

Review

Electrodeposition of Copper-Silver Alloys from Aqueous Solutions: A Prospective Process for Miscellaneous Usages

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Abstract: The electrodeposition of copper (Cu), silver (Ag), and their alloys has been a subject of interest since the 19th century. Primarily due to their exceptional features such as good mechanical hardness and electrical conductivity, high resistance to corrosion, and electromigration, Cu–Ag electrodeposits continue to be investigated and developed to improve their properties for different applications. This paper reviews the state of the art in the field of electroplated Cu–Ag alloys in an aqueous solution, with particular emphasis on the observed properties and variety of electrochemical processes used to produce high-quality materials. Moreover, this review paper focuses on the experimental conditions employed for Cu–Ag electrodeposition, intending to understand the basis and manipulate the processes to obtain coatings with superior characteristics and for attractive usage. Finally, the most trending applications of these coatings are discussed depending on different parameters of electrodeposition to provide prospects for potential research.

Keywords: Cu–Ag alloy; electrodeposition; coating; electrocatalyst; metal interconnection



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1. Introduction

A metallic alloy is a combination of two or more metallic elements resulting in either a mixture of distinct phases or a random solid solution of these elements [1]. Alloys have different properties from those of the initial metals they are composed with.

Electrodeposition, or electroplating, is an electrochemical process used to change the surface of materials. This method has a long and interesting history [2] and was first applied in 1805 by Italian inventor Luigi V. Brugnatelli. For instance, silver plating was patented in 1840 [3]. Nowadays, electrodeposition is one of the most implemented techniques utilized to fabricate different metals and alloys [4]. Using this method, the structure, shape, and thickness of the deposits are controlled on the surface of the substrates by modifying the conditions of the process. Furthermore, a large surface area of the deposited alloys can be obtained, a complex shape of the substrates can be used, and various kinetic advantages can be applied by electroplating [5].

The combination of excellent mechanical strength and high electrical conductivity makes Cu–Ag alloy materials of interest for various applications [6]. Compared to pure copper, Cu-based alloys have many advantages including higher chemical and electromigration resistance, mechanical hardness, and electrocatalytic performance [7].

2. Physico-Chemical Properties of Cu, Ag, and Their Alloys

It is widely acknowledged that the phase diagram of the Cu–Ag alloy system refers to the eutectic type with limited solubility of the components in each other (Figure 1). The maximum solubility of Cu in Ag is 14.1 at.%, and the solubility limit of Ag in Cu is 4.9 at.%. The eutectic temperature is between 778 and 779 °C [8].

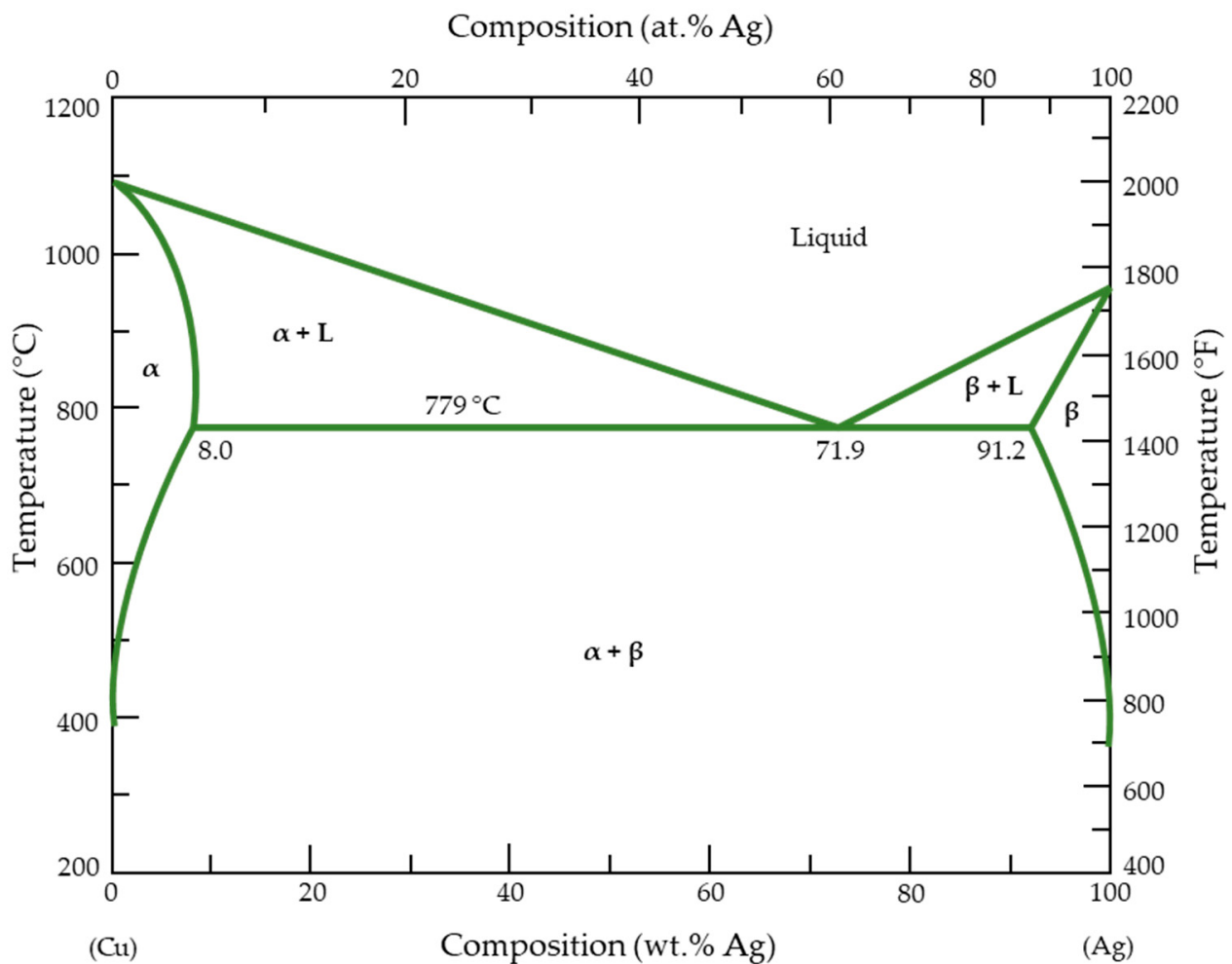


Figure 1. Phase diagram of the Cu–Ag alloy [9].

According to previously published results [9], if the content of Ag is <6 wt.%, the Cu–Ag alloy consists of a single Cu-rich α -phase [10]. When the Ag content is >6 wt.%, an Ag-rich solid β -phase appears in the primary α -phase dendrite. At 6–15 wt.%, the Cu–Ag microstructure is usually composed of the Cu-rich solid α -phase and the eutectic phase (α -phase + β -phase) [11]. However, the microstructure of Cu–24 wt.% Ag mostly consists of the Cu-rich phase and a reticular eutectic structure [12]. By increasing Ag content up to 71.9 wt.%, the whole microstructure becomes eutectic and is composed of both α - and β -phases [13]. The phase diagram also demonstrates that these two metals are almost entirely immiscible at room temperature, as a result of their positive heat of mixing [14]. Underpotential co-deposition does not happen in the Cu–Ag electrodeposition system because of Cu–Ag unmixing, in contrast to alternative alloy systems with complete miscibility [15]. Nevertheless, under specific synthesis conditions such as mechanical alloying for different milling times [16], Cu and Ag are known to form oversaturated solid solutions. For the production of solid solutions, ball milling in an inert atmosphere for 12 h is sufficient. Additionally, Ag precipitates can nucleate and grow in the grain interiors when the Ag concentration is oversaturated in the Cu matrix. This strengthens Cu by obstructing the dislocation motion [17]. Moreover, copper and silver crystallize in a face-centered cubic structure (Figure 2) and have different lattice constants (Table 1), making the manufacture of their alloys challenging.

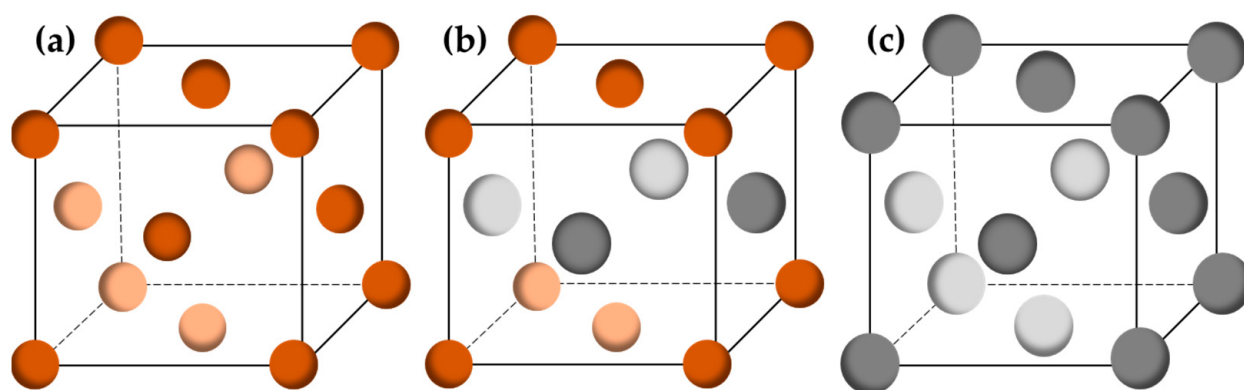


Figure 2. Crystal structures of Cu (a), $\text{Cu}_{0.5}\text{Ag}_{0.5}$ (b), and Ag (c). Brown for Cu; grey for Ag.

Various compositions of Cu–Ag alloys have exceptional malleability, which indicates that they have presumably reached superplastic behavior. The Cu–71.9 wt.% Ag eutectic composition exhibited superplasticity in its annealed equiaxed structure. According to Cline et al. [18], complementary research is needed to replicate this effect and identify the circumstances in which other compositions and microstructures will be able to demonstrate superplasticity.

Table 1. Lattice constants (in Å) of Ag, Cu, and Cu–Ag alloys with different atomic ratios [19].

Substance	a	b	c
Ag	4.147	4.147	8.295
Cu	3.638	3.638	7.276
$\text{Cu}_{0.125}\text{Ag}_{0.875}$	4.094	4.094	8.188
$\text{Cu}_{0.25}\text{Ag}_{0.75}$	4.037	4.037	8.075
$\text{Cu}_{0.5}\text{Ag}_{0.5}$	3.948	3.909	7.782

Cu and Ag metals have an identical electronic configuration since they are members of the same group of chemical elements in the periodic table. Jian et al. constructed Cu–Ag alloys [19] with various atomic ratios by setting several units of the Ag conventional cell and replacing one of the Ag atoms with a substitutional element—Cu. The crystal structures of Ag, $\text{Cu}_{0.125}\text{Ag}_{0.875}$, $\text{Cu}_{0.25}\text{Ag}_{0.75}$, and $\text{Cu}_{0.5}\text{Ag}_{0.5}$ were schematically shown. It was determined that Cu–Ag alloys in the investigated composition range are not thermodynamically stable and that non-equilibrium methods, for example, physical vapor deposition (PVD), should be used for their production.

The calculated lattice constants of Cu–Ag alloy unit cells are presented in Table 1. The lattice constants are 4.147 Å and 3.638 Å for Ag and Cu, respectively, which are comparable to the experimental results [20]. For the Cu–Ag alloys, their lattice constants are between that of Ag and Cu, which also gradually decrease as the Cu ratio increases. In contrast, the lattice constants for various alloy structures are nearly equivalent for the same atomic ratio.

Furthermore, due to the redox potential difference, it is difficult to manage a simultaneous reduction in Cu and Ag [21]. Another important obstacle is the instability of copper ions in an aqueous medium. Table 2 demonstrates some physical properties (intervals) of the Cu–6 wt.% Ag alloy obtained from different processes and/or metallurgical states [22], and their comparison with pure Cu and Ag at $T = 20\text{ }^{\circ}\text{C}$.

Nowadays, Cu–Ag alloys are extensively utilized in the manufacturing of electrodes, solders for circuit boards, coins, silverware, and jewelry. These alloys, with their high Ag content, are well-recognized due to their mechanical and electrical characteristics [24]. Numerous material properties such as, for example, electrical conductivity and Brinell hardness display a plateau between 30 wt.% and 80 wt.% of Cu as was shown by Broniewski et al. in Figure 3 [25]. The mechanical properties of Cu–Ag alloys are relatively comparable over

a wide range of compositions. In other words, there is no particular Cu–Ag ratio that can substantially enhance the mechanical properties of the alloy.

Table 2. Comparison of physical properties ($T = 20\text{ }^{\circ}\text{C}$) for Cu–6 wt.% Ag alloy and pure Cu and Ag. 100% IACS (International Annealed Copper Standard) is equivalent to $58 \times 10^6\text{ S}\cdot\text{m}^{-1}$ at $20\text{ }^{\circ}\text{C}$ [23].

Substance	Density	Electrical Conductivity	Thermal Conductivity	Ultimate Tensile Strength	Young’s Modulus
Cu–6 wt.% Ag	$9.2\text{ g}\cdot\text{cm}^{-3}$	60–87 (% IACS)	$270\text{--}380\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	230–1200 MPa	120 GPa
Cu	$8.96\text{ g}\cdot\text{cm}^{-3}$	100–102 (% IACS)	$386\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	210 MPa	117 GPa
Ag	$10.5\text{ g}\cdot\text{cm}^{-3}$	105 (% IACS)	$407\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	140 MPa	83 GPa

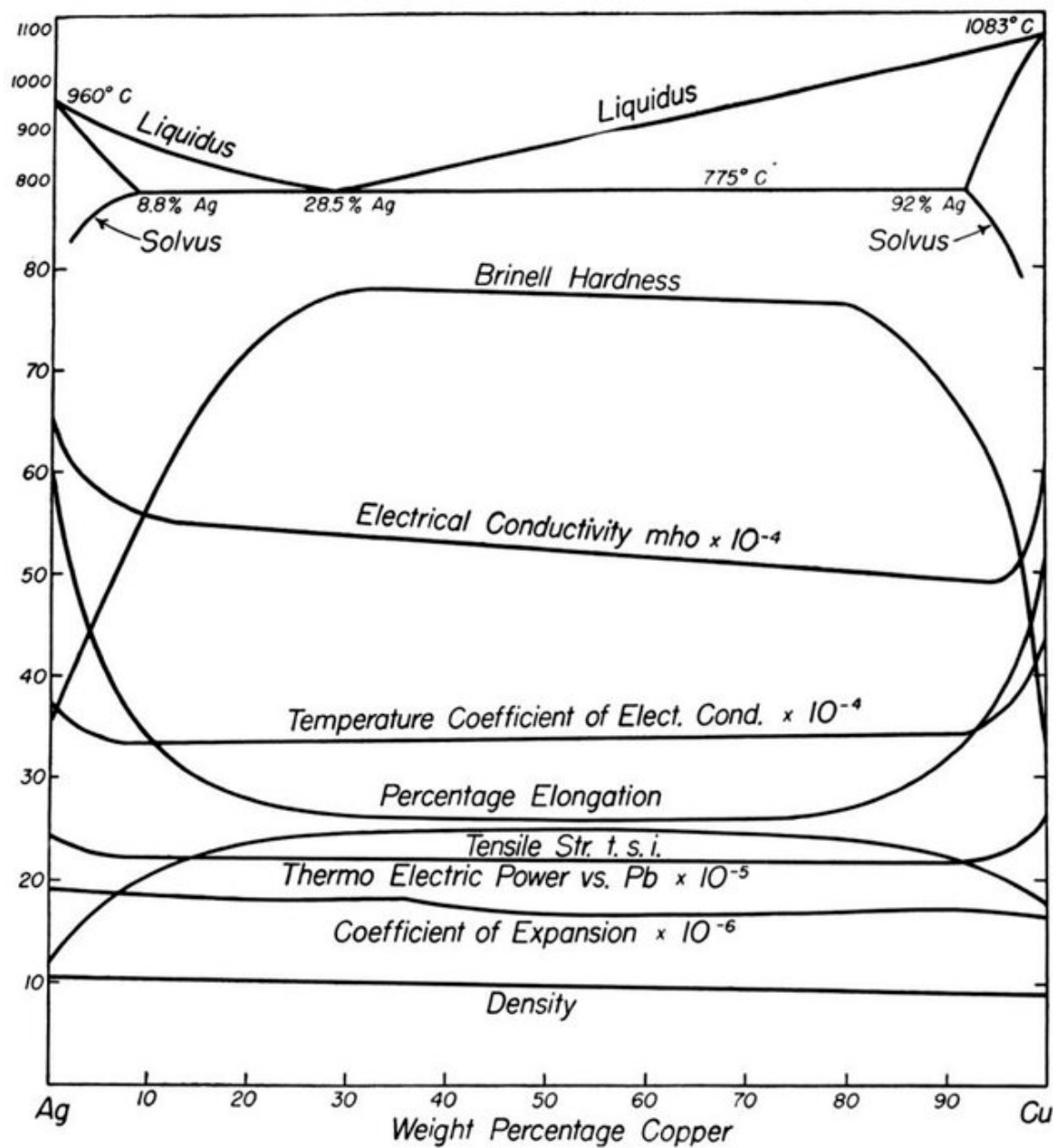


Figure 3. Properties of annealed Cu–Ag alloys at $25\text{ }^{\circ}\text{C}$ [25].

Considering the existence of many other beneficial properties of Ag (conductivity and antibacterial), it can also improve the Cu(II)/Cu(0) reduction kinetics. Shao et al.

implemented cyclic voltammetry of different electrolytes on various metallic substrates and used an electrochemical quartz crystal microbalance to observe the first Cu reduction peak at the copper substrate [1]. It was found that the depolarization of reactive species significantly depends on the presence of silver, either in ionic form, in the electroplating bath, or as a substrate, initiating the reduction in Cu(II) at the overpotential range during Cu deposition. The authors explained that such an effect may be caused by the catalytic behavior of Ag on the substrate in the intermediate step of Cu(II)/Cu(I). So, this feature can shift the reduction rate of Cu(II)/Cu(0), from Cu(II)/Cu(I) to Cu(I)/Cu(0).

3. Different Techniques Mentioned to Date for the Production of Cu–Ag Alloys

Methods such as laser cladding [26], blasting [27], microwaves [28], ball milling [29], pulsed laser deposition [30], ion beam mixing [31], PVD [32], the wet chemical method [33], and chemical vapor deposition [34] are usually used to fabricate Cu–Ag alloys by producing a metastable solid solution that kinetically prevents the separation of the constituent metals. Also, Cu–Ag structures with various Ag contents can be obtained via in situ alloying and laser powder bed fusion additive manufacturing [35]. In this case, increased Ag content from 10 at.% to 30 at.% led to a decrease in the amount of pore defects for produced and annealed samples [36]. On the other hand, it was found that annealing may enlarge the porosity by up to 164%. Moreover, this process causes atomic lattice contractions, which lead to improved yield strength, Young's modulus, and ultimate tensile strength (UTS).

There are many different possibilities to fabricate bulk alloys, for example, mechanical alloying [37], magnetron sputtering [38], cold spray [39], and cold drawing combined with intermediate heat treatments [40]. The last manufacturing method enabled the achievement of ultra-high strength at low reduction and large cross-section conductors. The optimized Cu–24 wt.% Ag alloy wire with a total drawing strain of $\eta = 5.8$ showed an electrical conductivity of 65% IACS and a UTS of 1.5 GPa at room temperature. The wires obtained via this technique could be suggested as prospective candidate conductors used in high-field pulse magnets [41].

A fine and dense micro-composite structure is gradually formed by the compression and elongation of two phases, a Cu-rich and an Ag-rich solid solution, during cold working operations such as forging, drawing, swaging, or rolling. The degree of deformation significantly increases the strength of this structure [40]. High strength with the maintenance of relatively high conductivity can be reached for the alloy if cold working is combined with an appropriate intermediate heat treatment [42].

Suitable quantity and process sequences of heat treatment allow the production of wires [43] composed of Cu and Ag fibers with nanometric transverse dimensions, providing the ideal possible superposition of high electrical conductivity and mechanical strength with satisfactory ductility of Cu–Ag alloys [44]. It was reported that a combination of thermal treatments and extensive cold forming achieved the required strength level [41]. The conceivable thermomechanical treatment can include homogenized annealing, prefinal cold rolling, solution annealing, and final cold rolling, as well as isochronal and isothermal annealing up to the recrystallization temperature.

Nestorovic et al. have shown that the anneal hardening effect appeared in the temperature range of 160–400 °C on the Cu–6.6 wt.% Ag alloy. Also, thermomechanical treatment influenced structural modifications and an improvement in electrical conductivity and hardness [45]. Up to 200 °C, the electrical conductivity did not change considerably; however, above 300 °C, it quickly increased. The microstructural coarsening of the heavily deformed linear band structure could be related to this improved conductivity [37].

Another research study presented the parameters of Cu–Ag alloy rods that were obtained by continuous casting [9]. The wires with a diameter of 0.2 mm exhibited a UTS of >1.25 GPa with a simultaneous electrical conductivity of 69% IACS for Cu–15 wt.% Ag, and a UTS of >1.1 GPa with 79.3% IACS for Cu–5 wt.% Ag. This study demonstrated that through reciprocal reactions of precipitation and drawing, the mutually variable solubilities of Cu in the Ag matrix and Ag in the Cu matrix, in addition to temperature changes,

provide valuable opportunities for enhancing the mechanical and electrical characteristics of Cu–Ag alloys.

Zhu et al. indicated that after the continuous cold drawing, the Cu–4 wt.% Ag alloy wire with a diameter of 40 μm had a UTS of 1048 MPa, yield strength of 886 MPa, and electrical conductivity of 75.2% IACS [46]. Following the drawing deformation, the Cu–Ag alloy was strengthened by work hardening, solid solution, and grain refinement strengthening, which resulted in yield strengths of 92.8 MPa, 117.9 MPa, and 626.1 MPa, respectively.

Tian et al. discovered that a UTS of 720 MPa was reached in the Cu–8 wt.% Ag alloy after multiple equal-channel angular pressing [47]. A banded structure was observed on the cross-section, and the UTS of the Cu–8 wt.% Ag alloy rose up to ~ 1.1 GPa after high-pressure torsion. Chang et al. measured the yield strength and UTS of the hot extruded Cu–0.1 wt.% Ag alloy, which were 75 and 168 MPa, respectively [48]. Its elongation was approximately 38%. After cold drawing, the yield strength was increased up to 280 MPa, and the elongation was reduced to 11%.

In addition to the above-mentioned techniques, Cu–Ag films have been obtained via electron beam evaporation [49], electrodeposition in supercritical fluid [50], or by deposition from the melted stage in the vacuum [51].

4. Electroplating of Cu–Ag Alloys

Regarding the application in the interconnections of electronic devices [52], the low-temperature wet-process of Cu–Ag co-deposition is the most relevant and controllable [53]. Due to the electrochemical potential values of copper and silver systems (Figure 4), it is possible to obtain these two metals via electroreduction in aqueous solutions without hydrogen evolution. Therefore, by combining the concentrations of the copper and silver ions and complexing species, alloys of these two metals with various compositions can be obtained using a cheap and green method, i.e., electrodeposition in aqueous electrolytes. This fact explains the very few published works [54–56] dealing with the electrodeposition of Cu–Ag alloys in eutectic solvents, which is a more expensive method requiring more stringent conditions (no trace of water, anaerobic conditions, etc.).

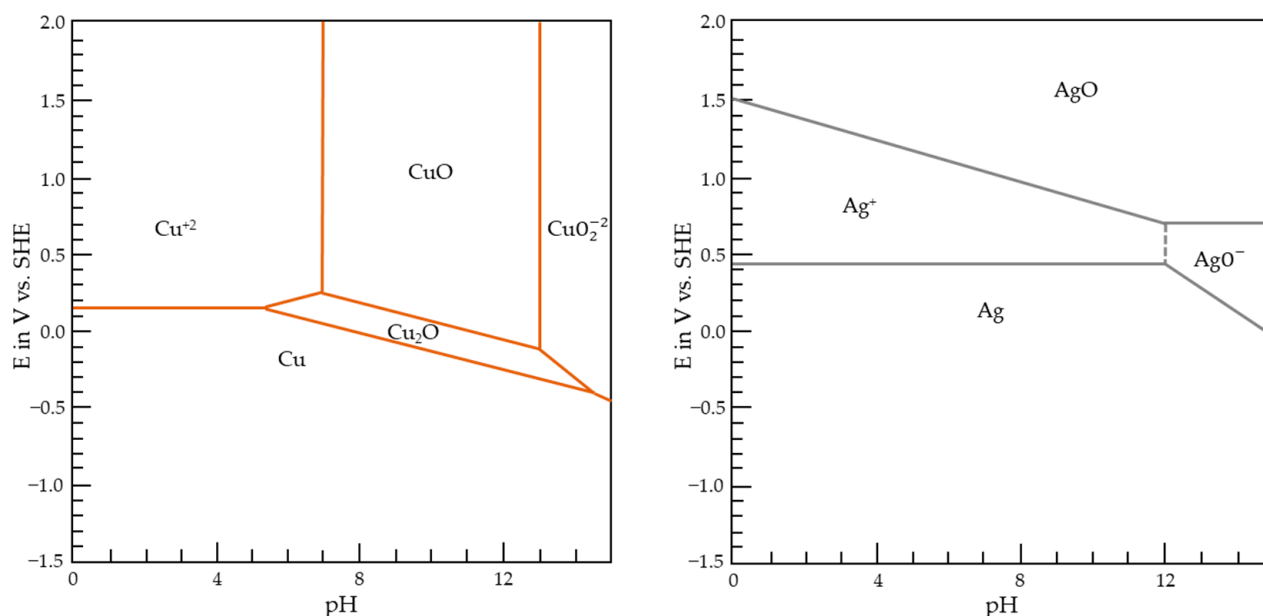


Figure 4. Potential-pH diagrams for Cu and Ag at 25 °C. The total concentration of copper ion and silver ion at pH = 0 is 10^{-6} mol/L.

Alloy films are usually obtained by applying a potential or current to conductive substrates submerged in electrolytes containing multiple metal precursors. The compo-

sition of electrolytes and applied current (or potential) can manage the contents of metal components. For example, in alloy electrodeposition, it is important to correctly select the electrolyte in order to produce uniform films without any spontaneous formation of the metal precipitates.

The electroplating technique has many benefits, including the ability to produce low-cost nanocrystalline films, the possibility to deposit compact pore-free dense coatings, and the ability to control crystal particle size, microstructure, and roughness [57]. In consequence, plating on any complex shape for antimicrobial touch surface application is achievable.

Bernasconi et al. synthesized Cu–Ag alloys using the electrodeposition method [6]. Different Ag percentages (3.2–15.4 at.%) were achieved by managing the conditions of deposition. Eventually, these as-deposited alloys demonstrated high hardness. The Cu–15.4 at.% Ag alloy, for example, exhibited a hardness of 628 VHN (Vickers hardness). Bao et al. sequentially examined the UTS of Cu, Cu–2 wt.% Ag, and Cu–6 wt.% Ag vs. drawing strain [58]. It was discovered that the strength of Cu–6 wt.% Ag reached approximately 1.24 GPa, more than twice the UTS of pure Cu when the drawing strain was $\eta = 6$.

Lee et al. implemented the electrodeposition of nanocrystalline Cu–Ag foil and investigated its properties [59]. The as-deposited foil showed moderate ductility, high UTS (993 MPa), and high electrical conductivity (66.7% IACS). The strength and conductivity were further enhanced with mild annealing (1043 MPa and 68% IACS, respectively), reaching characteristics similar to deformed Cu–Ag foils of greater thicknesses. Another efficient method of strengthening the Cu–Ag alloy without a significant reduction in conductivity is micro-alloying [60].

The electroplating process can be carried out through direct current (DC), pulse current (PC), and pulse reverse current (PRC) modes [61]. All these methods can be used for producing the Cu–Ag alloys. During the DC electrodeposition process, the electrical current is applied to the system continuously in an uninterruptible manner. This conventional technique has been widely implemented for the electroplating of metals and alloys, despite the fact that, in this case, the deposition process is slow, and often it has drawbacks in film defects, such as porosity and poor adhesion [62].

In the PC mode, the current or potential quickly alternates between two different values. This leads to a sequence of pulses separated by zero current that have the same amplitude, duration, and polarity. Each pulse is composed of two phases: an ON-time (t_{ON}) when potential and/or current are exerted and an OFF-time (t_{OFF}) when no current is applied. According to priorly attained research [63], electrodeposition via the PC method results in finer grain sizes and an improvement in adhesion to the substrate.

In the case of the PRC technique, the plating current is interrupted, and a stripping time is introduced into the plating cycle. PRC selectively dissolves the protrusions of the metal surface, ensuring uniform deposition. Also, the utilization of additives can be limited by the introduction of high-frequency PRC, which decreases the electrical conductivity and ductility of deposits. PRC avoids the disadvantages of additives, while the superimposed pulsation maintains control over the crystal structure.

Table 3 shows some examples of using electroplating in an aqueous solution with the synthesis conditions used and the following acquired properties.

Table 3. Examples of using the electrodeposition technique (synthesis conditions used and properties obtained).

Electrolyte for Cu–Ag Electrodeposition + Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties	References
0.78 M CuCN, 0.37–2.25 mM AgCN, 2.08 M KCN, 79 mM Rochelle salt, 0.27 M KOH, 0.36 M K ₂ CO ₃ + 0.5 mM <i>saccharin</i> , 75 μM <i>potassium antimonyl tartrate hydrate</i> , 3.0 mM <i>polyethyleneimine</i> , 5.0 mM <i>Triton-X</i>	Ni strike—chromate layer	DC at I = 7.5 mA/cm ² for 142 min and PC at I = 15 mA/cm ² , t _{ON} /t _{OFF} : 12 s/12 s for 142 min. + Annealing (N ₂) at 100–300 °C for 1 h.	1.5–5.0 wt. %	40 μm	The as-deposited Cu–Ag foil exhibited high ultimate tensile strength (993 MPa), high electrical conductivity (66.7% IACS), and moderate ductility. With mild annealing, both the strength and the conductivity were improved further (1043 MPa and 68% IACS, respectively).	Lee et al. [59]
50 g/L CuSO ₄ ·5H ₂ O, 150 g/L K ₄ P ₂ O ₇ , 150 g/L KI, 75 mL/L 0.1 M AgNO ₃ , 10 g/L KNO ₃	Glassy carbon	The pH = 8.9. Electroplating was done in non-stirred conditions at 50 °C. Current densities between 2 mA/cm ² and 30 mA/cm ² were used. + Annealing (N ₂) at 400 °C for 2 h.	3.2–15.4 at. %	nm-sized	As-deposited alloys exhibited high hardness values (628 VHN) and the contribution of solid-solution hardening.	Bernasconi et al. [6]
0.5 M H ₂ SO ₄ , 0.3 M CuSO ₄ , 0–2 mM AgNO ₃	Cu, Cu–Ag, Au, Ru	The scanning rate of 10 mV/s.	3.2–9.6 at. %	4.7–6.4 nm	The addition of AgNO ₃ to the copper solution enhanced Cu reduction and introduced an additional reduction peak, regardless of the property of the metallic substrate.	Shao et al. [1]

5. The Main Electrolytes Used in Electroplating of Cu–Ag Alloys

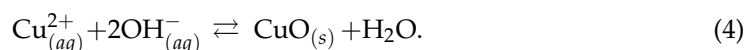
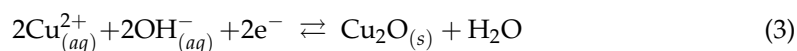
In general, copper electrodeposition in a bivalent Cu bath without complexing species occurs in two basic sequential steps, which are electrochemical reduction in the Cu(II) species to Cu(I) and then, from the Cu(I) species to Cu(0), as shown in Equations (1) and (2), respectively. The theoretical mass/charge values for these reactions are both equal to 63.6 g/mol ($M_{Cu}^{n+}/1e^-$) [64].



where $Cu_{(ad)}^+$ represents the Cu(I) ion, which is an intermediate species, not stable in solution but adsorbed on the surface of the electrode.

The global system (Cu^{2+}/Cu) has a redox potential E_{red}^0 (Cu^{2+}/Cu) equal to +0.34 V vs. SHE—volt vs. the standard hydrogen electrode.

The actual value of the redox potential for the copper system depends on the pH of the solution, and a high value of the pH can provoke the precipitation of CuO and Cu_2O , as demonstrated in the potential-pH diagram (Figure 4) and as was calculated from [65]. Copper electrodeposition can be put in competition with the electrodeposition of Cu_2O and the precipitation of CuO, as seen in Equations (3) and (4), respectively:



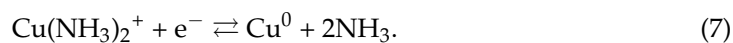
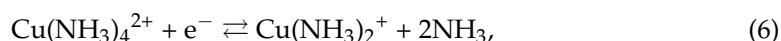
The potential-pH diagram for Ag in an aqueous system at 25 °C is shown in Figure 4. Thus, Ag(I) electrodeposition can be described by an electrochemical reduction to Ag(0) as follows in Equation (5):



E_{red}^0 (Ag^+/Ag) = +0.80 V vs. SHE.

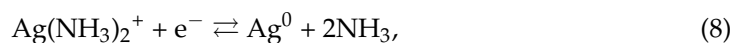
In particular, copper ions in aqueous baths can exist in diverse complex configurations depending on the used electrolyte.

For example, the electroplating bath prepared for Cu–Ag electrodeposition may consist of Cu(II) ions, Ag(I) ions, and ammonia (NH_3) as a complexing agent. NH_3 can form complexes with both Cu(II) and Ag(I) ions. The corresponding reactions for the copper complexes are shown in Equations (6) and (7) [7]:



The values of the standard redox potentials of these two systems are 0.00 V vs. SHE and −0.11 V vs. SHE, respectively.

A one-electron reduction in the silver complex occurs as in Equation (8):



This has a standard potential equal to 0.373 V vs. SHE.

The main positive point of the complexation of the ions by ammonia lies in the mass transport control of the kinetic velocities of the reduction reactions that allow us to obtain the desired composition of deposits without affecting the potential but only due to the concentrations of the ions in the electrolyte.

The delivery of a highly effective electrolyte composition is the most challenging direction in the development of Cu–Ag alloys' electrodeposition [66]. Generally, Cu electrodeposition is performed in an acidic sulfate bath, which frequently contains halogen ions in order to obtain better characteristics of the films [67]. However, Ag cannot be deposited

in the electrolyte containing halogen ions since precipitation from their spontaneous reaction with Ag(I) ions will form too easily. The electrolytes for Cu–Ag electroplating require suitable complexing agents (additives) to produce smooth and uniform Cu–Ag coatings. It was noted that the electrodeposition of Cu–Ag alloys from the H_2SO_4 -based bath comprised of CuSO_4 and AgNO_3 without any complexing agents led to an increase in the surface roughness and demixing of Cu and Ag into separate phases. The addition of thiourea (TU), a complexing agent for both Cu(II) and Ag(I) ions [68], allows the deposition of a homogeneous solid solution via a reduction in $[\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_9]^{4+}$ and $[\text{Ag}[\text{SC}(\text{NH}_2)_2]_4]^+$, respectively. Furthermore, cyanide [69] and citrate ions [70], as well as organic acids, give complexes with Cu(II) [71] and Ag(I) species [72]. Bernasconi et al. obtained a Cu–Ag alloy utilizing two different complexing agents [73]. It was realized from a solution containing pyrophosphate and iodide ions, which react with Cu(II) and Ag(I) ions to form the species $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$ and AgI_4^{3-} or AgI_3^{2-} , respectively [6].

Cyanide-based electrolytes are favorable in Cu–Ag super-filling, which is possible with the assistance of potassium selenocyanate (KSeCN) and TU [74]. However, researchers nowadays are looking for cyanide-free baths due to their extreme toxicity and the limitations of practicing ionic cyanide in the industry [70]. Less toxic pyrophosphate- and ammonia-based electrolytes can potentially replace the cyanide bath [53]. Previous studies focused on ammonia solution [75], hydrazine sulfate [76], methanesulfonic acid (MSA) [77], and protic ionic liquid baths [4]. Although, the results are not encouraging. For example, the parameters for dendritic or nodular cluster growth are still unknown.

Figure 5 presents the main aqueous electrolytes employed for the electroplating of Cu–Ag alloys with their principal advantages (in green) and disadvantages (in red).

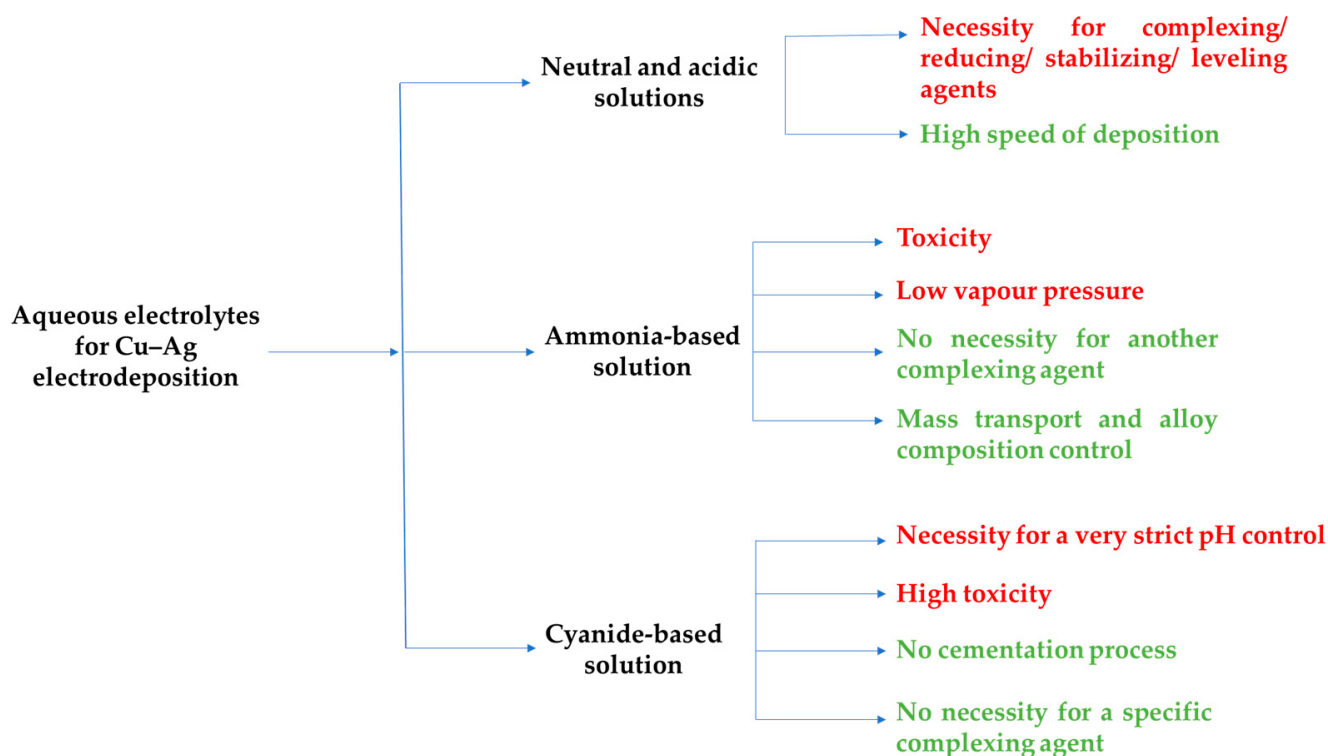


Figure 5. The summary of aqueous solutions used for electrodeposition of Cu–Ag alloys. Advantages are in green; disadvantages are in red.

Traditionally, electrodeposition is conducted in aqueous solutions containing additives to alleviate the deposition of metals with high negative reduction potentials, which is impeded by low current efficiencies and hydrogen embrittlement of the substrate [78]. The need to deposit refractory metals was the primary driving force behind the development of

non-aqueous electrolytes, and molten salts—so-called ionic liquids—have recently been employed for this purpose [79].

Many fundamental issues remain to be resolved, so this ionic liquid-based technology has not found broad industrial application. Firstly, the double-layer structure requires comprehensive analysis and the influence of electrolytes, temperature, composition, and brighteners must be further quantified [80]. The next step is to determine how complexing agents affect the redox characteristics of metals since this is essential for the creation of innovative methods in alloy plating [81]. To enhance mass transport properties, conductivity, and nucleation characteristics, diluents will likely be investigated [82]. The current systems used in aqueous solutions will likely be implemented first, and to produce materials with optimal interfacial properties, it will be necessary to rely on the results obtained from the aforementioned research [83].

For the electrodeposition of nanostructures, deep eutectic solvents (DESs) have been proposed as an alternative sustainable solution [84]. These substances are presently acknowledged as a variety of ionic liquids [56]. DESs are a mixture of Lewis and Brønsted acids and bases that considerably lower the freezing point compared to their constituent parts [85]. Due to their generally high conductivities, DESs can be beneficial in electrochemical processes [86]. Numerous metals were effectively solo electrodeposited in DESs [87] and also several bimetallic compounds [88]. Nevertheless, the electroplating of noble bi- or multimetallic nanostructures in these fluids is still a subject in its formative stages [89]. In addition, the use of a DES as a solvent slows the growth process [90]. Generating a current comparable to that in an aqueous medium requires a higher concentration and temperature in the DES [91].

Ternary Sn–Ag–Cu alloy coatings were electrodeposited by Huang et al. by employing DES-based electrolytes at various deposition potentials [54]. According to the experimental results, when the deposition potential rose, the crystal grain and the coating became finer and denser, respectively. Moreover, higher cathodic deposition potentials promoted the presence of the Cu_6Sn_5 phase, whereas lower potential values indicated the Ag_3Sn phase. The Sn–7.6 wt.% Ag–1.5 wt.% Cu alloy had a melting point of $\sim 215^\circ\text{C}$ and was suggested as an improved carrier printed circuit board.

Reyna-González et al. performed an electroplating of the Ag–22.5 wt.% Cu alloy on a glassy carbon electrode from a pyridinium-based ionic liquid. The co-deposit was obtained at high overpotentials from the extracted phase $\text{Ag}^+ - \text{Cu}^{2+} - [3\text{-BuPyr}][\text{NTf}_2] - \text{H}_2\text{O}$ [55].

There is a possibility to acquire ionic liquids that are non-flammable, green, and financially affordable to produce materials that cannot be reached in standard H_2O -based electrochemical baths. Despite previous research, the improvement of electrolytes for high-end Cu–Ag electrodeposition remains essential. Table 4 shows some examples of using the above-mentioned types of electroplating baths with the synthesis conditions used and the achievement of properties following prospective future applications.

Table 4. Examples of using different types of electroplating baths.

Electrolyte + Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
0.5 M Cu(MSA) ₂ , x mM Ag(MSA) (x = 0 or 5), 1.0 M MSA	Stainless steel plate	DC at I = 60 mA/cm ² for 20 min and PC at I = 60 mA/cm ² with varying frequencies from 0.1 to 1 Hz at a fixed duty cycle of 50%. The total amount of deposition was set at 72 C/cm ² .	3–7 wt.%	16 μm	High-quality Cu–Ag foil was formed in an additive-free system due to the double function of Ag(I) ion in an MSA-based bath: as a brightening agent and precursor for solute atoms. The as-deposited foil exhibited an UTS of 927 MPa even at low Ag content (2.37 wt.%). After annealing at 250 °C for 1 h, the nanostructure was stable despite a high fraction of the phase boundary.	Kong et al. [92]
160 g/L Cu(SO ₃ CH ₃) ₂ , 0–0.37 g/L AgSO ₃ CH ₃ , 100 g/L HSO ₃ CH ₃ , 40 ppm Cl [−] + 20 mL/L leveling agent, 0–1.4 g/L TU (CH ₄ N ₂ S)	Si wafer + 100 nm Ta and 200 nm Cu	The linear sweep voltammetry (LSV) measurement was set from −0.2 to −1.2 V (vs. Hg/Hg ₂ SO ₄ (0.658 V vs. SHE)) at a scan rate of 5 mV s ^{−1} . + Annealing (Ar) at 350 °C for 1 h.	0.7–43 wt.%	1 μm	For expected usage as <i>interconnects in microelectronics</i> , the microstructures of Cu–Ag deposits—Ag content, grain size, crystalline preferential orientation, and roughness—were properly compared.	Chiang et al. [77]
10 mM CuSO ₄ , 0–1 mM AgNO ₃ , 0.5 M H ₂ SO ₄	Ru(100 nm)/Ta(5 nm)/Si wafer	The deposition rate was ~0.212 nm/s with a steady state deposition current of 0.56 mA/cm ² , and the deposition potential of −0.85 V (vs. SMSE—saturated mercurous sulfate (0.64 V vs. SHE)).	0.4–11 at.%	~180 nm	No application for the deposit was mentioned. The presented estimation methods showed good agreement with experimental values, which can be applied in <i>designing and implementing procedures for alloy electrodeposition</i> .	Shao et al. [93]

Table 4. Cont.

Electrolyte + Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
0.1 M CuCN, 5 mM KAgCN, 0.2 M KCN, 0.1 M NaOH	Cu seed layer (60 nm, PVD)/Ta (7.5 nm, PVD)/TaN (7.5 nm, PVD)/Si	The potential range for LSV was from 0.0 V to −2.0 V (vs. Ag/AgCl), and a scan rate was fixed at 1 mV/s. The reduction of Cu and Ag took place from −1.2 V to −2.0 V, and the electrodeposition was carried out at −1.2, −1.4, −1.6, and −1.8 V. pH = 6.6–13.2, and various concentrations of KAgCN were used.	10 at.%	nm-sized	A porous and rough surface was obtained with a KAgCN concentration >0.02 M. The Cu–Ag film had a resistivity of 5.0 $\mu\Omega\text{cm}$ and was made with −1.6 V at pH = 6.6. It can be used to overcome electromigration—one of the problems in <i>Cu interconnections</i> .	Lee et al. [69]
50 g/L CuSO ₄ ·5H ₂ O complexed by 150 g/L K ₄ P ₂ O ₇ , 75 mL/L 0.1 M AgNO ₃ complexed by 150 g/L KI	Plated Ni on steel samples	Electroplating at 50 °C in non-stirred conditions, deposition time was in the range of 10–150 min. I = 2–30 mA/cm ² at the different current densities.	3–16 at.%	5–7 μm	Innovative opportunities in the electrodeposition of electromigration-resistant coatings with high mechanical qualities for <i>application in the electronic industry</i> .	Bernasconi et al. [73]
50–125 mM Cu(NO ₃) ₂ , 1–7 mM AgNO ₃ , 0–1 M NaNO ₃ , 0.5 M NH ₄ OH	Cu seed layer (PVD, 60 nm)/Ta (PVD, 35 nm)/SiO ₂ wafer	The pH = ~10.9. During electrochemical analyses and electrodeposition, the temperature of the electrolyte was maintained at 30 °C. The Cu–Ag films were obtained by applying potentials from −0.5 V to −1.5 V (vs. Ag/AgCl).	3.4–12.8 at.%	110 nm	Compared to pure Cu, an increase in mechanical hardness and oxidation resistance, a less toxic electrolyte. The films can be utilized for <i>formation of protective coatings, electrocatalysts, and fabrication of interconnects</i> .	Jeon et al. [7]

Table 4. Cont.

Electrolyte + Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
0.02 M Cu(NO ₃) ₂ ·3H ₂ O, 0.02 M AgNO ₃ + 0.2 M TU as a complexing agent	The Ni-coated copper strips	The LSV from the open circuit potential to −1.5 V (vs. Ag/AgCl) in 3.0 M KCl reference electrode with a scan rate of 10 mV/s. Samples were deposited with T _{ON} current densities of 1, 5, and 10 mA/cm ² . The T _{OFF} current was fixed at 0.1 mA/cm ² in each case.	40–80 wt. %	10 ± 1 μm, 14 ± 2 μm	The Cu–Ag coatings deposited at 1 and 5 mA/cm ² demonstrated a hardness of 382 ± 7.5 and 174 ± 5.0 VHN, respectively. These coatings have high electrical resistivity and can be promising candidates for <i>electrical contact materials</i> .	Satpathy et al. [68]

6. Various Applications of Electrodeposited Cu–Ag Alloys

Different structures can be formed by modifying the morphology of electrodeposited Cu–Ag alloys. This enables numerous applications from surface-enhanced Raman spectroscopy (EC-SERS) [94] to electrocatalysis [95]. Rajashekhar et al. have reported that a two-step reduction process was used to develop the Cu–Ag nanocrystalline coating via chronoamperometric co-deposition, optimizing precursor composition and deposition time/current [96]. The rate of nucleation and growth of the nanocrystalline alloy cluster were analyzed using scanning electron microscopy. The controlled 15 mA electro co-deposition led to a better overlay of Cu–Ag nanocrystallites with an average particle size in the range of 200–500 nm compared to the 5 mA for Si wafer of the $2.25 \times 10^{-4} \text{ m}^2$ mediated alloy. This Cu–Ag coating was performed as a SERS probe. The facile nanocrystallite cluster formation resulting from electro co-deposition could be utilized for other bimetallic components advantageous in biomarker, agro-livestock sensing, and trace chemical investigations.

The composition and surface structure of Cu–Ag catalysts can be regulated by adjusting the quantity of precursors in the electroplating bath. Włodarczyk et al. synthesized the Cu–Ag catalyst applied to the cathode using the electrodeposition method [97]. A Cu foam served as a substrate for the catalyst (Cu–Ag alloy). In their work, the bio-electricity production from yeast wastewater in membrane-less microbial fuel cells with a Cu–Ag cathode was described. According to the measurements, the most favorable catalytic parameters—a power of 6.38 mW and a cell voltage of 1.09 V—have been reached with a Cu–5 wt.% Ag alloy that was oxidized over 6 h and after 3 cycles of anodic charge. Also, compared to pure Cu, which has a film-like structure with a prominence-terminated surface, and pure Ag, which has a multi-pod structure, Cu–Ag catalysts were found to have hierarchical dendritic structures [95].

In addition, the morphology of Cu–Ag deposits is readily modulable from smooth films that were achieved at low electrodeposition rates to nanoparticles or dendrites [98], allowing their implementation in the electrochemical reduction in CO_2 . The nanoparticles of Cu–Ag alloy have demonstrated great optical, electronic, and catalytic characteristics [99]. Hoang et al. obtained nanoporous Cu–Ag alloys via electrochemical deposition with 3,5-diamino-1,2,4-triazole (DAT) as an inhibitor [100]. The addition of DAT to the electrolyte leads to a nanowire morphology of the Cu–Ag alloy and results in catalysts with a large surface area that are relevant for selective and active CO_2 electroreduction to multicarbon hydrocarbons and oxygenates. In comparison to Cu–Ag poly and monometallic copper nanowires, the Cu–6at.%Ag alloy film exhibited the highest reduction current density (nearly -300 mA/cm^2 at a cathode potential of -0.7 V vs. RHE —volt vs. the reference hydrogen electrode). Even though the concentration of generated hydrogen has not considerably changed, the Faradaic efficiency (FE) for C_2 products was enhanced, reaching $\sim 60\%$ of C_2H_4 and 25% of $\text{C}_2\text{H}_5\text{OH}$ [101]. Carbon monoxide is one of the most beneficial outputs of CO_2 reduction, and the electroreduction of CO_2 to CO was painstakingly researched [102]. Chen et al. electrodeposited Cu–Ag alloy films by using the same DAT inhibitor [103]. The results show that CO production begins at approximately -0.2 V vs. RHE and increases at more negative potentials to achieve a maximum FE value of $\sim 60\%$ at a cathode potential of -0.4 V vs. RHE . However, the FE improves the production of both C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ at increasing negative potentials, while the FE for CO production decreases. This trend confirms the hypothesis that the adsorbed CO serves as an important intermediate in the synthesis of C_2 products [104].

Sulfate-, nitrate-, and cyanide-based electrolytes containing Cu(II) and Ag(I) ions are widely used for the mentioned applications of Cu–Ag alloys including great prospects for electronic interconnections [105]. Since one of the major concerns in metal interconnection is electromigration failure, the Cu–Ag interconnects are good candidates to solve this problem without severe deterioration of the electrical performance [106]. Recently, the Cu–Ag alloy has been studied as a potential alternative for interconnections in microelectronic circuits and can possibly be implemented in high-field magnets [107]. Advanced research can be effectively conducted at extremely high magnetic fields (80–100 T) with the help of

non-destructive pulsed high-field magnets. The Cu–Ag micro-composites, among other materials, are considered to be promising for usage in the above-mentioned magnets [34].

Regarding the application in ultra-large-scale-integration interconnects, Cu–Ag alloys can increase reliability [108]. This may be the result of the interconnect architecture developed and tailoring copper microstructure in terms of the low-grain boundary and interface diffusion [109], low electrical resistivity, and high mechanical strength [110]. For complete utilization of their alloying effects [111], while keeping a moderately low electrical resistance, an auspicious material modification is necessary. However, alloying additions usually have detrimental effects on one or more of the important characteristics such as thermal stability, electrical resistivity, texture, grain size, and surface roughness. Therefore, the Cu–Ag alloy must offer enhanced mechanical strength and reliability, reduced electrical resistivity, and increased resistance against electromigration effects in order to be accepted as interconnections in future microelectronic devices. Fortunately, it was discovered that in comparison to other copper alloys, alloying Cu with Ag would lead to the lowest increase in resistivity [106].

Further uses of Cu–Ag alloys include the electrodeposition of their particles to ensure improved performance for Zn-air batteries. Also, Cu–Ag films can be used as antibacterial coatings for stainless steel [112].

In addition to the above-mentioned applications, researchers have reported that Cu–Ag alloys have exhibited success in fields such as bactericides [113], decorative artifacts [114], electrocatalysis (H_2O_2 reduction [115] and ammonia oxidation [116]), electrical contacts (flexible electronics [117] and conductive inks [118]), and electrochemical sensors [119], usually in the shape of nanoparticles or core-shell nanowires.

Also, the metal alloys containing Cu (and Ag) were found to have high antibacterial activity against several types of bacteria: *E. coli*; *S. aureus*; MRSA; *L. monocytogenes*; *M. tuberculosis* strain R432 and R267; *C. albicans*; *K. pneumoniae*; *P. aeruginosa*; *A. baumannii*; *Salmonella*; *Enteritidis*; *S. Typhimurium* DT193 S9, DT120 S19 and DT66 S20; *S. typhimurium*; *Streptococcus* sp. BY1; *Enterococcus* sp. BY2; and *B. cereus* BY3. Metallic materials with antibacterial properties can effectively inhibit bacterial adhesion, growth, and proliferation by using element alloying, suitable metal forming, and heat treatment [27].

Tables 5–7 include examples of implementing Cu–Ag alloys as interconnections, catalysts, and SERS investigations with the synthesis conditions used and the properties obtained.

Table 5. The use of Cu–Ag alloys as interconnections.

Electrolyte	Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
0.3 M CuCN, 5.0 mM KAg(CN) ₂ , 0.6 M KCN	5 µM KSeCN and 0.1625 mM TU are the adsorbates used for Ag super-filling	Cu (PVD, 40 nm)/Ta(PVD, 7 nm)/Si	The deposition potential was fixed at −1.3 V (vs. Ag/AgCl). + Annealing (N ₂) at 350 °C for 1 h.	7.73–9.28 at. %	240 nm	The Cu–Ag exhibited superior oxidation resistance and mechanical hardness without severe reduction in the electrical conductivity compared to pure Cu. The super-filling of Cu–Ag can be used for the fabrication of <i>metal interconnections</i> .	Kim et al. [120]
67 g/L CuSO ₄ ·5H ₂ O (0.24 M), 0–30 mL/L AgNO ₃ (0.1 M), 170 g/L H ₂ SO ₄ (1.8 M)	8 mL/L Cubath SC MD, 2 mL/L Cubath LO 70/30 (Enthone GmbH, Langenfeld, Germany)	Single crystalline Si wafers	An applied deposition voltage of 1 V and a substrate with d = 100 mm. The deposition was realized in the constant current density mode with 5 mA/cm ² and 15 mA/cm ² .	2 at. %	1 µm	The deposited Cu–Ag films fulfilled the electrical resistivity of $\rho_f < 2.2 \mu\Omega\text{cm}$ ITRS (International Technology Roadmap for Semiconductors) after heat treatment up to 500 °C. The electrical resistivity of films was low enough for <i>interconnect applications</i> .	Strehle et al. [121]
CuCN, 1.25–10.0 mM KAg(CN) ₂	0.2 M KCN as a complexing agent	Cu blanket wafers (PVD, 40 nm)/Ta (PVD, 7 nm)/Si	The LSV was carried out with a 10 mV/s scan rate, and the applied potential ranged from −0.6 to −2.0 V (vs. Ag/AgCl). Annealing (N ₂) at 350 °C for 1 h to decrease the electrical resistivity of the films, and the atomic distribution of metals. A corrosion test was performed in the air at 250 °C for 30 min.	3–11 at. %	130 nm	During annealing, Ag atoms appeared to be segregated at the surface through the grain boundaries, which decreased the surface roughness and enhanced the oxidation resistance. After annealing, Cu–Ag film had a resistivity comparable to that of pure Cu.	Kim et al. [53]

Table 5. Cont.

Electrolyte	Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
50 mM CuSO ₄ ·5H ₂ O, 2 mM AgNO ₃ , NaOH (pH = 6–10)	250 mM (NH ₄) ₂ HC ₆ H ₅ O ₇	Si wafers/100-nm thick SiO ₂ layer/10-nm thick W diffusion barrier layer	Cathodic voltammetry was performed up to −1.2 V (vs. Ag/AgCl) at a potential scan rate of 10 mV/s. The Cu–Ag alloy was electrodeposited for 20 s at a constant potential of −0.7 V (vs. Ag/AgCl).	3–5 wt.%	nm-sized	This seedless Cu–Ag electrodeposition can be used in fabricating <i>defect-free interconnect lines for microelectronic systems</i> .	Kim et al. [122]

Table 6. The use of Cu–Ag alloys as catalysts.

Electrolyte	Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
Cu(NO ₃) ₂ ·3H ₂ O, AgNO ₃	3 mM Sodium citrate	Ni foams	The open circuit voltage was 1.49 V and the maximum power density was 86.5 mW/cm ² at a constant current density of 100 mA/cm ² for the primary zinc-air battery. The electrodeposition time—50 s.	5–10 at.%	40–50 nm	The round-trip efficiency of the rechargeable zinc-air battery at 20 mA/cm ² was 56.4%. The <i>Cu–Ag electrocatalyst</i> showed high catalytic activity in the oxygen evolution reaction in an alkaline battery and excellent tolerance of carbonate ions on the cathode side. The innovative air cathode modified by the Cu–Ag catalyst exhibited good durability during the charge and discharge processes. The Cu–Ag catalysts are the candidates for <i>applications in metal-air batteries and alkaline fuel cells</i> .	Jin et al. [123]

Table 6. Cont.

Electrolyte	Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
0.2 M CuCN, 10–30 mM KAg(CN) ₂	0.4 M KCN	Cu foil	The LSV for selecting the deposition potential was conducted in the electrolytes across a potential range from −0.4 V to −2.0 V (vs. Ag/AgCl) at a sweep rate of 20 mV/s. The electrodes were deposited at −1.3 V (vs. Ag/AgCl), and the amount of charge was set at 400 mC/cm ² .	57 at.%	1–2 µm	The catalytic activity of the <i>Cu–Ag dendritic catalyst</i> was 2.2 times higher than that of the Ag dendrite catalyst, in terms of Ag mass activity. These Cu–Ag catalysts can be effectively used for the production of CO by electrochemical reduction of CO ₂ . They also offer significant benefits in terms of process expenses.	Choi et al. [95]
20 mM CuSO ₄ , 2 mM Ag ₂ SO ₄ , 1.5 M H ₂ SO ₄	0.1 M Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	Cu foil	I = −3 A/cm ² for 20 s. A mild thermal annealing treatment in air at 200 °C was applied to the deposited Cu–Ag foam for 12 h.	15 at.%	nm-sized	The as-deposited <i>catalyst</i> was selective towards CO at particularly low overpotentials (FE _{CO} = 81.45%, I _{CO} = −0.24 mA/cm ² at −0.3 V vs. RHE) and towards C ₂ H ₄ at higher overpotentials (FE _{C₂H₄} = 36.56%, I _{C₂H₄} = −11.32 mA/cm ² at −1.1 V vs. RHE).	Dutta et al. [124]
0.2 M CuSO ₄ , 10–50 mM AgNO ₃ , 1.5 M H ₂ SO ₄	–	Cu foil	Cu–Ag foams were electrodeposited at a constant current of 1 A/cm ² for 10 s.	~11–33 wt.%	1–5 µm	Increased selectivity and activity for CO production from CO ₂ for <i>Cu–Ag catalysts</i> . Compared to pure Ag catalyst, the nanostructuring of Ag with low-cost and CO ₂ RR active Cu highlights a synergy between the metal components in efficiently catalyzing CO ₂ reduction to CO at low overpotentials and with better stability.	Kottakkat et al. [125]

Table 6. Cont.

Electrolyte	Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
0.1 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 1 mM Ag_2SO_4 , H_2SO_4	10 mM 3,5-diamino-1,2,4-triazole as an inhibitor	The carbon paper coated with Cu	Up to a final deposition charge of 2 C/cm^2 , alloys were electrodeposited galvanostatically at a constant current density of 4 mA/cm^2 .	6 at. %	nm-sized	For the electroreduction of CO_2 in an alkaline flow electrolyzer, the <i>Cu–Ag catalyst</i> shows good selectivity towards C_2H_4 (~60%) and $\text{C}_2\text{H}_5\text{OH}$ (~25%) production at a relatively low applied potential -0.7 V vs. RHE and a high current density of -300 mA/cm^2 .	Hoang et al. [101]

Table 7. The use of Cu–Ag alloys for SERS investigations.

Electrolyte	Additives	Substrate	Synthesis Conditions	Ag Content	Thickness	Properties and Applications	References
CuSO_4 , AgNO_3	Reducing agent, tri-sodium citrate dissolved in H_2O	Pre-activated Si wafer	The electrodeposition of bimetallic coatings was achieved using the chronoamperometry technique at ambient temperature.	5.3 at. %, 6.2 at. %	$2.9 \text{ }\mu\text{m}$, $11 \text{ }\mu\text{m}$	Optical reflectance, high surface chemistry and topography, nanocrystallite cluster orientation. Applicable in <i>SERS</i> .	Rajashekhar et al. [96]
0.1 M $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 10^{-4} M AgNO_3	–	Carbon-based screen-printed electrode	The potential was at -0.3 V (vs. Ag/AgCl) for 180 s.	–	μm -sized	High-performance, low-cost <i>SERS</i> -active electrodes were made with a minimal concentration of Ag. The superior performance of this bimetallic Cu–Ag electrode over a monometallic Ag screen-printed electrode represents an eco-friendly solution for <i>EC-SERS investigations</i> in the future.	Clarke et al. [126]

7. Conclusions

This review article summarizes different aspects of Cu–Ag alloys' electrodeposition from aqueous solutions. The process, effective parameters, and related properties were described. Although much research in terms of synthesis, as well as applications, has already been conducted and reported in the literature, there are still many avenues that deserve exploration to gain a better understanding of Cu–Ag systems. Despite the previously carried out studies, it is necessary to further develop electrolytic baths for high-quality Cu–Ag electrodeposition. Moreover, the effects of aging treatment on the mechanical and electrical properties of these alloys remain unclear. Future research is also needed to investigate how Ag contributes to strengthening and creating nano-lamellar structures with a coherent interface that may be a practical method for obtaining Cu–Ag alloys with high strengths and stability. The main applications for these superior alloys are wires and microwires, conductors for DC and pulsed high magnetic fields or fusion magnets, metal sheets, cables for diagnostics, power supplies, and transformers, and electrodes used in resistance welding. To broaden the utilization of Cu–Ag alloys, more studies will be required to determine how organic additives affect Cu–Ag electrodeposition and surface morphology control. Furthermore, the production of materials with excellent resistance against electromigration effects in interconnected metallization is still one of the most promising directions.

Indeed, controlling the electrodeposition processes aims at adjusting the competing forces involved to achieve the desired mass transport. For instance, the formation of quasi-equilibrium structures becomes accessible via the close control of the driving force and is beneficial for the growth of ordered phases or intrinsic compounds. Furthermore, the degree of metastability of the structure during formation can be continuously tuned. This enables the corresponding modification of properties via dopant density, impurity concentration, and defects in products, as well as through alloy composition and atomic configuration in metals.

Therefore, the use of ultrasound during the electroplating process is suggested to improve the composition and physical properties of materials, in particular, corrosion resistance, magnetization, wear, and microhardness. Ultrasound technology showed a high potential in promoting the growth of smooth and uniform surfaces with homogeneously distributed particle content. Also, the imposition of ultrasound induces a decrease in the size of porous structures due to hydrogen absorption in the deposit. Regarding the stability of adhesion between the film and substrate along with the orientation of crystals, ultrasonic waves play an important role.

Concentration polarization and hydrogen evolution throughout electroplating readily affect the deposition efficiency and surface compactness. To improve this efficiency and avoid the cracking of fragile coatings caused by introducing ultrasonic energy, other physical treatments are proposed [127]. For example, the use of moving electrodes allows us to enhance mass transport and deal with slight reactant and ionic concentrations. However, such a method has limited effects and requires intricate cell construction.

The application of an external magnetic field develops the functionalization of the surfaces during the electrodeposition process and is advantageous for obtaining dense alloy films and refining grain size. Moreover, by changing the surface roughness and accelerating the rate of ion mass transfer, the Lorentz force produced through an interaction of the electric and magnetic fields will lead to magnetohydrodynamic phenomena on the cathodic surface, affecting the current distribution and increasing film thickness and hardness as well as the deposition efficiency.

Enhancing the characteristics of Cu–Ag alloys obtained via the electrodeposition technique may be an appropriate way to achieve materials with specific properties and large surface area, as was discussed in this review article.

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