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IntechOpen Series
Materials Science, Volume 23

Copper

Properties, Metallurgy and Applications

Edited by Daniel Fernández González



Copper - Properties, Metallurgy and Applications

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Published in London, United Kingdom

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<http://dx.doi.org/10.5772/intechopen.1008107>

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First published in London, United Kingdom, 2026 by IntechOpen

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British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

Copper – Properties, Metallurgy and Applications

Edited by Daniel Fernández González

p. cm.

This title is part of the Materials Science Book Series, Volume 23

Topic: Metals and Nonmetals

Series Editor: Chonghe Li

Topic Editor: Joan Josep Roa Rovira

Print ISBN 978-1-83635-394-2

Online ISBN 978-1-83635-393-5

eBook (PDF) ISBN 978-1-83635-395-9

ISSN 3049-8856

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IntechOpen Book Series

Materials Science

Volume 23

Aims and Scope of the Series

Materials science has always occupied an extremely high position in the human development process. As we explore the oceans of stars, various industries have put forward more stringent requirements for the performance of materials, forcing us to pay more and more attention to the development of new materials. At the same time, the formation of a data-driven scientific paradigm is dramatically shortening the development cycle of new materials. The huge data generated by synergistically combining theories, high-throughput experiments, high-throughput computation, and artificial intelligence is greatly contributing to our ability to utilize materials science to solve real-world problems. The three topics of this book series - Metals and Nonmetals; Composite Materials; and Surface Science - will address important areas of advancement in materials science. There will be a range of interesting works published under these topics.

Meet the Series Editor



Prof. Chonghe Li received his Ph.D. from the Chinese Academy of Sciences in 1995. From 1995 to 2000, he worked as a researcher at the Shanghai Institute of Metallurgy, Chinese Academy of Sciences, where he also served as director of the research laboratory. In 2000, he was appointed Professor at the Institute of High-Performance Computing in Singapore, where he worked on computation and simulation in materials science until 2004. Since then, he has been a professor at the School of Materials Science and Engineering, Shanghai University, China, as well as the director of the Shanghai Specialty Casting Engineering and Technology Research Center. Prof. Li's research focuses on titanium alloys, titanium-aluminum single crystals, intermetallic compounds, theoretical calculations, alloy design, and special refractory materials. His broad scientific expertise is well recognized by the scientific community around the world. He is a member of the editorial board of the journal *Metals*. As an author, he has published more than 200 peer-reviewed papers, 2 books, and over 40 patents.

Meet the Volume Editor



Daniel Fernández-González graduated with a bachelor's and master's degree in mining engineering in 2013, and he earned a Ph.D. in Materials at the University of Oviedo in 2029. He has worked as a researcher at the Nanomaterials and Nanotechnology Research Centre of the Spanish National Research Council since 2021. His research focuses on the synthesis and sintering of nanostructured materials in the form of ceramic-ceramic and ceramic-metal composites, using technologies such as spark plasma, laser, microwave, or cold sintering. He is also a pioneering researcher in the field of using concentrated solar energy to synthesise materials and valorise industrial by-products. From this investigation, more than 50 articles have been published in indexed journals, 6 books, several edited books, and numerous conference contributions.

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*by Futian Chen, Zhenyu Tian, Pingping Liu, Wentuo Han, Xiaou Yi, Qian Zhan
and Farong Wan*

Preface

Copper is one of the oldest metals used by humans, dating back to the Copper Age. Anyway, its relevance continues today and is expected to continue in the future, thanks to its unique properties and wide range of applications. The importance of copper can be approached from several perspectives: economic, industrial, technological, and environmental.

From an economic perspective, copper is a fundamental metal. The extraction and processing of the copper ores are important in terms of job generation regarding different points of the chain: geology, mining, metallurgy, logistics, and applications, among others, making the copper utilisation a global material, although some countries account for an important part of the mining resources (such as, for instance, Chile) but others are involved in the transformation or recycling. Therefore, due to the wide range of recycling options and transformations of the metal and its compounds, copper is a global metal. The significance of this lies in copper's importance for thermal management and electric power transmission, as well as in agriculture and corrosion-resistant applications.

In the industrial field, copper is well known for its excellent electrical and thermal conductivities. These properties make it an ideal metal for fabricating wires, electronic components, and thermal management devices. This way, in the current technological revolution, characterised by advances in electronics and renewable energy, copper has become increasingly important, and demand is expected to grow in the future. For example, electric vehicles and wind turbines are fundamental to our societies as more sustainable modes of transport and energy generation are demanded, and they depend heavily on this metal for batteries and electrical systems.

At a technological level, copper plays an important role in modern communications, i.e., printed circuits. This way, the contribution of copper-based technologies is fundamental for global telecommunications. Moreover, the investigation into new copper-based alloys and composites continues to expand the number of applications, potentially transforming the entire industry (and other fields) in the future.

Finally, from an environmental perspective, copper is important due to its recyclability. This metal can be recycled indefinitely without losing its properties, reducing the need to extract new resources and minimizing the environmental impact of mining operations. Within this context, where sustainability is increasingly a priority, the use of recycled copper is consolidating as a responsible and effective practice.

Definitely, copper is an invaluable resource for humans, and its importance extends far beyond economic and industrial considerations, impacting technology and society. As the world faces new challenges, the importance of copper will grow. Copper will be a fundamental metal in the future development of civilization.

As detailed, copper plays and will continue to play an important role in the progress of our society. Within this context, this book provides an overview of various aspects of copper, including fundamentals, metallurgical operations, and advanced applications. This book also includes relevant advances in research, presented as reviews of recent work on hot topics in copper.

The process of publishing this book was long and sometimes complicated, and I want to thank everyone for their support. Moreover, I want to acknowledge the authors for their interesting contributions, willingness to share their research and experience, and for their hard work in making this book possible. Finally, I want to express my gratitude to IntechOpen for the initiative to publish this book on copper, the third on this topic, following “Copper Overview - From Historical Aspects to Applications” (2024) and “Copper - From the Mineral to the Final Application” (2023). These edited books are always a good platform for sharing knowledge from a multidisciplinary perspective.

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Section 1

Fundamentals

Chapter 1

The Atomic Structure of Copper: Understanding Its Properties

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and Abdul Ghuffar*

Abstract

Understanding the atomic structure of a material provides the foundation for explaining its macroscopic behavior and predicting its properties. This chapter describes copper's atomic structure as the basis for its individual characteristics that have made it essential throughout human history. Copper's electronic configuration ($3d^{10}4s^1$) is also explored, highlighting how its single valence electron in the 4 s orbital enables exceptional electron mobility within its face-centered cubic (FCC) crystal structure. The chapter describes copper's metallic bonding, characterized by delocalized electrons forming a "sea" around positively charged ions, and demonstrates how this arrangement directly enables its outstanding electrical and thermal conductivity. Various structural defects, including vacancies, dislocations, and grain boundaries, are analyzed for their influence on mechanical properties, particularly copper's remarkable ductility and malleability. Advanced computational models simulating electron movement and atomic interactions at different temperatures provide further insights into structure-property relationships. Through a comprehensive examination of these structural features, the chapter establishes clear connections between atomic-level phenomena and macroscopic properties, offering a theoretical framework essential for understanding copper's technological applications and developing novel copper-based materials with improved performance characteristics.

Keywords: copper, atomic structure, electronic configuration, crystal structure, metallic bonding, electrical conductivity, thermal conductivity, ductility, malleability, defects

1. Introduction

Copper has been involved in human technological advancement for centuries, from the dawn of metallurgy to modern electronics and energy systems. As one of the earliest metals utilized by humans, copper's unique combination of properties has confirmed its continued relevance despite the development of numerous new materials [1]. The versatility of this transition metal stems directly from its atomic structure, which governs all aspects of its behavior on a macroscopic scale. Copper stands apart among metals with its distinctive reddish-orange color, exceptional electrical and thermal conductivity, excellent corrosion resistance, and remarkable

mechanical properties. These characteristics have made copper indispensable in diverse applications, including electrical wiring, heat exchangers, architectural elements, coinage, and antimicrobial surfaces [2]. Globally, copper production is a significant industry, with millions of metric tons produced annually, reflecting its extensive demand in electronics, construction, transportation, and industrial machinery. The trend in production has generally been rising, driven by global economic growth and the increasing electrification of society. While these properties are readily observable and measurable, their origin lies in copper's fundamental atomic architecture. This chapter provides a comprehensive explanation of copper's atomic structure and how it directly influences its macroscopic properties. Beginning with the arrangement of electrons around the copper nucleus and the resulting electronic configuration, we explore copper's position in the periodic table as a transition metal and analyze how its electronic structure leads to its characteristic properties. The crystalline arrangement of copper atoms, with particular attention to its face-centered cubic (FCC) structure, is then examined to understand how this specific spatial group contributes to copper's remarkable physical and mechanical properties [3]. The nature of metallic bonding in copper is investigated, focusing on the sea of delocalized electrons that gives rise to its outstanding electrical and thermal conductivity. Various types of crystal defects that occur in real copper structures are discussed, including vacancies, dislocations, and grain boundaries, with emphasis on how these imperfections impact mechanical properties such as ductility, malleability, and strength [4]. Modern computational approaches to model copper at the atomic level are also presented, highlighting how simulation techniques provide insight into electron movement and atomic interactions across different conditions.

This chapter will systematically inspect the key properties that make copper essential, its exceptional electrical conductivity, outstanding thermal conductivity, remarkable ductility and malleability, excellent corrosion resistance, and unique antimicrobial properties. Each of these macroscopic characteristics will be directly linked to copper's atomic structure and electronic configuration. Throughout the chapter, clear connections are established between atomic-level phenomena and observable macroscopic properties, offering a theoretical framework essential for understanding copper's current applications and informing the development of novel copper-based materials with enhanced performance characteristics.

2. Atomic structure and electronic configuration of copper

2.1 Fundamental atomic properties

Copper (Cu) is element 29 in the periodic table, positioned in period 4, group 11. With an atomic number of 29, a copper atom contains 29 protons in its nucleus, balanced by 29 electrons orbiting in shells around the nucleus. The most common isotope, Cu, has 34 neutrons, giving it an atomic mass of approximately 63.546 atomic mass units [5, 6]. The atom has an atomic radius of 128 pm and a covalent radius of 132 pm, dimensions that influence its packing behavior in crystalline structures and its interaction with other elements. The electronic structure of a copper atom is shown in **Figure 1**, along with the distribution of electrons in the shells: 1 s, 2 s, 2p, 3 s, 3p, 4 s, and 3d. The diagram also highlights the exception to the Aufbau principle, in which the 4 s orbital is filled before the 3d orbital during electron configuration.

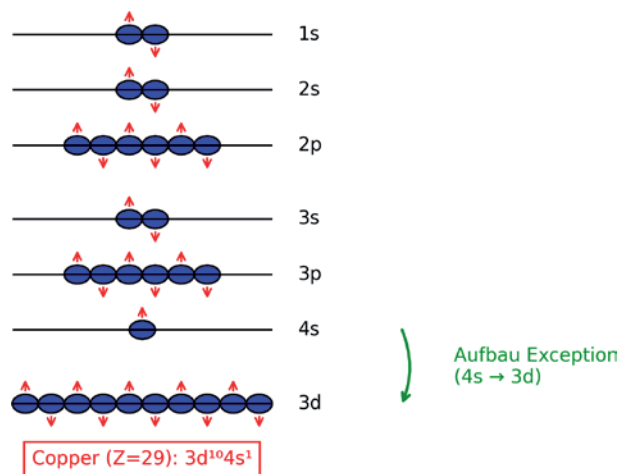


Figure 1.
A diagram illustrating the electronic configuration of copper.

Property	Value
Atomic number	29
Atomic weight	63.546
Atomic radius	128 pm
Atomic diameter	2.551×10^{-10} m
Covalent radius	132 pm
Melting point	1356 K (1083°C)
Boiling point	2868 K (2595°C)
Density at 293 K	8.94×10^3 kg/m ³
Fermi energy	7.0 eV

Table 1.
Fundamental properties of copper.

This exception plays a significant role in copper's electrical conductivity and bonding characteristics, making it essential to the metal's overall behavior and properties.

Some fundamental properties are summarized in **Table 1**.

2.2 Electronic configuration

The electronic configuration of copper presents an interesting anomaly compared to what might be expected from a straightforward application of the Aufbau principle. According to this principle, electrons should fill orbitals in order of increasing energy levels. For copper, this would theoretically yield a configuration of $[\text{Ar}]3d^94s^2$. However, copper's actual configuration is $[\text{Ar}]3d^{10}4s^1$, with a completely filled 3d subshell and a single electron in the 4s orbital [7]. This deviation occurs because a fully filled d subshell provides greater stability than a half-filled s subshell. The energy difference between the 3d and 4s orbitals is small enough that the energetic advantage of having a completely filled 3d subshell compensates for the slight energy increase

of keeping only one electron in the 4 s orbital. This phenomenon is characteristic of several transition metals and results from the interplay of electron-electron repulsion, nuclear charge, and orbital energies [8]. The electronic configuration of copper directly influences its chemical and physical properties. The filled 3d subshell contributes to copper's stability, while the single electron in the 4 s orbital is responsible for many of its characteristic properties. This 4 s electron is easily delocalized in the metallic state, becoming part of the “sea” of mobile electrons that enables copper's exceptional electrical conductivity [9].

2.3 Valence states and bonding potential

Copper mainly shows two valence states: Cu^+ (cuprous ion) and Cu^{2+} (cupric ion), corresponding respectively to the loss of the single 4 s electron or both the 4 s electron and one 3d electron. While in aqueous solutions the Cu^+ state is less stable, it forms stable compounds with some anions. More often occurring and giving many copper compounds and solutions a distinctive blue or green hue is the Cu^{2+} state [10]. Multiple valence states make copper advantageous in redox processes and catalytic uses. Copper can engage in many biological activities, such as electron transfer reactions in enzymes like cytochrome c oxidase and superoxide dismutase by means of the quite simple transition between Cu^+ and Cu^{2+} oxidation states [11]. When copper is metallic, the delocalization of its valence electrons, mostly the 4 s electron, dominates its bonding. This delocalization produces the metallic bond that defines copper and other metals, therefore preserving their mobility of electrons across the crystal structure [12] while giving cohesive strength.

3. Crystal structure of copper

3.1 Face-centered cubic (FCC) structure

Copper crystallizes in a face-centered cubic (FCC) structure, which is one of the most common crystal structures among metals. In this configuration, copper atoms are positioned at each corner of the cube and at the center of each face. This arrangement results in a total of four atoms per unit cell: eight corner atoms (each contributing 1/8 of an atom) and six face-centered atoms (each contributing 1/2 of an atom) [13]. The FCC unit cell of copper, with atoms at corners and face centers, and an extended view showing the packing of atoms, is shown in **Figure 2**.

The FCC structure is characterized by its high atomic packing factor of 0.74, which means that approximately 74% of the available space in the crystal is occupied by atoms. This close packing arrangement contributes to copper's relatively high density of 8.94 g/cm^3 at room temperature. The lattice parameter (a) of copper at 293 K is $3.6147 \times 10^{-10} \text{ m}$, which represents the length of the side of the cubic unit cell [14]. The closest approach distance between copper atoms in the FCC lattice is $2.556 \times 10^{-10} \text{ m}$, which also corresponds to the Burgers vector, a critical parameter for understanding dislocation movement in the crystal. Each copper atom in the FCC structure is coordinated with 12 neighboring atoms, a coordination number that maximizes the efficiency of metallic bonding and contributes to the cohesive energy of the crystal [15]. Crystallographic features of copper are summarized in **Table 2**.

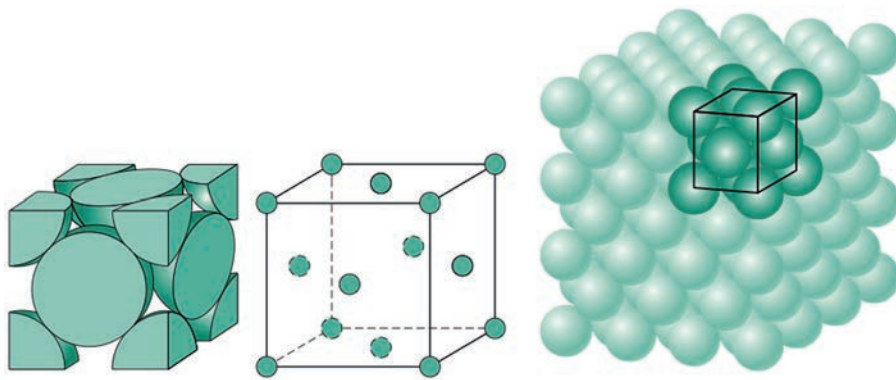


Figure 2.
Face-centered cubic (FCC) crystal structure of copper.

Feature	Value
Crystal structure	Face-centered cubic (FCC)
Space group	$Fm\bar{3}m(O_h^5)$
Atoms per unit cell	4
Lattice parameter at 293 K	3.6147×10^{-10} m
Closest atomic approach (Burgers vector)	2.556×10^{-10} m
Coordination number	12
Atomic packing factor	0.74
Atomic volume	1.182×10^{-29} m ³

Table 2.
Crystallographic features of copper.

3.2 Crystallographic planes and directions

The FCC structure of copper has several significant crystallographic planes and directions that determine its physical and mechanical properties. The most densely packed planes in the FCC structure are the {111} planes, which contain the maximum number of atoms per unit area. These close-packed surfaces enable dislocation movement during plastic deformation, contributing to copper's exceptional ductility and malleability [16]. The principal slip systems in copper consist of the {111} planes and the $\langle 110 \rangle$ directions, producing a total of 12 separate slip systems. This profusion of slip systems allows for substantial plastic deformation before fracture, a fundamental element in copper's mechanical behavior. The ease of slip along these planes is closely connected to the low critical resolved shear stress (CRSS) required to commence dislocation movement in copper [17]. The crystallographic texture, the preferred orientation of crystals in a polycrystalline material, strongly affects the anisotropic properties of copper. During processing activities such as rolling, drawing, or extrusion, copper grains prefer to align in specific orientations, resulting in directional changes in mechanical and physical properties [18].

3.3 Thermal expansion and structural stability

The FCC structure of copper remains stable from very low temperatures to its melting point of 1083°C. The lattice parameter increases with temperature due to thermal expansion, following a nearly linear relationship in the temperature range of practical interest. The coefficient of thermal expansion for copper is approximately 16.5×10^{-6} K⁻¹ at an ambient temperature [19]. Thermal vibrations of atoms about their equilibrium locations increase with temperature, affecting numerous attributes such as electrical resistance, thermal conductivity, and mechanical strength. The amplitude of these vibrations can be defined by the Debye temperature, which for copper is roughly 343 K. Below this temperature, quantum effects become significant in characterizing atomic vibrations [20]. At elevated temperatures closer to its melting point, copper can develop substantial concentrations of point defects, particularly vacancies, which influence diffusion processes, electrical resistivity, and mechanical characteristics. The equilibrium concentration of vacancies in copper follows an Arrhenius relationship with temperature, given by:

$$c_v = \exp\left(-\frac{E_f}{kT}\right) \quad (1)$$

where c_v is the vacancy concentration, E_f is the vacancy formation energy (approximately 1.17 eV for copper), k is the Boltzmann constant, and T is the absolute temperature [21].

4. Metallic bonding in copper

4.1 Nature of metallic bonding

Metallic bonding in copper is described by the delocalization of valence electrons throughout the crystal lattice. Unlike covalent or ionic bonding, metallic bonding does not require directed connections between specific atoms but rather generates a “sea” of movable electrons that penetrates the entire crystal structure. In copper, the solitary 4s electron from each atom becomes divorced from its parent atom and enters this collective electron sea, whereas the positively charged copper ions (Cu^+) form a regular crystalline array [22], as shown in **Figure 3**.

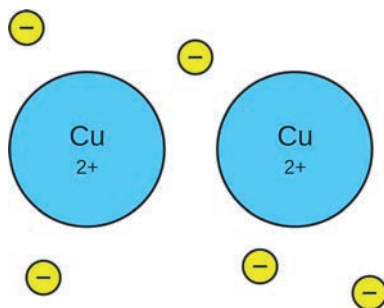


Figure 3.
Schematic representation of metallic bonding in copper.

The free electron model offers a simplified but effective description of metallic bonding in copper. According to this model, the valence electrons behave like a gas of noninteracting particles traveling through a periodic potential formed by the ion cores. This paradigm helps explain several of copper's electronic properties, including its electrical conductivity and specific heat capacity [23]. A more advanced method, the tight-binding model, incorporates the overlap of atomic orbitals from adjacent atoms, resulting in the development of energy bands. For copper, the valence and conduction bands overlap, eliminating any energy gap and allowing electrons to travel freely when an electric field is applied. This band structure is crucial to understanding copper's electrical properties [24].

4.2 Cohesive energy and bond strength

The cohesive energy of copper—the energy required to separate the solid into isolated atoms—is approximately 3.49 eV/atom (337 kJ/mol). This relatively high value reflects the strength of metallic bonding in copper and contributes to its melting point of 1083°C, which is higher than that of many other metals [25]. The strength of metallic bonding in copper can also be assessed through its bulk modulus, which measures a material's resistance to uniform compression. For copper, the bulk modulus is approximately 140 GPa, indicating substantial resistance to volume change under hydrostatic pressure. This property is directly related to the interatomic forces in the copper crystal [26]. While metallic bonding provides substantial cohesive energy, it also allows for considerable atomic mobility, particularly at elevated temperatures. This characteristic facilitates processes, such as diffusion, recrystallization, and grain growth, which are important in the processing and performance of copper products [27].

4.3 Electronic structure and bond characteristics

The electronic structure of copper significantly influences its bonding characteristics. While the simplified free electron model provides a useful approximation, the actual behavior of electrons in copper is more complex due to the presence of the d-band electrons. The filled 3d orbitals in copper do not directly participate in metallic bonding but do influence the electronic properties through interactions with the conduction electrons [28]. The density of states (DOS) of copper shows a characteristic structure with a narrow d-band located below the Fermi level and a broad s-band that crosses the Fermi level. This electronic structure results in a relatively low density of states at the Fermi level, which has implications for copper's electrical and thermal properties [29]. The Fermi surface of copper, which represents the surface of constant energy in momentum space corresponding to the Fermi energy, has a nearly spherical shape with necks along the [111] directions. This geometry of the Fermi surface directly influences electron transport properties and is critical for understanding phenomena such as the anomalous skin effect and cyclotron resonance in copper [31].

5. Electrical conductivity properties

5.1 Mechanisms of electrical conduction

Copper's high electrical conductivity, second only to silver among pure metallic materials, comes directly from its atomic structure and metallic bonding.

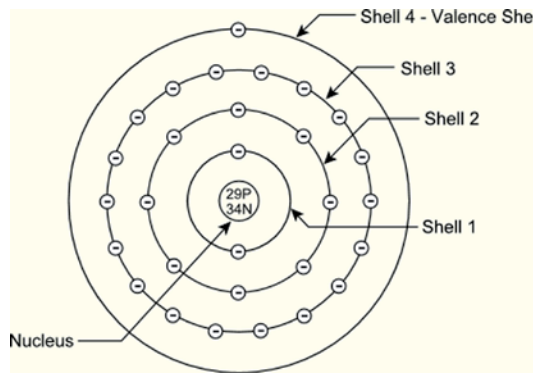


Figure 4.
Illustration of electrical conduction mechanism in copper.

The delocalized 4 s electrons, released from their parent atoms, generate a “sea” of mobile carriers that can rapidly respond to an applied electric field. This electron mobility is the main process behind copper’s electrical conductivity, which reaches 5.96×10^7 S/m at ambient temperature [32]. A Bohr model of a copper atom showing the nucleus (29P, 34 N) and electron shells, emphasizing the valence electron in Shell 4 in **Figure 4**.

The classical Drude model provides a simplified description of electrical conduction in copper, treating conduction electrons as a gas of free particles that occasionally scatter with the ionic cores. According to this model, the electrical conductivity (σ) can be expressed as:

$$\sigma = \frac{ne^2\tau}{m} \quad (2)$$

where n is the electron density, e is the elementary charge, τ is the mean free time between scattering events, and m is the electron mass. For copper, the electron density is approximately 8.47×10^{28} electrons/m³, corresponding to one conduction electron per copper atom [33]. While the Drude model provides useful insights, a more accurate description requires quantum mechanical considerations, particularly the Fermi-Dirac statistics governing electron behavior. In the quantum mechanical

Property	Value	Condition
Electrical conductivity	5.96×10^7 S/m	At 20°C (293 K)
Electrical resistivity	$1.68 \times 10^{(-8)} \Omega \cdot \text{m}$	At 20°C (293 K)
Temperature coefficient of resistivity	$3.93 \times 10^{(-3)} \text{K}^{-1}$	Near room temperature
IACS conductivity rating	100%	Standard for annealed copper
Mean free path of electrons	~39 nm	At room temperature
Fermi velocity	1.57×10^6 m/s	At room temperature

Table 3.
Electrical properties of copper.

picture, only electrons near the Fermi level participate in conduction, as these are the only ones capable of accessing nearby unoccupied states when responding to an electric field [34]. Electrical properties are summarized in **Table 3**.

5.2 Factors affecting electrical conductivity

Several factors influence the electrical conductivity of copper, including temperature, impurities, defects, and strain. The electrical resistivity of copper increases with temperature due to increased lattice vibrations (phonons) that scatter conduction electrons. This relationship is approximately linear over a wide temperature range and is characterized by the temperature coefficient of resistivity, which for copper is $3.93 \times 10^{-3} \text{ K}^{-1}$ near room temperature [35]. Impurities in copper can significantly reduce its electrical conductivity, as they introduce scattering centers for the conduction of electrons. According to Matthiessen's rule, the total resistivity of a metal can be expressed as the sum of contributions from thermal vibrations, impurities, and defects:

$$\rho_{\text{total}} = \rho_{\text{thermal}} + \rho_{\text{impurity}} + \rho_{\text{defect}} \quad (3)$$

The impact of impurities depends on their concentration and atomic characteristics. Elements with an atomic size similar to copper, such as silver and gold, have relatively little effect on conductivity, while elements with significantly different sizes, such as silicon or phosphorus, can drastically reduce it [36]. Crystal defects such as vacancies, dislocations, and grain boundaries also contribute to electrical resistivity by scattering conduction electrons. The resistivity contribution from dislocations depends on the dislocation density (ρ), with a typical relationship of:

$$\rho_{\text{defect}} = \alpha \rho_d \quad (4)$$

where (α) is a material-specific constant. For copper, this constant is approximately $2.0 \times 10^{-25} \Omega \cdot \text{m}^3$ [37].

5.3 Electronic structure and conductivity

The electronic band structure of copper plays a crucial role in determining its electrical conductivity. The nearly free electron model provides a reasonable approximation for the conduction band, which is derived primarily from the 4s orbitals. However, the presence of the filled 3d band near the Fermi level introduces complications that require more sophisticated models [38]. The density of states at the Fermi level in copper is relatively low compared to other metals due to the position of the d-band just below the Fermi energy. This characteristic influences the electronic specific heat, the Pauli paramagnetism, and other properties related to the behavior of conduction electrons [39]. Recent computational studies using density functional theory (DFT) have provided detailed insights into the electronic structure of copper and its relationship to electrical conductivity. These calculations have confirmed the dominant role of s-band electrons in conduction while also highlighting the influence of d-band electrons through hybridization effects [40]. Gan et al. (2024) investigated the electrical conductivity of copper under ultrahigh pressure and temperature conditions through experiments and first-principles simulations. Their results revealed that the electrical resistivity of face-centered cubic total thermal impurity defect (FCC) copper diminishes with increasing

pressure and displays a linear augmentation with rising temperature, providing valuable insights into copper's behavior under extreme conditions [41].

6. Thermal conductivity properties

6.1 Mechanisms of thermal conduction

Copper exhibits exceptional thermal conductivity, with a value of approximately 400 W/(m·K) at room temperature, second only to silver among metals. This high thermal conductivity arises from two primary mechanisms: electronic heat transport and lattice (phonon) heat transport, with the electronic component being dominant in metals like copper. The primary mechanism for copper's remarkable thermal conductivity is electronic heat transport. This occurs through the movement of free electrons, which are highly mobile within the metallic structure. As illustrated in **Figure 5**, when a heat source is applied, electrons in the hotter region gain kinetic energy. These “Free flowing conduction electrons” then move or drift toward cooler regions of the metal, carrying thermal energy with them. This movement of energy-carrying electrons through the lattice of “Metal atoms” (ions) is the main reason for copper's high thermal conductivity.

While phonon conduction contributes to the overall thermal conductivity, the electronic component is typically dominant in metals like copper. Electronic thermal conduction in copper occurs through the movement of free electrons, which carry thermal energy from higher to lower temperature regions. The relationship between electrical and thermal conductivity due to electrons is described by the Wiedemann-Franz law, which states that the ratio of thermal conductivity (κ) to electrical conductivity (σ) is proportional to temperature (T):

$$\frac{\kappa}{\sigma T} = L \quad (5)$$

where L is the Lorenz number, approximately $2.44 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ for metals. For copper at room temperature, this relationship holds remarkably well, confirming the

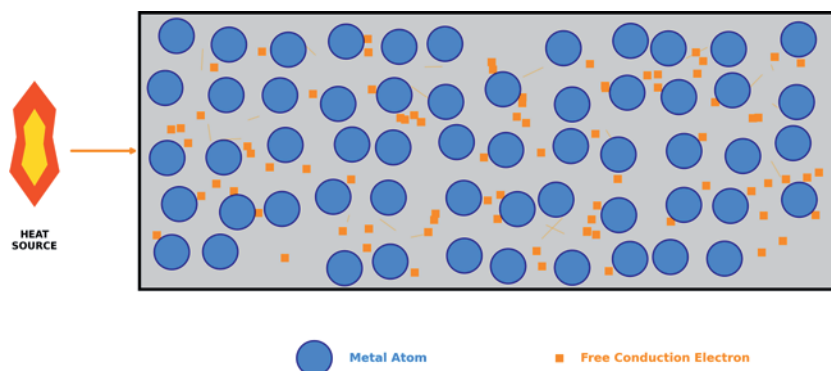


Figure 5.
Mechanism of electronic thermal conduction in a metal [42].

dominant role of free electrons in thermal transport [43]. Lattice thermal conduction, which involves the propagation of phonons (quantized lattice vibrations), plays a minor role in copper compared to electronic conduction. However, it becomes increasingly important at lower temperatures, where electron-phonon scattering is reduced. The total thermal conductivity of copper can be expressed as the sum of electronic and lattice contributions:

$$\kappa_{\text{total}} = \kappa_{\text{electronic}} + \kappa_{\text{lattice}} \quad (6)$$

At room temperature, κ accounts for approximately 95% of the total thermal conductivity in copper [44]. Thermal properties are summarized in **Table 4**.

6.2 Factors affecting thermal conductivity

Like electrical conductivity, the thermal conductivity of copper is influenced by temperature, impurities, defects, and microstructure. The temperature dependence of thermal conductivity in copper follows a more complex pattern than electrical conductivity. At low temperatures, thermal conductivity increases with temperature as more phonon modes become excited. However, above the Debye temperature (343 K for copper), thermal conductivity decreases with increasing temperature due to enhanced electron-phonon scattering [45]. Impurities significantly reduce the thermal conductivity of copper by scattering both electrons and phonons. The effect is particularly pronounced for elements that form solid solutions with copper, such as zinc, nickel, or aluminum. Even small amounts of impurities can cause substantial reductions in thermal conductivity, emphasizing the importance of high-purity copper for thermal management applications [46]. Crystal defects, including vacancies, dislocations, and grain boundaries, also reduce thermal conductivity by scattering heat carriers. Grain boundaries are particularly effective at scattering phonons, making polycrystalline copper's thermal conductivity generally lower than that of single-crystal copper. The effect becomes more pronounced as the grain size approaches or becomes smaller than the mean free path of the heat carriers [47]. Microstructural effects on thermal conductivity are crucial in copper alloys and composites. For example, precipitation-hardened copper alloys often show reduced thermal conductivity compared to pure copper due to the scattering effects of precipitates. However, carefully designed copper matrix composites can potentially offer combinations of mechanical strength and thermal conductivity that exceed what is possible with conventional copper alloys [48].

Property	Value	Conditions
Thermal conductivity	401 W/(m·K)	At 20°C (293 K)
Electronic contribution to thermal conductivity	~95%	At room temperature
Specific heat capacity	0.385 J/(g·K)	At 20°C (293 K)
Thermal diffusivity	1.17×10^{-4} m ² /s	At 20°C (293 K)
Linear thermal expansion coefficient	16.5×10^{-6} K ⁻¹	At 20°C (293 K)
Debye temperature	343 K	Characteristic phonon temperature

Table 4.
Thermal properties of copper.

6.3 Atomic-level heat transfer mechanisms

At the atomic level, heat transfer in copper involves complex interactions between electrons and the crystal lattice. The primary mechanism involves electrons absorbing thermal energy in hot regions, moving to cooler regions, and transferring this energy to the lattice through electron-phonon coupling [49]. The electron-phonon coupling in copper is characterized by a coupling constant (λ) of approximately 0.3–0.4, indicating a moderate strength of interaction between electrons and lattice vibrations. This coupling is essential for understanding not only thermal transport but also related phenomena such as electrical resistivity, superconductivity, and thermoelectric effects [50]. Recent computational studies have provided detailed insights into the microscopic mechanisms of heat transfer in copper. Molecular dynamics simulations using embedded-atom method (EAM) potentials have successfully reproduced the temperature dependence of thermal conductivity and revealed the contributions of different phonon modes to thermal transport [51]. First-principles calculations based on density functional theory have also been applied to study phonon transport and electron-phonon interactions in copper. These calculations have confirmed the dominant role of electrons in thermal conduction and provided quantitative predictions of thermal conductivity that agree well with experimental measurements [52].

7. Ductility and malleability characteristics

7.1 Plastic deformation mechanisms

Copper's remarkable ductility and malleability, its ability to deform under tensile stress and compressive stress without fracturing, are direct consequences of its atomic structure and crystalline arrangement. As an FCC metal, copper primarily deforms through the movement of dislocations along slip systems, with twinning serving as a secondary deformation mechanism under certain conditions, as shown in **Figure 6** [53].

Dislocation slip in copper occurs predominantly on the $\{111\}$ planes in the $\langle 110 \rangle$ directions, which constitute the close-packed planes and directions in the FCC lattice.

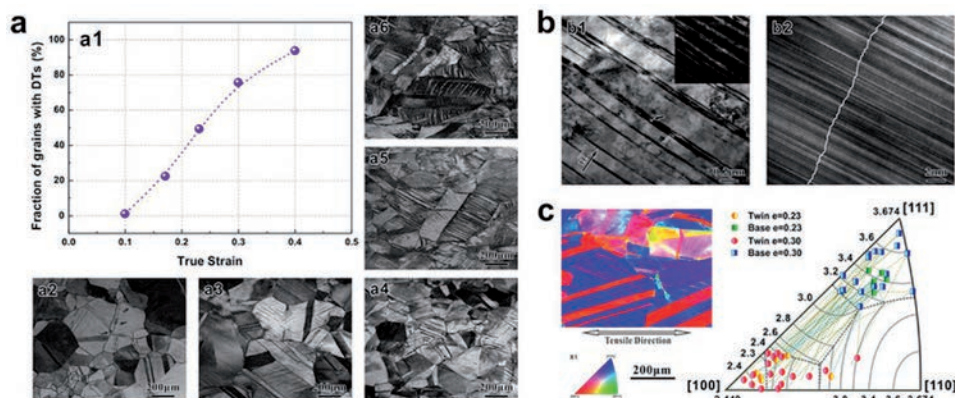


Figure 6. Deformation mechanisms in copper: twins, showing how twins form and grow during plastic deformation, contributing to copper's exceptional ductility and malleability [53].

Property	Value range	Conditions
Tensile strength	220–380 MPa	Depending on work hardening
Yield strength	70–320 MPa	Depending on work hardening
Elongation to failure	10–60%	Depending on work hardening
Young's modulus	110–130 GPa	At room temperature
Poisson's ratio	0.34	At room temperature
hardness (Vickers)	40–120 HV	Depending on work hardening
Shear modulus	45–50 GPa	At room temperature
Stacking fault energy	45–78 mJ/m ²	At room temperature

Table 5.
Mechanical properties of pure copper.

The critical resolved shear stress required to initiate slip in pure copper is extremely low, approximately 0.5–1.0 MPa for single crystals, facilitating easy plastic deformation. This explains why annealed copper can be deformed to extraordinary degrees before failure [54]. The 12 independent slip systems in copper's FCC structure satisfy the von Mises criterion, which states that at least five independent slip systems are necessary for arbitrary shape change without cracking or void formation. This abundance of slip systems is a key factor in copper's exceptional formability compared to metals with fewer available slip systems [55]. Deformation twinning, though less common in copper than in lower stacking fault energy metals, can occur under conditions of high strain rate or low temperature. Mechanical twins form on {111} planes in FCC metals, creating mirror images of the crystal structure across the twin boundary. These twins can contribute to work hardening and influence texture evolution during processing [56]. Mechanical properties are summarized in **Table 5**.

7.2 Role of stacking fault energy

The stacking fault energy (SFE) of copper, estimated to be between 45 and 78 mJ/m, plays a crucial role in determining its deformation behavior. SFE influences the ease with which dislocations can cross-slip, affecting work hardening, recrystallization, and creep processes [57]. In FCC metals like copper, dislocations typically dissociate into partial dislocations separated by a stacking fault. The width of this dissociation is inversely proportional to the SFE. Copper's moderate SFE results in partial dislocations separated by a few nanometers, striking a balance that allows for good ductility while maintaining moderate work hardening capability [58]. The SFE of copper can be modified by alloying elements, with some elements (such as zinc, aluminum, and tin) decreasing the SFE and others (such as nickel) increasing it. Lower SFE promotes planar slip and deformation twinning, enhancing work hardening but potentially reducing ductility at high strain rates. This relationship between composition, SFE, and mechanical properties is exploited in the design of copper alloys for specific applications [59]. Computational studies have provided insights into the atomic-level mechanisms underlying the effect of SFE on deformation behavior. Molecular dynamics simulations have shown how changes in SFE influence dislocation core structures, cross-slip propensity, and twin nucleation, offering guidance for alloy design to optimize mechanical properties [60].

7.3 Work hardening and recrystallization

Work hardening (strain hardening) in copper occurs as dislocations multiply and interact during plastic deformation, increasing resistance to further deformation. The rate of work hardening is related to the ease of dislocation cross-slip, which depends on the SFE. Copper's moderate SFE results in significant work hardening during cold working, allowing its strength to be substantially increased through deformation processing [61]. The dislocation density in copper increases from approximately 10^{12} m^{-2} in the annealed state to 10^{15} m^{-2} in heavily cold-worked material. This increase in dislocation density is responsible for the observed hardening effect. The flow stress (σ) relationship with dislocation density (ρ) can be approximated by the Taylor equation:

$$\sigma = \sigma_0 + \alpha Gb\sqrt{\rho} \quad (7)$$

where (σ_0) is the friction stress, (α) is a constant (approximately 0.3–0.5 for copper), (G) is the shear modulus, and (b) is the Burgers vector [62]. Recrystallization of work-hardened copper occurs through the nucleation and growth of new, strain-free grains, typically initiated at regions of high strain heterogeneity such as grain boundaries, deformation bands, or around large particles. The recrystallization temperature of copper depends on prior deformation, purity, and heating rate, but is generally around 200–300°C for commercially pure material with moderate cold work [63]. The balance between work hardening and recovery/recrystallization processes is central to the thermomechanical processing of copper and its alloys. Controlled combinations of deformation and heat treatment allow for precise tailoring of grain structure, texture, and dislocation configurations to optimize mechanical properties for specific applications [64].

8. Crystal defects and their influence

8.1 Point defects

Point defects in copper include vacancies (missing atoms), self-interstitials (extra copper atoms in interstitial positions), and impurity atoms (either substitutional or interstitial). These defects, though atomic in scale, significantly influence copper's physical and mechanical properties [65]. A diagram illustrating different crystal defects like vacancies, interstitial atoms, substitutional atoms, edge dislocations, grain boundaries, and precipitates within a crystal lattice **Figure 7**.

Vacancies are the most common point defects in copper, with an equilibrium concentration (c_v) that increases exponentially with temperature according to the Arrhenius relationship:

$$c_v = \exp\left(-\frac{G_f}{kT}\right) \approx \exp\left(-\frac{E_f}{kT}\right) \quad (8)$$

Where G_f is the Gibbs free energy of vacancy formation, E_f is the formation energy. (Approximately 1.17 eV for copper), k is the Boltzmann constant, and T is the absolute temperature. At copper's melting point, the equilibrium vacancy

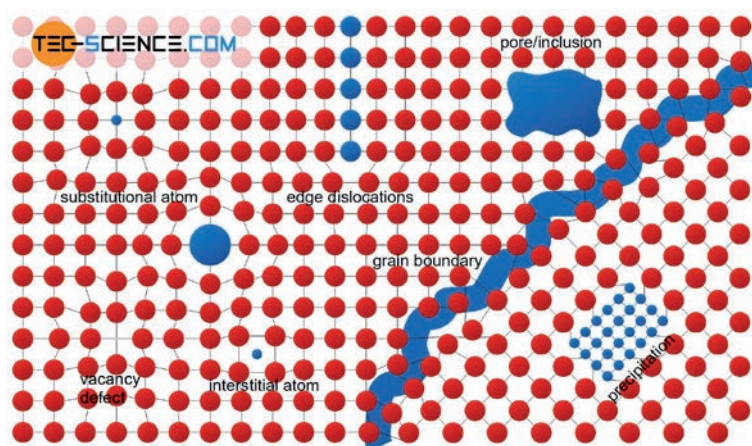


Figure 7.
 Various crystal defects in copper [66].

concentration reaches approximately 10^{-4} , or one vacancy per 10,000 atomic sites [67]. Self-interstitials have a much higher formation energy (approximately 3–4 eV) and are therefore extremely rare in thermal equilibrium. However, they can be produced in significant concentrations through irradiation or quenching from high temperatures. These defects are highly mobile even at low temperatures and play important roles in radiation damage and diffusion processes [68]. Impurity atoms in copper can occupy either substitutional or interstitial positions depending on their size and electronic structure. Common substitute impurities include zinc, tin, and nickel, while small atoms like hydrogen, carbon, and oxygen typically occupy interstitial positions. These impurities affect properties including electrical conductivity, thermal conductivity, and mechanical strength through electron scattering and lattice distortion mechanisms [66].

8.2 Line defects: Dislocations

Dislocations are line defects that enable plastic deformation in copper through their movement under applied stress. The two basic types—edge and screw dislocations—often combine to form mixed dislocations with varying character along their length. In copper's FCC lattice, perfect dislocations have a Burgers vector of $a/2\langle 110 \rangle$, where a is the lattice parameter [69]. The core structure of dislocations in copper influences their mobility and interaction with other defects. Perfect dislocations in copper typically dissociate into Shockley partial dislocations with Burgers vectors of $a/6\langle 112 \rangle$, separated by a stacking fault. The equilibrium separation distance (d) between these partials is given by:

$$d = \frac{Gb^2}{2\pi\gamma} \quad (9)$$

where (G) is the shear modulus, (b) is the magnitude of the Burgers vector of the partial dislocation, and (γ) is the stacking fault energy. For copper, this separation is typically a few nanometers [70]. Dislocation density in copper varies widely depending on processing history, from approximately 10^{10} m^{-2} in well-annealed material to

10^{15} m^{-2} in heavily cold-worked copper. This increase in dislocation density during plastic deformation is responsible for work hardening, as dislocations interact with each other to impede movement [71]. Experimental and computational studies have provided detailed insights into dislocation behavior in copper. Transmission electron microscopy (TEM) has revealed the arrangement of dislocations in various deformation structures, while atomistic simulations have elucidated dislocation core structures and mobility mechanisms at the atomic level [72].

8.3 Planar defects

Planar defects in copper include grain boundaries, twin boundaries, stacking faults, and antiphase boundaries. These two-dimensional defects separate regions of the crystal with different orientations or stacking sequences and significantly influence mechanical and physical properties [73]. Grain boundaries—interfaces between crystals of different orientations are classified as either low-angle (misorientation $<15^\circ$) or high-angle boundaries. Low-angle boundaries can be described as arrays of dislocations, while high-angle boundaries have more complex structures. The energy of grain boundaries in copper increases with misorientation angle up to about 15° , after which it remains relatively constant at approximately $0.6\text{--}0.8 \text{ J/m}$ for general high-angle boundaries [74]. Special boundaries with misorientation relationships, such as coherent twin boundaries ($\Sigma 3$) or $\Sigma 9$ boundaries in the coincident site lattice (CSL) model, have lower energies and distinct properties. Coherent twin boundaries in copper have an energy of only about $0.02\text{--}0.04 \text{ J/m}$, making them considerably more stable than general high-angle boundaries [75]. Stacking faults in copper are interruptions in the normal ABCABC... stacking sequence of $\{111\}$ planes in the FCC lattice. Intrinsic stacking faults (removal of a plane) create a local ABCABABC... sequence, while extrinsic stacking faults (insertion of an extra plane) create an ABCBABCABC... sequence. The energy of stacking faults, the stacking fault energy, is a critical parameter that influences deformation behavior, as discussed earlier [76]. Grain boundaries and other planar defects affect properties including strength, ductility, creep resistance, and corrosion behavior. They also serve as high-diffusivity paths, enhancing atomic transport along these interfaces compared to bulk diffusion. The engineering of grain boundary character distributions through thermomechanical processing is an important strategy for optimizing copper's properties for specific applications [77].

8.4 Defect interactions and property influence

The interaction between different types of defects in copper leads to complex behaviors that significantly influence macroscopic properties. For example, solute atoms and point defects interact with dislocations through size misfit and electronic effects, leading to solid solution strengthening. The resulting pinning forces increase the stress required for dislocation motion, enhancing strength but potentially reducing ductility [78]. Precipitate particles formed during heat treatment of copper alloys interact with dislocations through cutting or bypassing mechanisms (Orowan looping), depending on their size, spacing, and coherency with the matrix. These interactions are the basis for precipitation hardening, an important strengthening mechanism in many copper alloys [79]. Grain boundaries interact with dislocations by serving as both sources and sinks, as well as barriers to dislocation motion. The Hall-Petch relationship describes the strengthening effect of grain refinement:

$$\sigma_y = \sigma_o + k_y d^{-1/2} \quad (10)$$

where (σ_y) is the yield strength, (σ_o) is the friction stress, (k_y) is the Hall-Petch coefficient (approximately 0.1–0.2 MPa·m for copper), and d is the grain diameter. This relationship explains why fine-grained copper typically exhibits higher strength than coarse-grained material [80]. The collective influence of defects on properties is particularly evident in electrical and thermal conductivity. According to Matthiessen's rule, different scattering mechanisms contribute additively to resistivity, with point defects, dislocations, and grain boundaries all reducing conductivity to varying degrees. This understanding guides the development of copper alloys that balance conductivity with mechanical properties [81].

9. Computational modeling approaches

9.1 Atomistic simulation methods

Computational modeling at the atomistic level has become an indispensable tool for understanding copper's properties and behavior. Molecular Dynamics (MD)

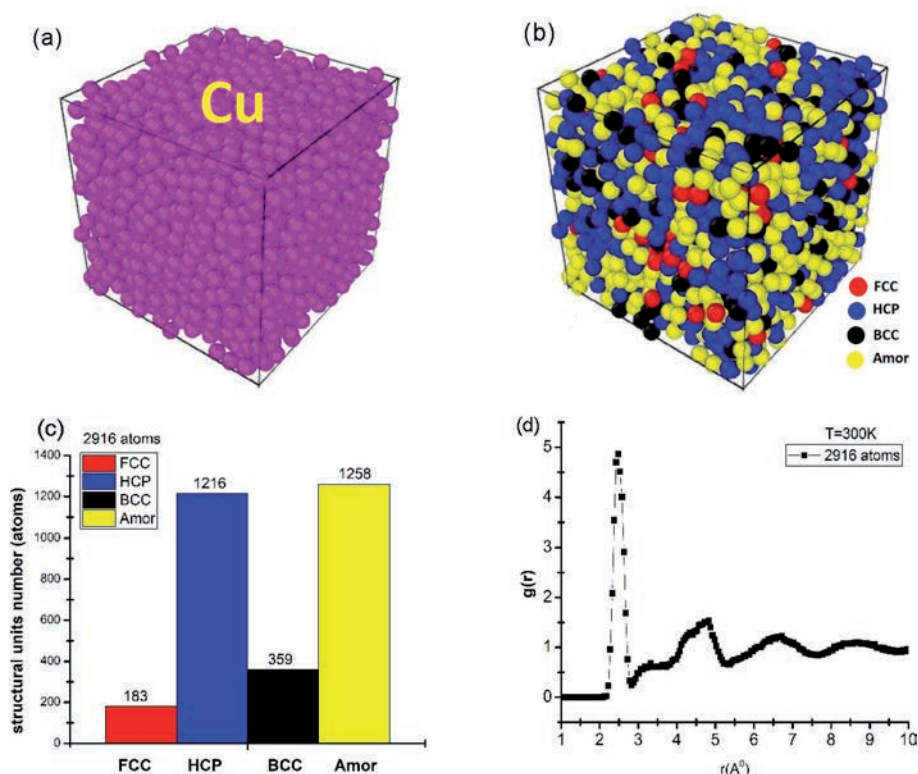


Figure 8. Molecular dynamics simulation showing atomic-level processes (a) initial FCC structure of Cu, (b) structure after impact showing FCC, HCP, BCC, and amorphous regions, (c) bar chart of structural units, and (d) radial distribution function $g(r)$ [82].

simulations using interatomic potentials have been widely applied to study various aspects of copper, including defect structures, mechanical properties, and phase transformations [82] as shown in **Figure 8**.

The embedded-atom method (EAM) represents atoms through embedding energy functions that account for the local electron density environment, providing accurate descriptions of metallic bonding. Density functional theory (DFT) solves quantum mechanical equations for electrons using exchange-correlation functionals to predict electronic structure and properties from first principles. Molecular Dynamics (MD) simulations integrate Newton's equations of motion for thousands of atoms to study dynamic processes and thermal properties. Monte Carlo methods use statistical sampling to explore configuration space and study equilibrium properties efficiently. EAM potential has been particularly successful for modeling copper, capturing many essential features of metallic bonding, including its many-body character. The total energy in the EAM is expressed as [83]:

$$E_{\text{total}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{ij} \phi_{ij}(r_{ij}) \quad (11)$$

where (F_i) is the embedding energy function, (ρ_i) is the electron density at atom i due to all other atoms, and (ϕ_{ij}) is the pair potential between atoms (i) and (j) . Highly optimized EAM potentials for copper accurately reproduce properties including lattice parameter, elastic constants, vacancy formation energy, and stacking fault energy. More sophisticated interatomic potentials, such as the modified embedded-atom method (MEAM) and angular-dependent potentials, offer improved accuracy, particularly for nonequilibrium structures and surfaces, at the cost of increased computational complexity. Quantum-mechanical methods based on DFT provide even greater accuracy but are limited to smaller systems due to their computational demands [84]. Monte Carlo methods complement MD simulations by efficiently sampling configuration space, particularly for phenomena involving rare events or longer time scales. Kinetic Monte Carlo (KMC) simulations have been applied to study diffusion, precipitation, and recrystallization processes in copper, bridging the gap between atomic-scale events and microstructural evolution [85].

9.2 Electronic structure calculations

First-principles calculations based on DFT have provided fundamental insights into copper's electronic structure and its relationship to various properties. These calculations solve the quantum mechanical equations for electrons without employing empirical parameters, offering predictive capability for properties that derive directly from electronic structure [86]. DFT calculations have accurately reproduced copper's band structure, density of states, and Fermi surface, confirming the importance of the filled 3d band and its position relative to the Fermi level. These electronic structure features directly influence properties including electrical conductivity, thermal conductivity, and optical response [87]. The treatment of electron correlation effects in copper requires careful consideration of exchange-correlation functionals. While the local density approximation (LDA) and generalized gradient approximation (GGA) provide reasonable results for many properties, more sophisticated approaches such as hybrid functionals or GW methods may be necessary for accurate descriptions of spectroscopic properties or strongly correlated states [88]. Recent

advances in computational methods have enabled first-principles calculations of transport properties in copper. The combination of DFT with Boltzmann transport theory has yielded predictions of electrical conductivity and thermoelectric properties that agree well with experimental measurements. Additionally, time-dependent DFT (TDDFT) calculations have provided insights into copper's optical properties and plasmonic response [89]. Maier et al. (2019) utilized density functional theory calculations together with the nonequilibrium Green's functions approach to investigate the influence of alloying on the electronic transport properties of copper. Their research revealed how impurities affect the electronic transmission and conductance, showing that higher impurity concentrations generally lead to lower electronic transmission compared to pure copper [90].

9.3 Multiscale modeling approaches

Bridging the gap between atomic-scale processes and macroscopic behavior requires multiscale modeling approaches that connect different length and time scales. For copper, these approaches have been particularly valuable in understanding mechanical behavior, microstructural evolution, and property development during processing [91]. Dislocation dynamics (DD) simulations model the collective behavior of dislocations at the mesoscale, typically spanning lengths of micrometers and times of microseconds to milliseconds. These simulations capture essential aspects of copper's plastic deformation, including work hardening, size effects, and strain localization, by tracking the motion and interaction of large numbers of discrete dislocations [92]. Phase field models describe microstructural evolution in copper and its alloys, including grain growth, recrystallization, and phase transformations. By representing interfaces as diffuse rather than sharp boundaries, these models efficiently capture complex morphological changes driven by interfacial and bulk free energy minimization [93]. Crystal Plasticity Finite Element Method (CPFEM) models integrate crystallographic slip mechanisms into continuum mechanics frameworks, enabling prediction of texture evolution, localized deformation, and anisotropic mechanical response in polycrystalline copper. These models have proven particularly valuable for simulating forming operations and predicting property anisotropy in processed copper products [94].

Computational thermodynamics and kinetics, often implemented through the Calculation of Phase Diagrams (CALPHAD) approach, enable the prediction of phase equilibria, diffusion processes, and microstructural evolution in copper alloys. These methods provide essential inputs for process design and alloy development, connecting composition, processing, microstructure, and properties [95].

9.4 Simulation of electron movement and thermal transport

Atomic-level simulations of electron transport in copper provide insights into conductivity mechanisms beyond what is possible with classical approaches. Time-dependent quantum mechanical simulations have revealed how electrons interact with lattice vibrations (phonons) and defects, leading to a detailed understanding of scattering processes that limit conductivity [96]. Nonequilibrium Green's Function (NEGF) methods have been applied to model quantum transport in copper nanostructures, capturing effects such as quantized conductance and ballistic transport that become important at the nanoscale. These simulations have implications for copper's role in nanoelectronics and quantum devices [97]. Molecular dynamics

simulations using appropriate interatomic potentials can model thermal transport in copper through the direct calculation of heat fluxes and application of the Green-Kubo relations. These simulations have demonstrated how phonon scattering from defects, interfaces, and other phonons determines thermal conductivity across different temperature ranges [98]. Ab initio Molecular Dynamics (AIMD), which combines MD with electronic structure calculations, provides the most accurate description of the coupled dynamics of electrons and ions in copper. Although computationally intensive, AIMD simulations have offered unique insights into temperature-dependent properties, including electrical resistivity and the phonon frequency spectrum [99]. Researchers combined experimental measurements with first-principles simulations to investigate copper's electrical conductivity under extreme conditions. Their computational approach accurately captured how pressure and temperature affect copper's electronic structure and transport properties, demonstrating the predictive power of modern simulation techniques [41, 100].

10. Structure: Property relationships

10.1 Electronic structure-conductivity relationships

The relationship between copper's electronic structure and its exceptional electrical and thermal conductivity properties represents one of the clearest examples of structure-property connections in materials science. The specific features of copper's electronic configuration, particularly its filled 3d band and single 4s electron, create ideal conditions for electron transport [101]. Copper's high conductivity stems from a combination of factors: a high concentration of conduction electrons (one per atom), low effective mass of these electrons due to the nearly free-electron-like 4s band, and relatively weak electron-phonon coupling. This combination results in a long mean free path for electrons, approximately 39 nm at room temperature [102]. Band structure calculations reveal that copper's Fermi surface consists primarily of s-p bands that cross the Fermi level, with the d bands fully occupied and residing just below the Fermi level. This arrangement minimizes d-band scattering while providing abundant conduction electrons, optimizing conditions for both electrical and thermal transport [103]. The relationship between electronic structure and conductivity is further evidenced by the behavior of copper alloys. Introduction of elements that disturb copper's electronic structure, particularly those that promote s-d hybridization or scatter electrons through size or valence effects, dramatically reduces conductivity. This understanding guides the development of copper alloys that preserve conductivity while enhancing other properties [104].

10.2 Crystal structure: Mechanical property relationships

Copper's crystal structure directly determines its mechanical behavior, particularly its outstanding ductility and malleability. The close-packed arrangement of atoms in the FCC structure facilitates dislocation movement along multiple slip systems, allowing for extensive plastic deformation without fracture [105]. The 12 independent slip systems in copper's FCC structure (formed by the combination of four {111} planes and three $\langle 110 \rangle$ directions on each plane) provide numerous pathways for plastic deformation. This abundance of slip systems ensures that at least five independent systems can be activated regardless of crystal orientation, satisfying the

von Mises criterion for homogeneous deformation [106]. The stacking fault energy (SFE) of copper—a direct consequence of its atomic bonding and crystal structure—influences dislocation behavior and deformation mechanisms. Copper's moderate SFE (approximately 45–78 mJ/m²) leads to partial dislocation separation of a few nanometers, promoting planar slip and contributing to its hardening characteristics [107]. Grain boundaries in copper, which separate regions of different crystallographic orientation, significantly affect mechanical properties through various mechanisms including dislocation pile-up (Hall-Petch strengthening), dislocation emission and absorption, and diffusional creep. The nature of these boundaries, whether special low-energy configurations or general high-angle boundaries, further modulates their influence on mechanical behavior [108].

10.3 Defects-property correlations

Crystal defects in copper establish direct correlations with various properties, creating opportunities to engineer performance through defect control. Point defects such as vacancies and impurities primarily affect diffusion rates and electrical conductivity, while line and planar defects dominantly influence mechanical properties [109]. The density and distribution of dislocations in copper directly correlate with its strength and work hardening behavior. As dislocation density increases from 10¹⁰ m⁻² in annealed material to 10¹⁵ m⁻² in heavily deformed copper, yield strength can increase by a factor of 3–4 through the mechanism of dislocation-dislocation interactions [110]. Grain size and grain boundary characters establish strong correlations with both mechanical and physical properties. The Hall-Petch relationship quantifies the strengthening effect of grain refinement, while the proportion of special boundaries influences intergranular corrosion resistance, creep behavior, and electrical conductivity [111]. Experimental and computational studies have elucidated quantitative relationships between specific defects and resulting property changes. For example, the electrical resistivity contribution from dislocations in copper is approximately (1.1–1.3) × 10⁻⁸ Ω·m per dislocation, allowing precise prediction of conductivity changes resulting from plastic deformation [30]. Kogure et al. (2006) investigated the mechanical response of point defects in copper using molecular dynamics simulations with an embedded-atom method potential. Their research revealed how interstitials interact with elastic vibrations and contribute to internal friction, providing insights into the atomic-level mechanisms underlying copper's mechanical damping behavior [110].

10.4 Processing-structure-property linkages

The processing-structure-property paradigm provides a framework for understanding how manufacturing methods influence copper's atomic and microstructural features, which in turn determine its performance characteristics. Various processing routes, including casting, deformation processing, heat treatment, and powder metallurgy, create distinct structural features that directly affect properties [112]. Deformation processing of copper, through techniques such as rolling, drawing, or extrusion, increases dislocation density and potentially introduces deformation twins, resulting in strength enhancement through work hardening. The development of crystallographic texture during these processes also induces property anisotropy, with electrical conductivity and elastic modulus varying with direction relative to the processing orientation [113]. Heat treatment processes, including recovery,

recrystallization, grain growth, and precipitation, modify copper's defect structure and phase constitution. Annealing of cold-worked copper reduces dislocation density and internal stress, decreasing strength but enhancing ductility and electrical conductivity. Precipitation heat treatments in copper alloys create dispersed particles that obstruct dislocation movement, increasing strength while typically reducing conductivity [114]. Powder metallurgy and additive manufacturing processes for copper components introduce unique structural features, including fine grain sizes, porosity, and oxide inclusions. These features create distinctive property combinations that can be advantageous for specific applications, such as high strength with controlled electrical conductivity or enhanced damping capacity [115]. Li et al. (2016) demonstrated a processing strategy to balance strength and electrical conductivity in copper alloys by introducing precipitated particles into a structure composed of deformation twins. By dissolving zirconium into the copper matrix through solution treatment before cryorolling and precipitating it during subsequent aging, they achieved superior tensile strength (602 MPa) while maintaining high electrical conductivity (81.4% IACS) [116].

11. Technological applications and future developments

11.1 Current applications leveraging atomic structure

Copper's unique atomic structure and resulting properties have made it indispensable in numerous technological applications, each exploiting specific aspects of its structure-property relationships. Electrical and electronic applications leverage copper's exceptional conductivity, which stems directly from its electronic configuration and crystal structure [117]. In electrical power transmission and distribution, copper conductors efficiently transport electricity with minimal losses. The delocalized electrons from copper's 4s orbitals move readily through the FCC lattice, enabling current densities that would cause rapid heating in less conductive materials. High-performance motors and generators similarly depend on copper's conductivity for efficient energy conversion [118]. Thermal management applications exploit copper's high thermal conductivity, which shares the same structural origin as its electrical conductivity, free electrons efficiently transport energy through the crystal lattice. Heat sinks, heat exchangers, cooling systems in electronics, vehicle radiators, and HVAC equipment rely on copper's ability to rapidly conduct heat away from critical components [119]. Antimicrobial applications utilize copper's ability to release Cu and Cu ions, which can disrupt cell membranes and destroy bacteria, viruses, and fungi. This ability derives from copper's electronic structure and oxidation behavior. Touch surfaces in healthcare facilities, public transportation, and food preparation areas increasingly incorporate copper for its self-sanitizing properties [120].

11.2 Emerging materials based on copper's atomic structure

Advanced copper alloys and composites designed at the atomic level are expanding the material's application range by enhancing specific properties while preserving its essential characteristics. Precipitation-strengthened copper alloys achieve high strength while maintaining good electrical conductivity through careful control of precipitate size, distribution, and coherency with the copper matrix [121]. Nanostructured copper materials, including nanocrystalline and nano-twinned

copper, exhibit exceptional combinations of strength and electrical conductivity by exploiting the distinctive properties of nanoscale structural features. Nano-twinned copper, for example, achieves ultrahigh strength through twin boundary strengthening while maintaining high conductivity because twin boundaries cause minimal electron scattering compared to grain boundaries [122]. Copper-based metal matrix composites incorporate reinforcing phases such as carbon nanotubes, graphene, ceramic particles, or refractory metal fibers to enhance specific properties, including mechanical strength, wear resistance, thermal stability, and reduced thermal expansion. These composites find applications in electrical contacts, heat sinks, and wear-resistant components [123]. Copper-based shape memory alloys, particularly Cu-Al-Ni and Cu-Al-Mn systems, exploit specific atomic-level phase transformations to achieve reversible shape changes in response to temperature or stress. These materials offer lower-cost alternatives to Ni-Ti alloys for applications in actuators, sensors, and medical devices [124].

11.3 Computational design of novel copper materials

Computational materials design is revolutionizing the development of copper-based materials by enabling the prediction of properties based on atomic and electronic structure before physical synthesis. High-throughput computational screening of copper alloy compositions identifies promising candidates with targeted property combinations, accelerating the discovery of new materials for specific applications [125]. Machine learning approaches combined with computational modeling enable the exploration of vast composition-processing-structure-property spaces to identify optimal copper alloys for requirements. These techniques have led to the development of novel copper alloys with previously unachievable combinations of strength, conductivity, and thermal stability [126]. Integrated computational materials engineering (ICME) frameworks link atomistic, microstructural, and continuum models to predict how processing conditions affect copper's structure and properties across multiple length scales. These frameworks guide the optimization of manufacturing processes to achieve desired performance characteristics with reduced development time and cost [127]. Quantum mechanical modeling of electron transport in copper nanostructures and interfaces enabling the design of next-generation interconnects and quantum devices with enhanced performance. These models account for quantum confinement effects, surface scattering, and interface phenomena that become dominant at the nanoscale [128].

11.4 Future directions and challenges

Future developments in copper-based materials will likely focus on addressing several key challenges through atomic-level engineering. Enhancing the stability of copper's structure and properties at elevated temperatures remains a significant challenge, particularly for applications in increasingly powerful and compact electronic devices, electric vehicles, and sustainable energy systems. Balancing competing properties—particularly strength and conductivity—continues to drive innovation in copper alloy design. Computational modeling combined with advanced processing techniques promises further improvements in this balance by creating optimized microstructures with minimal electron scattering [129]. Sustainability considerations are increasingly influencing copper materials development, with a focus on recyclability, reduced energy consumption in processing, and minimized

use of critical or environmentally problematic alloying elements. These challenges require an atomic-level understanding of how alternative elements and processing routes affect copper's structure and properties [130]. Integration of copper with emerging materials systems, including semiconductors, two-dimensional materials, and quantum materials, presents opportunities and challenges related to interfaces, diffusion barriers, and thermal management. Atomic-level control of these interfaces will be critical for next-generation electronic and quantum technologies [131]. The continued development of in situ and operando characterization techniques, coupled with advanced computational modeling, promises a deeper understanding of copper's dynamic behavior during processing and in service. These insights will enable more precise control of copper's structure and properties for increasingly demanding applications across multiple technology sectors [132].

12. Conclusion

This chapter has provided a comprehensive review of copper's atomic structure and its direct influence on macroscopic qualities that have made this metal indispensable throughout human history and modern technology. Beginning with copper's electronic configuration ($3d^{10}4s^1$), we have investigated how its single valence electron in the 4 s orbital creates optimal circumstances for electrical and thermal conductivity when combined into copper's face-centered cubic crystal structure. The nature of metallic bonding in copper, characterized by delocalized electrons forming a "sea" around positively charged ions, directly enables its excellent electrical conductivity (5.96×10^7 S/m) and thermal conductivity (401 W/(m·K)). This electronic structure also contributes to copper's distinctive reddish hue and its chemical behavior, including its many valence states and corrosion properties. Copper's high ductility and malleability derive from its FCC crystal structure, which provides 12 separate slip systems that promote dislocation movement during plastic deformation. The modest stacking fault energy of copper (45–78 mJ/m²) maintains a balance that allows for significant plastic deformation while maintaining work hardening capacity, making copper ideally suited for forming processes. Crystal flaws, including point defects, dislocations, and grain boundaries, significantly influence copper's characteristics. Understanding and managing these flaws through processing is crucial to designing copper materials with specific property combinations. Advanced computer models now provide unparalleled insights into how these flaws arise, interact, and alter characteristics at the atomic level [133]. The structure-property correlations revealed in this chapter serve as the foundation for designing innovative copper-based materials with increased performance characteristics. Continued advancements in computational modeling, characterization techniques, and processing methods promise additional advances in copper materials for applications ranging from electrical transmission and thermal management to antimicrobial surfaces [134] and quantum technologies [135]. By establishing explicit linkages between atomic-level occurrences and macroscopic features, this chapter gives a theoretical foundation crucial for analyzing copper's technological uses and directs the creation of next-generation copper materials. As demands for higher-performance materials continue to expand across different sectors, atomic-level engineering of copper will remain an interesting and crucial subject of research and development.

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Section 2

Metallurgical Operations

Sustainable Technologies in the Synthesis, Sintering and Recycling of Copper Compounds

Daniel Fernández-González

Abstract

Copper has been and remains a key metal for societies throughout history: From the first utensils used to prepare food to the special alloys for space applications, passing through the massive utilization of this metal in power transmission. In fact, the production of copper has increased in the last decades to around 27 Mt in 2024, which is almost twice the production in 2004 (14.5 Mt). This emphasizes the growing importance of this metal, particularly in the electrification of societies. Nevertheless, different sectors are demanding copper products, sometimes in the form of composites, with improved properties for advanced applications. Within this context, new emerging fabrication technologies are being investigated to achieve these improved functionalities while enhancing productivity and considering sustainability as a key factor. As novel technologies, this chapter considers cold sintering, spark plasma sintering, and laser sintering. Finally, a step further in copper metallurgy sustainability involves the utilization of environmentally friendly technologies, such as concentrated solar energy utilization, which is the second part of this chapter.

Keywords: copper, spark plasma sintering, cold sintering, solar energy, laser

1. Introduction

Copper is an essential metal for humanity, valued for its high ductility, malleability, thermal and electrical conductivity, as well as its resistance to corrosion in specific environments. These characteristics make copper widely utilized in various electrical applications, including power transmission, generation, building wiring, and telecommunications, which collectively account for approximately three-quarters of overall copper consumption. Additionally, copper plays a significant role in construction (such as plumbing and roofing), medical applications (including diagnostic devices), and agriculture. As a result, copper production reached 23 million tons in 2024, based on mine production, and 27 million tons when including refined copper, which also accounts for recycled material, according to data from the United States Geological Survey. The production of copper has significantly increased in the last decades due to the increasing demand

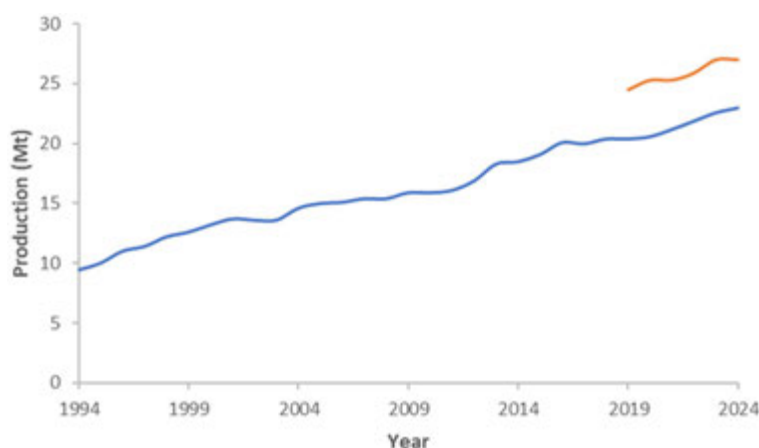


Figure 1.

This figure describes the copper production in the last 30 years. On the one hand, the blue line represents the production of copper in terms of copper mine concentrates. On the other hand, the orange line represents the copper production from the refinery (which includes the recycled copper).

resulting from the electrification of society. It is important to consider the importance of copper production from refineries because it indicates the copper obtained from mine concentrates but also the recycled copper. It is possible to see in **Figure 1** how copper production has changed in the last 30 years.

As previously reported, copper is a fundamental metal in the electrification of societies due to its applications in wiring, motors, and various components. In this regard, the International Copper Association projects that copper demand will reach approximately 50 million tons by 2050, nearly doubling the levels expected in 2024. Companies are particularly interested in high-grade ore mines, as they offer richer returns. However, it is anticipated that high-grade resources will experience a gradual decline [1]. For instance, well-known copper mines such as Bingham Canyon (USA), El Teniente (Chile), and Mt Lyell (Australia) are showing a noticeable decrease in ore grade [2]. In the 2010s, the average mined ore grade for copper was around 0.62% Cu [3], while recent data indicates that this average has fallen to between 0.4% and 0.8% Cu [4]. The International Energy Agency also reports that from 2005 to 2019, the average copper ore grade in Chile, based on production route, ranged from 1.1% to 0.8% (concentrate), further illustrating the ongoing reduction in copper ore grade. Within this context of depletion of high-grade copper ores, the extraction of copper from secondary ores or residues is gaining importance.

On one hand, there is an increasing demand for new features in materials, and, in the case of copper-based materials, the situation is no different. Within this context, it is possible to observe the implementation of new processing technologies that allow for reducing sintering cycles or maintaining a more precise control over grain size. This is, for instance, the case with cold sintering or spark plasma sintering (SPS). On the other hand, other technologies, such as laser sintering, allow for the progressive introduction of additive manufacturing technologies in the fabrication of copper parts. In this way, this chapter focuses, in the first part, on reviewing the application of these agglomeration technologies in the fabrication of copper-based parts.

On the contrary, sustainability is fundamental in the advancement of societies and in reducing the environmental impact of various processes. Despite the fact that some of the above-reported technologies can contribute to reducing the environmental impact by shortening processing times, the utilization of a renewable energy source seems to be the most attractive alternative. In this regard, the second part of the chapter emphasizes the utilization of concentrated solar energy in various processes of copper metallurgy.

2. Cold sintering

The Randall group at Pennsylvania State University (Penn State) has developed, in recent years, the cold sintering process (CSP; first publications in 2016) [5–7]. The premise of this low-temperature sintering process was demonstrated by the preparation of a large number of ceramics (more than 50 inorganic compositions, including binary, ternary, and even some quaternary and quinary compounds) and composites (ceramic/polymer, ceramic/ceramic). In CSP, the starting powder is mixed with a small amount of liquid (1 to 10 vol.%), and the sintering is performed at a temperature below 300°C and under a uniaxial pressure of up to 500 MPa. This process allows ceramic powders to be sintered in short times (15 to 60 minutes) and to reach densities of the order of 80% to 99% of the theoretical [5–7].

Investigations involving copper, copper compounds, or copper alloys using cold sintering are limited in number due to the novelty of the technique. Computer-aided analysis tools were applied to compare the results obtained in the high-pressure consolidation of bimetallic nanoparticles composed of two immiscible metals – Fe and Cu – using cold sintering, atomistic molecular dynamics simulations, and the embedded atom method [8]. They analyzed the effect of cold-sintering parameters on the structure, density, and topology of the Fe–Cu nanocomposites, obtaining dependences that are in good agreement with the experimental data. Other researchers used the cold sintering technique to avoid changes in grain size and orientational effects in the ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO), which is important in this material for the critical current density that is strongly dependent on the orientation [9]. On another note, the densification occurs at 180°C, while it occurs at 1,000°C in the solid-state method, maintaining an orientational behavior. Other composites were also prepared by cold sintering: $(1-x)\text{Na}_2\text{WO}_4-x\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ (NWO-NCZO), where $x = 0-0.6$ [10]. For reference, cold sintering conditions consisted in an applied uniaxial pressure of 200 MPa at 150°C for 30 minutes. The sintered composite exhibited good properties to be used in miniaturized antennas.

There were some other compounds fabricated; for instance, bulk Cu_2Se was prepared by a liquid-phase-assisted CSP, reporting a dense sample (90%) at a low sintering temperature (200°C) [11]. The sintered specimen exhibited inhibited grain growth, which translated into ultralow thermal conductivity. Moreover, the thermoelectric properties were improved compared to the hot-pressed sample, being more than three times greater in the cold-sintered sample [11]. Other researchers also focused on obtaining dense components of CuO [12]. These researchers employed CuO nanoparticles that were sintered under a pressure of 400 MPa at temperatures ranging from 150°C to 300°C for 30 minutes, reporting values of relative density >81.9%, which is greater than that achieved by the non-CSP. Afterward, annealing at a temperature of 750°C increased the relative density above 90%. These samples

exhibited a giant dielectric permittivity under these sintering conditions, which was not observed in the case of samples fabricated by conventional methods [12].

Another application of cold sintering involving copper is the preparation of ceramic substrates with a copper layer, which has reported good results [13]. It is possible to see from these investigations the potential fields where the cold sintering technique might find future applications. Nevertheless, cold sintering investigation is still at the laboratory scale. Advancing in the Technology Readiness Levels is still challenging due to several reasons, which include understanding the sintering mechanisms, restrictions in materials to be consolidated (it is necessary to employ materials with high solubility), difficulties in ensuring good mechanical properties (sometimes specimens of this material exhibit lower toughness than conventional parts), the complexity of ensuring microstructural homogeneity, concerns about the removal of residual additives or the presence of superficial degradation. Moreover, cold sintering parts sometimes require post-processing treatments to ensure good final properties. Scaling also faces some other problems related to the management of transient liquid evaporation, the achievement of uniform densification, limitations in terms of productivity, or the requirements of equipment to produce discs of greater diameter: the pressure applied to the sample is inversely related to the area in such a manner that increasing the area of the sample requires increasing the force applied by the machine to provide the same pressure to the sample (increasing the force requires more expensive equipment).

3. Laser sintering

Laser sintering has also been applied to the sintering of copper, particularly in combination with 3D printing, although it is necessary to make a distinction between selective laser sintering (which is based on the sintering of powders, meaning that the melting of the powders is not produced) and selective laser melting (which involves melting the powder material to obtain dense components). In this context, printing circuits is a promising research area. An example of this is the fabrication of copper wire electrodes for glucose quantification by combining fusion deposition modeling (FDM) 3D printing and laser sintering (LS) [14]. This was not the only investigation in this area; other researchers have proposed employing laser sintering to fabricate low-cost and reliable flexible printed electronic devices [15].

Apart from these investigations in the field of printed circuits, laser sintering has been applied to sinter copper and copper-based alloys for rapid tooling [16]. This topic has been widely studied in the literature, varying the different parameters. The objective was to obtain sound parts with suitable properties for the considered application. An example was the investigation by Chinese universities, which attempted to overcome the problems related to the poor optical absorptivity (high reflectivity) in the near-IR wavelength and the high thermal diffusivity of pure copper, making sintering copper for heat sinks and exchangers complicated [17]. In this context, only 10% of the beam energy was absorbed during printing, making the densification of pure copper parts difficult [17].

Laser sintering has been applied in other applications. This includes the fabrication of electrical discharge machining (EDM) electrodes with improved properties in terms of wear rate. It also includes the manufacturing of TiB₂ and TiC reinforcement particulates in a Cu matrix for EDM electrodes [18]. Other copper

compounds were also sintered using laser technologies, that is, tin–copper composites with strength and ductility comparable to high-porosity materials produced using other techniques, although for other applications [19].

On another note, the fabrication of complex copper parts for thermal structures is another of the objectives of three-dimensional (3D) printing and laser sintering, but it represents a challenge due to the above-reported problems of copper's high optical reflectivity. Researchers have managed to obtain complex-shaped copper parts with values of relative density of 95% and low surface roughness, reporting values of thermal conductivity above $350 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is close to the value obtained by conventional powder metallurgy methods [20]. Regarding the complexity and advances in the printing of 3D parts of pure copper, the following review reports the investigations conducted in this line [21], and it is possible to see that complex-shaped parts can be achieved using this technology, leading to potential applications in induction heat coils [22] or complex heat exchangers [23].

Other investigations conducted in this line include producing near-net-shape components of Cu–Ni alloy having low porosity levels and superior mechanical properties, while providing good behavior in terms of corrosion resistance in seawater conditions [24]. Other investigated composites include copper–zirconium–boron (Cu–Zr–B) for applications in aerospace engineering, military, electronics, and nuclear complexes due to their extraordinary characteristics in terms of mechanical, thermal, and electrical properties, including suitable chemical stability [25].

4. Spark plasma sintering

Sintering copper and copper compounds using the SPS technique has been widely reported in the literature [26]. This can be explained by the specific features associated with this technology, mainly the operation under vacuum or controlled atmosphere, the applied pressure, or the fast heating and cooling rates achieved with Joule heating. Within this context, the fundamentals of SPS involve applying pulsed DC or AC current directly through a conductive die containing the powder, inducing Joule heating predominantly within the powder particles and/or the die (see **Figure 2**). The following parameters are the main ones used in the SPS technology:

Pressure, which usually ranges from a few MPa to around 100 MPa (in the case of using graphite utensils), assists particle rearrangement and plastic deformation, leading to higher densification.

- Temperature and heating rate. SPS enables rapid heating (up to hundreds of °C/min) and maximum temperatures above 2,500°C. Sintering occurs at temperatures significantly lower than those required in conventional sintering due to the combination of temperature, pressure, and vacuum conditions. Grain coarsening is minimized, allowing a very fine-grained microstructure if the initial powders are fine.
- Dwelling time: Short dwell times (minutes) minimize grain growth while ensuring adequate densification.

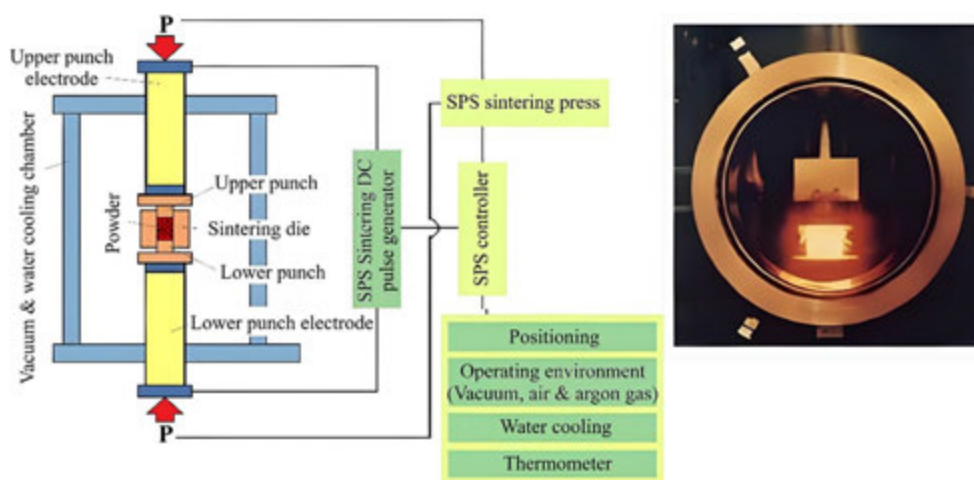


Figure 2.

The figure on the left side provides a scheme of the spark plasma sintering equipment. On another note, the figure on the right side provides a real image of the vacuum chamber [27].

- **Electrical parameters:** The current pulsing pattern, magnitude, and waveform influence local heating, plasma formation, and possibly spark discharge effects, which can enhance diffusion and impurity removal.
- **Die and tooling:** Typically, graphite molds and dies are used, but it is possible to employ other utensils, allowing different conditions of sintering. Material choice and design impact uniform heating and stress distribution.

In the case of copper, many different copper alloys have been studied using SPS technology: Cu–Zn (brass), used in construction, electrical, and other sophisticated applications due to its ductility, machinability, and electrical conductivity [28]; Cu–Al–Ni, a shape memory alloy [29]; and Cu–Pb, an alloy widely employed in engineering applications as bearings [30]. Many other different copper alloys were studied employing SPS technology: Ti–Cu [31], Cu–W [32], Cu–Nb–graphite [33], Cu–Ti–Ni [34], Cu–Al [35], or Cu–TiB₂ [36], among others. Apart from the alloys, metallic copper was also spark plasma sintered, reporting better results in terms of mechanical properties than other techniques like hot pressing [37].

One of the topics of greater interest involving copper and SPS technology is the fabrication of composites for heat dissipation, either as individual parts or for use in other engineering applications where tribological properties are necessary. Researchers are studying the densification of copper-10 wt.% graphite composites with 2 wt.% Al in the SPS apparatus at temperatures as low as 600°C [38]. It is precisely the self-lubricating properties of graphite combined with the thermal conductivity of copper that make this a promising research line. Polish researchers investigated Cu-graphite composites (15–80 vol.% graphite), reporting that 15 vol.% is the critical graphite concentration required to achieve a suitable coefficient of friction, supported by the lubricant properties of graphite [39]. Other authors studied the incorporation of graphite flakes, reporting greater relative density and electrical conductivity compared to conventional methods, while maintaining an

acceptable friction coefficient and wear rate [40]. Additionally, other researchers reported very high directional thermal conductivity values in studies of composites with 20–60 wt.% Cu, highlighting the potential advantages of this type of composite not only for the self-lubricating properties of graphite but also for thermal conductivity applications [41]. Finally, composites incorporating a third phase, that is, WS₂, for thermal conductivity and tribological applications are also a hot topic in terms of investigation [42].

5. Concentrated solar energy

Solar energy is an attractive technology for the fabrication of materials due to the high temperatures that can be reached when it is adequately concentrated using lenses and mirrors. Apart from the high temperatures, it is possible to mention some other advantages related to the utilization of controlled atmospheres (inert, vacuum, reductant, or ambient atmospheres), the zero pollutant emissions (pollutants are only related to the process being conducted and not to the energy source employed to reach the temperature required for the process), or the price (the energy is free, although the technology employed to reach the temperature is not). Nevertheless, solar energy faces some problems or disadvantages related to weather conditions and the day-night cycles. Moreover, concentrated solar energy applications in the field of materials also face problems related to the maturity of the technology: there are no studies at the pilot plant scale to evaluate productivity over long periods, that is, one year of continuous operation under real conditions.

The utilization of concentrated solar energy in the field of materials dates back to the Roman period, when Archimedes employed concave mirrors to sink the Roman Army during the Siege of Syracuse (213–212 BC, Second Punic War). Regarding investigations, Ehrenfried Walter von Tschirnhaus worked with lenses and mirrors to concentrate the energy of the sun, melting iron and obtaining ceramics (porcelain). In the Modern Period, too, Antoine Lavoisier, considered the father of modern chemistry, established the Law of Conservation of Mass (“nothing is lost, nothing is created, everything is transformed”) using solar-based technology. Using large lenses to concentrate solar energy (see **Figure 3**), Lavoisier studied combustion and other changes, proving that mass remains constant even when substances change form (like wood burning to ash, gas, and water vapor). These experiments also served to demonstrate that special atmospheres can be used in the treatment of materials with concentrated solar energy.

After a long period without investigation in this field, following World War II, Felix Trombe restarted these investigations in France together with Marc Foex and Charlotte Henry La Blanchetais. Initially, they conducted the investigations in Meudon (a 2-kW parabolic concentrator) and later in Mont-Louis (a 50-kW solar furnace), focusing on achieving the melting of high melting point refractory ceramics, such as alumina, chromium oxide, or zirconia, among others [43]. As a result of these research efforts, the solar furnace of Odeillo was constructed during the period 1962–1968 and began operation one year later, where it became possible to operate solar furnaces of different power levels (0.9 kW, 1.5 kW, 6 kW, and 1000 kW). The Odeillo solar furnace, located in Font-Romeu-Odeillo-Via (France), belongs to PROMES (Procédés, Matériaux et Énergie Solaire), CNRS, Centre National de la Recherche Scientifique.

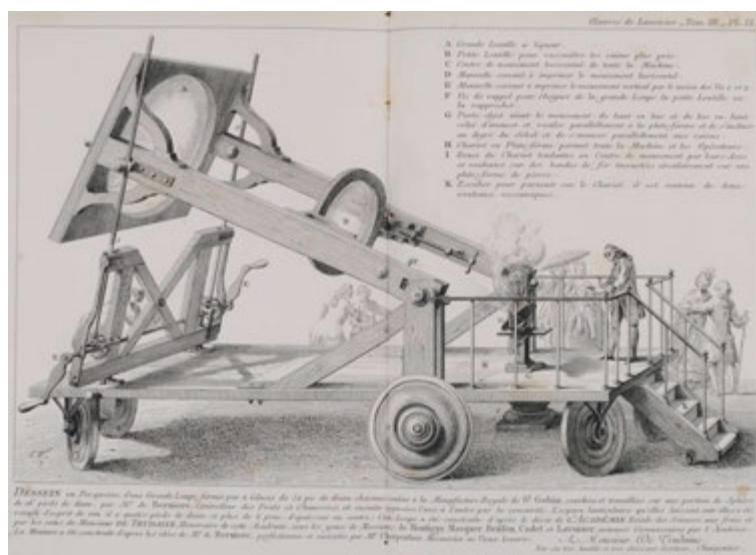


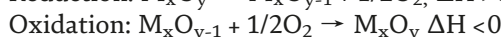
Figure 3.
Lavoisier's solar furnace.

The investigation into the utilization of solar energy in the field of materials has encompassed different topics: metallurgy, ceramics, materials processing, or valorization of residues [44, 45]. Among these topics, some lines have reached a larger development. It is possible to mention the following ones:

- Metal fuels, which are recyclable energy carriers with high energy density, can be burned with air or reacted with water to release chemical energy. In this context, concentrated solar energy is employed to regenerate the metal after it has been burned. Different chemical loops have been studied: $\text{CeO}_2\delta/\text{CeO}_2$ [46], $\text{Fe}_3\text{O}_4/\text{Fe}$ [47], SnO_2/SnO [48], $\text{Mn}_2\text{O}_3/\text{MnO}$ and MnO_2/MnO [49], CaCO_3/CaO [50], $\text{Co}_3\text{O}_4/\text{CoO}$ [51], MgO/Mg [52], and $\text{Al}_2\text{O}_3/\text{Al}$ [53]. Nevertheless, the pair $\text{ZnO}-\text{Zn}$ is probably the most successful technology based on solar energy within the field of materials, as it has reached the pilot plant scale [54] (TRL 5–6?).
- Cement, particularly the calcination of limestone [55], although Portland clinker was produced [56], as well as other varieties of cement, such as calcium aluminate cement [57].
- Refractory hard carbides, from nitrides to carbides: silicon carbides and/or nitrides [58], tungsten carbides and/or nitrides [59], titanium carbides and/or nitrides [60], or molybdenum nitrides and/or carbides [61], among others.

Despite the largest developments regarding the utilization of concentrated solar energy in the field of materials being found in the above-reported topics, research has reached many other different fields. In this section, the investigation focused on copper is described.

Regarding thermochemical storage, copper oxide has been proposed as a valid metal oxide. Chilean and Mexican researchers studied the performance of CuO reduction in a rotary kiln under an argon atmosphere and the cyclability of the CuO/Cu₂O pair in air [62]. This redox pair of metal oxides has been proposed as a promising alternative for thermochemical energy storage at high temperatures. The system employs cycles of reduction and oxidation (redox) reactions to store and release heat:



Therefore, the system is based on cycles of reduction and oxidation (redox), where reactions are used to store and release heat. The temperature of operation depends on the redox pair, but it usually ranges between 623 and 1,373 K. In the case of the copper oxide pair (CuO/Cu₂O), re-oxidation of Cu₂O takes place at a temperature significantly lower than the equilibrium transition. This capacity provides flexibility in the design and operation of the storage system, with the theoretical transition temperature being 1,120°C in air and the storage density being 811 kJ/kg.

Alonso et al. [62] conducted the experiments in the rotary solar reactor installed at the HoSIER solar furnace in IER-UNAM (Renewable Energy Institute of the National University of México). The conversion reached almost 80% when reducing CuO in an argon atmosphere, while in air, after several cycles of reduction and oxidation, they observed that reduction was disfavored by the presence of air in comparison to argon. Moreover, the stronger coalescence of the particles resulted in a handicap for the progression of the redox reactions. Additionally, conversion was lower for oxidation than for reduction. Despite the potentially promising results, it is necessary to optimize several of the operational parameters, including rotational speed, particle size, gas flow, and initial mass of reactant.

Apart from the utilization of copper compounds in chemical loops for energy storage, concentrated solar energy has also been used to produce metallic copper. This is an interesting alternative to reduce energy costs and environmental impact in copper metallurgy. It is important to consider that copper metallurgy is based on the sulfides of copper. Therefore, the main research line in this topic has consisted of the dissociation of copper sulfides into metallic copper and sulfur. In this way, the production of copper would be conducted without carbon dioxide emissions, nor with sulfur dioxide release. The first investigations in this line date back to the early 2000s when Guesdon and Sturzenegger [63] reported that solar energy could be employed to extract Cu from Cu₂S. In this route, metallic copper is obtained at 1,323 K, and it is possible to easily separate copper from S₂ (g). This research line was further explored by other authors such as Winkel et al. [64], and Winkel et al. [65]. A detailed study by Winkel et al. [66] in a solar simulator at the Paul Scherrer Institute with copper sulfide concentrates quantified the extent of sulfur removal at high temperatures. This study reported information about the rates of sulfur volatilization, provided phase relations at high temperatures, and assessed the feasibility of separating metallic copper from the residual sulfide phases. This in-depth study revealed that after 330 seconds of irradiation under an argon atmosphere, 40% of the initial sulfur content was removed, and elemental copper was formed, highlighting the importance of operating with submillimeter particles for favorable results. Later on, Winkel et al. [67] conducted experiments with copper sulfide concentrates (chalcocite (Cu₂S), chalcopyrite (CuFeS₂), and enargite (Cu₃AsS₄), as well as two multiphase

copper concentrates) using a solar flux simulator at the Paul Scherrer Institute under an inert atmosphere at maximum temperatures of 1,773 K. The conditions of the experiments allowed for the removal of impurities, particularly heavy metal impurities, which could be efficiently separated under reduced oxygen partial pressures as proposed in these experiments.

Despite the potential interest of this technology at an industrial scale to reduce carbon dioxide emissions in copper metallurgy, the investigation did not progress beyond the laboratory scale. Anyway, Sturzenegger et al. [68] provided a detailed study on the potential solar extraction of copper through the direct decomposition of copper sulfides under an oxygen-free atmosphere. As potential zones for implementation, they suggested that the main copper mining districts located in Chile or Southern Africa are areas that receive sufficient sunlight radiation. From a numerical point of view, they proposed that 200 tons of copper might be produced with a thermal input onto the heliostat field ranging between 40 and 165 MW, leading to temperatures exceeding 2,000 K. The costs of production might be 30% lower than those of conventional production because SO₂ would not need to be processed, and an oxygen plant would not be necessary.

Solar energy has been proposed by other researchers as an instrument to make copper production more sustainable. For example, Cruz-Robles et al. [69] suggested that almost 20% of copper could be produced using solar-based systems due to the irradiation levels available in locations where copper metallurgical factories are currently found, reducing energy consumption by half through preheating the input blast with solar energy. This was also the proposal of Parra-Ramos [70], whose aim was to integrate a central tower system to supply energy for preheating the blast of an Outokumpu Flash Furnace. Going a step further, Moreno-Leiva et al. [71] identified 12 technologies involved in copper production where solar energy could be integrated. These technologies exhibit different degrees of maturity: the replacement of conventional electric power with solar-generated power is the most mature technology, as well as employing solar-thermal technologies in low-temperature processes. On the other hand, solar energy has the potential to replace conventional energy sources in almost every operation involved in copper production processes (except blasting), although the degree of maturity is still low. In this way, it is possible to see the potential importance of solar energy in copper metallurgy. Within this context, due to the importance of copper mining and metallurgy in Chile, other researchers have studied the implementation of solar energy in this country, considering the significance of copper metallurgy and the adequate irradiation levels. For instance, Chandia et al. [72] analyzed the implementation of solar thermal heating in each mining process and the generation of solar thermal electricity. Moreover, they proposed that flat plate collectors to heat water for mining operations (i.e., electrowinning) are an interesting option, while electric power could be supplied using solar-based technologies. Quiñones et al. [73] also conducted a detailed study on the use of three different solar collectors in the electrowinning process. Cuevas et al. [74] studied the integration of solar energy in copper electrowinning processes, based on concentrating and non-concentrating technologies, with promising results.

Apart from the potential integration of solar-based technologies in copper metallurgy, researchers, such as Moreno-Leiva et al. [75], evaluated the global warming potential (GWP) changes resulting from the integration of solar energy in copper metallurgy, reporting that GWP would be reduced by 63% and 76% for pyrometallurgical and hydrometallurgical routes, respectively, considering only that

solar energy was used to produce the electricity taken from the grid. Additionally, GWP reduction using solar technologies would be greater by means of the substitution of on-site fossil fuels.

Apart from the above-reported investigations, other researchers have proposed alternative processes to produce copper, such as the utilization of hydrogen reduction, although this alternative has limited interest due to the fact that the main copper ores are sulfides. Arenas et al. [76] proposed the reduction of copper (II) oxide with concentrated solar energy under a stream of 5–95 v/v H₂/N₂ at a pressure of 8 bar using a 1.5 kW vertical parabolic concentrator, with samples consisting of two types: powders and compacted specimens. Results (microstructure and corrosion behavior) suggested that the characteristics of the solar metal were similar to the commercial product, where, for instance, the reduction of CuO to elemental Cu was more effective for compacted specimens with an electrochemical behavior similar to that exhibited by the commercial metal. Regarding powdered specimens, a composite metal/oxide (Cu/Cu₂O) block was obtained as a macroporous material with different properties. An alternative research study, conducted by Yepsen et al. [77], suggested the possibility of photocorrosion of copper sulfides, although the copper leached using this procedure is still low (<15%). On another note, solar thermal energy has been employed in the heap bioleaching of chalcopyrite. The objective was to increase the temperature in the heap and enhance the extraction of copper [78].

Finally, from the applications of solar energy in the case of copper, it is possible to mention its utilization in the treatment of slags [79, 80], particularly copper slag [81]. The objective was to promote the dissociation of fayalite (Fe₂SiO₄) into iron oxides, particularly magnetite (Fe₃O₄), and silica (SiO₂), leading also to the liberation of copper, which might appear as occluded matte or in other forms. The reason for this investigation is that this type of slag contains up to 40% iron and 1%–2% copper. In this way, the sample becomes magnetic after the treatment with concentrated solar energy. Then, the sample was crushed and milled, and magnetic separation was applied, which resulted in copper concentrating (5%–10% Cu) in the non-magnetic fraction in the form of nodules with 65–85 wt.% Cu, and the non-magnetic fraction mainly comprising magnetite. Nevertheless, the sample consisted of a significant quantity of non-transformed fayalite.

6. Discussion

The synthesis and sintering techniques have a fundamental impact on the properties of the final product and, additionally, on the economic and environmental impacts. It is possible to find a comparison between the different technologies in **Table 1** [82–85]. Depending on the technology, it is reasonable to conduct different processes that provide different products with different characteristics, which are adequate for one or another application. For that reason, it is not rational to define a better or worse technology but a technique more or less acceptable for one or another application. Solar energy is included here due to its potential application in the sintering of materials, apart from in the synthesis.

In **Table 1**, the environmental impact is presented. The environmental impact is directly related to energy consumption. Considering that the energy consumed in each process is electric power, the environmental impact is associated with the

Parameter	Conventional sintering	Cold sintering	Spark plasma sintering	Laser sintering	Solar energy
Temperature (°C)	Up to 2,000	Below 400	Up to 2,600	Up to 2,000	Up to 3,500
Time	From several hours to days	Minutes, hours	Minutes	Depending on the part (powder bed melting).	Minutes
Pressure	Pressureless (starting from green compacts)	Up to 1 GPa	Up to 100 MPa in graphite utensils.	Pressureless (starting from powder bed)	Pressureless (starting from green compacts or powder bed melting)
Energy consumption	High	Very low	Moderate	Moderate	High
Environmental impact	High	Low	Moderate	Moderate	Very low
Densification mechanism	Thermal mechanisms (convection-radiation)	Solvent-assisted transport and pressure induced	Joule heating & electrical field activation	Thermal mechanisms	Thermal mechanisms
Grain growth avoidance	Poor	Excellent	Excellent	Limited	Depends on the technology (heating chamber or powder melting).
Scalability	Fully industrial	Limited	Scalable	Scalable	Limited (still not analyzed)
Productivity	Adequate	Limited	Limited	Limited	Limited
Cost of the equipment	Low	Low to moderate	Very high	High	High (it depends on the technology).
Materials to be treated	Ceramics, metals	Ceramics, metals, polymers, composites	Ceramics, metals	Ceramics, metals	To be studied in depth (current studies limited to metals and ceramics).
Microstructural control	Coarse grains	Fine-grained, minimal growth	Ultra-fine, nanostructured	Grain growth occurs	Depends on the technology (heating chamber or powder melting).
Key challenges	High energy demand, grain growth	Process control, solvent removal, scalability, post-annealing.	Expensive equipment, limited material choices	Economic costs, surface finishing of parts, limited material variety, and complexity in the management of powders.	Operating under variable weather conditions, scalability, control of the power source, and limited literature.

Table 1.
Comparison of the different technologies in terms of several parameters (sintering).

source used to generate the electric power, that is, in a country whose generation is only associated with fossil fuels, the environmental impact will be higher (carbon footprint associated with indirect carbon emissions). On the contrary, in a country whose generation is only associated with renewable energy sources, the environmental impact will be almost zero. Within this context, the utilization of concentrated solar energy would be the technology with the lowest environmental impact. Nevertheless, the utilization of one or another technology is defined by other factors also considered in the table, such as the cost of the equipment or the grain growth control during the process (which affects the properties). Moreover, there are technologies that are still at the laboratory scale (i.e., cold sintering and solar-assisted sintering), while some others have been implemented at the industrial scale (i.e., SPS and conventional sintering). For instance, selective laser sintering is being widely used to fabricate parts of different materials at a commercial scale [86, 87].

7. Conclusions

Copper is a fundamental metal for the progress of our society, not only in modern times but also throughout all periods of history, first with weapons and utensils and now in many different applications, primarily in power transmission and heat dissipation. The importance of copper in the electrification of societies is highlighted by the increasing demand for this metal. To overcome some of the limitations posed by traditional fabrication technologies, different methods have been implemented in the production of copper, copper alloys, or copper composites. These include laser sintering, SPS, and cold sintering technologies. On another note, the incorporation of sustainable concepts into the production of copper is also important to progress beyond the current state-of-the-art.

Regarding the cold sintering technology, due to the incipience of this technology, the number of investigations is very limited and corresponds to different attempts to obtain dense parts, but without a dominant field of research. This is not the case with laser sintering or SPS technologies, where the focus of investigation in particular areas is evident. In the case of laser sintering, there is a combination of 3D printing and laser sintering to fabricate printed circuits. Regarding SPS, the dominant field seems to be the fabrication of dense composites, such as copper with graphite, for applications in heat dissipation and tribology, although research has also been conducted with other copper alloys and composites.

Finally, the utilization of concentrated solar energy in copper metallurgy can offer a sustainable approach, with zero carbon dioxide emissions, to produce metallic copper. Research in this line has included the integration of solar technologies in different operations of the copper metallurgical process, chemical fuels, and the recovery of metallic copper from secondary sources, such as by-products of the metallurgical process.

Acknowledgments

The author of the chapter thanks the Government of the Principality of Asturias for its support via the call “Convocatoria de subvenciones para grupos de investigación de organismos del Principado de Asturias” (IDE/2024/000637).

Conflict of Interest

The authors declare no conflict of interest.

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Chapter 3

Enhancing Productivity, Energy Efficiency, and Sustainability in Pyrometallurgical Copper Production

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Abstract

This chapter explores the latest advancements and case studies in copper pyrometallurgy, focusing on the use of industrial gases to achieve increased productivity, energy efficiency, and reduced environmental impact. It begins with an overview of the use of industrial gases in copper production, both in primary and secondary processes, and its historical development. It then explores the pathway to decarbonization using the latest oxyfuel and hydrogen technologies. The optimized use of nitrogen across the value chain is also discussed. Key case studies and their results are discussed to illustrate the practical application of oxyfuel combustion in various processes, including flash smelting, flash converting furnaces, copper fire refining, and pyrometallurgical recycling. Emphasizing continuous innovation, the chapter highlights efforts to improve productivity, optimize energy use, and minimize environmental impact (carbon footprint, emissions, resource use, etc.), in line with global sustainability goals. It showcases how the increasing use of industrial gases supports transformation into greener and more resource efficient copper production, for instance, by oxygen-based technologies in copper smelting and recycling operations.

Keywords: industrial gas, oxyfuel, oxygen, productivity, efficiency

1. Introduction

Copper is mainly mined as copper-iron-sulfide minerals whereof chalcopyrite (CuFeS_2) is the dominant mineral. Chalcopyrite copper concentrate is typically processed using pyrometallurgical processing. Pyrometallurgical copper processes deliver about 80% of the world's mined (and recycled) copper [1]. The remaining 20% of mined (also referred to as "primary") copper is processed using hydrometallurgy processes of which heap-leaching, solvent-extraction, and electrowinning is the main process that recovers copper, generally from oxide ores.

This chapter focuses on recent developments in pyrometallurgical copper processing and the important role of industrial gases in the copper smelting industry. The industrial gases industry works with copper smelters and refineries owing to increasing amounts of industrial gases being applied to improve copper production. The primary benefits of applying industrial gases to copper smelting are gains in efficiency, productivity, and environmental (sustainability) performance.

Copper pyrometallurgy is an ancient art closely linked to human civilization. Evidence of ancient copper smelting is found in West Asia and in Cyprus [2]. Copper smelting in Europe is referenced by Agricola [3], using air to support a fire to smelt copper ore in blast or shaft-type furnaces producing copper. The copper was then refined and alloyed to produce useful alloys like bronze. Such was its importance that copper, and copper smelting, is the cornerstone of the bronze age of ancient civilizations.

Air-based smelting has been practiced for thousands of years. Around the year 1900, global copper consumption boomed with the onset of widespread electrification needing copper wire as an electrical conductor. Copper industry growth led to larger copper smelting furnaces for improved economies of scale. Copper smelting using air-fired reverberatory furnaces became the dominant smelting technology by the 1950s. A state-of-the-art reverberatory furnace in 1960s could smelt 300 tons per day of copper [4]. The transition to oxygen-enhanced smelting and processing and then oxygen-fired processes started in the 1950s. This development followed parallel developments of oxygen-based steelmaking and the increased availability of lower cost oxygen production methods [5].

In 1994, oxygen-based copper converting technology was commercialized at Kennecott Utah Copper Smelter in Salt Lake City, USA. Subsequently, several modern smelters employed oxygen-based smelting and converting based on Kennecott Copper's flow sheet (termed the "double-flash" flow sheet). According to D.B. George (personal communication, August 11, 2025), today about 20% of the global copper production is oxygen-based, and this development continues, the most recent being Freeport McMoRan's Manyar Indonesia copper smelter commissioned 2024–2025. One reason for the rapid adoption of the "double-flash" process is sulfur dioxide rich gases are completely captured, processed, and then sold as sulfuric acid. Sulfur dioxide emission is virtually removed from the workplace. This technology increased the oxygen intensity in copper smelting by about 50% compared to smelting techniques reliant on Peirce-Smith copper converting (which remains the dominant copper converting process, and which is air-based). Smelter productivity of 1000 tons per day of copper or larger produced by a modern "double-flash" smelter is closely linked to the smelter's increased oxygen consumption relative to other processes.

Improved energy efficiency, productivity, and sustainability continue to be important drivers, thereby supporting the continued application of industrial gases in symbiosis with modern copper smelting processes.

Modern copper processing uses large and increasing amounts of industrial gases. Oxygen is used to improve copper smelting efficiency. Existing smelters seeking to increase production and improve their efficiency achieve dramatic increases in production by replacing air with oxygen. Virtually all modern smelters have either a pipeline oxygen supply or an oxygen plant on site. Modern copper smelters increasingly employ oxygen-based processes. Nowadays, the oxygen supply is designed and integrated into the overall smelting process, so a reliable oxygen supply is imperative.

Today, oxygen and nitrogen may be found throughout smelter flow sheets. Nitrogen may be used for concentrate drying. Nitrogen may also be used to inert concentrate storage, for example, at Chagres Smelter in Chile where a spontaneous combustion event occurred in a concentrate storage bin. Nitrogen was then applied to the concentrate storage to prevent spontaneous combustion during storage. Oxygen is used for Metso flash smelting and Kennecott-Metso flash converting. Oxygen is used in Metso Ausmelt and Glencore Isasmelt reactors by replacing air with oxygen in the top-lancing system. Air is still predominantly used in Peirce-Smith converters and in anode furnace fire refining. Nitrogen is widely applied in porous plugs for stirring in anode furnaces. Moreover, nitrogen is used for copper fire refining at two locations, Kennecott Copper and Jinlong Copper [6]. Linde oxyfuel burners are installed at about forty smelters. The main drivers for oxyfuel burners are lower capital costs for the gas handling system (due to substantially lower flue gas volumes), fuel savings of about 45%, and increased productivity for the smelting process.

The economics of oxyfuel combustion are typically driven by fuel price, but as metal producing plants adopt clean hydrogen fuel to decarbonize, oxyfuel combustion will become economically necessary. This is because hydrogen will always be a relatively expensive fuel; accordingly, oxyfuel combustion is required to minimize its use. Therefore, the recommendation is to convert to oxyfuel combustion now to achieve 20–50% CO₂ reduction and be prepared to blend in clean hydrogen as and when it becomes available to achieve full decarbonization in the future; see **Figure 1**.

Recently commissioned copper smelters, for example at Freeport McMoRan at Manyar in Indonesia, have employed what is termed the double-flash smelter flow sheet. This flow sheet comprises a flash smelting furnace followed by matte granulation and subsequent flash converting. This configuration increases unit oxygen consumption to about 1.5 ton of oxygen per ton of copper produced.

The double-flash copper smelting flow sheet employs oxygen to greatly reduce the flue-gases treatment volumes. This enables 99.9 percent sulfur capture as sulfuric acid (**Figure 2**).

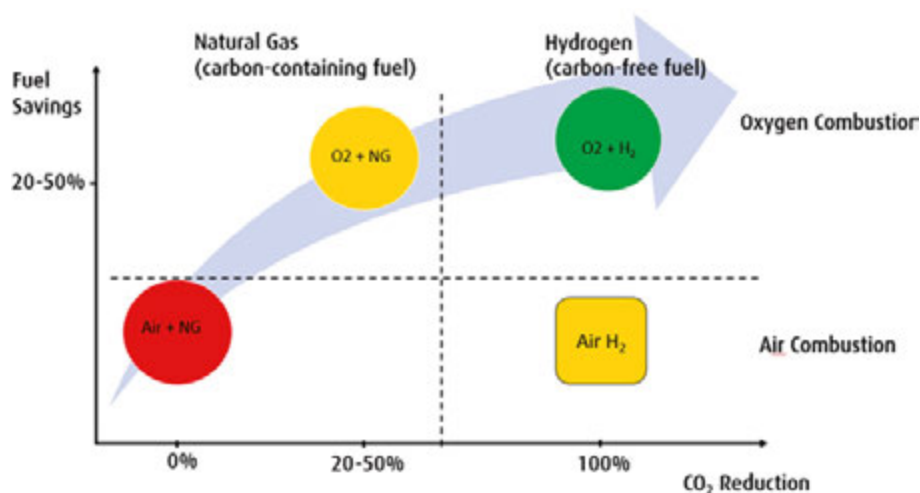


Figure 1.
The suggested pathway to decarbonization via energy-efficiency to using hydrogen as a fuel in a second step [7].

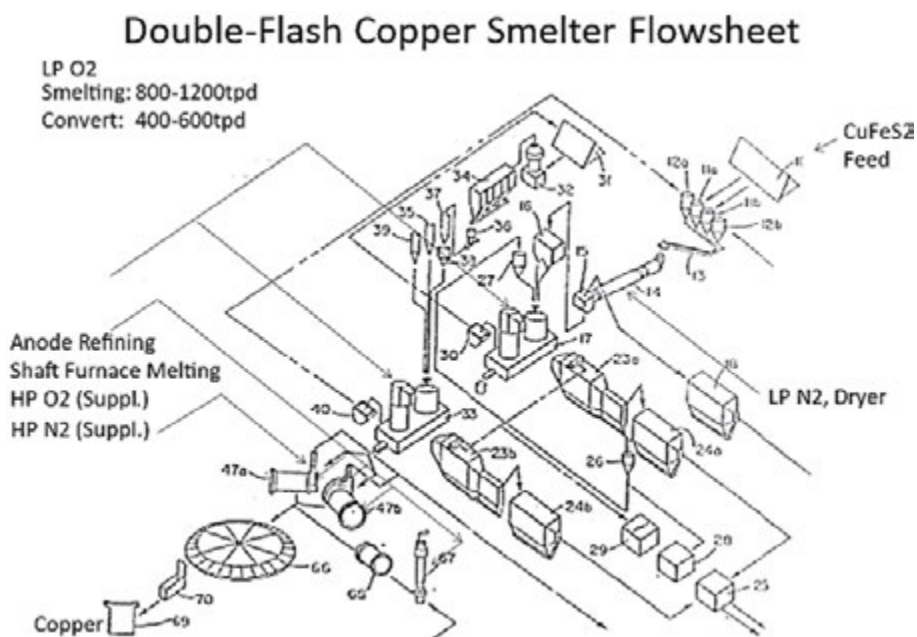


Figure 2.
Double-Flash Metso Smelter showing industrial gases piping network integrated into the smelter flow sheet; this configuration has a unit oxygen consumption of about 1.5 tons of oxygen per ton of copper produced [8].

This chapter highlights the major steps in copper pyrometallurgy, which include the following areas of the copper production process.

- Mining—Liquid nitrogen is used for mining truck tires and workshop uses, like shrink fitting bearings
- Concentrate production—Copper-molybdenum separation is facilitated using nitrogen and carbon dioxide in the molybdenum-copper flotation separation stage
- Concentrate preparation for smelting—Nitrogen may be used for concentrate-drying
- Smelting—Oxygen, low pressure, high oxygen tonnages used to remove iron and sulfur
- Converting—Flash converting oxygen and oxygen enrichment for Peirce-Smith converting
- Refining—Oxygen enrichment for air refining, oxyfuel burner, nitrogen-oxygen refining; oxygen enrichment for shaft furnace copper anode-scrap melting (**Figure 3**).

Decarbonization and greenhouse gases emission reduction in copper production are strongly supported by increasing use of industrial gases improving

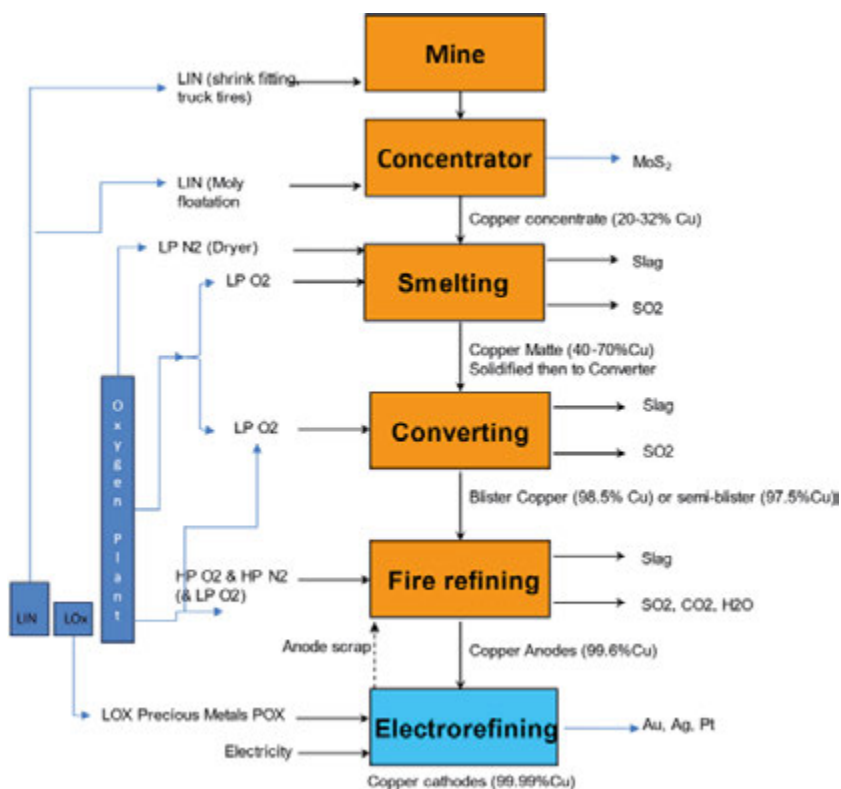


Figure 3.
 Integrated copper extraction flow sheet from mine to smelter to refinery; oxygen plant and industrial gases used.

energy-efficiency and minimizing environmental impact. However, perhaps we may anticipate alternative production processes, such as in the applications of vacuum refining in copper-making. In 1985, Ozberk and Guthrie provided a critical assessment in a review that explored the history, theoretical framework, and applications of vacuum metallurgy to copper production, with the latter including blister copper, anode and/or cathode-type copper, and the treatment of copper matte. Historically, the vacuum treatment of steels was recognized as being important in the late 1800s, while, on the other hand, the first investigations of vacuum metallurgy to copper date back only to the late 1940s. It was noted at the time [9] (ca. 1985) that there were no known commercial installations in use for the vacuum refining of copper, although the vacuum treatment of steel was well established.

Industrial practices for oxygen utilization, pneumatic injection, and oxyfuel know-how developed in the steel industry will continue to be migrated into copper production. For example, Queneau and Marcuson [10] in 1996 discuss the history of oxygen pyrometallurgy applications at Copper Cliff. Following oxygen steelmaking, referring to copper-making, “The pyrometallurgist will gain further benefits from the advent of low-cost oxygen. The dead hands of nitrogen have been lifted from oxidation reactions...The tuyere-less, top-blown oxygen steel converter will invade and conquer the smelters and refineries...”

In terms of vacuum applications in steelmaking, the RH degasser, as an example, utilizing the vacuum-lift technique to promote turbulent conditions in the melt to expose large surface area continuously to the vacuum may ultimately find commercial application

in copper production [11]. In the other direction, the Linde argon-oxygen decarbonization (AOD) process for stainless steel production, as described by Krivsky [12], supplanted much of the industrially produced vacuum refined stainless steel at the time.

Research and development work continues today on vacuum refining of copper. More recently, in 2023, Wang et al. [13], in China, described the preparation of high-purity copper through vacuum distillation. Their focus is on smaller applications pertinent to the production of copper films from sputtering and aerospace applications. They demonstrated 5 N purity production with no wastewater and no waste gas generation. Comparing electrolytic, zone melting, ion exchange and vacuum distillation production processes, their focus is on the latter to minimize pollution in the processing of copper.

2. Copper history and the role of oxyfuel in recycling

Copper has been part of human history for over 5000 years. Early civilizations smelted it using wood and air, relying on simple methods and local materials. Over time, as our understanding of chemistry and engineering advanced, so did the ways we process copper. The introduction of industrial gases like oxygen and nitrogen marked a turning point—making copper production faster, cleaner, and more efficient.

Today, the demand for copper continues to grow, driven by its essential role in everything from electronics to renewable energy [14, 15]. By 2023, global refinery production had reached 27 million tons, with projections aiming even higher [16, 17]. To meet this demand, copper is sourced from both mined ores and recycled materials. In the U.S., about a third of copper comes from recycling, and new facilities—like the one being built by Aurubis in Georgia—are expanding this capacity.

While mining still supplies most of the world's copper, it is energy-intensive and environmentally taxing. That is why secondary copper—recycled from scrap—is becoming increasingly important. It is not only more sustainable but also more energy efficient [18, 19].

This is where oxyfuel technology comes in. By replacing air with pure oxygen in the melting process, oxyfuel systems dramatically reduce energy use and emissions. For secondary copper producers, this means faster melting, lower costs, and a smaller carbon footprint. As the industry shifts toward greener practices, oxyfuel is proving to be a key tool in making copper recycling cleaner and more efficient. Currently, most conventional copper furnaces still operate with air-fuel burners or use only low levels of oxygen enrichment of the combustion air.

To meet rising demand while reducing emissions, more copper scrap furnaces are being installed. These furnaces are essential for recycling, but they consume a lot of energy—up to 1000 kWh per ton of copper when using traditional air-fuel burners. This high energy use poses both economic and environmental challenges.

Oxyfuel burner technology offers a solution (**Figure 4**). By replacing air with pure or enriched oxygen, it boosts melting speed and cuts energy use—down to as low as 400 kWh per ton [20]. This means a 30–50% reduction in energy consumption, along with lower emissions and off-gas volumes. As a result, oxyfuel is becoming a key technology for making copper recycling cleaner and more efficient. The benefits of oxyfuel technology in copper scrap smelting include:

- Fuel savings: Significant reduction in fuel consumption.



Figure 4.
Examples of copper furnace running with oxyfuel and JL flameless oxyfuel burner.

- Lower carbon footprint: Reduced CO₂ emissions (Scope 1).
- Increased melting rate: Faster production cycles.
- Yield improvement: Higher quality and quantity of recovered copper.

Lancing technologies play a crucial role in copper production in the oxidation and poling processes, especially when dealing with dirty scrap, and when the requirements of the final product are considered. These processes involve:

- Oxidation: Removing impurities through oxidation reactions, usually reaching up to 10,000 ppm of dissolved oxygen [O].
- Chemical refining: Further refining copper to achieve the desired purity and remove contaminants.
- Poling: Reducing the oxygen content in the molten copper to improve its quality, reaching concentrations of dissolved oxygen [O] as low as 200–400 ppm.

2.1 Coherent jet technology—CoJet: Copper smelting and refining

The CoJet[®] technology, developed by Linde, is a gas injection system designed to enhance copper refining and scrap melting processes. It combines an oxyfuel burner with a high-velocity gas injection lance, allowing independent control of chemical and kinetic energy in pyrometallurgical reactors [21] (**Figure 5**).

CoJet technology, as applied to copper smelting and refining, delivers high-efficiency gas injection through supersonic coherent jets tailored for low-pressure environments typical of copper operations. In the MK Reactor and anode furnace applications, CoJet achieves up to 94% oxygen efficiency at lance-to-bath distances exceeding 2.5 meters, significantly reducing splash and enhancing gas-liquid interaction [24]. The system supports a wide range of gas compositions—including oxidizing and reducing mixtures—and operates in multiple modes for scrap melting, accretion removal, and bath heating. With extended lance life exceeding one year—compared to conventional tuyeres that last only a few batches or weeks,



Figure 5.
CoJet installed in an anode furnace [22, 23].

CoJet enhances safety, energy efficiency, and metallurgical performance in copper pyrometallurgy.

In copper refining, CoJet technology improves scrap melting efficiency, increases furnace capacity, and helps maintain optimal copper temperature. It has been successfully implemented in anode furnaces, where it has contributed to higher scrap melting rates and better process control [23]. The system also supports efforts to reduce furnace accretions and optimize oxidation and reduction processes (**Figure 6**).

Benefits

- **Enhanced scrap melting:** CoJet technology significantly increases the rate at which scrap copper melts, improving furnace productivity.
- **Improved temperature control:** The system helps maintain optimal copper temperature, reducing heating delays, and improving refining efficiency.
- **Furnace integrity:** By optimizing oxidation and reduction processes, CoJet technology minimizes furnace accretions and extends refractory life.
- **Energy efficiency:** The coherent jet system allows for precise control of gas injection, reducing fuel consumption and emissions.

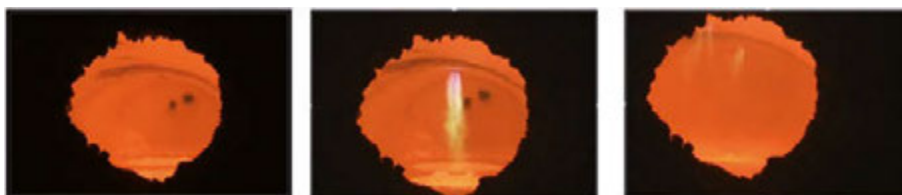


Figure 6.
CoJet operation in a MK reactor with mounting distance of 2.4 m from the bath surface: Only porous plugs with no CoJet operation (left), CoJet in burner mode (center), CoJet in lancing mode with shroud flame and coherent jet (right) [24].

2.2 Computational fluid dynamics driven gas injection and oxyfuel technologies

In the primary (smelting) and secondary (recycling) copper sectors, industrial gases and associated injection equipment are applied to oxyfuel burners and pneumatic injection technologies. The former is today often applied to decarbonization efforts through the increased utilization of alternative fuels (of all forms), including a growing interest in industrial hydrogen trials. The latter is generally concerned with controlled gas jetting into reactors/ furnaces for refining (oxidation, reduction) and metal mixing power delivery (stirring).

Computational fluid dynamics (CFD) can be utilized to support the design, installation, and operation of oxyfuel burners and pneumatic injection equipment. These studies contribute toward risk minimization and the reduction of time required for process optimization.

Pneumatic injection: Two CFD examples illustrating gas jetting into liquid copper are highlighted. We draw upon industrial examples in the following reactors: (1) a top-blown bottom stirred (TBBS) utilizing Linde' CoJet coherent jet technology and (2) submerged supersonic tuyere injection (Mach 1.5) into a horizontal cylindrical furnace (Figures 7 and 8).

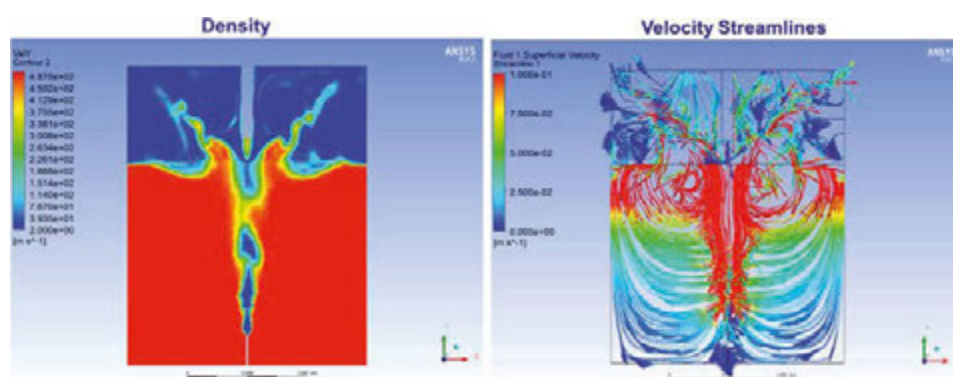


Figure 7.
 Top-Blown Bottom Stirred (TBBS) CFD example: Density (left) and Velocity Streamlines (right), utilizing CoJet Coherent Jet Technology.

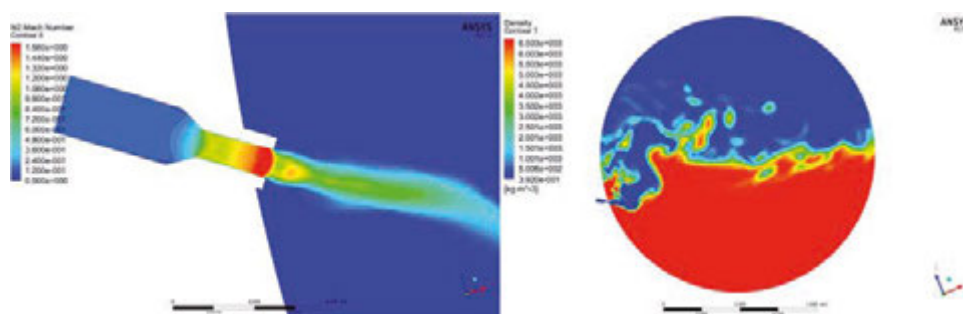


Figure 8.
 Submerged supersonic tuyere CFD example. The tuyeres are designed for Mach 1.5. Mach No. Field (left) and Density Contours (Right).

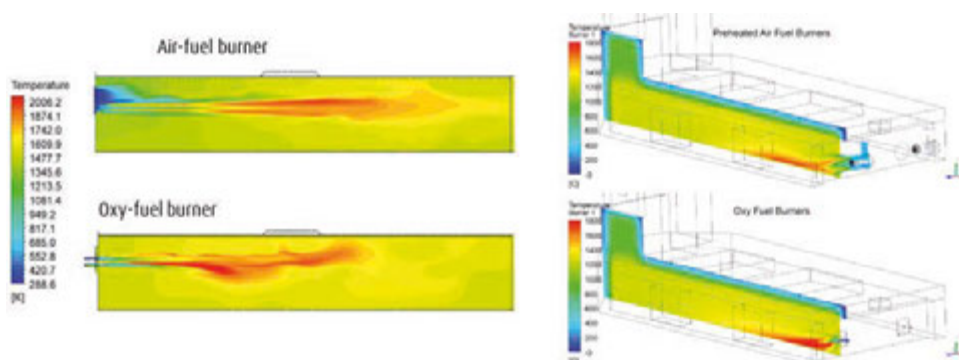


Figure 9.
CFD Temperature comparison of an air-fuel burner and a flameless oxyfuel burner in a cylindrical furnace (left) and a reverberatory furnace (right).

Oxyfuel burners: One CFD example is highlighted comparing air-fuel to oxyfuel furnace heating, utilizing Linde’s JL flameless burner technology in a horizontal cylindrical furnace. The CFD highlights the near-field heating in the furnace (**Figure 9**).

2.3 Oxyfuel installations on small copper scrap (secondary) reverberatory furnaces

In some parts of the world, a different approach to that discussed above has been taken for copper recycling. In these cases, many smaller air-fuel fired furnaces are used instead of large, complex, and capital-intensive technology (**Figure 10**).

They utilize relatively small—typically 50 to 120 ton—and inexpensive reverberatory furnaces that are used to melt relatively clean copper scrap to produce copper wire directly from the furnace. All refining steps occur within these furnaces, and they are operated manually with little process control. These furnaces are inexpensive and do not require highly skilled or well-trained operators and are frequently treated as a consumables item rather than a capital investment. At least thirty of these



Figure 10.
Poling with wood in a 100-ton reverberatory furnace.

furnaces have been converted to oxyfuel technology by industrial gas companies in China over the last 15 years.

2.3.1 The furnace

Two ambient air-fired natural gas burners are installed with a combined capacity of 80 to 100 kW/ton of charge and a specific fuel consumption of 1000 to 1300 kWh/ton of copper produced. The burner capacity is often difficult to determine precisely because of the lack of flow meters.

Process control and monitoring equipment is minimal. It often consists of a simple manual isolation valves used for natural gas and air flow adjustment. There is normally no flame supervision, no integrated ignition system, and neither process nor flue gas temperature control or measurement. The process is very rough and hard on the furnace and equipment. The copper bath temperature, which is a critical process parameter, is measured using expendable (single use) immersion thermocouples, for example, the Heraeus Electronite system.

The furnaces are relined or rebuilt every 8 to 12 months at a cost of approximately EUR 80,000 per lining (data from 2014). They are often not sintered very carefully and heat up is much faster than would be expected.

A single charging door is in the middle of the furnace. The door is opened and shut with a chain and does not seal very well toward the end of life of the furnace refractory.

Slag removal is through a small opening opposite the burners. Tapping is through an opening at the side of the furnace, normally in the corner below the burners and diagonally opposite the charging door. The location of the tapping hole may be different and depends on the position of the casting and wire drawing equipment. The hole is closed with refractory mortar during normal operation and drilled open for tapping.

The refractory material must be able to withstand the hot and strongly reducing environment prevalent in the furnace during reduction and tapping. In addition, it must also withstand the mechanical impact of the manual charging process and be able to deal with the slightly oxidizing environment present during more than half of the process cycle. The refractory composition is primarily MgO with some Cr₂O₃, Fe₂O₃, SiO₂, Al₂O₃, and CaO plus a few other trace compounds.

They cast directly into a tundish that flows to a continuous wire pulling machine. The final product is mostly 8 mm wire rod that is then further processed to electrical cables, sometimes in-house.

2.3.2 The process

Air-fuel tap-to-tap process times are normally between 22 and 25 hours and are broken down as shown in **Table 1**.

The furnaces are charged manually, normally with pressed bails of relatively clean copper scrap weighing 100 to 200 kg each. Clean scrap must be used because all the refining steps occur within the furnace.

Once full, the door is shut, and the burners are operated at full power until the copper is molten. The furnace is then charged once again, and the process repeated. Usually, the furnace is charged 3 to 5 times. The charging process is very rough, and the furnace refractory is exposed to a lot of impacts and blows. Thereafter, the

Process step	Time (hours)	Remarks
Charging	2 to 4	manual charging—alternate charging and melting
Melting	6 to 8	at full power after charging is completed
Oxidation	1.5 to 2.5	depends on scrap purity
Reducing	1 to 3	depends on scrap purity and amount of oxidation
Heat-up	1 to 2	performed if required
Tapping	7 to 8	a heat-up is performed if the copper temperature drops too low

Table 1.
Typical process description.

burners are operated at full power until all the copper has been melted and a bath temperature of 1150–1160°C reached.

The next step is *oxidation*. The burners should be removed from the furnace prior to starting the oxidation step if they are not in service at more than half load. Compressed air is blow in below the liquid copper surface with consumable steel lances covered with a thin layer of refractory mortar. The air pressure is >5 bar(g) and hot liquid copper and slag is splashed all over the furnace—this is the reason why the burners should be removed. Silica and calcium carbonate (CaCO_3) are added as fluxing agents to promote the formation of slag with the impurities present in the scrap copper. Impurities like iron, lead, and zinc are oxidized, and these solid oxides are then trapped in the slag that floats on the surface of the liquid metallic copper bath. These oxidation processes are exothermic and generate heat in the furnace. The slag is manually removed through the de-slagging hole located on the opposite side of the furnace to the burners. **Table 2** lists the main reactions taking place during oxidation.

The burners are normally kept in service to heat the slag and reduce its viscosity, which eases the slag removal during de-slagging. A few bags off charcoal are also added just prior to de-slagging to help heat up the slag and further lower the viscosity. There is always an unavoidable carryover of copper into the slag. Typically, the slag will have a copper content of between 1.8% and 2%.

The oxidation step is complete when a layer of liquid, oily looking, cuprous oxide (Cu_2O) can be seen floating on the surface of the liquid copper and no more slag is being produced. At this stage, the liquid copper is saturated with oxygen. Cu_2O is a liquid at the process temperature, and it is soluble in liquid metallic copper. The solubility is temperature-dependent with the lowest solubility at 1065°C; refer to **Figure 11** for a graph showing the Cu_2O solubility temperature dependence.

Oxygen dissolved in the melt	$\text{O}_2 \rightleftharpoons 2\text{O}$ dissolved in Cu
Copper oxidation	$2\text{Cu} + \text{O dissolved in Cu} \rightleftharpoons \text{Cu}_2\text{O}$
Oxidation of tramp elements	$\text{O dissolved in Cu} + (\text{Fe, Pb, Zn}) \text{ in Cu} \rightleftharpoons [(\text{Fe, Pb, Zn})\text{O}]\text{slag}$
Copper reduction by tramp elements	$\text{Cu}_2\text{O dissolved in Cu} + (\text{Fe, Pb, Zn}) \text{ in Cu} \rightleftharpoons 2\text{Cu} + [(\text{Fe, Pb, Zn})\text{O}]\text{slag}$

Table 2.
Simplified reactions occurring during oxidation.

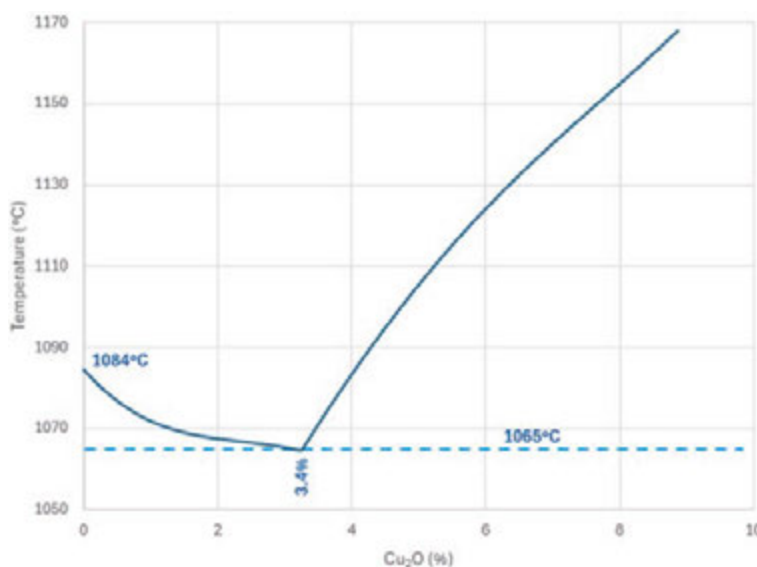


Figure 11.
 Temperature dependence of Cu_2O solubility in molten copper. Adapted from Hofman [25].

The goal is to keep the temperature of the copper bath as close to this temperature as possible to simplify the next oxygen removal (reduction step). Too much oxidation can result in an extended reduction step but can also cause other quality issues that cannot be corrected by a longer reduction step. Care must be taken to ensure that the air used for oxidation has been properly dried.

The next step is reduction. The purpose of this step is the dissolved oxygen from the copper and to reduce the cuprous oxide back to metallic copper. The target is to reach an oxygen concentration of 200 to 250 ppm, with the upper limit being 350 ppm. If the oxygen concentration is >400 ppm, then the wire rod becomes brittle, and it cannot be pulled to produce electrical wire. The Cu purity goal is >99.85%. A copper reverberatory furnace producing anodes would have a less strict oxygen target of <1000 ppm because it has another refining step in the form of the downstream electrolysis system.

Reduction is done with wood, ideally green or similar fresh (wet) wood, although this is being changed to natural gas for environmental reasons. This step is performed through the charging door. Coal powder is still used at a few recycling plants. The wood quality is sometimes poor and variable, which can have a significant impact on the reproducibility of the reduction step. This process is often referred to as *poling*; this name comes from the English word pole, referring to the use of wooden poles or tree trunks for the reduction step.

The wood produces H_2O , CO , H_2 and other hydrocarbons, which reduce the cuprous oxide to metallic copper. The consumption is between 20 and 30 kg of wood per ton of copper. **Table 3** lists the main reactions taking place during reduction.

The copper temperature MUST be kept well below 1200°C , better is always $<1170^\circ\text{C}$. This is to prevent the dissolution of too much Cu_2O in the liquid copper.

Care must be taken to avoid over-poling as the remaining metallic oxide impurities will then be reduced back to their metallic form. These metals then form alloys with the copper, which lowers the electrical conductivity of the final copper wire product. A small amount of metallic oxides have no measurable impact on the quality; once

$2H_{Cu} + O_{Cu} \leftrightarrow H_2O$
$C + O_{Cu} \leftrightarrow CO$
$CO + Cu_2O \leftrightarrow 2Cu + CO_2$
$C + 2Cu_2O \leftrightarrow 4Cu + CO_2$

Table 3.
Simplified reactions occurring during reduction.

reduced, their impact is significant. Over-poling also results in excess dissolved CO and H₂ that makes the final product brittle and porous that effects the ability to be pulled and increases the electrical resistance (Ω).

Finally comes that *tapping* step. If the liquid copper temperature is too low for tapping, the burners are operated at full power until the required temperature has been reached. The target temperature is $\geq 1180^\circ\text{C}$. Care must be taken not to overheat the copper at this stage as this would increase the Cu₂O solubility, should any oxygen come into contact with the copper during the tapping phase.

The uptake of water vapor by the hot copper bath can also result in an excess of dissolved hydrogen, causing a too brittle product. The water can originate from the air in contact with the hot copper being cast from the furnace, especially in hot and humid summer months or in regions where it is always hot and humid.

The liquid copper bath and entire tapping, launder, and tundish system is covered with charcoal to keep the copper from taking up and reacting with oxygen. The charcoal consumption is around 10–11 kg/ton copper. The charcoal is thrown in by hand through the charging door. The charcoal helps to keep the copper free of oxygen and helps to maintain the temperature of the copper during tapping. The copper temperature in the launder and tundish system should be around 1125–1135°C.

The typical recovery rate is 98–99% of the copper mass charged. The recovery is dependent on the quality of the scrap charged; poor quality scrap reduces the recovery rate.

A positive pressure is maintained in the furnace during tapping. Carbon monoxide generation is extremely high during reduction and tapping resulting in a very strong reducing environment that is both very poisonous and highly flammable, as is clearly seen in **Figure 12**. Tapping and the associated casting and rolling can take from 7 to 8 hours.

2.4 Customer benefits of an Oxyfuel conversion

A reduction in the specific natural gas consumption to less than 50 Nm³ per ton of copper is easy to achieve. Values as low as 35–40 Nm³ per ton of copper can be achieved on very well operated and properly maintained furnaces.

There is a small increase in production by reducing the melting time. Oxyfuel can only influence the melting time with oxyfuel, the balance of the process times; that is, charging, oxidation, reduction, and tapping cannot be altered as these are independent of the use of oxyfuel. The melting time can often be reduced by 5–20%.

Another significant benefit is better process control and vastly improved safety. The latter is achieved when the oxyfuel control system complies with combustion safety standards, for instance, ISO EN 13577-2 or NFPA 86, and is generations ahead of the air-fuel systems with minimal process control or safety systems.



Figure 12.
Flames resulting from carbon monoxide generating during tapping.



Figure 13.
Example of a retractor and burner installation.

Two burners are normally installed in the positions of the original air fuel burners. One burner is in service while the other burner is on standby. The ideal situation would be one burner installed along the center line of the furnace, but most customers generally want the security of a second burner to guarantee operation of the furnace in the event of a burner or retractor failure. **Figure 13** shows a typical burner installation with a pneumatic retractor system.

2.5 Copper refining with hydrogen

In 1998, Mansfelder Kupfer und Messing GmbH (MKM) and Linde performed full-scale hydrogen reduction trials on their 150-ton anode furnace at the MKM plant in Hettstedt, Germany.

The last stage of the copper refining process to produce anode copper involves a reduction reaction in the molten copper bath just prior to tapping. The goal is to reduce the oxygen content prior to casting the anodes. If present, sulfur dioxide is also removed. It is very important that the metallic oxide impurities are transferred into the slag and that the bath surface is thoroughly cleaned before the reduction process begins; else the metal oxides will be reduced back to the metal phase. This results in metallic impurities in the anode that interfere in the subsequent hydrometallurgical processing steps.

Previous tests with oil and methane were unsuccessful. Oil was environmentally unacceptable, and methane was not economically viable due to the higher temperature required to achieve the higher copper starting temperature for producing anodes. The latter is because the methane must first be split into H_2 and CO to drive the Cu_2O reduction step, and this requires additional energy.

The refining tests showed that good reduction results are achieved with a hydrogen/nitrogen mixture within a range of 60/40 to 70/30 volume %. The injection lances were immersed at an angle of about 40° , and a lance inlet pressure of approximately 10 bar(g) was required at a flow rate of between 280 and 350 Nm^3/h .

Poling was achieved within 3 hours with two lances, versus 3 to 4 hours when using wood. A further reduction of another hour would be achieved if an additional lance was used. By adjusting the flow rate, the reduction rate and flue gas composition can be better controlled; the latter is not possible when using wood. The use of porous plugs in newer furnaces would likely further reduce the refining time.

Another advantage is that a higher copper bath temperature is not required at the start of poling, as is the case when poling with natural gas. This is because the thermal decomposition of 1 Nm^3 of methane requires approximately 3500 kJ, and temperatures above $1200^\circ C$ to achieve a reasonable yield.



Figure 14.
A hydrogen tube trailer delivering H_2 for the trials at Codelco facility [26].

Test	N ₂ (%)	H ₂ (%)	Oxygen [O] (ppm)		Sulfur (ppm)		Removal Efficiency (%)		Copper Temperature (°C)		Time (h)	Consumption (m ³)	
			Initial	Final	Initial	Final	Oxygen	Sulfur	Initial	Final		N2	H2
2	69	31	6760	4080	75	8	31	89	1244	1280	2.5	4500	1975
3	60	40	4700	1030	170	30	78	82	1241	1292	1.9	3399	2261
4	50	50	5820	1020	88	28	82	68	1230	1296	1.5	2850	2850

Table 4.
 Summary of Experimental Results using H₂/N₂ mixtures for Poling [26].

At the time, although technically feasible and advantageous, the use of hydrogen was not economically viable.

Later in 2008, a new test was conducted by Linde in collaboration with Codelco – División Ventanas. The objective was to evaluate the use of a hydrogen-nitrogen (H_2/N_2) gas mixture as a substitute for natural gas in the reduction stage of the tilting furnace during the fire refining process, as at MKM (**Figure 14**).

One test was performed to check the trial setup, and three tests were performed using different ratios of H_2 and N_2 for process evaluation:

- Test 2: 31% H_2 / 69% N_2
- Test 3: 40% H_2 / 60% N_2
- Test 4: 50% H_2 / 50% N_2

The tests using H_2/N_2 mixtures in the reduction stage of the tilting furnace demonstrated significant improvements over traditional natural gas, as shown in the **Table 4**. Process time was reduced from 3 hours (natural gas) to as little as 1.5 hours (Test 4, H_2/N_2). Concentrations of oxygen and sulfur were notably decreased, and black smoke was eliminated due to the use of hydrogen, which produces water vapor, in contrast to natural gas, which generates CO_2 , CO, and soot. Additionally, productivity increased by up to 1200 additional tons per month thanks to the reduced poling time. Operating costs remained comparable to those of natural gas, making the new method both efficient and economically viable while also reducing the operation's carbon footprint (scope 1).

In 2024, Aurubis conducted full-scale tests on the use of hydrogen in an anode furnace at its Hamburg, Germany plant [27]. These trials replaced natural gas as the refining agent with a hydrogen-nitrogen (H_2/N_2) mixture, demonstrating that hydrogen could be seamlessly integrated without disrupting or altering the existing process. A key advantage of this technology is its environmental sustainability, as the only byproduct emitted from the furnace is water vapor.

The effectiveness of the H_2/N_2 mixture is largely due to hydrogen's high reactivity with oxygen, which facilitates the formation of water vapor while releasing energy without generating carbon-based emissions. This makes hydrogen a cleaner alternative to natural gas, significantly reducing the carbon footprint of the refining process. Meanwhile, nitrogen's inert properties play a crucial role in stabilizing the reaction environment—maintaining optimal jet velocities, ensuring thorough mixing, and controlling the reduction potential. These combined characteristics not only improve the efficiency of the refining process but also align with modern environmental standards, toward a cleaner and more sustainable, low-carbon metallurgical operations.

3. Conclusion

The integration of industrial gases, oxyfuel systems, and hydrogen technologies marks a transformative era in copper pyrometallurgy. These innovations not only enhance productivity and reduce costs but also align with global sustainability goals. As the industry continues to evolve, the synergy between technology and environmental responsibilities will be key to meeting future greener copper demand, supported by energy-efficient combustion and injection and paving the way for use of hydrogen as a fuel.

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Section 3

Applications

Chapter 4

Antimicrobial Copper Coatings: Mechanisms, Applications, Challenges, and AI-Driven Advancements

Mohamed E. A. Abdelmonaem

Abstract

Antimicrobial coatings are engineered surface treatments applied to reduce, or even eliminate, the microbial burden on high-touch surfaces. Among the materials explored for this purpose, copper and its derivatives stand out as particularly compelling candidates. This chapter presents a comprehensive overview of the antimicrobial potential of copper in its various forms, including pure copper, copper oxides, and copper alloys, as well as macro- and nanostructured architectures. It first examines the fundamental surface chemistry governing ion release and the associated antimicrobial mechanisms. The discussion then shifts to practical applications in medical and healthcare environments, highlighting current implementation challenges and emerging strategies to address them. Finally, the chapter evaluates the prospects and constraints of applying machine learning to predict the antimicrobial efficacy and durability of copper-based coatings, and to assist in designing novel formulations. Bringing together insights from materials science, microbiology, and artificial intelligence (AI), this chapter offers a state-of-the-art overview and identifies critical research gaps. It also provides research and development (R&D) teams, startups, and industry stakeholders with a forward-looking roadmap for integrating AI-driven approaches into next-generation antimicrobial copper technologies.

Keywords: copper, copper nanostructures, antimicrobial coatings, copper coatings, antimicrobial mechanisms, smart materials, artificial intelligence (AI), machine learning (ML)

1. Introduction

The antimicrobial properties of copper have been recognized for decades, inspiring extensive research and industrial efforts to uncover their underlying mechanisms, optimize their performance, and apply them effectively in real-world settings to prevent or even reduce the spread of pathogenic microbes, particularly antibiotic-resistant bacteria. This chapter aims to present a comprehensive review, drawn from existing literature, on the utilization of copper-based materials – such as

pure copper, copper oxides, and copper alloys – in various forms, including micro- and nanostructured coatings, for medical and healthcare applications. Throughout this chapter, these materials will collectively be referred to as “copper coatings.”

The antimicrobial effect of copper coatings is primarily mediated by the release of copper ions, which subsequently attack microbes on the coated surface. However, the coating’s antimicrobial potency is not merely an intrinsic property; rather, the coating’s efficacy to release these ions is a dynamic characteristic, dictated by its interaction with the ambient environment from the first moment of application.

Among ambient conditions, temperature (T) and relative humidity (RH) are the most critical, as they govern the copper coating’s dominant oxidation state, which, in turn, dictates the primary mechanism of antimicrobial action. However, since this chapter focuses on medical applications of copper coatings, the temperature ranges the copper coating will be exposed to will vary from room temperature (for example, in the case of coating high-touch surfaces in hospitals) to body temperature (for example, in the case of coating implants). All these temperature ranges, under which we will address the antimicrobial effect of copper coatings throughout this chapter, are referred to as “low temperature.”

Since the surface chemistry and corrosion mechanism of copper are almost the same for all temperatures under 80°C [1], this means that temperature variations play a minor role in defining the antimicrobial efficacy of copper coatings in medical real-world applications. Relative humidity, however, is the paramount factor, dramatically shifting the oxidation state and, consequently, the resulting antimicrobial efficacy.

The following section examines the specific effects of varying relative humidity levels at low temperatures. It details how this important parameter governs the coating’s ability to release copper ions and exhibit its antimicrobial behavior.

In this regard, unless otherwise stated throughout this chapter, “Low humidity” means relative humidity below 70%, while “High humidity” means relative humidity above 70%–80%. However, in this context, it is worth noting that the ranges of relative humidity mentioned here are flexible and subject to change based primarily on the surface coating characteristics, particularly the roughness, since the thickness of the adsorbed water layer increases with increasing surface roughness of the coating [2].

2. How copper ions are released from copper coatings: The journey’s first station

Since the release of copper ions from copper coatings depends on the environmental conditions to which the copper coatings are exposed, we will start by addressing ion release from pure copper coatings under conditions of low temperature and low humidity. This may occur when the copper coating is applied to high-touch surfaces in healthcare facilities, where it is usually exposed to a low-temperature and low-humidity environment ($T < 80^\circ\text{C}$ and $\text{RH} < 70\%$).

2.1 Copper oxidation state under low temperature and low humidity

Under low temperature and low humidity, the copper coating stabilizes in its reduced forms, comprising metallic copper (Cu^0) and cuprous oxide (Cu_2O), with no significant formation of cupric oxide (CuO) [3, 4].

In detail, the low-humidity environment prevents the formation of a continuous water layer on the copper coating. Instead, ambient water vapor forms only small, isolated clusters of a few molecules. These clusters lack the extensive hydrogen-bonding network required for the dissociation of water into protons (H^+) and hydroxyl ions (OH^-). Consequently, the absence of free protons negates the electrochemical driving force needed for the dissolution of metallic copper (Cu^0). This results in suppression of the primary release mechanism for antimicrobial copper ions under these dry conditions [5, 6].

However, even under these relatively dry conditions, atmospheric oxygen remains present and available for chemisorption at specific, high-energy sites on the copper coating surface, such as step edges and kinks. These surface artifacts act as favorable points where oxygen molecules (O_2) are captured. Following adsorption, the oxygen molecules dissociate into atomic oxygen, which subsequently reacts with copper atoms to form localized islands of cuprous oxide (Cu_2O) through selective oxidation (see **Figure 1**) [7].

Over time, these Cu_2O islands can slowly propagate. This slow propagation is characterized by highly anisotropic growth. The vertical growth of the Cu_2O islands proceeds rapidly, reaching the self-passivating thickness of a few nanometers. This layer effectively hinders further oxidation beneath this thickness. In contrast, horizontal growth to form a continuous layer is exceptionally slow. This stark difference in growth rates is attributed to the Cabrera–Mott effect [8], wherein Cu_2O islands create local electric fields that suppress oxidation of the metallic copper (Cu^0) located in the inter-islands' gaps. In other words, metallic regions between the Cu_2O islands are electronically passivated, which prevents copper ions release and slows down horizontal coalescence of these isolated islands into a continuous Cu_2O layer. Furthermore, under these conditions, no cupric oxide (CuO) is formed [4].

Therefore, under sustained exposure to this low relative humidity, the coating's composition remains predominantly metallic copper, with surface oxidation limited to minor Cu_2O islands at the high-energy surface artifacts [9]. Since the antimicrobial effect of copper coatings is driven mainly by the released copper ions, under these low relative humidity conditions no copper ions are released – neither

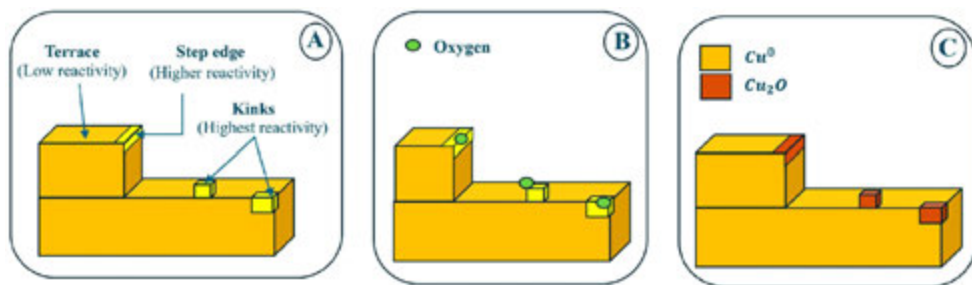
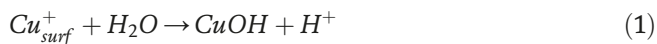


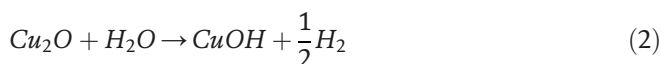
Figure 1.
 (a) Schematic shows the atomic-scale surface features of copper coatings with their respective reactivity, including the flat surface regions (terrace) in which atoms have neighbors on all sides except above, thus its low reactivity; the region where one atomic layer ends and the next begins (step edge) in which atoms have fewer neighbors, thus higher reactivity; and irregularities on steps or the corner site of the step (kinks) with much fewer neighbors and thus much higher reactivity. (b) Schematic shows the preferred sites for oxygen chemisorption at the highly reactive sites including surface edges and kinks. (c) Schematic shows where the Cu_2O is developed through selective oxidation under low temperature and low relative humidity.

from metallic regions between Cu_2O islands nor from the Cu_2O islands itself – copper coatings cannot exhibit efficient antimicrobial effect under low humidity conditions.

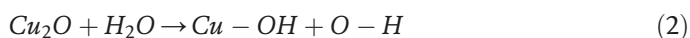
In this context, it is worth mentioning that Cu_2O is formed at the surface's artifacts in a crystal structure that contains both copper ions (Cu^+) and oxygen ions (O^{2-}) in a characteristic atomic arrangement. The adsorbed water clusters or monolayers can hydroxylate the surface Cu^+ sites ($\text{Cu}_{\text{surf}}^+$) of the Cu_2O lattice into copper hydroxide (CuOH), as shown in Eq. (1). In addition, the released protons bind to surface O^{2-} sites of the Cu_2O lattice, forming transient OH^- groups that stabilize the surface. This hydroxylation process forms a thin reactive CuOH layer (only the top one to three atomic layers of the Cu_2O islands are converted to CuOH , no bulk oxidation occurs) [9].



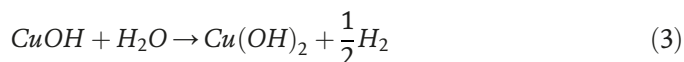
To understand why this hydroxylation process is superficial and cannot propagate beyond the top one to three atomic layers, we have to know the difference between the surface $\text{Cu} - \text{O}$ bonds and the bulk $\text{Cu} - \text{O}$ bonds in the Cu_2O lattice. Apart from the detailed crystallographic structure of Cu_2O lattice, which goes beyond the main scope of this chapter, to understand why water dissociates easier, and thus hydroxylation occurs easier, on surface Cu_2O , imagine surface copper atoms (Cu^+) as “incomplete” versions of bulk copper atoms. In other words, while bulk atoms are fully “handshaked” with oxygen neighbors, surface copper atoms have fewer partners – making them electron-hungry (Lewis acidic). On the contrary, water (H_2O) has a polarized bond, that is, oxygen (δ^-) acts as a nucleophile (electron-rich), while hydrogens (δ^+) are electrophilic (electron-deficient). Consequently, electron-hungry surface Cu^+ electrophiles attract water's nucleophilic oxygen (δ^-), and electron-rich surface nucleophiles attract water's electrophilic hydrogens (δ^+). This dual electrostatic pull strains $\text{H} - \text{O}$ bonds like “stretching a rubber band,” lowering the dissociation energy barrier (tug-of-war effect). In other words, the first adsorbed water layer is localized by double hydrogen bonding of a single water molecule to two surface hydroxyls (i.e., CuOH and OH), as shown in Eq. (2) [9–13].



which can be rewritten for clarity as:



Since the concentration of hydroxyls on the copper coating determines its hydrophilicity, formation of these hydroxyls makes the copper coating more hydrophilic and encourages adsorption of more water monolayers, that can react with CuOH and forming $\text{Cu}(\text{OH})_2$ [9], as shown in Eq. (3).

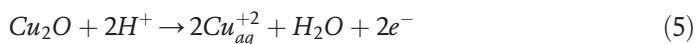
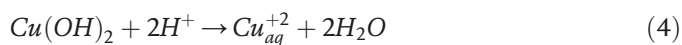


To this point, the composition of the copper coating is dominated by the Cu_2O covered by $\text{Cu}(\text{OH})_2$ on the surface artifacts in the form of islands, and the metallic copper between these islands. In this case, the copper coating cannot undergo electrochemical dissolution, thus no copper ions released, and the coating cannot exhibit ions release-based antimicrobial potency.

But what will happen if this copper coating is now exposed to high relative humidity beyond 70%–80%? This can occur if the relative humidity of the ambient air around the entire coating (macro-environment) increases, or if some water drops (e.g., saliva or mucus drops from coughing or sneezing near this surface) fall locally on the surface (micro-environment). In these cases, electrochemical dissolution can entirely or locally occur on the coating, as detailed below.

2.2 Copper oxidation state under low temperature and high humidity

When the relative humidity exceeds 70%–80%, the adsorbed water layer becomes more than three molecules thick and behaves like bulk solutions; that is, this water layer acts as an electrolyte, enabling electrochemical dissolution reactions. In addition, the thickness of this adsorbed water layer increases with the relative humidity of the ambient environment [2, 14, 15]. The continuous water layer provides protons required for proton-catalyzed dissolution of copper hydroxide and cuprous oxide islands, thus releasing copper ions [16, 17], as shown in Eqs. (4) and (5).



For the inter-islands metallic copper regions, when the humidity exceeds 70%–80%, copper ions Cu^{+2} are released also through the electrochemical dissolution, including anodic and cathodic reactions [16, 17], as shown in Eqs. (6), (7) and (8).

Anodic reaction: $\text{Cu} \rightarrow \text{Cu}_{\text{aq}}^{+2} + \text{e}^-$ (6)



Cathodic reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ (8)

This means that the coating is ready to release copper ions Cu^{+2} whenever the humidity exceeds 70%–80%, either from the whole coating (including both the islands and inter-islands regions, but through different mechanisms as shown earlier) or partially from the smaller area of the micro-environment on which water drops fall, thus exhibiting the copper ions-based antimicrobial effect.

However, if the copper coating is exposed directly to humidity levels exceeding 70%–80%, the entire metallic copper surface will undergo electrochemical dissolution in the available water film, including both anodic and cathodic reactions as shown in Eqs. (6), (7), and (8). This leads to a high flux of copper ions, thereby exhibiting the copper ions-based antimicrobial effect. This can occur, for example, in the case of certain medical applications that involve exposing the copper coating to highly humid or even liquid environments, such as copper-coated implants that are directly exposed to body fluids (see **Figure 2**).

3. The antimicrobial mechanisms of copper coatings: How do the released copper ions kill the adsorbed microbes?

The released copper ions from copper coatings are the spearhead attacking microbes adsorbed on the coated surfaces. In other words, we can consider copper

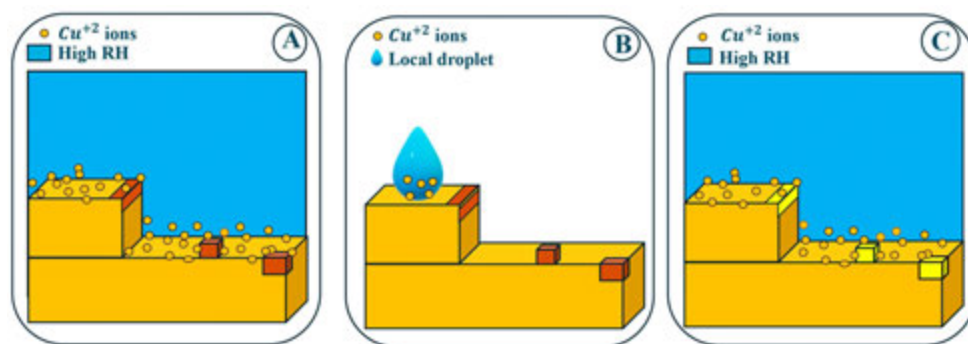


Figure 2.

(a) Schematic shows releasing Cu^{+2} ions from the whole copper coating, including both $\text{Cu}_2\text{O}/\text{Cu}(\text{OH})_2$ and Cu^0 under high relative humidity in the whole surrounding (macro-environment). (b) Schematic shows releasing Cu^{+2} ions locally where a fluid drop was fallen (micro-environment). (c) Schematic shows releasing Cu^{+2} ions from the whole copper coating, including all its regions when the copper coatings is exposed directly to high relative humidity.

coatings as a sustainable source of copper ions, apart from various physicochemical characteristics (e.g., surface charge, roughness, hydrophilicity, porosity, etc.) that collectively formulate the intrinsic fingerprint of each coating in terms of its sustainability and efficiency to exhibit its antimicrobial effect. However, the precise weight of contribution from each physicochemical characteristic to the overall antimicrobial efficacy of the coating under different conditions has not been determined precisely yet. According to previous studies, it is expected that this weight may depend on the targeted microbe(s) and the ambient conditions. Filling this knowledge gap enables materials designers to prioritize optimizing the most decisive characteristic(s) of the coatings, thus accelerating the discovery of novel antimicrobial coatings.

The interaction between the antimicrobial coating and any microbe (e.g., bacteria or virus) starts with the falling of this microbe, contained in droplets of biofluids (e.g., saliva or mucus from coughing or sneezing), onto the surface of the antimicrobial coating. In the following, antibacterial and antiviral mechanisms of copper coatings will be addressed.

3.1 Antibacterial mechanisms

Basically, it is worth mentioning that bacterial membrane potential is the electrical charge difference across a bacterial cell's plasma membrane, generated by differences in ion concentrations between the inside and outside of the cell. In bacteria, this potential is typically around -150 mV [18].

In this context, the bacterial membrane is negatively charged under physiological conditions due to components like lipopolysaccharides (LPS) in gram-negative bacteria and teichoic acids in gram-positive bacteria [19, 20]. Upon falling of bacteria on the coated surface, long-range Coulombic forces cause attraction and attachment of the negatively charged bacteria to the positively charged coating. This electrostatic attraction is highly dependent on charge density of the coating. Research indicates that a minimum threshold of approximately 10^{12} to 10^{16} positive charges per cm^2 is required on the coating surface to induce sufficient electrostatic pressure for lethal

bacterial membrane damage. This electrostatic interaction leads to depolarization and disruption of the bacterial membrane potential. This electrostatic interaction can contribute significantly to bacterial death [21].

Furthermore, copper ions released from the surface directly bind to the membrane lipids and catalyze their peroxidation, which creates holes and causes physical breakdown of the bacterial membrane. However, research has demonstrated that physical contact between the bacterium and the coating is essential for killing. In this regard, one study engineered a copper surface covered with an inert polymer grid that prevented direct contact but still allowed copper ions to be released. On these surfaces, bacterial killing was strongly suppressed, showing that both direct contact and copper ions are necessary for the full “contact killing” effect [22]. Also, copper ions disrupt the bacterial cell membrane by electrostatically interacting with key electronegative functional groups (e.g., thiol, carboxyl groups) [23], and through nonenzymatic peroxidation of membrane phospholipids [24], leading primarily to contact-killing of bacteria.

After the released copper ions invade the adsorbed bacteria through the depolarized regions of the membrane, copper ions can competitively replace divalent cationic cofactors (e.g., Fe^{+2}) of bacterial enzymes, leading to inhibiting their function [25]. In addition, copper ions induce generation of reactive oxygen species (ROS) in the bacteria through Fenton-like reactions that generate highly destructive hydroxyl radicals and other ROS. These radicals cause widespread oxidative damage to proteins, lipids, and DNA of bacteria. ROS cause lipids peroxidation with highly toxic end-products such as 4-hydroxynonenal (4-HNE) and malondialdehyde (MDA) that can diffuse within the cell, forming damaging adducts with proteins and DNA, which amplifies the initial oxidative insult. In addition, ROS can directly oxidize sensitive amino acid residues in proteins, such as cysteine and methionine. This oxidation can lead to protein carbonylation which is often an irreversible modification that leads to a loss of protein function. Oxidation can also cause misfolding of proteins, disruption of active sites in enzymes, and abnormal aggregation of proteins. This damages critical cellular machinery and vital signaling pathways. Furthermore, ROS oxidize nitrogenous bases and sugar backbone of the bacterial DNA, leading to mutations, single/double-strand breaks, and impaired replication, all these events lead collectively to bacterial cell death (see **Figure 3**) [24, 26]. The antibacterial efficacy of copper coatings was studied against many bacteria including, for example, vancomycin-resistant *Enterococci* [27], *Streptococcus mutans*, *Porphyromonas gingivalis* [28], *S. aureus*, and *K. pneumoniae* [29].

3.2 Antiviral mechanisms

The released copper ions are considered the main antiviral effector of the coating against a broad spectrum of viruses, including enveloped, non-enveloped, single-stranded, and double-stranded DNA/RNA viruses. Copper ions can affect viral envelope lipids and capsid proteins, causing a loss of viral integrity. In addition, copper ions participate in Fenton-like reactions, generating ROS, which leads to viral inactivation [30]. The generated ROS can oxidize the viral genome, leading to its disordering and fragmentation [31, 32]. Furthermore, copper ions can replace many other divalent metal ions, resulting in the inactivation of viral metalloproteins (see **Figure 4**) [33, 34].

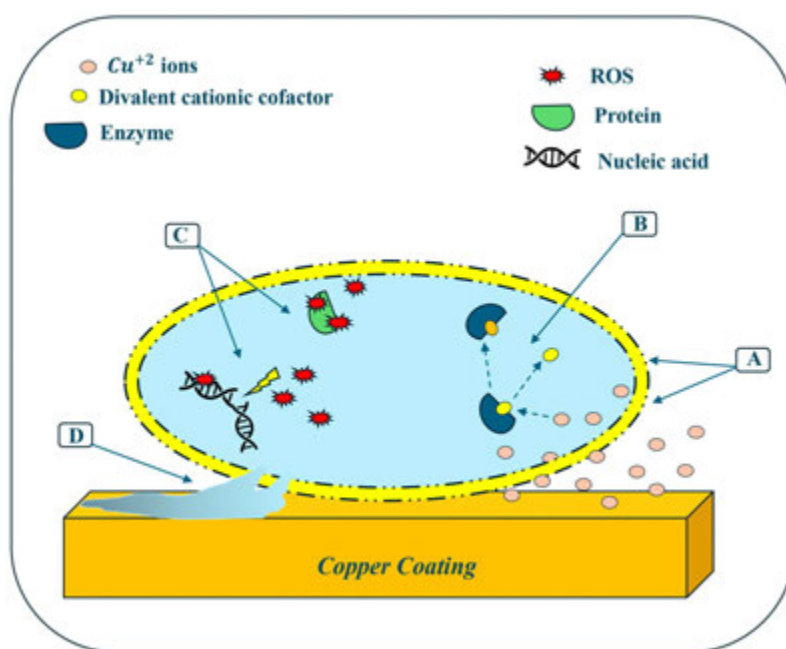


Figure 3.

Schematic shows the antibacterial mechanisms of copper coatings under high humidity including (a) disruption of the bacterial membrane potential due to the electrostatic pressure caused by the coating's charge and the released copper ions; (b) inhibition of bacterial enzymes by replacing divalent cationic cofactors (e.g., Fe^{+2}); (c) ROS generation due to the accumulation of copper ions inside the bacterial cell, leading to destructive effects on various macromolecules including proteins, lipids and nucleic acids; and (d) leakage of biofluids and thus bacterial cell death.

In this context, it is worth mentioning that viruses have two weak points that make antimicrobial copper coatings effective antiviral agents against a broad spectrum of viruses, regardless of their varieties. The first is the vulnerability of enveloped viruses (like SARS-CoV-2 and influenza) to copper-induced damage to their membrane lipids. The second is the lack of nucleic acid repair mechanisms in viruses, in contrast to bacteria, which makes viruses more susceptible to any genomic damage and makes copper coatings a promising antiviral agent. The antiviral efficacy of copper coatings was studied, for example, against SARS-CoV-2 [35–37] and Influenza A [38].

4. Medical applications of copper coatings

4.1 High-touch surfaces and medical devices

Many bacterial and viral pathogens can be transmitted by contact through various surfaces in healthcare settings; thus, the main motive for adopting such antimicrobial coatings, especially copper coatings, is to mitigate or even eliminate healthcare-acquired infections (HAIs), particularly those caused by antibiotic-resistant pathogens, such as ESKAPE bacteria [39–41]. In this regard, copper

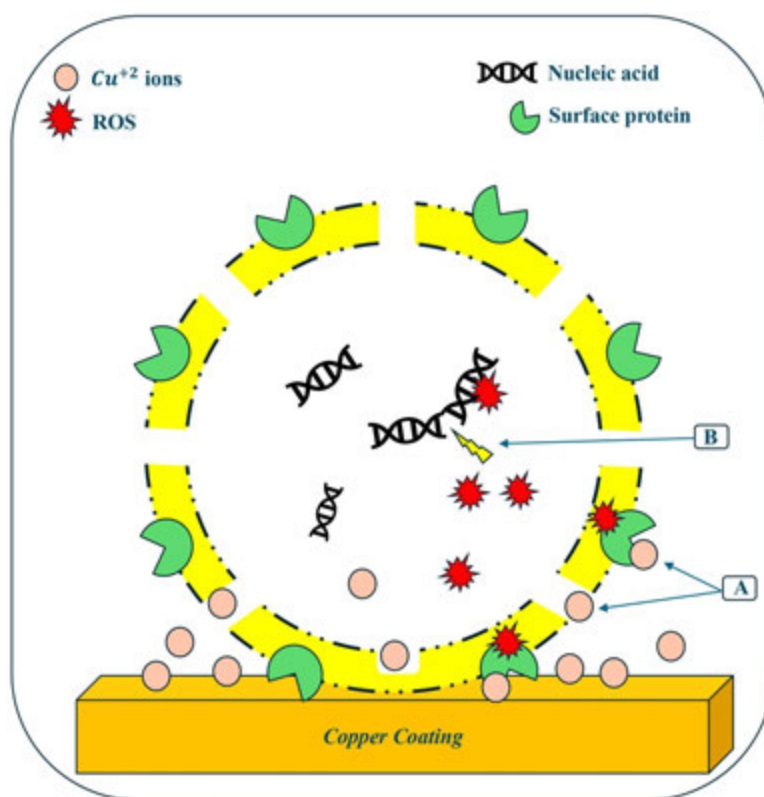


Figure 4.
 The schematic shows the antiviral mechanisms of copper coatings, including (a) viral capsid damage, generation of ROS, inactivation of surface proteins, and (b) degradation of the viral genome, collectively leading to losing viral activity.

coatings offer a promising solution due to their unique antimicrobial potency, even after developing a self-passivating layer, low cost, and mild toxicity to the environment [42, 43].

In the context of assessing the efficacy and longevity of antimicrobial copper coatings on high-touch surfaces in healthcare settings, and since, in real practice, these coatings are complementary rather than alternative to other conventional chemical disinfectants, it is worth considering assessing the efficacy and longevity of the coating under real-world conditions. Under the real-world conditions of healthcare facilities, all surfaces are subjected to routine cleaning and disinfection with special cleaning agents that are always selected in light of the ASTM E2871–21 standard, including strong disinfectants like quaternary ammonium compounds and sodium hypochlorite, as well as other antimicrobials, including phenolics, peracetic acid, hydrogen peroxide, ozone, and steam [44].

The release rate of copper ions and the antimicrobial efficacy of copper coatings should be assessed under these real-world conditions. Additionally, probable interactions with these disinfectants and any possible effects of these harsh detergents on the topography and/or composition of copper coatings – and thus their longevity and antimicrobial efficacy – should be considered.

Furthermore, antimicrobial coatings can also be used to protect medical devices (e.g., dental and surgical tools, catheters, ventilator tubing, endoscopes, etc.) from failure due to adhesion and proliferation of microbes on their surfaces and the subsequent formation of biofilms with biochemical and physicochemical characteristics that can damage these devices [45, 46].

In this regard, setting safety standards for applying copper coatings on medical tools and devices, despite its importance, is not of the highest priority because patients, in this case, will not be exposed to these copper-coated tools for a long time; that is, it is not expected for the patients to acquire toxic concentrations of copper ions from the coated medical tools and devices. However, the more important aspect is studying the durability, longevity, and antimicrobial efficacy of the copper coating under the regular sterilization measures for these tools, such as autoclave sterilization (high temperature and pressure), since it is not expected that surgeons or dentists will depend solely on copper coatings for ensuring sterilization of their toolkits.

Filling these knowledge gaps can significantly boost the extension of the applicability of copper coatings in healthcare facilities, making use of their superior antimicrobial potency.

4.2 Masks, wound dressings, and curtains

Another promising area of applying antimicrobial coatings in the healthcare sector, which escalated particularly after the Covid-19 pandemic, is antimicrobial masks, especially antiviral masks. In this regard, many studies have referred to the proven antiviral potency of copper-containing face masks and their ability to inactivate pathogenic viruses, like the SARS-CoV2 virus to some extent [47–49]. This approach is highly safe due to indirect contact with the human user. In addition, the vicinity of the coated mask to the mouth maintains a relatively high humidity level and ensures its efficiency.

The same approach can be extended to copper-containing wound dressings. However, in this case, the effect of other liquids, such as wound disinfectants, blood, or drugs, on the release of copper ions and the antimicrobial potency should be studied.

Furthermore, this approach can be extended to other non-disposable textiles in medical settings, such as curtains, for example. However, the laundry conditions and their effect on the longevity of the antimicrobial copper coating should be considered. In this regard, it might be possible to re-apply the coating after each laundry cycle, especially for the easy application methods such as immersion and roll-to-roll dipping. In this regard, a recent study [50] referred to the synergistic antimicrobial efficacy of multiple antimicrobial agents (copper ions, chitosan, and citric acid) for textiles against *E. coli* and *S. aureus* with a reduction efficiency of 99.9%, and against *Influenza A H1N1* virus with a reduction efficiency of 99.8% after 30 minutes on polyethylene terephthalate (PET). This approach reduced both the required coating concentration and bacterial contact time. Also, selecting “Citrate” enhanced the antimicrobial effect due mainly to the crosslinked complex formed. Additionally, the application method is very simple and fast, thus it can be repeated for the non-disposable textiles after each laundry cycle; however, the cost-effectiveness of re-applying the coating regularly should be assessed to ensure real-world applicability.

4.3 Dental and orthopedic implants

To endow implants with antimicrobial power, one promising strategy involves incorporating copper, either by blending it with implant materials (e.g., titanium) or by applying it as a surface coating on implants. This approach effectively hinders biofilm formation by a range of bacteria, including *Streptococcus mutans*, *Porphyromonas gingivalis*, and *Staphylococcus epidermidis*, on both dental and orthopedic implants [23, 28, 51–54]. However, for permanent implants, the safety of long-lasting, uncontrolled local exposure of the human body to copper ions released from the coated implants should be studied. *In vivo* studies on copper-coated implants and dental caps are required to assess their long-term safety.

Generally, it seems that the main criteria based on which we can assess the safety of copper-containing or copper-coated implants are:

- (1) The maximum concentration of copper ions, which is considered safe for human intake, as per the WHO recommendations.
- (2) The minimum inhibitory concentration of copper ions for the target microbe(s).
- (3) The release rate of copper ions in the *in vivo* media under physiological conditions. This urges the need for precise assessment techniques of copper ion release rates *in vivo*. In this regard, this study [55] proposed a protocol for evaluating copper ion release rates; such studies should be adopted and developed for assessing the biosafety of copper-containing and copper-coated implants.

In this context, it might be helpful to improve the safety of the coated implants by coating them with a certain thickness of the coating layer, such that complete depletion of the copper coating is ensured after a certain period of time (which can be predicted through AI predictive models, for instance) to ensure long-term safety and prevent the prolonged, unnecessary exposure of the human body to ions released from the copper coating. The same approach can be adopted in the case of mixing the main material of implants (e.g., titanium) with a certain amount of copper micro- or nanostructures that are predictively depletable after a certain period.

Conditional localized release of copper ions from implants only in the targeted micro-environment is another promising approach for maximizing the biosafety of copper-containing or copper-coated implants [56].

5. Challenges and artificial intelligence–driven potential solutions

Although copper coatings hold remarkable potential, several challenges still hinder their broader applicability. Emerging advances in artificial intelligence (AI) and machine learning (ML), however, offer a promising route to overcome these limitations.

AI is a broad field that addresses creating computer systems that perform tasks that would normally require human intelligence (e.g., reasoning, learning, decision-making, pattern-recognition, language, etc.). Under the broad umbrella of AI, ML is

a powerful subfield that uses statistical algorithms and mathematical optimizations, instead of hard-coded rules, to let a system learn from the data, such that once the system is trained, it can generalize the learned rules (optimized models) to new, unseen data to perform tasks (e.g., classification, prediction, or generating new items, etc.) without explicit instructions [57].

In the context of ML, there are two main categories of ML models, i.e., predictive models and generative models. Predictive models are a group of algorithms that can take a set of coating characteristics (e.g., coating composition, thickness, roughness, etc.) as inputs to predict a certain property of the coating (e.g., ion release rate, antimicrobial efficacy, longevity, etc.) as its output. On the other hand, generative models are a group of algorithms that can explore the coating characteristics space to generate new, previously unseen coating designs that fulfill a predetermined set of constraints (e.g., high antimicrobial efficacy and low cytotoxicity).

In the last decade, various ML models have been involved in materials science research, including antimicrobial peptides and nanomaterials, with promising capabilities in predicting materials' properties and generating novel materials with desirable properties [58–62].

The application of copper coatings involves a three-dimensional interplay among the microbe, the coating itself, and the human user. Accordingly, the following is a focused discussion of the key challenges associated with each dimension: (1) the emergence of bacterial metal resistance against copper coatings, (2) the functional performance and durability of copper coatings under realistic conditions, and (3) the safety and biocompatibility considerations for human users. Potential ML-driven approaches to address these challenges are also highlighted.

5.1 Developing metal resistance against copper coatings

One critical barrier to controlling bacteria is its ability to develop metal tolerance. This is mainly because copper resistance and antibiotic resistance were proven many years ago to be simultaneously transferred in some pathogens, such as *Enterococci* [63]. In addition, the relevant resistance genes are often located on mobile genetic elements, facilitating their transfer between bacteria within and across different ecosystems [64]. In other words, the coexistence of significant copper levels in the environment with bacterial antibiotic resistance genes implies that employing copper as an antimicrobial agent might induce the development of multi-drug-resistant bacteria [65–67]. Furthermore, the use of copper as a supplement in animal feeds may enhance the emergence of these metal-resistant microbial strains [68] and triggers a new challenge against extending the use of such antimicrobial copper coatings, raising an important knowledge gap regarding the effectiveness of copper coatings against copper-tolerant bacteria [69].

Careful and wise use of antimicrobial copper coatings, without needless use, should be adopted. In addition, for eliminating or even mitigating bacterial metal resistance, it might be helpful to attack bacteria with multiple antibacterial agents simultaneously, with synergistic antimicrobial mechanisms, since the possibility for the targeted bacteria to develop resistance against all the antibacterial agents at the same time is less than the possibility of developing resistance against only one, especially when each antibacterial agent targets a different pathway.

A striking example of this synergistic antibacterial strategy comes from a recent study where researchers engineered a bimetallic polyphenol coating capable of

releasing both Cu^{+2} and Ga^{+3} ions. While Cu^{+2} disrupting bacterial membranes, Ga^{+3} acts as a deceptive iron mimic, obstructing bacterial iron acquisition and metabolism through a “Trojan horse” mechanism. Together, these effects form a potent alliance: Ga^{+3} -induced iron deprivation heightens bacterial susceptibility to Cu^{+2} toxicity, whereas Cu^{+2} -mediated membrane disruption facilitates Ga^{+3} uptake [56].

Predictive ML models can be used to predict the synergistic effect of the composite of two or more antimicrobial agents (e.g., antimicrobial peptides or drugs and copper or copper nanostructures) [70, 71]. In addition, copper coatings can be functionalized with novel, highly specific antimicrobial peptides that can mitigate bacterial resistance. Generative ML models can efficiently generate these novel antimicrobial peptides with superior specificity. However, it is worth mentioning that generating novel coating designs or novel antimicrobial peptides implies a subsequent step of evaluating their synthesizability, stability, and efficiency, which can be predicted by predictive ML models and performed using molecular dynamics (MD) simulations [72].

5.2 The performance of copper coatings under real-world conditions

Precise prediction of the antimicrobial potency and longevity of the coating under the real-world conditions of each application is highly needed for reliable application, avoiding the use of depleted coatings, and compromising safety. In this regard, it is worth mentioning that many studies conducted were executed on copper coatings under various laboratory conditions, which impose uncertainty about the sustainability of the antimicrobial effect and make these studies indicative rather than reliable in setting standards for testing and validating the antimicrobial efficacy and longevity of copper coatings under real-world conditions.

In this regard, ML predictive models can be used to predict the antimicrobial efficacy, *in vivo* toxicity, and longevity of coatings. For example, supervised ML (random forest) was used to predict the sustainability of the antimicrobial effect exhibited by coated textiles after several washes. The study revealed that the type, shape, and application method of nanomaterial coating are the most decisive input descriptors determining prediction accuracy [73].

Using ML predictive models saves time and cost, orients experimental efforts toward the more promising antimicrobial combinations, and highlights the most decisive parameters in designing these composites. However, the predictive performance of these models is highly dependent on the number and quality of the input variables from the experimental studies. This requires many experiments to be conducted under standardized, unified conditions, which can significantly enhance the leveraging of research outcomes obtained from various research teams globally. Some studies [73, 74] rely, in developing their predictive models, on collecting their input variables from other studies, which imposes standardization-related errors and limits the reliability of their findings.

To build reliable ML predictive models for forecasting the antimicrobial and/or biosafety of copper coatings, model training should be done using a large space of input descriptors that directly or indirectly affect the antimicrobial potency. This underscores the need to build large, standardized datasets for all the relevant material characteristics and pool them in open-access materials databases. Adopting

such large projects can boost ML-guided material design and accelerate discovery pipelines for novel material designs.

5.3 Safety and biocompatibility of copper coatings for human users

Among the most important challenges in extending the applicability of copper coatings, especially for *in vivo* applications (e.g., implants), are concerns about biocompatibility and long-term biosafety. Copper coatings intended for medical applications must satisfy the **ISO 10993** standards for biocompatibility, which address genotoxicity, cytotoxicity, hemocompatibility, and implantation studies. These concerns are heightened toward copper coatings that include novel alloys, which are not fully characterized yet, and nanostructures, due to the probability of leaching.

Although *in vivo* studies represent the most reliable source of information in this regard, these studies are hindered by ethical dilemmas in humans and by the 3R principles (replacement, reduction, and refinement) for minimizing animal use in research. In this context, *in silico* tools, including ML predictive models, can be exploited to predict the biocompatibility and biosafety of designed coatings based on their structural descriptors, since ML-based prediction, combined with molecular docking and MD simulations of biocompatibility, showed promising findings during the last years in various applications [73, 75–77]. However, the reliability of ML to predict biocompatibility is still highly dependent on the availability of large, standardized datasets from *in vivo* studies, or even standardized *in vitro* studies that mimic real-world conditions.

6. Conclusion and future perspectives

In this chapter, the principal antimicrobial mechanisms of copper-based coatings were systematically examined, with emphasis on ion-release dynamics and the associated bactericidal and antiviral modes of action. Key medical applications – particularly their deployment on high-touch surfaces, medical textiles, and implants – were also critically reviewed. Moreover, three major barriers to the broader adoption of copper coatings were outlined, alongside an evaluation of how emerging ML models may offer viable pathways to overcome these limitations.

In conclusion, copper coatings constitute a promising technological intervention for mitigating healthcare-associated infections and addressing the escalating threat of antibiotic-resistant pathogens. Nevertheless, indiscriminate or excessive application is inadvisable, as it may impose selective pressures that contribute to the evolution of copper-resistant microbial populations. Rigorous biocompatibility assessments remain indispensable, especially for coatings intended for direct biological contact or *in vivo* use. Looking forward, the establishment of standardized, comprehensive datasets capturing the physicochemical and biological attributes of copper coatings – and their integration into openly accessible repositories – will be essential for advancing machine-learning-enabled design and optimization of next-generation antimicrobial coatings. Such data infrastructures will enhance the predictive accuracy regarding coating efficacy and biosafety, ultimately reducing experimental burdens and accelerating translational progress in the field.

Acknowledgment

I dedicate this work to everyone who taught me even one letter, to my wife Dr. Asmaa H. Raslan, and to my sons Ahmed & Malek.

I also dedicate this work to my colleagues at the National Institute of Chemistry, Slovenia: Janez Mavri, Jože Grdadolnik, Simona Golič Grdadolnik, Franci Merzel, Barbara Zupančič, Urban Novak, Tjaša Goričan, Iza Ogris, Anže Hubman & Neli Sedej

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Chapter 5

Copper's Encore: (Dry)Etching a Path from Stardom to Survival in Next-Gen Interconnects

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Abstract

Copper, once the undisputed star of semiconductor interconnects, now risks being written out of the script as next-generation technologies demand ever-tighter pitches. This chapter explores copper's most infamous diva trait: its stubborn resistance to dry etching. Where aluminum took direction with grace, copper clings to the stage, its low-volatility byproducts refusing to bow out cleanly. We trace decades of creative etching attempts—using non-halogens, halogens, and hydrocarbons—all with mixed reviews. Rather than delivering a polished performance, copper dry etching has often culminated in a cluttered stage. But the show must go on. Drawing from our own work and that of the broader research community, we look beyond chemistry to spotlight the understudied role of copper's microstructure—its grain boundaries, surface oxides, and crystallographic quirks—as critical players in this performance. The verdict? It may not be a curtain call for copper just yet. With the right script—balancing chemistry, anisotropy, and process integration—it could still earn a standing ovation. After all, even the most capricious divas deserve an encore.

Keywords: copper, dry etching, plasma processing, interconnects, next-gen nodes

1. Introduction

Once waiting in the wings, copper became the surprise lead in the semiconductor saga, replacing aluminum with a dramatic entrance at the turn of the millennium. Celebrated for its superior electrical and thermal conductivity, copper was heralded as the material that would carry interconnect technology into the nanoscale era. But there was one major hurdle: copper did not always follow the script. Traditional subtractive etching methods—so effective for aluminum—simply would not work. IBM's inventive solution was the now-legendary damascene process, which cleverly sidestepped the need for subtractive dry etching by filling trenches instead of removing material [1].

For a while, copper played its part brilliantly. But as the semiconductor industry pursued ever-smaller technology nodes, the stage began to shift. With tighter interconnect pitches comes a significant rise in resistivity—largely a consequence of the very fine grain structures that result from the damascene process, which increase electron scattering at grain boundaries and line sidewalls. Copper, once the rising star of interconnects, began to struggle under the spotlight.

Driven by the industry's roadmap toward ever-smaller interconnect pitches [2], the search for new materials has become a high-stakes casting call. Cobalt and ruthenium have stepped into the spotlight as serious contenders for the lead role—a part that, for decades, belonged to copper. Most recently, our own research group has participated in an effort led by IBM to audition iridium as a promising alternative [3]. Still, writing copper out of the script is not a decision made lightly. Its legacy is profound, and its potential remains—if only it was not quite so difficult to direct. Copper has long shown a diva-like reluctance when it comes to dry etching. A viable subtractive etch process could change the narrative, though, enabling larger grain sizes and consequently lower resistivity [4]—thereby restoring copper's competitiveness as a front-end-of-line (FEOL) interconnect material. Realizing this potential would also depend on the availability of ultrathin, conformal diffusion barriers compatible with FEOL requirements. Beyond FEOL, such a process could also unlock new possibilities for advanced packaging, where the semi-additive process (SAP) is used to fabricate interconnects on organic substrates. In this context, a directional dry etch process for removing the copper seed layer—currently done by isotropic wet etching—would overcome key limitations related to profile control and feature scaling, enabling reliable high-density interconnects at sub-5 μm line/space (L/S) dimensions.

This chapter traces the decades-long effort to steer copper into that performance. We explore the evolution of plasma-based techniques for etching copper, reviewing the major strategies that have been attempted and the chemistry that underpins them. By critically examining these approaches, we aim to provide insight into the challenges ahead—and the possibilities still waiting just offstage.

2. Taking the stage: Dry etching approaches for copper

One of the earliest documented attempts to dry etch copper in the context of semiconductor manufacturing dates back to a 1980 patent filed by IBM [5]. In this early proposal, copper films were patterned using a combination of magnesium oxide (MgO) or aluminum oxide (Al_2O_3) hard masks and a carbon tetrachloride (CCl_4)/argon plasma. Etching was conducted at substrate temperatures equal to or greater than 225°C. This approach marked the opening act in what would become a decades-long drama: the quest to convince copper to perform under plasma conditions. From the very beginning, it was clear that this material would not follow the script written for its predecessor, aluminum.

At the heart of this challenge lies a seemingly simple yet profoundly limiting material property: the low volatility of copper's etch byproducts. In contrast to aluminum, which forms volatile compounds such as AlCl_3 and Al_2Cl_6 under halogen-based plasmas, copper tends to form chlorides, oxides, and organometallic complexes that are either non-volatile or decompose only at elevated temperatures. This makes it extremely difficult to achieve directional (anisotropic) etch profiles without undesirable side effects, such as surface residue, redeposition, or plasma-induced damage to underlying layers.

To appreciate the scope of this limitation, it is instructive to examine the thermal properties of various copper-containing compounds that may form during plasma exposure. **Table 1** presents the melting and boiling points of selected copper hydroxides, nitrates, and other inorganic compounds. This thermochemical landscape underscores the central dilemma: most copper etch byproducts do not readily enter the gas phase under standard process conditions, severely hampering the efficiency and cleanliness of any dry etching process.

This table provides more than just thermodynamic context—it frames the creative tension that underlies decades of plasma chemistry research. If copper refuses to “leave the stage” voluntarily, researchers have been forced to script more persuasive exits. From temperature-assisted halogen plasmas to hydrocarbon-enhanced etching schemes, a wide spectrum of chemical approaches has been tested, each one attempting to address the volatility bottleneck in its own way.

What follows is a detailed review of these methods, organized not by chronology but by the type of chemical strategy employed. Grouping them into non-halogenated, halogen-based, and hydrocarbon-based approaches allows us to compare not only their fundamental mechanisms, but also their effectiveness, limitations, and potential paths forward in the relentless pursuit of a viable copper dry etch process.

2.1 Approaches using non-halogen plasmas

2.1.1 Etching of copper by argon plasma

One of the most straightforward attempts to dry etch copper involved the use of pure argon plasma. Raj et al. [7] investigated copper seed layer removal using pure Ar plasma, achieving etch rates of up to 5 nm/min. The mechanism in this case is purely physical sputtering, where energetic Ar^+ ions transfer momentum to surface atoms, ejecting them without the aid of chemical reactions.

Despite its simplicity, this method presents significant drawbacks. The lack of volatile byproducts leads to extensive redeposition of sputtered copper onto adjacent features, resulting in contamination and degraded pattern fidelity. In addition, the etch rate is far too low to be viable for a production-scale use as an alternative to wet etching in SAP workflows. To mitigate the redeposition issue, a post-etch wet cleaning step using sulfuric acid was employed, yet it proved insufficient in fully eliminating the redeposited material [7]. As a result, while argon plasma can remove copper, its

Copper compound	Melting temperature (°C)	Boiling temperature (°C)
Cu(OH)_2	80	—
$\text{Cu(NO}_3)_2$	114.5	170
CuCl	426	1490
CuCl_2	498	993
CuBr	492	1345
CuBr_2	498	900
Cu_2O	1232	1800
CuO	1326	2000

Table 1.
Melting and boiling points of representative copper compounds (adapted from [6]).

inability to ensure clean, directional and high-throughput etching limits its viability for advanced patterning applications.

It could be said that, while argon plasma could direct copper off the stage, it did so through sheer force—leaving the set in disarray and taking far too long between scenes.

2.1.2 Etching of copper by hydrogen plasma

Hydrogen plasma represents one of the more intriguing approaches to the dry etching of copper, offering low-temperature compatibility and promising etch profiles, all while operating through a mechanism that remains only partially understood. Wu et al. [8–12] demonstrated that copper could be etched using hydrogen plasma in an inductively coupled plasma (ICP) system, achieving etch rates of up to 13 nm/min at substrate temperatures as low as 10°C. The resulting features displayed notable anisotropy, with sidewall angles exceeding 80°, suggesting a degree of directional control not typically associated with such a chemically passive gas. Despite these promising characteristics, the nature of the etching mechanism remains unclear. Traditional chemical etching appears unlikely, as copper hydrides (e.g., CuH and CuH₂) are thermodynamically unstable and possess extremely low vapor pressures [13], making them ineffective as volatile etch products. At the same time, a purely physical sputtering process is improbable, given the low mass and limited momentum transfer capacity of hydrogen ions. Wu et al. nonetheless proposed that under high hydrogen activity, CuH may transiently form on the copper surface, with its desorption facilitated by ion or photon bombardment. The absence of redeposition and the sharp profile of the etched features suggest that the mechanism may incorporate both chemical and directional components. Additional insight comes from process behavior under varying plasma conditions. Higher etch rates were observed when ion bombardment was introduced—specifically when platen power was applied in tandem with coil power—indicating that energetic input plays a critical role in assisting the removal of surface-bound species. To account for the apparent chemical contribution despite the instability of neutral CuH_x species, Choi and Hess [14] proposed the involvement of a more stable anionic species, CuH₂[−]. In their model, this anion forms at the surface and is repelled by negative surface potentials, enabling desorption through electrostatic forces rather than thermal volatility.

Interestingly, Wu et al. [15] observed that etch rates peaked around 10°C, above which the process efficiency declined. This behavior likely reflects a shift in the dominant etching pathway. As CuH_x species become increasingly unstable above 0°C [13], the observed transition may indicate a change from CuH_x-mediated etching to a mechanism involving CuH₂[−].

Despite the limitations imposed by the instability of hydrogen-copper reaction products, hydrogen plasma has been shown to enable copper etching at temperatures up to 150°C. However, its practical use is not without complications. Ohmi et al. [16] reported etch rates as high as 500 nm/min using a sub-atmospheric pressure H₂ glow discharge. Unlike the results of Wu et al., this process showed minimal temperature dependence but introduced substantial surface roughness—highlighting a key drawback of hydrogen-based approaches. This surface degradation may stem from a well-known metallurgical phenomenon: hydrogen embrittlement. Atomic hydrogen, capable of diffusing deep into the copper lattice, can recombine into H₂ molecules within the bulk. The internal pressure exerted by these molecular species leads to stress accumulation, void formation, and ultimately, surface damage [17, 18]. Copper,

in particular, is known to be highly susceptible to this form of degradation [19, 20]. The roughness observed by Ohmi et al. is likely a direct consequence of this internal disruption.

Thus, while hydrogen plasma has shown the ability to pattern copper under gentle conditions and produce directionally etched features, its role remains enigmatic. Its performance hints at a nuanced and fleeting chemistry—like a soft-spoken understudy who unexpectedly commands the audience's attention, only to leave behind questions, and a few broken props, in their wake.

2.1.3 Etching of copper in hydrogen/nitrogen/argon plasma

To address the issue of internal void formation caused by hydrogen diffusion into bulk copper, Ohmi et al. [21] introduced nitrogen into their sub-atmospheric pressure hydrogen glow discharge system. In this configuration, a localized plasma is generated in a narrow gap between a small-diameter pipe electrode and the copper sample. Process gases are delivered through the pipe, and the resulting discharge is confined to a ~1 mm region beneath the electrode tip—accounting for the highly localized nature of the etch. By adding 10% N₂ to the plasma, the aim was to promote the formation of a copper nitride layer at the surface, which would act as a diffusion barrier to atomic hydrogen during etching.

This modification yielded a dramatic increase in etch rate, exceeding a fivefold improvement and reaching values as high as 2.4 μm/min. Notably, the addition of argon to the plasma had no measurable effect on the etch rate, allowing the authors to rule out physical sputtering as the dominant mechanism. At the same time, the formation of the nitride layer appeared to suppress hydrogen-induced damage: internal voids in the copper were significantly reduced, resulting in a much smoother etched surface. Despite these promising indicators, the etch mechanism remained unclear. Outside the small plasma treatment zone, the process showed strong non-uniformity and significant redeposition. Moreover, although the substrate holder was cooled to 0°C, the copper surface itself reached temperatures approaching 250°C during etching, indicating intense localized heating within the discharge region. These factors—limited etch area, surface redeposition, elevated local temperature, and uncertainty around the etching chemistry—present significant challenges for scaling the process to practical semiconductor applications.

In the end, while this approach managed to extract a high-performance moment from copper, the spotlight shone only briefly and narrowly. For broader application, the performance would need to be far more consistent—and far less temperamental.

2.1.4 Etching of copper in hydrogen/argon plasma

Wu [8] studied the effect of introducing argon into a hydrogen plasma during copper etching and reported a slight improvement in both etch rate and surface smoothness. While no quantitative surface roughness data were provided—and no clear differences could be discerned from the accompanying images—the enhancement was attributed to the role of Ar⁺ ions in promoting the desorption of copper etch products through additional ion bombardment.

The best results were obtained with a 1:1 H₂:Ar ratio. At this balance, the system seemed to have enough chemical activity from hydrogen species, while benefiting from the additional physical energy input provided by argon. However, increasing the

argon content beyond this ratio led to degradation in sidewall slope, likely due to an elevated sputter rate of the SiO₂ mask and a concurrent reduction in the chemically driven component of the etch process.

In this combination, argon seemed to act as an energetic co-star—helping hydrogen to move the scene along, but too much screen time tilted the balance toward disruption.

2.1.5 Etching of copper in helium plasma

The etching of copper under pure He plasma has been reported in the literature [10] despite helium's chemical inertness and its notably low sputter yield—especially when compared to argon [22]. In this study, an etch rate of 10 nm/min was observed—more than double the 4 nm/min reported under Ar plasma in the same work [22]—raising questions about the underlying mechanism.

Given helium's limited physical and chemical interaction potential and the difficulty in accurately measuring such small etch rates, the precision of the reported results is open to scrutiny. Nevertheless, the authors attributed the apparent enhancement to high-energy vacuum ultraviolet (VUV) photons—particularly around 58.4 nm—emitted by the helium plasma, proposing that these photons may weaken Cu–Cu bonds and facilitate surface ablation.

If the claim holds, helium's role is not that of a reactive participant nor a forceful actor but rather a subtle manipulator—altering the mood of the scene through light rather than motion. Whether it truly moved copper off the stage, or simply cast a flicker of illusion across the surface, remains open to interpretation.

2.1.6 Etching of copper in plasmas of nitrogen oxides

As shown in **Table 1**, the formation of copper nitrate [Cu(NO₃)₂]*—*a compound with relatively high volatility*—*presents a promising pathway for etching copper at temperatures below 200°C.

This potential has led to several patented approaches. Shinohara et al. [23] filed a claim involving a plasma containing nitrate species (NO₃), though no details were disclosed regarding copper etch rates or resulting feature characteristics, leaving the effectiveness of the method uncertain. Nakatani [24] introduced a NO₂/H₂ plasma process that reportedly achieved a copper etch rate of 120 nm/min, along with a sidewall slope of 86°. The mechanism was attributed to the sublimation of Cu(NO₃)₂ as the primary volatile byproduct. However, the treatment temperature was not specified, and visible redeposition can be observed, suggesting process limitations in terms of cleanliness and profile fidelity.

Nitrogen oxides may have had the right chemistry, but with missing cues and unclear directions, the act never quite came together. Fortunately, the next scene brings a far more reactive cast to the stage.

2.2 Halogen-based plasma approaches

Having explored non-halogenated strategies, which typically rely on physical sputtering or unstable intermediate species, we now turn to halogen-based plasma chemistries. These systems—richer in chemical reactivity—offer pathways for more efficient copper removal, though they often come with trade-offs in volatility,

selectivity, and thermal requirements. These approaches, while promising, must be precisely directed. Like a fiery co-star with undeniable presence, halogen plasmas can either elevate the performance—or completely upstage it.

2.2.1 Etching of copper by chlorine plasma

Chlorine-based plasmas have been extensively investigated for copper etching, as copper chlorides—though generally exhibiting low volatility—are the most volatile among the copper-halogen compounds (see **Table 1**) [8, 25–27]. Chlorine reacts rapidly with copper, forming a CuCl_x surface layer. However, due to the weak vapor pressures of these compounds, effective desorption typically requires elevated substrate temperatures. Among the possible etch products, the six-membered ring trimer Cu_3Cl_3 is considered the most favorable in the intermediate temperature range between $\sim 150^\circ\text{C}$ and 580°C , while CuCl becomes the dominant desorption species above $\sim 600^\circ\text{C}$ [28]. Although Cu_3Cl_3 lacks well-documented thermodynamic data—likely due to its polymeric nature and thermal instability—Winters et al. [28] showed that it can desorb from the surface around 150°C , indicating that its volatility becomes kinetically relevant under plasma exposure, even in the absence of high intrinsic volatility.

Miyazaki et al. [29] demonstrated that etch rates up to 320 nm/min could be achieved using a Cl_2 -based reactive ion etching (RIE) plasma at a substrate temperature of 260°C . However, the process exhibited strong temperature dependence. At elevated temperatures, particularly above 270°C , severe undercutting was observed in submicron features, suggesting a transition in the dominant etching mechanism. Below this threshold, the process appeared to be driven primarily by ion bombardment, yielding more anisotropic profiles, whereas at higher temperatures, chemical reactions took over—resulting in isotropic etching behavior.

In this regime, chlorine proves to be a reactive and efficient partner—but one that requires careful direction. Without tight thermal and process control, its performance shifts from precision to excess, like a powerful performer who, unrestrained, overwhelms the scene.

2.2.2 Etching of copper by hydrochloric acid plasma

Hydrochloric acid (HCl) plasma has been explored as an alternative to Cl_2 discharges for copper etching, though both experimental studies and computational modeling indicate its effectiveness is comparatively limited [30]. Etch rates under HCl plasmas tend to be lower than those achieved with Cl_2 , primarily due to differences in dissociation rate constants. According to the same study, Cl_2 plasmas generate a higher flux of positive ions and a denser concentration of reactive species, which enhances the overall reactivity of the system.

To address the limitations of HCl plasma alone, Kuo et al. [31] proposed a dual-step process combining a plasma etch step with subsequent wet etching in an HCl solution to remove residual reaction products. This method enabled the patterning of a 500 nm-thick copper layer in under 4 minutes of total processing time. However, the plasma step required a substrate temperature of 250°C , and the resulting features showed pronounced surface roughness. In a follow-up study, replacing HCl with Cl_2 allowed the plasma etching to proceed at room temperature (25°C), but the improvement in surface quality was minimal—images provided in the study indicate that roughness remained significant [32].

While HCl plasma brings some reactive potential to the stage, its performance appears limited—like a supporting actor delivering lines that lack the clarity or impact needed to carry the scene. Even when assisted by a wet chemistry encore, the result falls short of a clean, convincing performance.

2.2.3 Etching of copper by chlorine/argon plasma

The addition of argon to a Cl_2 plasma has been shown to enhance copper etching performance by promoting greater Cl_2 dissociation and increasing the desorption of reaction products. This improvement is attributed to both the energetic Ar ion bombardment and the presence of ultraviolet (UV) photons—particularly at 256 and 307 nm—emitted by excited chlorine species, which contribute to weakening Cu–Cl bonds and promoting product desorption [25]. Interestingly, this mirrors the proposed mechanism in He plasmas (as discussed in Section 2.1.5), where high-energy photons are also believed to assist in breaking surface bonds, offering a potential unifying thread between these otherwise distinct systems. Using a Cl_2/Ar electron cyclotron resonance (ECR) plasma at 200°C, Lee et al. [33] reported copper etch rates of up to 500 nm/min. They observed a strong dependence of the etch process on the source power: at lower power levels, the ion flux was insufficient to remove the copper chloride layer formed on the surface, resulting in deposition rather than etching. In these conditions, the CuCl_x compounds accumulated rather than volatilized, halting material removal. The role of bias power was also found to be critical in determining etching efficiency. Jang et al. [34] reported that with a bias power of 75 W, they achieved an ultra-smooth copper surface, exhibiting a root mean square (RMS) roughness of just 0.5 nm—comparable to that of the underlying glass substrate. However, the etched sidewalls under these same conditions were significantly roughened. According to the authors, this may originate partly from the irregular profile of the photoresist (PR) mask used in the process, but is more likely related to the preferential attack of copper grain boundaries by chlorine radicals. They suggest that sidewall roughness could be reduced by adjusting the Cl_2/Ar ratio and increasing bias power, as more energetic—and therefore more directional—ion bombardment may help suppress lateral chemical attack. In this chemistry, argon serves not just as a carrier or enhancer but as a kind of stage technician—tuning energy and direction to help chlorine deliver effectively and with precision. When the balance of plasma conditions is right, the performance is clean and well-defined. But when that balance slips—whether through excessive chemical reactivity or insufficient control over ion bombardment—the scene becomes uneven, and the cast ends up producing a rougher performance than intended.

While Cl_2/Ar plasmas offer high copper etch rates, their effectiveness is often constrained by challenges such as sidewall roughness, the need for elevated temperatures, and post-etch corrosion. To address these limitations, several enhancements have been proposed—each targeting a specific aspect of process performance. Although these strategies have been most extensively studied in the context of chlorine-based plasmas, many of the underlying principles may also be applicable to other halogen-containing etching systems.

2.2.3.1 Dressing the stage: Role of passivation layers in profile control

To improve etch anisotropy and reduce sidewall roughness in Cl_2 -based plasmas, several strategies involving passivation layers have been investigated. One of the key

challenges in these systems is that the high temperatures required to volatilize CuCl_x products typically preclude the use of PR masks. As a workaround, polymer-based passivation has been explored by adding CH_4 to the gas mixture. This approach forms a protective film along the sidewalls during etching, improving anisotropy—but at the cost of significantly reduced etch rates [35]. To overcome this limitation, a two-step process has been proposed: CH_4 is initially introduced to form the passivation layer, and its flow is then reduced in a subsequent etch step [36]. This approach enables both improved sidewall quality and high throughput, with etch rates reaching 500 nm/min.

Additional methods have also been reported to enhance profile control. The introduction of NH_3 in the presence of a SiO_2 hard mask has been shown to promote the formation of SiON passivation layers, further improving sidewall integrity [37]. When SiCl_4 is present in the plasma, NH_3 can instead lead to the formation of a protective Si_3N_4 film [27]. Interestingly, the addition of fluorine-containing gases such as SF_6 or C_2F_6 has also been found to result in cleaner etch grounds, although the underlying mechanism remains unclear [35].

Think of these passivation approaches like good stage makeup—their goal is not to steal the show, but to keep the edges sharp under the spotlight.

2.2.3.2 Lighting the stage: Enhancing etching with UV and laser

The high substrate temperatures typically required for Cl_2 -based copper etching—often exceeding 150°C —present a major limitation, particularly with respect to PR compatibility and integration into thermally sensitive process flows. To address this, a range of photon-assisted techniques have been explored, including UV and infrared radiation as well as laser irradiation. These approaches rely on the principle that absorbed photon energy can locally heat the substrate or weaken Cu–Cl bond strength, thereby facilitating the desorption of copper chloride reaction products. While CuCl_2 can absorb UV light, the observed increase in etch rate under UV exposure is not attributed to its direct photochemical decomposition. As detailed in reference [38], the enhancement arises instead from photo-assisted processes involving CuCl. Upon UV absorption, CuCl undergoes electronic excitation that destabilizes the surface layer, promoting the release of volatile species through reactions such as $\text{CuCl}(s) + h\nu \rightarrow \text{Cu}(g) + \text{Cl}(g)$. The overall effect is strongly dependent on both UV intensity and the prior formation of the chlorinated surface.

Etch rates as high as 300 nm/min have been reported at or near room temperature, significantly reducing the thermal budget of the process [34, 38–47]. Despite this promise, photon-assisted techniques introduce several challenges. Precise control over photon flux and spatial uniformity is difficult to achieve across large substrates, and the process setup becomes significantly more complex. Lasers, in particular, have been associated with issues such as redeposition, limited resolution, and low throughput, all of which limit their practicality for industrial-scale implementation [39, 46]. One potential alternative could be to generate UV photons directly within the plasma—using species like He or HBr—rather than relying on external light sources. While this approach could, in principle, offer a more integrated solution, our own attempts to introduce HBr into Cl_2 -based plasma mixtures led to the formation of non-volatile copper bromide species on the surface, which ultimately hindered rather than enhanced etching. This highlights the need for further investigation into UV-generating plasma chemistries that could offer the benefits of photon-assisted etching without compromising byproduct volatility.

Shining a light on the process may help coax copper into action—but without careful control, the spotlight can just as easily leave uneven lighting, scattered props, and a show too expensive to take on tour.

2.2.3.3 Cleaning the stage: Post-etch chlorine removal

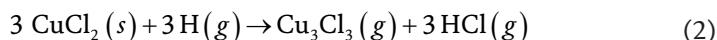
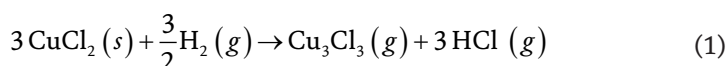
One of the primary concerns with Cl_2 -based copper etching is the potential for corrosion following plasma treatment. Residual chlorine species left on the etched surfaces can react with ambient humidity, triggering unwanted chemical reactions over time. These reactions may lead to undercutting, degradation of feature integrity, and, in severe cases, even short circuits—ultimately compromising the long-term reliability of the device. To mitigate these risks, post-etch cleaning steps have been developed to effectively remove chlorine residues before further processing.

Lee et al. [33] compared hydrogen- and oxygen-based plasma cleaning approaches. Their results indicated that hydrogen plasma was significantly more effective in eliminating residual chlorine, likely through the formation and volatilization of HCl . This simple yet critical step can help preserve etched features and improve the overall reliability of the process.

Post-etch cleaning may not be glamorous but skip it, or bring in the wrong cleaning crew, and what looks like a standing ovation might just be the calm before corrosion sets in and the stage collapses. And having a clean sample is only half the job: a major challenge for etch process engineers is keeping the chamber itself clean. Non-volatile copper byproducts can deposit on reactor walls, potentially contaminating subsequent wafers and degrading long-term process stability. While this chapter focuses primarily on wafer-level strategies, chamber contamination remains a critical—and ongoing—concern in the pursuit of sustainable copper etch processes.

2.2.4 Etching of copper by chlorine/hydrogen plasma

In an effort to develop a low-temperature plasma-based planarization alternative to chemical mechanical polishing (CMP), Kulkarni and DeHoff [48] investigated the effect of hydrogen on the volatility of copper chloride species. Based on equilibrium calculations, they proposed that both molecular and atomic hydrogen could significantly increase the volatility of Cu_3Cl_3 , the key etch product, through the following reactions (where s = solid, g = gas):



These findings suggest that copper could be etched at or near room temperature, provided that CuCl_2 is present on the surface. However, under low-temperature conditions, CuCl is thermodynamically favored over CuCl_2 . To address this, Kulkarni and DeHoff proposed a two-step approach: (1) chlorination of the copper surface using Cl_2 plasma, followed by (2) hydrogen plasma exposure to volatilize the resulting chlorinated layer. These steps are repeated cyclically to achieve the desired etch depth. This method was experimentally validated for etching copper at 10°C , although the

reported etch rate was relatively low (~5 nm/min), and sidewall profiles were notably rough [49–51]. Wu et al. [51] demonstrated that the addition of argon during the hydrogen step could double the etch rate and improve anisotropy.

While this two-step method is justified at low temperatures, a potentially more efficient alternative at elevated temperatures is the use of a single Cl_2/H_2 plasma. Elevated temperatures favor the formation of CuCl_2 over CuCl at the surface [52]—an important condition for enabling hydrogen-assisted volatility in chlorinated copper species. Complementary optical emission spectroscopy (OES) data from Efremov et al. [53] indicated that etching could be enhanced using an 80% H_2 /20% Cl_2 plasma mixture at 300°C.

In the end, hydrogen may help keep the show cool and the chlorides volatile—but without just the right supporting cast, the performance is slow, rough, and rarely ready for prime time. Fortunately, help is waiting in the wings.

2.2.5 Etching of copper by chlorine/hydrogen/argon plasma

Given the promising results from the cyclic Cl_2/H_2 approach discussed in the previous section—and the improvements observed with Ar in the H_2 step—our group, taking a cue from the controlled chaos of *Everything Everywhere All at Once*, decided to simplify the sequence by combining Cl_2 , H_2 , and Ar into a one-step approach. While the concept was appealing in terms of process efficiency, it was not without concern: previous studies have shown that Ar^+ bombardment can reduce CuCl_2 to CuCl [54], potentially undermining the etching mechanism.

Our objective was to develop a plasma-based alternative to wet etching for the removal of copper seed layers in the SAP used to fabricate high-density interconnects (HDI) on organic substrates. Although wet etching is simple, it is isotropic and can lead to undercutting and contamination—especially at L/S dimensions below 5 μm . Replacing it with a dry, directional etching method would represent a significant advancement for advanced packaging.

The one-step $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasma process was implemented in an ICP reactor at 200°C—a temperature selected based on the thermal budget of the organic substrate [55]. A key finding was the critical role of surface preparation: even a native oxide layer was found to inhibit etching and instead promote the formation of a thick, rough copper chloride film. As further discussed in Section 3, this behavior underscores the importance of surface condition in copper plasma etching. A brief deoxidation step prior to plasma exposure enabled smooth, uniform etching.

Etch rate was highly sensitive to Cl_2 concentration. A peak rate of ~150 nm/min was achieved near 8% Cl_2 ; higher concentrations led to surface deposition, likely due to low-volatility CuCl formation.

When applied to SAP structures, the process revealed that electrochemically deposited (ECD) copper—used to fill interconnect features—etched nearly 10 times faster than physical vapor deposited (PVD) copper used for seed layers. This behavior is likely influenced by grain structure, crystallographic orientation, and potential plating-induced contamination, as also discussed in Section 3. To address this, a protective and permanent cap layer was developed to shield the ECD copper during plasma exposure while maintaining electrical performance. With this cap in place, the optimized $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasma process demonstrated clean, undercut-free etching with no measurable chlorine contamination. L/S patterns as small as ~1.65 μm were successfully fabricated on organic substrates using this advanced plasma-enhanced SAP process. Importantly, the resulting interconnects exhibited excellent electrical

performance, confirming that the plasma exposure did not degrade signal integrity or increase resistivity [56]—an essential requirement for HDI in packaging applications.

Sometimes, bringing the right supporting cast into the plasma is exactly what it takes to get copper to follow the script.

2.2.6 Etching of copper by silicon tetrachloride plasma

In studies by Howard and colleagues [57, 58], silicon tetrachloride (SiCl_4) was investigated as part of a mixed-gas plasma—either with argon or nitrogen—for copper etching applications. Effective surface chlorination required substrate temperatures above 190°C , followed by a wet etch step in ammonium hydroxide (NH_4OH) to remove the reaction products. This two-step approach imposed limitations in terms of thermal budget and process complexity.

The choice of carrier gas was found to significantly affect etch performance. While SiCl_4/Ar plasmas produced measurable etching, the use of nitrogen instead of argon led to a notable improvement in etch rate—allegedly due to enhanced production of reactants. In SiCl_4/N_2 plasmas, etch rates reached up to 85 nm/min . However, the resulting surface morphology exhibited roughness and sloped sidewalls, indicating limited anisotropy.

We could think of SiCl_4 as having passed the chemistry audition—but when it came to performance, it never quite nailed the role.

2.2.7 Etching of copper by boron trichloride plasma

Building on their earlier investigations into copper etching using halogenated plasmas, Howard and Steinbrüchel [59] evaluated boron trichloride (BCl_3) as a potential candidate for single-step dry etching. In this study, nitrogen was introduced into the plasma to enhance the production of reactive species, enabling copper patterning at substrate temperatures exceeding 275°C . Etch rates around 55 nm/min were achieved across a range of BCl_3/N_2 ratios. However, the resulting surfaces were notably rough, limiting the method's viability for applications requiring precise dimensional control.

BCl_3 seemed like the next hopeful in Howard's casting call—following SiCl_4 in the lineup, only to flub its lines and scuff the set on the way out.

2.2.8 Etching of copper by hydrogen bromide plasma

The use of hydrogen bromide (HBr) for copper dry etching has been explored with varying success. Foundational work by Nakakura and Altman [60], who exposed copper surfaces to Br_2 gas and analyzed the resulting products *via* mass spectrometry, showed that CuBr_x species begin to sublime at approximately 177°C . While this indicated some degree of volatility, it has been interpreted that the CuBr_x species are likely not sufficiently volatile to enable a fast or complete dry etching process.

To address this limitation, Lee and Kuo [61] proposed a dry-wet hybrid approach involving HBr plasma followed by immersion in an HCl solution. This process enabled copper patterning at room temperature with an etch rate of approximately 340 nm/min . However, the resulting sidewalls were significantly rougher than those achieved using Cl_2 -based plasmas. The authors attributed this to bromine's more aggressive attack on copper grain boundaries.

More recently, Lim et al. [62] investigated a cyclic etching strategy involving alternating exposure of the copper surface to an HBr/Ar gas mixture and Ar plasma

sputtering of the resulting CuBr_x layer. While this method achieved successful patterning at room temperature and produced smooth sidewalls, the etch rate was extremely low—on the order of 1 nm/min.

HBr entered with potential, offering a low-temperature act and a few technical flourishes—but in the end, its performances were either too rough or too slow to carry the show. Still, the script is not finished—another act is about to begin.

2.3 Hydrocarbon-based approaches

2.3.1 Etching of copper by methane plasma

Hydrocarbon plasmas have been explored as an alternative to halogen- and hydrogen-based systems for copper dry etching, particularly for low-temperature processes compatible with polymer-based masking materials. This is particularly relevant because, while hydrogen plasmas can etch copper at low temperatures (as discussed in Section 2.1.2), they also cause severe degradation of PR masks due to carbon-hydrogen reactions that readily form volatile compounds—resulting in poor etch selectivity. To address this, Choi et al. [63] investigated whether methane (CH_4) plasmas could achieve similar etching effects while offering better compatibility with organic masks. The authors hypothesized that methane dissociation would yield etching-active species similar to those in H_2 plasmas, while offering improved mask protection due to the passivation of the PR surface by deposited hydrocarbon layers. Additionally, the resulting methylated copper compounds were expected to be more stable than copper hydrides. Their results showed that, as in Cl_2 and H_2 ICP plasmas, etch rates were enhanced by increased platen and coil powers. By adding 50% H_2 to the CH_4 plasma, they achieved an etch rate of 20 nm/min at 10°C —compared to 13 nm/min for pure H_2 plasma—with a sidewall angle of approximately 80° . The improvement was attributed to both the higher momentum transfer from CH^+ and C^+ ions and the increased stability of the CH_3Cu and CH_3CuH^- reaction products compared to CuH_x . Additionally, the presence of hydrogen contributed to the formation of CH_x radicals, which enhanced reactivity with copper. The authors noted that no methyl-containing copper species were detected in the OES—only Cu emission lines—likely due to rapid byproduct dissociation by electron impact. Ultimately, while the PR mask/Cu selectivity improved by over $17\times$ compared to H_2 plasma, it remained poor in absolute terms—on the order of 0.25.

Noting the presence of redeposition in the profiles reported by Choi et al., Lim et al. [64] explored an alternative gas mixture combining CH_4 , O_2 , and Ar. They observed that at high CH_4 concentrations, polymer deposition dominated rather than etching. However, under optimized conditions—50% CH_4 , 15% O_2 , and 35% Ar—they achieved redeposition-free etching at 14°C with a sidewall slope of 75° and an etch rate of 70 nm/min. The addition of O_2 and Ar was believed to promote ion sputtering and generate volatile byproducts such as $\text{Cu}(\text{OH})_2$ (see **Table 1**), thus improving etching performance relative to pure CH_4 .

It may not have delivered a breakout performance, but methane managed to stay cool and protect the cast—a respectable turn for a gas better known for clearing the room.

2.3.2 Etching of copper by alcohol plasmas

In response to environmental concerns surrounding CH_4 —specifically its role as a potent greenhouse gas—Lim et al. [65] proposed the use of alcohol-based plasmas

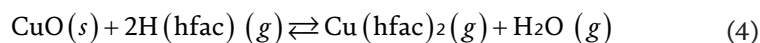
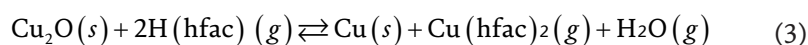
as more sustainable alternatives for copper etching. Their study in an ICP reactor at 10°C compared methanol and ethanol, revealing that while methanol yielded slightly higher etch rates, it also caused considerable redeposition. Ethanol, on the other hand, produced cleaner etch profiles, and the addition of 10% O₂ further improved anisotropy, allegedly by enhancing the reactivity of CuO_x with C₂H₅OH. Under optimized conditions, the etch rate reached 25 nm/min with a sidewall angle of 70°. The etching mechanism was attributed to a combination of chemical reactions with OH*, CH_x*, and H* species and physical sputtering by O₂⁺, O⁺, and CH_x⁺ ions.

Alcohols have also shown promise as additives in hybrid etching systems. In one study, butanol was added to an ethylenediamine (EDA)/Ar plasma at 10°C. Although the resulting Cu etch rate was modest (~15 nm/min), the profile was notably cleaner, likely due to passivating sidewall layers and the formation of copper oxides subsequently sputtered by Ar⁺ ions [66]. Seeking higher rates, the same group replaced EDA with piperidine—another Cu-chelating amine with only one bridging group—paired with ethanol for its similar boiling point. This mixture (10% C₂H₅OH, 35% piperidine, and 55% Ar) achieved a 35 nm/min etch rate and clean 300 nm L/S patterns with sidewall angles of around 75°. X-ray photoelectron spectroscopy (XPS) and OES data suggested etching occurred through desorption and sputtering of CuCN, CuO_x, and CuH_x species [67].

Often associated with wild nights and bad decisions, alcohol surprised the audience with a disciplined performance—etched lines, not lines forgotten.

2.3.3 Etching of copper by hexafluoroacetylacetone [H(hfac)]

H(hfac) has garnered interest as a vapor-phase reagent for copper etching due to its strong affinity for copper oxides and negligible reactivity with metallic Cu. George et al. [68] demonstrated that H(hfac) can etch oxidized copper surfaces selectively *via* the following reactions:



These reactions are highly sensitive to process conditions, requiring at least 1000 Pa of pressure and temperatures around 170°C to initiate. Etching slows significantly above 240°C, likely due to the thermal reduction of the copper oxide layer back to metallic copper [69].

Very high etch rates—up to 1 µm/min—have been achieved when H(hfac) exposure is combined with vapor-phase oxidation using H₂O₂ at 190°C [70]. However, this rapid oxidation leads to void formation, causing rough surfaces and isotropic profiles. As a result, such processes are generally better suited for chamber cleaning than for patterning.

Kang et al. [71] explored an alternative method in which ozone radicals (O₃) were generated *via* ICP and reacted with H(hfac) downstream. Although etch rates of 110 nm/min at 200°C were observed, surface roughness remained a limitation.

In a more direct plasma-assisted approach, H(hfac) was introduced alongside O₂ into an ICP reactor. When oxidation was performed first and followed by H(hfac) exposure, etch rates of ~25 nm/min at 210°C were obtained. A simultaneous O₂/H(hfac) plasma, introduced *via* a showerhead above the substrate, improved the

rate to 70 nm/min under the same temperature. However, due to the isotropic nature of the reaction, the resulting sidewall angles remained shallow—around 30°—making it unsuitable for patterning fine features [72, 73].

H(hfac) brought selective chemistry and dramatic speed to the stage—but with rough surfaces and imprecise profiles, it is better suited to backstage cleanup than a starring role.

2.3.4 Etching of copper by organic acids

Organic acids such as acetic and formic acid have emerged as low-temperature candidates for copper etching due to the relatively low volatility of their copper reaction products—particularly $\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2$ (see **Table 1**). These compounds offer the potential for enhanced etch rates and improved surface quality, though each method presents unique limitations in terms of anisotropy, throughput, or process complexity.

Ryu et al. [6] investigated copper etching in an ICP reactor using vapor-phase acetic acid at 10°C. The best results were obtained with a 50% $\text{CH}_3\text{COOH}/\text{Ar}$ mixture, which yielded an etch rate of 35 nm/min and redeposition-free features, albeit with sloped sidewalls. Drawing from trends observed in previously discussed O_2 -enriched plasmas, it is likely that the addition of O_2 could have improved etching performance, though this was not explored in the study.

Toyoda et al. [74] adopted a two-step process in which a copper surface was first exposed to acetic acid vapor and then bombarded with an O_2 cluster ion beam—an aggregate of thousands of O_2 molecules electrostatically accelerated toward the sample. The beam successfully removed a monolayer of the resulting $\text{Cu}(\text{CH}_3\text{COO})_2$ reaction product, though the etch rate was low (~0.2 nm/min). Reversing the process order—oxidizing the surface first, then exposing it to acetic acid—did not significantly enhance the rate but interestingly produced exceptionally smooth surfaces, free of preferential etching on grain boundaries and ion channeling effects [75].

Formic acid (CH_2O_2) was evaluated by Sheil et al. [76], who demonstrated that the liquid reacts ~300× faster with CuO_x than with metallic copper. As liquid-phase treatments cannot provide anisotropic profiles, the team proposed a cyclic process combining plasma oxidation with gas-phase CH_2O_2 exposure. Oxidation was performed in an ICP reactor at room temperature, followed by transfer to a secondary vacuum chamber (80°C) for the reduction step. While clean profiles were obtained, the vacuum break between steps limited throughput, resulting in an etch rate of only ~0.2 nm/min. Raising the temperature to accelerate the process may not be viable, as CH_2O_2 decomposes above 187°C [77], potentially reducing the oxide layer and reversing the intended etch [78]. Density functional theory (DFT) simulations further showed that CH_2O_2 -based etching is thermodynamically favorable under water-deprived conditions [76], suggesting that a single-step $\text{CH}_2\text{O}_2/\text{O}_2$ plasma may offer a promising path forward.

Organic acids took the stage with elegance—but delivered their lines so slowly, they risked losing the crowd. In the next act, we shift focus from the performance to the protagonist itself—and how its inner nature can shape the plot.

3. Behind the scenes: Copper's surface and structure impact on etching

Even the most seasoned actor can stumble if the stage is uneven—or if their costume pulls in all the wrong places. Likewise, copper's behavior during dry etching

is not just dictated by chemistry. It also hinges on subtle but significant structural features. Surface oxides, grain boundaries, and crystallographic orientation can all hinder, delay, or unevenly advance the etching process—sometimes stalling the scene entirely. In this act, we take a focused look at how copper's physical structure shapes its interaction with plasma, drawing from the limited but telling studies available.

Although few studies have directly examined the role of copper's surface condition prior to plasma treatment, it has been postulated that the formation of copper oxychloride may inhibit etching in Cl_2 plasmas [79]. Our own results, discussed in Section 2.2.5, confirmed that surface oxides can severely hinder copper removal, highlighting the need for proper deoxidation prior to etching. These findings suggest that removing native oxides and contamination layers is essential for ensuring uniform etching. Surface preparation, in turn, plays a central role in minimizing plasma-induced roughness—especially in applications where plasma etching is considered as an alternative to CMP, such as for overburden copper removal. Beyond surface cleanliness, copper's microstructure also contributes significantly to local etch non-uniformities and resulting roughness [80]. Zhang and Machlin [81] showed that CuCl_x forms preferentially at grain boundaries. Because chlorination progresses at different rates along boundaries and within the bulk, Lee and Kuo [82] observed that Cl_2 plasma etching could result in substantial surface roughness. Controlling grain size may help mitigate this effect, and Liu et al. [83] explored this hypothesis. As expected, larger grains reduce electrical resistivity; however, their study found that surface roughness increased with grain size during etching in a Cl_2 -based plasma.

Although smaller grains have been shown to reduce surface roughness during Cl_2 -based plasma etching, maintaining a fine-grained structure in copper is far from straightforward. Due to its strong tendency to self-anneal—even at room temperature [84, 85]—copper naturally undergoes grain growth over time, especially in ECD films. Yet this evolution is not entirely detrimental: recrystallization can reorient grains in favorable ways. For instance, Cl adsorption and etch rates are influenced by crystal orientation [54, 86], with (111)-oriented grains often showing enhanced reactivity. A copper surface dominated by (111) grains may also reduce the impact of ion channeling—an effect in which regions of different crystallographic orientation exhibit varied sputtering yields, often worsening roughness [87].

The crystallographic texture of copper films is strongly influenced by the underlying adhesion layer. X-ray diffraction (XRD) studies have shown that titanium adhesion layers tend to promote (111) grain orientation, while tungsten coatings favor (100) alignment [88]. In contrast, ECD copper films typically exhibit random grain orientations, which can exacerbate ion channeling effects under directional ion bombardment [89].

If ion channeling leads to unacceptable roughness, alternative strategies may be necessary. One such approach, proposed by Gale [90], involves pre-irradiating the copper surface with species capable of creating point defects. These disruptions may reduce crystal order, thereby lessening sputtering anisotropy.

The discussion presented here underscores a critical, and often underappreciated, dimension of copper dry etching: the influence of the metal's own structural characteristics. While most research efforts have focused on plasma chemistries, it is increasingly clear that copper's surface condition, grain structure, and crystallographic orientation must also be treated as central variables. As discussed in Section 2.2.5, ECD-Cu etched nearly 10 times faster than PVD-Cu under identical plasma conditions. This difference stems not only from variations in grain size and orientation but possibly from differences in contamination levels introduced

during deposition—particularly in ECD films—which warrants further investigation. Properly addressing these microstructural and compositional factors may be essential for optimizing etch performance. For instance, crystal orientation could prove critical for enabling plasma etching as a viable alternative to CMP in the planarization of damascene structures. Notably, copper recrystallization proceeds significantly faster in the wider turnaround regions of damascene features [84]. This results in substantial local variation in grain size and orientation within the same structure—conditions that could severely hinder uniform etching. Ultimately, realizing the full potential of copper dry etching will require a more holistic approach—one that considers not just the plasma above the surface but the nature of the copper beneath it.

In short, a flawless performance is not only about the chemistry between actors. Likewise, if we want copper to hit its marks under plasma, we will need to pay closer attention to its posture, its wardrobe, and what lies beneath the makeup.

4. Conclusion: The final act?

Over the course of this chapter, we have traced copper's complicated relationship with plasma etching—through the many inventive chemistries and strategies developed in pursuit of a clean, scalable process, and the persistent challenges that have accompanied them. Whether halogenated, non-halogenated, or hydrocarbon-based, one message emerges clearly: copper is difficult to direct under plasma, but its role is far from over.

Despite decades of research, no single subtractive dry etch strategy has yet proven technically and industrially viable at scale for FEOL interconnects. However, recent progress—including new process chemistries, hybrid etching schemes, and microstructural insights—suggests the field is anything but stagnant. With careful attention to surface preparation, plasma design, and copper's own structural properties, dry etching no longer feels like an impossible act—just an unfinished one.

Crucially, this is not only a reflection on copper's past or present—it is a question about its future. While copper will likely remain dominant in larger-pitch interconnects and traditional back-end-of-line and packaging applications, its place in the most advanced nodes is increasingly under pressure. Exotic alternatives—such as cobalt, ruthenium, and iridium—have stepped into the spotlight, vying for the lead role. And yet, copper's intrinsic performance advantages remain compelling—if, and only if, we can develop a scalable, directional, and residue-free dry etch solution. Equally important is the availability of ultrathin, conformal diffusion barriers that can meet the stringent scaling and reliability demands of fine-pitch integration—another key obstacle in efforts to maintain copper's position in advanced FEOL nodes. However, it is worth noting that the development of a subtractive copper etch process could ease some of these constraints: rather than requiring barriers to line complex damascene structures, future architectures could allow copper to be patterned first, then encapsulated—potentially enabling simpler and more scalable barrier integration.

Importantly, etching is only part of the story. Any viable copper etch process must also account for tool integration and long-term stability. Redeposited byproducts can foul reactor surfaces, and corrosive gases or reaction products may accelerate wear in pumping systems—introducing reliability risks and maintenance overhead. In this sense, developing a copper dry etch solution is not just a chemistry challenge but a

manufacturing scalability problem, where behind-the-scenes logistics matter as much as the performance under the lights.

We therefore call on the scientific community to revisit copper—not as a fading star, but as a protagonist still capable of carrying the story. The development of a sustainable dry etch process is not just about honoring copper's legacy; it is about enabling the next generation of interconnects. The pursuit is bigger than any one material—it is about expanding what is possible in etch chemistry, integration engineering, and semiconductor manufacturing.

If we can rise to meet that challenge—balancing chemistry, process control, and tool robustness—then copper may not be stepping off the stage after all. It may simply be waiting, quietly and stubbornly, for its deserving encore.

Acknowledgements

The authors wish to thank the NSERC/IBM Industrial Research Chair and PROMPT Québec for supporting this work. LN2 is a joint International Research Laboratory (IRL 3463), co-funded and co-operated in Canada by the Université de Sherbrooke (UdeS) and in France by the CNRS, École Centrale de Lyon (ECL), INSA Lyon, and Université Grenoble Alpes (UGA). It is also supported by the Fonds de recherche du Québec—Nature et technologies (FRQNT).

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Research Advances and Practical Applications of Cu-Al-Mn Shape Memory Alloys

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Abstract

Cu-Al-Mn shape memory alloys (SMAs), as a new generation of low-temperature responsive functional materials, exhibit excellent shape memory effect, super-elasticity, high damping capacity, and good workability. These properties make them highly promising for applications in aerospace, civil engineering, mechanical electronics, and biomedical fields. This review systematically summarizes the fundamental principles and key characteristics of Cu-Al-Mn SMAs, including thermoelastic martensitic transformation mechanisms, super-elastic behavior, damping properties, and phase diagram structures. In terms of alloy design, researchers have optimized transformation temperatures, recovery strain, and thermal stability by adjusting the Al/Mn ratio and introducing trace elements, such as Ti, V, and Zr. In manufacturing, advanced processes such as laser powder bed fusion, powder metallurgy, and rapid solidification significantly improve microstructural uniformity and performance stability. The paper further discusses microstructural control, multi-physical field coupling effects (magnetocaloric and elastocaloric effects), and fatigue life enhancement strategies. Through bibliometric and visualization analysis, current research hotspots and trends are also highlighted. Despite the great potential of Cu-Al-Mn SMAs in low-temperature functional applications, challenges remain in understanding the reverse martensitic transformation mechanism, improving cyclic stability, and adapting to extreme service environments. Future research can focus on integrating multiscale simulations, additive manufacturing, and multifunctional material design to accelerate the engineering application of Cu-Al-Mn SMAs in structural health monitoring, intelligent actuation, and energy conversion.

Keywords: Cu-Al-Mn SMAs, martensitic phase transformation, super-elasticity, shape memory effect, high damping capacity

1. Introduction

Shape memory alloys (SMAs) are a class of intelligent materials characterized by a shape memory effect (SME) and super-elasticity (SE). In SMAs, the original shape

can be regained by heating it to above a characteristic temperature if it is deformed at low temperature, which is known as the SME. If the material is deformed at high temperature, the original shape can be recovered by simply removing the applied load, which is known as the SE. These unique behaviors of Au-Cd alloys, which originate from the thermoelastic reversible martensitic transformation, were first discovered by Olander in the 1930s [1]. SMAs have found extensive applications in aerospace, biomedicine, civil engineering, mechanical manufacturing, and other fields.

According to their matrix compositions, SMAs are primarily classified into three categories: nickel-titanium-based (NiTi), iron-based (Fe-based), and copper-based (Cu-based) alloys. NiTi alloys are the most widely used and commercially mature SMA type, renowned for their excellent shape memory effect, high damping capacity, biocompatibility, and super-elastic mechanical properties. However, they suffer from high costs and complex processing technologies. Fe-based alloys are cost-effective and mainly used in damping systems, but they exhibit narrow phase transformation temperature ranges and weaker shape memory effects. Cu-based alloys, featuring low cost, good thermal stability, high thermal conductivity, and superior formability, have become a significant research focus in the SMA field [2]. Thanks to their good plasticity and processability, they can be easily fabricated into various shapes through traditional processing methods, such as rolling, forging, and extrusion, with relatively low processing costs that meet the forming requirements of different applications. Nevertheless, in specific corrosive environments, Cu-based alloys are prone to corrosion, affecting their service life and performance stability. Surface protection is often required to enhance their corrosion resistance [3].

Copper-based shape memory alloys mainly include Cu-Zn-Al, Cu-Al-Ni, and Cu-Al-Mn systems. Among them, Cu-Al-Mn alloys have garnered increasing attention due to their excellent low-temperature shape memory performance, good super-elasticity, high damping capacity, superior processability, and low heat treatment costs. They exhibit remarkable potential, particularly in low-temperature application scenarios.

Research on Cu-Al-Mn shape memory alloys can be traced back to the 1990s, when Kainuma and colleagues first systematically investigated the martensitic phase transformation behavior and shape memory characteristics of Cu-Al-Mn alloys [4]. With deepening explorations of phase transformation mechanisms, microstructural regulation, and process optimization, the functional properties of these alloys have been continuously improved, making them a research hotspot in low-temperature SMAs. In recent years, the introduction of advanced technologies, such as additive manufacturing, nanocomposite modification, and microstructural tailoring, has significantly enhanced the performance of Cu-Al-Mn alloys and expanded their application scope.

This paper provides a systematic review of the fundamental principles, key properties, research advancements, and typical applications of Cu-Al-Mn shape memory alloys in the fields, such as aerospace, civil engineering, biomedicine, and other fields. Focusing on the latest research achievements, it evaluates their development trends and future potential while identifying the remaining scientific and engineering challenges.

2. Fundamental principles and characteristics of Cu-Al-Mn SMAs

As a key representative of copper-based SMAs, the core properties of Cu-Al-Mn shape memory alloys rely on the thermoelastic martensitic phase transformation

occurring within specific temperature ranges, endowing them with shape memory, super-elasticity, and excellent damping performance.

2.1 Shape memory effect of the Cu-Al-Mn SMAs

The shape memory effect of Cu-Al-Mn alloys originates from the reversible thermoelastic martensitic phase transformation. As the temperature decreases below the M_s point (the martensitic transformation start temperature), the high-temperature austenite (β) phase of the alloy transforms into the low-temperature martensite (β' or γ') phase. When the material is deformed in the low-temperature martensitic state, martensitic variants undergo preferential orientation (or “preferential growth”). When the temperature rises above A_f (austenite finish temperature), the material fully recovers to its original austenitic state through reverse transformation, achieving shape memory function. Thermodynamically, the phase transformation is accompanied by latent heat absorption/release, following the principle of Gibbs-free energy minimization. Crystallographically, the martensite in Cu-Al-Mn alloys typically has an 18R or 2H structure with a dodecahedral twin structure, which can stabilize into different sub-type structures after varying Mn contents or heat treatments [5]. For example, Jain et al. [6] regulated the Al/Mn ratio and found that the martensite sub-type structure can evolve from 18R to 6R, affecting the phase transformation temperature and recovery strain rate.

Additionally, Salgado et al. [7] studied the bainite precipitation behavior of the Cu-74.5Al-15Mn-10.5 alloy under non-isothermal conditions and found that the precipitation of bainite competes with the martensitic phase transformation process, inhibiting its reversibility and thus weakening the shape memory effect.

2.2 Super-elasticity of the Cu-Al-Mn SMAs

In the austenite stable region above the A_f temperature, the Cu-Al-Mn alloy exhibits excellent super-elasticity, meaning that under an applied load, martensite structures are generated through stress induction, and upon removal of the stress, the austenite phase recovers, thereby demonstrating complete strain resilience [8]. At the crystalline scale, this behavior is manifested as a cycle of stress-induced martensite formation and disappearance (**Figure 1**) [9].

For example, Wang et al. [10] developed a Cu68.5Al17.5Mn14 single-crystal alloy exhibiting an ultra-wide operating temperature range (up to 150 K) and excellent super-elasticity, with a maximum recovery strain exceeding 10%, demonstrating its potential in thermal actuators and elastic cooling systems. Liu et al. [11] enhanced the super-elastic stability of Cu-Al-Mn alloys across different temperature zones through gradient hot-rolling technology, making them suitable for multi-temperature mechanical components.

Additionally, the stability of stress-induced phase transformation behavior depends on grain orientation, defect density, and heat treatment conditions. Kwon et al. [12] used white-light X-ray microdiffraction to reveal strain response differences among grains in polycrystalline alloys, showing that stress distribution heterogeneity exists both between grains and within individual grains. Reversible martensitic phase transformation leads to reversible phenomena in strain/stress evolution processes associated with the material's super-elastic behavior.

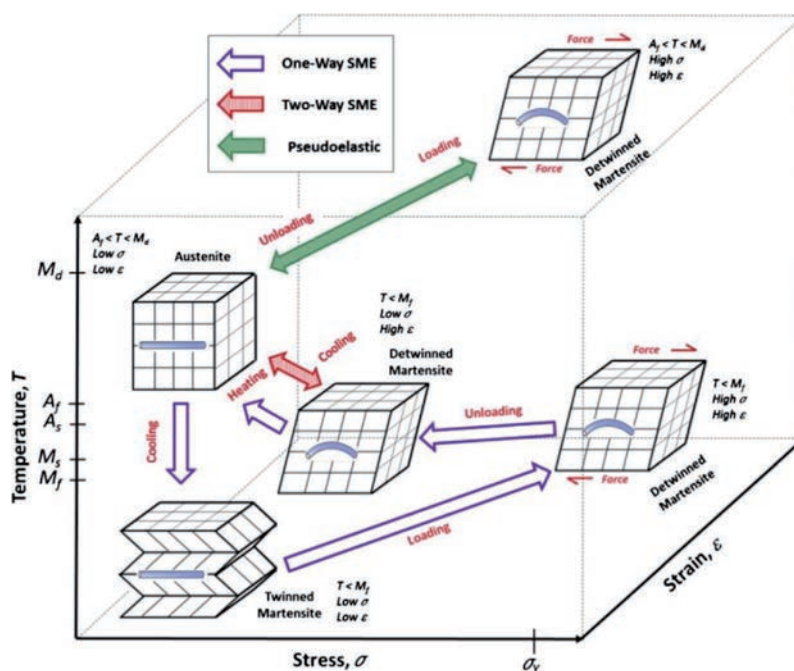


Figure 1.
Shape memory effect and super-elasticity.

2.3 Damping performance of the Cu-Al-Mn SMAs

Cu-Al-Mn alloys also exhibit good internal friction properties, that is, high damping characteristics. Under loading, reversible phase interface/twin boundary slip in materials serves as the primary energy dissipation mechanism. Furthermore, phase transformation hysteresis under thermal loading causes internal energy loss, further enhancing damping effects.

Jiao et al. [13] systematically studied the relationship between internal friction and strain amplitude in Cu-Al-Mn alloys and found that their damping performance exhibits plateau-like enhancement in specific strain intervals, attributed to the slip and recovery mechanisms of martensite twin boundaries. Li et al. [14] enhanced internal energy dissipation pathways by designing porous structures, enabling materials to maintain strength while demonstrating higher damping capacity, suitable for seismic and dynamic response components. Additionally, certain heterostructure designs (e.g., graphene composites [15], nano-precipitate strengthening [5]) can further amplify internal friction responses.

2.4 Phase diagram of the Cu-Al-Mn SMAs

The phase diagram of the Cu-Al-Mn ternary alloy system contains multiple metastable and stable phase regions, where the high-temperature stable β -phase can transform into reversible β' martensite (18R type) or irreversible bainite under rapid cooling or controlled cooling conditions. This transformation is governed by Al and Mn contents, cooling rate, and subsequent aging treatment methods.

Figure 2 [16] represents the liquidus surface phase diagram of the Cu-Al-Mn ternary alloy. The coordinate axes represent the atomic percentage (at.%) of the three elements (Cu, Al, and Mn). The curves in the figure are the liquidus lines at different temperatures, and the numerical values (such as 800, 900, etc.) represent the temperature (usually in °C), which is used to indicate the temperature boundary at which the alloy starts to solidify (solid phase appears) from the liquid phase.

Analysis of Phase Transformation Process (Understanding the Starting Point of Solidification Phase Transformation Based on the Liquidus Surface).

Starting Point of Liquid Phase → Solid Phase Transformation:

For any Cu-Al-Mn alloy with a specific composition, the corresponding point can be found in the diagram, and the temperature of the liquidus line, where it is located, is the initial temperature of the solidification phase transformation of the alloy (the temperature at which the liquid phase → solid phase transformation begins). For example, if the liquidus temperature corresponding to the composition of a certain alloy is 900°C, it will be completely liquid when heated above 900°C, and when cooled to 900°C, the solid phase will start to precipitate from the liquid phase (the specific type of solid phase needs to be judged in combination with other phase diagrams or data, as this diagram only reflects the temperature boundary of the liquid phase → solid phase transformation).

Influence of Composition on Phase Transformation Temperature:

Changes in the content of different elements alter the starting point of phase transformation: for instance, the liquidus temperatures in the high-Al region (close to the Al vertex) and the high-Cu region (close to the Cu vertex) differ significantly, indicating that the contents of Al and Cu significantly affect the initial temperature of solidification phase transformation in the alloy.

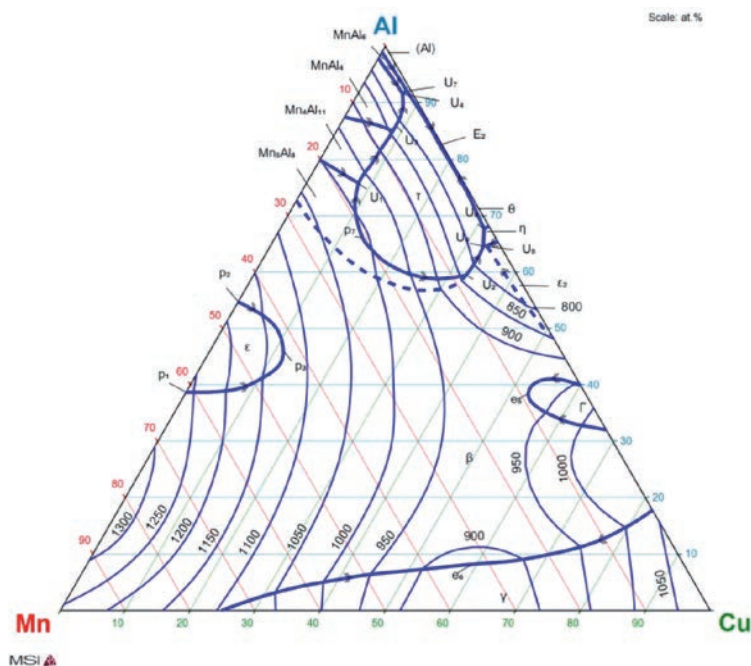


Figure 2.
 The ternary phase diagram of Cu-Al-Mn [16].

The role of the Mn element: Changes in the Mn content also cause the liquidus temperature to shift, reflecting the regulatory effect of Mn on the starting point of solidification phase transformation in Cu-Al-Mn alloys.

The phase transition reactions shown in **Figure 3** involve order-disorder transitions and martensitic transformations in the Cu-Al-Mn system:

2.4.1 Order-disorder transitions in the β -phase region

A2 to B2 transition.

In the β -phase field, there is an order-disorder transition from the A2 (disordered body-centered cubic, bcc) structure to the B2 (CsCl-type ordered bcc) structure. As the aluminum content decreases, the critical temperature for this transition T_c^{A2-B2} drops significantly. This transition represents a change in the atomic arrangement from a random sub-distribution in A2 to a more ordered one in B2, where atoms occupy specific sub-lattice sites.

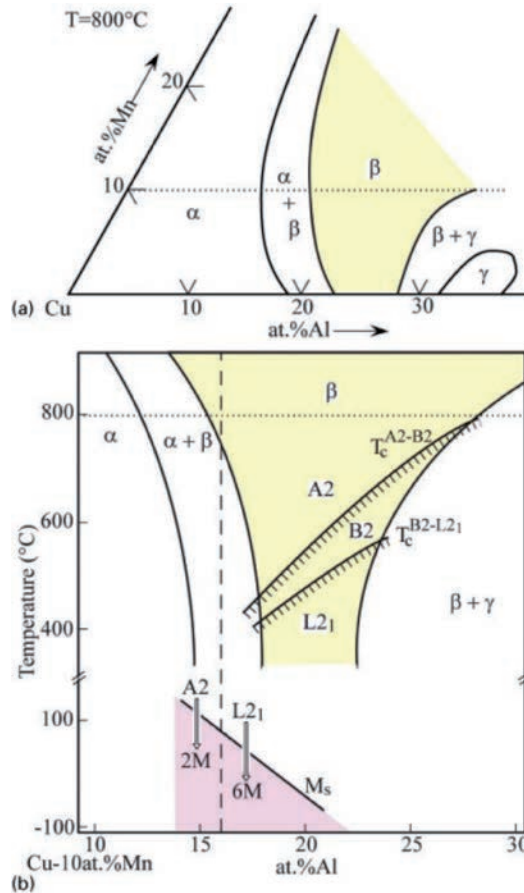


Figure 3. (a) isothermal section diagram at 800°C and (b) vertical section diagram in Cu-Al-10 at.-%Mn ternary system with A2/B2 (T_c^{A2-B2}) and B2/ $L2_1$ ($T_c^{B2-L2_1}$) order-disorder transformation and martensitic transformation starting M_s temperatures [17].

B2 to L2₁ transition.

Subsequently, within the β -phase, there is another order-disorder transition from the B2 structure to the L2₁ (Heusler-type ordered) structure. The critical temperature for this transition $T_{C}^{B2-L2_1}$ also shows a drastic decrease with reducing Al content. The L2₁ structure has a higher degree of atomic ordering compared to B2, with a more complex arrangement of atoms in the unit cell.

2.4.2 Martensitic transformations

For high Al content (> 16 at.% Al).

When the Al content is relatively high (greater than 16 at.% Al), quenching from the disordered A2 phase region cannot suppress the ordering to the L2₁ structure. Then, the L2₁ phase undergoes a martensitic transformation to a 6 M structure. This 6 M structure has a six-layered modulation, which is a characteristic of the martensitic product in this composition range. Martensitic transformations are diffusionless, and the 6 M structure forms through a shear-dominated mechanism, resulting in a new crystal structure with a specific orientation relationship to the parent L2₁ phase.

For low Al content (< 16 at.% Al).

At lower Al contents (less than 16 at.% Al), quenching can suppress the ordering from the A2 to the L2₁ structure. Instead, a martensitic transformation occurs directly from the A2 (disordered face-centered cubic, fcc, like in terms of the parent phase's behavior here) structure to a 2 M (disordered fcc-related martensitic) structure at low temperatures. This transformation also proceeds via a diffusionless, shear-based mechanism, leading to the formation of the 2 M martensitic structure, which has a different crystal structure and properties compared to the 6 M structure formed at higher Al contents.

These phase transitions are crucial for understanding the microstructural evolution and properties of the Cu-Al-Mn alloys, as they affect aspects, such as mechanical properties and functional properties.

Jain et al. [6] and Arlic et al. [5] systematically mapped the thermally stable phase transformation pathways of Cu-Al-Mn alloys, indicating that within the composition range of 15–18 at.% Al and 10–14 at.% Mn, thermoelastic martensite structures with good reversibility and high recovery strain can be achieved; higher Mn content decreases martensite stability and even promotes transformation to bainite or γ_2 phase.

Yang et al. [18] found that during rapid heating (step-quenching), higher heating rates enhance martensite stabilization, thereby inhibiting phase transformation reversibility. Therefore, controlling the heating rate is necessary in applications to improve material service life.

3. Research progress of Cu-Al-Mn SMAs

As a cost-effective and reliable material system, Cu-Al-Mn shape memory alloys have garnered extensive attention from both academia and industry with the development of functional materials science. Since 2012, the number of research papers on Cu-Al-Mn SMAs has shown a nearly annual growth trend. In recent years, remarkable advancements have been achieved in composition optimization, development of novel preparation processes, and multifunctional property regulation.

To systematically summarize the research progress of Cu-Al-Mn SMAs, this study employs a multi-dimensional bibliometric approach based on databases, such as Web of Science, ESI, and CNKI [Note: Including web citations from application sources, such as Web of Science]. Using keywords such as “Cu-Al-Mn shape memory alloy,” “copper-based SMA,” “martensitic transformation,” and “super-elasticity,” a total of 370 relevant literatures from 2012 to 2024 were retrieved. Through theme clustering, co-citation analysis, and research hotspot mining using tools such as VOSviewer [19], 112 core papers were identified, including 82 experimental studies, 12 review articles, and 18 simulation calculations.

Figure 4 illustrates the trends in publication counts and citation frequencies from 2000 to 2025. The horizontal axis denotes the year, while the vertical axis shows the number of publications and citations. Notably, citation frequencies have shown a significant overall growth: starting from a low level in 2000, they increased year by year and reached a peak of 800 citations in 2023. The correlation between the growth in publication numbers and citation frequencies reflects the synchronous enhancement of academic research output and its influence. Overall, the data trends indicate that the research activity and academic influence of Cu-Al-Mn shape memory alloys have continuously intensified over the past 25 years.

In terms of analytical methods, this paper employs a strategy combining bibliometrics with visual analysis. Keyword co-occurrence maps and author collaboration networks were constructed based on VOSviewer [19]. The keyword co-occurrence map (**Figure 5**) indicates that current research on Cu-Al-Mn alloys has expanded from early focuses on martensitic phase transformation mechanisms and shape memory effects to emerging directions, such as super-elasticity, damping performance, elastocaloric effect, and additive manufacturing. The research themes are closely interconnected, demonstrating a trend of interdisciplinary integration and collaborative development.

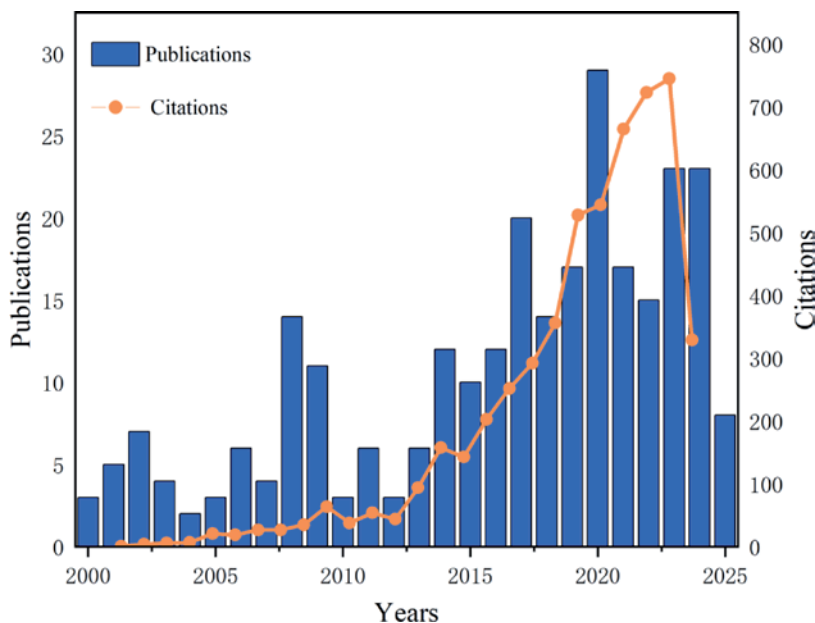


Figure 4.
Number of publications and citation counts.

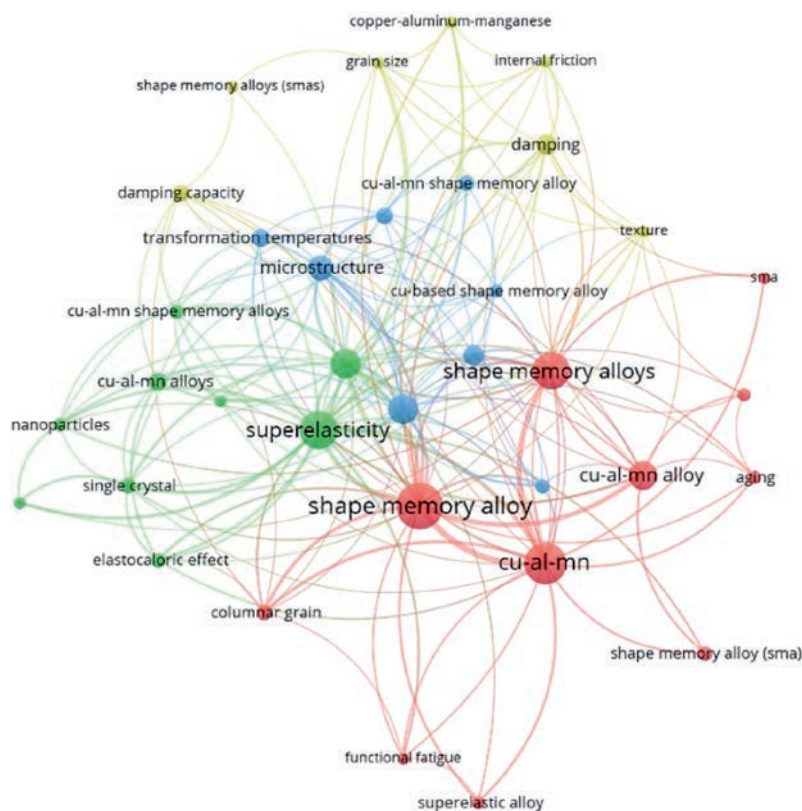


Figure 5.
 Keyword co-occurrence network diagram [19].

The author collaboration network diagram (**Figure 6**) reveals the formation of multiple relatively independent research clusters in this field. Notable examples include the team led by Kainuma Ryosuke in Japan and Wang Qingzhou in China, which have made significant contributions to martensitic mechanism and microstructural control, as well as additive manufacturing and structural applications, respectively. However, the overall collaboration network remains predominantly regionally focused, indicating substantial room for enhancing international collaborative research.

3.1 Alloy composition design and development of novel alloys

The performance of Cu-Al-Mn alloys is extremely sensitive to composition, with the Al/Mn ratio directly determining martensitic phase transformation temperature, structural type, and super-elasticity window width. To further enhance their comprehensive properties, researchers have introduced various alloying elements for composition optimization.

3.1.1 Elements influencing phase structure and phase transformation behavior

Jain et al. [6] studied the effects of different Al/Mn ratios on phase transformation behavior, indicating that moderate Mn content can significantly improve martensite

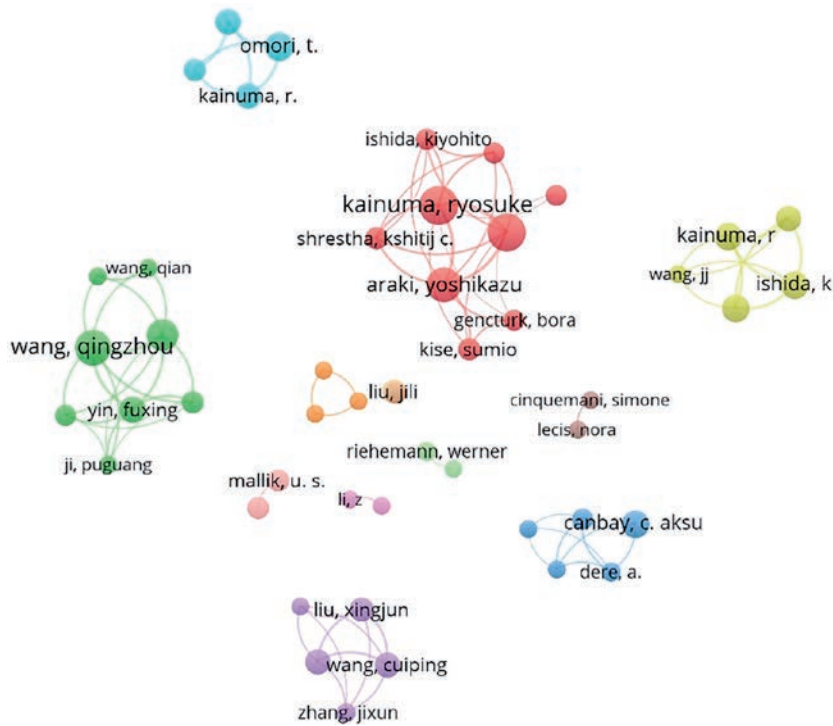


Figure 6.
Author collaboration network map [19].

formation capability, while excessively high Mn content tends to cause poor stability and premature transformation to bainite. Yang et al. [11] further discovered that supersaturated Mn easily induces martensite stabilization, which is detrimental to shape memory recovery. Li et al. [20] investigated the relationship between the microstructure and martensite start temperature (M_s) in Cu-Al-Mn low-temperature SMAs, revealing that the M_s point decreases significantly with increasing Al and Mn contents. Through appropriate composition design, a Cu-Al-Mn SMA with $M_s \approx 110$ K was developed.

Introducing trace elements has become an effective strategy to enhance SMA performance:

Vanadium (V) [21]: V addition promotes β -phase separation, forming $\delta(V, Mn)$ phases and inducing stable β_1 martensite. At room temperature, the microstructure comprises $\beta_3(L21)$ parent phase, minor cubic bcc($\delta(V, Mn)$) precipitates, and ($\beta_1'(18R)$) and ($\gamma_1'(2H)$) martensite. Additionally, V raises A_f and M_s temperatures, triggering multi-stage $\beta_1' \rightarrow \gamma_1' \rightarrow \beta_3$ phase transformations and significantly altering thermodynamic parameters.

Tin (Sn) and Gadolinium (Gd) [22]: The addition of Sn stabilizes the ferromagnetic β_3 phase. In Sn-containing alloys, martensitic transformation occurs at approximately 560 K following mixed interstitial transformation. Both Sn and Gd expand the stable region of the ferromagnetic β_3 phase. However, the formation of Cu_5Gd precipitates by Gd retards the mixed interstitial transformation during heating, thereby reducing the proportion of ferromagnetic phases at room temperature.

Zirconium (Zr) and Hafnium (Hf) [23]: These elements lower austenite transformation temperatures, raise martensite transformation temperatures, significantly

narrow temperature hysteresis, and alter thermodynamic parameters such as enthalpy and entropy changes. Concomitant changes in crystal structure and microstructure reduce crystal size, with magnetism transitioning from superparamagnetic to paramagnetic.

Yttrium (Y) [24] refines grains and enhances strength; titanium (Ti) [25] improves thermal stability and super-elasticity via solid solution strengthening and precipitation control; silicon (Si) [26] forms coherent nano-precipitates, enhancing plasticity and damping performance, while nickel (Ni), iron (Fe), and chromium (Cr) [27–29] regulate martensite start temperatures and hysteresis zone widths.

3.1.2 Elements influencing mechanical properties

Tantalum (Ta) [30]: Using spark plasma sintering technology, Cu-11Al-5Mn-0.7Ti alloys with different Ta contents were prepared. It was found that adding 1 wt.% Ta significantly improves comprehensive properties, with ultimate tensile strength (UTS) reaching 386.1 MPa, compressive strength 1269.9 MPa, and room-temperature damping capacity 0.026. Compared with the matrix, the hardness is increased by 18.2%, the tensile strength is increased by 44.9%, and the compressive strength is increased by 28%. The strengthening mechanisms primarily involve fine-grain strengthening and dispersion strengthening by secondary phases.

TiB₂ nanoparticles [31]: Serving as effective heterogeneous nucleation sites, TiB₂ nanoparticles significantly refine Cu-Al-Mn SMA grains. Electromagnetic field treatment inhibits their agglomeration, further enhancing refinement and reducing spherical pore defects.

Niobium (Nb) [32]: Adding 2% Nb refines grains, forms an ideal martensitic microstructure, nearly doubles alloy strength, increases strain by ~33%, and achieves a shape memory recovery rate of 95%.

Zirconium (Zr) [33]: Refines α -Cu phase grains and improves microhardness. Adding 5% Zr can increase the melting point of the alloy from 1220 K to 1260 K, promote Cu₂ZrAl phase formation, and alter β 3(L21) phase stability and saturation magnetization, without affecting the Curie temperature.

3.1.3 Elements influencing functional properties

Nickel (Ni) [34]: Alloying inhibits vacancy movement, effectively improving damping performance in Ni-containing alloys. Solid solution strengthening enhances UTS (~6% increase) and shape memory effect (SME), raises martensite transformation temperatures (M_f and A_s) by 7°C, and increases strain energy dissipation at high temperatures (above A_f), making it suitable for smart structural materials.

Silver (Ag) [35]: Ag addition alters phase stability ranges, with Ag nano-precipitates forming after quenching. Ag promotes β -phase formation, and its precipitation dissolves Mn and Al atoms, reducing the proportion of reactive elements; low-concentration Ag preferentially dissolves in Mn, while high-concentration Ag (4–5%) dissolves in the Cu matrix. However, Ag > 2% inhibits martensite formation, reduces damping capacity, and embrittles the alloy.

Chromium (Cr) [36]: Influences phase composition and grain size, enabling super-elasticity and shape memory effect. For example, the Cu-12.7Al-6.9Mn-1.8Cr alloy exhibits 5.0% super-elastic strain, while Cu-12.5Al-5.8Mn-4.1Cr achieves a maximum 2.5% shape memory effect, with universal stress-induced martensite stabilization.

Iron (Fe) [37]: Together with Al, Fe affects characteristic transformation temperatures, enthalpy-entropy values, and crystal size in Cu-Al-Mn-Fe SMAs. Al and Fe have minor effects on transformation temperatures but decrease enthalpy-entropy values in parallel with concentration, shifting martensitic transformation toward lower temperatures.

Zinc (Zn), silicon (Si), and magnesium (Mg) [38]: Quaternary additions reduce martensite retention ranges, where Ni delays austenite formation, while Zn, Si, Fe, Cr, and Ti advance austenite formation temperatures.

Influencing	Elements	Function or effect	Reference
Phase structure and phase transformation behavior	V	V addition promotes β -phase separation, forming δ (V, Mn) phases and inducing stable β_1 martensite.	[21]
	Sn and Gd	Both Sn and Gd expand the stable region of the ferromagnetic β_3 phase.	[22]
	Zr and Hf	Lower austenite transformation temperatures, raise martensite transformation temperatures, and significantly narrow temperature hysteresis	[23]
	Y	Refines grains and enhances strength	[24]
	Ti	Improves thermal stability and super-elasticity via solid solution strengthening and precipitation control	[25]
	Si	Forms coherent nano-precipitates, enhancing plasticity and damping performance	[26]
	Ni, Fe, and Cr	Regulate martensite start temperatures and hysteresis zone widths.	[27–29]
Mechanical properties	Ta	Significantly improves comprehensive properties	[30]
	TiB ₂	Refines the grain size and reduce defects.	[31]
	Nb	Refines the grain size to improve strength	[32]
	Zr	Refines the grain size and increases the melting point.	[33]
Functional properties	Ni	Inhibiting the movement of vacancies can effectively improve the damping performance.	[34]
	Ag	Changes the stability range of alloy phases	[35]
	Cr	Influences the phase content and grain size, causing the alloy to exhibit super-elasticity and shape memory effect.	[36]
	Fe	Influences the characteristic transition temperature, enthalpy-entropy values, and crystal size of the alloy.	[37]
	Zn, Si, and Mg	Reduce the retained range of martensite. Among them, Ni delays the formation of austenite, while elements, such as Zn, Si, Fe, Cr, and Ti, advance the formation temperature of austenite.	[38]
	Co, Gd, and Sb	Induce the formation of intermetallic compounds and new solid solutions.	[39]

Table 1.
The influences and effects of elements on alloys.

Cobalt (Co), gadolinium (Gd), and antimony (Sb) [39]: Induce intermetallic compounds and new solid solutions, highlighting atomic and electronic properties as critical parameters for evaluating phase equilibrium changes and their effects on phase transformations.

The influence of elements is briefly summarized in **Table 1**.

3.1.4 Development of novel alloys

Cu-Al-Mn-Fe single crystals [40]: Yang et al. developed a novel Cu-Al-Mn-Fe SMA single crystal exhibiting excellent room-temperature super-elasticity (7%) and shape memory effect (8.8%), with near-zero reverse phase transformation hysteresis and a wide 166 K response temperature range.

Monocrystal microfilaments [41]: Yuan et al. prepared single-crystal microfilaments via the Taylor-Ulitovsky method and multi-step cold drawing, showing fully recoverable super-elasticity at room temperature. Cold drawing refined grains and induced preferred <101> orientation, enhancing elastocaloric effects (eCE).

Porous Shape Memory Foams [42]: Li et al. fabricated polycrystalline shape memory foams (porosity ~70%, pore size 0.8–1.1 mm) via silica bead infiltration. Post-cyclic heat treatment increased average grain size to 3.44 μm (20 cycles), with polycrystallinity enhancing peak damping.

Yang et al. designed novel cast Cu-Al-Mn-V [43] and Cu-Al-Mn-W [44] shape memory alloys composed of an $\text{L2}_1\text{-Cu}_2\text{AlMn}$ matrix and fully coherent bcc A2(V/W) nanoparticles. Through annealing of as-cast polycrystalline alloys, abnormal grain growth (AGG) induced by orientation gradients from dissolution of A2(V/W) nanoparticles yields centimeter-scale large grains and single crystals. Single crystals with near-[45] orientation exhibit excellent super-elasticity and fatigue resistance: the Cu-13.7Al-8.6Mn-1.4 V single crystal shows a maximum full super-elasticity of 7.0% and a super-elastic strain of 5.4%, while Cu-Al-Mn-W achieves up to 12% full super-elasticity and 8.5% super-elastic strain, maintaining performance over 5000 cycles. These alloys offer significant advantages in raw material cost, processing simplicity, and functional properties, holding promise as new super-elastic materials.

3.2 New preparation and post-processing techniques for Cu-Al-Mn SMAs

The performance of Cu-Al-Mn SMAs depends not only on their chemical composition but also on their preparation and heat treatment processes. Although traditional smelting methods are mature, they suffer from issues, such as coarse grain size and compositional segregation. In recent years, various advanced techniques have been introduced to optimize their microstructure and functional response.

3.2.1 Additive manufacturing (AM)

Laser powder bed fusion (L-PBF) and selective laser melting (SLM) technologies are widely used because of their high cooling rates and controllable microstructures. Xiang et al. [46, 47] prepared Cu-Al-Mn-Si alloys via L-PBF, obtaining a dual-phase structure and further enhancing shape memory performance through aging treatment. Xi et al. [48, 49] studied the effect of SLM processing on microstructure and found that Nb addition inhibits grain boundary oxidation and improves phase transformation behavior, with a shape recovery strain as high as 8.7%.

In the field of additive manufacturing (AM), Babacan [50] demonstrated that scanning vector rotation angles in laser powder bed fusion (L-PBF) have minimal impact on the porosity and transformation temperature of SMA alloys. A 90° rotation sample exhibited optimal super-elasticity, with a recoverable strain of 6.05% (under 8% applied strain). The Cu-11.85Al-3.2Mn-0.1Ti alloy prepared by this technique features a fully β_1 martensitic microstructure with high-density stacking faults and twins, showing good super-elasticity and shape memory effect—achieving up to 87% super-elastic recovery and 100% shape memory recovery at 6% pre-strain. Huang et al. [51] used arc fusion deposition to prepare Cu-12.5Al-xMn alloys, where increasing Mn content reduces γ_2 phase precipitation and increases Al_2O_3 phase formation in as-cast structures, transforming the quenched structure from hypoeutectoid to eutectoid. The Cu-12.5Al-3Mn alloy achieves shape recovery rates of 79.41 and 84.43% under 4 and 6% pre-strain, respectively. Luo et al. [52] found in SLM processing that laser power significantly affects alloy performance: at 325 W, the sample achieves over 99% shape memory recovery rate and maximum microhardness, enabling the fabrication of near-full-density alloys with ~100% one-way shape memory effect and ~780 MPa tensile strength. Moskvichev et al. [53] used electron beam additive manufacturing (EBAM) to show that heat input significantly influences microstructure and phase composition, with alloy hardness distributed in gradients and friction coefficients ranging from 0.1 to 0.175—softer phase-rich samples exhibiting lower friction coefficients. Wu et al. [54] prepared Cu-71Al-18Mn-11 alloys via SLM, achieving a density of 7.3204 g/cm³ (99.18% relative density) through process optimization. The alloy is nearly fully β -phase at room temperature, with superior compressive strength and fracture strain along the build direction and super-elasticity up to 2.50% along the scanning direction.

3.2.2 Powder metallurgy and rapid solidification

Powder metallurgy significantly reduces grain size and improves nucleation uniformity, making it particularly suitable for preparing complex-composition materials with microalloying elements. Aldirmaz et al. [55] showed that bainite transformation is strongly suppressed in rapidly solidified Cu-9.97Al-4.62Mn alloys, promoting the formation of thermoelastic martensite. Ouyang et al. [56] prepared Cu-Al-Mn ribbons via rapid solidification, which exhibit as-cast columnar grain structures and transform into bamboo-like grain structures after annealing and aging, effectively inhibiting harmful order-disorder transitions and enhancing alloy ductility. Karthick et al. [57] developed a fiber optic sensor with a Cu-Al-Mn-Ni shape memory alloy coating on polymer optical fibers via flash evaporation physical vapor deposition. The coating is uniform and well-crystallized, enabling its application in status monitoring of 3D printers and providing a new solution for temperature sensing in the field of smart manufacturing.

3.2.3 Complex structure fabrication and casting techniques

Wu et al. [58] enhanced super-elastic performance through triply periodic minimal surface (Gyroid) structures, demonstrating the potential of Cu-Al-Mn alloys in structural materials. Alves et al. [59] used rapid investment casting to fabricate porous honeycomb structures with super-elastic response, providing new pathways for mechanical and thermal response structures.

In microstructure regulation, Li et al. [60] used directional recrystallization (DR) to prepare columnar grains in super-elastic Cu-Al-Mn alloys, significantly improving super-elasticity. Li et al. [61] developed novel strong-textured porous (STP)

Cu-Al-Mn alloys via multi-stage sintering, with adjustable porosity (31.1–11.4%), strong $\langle 001 \rangle$ and $\langle 101 \rangle$ textures, and low-angle grain boundaries, facilitating large near-elastic deformation. Zhu et al. [62] induced nonlinear gradient distributions of residual martensite through torsional pre-deformation (TPD), creating austenite/martensite dual-phase structures that significantly suppress the temperature dependence of super-elastic stress.

3.2.4 Heat treatment and aging strategies

Heat treatment processes play a key role in martensite stability and shape memory behavior. Jiao et al. [63] studied precipitate behavior during austenite phase aging and proposed that moderate aging enhances recovery strain rate. Yang et al. [64] developed a “constrained solution treatment” method to control grain boundary movement via external constraints, improving thermal cycle stability.

Liu et al. [11] used gradient hot rolling to maintain excellent super-elasticity in Cu-Al-Mn alloys across multiple temperature zones, expanding their application scope—particularly for thermal-mechanical components in low-temperature to room-temperature transition regions.

Milosavljevic et al. [65] showed that thermomechanical treatment significantly affects shape memory and damping properties: thermal cycling stabilizes transformation temperatures, but high temperatures induce martensite stabilization; damping performance is influenced by strain amplitude, frequency, and static preload, with treated alloys comparable to commercial NiTi SMAs, and adjustable damping via static preload. Zhou et al. [66] used gradient heat treatment to control the quantity and size of acicular bainite precipitates, creating gradient distributions in hardness, transformation temperature, and shape memory performance—providing new insights for microstructure design and property control.

3.3 Mechanical property research

The mechanical properties of Cu-Al-Mn shape memory alloys (SMAs) are critical indicators for evaluating their engineering feasibility and application reliability. Traditional Cu-based SMAs suffer from brittle fracture and short fatigue life, but microalloying and novel processing techniques have effectively improved their comprehensive mechanical performance.

Tu et al. [67] proposed optimizing grain morphology through Fe addition and grain boundary engineering, increasing yield strength by 200 MPa and fracture strain to 11.6–14.1%, meeting industrial application requirements. Naresh et al. [68] compared Cu-Al-Mn with Cu-Al-Be-Mn and found that Be refines grains and enhances fatigue life, particularly maintaining good stress-strain recovery under high-cycle conditions.

Additionally, Jiao et al. [15] developed graphene/metal composite structures that not only increased tensile strength from 390 MPa to 565 MPa but also significantly improved ductility and energy absorption, validating the effectiveness of nano-reinforcement in performance enhancement. Yang et al. [69] studied the effects of grain refinement on phase-transformation-induced strain and strength via a fine-grain strengthening pathway, revealing that grain sizes below 10 μm exhibit more stable strain recovery.

In functional fatigue, Shrestha et al. [70] evaluated functional degradation under tensile cycling and found that Cu-Al-Mn retained over 95% recovery strain after 50 cycles, indicating better durability in structural control components than some NiTi SMAs. Karami et al. [71] further revealed significant differences in fatigue

behavior between single crystals and polycrystals from a grain orientation perspective, where grain boundaries in polycrystals accelerate crack initiation.

3.3.1 Influence of crystal orientation on mechanical properties

Crystal orientation significantly affects the plasticity and fracture behavior of Cu-Al-Mn alloys. Kise et al. [72] showed that alloys exhibit poor-to-moderate ductility when specimen orientations are near the $\langle 101 \rangle$ direction, while orientations near $\langle 112 \rangle$, $\langle 113 \rangle$, or $\langle 001 \rangle$ significantly improve ductility, with fracture strains reaching 47–92%. This is primarily attributed to large-angle lattice rotation and long-range propagation of slip bands along the longitudinal direction. Fornell et al. [73] further confirmed through micropillar compression tests that single-crystal micropillars near the $[001]$ orientation exhibit high total strain and low stress, while those near $[74]$ show the opposite trend. In situ X-ray microbeam diffraction experiments revealed that grains with high Schmid factors have larger Laue spot 2θ diffraction angle dispersions, facilitating martensitic phase transformation and causing intragranular deformation heterogeneity. The tension-compression asymmetry of Cu-Al-Mn alloys is significantly anisotropic [75], with the largest transformation strain asymmetry ratio along the $\langle 011 \rangle$ crystallographic direction and the smallest along $\langle 111 \rangle$. Super-elastic properties exhibit significant tension-compression asymmetry parallel or perpendicular to the solidification direction.

3.3.2 Effect of processing techniques on mechanical properties

Different processing techniques significantly influence the mechanical properties of Cu-Al-Mn alloys. Kise [76] studied 16-mm diameter $\times$ 300-mm long single-crystal rods and found that operations between quenching and aging are feasible and simple. Compared with cut threads, rolled threads have smoother surfaces and significantly improved fatigue resistance, providing process support for large-scale structural engineering applications. Simões et al. [77] laser-welded Cu-17Al-11.4Mn alloys with 316 L stainless steel, resulting in increased hardness in the fusion zone and changes in grain size and orientation. Although the maximum tensile strain of welded joints is lower than unwelded samples, they withstand higher stress and exhibit superior energy absorption and maximum stress in mechanical cycle tests.

Liu et al. [78] adjusted microstructures and textures through multi-pass hot rolling (HR) and single-pass hot rolling followed by multi-pass cold rolling (HR + nCR) to improve workability and super-elasticity. Accumulative roll bonding (ARB) refines grains and enhances strength, while equal-channel angular rolling (ECAR) forms coexisting bainite and martensite structures, improving mechanical properties. Yuan et al. [79] achieved grain refinement and preferred orientation in microfilaments via cold drawing, enhancing elastocaloric effect cycle stability.

3.4 Martensitic phase transformation research

Martensitic phase transformation is the fundamental mechanism, enabling the functional behavior of Cu-Al-Mn shape memory alloys. In this alloy system, a reversible thermoelastic transformation occurs from the high-temperature β -phase (cubic structure) to low-temperature martensite (structures such as 18R, 2H, 6R with stacking fault, dislocation or twin crystal substructures), with the phase transformation temperature window adjustable via alloy design and heat treatment.

Salgado et al. [7] studied bainite precipitation in Cu-74.5Al-15Mn-10.5 alloy under non-isothermal conditions using differential scanning calorimetry (DSC) and Avrami kinetic models. They found that higher cooling rates inhibit bainite formation, promote martensitic transformation, and preserve reversibility. Yang et al. [18] demonstrated that heating rates significantly affect reverse martensitic transformation—particularly during rapid heating (step-quenching), where insufficient kinetic energy prevents residual martensite structures from recovering, degrading the shape memory effect. Subsequent research [64] proposed a “constrained solution treatment” strategy to effectively mitigate martensite stabilization and enhance reversibility.

Lei et al. [80] observed that during martensitic transformation, martensite grains gradually grow with decreasing temperature and shrink upon heating. Multiple differently oriented martensites form within a single grain, interacting with each other. They hypothesized that martensite nucleation sites may exist ubiquitously, with higher nucleation rates at grain boundaries and sample edges, and martensite can grow across grain boundaries into adjacent grains. Intersection points can also serve as new nucleation sites. Bian et al. [81] observed martensite formation in Cu-Al-Mn under compressive stress via in situ compression tests, confirming significant differences in phase transformation pathways between stressed and unloaded conditions. In polycrystalline systems, local stress concentrations lead to non-uniform transformation and residual martensite zones.

Kainuma et al. [1] early revealed that martensite in Cu-Al-Mn alloys exhibits an 18R structure with stacking fault sequences, offering good deformation compatibility and reversibility. In single-crystal Cu-68.5Al-17.5Mn-14 alloys studied by Wang et al. [10], the 18R structure undergoes stress-induced transformation under loading followed by automatic recovery, demonstrating excellent elastic rebound performance.

Xiang et al. [46, 47] further showed that directional grain structures obtained via L-PBF additive manufacturing stabilize single martensite subtypes, reduce coexisting multi-martensite phases, and improve strain consistency and stress-strain controllability. Grguric et al. [82] indicated that process parameters (e.g., cooling rate) significantly affect martensite start temperature (M_s) and finish temperature (M_f), while residual stress widens the hysteresis zone, influencing shape memory recovery accuracy. Lu and Chen [83] investigated martensite induction in Cu-Al-Mn single crystals under compressive loading and found significant elastocaloric effects under stress-temperature co-control, providing new insights for solid-state cooling devices. Xu et al. [84] reported columnar-grained Cu-71.5Al-17.5Mn-11 alloys exhibiting large elastocaloric responses across broad temperature ranges, with maximum temperature changes exceeding 15 K, highlighting the potential of Cu-based SMAs in functional energy applications.

Dang et al. [85] fabricated Cu-11.85Al-3.2Mn-0.1Ti copper-based shape memory alloys with ideal super-elasticity and shape memory effect via laser powder bed fusion (L-PBF). The shape memory effect originates from reverse martensitic transformation and γ_2 (Cu₉Al₄) phase precipitation along grain boundaries. For example, the Cu-11.85Al-3.2Mn-0.1Ti SMA achieves 100% shape memory recovery at 6% pre-strain.

3.5 Research on super-elasticity, damping, magnetic, and other special properties

Beyond shape memory and martensitic transformation, Cu-Al-Mn SMAs exhibit a range of tunable special functional properties.

3.5.1 Super-elasticity

Research on super-elasticity in Cu-Al-Mn alloys encompasses composition design, processing techniques, and performance characteristics:

Compositional Effects:

Boron (B) refines grains and optimizes microstructures to enhance super-elasticity.

Vanadium (V) promotes β -phase separation, induces stable β_1' martensite, alters phase transformation thermodynamics, and significantly improves super-elasticity.

Processing and Heat Treatment Effects:

Multi-pass hot rolling (HR) and hot-rolling followed by multi-pass cold rolling (HR + nCR) adjust microstructures and textures to enhance workability and super-elasticity. Cold drawing refines grains in microfilaments, induces preferred orientation, and improves elastocaloric effect cycle stability, closely linked to super-elasticity.

Quenching forms ordered Cu_2AlMn (L21) structures, providing a basis for super-elasticity. Tempering and aging alter hardness, strength, super-elasticity, and microstructures.

Cyclic heat treatment induces abnormal grain growth to produce ultra-large single-crystal rods, enhancing super-elastic strain.

Scanning vector rotation during laser powder bed fusion (L-PBF) regulates microstructures (e.g., grain size, and texture). A 90° rotation yields optimal super-elasticity.

Thermomechanical treatment stabilizes phase transformation temperatures via thermal cycling, influencing martensite stability and super-elasticity.

Anisotropy:

Kwon et al. [12] found that super-elasticity in columnar-grained Cu-Al-Mn alloys exhibits a “V”-shaped variation and significant anisotropy with the angle between the tensile and solidification directions. Critical martensitic transformation stress also changes, attributed to grain orientation and grain boundary effects with orientation-dependent influences.

3.5.2 Damping performance

Jiao et al. [13] confirmed that strain amplitude significantly affects damping coefficients, particularly in the 5–10% strain range, where high internal friction occurs. Li et al. [14] enhanced energy dissipation pathways via microporous structures, suitable for high-frequency vibration control systems.

Nickel (Ni) alloying inhibits vacancy movement, improving damping in Ni-containing alloys. Step quenching and upward quenching further enhance damping. Adding Ag or Nb to Cu-12Al-5Mn refines grains and increases hardness but reduces damping capacity and internal friction peak temperature. Ag decreases transformable martensite volume, while Nb-forming AlNb_3 phases restrict martensite variant boundary movement. Beryllium (Be), Mn, and Ag substitution for Cu in $\text{Cu}_{81}\text{Al}_{19}$ alloys hinder α -phase ordering, delay β -phase decomposition, reduce grain boundary area, and affect damping performance.

Heat Treatment Effects:

Parent phase aging [86] improves low-temperature damping and the reverse martensitic transformation internal friction peak height, with optimal damping at

600°C aging. For ductile Cu-16.59Al-10.55Mn alloys, damping performance first decreases, then increases, and decreases again with aging time at 250–400°C due to bainite precipitation [87]. In Cu-16.59Al-10.55Mn, increased quenching time raises martensite content and damping, with varying rates before/after 15 minutes due to vacancy concentration changes; damping is limited at low strain after 180 minutes [88]. Thermal cycling (10 cycles) enhances room-temperature damping in porous Cu-Al-Mn alloys, while >20 cycles weaken it due to dislocations and martensite phase changes [89].

Polycrystalline Cu-Al-Mn shape memory foams show increased peak damping, high-strain martensite damping, and recovery strain with larger grain sizes from cyclic heat treatment, while low-strain damping first increases then decreases [42]. In situ LaB6/Al inoculants refine grains, increase phase boundary density, and improve damping; hot-rolled samples further enhance damping by eliminating casting defects [90].

3.5.3 Special property research

Zhao et al. [91] and Gerdan et al. [92] reported that Cu-Al-Mn alloys transition from paramagnetic (PM) to ferromagnetic (FM) after low-temperature aging. XRD reveals that this stems from β 1-phase decomposition into FM β 3-phase and FM nanoparticle formation during aging. Mn atom spin synergizes with martensitic transformation. Gerdan's study on Cu-13Al, Cu-13Al-4Mn, and Cu-13Al-4Mn-2Zn showed Mn induces weak ferromagnetism, reducing magnetic saturation (from 0.03306 emu/g in Cu-Al to 0.00006 emu/g in Cu-Al-Mn) and coercivity (from 110 Oe to 50 Oe), indicating a hard-to-soft magnetic transition and enabling magneto-elastic shape memory effects (MSME). Sunbul et al. [93] observed nonlinear magnetic property changes with Mn content in rapidly solidified Cu-87-xAl-13Mn-x ($x = 5\text{--}15$) ribbons, with saturation values of 6.178–26.204 emu/g for CAM7–CAM14, providing a basis for multi-physical field applications. Canbay et al. [94–96] developed Cu-Al-Mn SMA films and devices for photodetectors and solar tracking systems, demonstrating feasibility in smart control components.

4. Applications of Cu-Al-Mn SMAs

Cu-Al-Mn shape memory alloys (SMAs) exhibit broad application potential in various fields due to their excellent low-temperature responsiveness, shape memory effect, super-elasticity, and high damping performance. These alloys are transitioning from laboratory research to practical engineering applications, particularly in aerospace, mechanical electronics, civil engineering, and smart structures (**Figure 7**).

4.1 Aerospace applications

Low-temperature environments are common operating conditions for aerospace systems. The superior low-temperature responsiveness and phase transformation stability of Cu-Al-Mn alloys make them ideal materials for automatic deployment systems in space structures. Trehern et al. [53] developed a Cu-Al-Mn alloy suitable for extreme low-temperature conditions (<100 K) and validated its elasticity and phase stability in deep-space environments, providing a feasible solution for spacecraft folding structures.

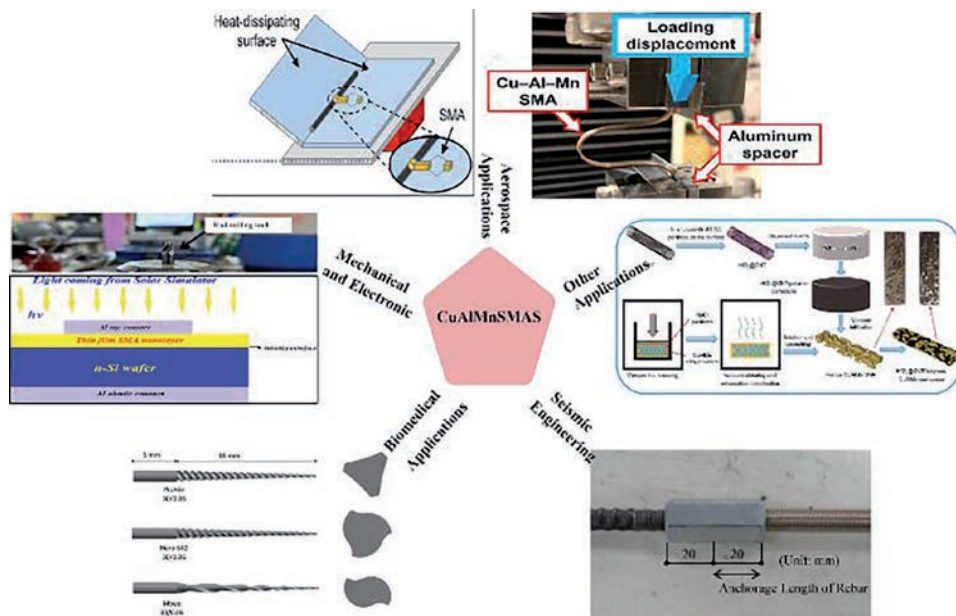


Figure 7. Applications of copper-aluminum-manganese shape memory alloys in aerospace, mechanical electronics, civil engineering, and smart structures [45, 97–101].

Zheng et al. [102] utilized 3D printing technology to fabricate Cu-Al-Mn super-elastic lattice structures with complex geometries. These intelligent flexible structures can serve as lightweight deployable antennas, solar array supports, and other components, demonstrating high shape recovery rates and deformation resistance. Jiang et al. [103] successfully prepared Cu-Al-Mn/polymer/carbon nanomaterial multiscale composites with high damping performance across a wide frequency and temperature range. Their exceptional damping properties show promising prospects for aerospace applications in vibration- and noise-intensive environments.

4.2 Mechanical and electronic applications

In precision machinery and microelectronic systems, SMAs are widely used in actuators, micro-grippers, and thermally driven devices. Compared with NiTi alloys, Cu-Al-Mn alloys offer lower costs and superior damping responses, making them suitable for high-frequency micro-actuation and stable gripping tasks.

Oliveira et al. [104, 105] significantly enhanced the mechanical properties and damping capacity of Cu-Al-Mn SMA wires through laser welding and laser remelting processes, achieving breakthroughs in microstructural joining and smart components. Praveen et al. [97, 106] investigated the machinability of this alloy in wire electrical discharge machining (WEDM), demonstrating its excellent processability.

Additionally, Canbay et al. [94, 95] developed photodetection and solar tracking devices based on Cu-Al-Mn-Cr thin-film structures, which exhibit high sensitivity and response speed, opening new pathways for micro-electro-mechanical system (MEMS) applications.

In thermal switch design, Ram et al. [107] established an empirical correlation to predict the phase transformation temperature of Cu-Al-Mn-based SMAs. Studies

on alloys with varying compositions revealed a prediction error within $\pm 18\%$. The research also analyzed the effects of the Cu/Mn and Cu/Al ratios, and the respective Mn and Al contents, on the start and end temperatures of martensitic and austenitic transformations. Higher Mn and lower Al content were found optimal for low-temperature space applications, providing critical guidance for thermal switch design.

In optoelectronic devices, Canbay et al. [98] fabricated multiple photodiodes based on Cu-Al-Mn SMAs. For instance, an Al/Cu-Al-Mn/n-Si/Al Schottky-type photodiode, prepared via arc melting, exhibited excellent rectification and photoelectric properties, with a photosensitivity of $\sim 10^5$ and detectivity exceeding 10^{10} Jones.

For sensors and connectors, Karthick et al. [57] developed SMA-coated polymer optical fiber sensors using flash-physical vapor deposition. The uniform, crystalline coatings enable 3D printer condition monitoring, offering novel solutions for temperature sensing in smart manufacturing. Furthermore, Cu-Al-Mn super-elastic alloy rods have been proven to function as self-sensing materials, with linear resistance-strain relationships (up to 10% strain), minimal hysteresis, high repeatability, and saturation limits, combining structural and sensing functionalities.

4.3 Biomedical applications

Although research on Cu-Al-Mn alloys in biomedicine remains in its early stages, their low-temperature phase transformation and recovery properties hold potential for low-temperature or deformable implants. Compared with NiTi alloys, Cu-Al-Mn alloys may offer cost advantages for disposable, temperature-controlled devices.

For example, alloying with Fe and Zr can enhance biocompatibility and corrosion resistance [108, 109]. Future integration of laser processing and nanocomposite reinforcement (e.g., graphene/carbon nanotube coatings [15, 110]) may expand their use in medical micro-devices. Babacan et al. [99] identified Hero 642 Cu-Al-Mn alloy as a promising material for endodontic instruments due to its superior torsional performance from large cross-sectional area and moment of inertia.

4.4 Smart materials, structural applications, and seismic engineering

Cu-Al-Mn SMAs demonstrate significant potential in smart structures and civil engineering, particularly for self-healing, self-sensing, and seismic control components. Their exceptional recovery and energy dissipation capabilities enhance structural safety under seismic and wind loads.

Mirzahosseini et al. [111] incorporated these alloys into concentrically braced structures, validating their self-recovery capacity post-large deformations. Pareek et al. [100] designed a relocatable plastic hinge for reinforced concrete beams using Cu-Al-Mn alloys to achieve controlled energy dissipation, significantly improving structural ductility. Shrestha et al. [74] proposed “self-sensing” structural components, leveraging the super-elasticity of Cu-Al-Mn alloys for simultaneous load-bearing and condition monitoring in bridges and high-rise buildings. Qian et al. [112] developed a novel prefabricated beam-column friction hinge joint, comprising a rotational friction hinge and a self-centering buckling-restrained damper. Cyclic solution treatment of Cu-Al-Mn SMA plates enhanced super-elasticity, endowing the joint with excellent seismic resistance, self-centering, and repairability.

In bridge column optimization, Hosseini et al. [113] combined engineered cementitious composites (ECC) with Cu-Al-Mn super-elastic alloys. ECC enhances lateral strength, while adjusting the number of SMA rebars balances energy

absorption and self-centering. Additionally, a quasi-zero stiffness vibration isolator using Cu-Al-Mn SMA bars was proposed, reducing input acceleration by ~50% with a resonance frequency of ~0.6 Hz, offering high feasibility and compact design. Kwon et al. [12] utilized directionally solidified columnar-grained SMAs for seismic isolation, leveraging high critical transformation stress in the thickness direction for load-bearing and horizontal super-elasticity for energy absorption.

4.5 Other applications: High damping and functional composites

Cu-Al-Mn SMAs exhibit exceptional energy dissipation in high-damping applications, such as rail transit, wind power, and precision machinery. Li et al. [14] developed porous structures with significant vibration absorption and mechanical stability.

For high-damping martensitic Cu-Al-Mn sheets, Haghdoust et al. [114] demonstrated that the duration of heat treatment influences damping and stiffness, making them suitable for use in glass-fiber-reinforced polymer hybrid composites. Columnar-grained Cu-Al-Mn SMAs show anisotropic damping enhancement with increasing tensile strain and improved performance after super-elastic training. These alloys achieve functional fatigue lives exceeding 10^3 cycles at 4–10% strain, with a super-elastic recovery decay coefficient of ~1.4, outperforming polycrystalline counterparts in stability and suitability for damping and refrigeration.

Furthermore, composites integrating Cu-Al-Mn alloys with polymers or ceramics offer multifunctional solutions. For example, Jiang et al. [101] developed lightweight $\text{HfO}_2\text{@CNT/polymer/Cu-Al-Mn}$ composites with high damping and strength, providing novel materials for aerospace, acoustics, and high-frequency mechanical systems.

5. Current challenges and future directions

Despite their potential in low-temperature responsiveness, super-elasticity, and damping, the widespread engineering use of Cu-Al-Mn SMAs faces challenges, particularly in long-term stability, micro-mechanisms of reverse phase transformations, and multifunctional synergy.

5.1 Current challenges

5.1.1 Controversies surrounding reverse martensitic transformation mechanisms

While macroscopic thermoelastic martensitic transformations are well-documented, the microscopic reverse transformation (martensite→austenite) mechanisms in Cu-Al-Mn systems remain unclear. Debates persist on whether nucleation and growth processes are involved. Based on in situ microstructural observations and XRD analysis, Bian et al. [81] found that even when the temperature is lowered below M_f and held for a sufficient amount of time, some residual austenite still exists. They inferred that the transformation from austenite to martensite follows the classical nucleation and growth theory, while the reverse transformation of martensite may only involve the growth process. This can also explain why the alloy can fully “remember” its “original” state. This process reflects the “asymmetry” of the martensitic

transformation and its reverse transformation in shape memory alloys. Although this inference needs further in-depth research, it provides a new perspective on the reverse transformation mechanism of martensite and may promote the study of the reverse martensitic transformation mechanism. Salgado et al. [7] reported that bainite precipitation induces interface pinning, hindering reversibility. Yang et al. [18, 64] further revealed nonlinear relationships between heating rates and residual martensite stabilization, necessitating quantitative models for thermo-mechanical coupling. Additionally, under complex loading (biaxial stress, thermo-mechanical cycling), phase transformation paths may exhibit hysteresis or reorientation, reducing shape recovery. In situ testing and multiscale simulations are required to unravel these phenomena.

5.1.2 Insufficient fatigue performance and cyclic stability

Cu-based SMAs generally suffer from performance degradation under thermal or mechanical cycling. Although adding Fe or Ti mitigates this issue [25, 68], their low-cycle fatigue life remains inferior to NiTi alloys. Strain accumulation in long-term applications (e.g., bridges, aerospace components) may initiate microcracks, leading to failure.

5.1.3 Limited adaptability to harsh service environments

Cu-Al-Mn alloys exhibit insufficient stability in corrosive, radiative, or rapidly varying thermal environments. For instance, they are prone to pitting or oxidation in NaCl environments [109]. Systematic models are lacking to evaluate thermal conductivity and electromagnetic interference in electronic devices.

5.2 Future research topics

5.2.1 Multiscale modeling and phase transformation studies

Integrating in situ phase transformation observations, atomic-scale first-principles calculations, phase-field simulations, and finite element modeling will help map energy barriers, track the martensitic transformation and its reverse process in situ, analyze the structural transformation relationships of the martensitic transformation, investigate the nucleation or growth mechanisms, study the role of stress-strain, dislocations, or twin-slip in the reverse martensitic transformation, and explore the mechanisms of crack initiation. For example, Yang et al. [27] employed density functional theory (DFT) to explore Ni-doping effects on martensite stabilization, offering quantitative design parameters.

5.2.2 Additive manufacturing-driven structural innovations

Advancements in laser powder bed fusion (L-PBF) and selective laser melting (SLM) enable the fabrication of functionally integrated Cu-Al-Mn components. Xiang et al. [46, 47] and Xi et al. [48, 115] demonstrated that laser path design, energy input, and post-processing can achieve gradient grains, oriented martensite, and localized stress control, laying the foundation for self-healing and self-regulating structures.

Future integration of 3D printing and topology optimization may yield “structure-property synergy” devices, such as temperature-controlled valves and flexible supports.

5.2.3 Multifunctional integration and physical coupling effects

Developing SMAs with magneto-thermo-mechanical coupling is a promising frontier. Zhao et al. [91] and Gerdan et al. [92] suggested that adjusting Mn/Cr/Ni content and heat treatment could introduce magnetic responsiveness, enabling cost-effective magnetostriuctive actuation and refrigeration.

Combining functional coatings or composites can create intelligent systems. For instance, Jiang et al. [101] designed HfO₂/CNT/Cu-Al-Mn composites for aerospace buffering and electronics damping. Further exploration in emerging fields—such as thermal management for renewable energy, MEMS components, and biodegradable implants—will unlock new applications.

6. Conclusions

As a new-generation low-temperature functional material, Cu-Al-Mn SMAs demonstrate remarkable potential in aerospace, smart structures, and civil engineering due to their shape memory effect, super-elasticity, high damping, and processability. This review systematically summarizes advances in phase transformation mechanisms, microstructural evolution, alloy optimization, advanced manufacturing, and multifunctional performance.

Material design strategies, including rare-earth/transition metal doping, and graphene/nanoparticle incorporation, have improved stability, recovery rates, and fatigue life. Additive manufacturing techniques such as SLM enable precise microstructure control, facilitating complex component fabrication. Functional advancements extend beyond thermal-mechanical responses to magneto-responsive and elastocaloric effects, driving Cu-Al-Mn SMAs toward multifunctional smart materials.

However, challenges persist, including unclear reverse transformation mechanisms, cyclic instability, and environmental adaptability. Future efforts should combine in situ characterization, multiscale modeling, and structure-property co-design to deepen mechanistic understanding and enable high-throughput optimization. These efforts will propel Cu-Al-Mn SMAs toward large-scale applications in low-temperature refrigeration, energy conversion, and structural health monitoring.

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Edited by Daniel Fernández González

This book aims to compile investigations and reviews on copper, as it has long been one of humanity's most vital metals. This is due to its exceptional properties and versatility, which make it indispensable across various domains. Characteristics such as malleability, ductility, and superior thermal and electrical conductivity have made copper a key material for thousands of years, dating back to the Copper Age. Its significance extends beyond history into the Modern and Contemporary eras, particularly as societies increasingly rely on electrification. Thanks to its remarkable electrical and thermal conductivities, copper has become a cornerstone in the electronics and electrical industries, as well as in heat management. Moreover, its unique antibacterial properties and the versatility of copper compounds have expanded its applications into numerous fields, including health. An integral aspect of the copper industry is its production, where pyrometallurgy, primarily the processing of sulfide ores, remains the dominant method, even as hydrometallurgical techniques gain prominence. Copper also serves as a base for creating various alloys, each tailored to meet specific needs. Brass, an alloy of copper and zinc, and bronze, a combination of copper and tin, are the best known due to their corrosion resistance. However, many others are important in many different applications. In summary, copper continues to play an indispensable role in human civilization. This book delves deeply into the many facets of copper, covering its fundamental properties, metallurgical processes, and wide-ranging applications, to underscore its significance. As the world moves toward a technology-driven future, the value of copper will only continue to grow, cementing its status as a fundamental resource for modern society. Whether powering electronics, advancing medical innovations, or forming essential alloys, copper remains a crucial element that supports daily life and drives technological advancement.

Chonghe Li, Materials Science Series Editor

Published in London, UK

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ISSN 3049-8856

ISBN 978-1-83635-394-2

