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Hydrometallurgical Method for AgCu Alloy Powder Synthesis and Its Application in Pd(II) Recovery Through Cementation

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Abstract: This study investigates the synthesis, characterization, and potential applications of silver-copper (AgCu) alloy powders produced from co-precipitated carbonates. The Cu/Ag carbonate samples were analyzed using EDXRF, TGA-DSC, XRD, SEM, and electrical conductivity tests to examine their composition, thermal behavior, structure, and morphology. The results showed slight deviations from the theoretical Cu/Ag ratios in the carbonates, attributed to equilibrium effects during precipitation. Thermal analysis indicated that the reduction process of carbonates with hydrogen was completed at 300 °C, while alloy formation was confirmed by endothermic peaks around 780 °C. XRD and SEM analyses revealed that AgCu alloys formed a solid solution, with smaller crystallite sizes observed at higher Cu contents. Electrical conductivity tests demonstrated that while pure Ag and Cu powders exhibited conductivity increases with compaction, the AgCu alloy showed stable conductivity without a significant decrease. In Pd(II) cementation experiments, AgCu alloys demonstrated higher efficiency in Pd(II) recovery than pure Ag and Cu. These findings suggest that AgCu alloys, particularly with a balanced composition, may offer improved performance for metal recovery applications, providing a promising approach for industrial cementation processes.

Keywords: copper; silver; alloy; palladium; cementation



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1. Introduction

Platinum-group metals (PGMs) are among the rarest elements on Earth, occurring in concentrations of less than 0.01 g per ton [1]. One of these metals is palladium (Pd), which is primarily used in automotive catalytic converters that reduce harmful emissions [2]. Its applications extend beyond this to include electronics [3], pharmaceuticals [4], jewelry [5], and clean energy [6]. Pd is classified as a critical raw material due to its highly concentrated supply chain, which is predominantly reliant on Russia and South Africa [7]. This dependence contributes to its significant market value, which was approximately USD 1000 per ounce by the end of 2023 [8]. Consequently, the development and improvement of Pd recycling technologies are of paramount importance, especially for Europe, which lacks significant deposits of this critical metal. The main Pd-bearing materials being globally recycled are spent catalytic converters, typically processed through pyrometallurgical methods [9]. An alternative would be hydrometallurgical processing. While the pyrometallurgical route requires high temperatures to melt the raw material, the hydrometallurgical route offers lower energy consumption [10], as well as high selectivity [11]. However, hydrometallurgical recycling faces challenges such as a difficult scale-up to an industrial scale and complex wastewater handling compared to pyrometallurgical recycling. Catalytic converters are the primary source for Pd recycling, but other notable sources exist, such as wastewater from mints and mines [12,13]. While the majority of Pd(II) is recovered in these facilities, they still generate large volumes of wastewater containing trace amounts of noble metal ions, which are not efficiently recovered [14]. These wastewaters can only be efficiently processed by means of hydrometallurgical methods, such as adsorption on

activated carbon [15] or anion exchange resins [16], direct chemical reduction [17], solvent extraction [18], and cementation [19].

In metallurgy, cementation is an electrochemical process in which an active metal reacts with an electrolyte solution containing ions of a more noble metal, leading to the deposition of the noble metal onto the active metal's surface [20]. This process is often employed for the recovery of noble metals, with the Merrill–Crowe process being a notable example, where zinc powder is used to recover Au [21]. However, a significant limitation of cementation is its low efficiency when applied to solutions with trace amounts of noble metals, even when an excess of the cementing metal is used [22]. Additionally, these wastewaters frequently contain nitrate and chloride ions, often originating from the use of aqua regia to dissolve noble metals [23]. Chloride ions tend to form complexes with noble metals, which typically exhibit lower standard potential values than pure cations [24], further reducing the efficiency of cementation. The presence of nitrate ions could also affect the effectiveness of cementation [25]. Theoretically, using metals with negative standard potentials should result in fast reaction kinetics and minimal residual noble metal ions in the solution [26]. However, the actual efficiency is often compromised by hydrogen evolution during the process, which can lead to the dissolution of the cementing metal. Moreover, hydrogen bubbles may adhere to the surface of the cementing metal, reducing its contact with the solution and further diminishing cementation efficiency [27]. While metals with positive standard potentials do not induce hydrogen evolution when used as cementing agents, the small difference in standard potentials between them and the noble metals being cemented negatively impacts the process. One promising approach to improving cementation efficiency is the use of alloys instead of pure metals. When two different metals are in contact within an electrolyte, with an electron-conductive path, the corrosion of the less resistant metal increases while that of the more resistant metal decreases; the more active metal acts as an anode (corroding), while the more resistant metal acts as a cathode [28]. Alloying metals ensures constant contact, which could alter effective potentials and influence the cementation process, although comprehensive studies on this influence appear to be lacking.

In this study, we synthesized and analyzed AgCu alloy powders with varying ratios of silver and copper, along with pure metal powders of silver and copper. The purpose of this investigation was to evaluate the effectiveness of these materials in the cementation of Pd(II) from an aqueous chloride medium, a common scenario in the recovery and purification of noble metals. The results suggest that using alloy powders yields greater process kinetics when compared to pure metals.

2. Materials and Methods

2.1. Synthesis of AgCu Alloy Powders

To synthesize AgCu alloy powders, multiple mixtures were prepared using a 267.2 g/L AgNO₃ solution and a 203.1 g/L Cu(NO₃)₂ solution, both made by dissolving appropriate amounts of 99.99% pure metals in nitric acid (65%, analytical grade, Pol-Aura, Kraków, Poland). The concentration of solutions was analyzed using AGILENT 4200 MP-AES microwave emission spectrometer (Agilent, Santa Clara, CA, USA). Solutions were then mixed in different proportions to achieve the desired metal mass ratios. A 106 g/L Na₂CO₃ solution, prepared by dissolving analytical grade Na₂CO₃ (Sigma-Aldrich, St. Louis, MO, USA) in deionized water, was then added to each mixture under vigorous stirring at 400 RPM, resulting in the co-precipitation of copper(II) and silver(I) carbonates.

The resulting carbonates were filtered, rinsed with deionized water, and dried in a laboratory dryer (SML-32/250, Zalmed, Skierniewice, Poland) at 60 °C for 24 h. After drying, the carbonates were milled using a commercial coffee grinder model KG200 (DeLonghi, Treviso, Italy). The final step in the production of AgCu alloy powders involved the reduction and decomposition of the carbonates in a tube furnace (Czyłok, Jastrzębie-Zdrój, Poland) under an Arcal gas mixture (95% Ar + 5% H₂, 99.999% purity, Air Liquide, Paris, France) with a gas flow rate of 20 L/h. The furnace was programmed with the following

parameters: a 0.5 h waiting period to ensure proper filling with the Arcal atmosphere, followed by a 1 h heating phase from room temperature to 300 °C, and then a 2 h holding period at 300 °C to allow for the reduction process. Finally, the furnace was cooled gradually back to room temperature before the samples were removed. The carbonates were placed in cylindrical quartz containers (2 cm in diameter and 2 cm in height), which were then positioned in a quartz boat for stability before being placed in the furnace.

2.2. Characterization of Ag/Cu Carbonates and AgCu Alloy Powders

The Cu and Ag content in the co-precipitated carbonates was determined using a Minipal 4 EDXRF spectrometer (PANalytical, Almelo, The Netherlands). To identify the optimal reduction temperature, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on the carbonates using an SDT Q600 instrument (TA Instruments, New Castle, DE, USA) in an Arcal atmosphere with a gas flow rate of 20 L/h, and the temperature was increased in steps of 0.1 °C.

Both the carbonates and the resulting metal powders were analyzed by means of X-ray diffraction (XRD) using a Primini instrument (Rigaku, Tokyo, Japan) equipped with a copper tube ($\lambda = 1.54059 \text{ \AA}$). Scanning electron microscopy (SEM) analysis was conducted on both the carbonates and the metal powders using a JCM-6000 Plus instrument (JEOL, Tokyo, Japan).

The electrical conductivity of the obtained metal powders was assessed using a custom-designed system based on the assembly presented by Juan et al. [29]. Resistance measurements were conducted using a Keithley 2000 Series 6.5 Digit Multimeter (Keithley Instruments, Cleveland, OH, USA).

2.3. Pd(II) Cementation

The metal powders were further examined for their effectiveness in the Pd(II) cementation process. A solution containing Pd(II) ions was prepared by diluting a stock solution, as described in our previous work [13], in 0.1 M HCl, resulting in a final Pd(II) concentration of 0.1 mM. The cementation experiments were conducted in Hellma GmbH quartz cuvettes (Müllheim, Germany) with a chamber volume of 3.5 mL, placed in a thermostat with magnetic stirring.

For each experiment, 3 mL of the Pd(II) solution was used, and AgCu metal powders were added to achieve a solid-to-liquid ratio of 0.33 g/L. A magnetic stirring bar was included in each cuvette to enable mixing, and the process was performed at a constant temperature of 10 °C with stirring at 1000 RPM. For each powder composition, two analyses were conducted. After one hour of cementation, the solution was filtered at room temperature. This filtration step was performed immediately after the solution was removed from the thermostat, and the small solution volume minimized any potential errors. The remaining Pd(II) concentration was then determined using the MP-AES technique, as described earlier.

3. Results and Discussion

3.1. EDXRF Analysis of Carbonates

After the precipitation process, the resulting carbonates were analyzed using the EDXRF method to confirm the Cu and Ag ratios. The goal was to precipitate Cu/Ag carbonates with a Cu content ranging from 0% to 100% in 10% increments. We are aware that copper carbonate reacts with water and forms insoluble basic carbonate [30]; for clarity, we refer to the samples prior to the reduction process simply as carbonates. The results of the EDXRF analysis are shown in Table 1.

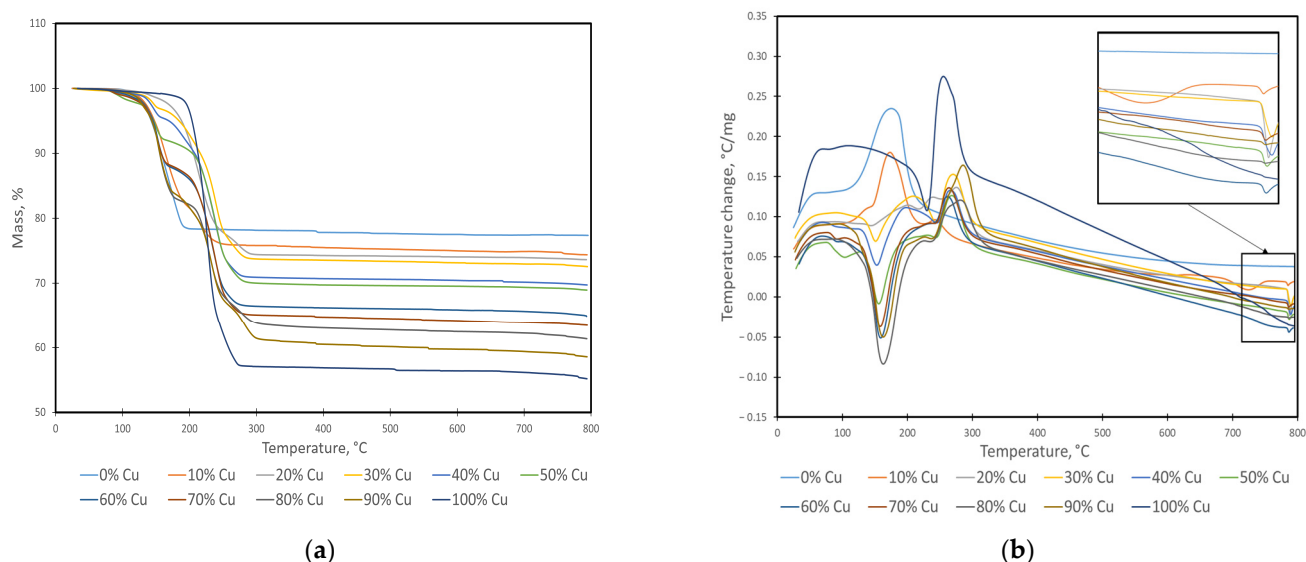
Table 1. Cu and Ag content of precipitated carbonates.

Theoretical wt%		Actual wt% (Based on EDXRF Analysis)	
Cu	Ag	Cu	Ag
0	100	0	100
10	90	11.1	88.9
20	80	22.4	77.6
30	70	34.6	65.4
40	60	42.7	57.3
50	50	52.9	47.1
60	40	66.1	33.9
70	30	75.2	24.8
80	20	82.6	17.4
90	10	89.3	10.7
100	0	100	0

The results from Table 1 show that the actual Cu and Ag ratios in the carbonates are slightly different from the theoretical ones. The greatest deviation from theoretical values is present at 60% and 70% theoretical Cu content. These discrepancies are likely not due to the secondary dissolution of carbonates, as the solubility of these compounds in water is very limited [31]. Instead, the variation in values likely arises from the establishment of an equilibrium between metal ions and carbonate anions in solution during the precipitation process. Mixtures with Cu content over 50% were still visibly blue (indicating the presence of Cu(II) ions); however, the further addition of sodium carbonate did not result in additional precipitation. In this paper, we will refer to the theoretical content of Cu and Ag in the resulting powders for clarity.

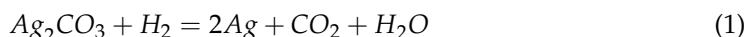
3.2. TGA-DSC Analysis of Carbonates

To determine the optimal temperature for the reduction of co-precipitated carbonates, a TGA-DSC analysis was conducted under the reducing Arcal (H_2/Ar) atmosphere. The results are detailed in Figure 1a,b.

**Figure 1.** The results of TGA (a) and DSC (b) analysis for AgCu alloy powders.

The TGA results in Figure 1a show the mass changes of carbonates as the temperature increases. The resulting mass loss is proportional to the metal content, with higher copper content leading to greater mass loss. All samples reached a semi-stable state before 300 °C, after which the mass did not change significantly. This indicates that at this point, no further reduction or thermal decomposition was occurring, and the carbonates had been

fully converted into metals, as shown in Equations (1) and (2). Therefore, the reduction of carbonates in Arcal atmosphere for subsequent tests was conducted at 300 °C.



The DSC results in Figure 1b show the thermal changes in the samples, allowing the observation of endothermic and exothermic processes. Up to 300 °C, both exothermic and endothermic processes are observed, corresponding to the reduction and decomposition of carbonates. After 300 °C, no further mass loss is observed, indicating that the sample consists of metallic powders. These powders could either be a mixture of Cu and Ag powders or a AgCu alloy. Distinguishing between a mixture of powders and a true alloy is challenging. However, the presence of an endothermic peak around 780 °C provides crucial evidence of alloy formation. Samples containing co-precipitated Cu and Ag carbonates show an endothermic peak at around 780 °C, while this peak is not observed for pure Cu or pure Ag carbonates. This peak can be attributed to the partial melting of the AgCu alloy, as the phase diagram of the AgCu system shows that for compositions near the eutectic point at 71.9 wt.% Ag, the melting temperature is 779 °C [32]. Variations in the composition of Cu and Ag would shift the melting temperature accordingly, as observed in the DSC curve. Thus, the presence of this peak in mixed carbonates indicates successful alloying. The absence of further mass changes after 300 °C, along with the endothermic peak near 780 °C, confirms that the observed process corresponds to the melting of the AgCu alloy, rather than any residual decomposition of carbonates.

3.3. XRD Analysis of Carbonates and Alloy Powders

The XRD analysis was conducted to identify the crystalline phases present in the samples and confirm the successful formation of the alloys. For the Cu/Ag carbonates, the XRD patterns were examined to detect individual carbonate phases and any potential mixed phases. The analysis was performed over a 2θ range of 20–80°, with a step size of 0.01° and a scan speed of 1°/min. Each sample required 1 h for analysis and was examined immediately after cooling to room temperature in the furnace, during which a H₂/Ar atmosphere was maintained. Phase identification was performed using the ICDD card number 03-065-6490. The results of this analysis are presented in Figure 2.

As shown in Figure 2a, the XRD analysis of co-precipitated copper and silver carbonates revealed the presence of additional phases that were not observed in systems containing only the pure carbonates of the individual metals. For the 0% Cu sample, the identified phase was Ag₂CO₃, while for the 100% Cu sample, it was Cu₂(OH)₂CO₃. With varying compositions, new peaks emerged in the XRD patterns, suggesting the formation of mixed phases. However, we were unable to specifically identify these phases, as no perfect matches were found in the ICDD database, and detailed crystallographic studies were not within the scope of this research.

The analysis of metal powders obtained after reduction, shown in Figure 2b, includes results for both pure metals (Ag and Cu) and the resulting alloy powders. In all alloy samples (containing 10–90% Cu), closely spaced diffraction peaks, such as Ag(200)/Cu(111) and Ag(311)/Cu(220), merge into single peaks. This behavior indicates the formation of a solid solution phase across the alloy compositions. An exception occurs at 90% Cu content, where the Ag(311) and Cu(220) peaks remain distinct, suggesting limited solid solution formation with this composition. At Cu contents of 50% and above, additional peaks in the range of 32° < 2θ < 36.5° corresponding to copper oxide phases appear, indicating partial oxidation of the alloy. Interestingly, these oxide peaks are absent in the pure Cu (100%) sample, possibly reflecting differences in oxidation resistance.

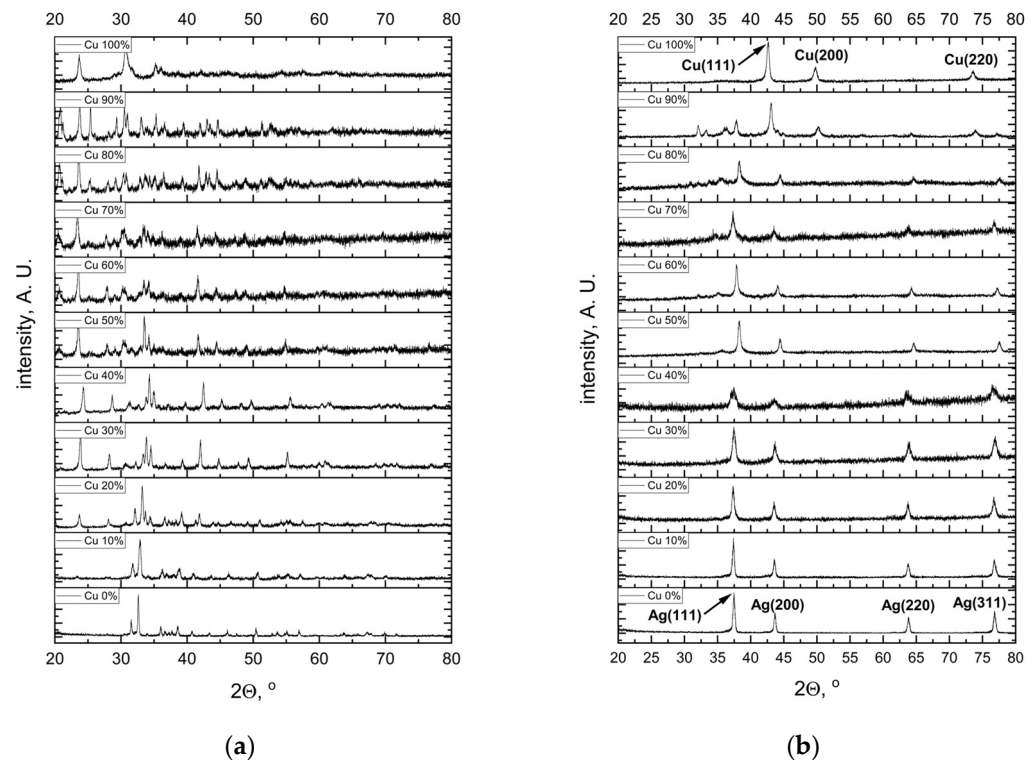


Figure 2. XRD analysis: (a) co-precipitated copper and silver carbonates; (b) metallic powders obtained by the reduction of carbonates in Arcal (H_2/Ar) atmosphere.

XRD results were utilized to analyze the structural properties of the samples, particularly to calculate crystallite sizes. The (111) planes of both Ag and Cu were specifically selected for these calculations, as they represented the most intensive reflections for each metal in the XRD patterns. These calculations were performed using the Scherrer equation, as shown in Equation (3), and the results are presented in Table 2.

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (3)$$

where D is the crystallite size; K is the shape factor (in the case of our calculations, this value was equal to 0.95, as commonly used for spherical crystals); λ is the wavelength of the X-ray radiation used (in our case Cu $K\alpha$ radiation, $\lambda = 0.154$ nm); β is the full width at half maximum (FWHM) of the diffraction peak; and θ is the Bragg's angle.

Table 2. Calculated crystallite sizes for (111) planes of Ag and Cu.

%Cu	Crystallite Size [nm]											Mean (SD)
	0	10	20	30	40	50	60	70	80	90	100	
Ag(111)	33.6	35.2	25.6	18.6	36.1	20.8	18.2	12.5	18.6	12.7	-	23.2 (9.0)
Cu(111)	-	32.9	27.8	23.3	28.8	31.9	18.1	26.3	15.4	15.3	21.1	24.1 (6.5)

The results presented in Table 2 show that for the Ag(111) plane, the crystallite size decreased with increasing Cu content, with values ranging from 33.6 nm at 0% Cu to 12.5 nm at 70% Cu. The average crystallite size for Ag was 23.2 nm, with a standard deviation of 9.0 nm. For the Cu(111) plane, the crystallite size also showed a decreasing trend, from 32.9 nm at 10% Cu to 15.3 nm at 90% Cu, with an average size of 24.1 nm and a

standard deviation of 6.5 nm. Although the trend is not exactly linear, these results indicate that increasing Cu content generally leads to smaller crystallite sizes for both metals.

3.4. SEM Images of Carbonates and Metal Powders

Scanning electron microscopy (SEM) was employed to examine the morphology of carbonates and metal powders. The samples analyzed included Ag_2CO_3 , $\text{Cu}_2(\text{OH})_2\text{CO}_3$, co-precipitated Ag_2CO_3 and $\text{Cu}_2(\text{OH})_2\text{CO}_3$, and their respective metallic forms obtained through reduction by hydrogen, namely Ag, Cu, and AgCu alloy. The results are shown in Figures 3 and 4.

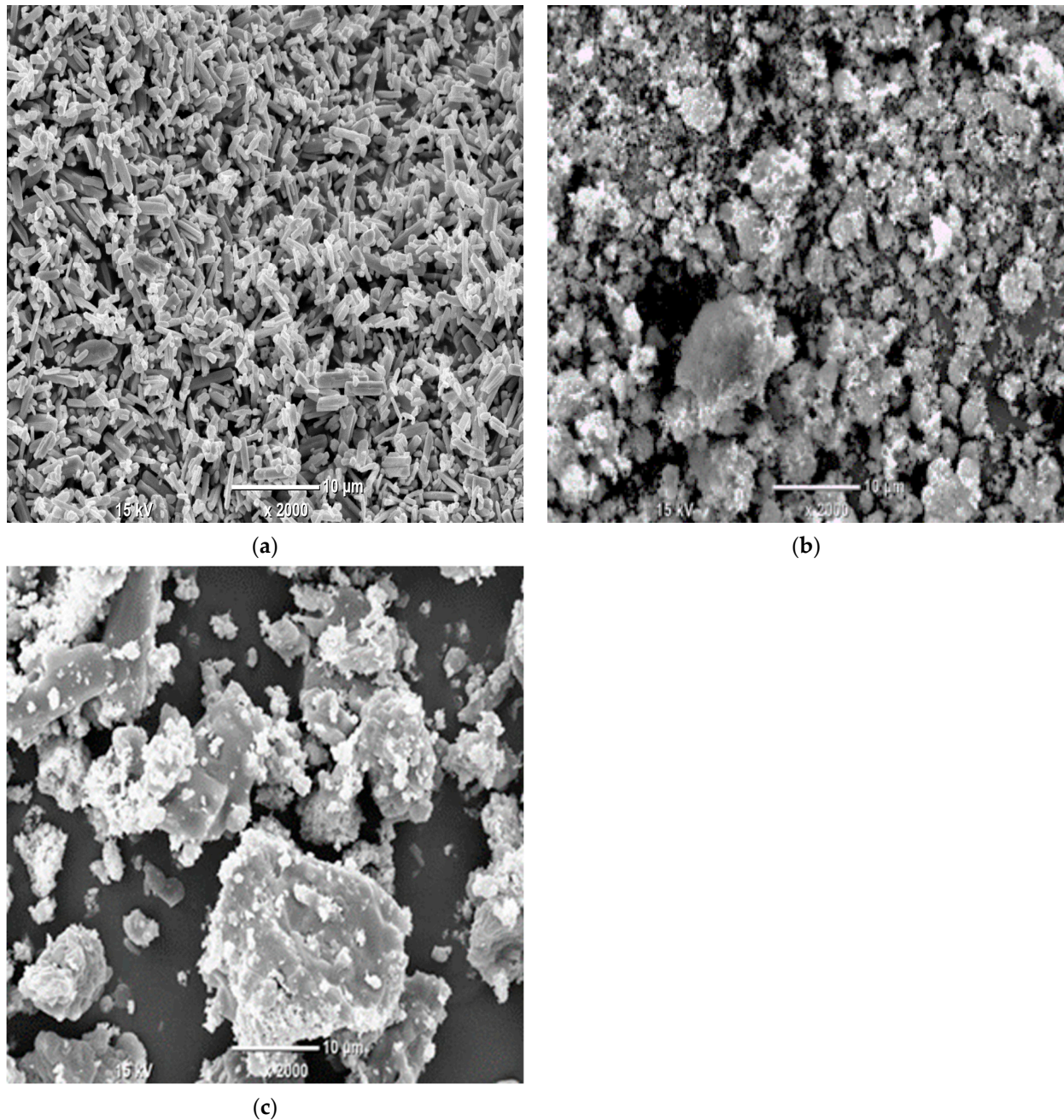


Figure 3. SEM images: (a) Ag_2CO_3 ; (b) $\text{Cu}_2(\text{OH})_2\text{CO}_3$; (c) co-precipitated Ag_2CO_3 and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (50% Ag, 50% Cu).

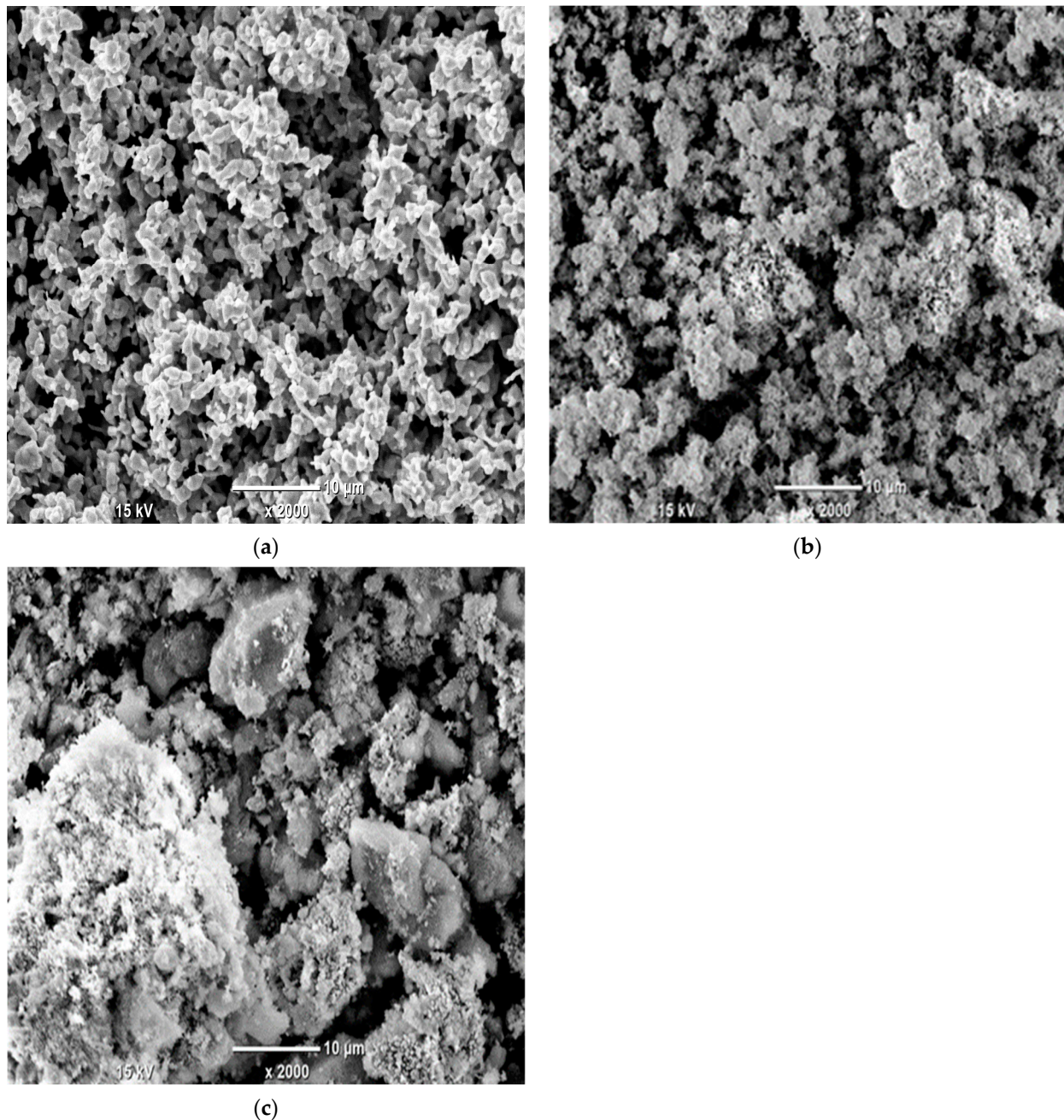


Figure 4. SEM images: (a) Ag powder; (b) Cu powder; (c) AgCu alloy powder (50% Ag, 50% Cu).

Figure 3a shows that Ag_2CO_3 is composed of relatively uniformly sized particles with a highly regular rod-like morphology, which is in accordance with the literature [33,34]. $\text{Cu}_2(\text{OH})_2\text{CO}_3$, presented in Figure 3b, shows an irregular morphology and size distribution, although the literature suggests that $\text{Cu}_2(\text{OH})_2\text{CO}_3$ should consist of spherical agglomerates [35]. Co-precipitated carbonates shown in Figure 3c are characterized by a different morphology than pure carbonates, forming larger agglomerates, and the regular structure of Ag_2CO_3 is not observed.

The Ag powder shown in Figure 4a exhibits a morphology characteristic of its carbonate form, as it is highly regular, with some rod-shaped particles still visible. The Cu powder in Figure 4b displays an irregular morphology similar to $\text{Cu}_2(\text{OH})_2\text{CO}_3$, but the particle sizes appear to be relatively uniform. In contrast, the AgCu powder in Figure 4c has larger particle sizes compared to the individual metal powders, suggesting that the

metals likely agglomerate during the reduction process. Although the particle sizes are not entirely uniform, the smallest observed particles have a diameter of at least 1 μm .

When considering the results from Section 3.3 (crystallite sizes), where the average diameters were 23.2 nm for Ag and 24.1 nm for Cu, it can be concluded that the obtained particles are polycrystalline. This discrepancy between the particle and crystallite sizes indicates that each particle comprises multiple smaller crystallites aggregated together.

3.5. Conductivity of Metal Powders

This subsection discusses the conductivity results of the synthesized metal powders: pure Ag, a 50% Cu/50% Ag alloy, and pure Cu. The analysis aimed to compare the electrical properties of these different compositions under different compaction degrees. A 100% compaction degree would relate to metal powder achieving the theoretical density of a solid metal. Conductivity is influenced by factors such as the presence of oxide layers, grain boundaries, and structural defects in the metals [36], all of which could also affect their reactivity and efficiency during cementation [37]. The results of this analysis are presented in Figure 5.

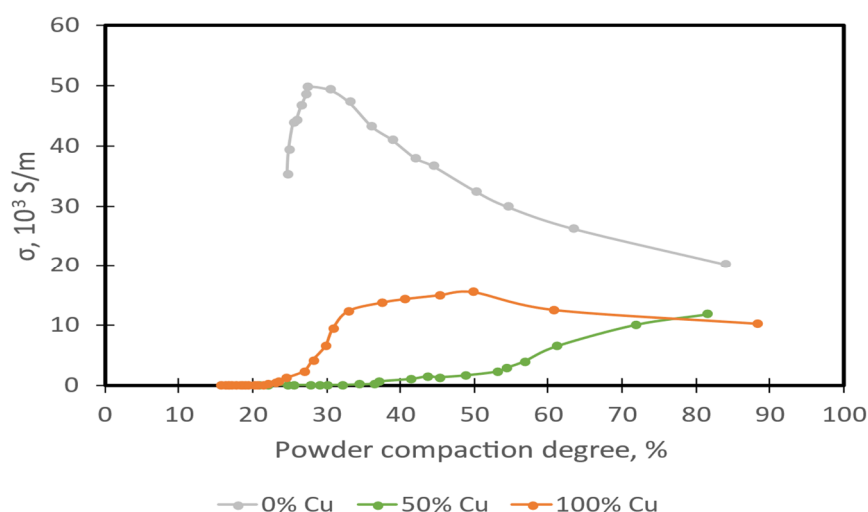


Figure 5. Changes in the electrical conductivity of metal powders depending on their compression degree. 0% Cu refers to a sample of pure Ag; 50% Cu refers to the AgCu alloy.

The closest conductivity match for silver ($6.30 \times 10^7 \text{ S m}^{-1}$ at 20 °C) is copper ($5.96 \times 10^7 \text{ S m}^{-1}$ at 20 °C).

The results presented in Figure 5 reveal a notable relationship between conductivity and the compaction degree of the powders. For pure metals, Ag demonstrated a higher conductivity compared to Cu, consistent with its known superior electrical properties. However, the obtained values are significantly smaller than the theoretical conductivities of pure metals ($6.30 \times 10^7 \text{ S m}^{-1}$ at 20 °C for Ag and $5.96 \times 10^7 \text{ S m}^{-1}$ at 20 °C for Cu [38]), likely due to factors such as oxide layers, structural defects, and particle boundaries inherent in powders. Both metals initially showed increasing conductivity with compaction (up to about 30% compaction), attributed to improved electrical contact between particles and the reduction of insulating oxide layers. Similar phenomena are documented in the literature; for example, Sergey Gilev observed comparable behavior in compressed Al powders [39]. His explanation is that metal powders initially lack macroscopic conductivity. Increased pressure improves electrical contact between particles and mechanically damages any oxide films on the metal surface. However, at higher pressures, conductivity can decrease due to intense heating and reduced density of the compressed material. Another theory is that the intense pressures present during the compacting of powders result in material stress, which is known to negatively affect the conductivity of metals [40].

The AgCu alloy, on the other hand, does not show a decrease in conductivity within the analyzed compaction range, but exhibits the lowest electrical conductivity compared to the pure metals, except at a compaction degree of over 80%, where it exhibits better conductivity than pure Cu. This finding aligns with the literature, which indicates that copper alloys generally have lower electrical conductivity than pure copper [41]. This trend holds for AgCu alloys, despite silver having higher conductivity than copper [42]. The lower conductivity of the alloy at lower compaction levels likely reflects the influence of grain boundaries and intermetallic interfaces, which could play a role in providing more active sites for Pd(II) reduction.

3.6. Recovery of Pd(II) by Cementation

In the recovery of Pd(II) from aqueous solutions, a variety of methods can be employed, each offering distinct advantages and limitations. The choice of method depends on factors such as Pd(II) concentration, the presence of other metals, the chemical composition of the solution (e.g., chloride-based, cyanide-based), economic considerations, and specific application requirements. A summary of the most commonly used methods is presented in Table 3.

Table 3. General comparison of common methods for Pd(II) recovery from aqueous solutions.

Pd(II) Recovery Methods	Materials Used	Advantages	Limitations
Ion exchange [43,44]	Ion-exchange resin	• Highly cost-effective • High selectivity	• Resin poisoning and swelling • Requires subsequent stripping and reduction steps
Solvent extraction [45]	Organic solvents	• Highly cost-effective • High selectivity	• Environmental concerns • Requires subsequent stripping and reduction steps
Adsorption on carbon [46]	Activated carbon	• Highly cost-effective • Activated carbon can be produced from biowaste	• Low selectivity • Requires subsequent stripping and reduction steps
Electrodeposition [47]	Electrodes	• Allows precise control over process parameters • Direct reduction to metallic Pd	• Low selectivity • Requires electricity
Chemical Precipitation [48]	Precipitating agents	• Highly efficient • Produces easily recoverable solid Pd compounds	• Low selectivity • Chemically intensive
Cementation [49,50]	Metal powders	• Highly cost-effective • Direct reduction to metallic Pd	• Low selectivity • Hydrogen evolution

No single method for Pd(II) recovery can be considered universally optimal, as each has its own specific applications within industrial settings, whether on a large or a small scale. In the case of cementation, the primary limitation is hydrogen evolution, which occurs when the cementator has a standard reduction potential that is lower than that of hydrogen. For instance, in industrial settings, Zn powder is commonly used as the cementing agent to recover Pd(II) through the process of cementation, such as in the case of spent electroplating solutions where this method is often employed [51]. An unwanted side reaction when using Zn in an acidic medium is hydrogen evolution, which occurs as described in Equation (4):



This reaction not only generates hydrogen, which may adhere to the zinc surface and reduce the available area for cementation, but also leads to the dissolution of zinc, rendering it unavailable for further use as a cementing agent. Furthermore, the generation

of hydrogen can be potentially hazardous when mixed with oxygen, creating flammable or explosive mixtures, which complicates safety considerations and makes industrial scale-ups more difficult [52]. One potential solution to this issue is to use cementing agents with higher standard potential values than hydrogen (such as Ag and Cu), thereby preventing the formation of gaseous hydrogen. However, this approach has a drawback: a smaller difference in standard potential values between Pd(II) and the cementing agent reduces the driving force of the cementation process. In the case of alloys, there are many factors to consider, such as galvanic corrosion, which can influence the cementation process. Galvanic corrosion occurs within an alloy when metals with different electrochemical potentials interact, leading to internal electron transfer. In this interaction, the metal with the lower electrochemical potential donates electrons more readily, facilitating the reduction of Pd(II) ions to metallic palladium. The magnitude of galvanic corrosion is, however, difficult to quantify, as it depends on factors such as the cathode and anode area ratio between the metals [53], which is nearly impossible to accurately describe in alloy powders. As such, we decided to experimentally test our AgCu alloy powders as potential cementators for Pd(II) recovery. Details of the procedure were described in Section 2.3, and the general setup for the experiment is depicted in Figure 6.

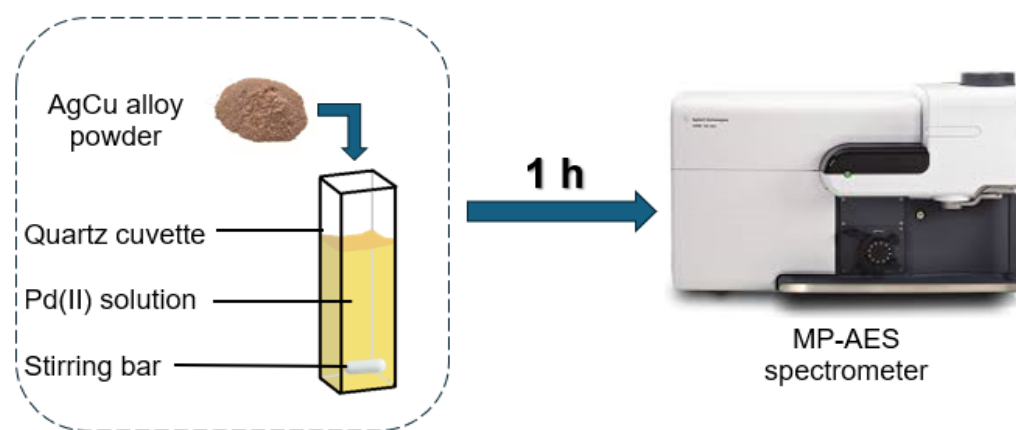


Figure 6. Experimental setup used for cementation experiments.

To investigate the differences in kinetics for various powder compositions during the cementation process, the experiments were conducted at 10 °C. This temperature is close to the average annual temperature of several countries, including the US, UK, and Poland, making the results relevant to practical applications in these regions. Conducting the experiments at this temperature also ensured that the Pd(II) concentration would not drop to zero within the selected timeframe, allowing the differences in performance between the compositions to remain visible. The cementation process was carried out for 1 h, focusing on analyzing the kinetic performance of the powders rather than determining the time required to reach equilibrium. Thermodynamically speaking, if an adequate amount of cementing agent is present, nearly all Pd(II) ions should be cemented, leaving only trace amounts [25]. However, as the system approaches equilibrium, the reaction rate diminishes significantly. We chose a 1 h timeframe to evaluate the kinetics of the process, which is more relevant in industrial applications where the speed of recovery and operational throughput are often of greater importance than achieving complete equilibrium. The experimental results, illustrating the efficiency of each alloy composition in Pd(II) cementation, are presented in Figure 7.

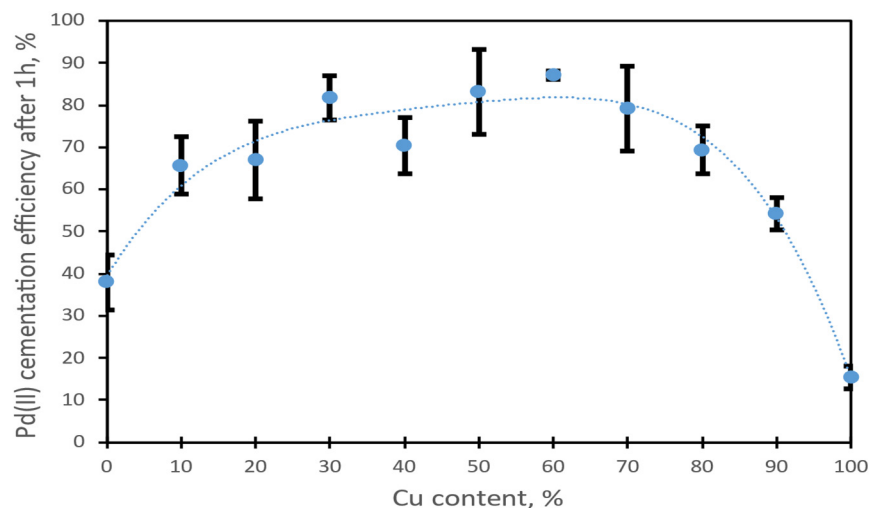


Figure 7. Pd(II) cementation results.

Cementation tests indicate that alloy powders exhibit higher efficiency in Pd(II) recovery compared to pure Ag and Cu. However, the results show relatively high standard deviations, making it challenging to precisely identify the optimal alloy composition. The general trend suggests that AgCu alloys with a composition close to a 50:50 Cu to Ag mass ratio tend to achieve the highest efficiency in Pd(II) cementation. Among the tested compositions, pure Cu powder proved to be the least effective cementator from a kinetic perspective, with an efficiency of only 15.4% after 1 h. While thermodynamically, the same mass of pure Cu should cementate more Pd(II) than pure Ag, the results indicate that pure Cu does so at a much slower rate.

To the best of our knowledge, there is no existing research on using metal alloys as cementators. Therefore, no broad conclusions can be drawn from our results on AgCu alloys regarding other alloys. If the observed trend—where metal alloys are more efficient cementators than pure metals—holds true for other alloys, it could indicate a promising approach for industrial applications. For instance, adding Pb to Zn as a cementator is known to increase the hydrogen overpotential, reducing its evolution during the process [54]. Thus, alloying these metals could form highly efficient cementators.

4. Conclusions

This study confirmed that co-precipitated Cu/Ag carbonates exhibit slight deviations from theoretical Cu/Ag ratios due to equilibrium dynamics during precipitation. Thermal analysis showed that the reduction of carbonates in an Arcal (H_2/Ar) atmosphere was completed at 300 °C, with alloy formation indicated by endothermic peaks around 780 °C, corresponding to the AgCu eutectic point. XRD and SEM results demonstrated the formation of a solid solution in AgCu alloys, with crystallite sizes decreasing as Cu content increased, suggesting smaller particles in alloys compared to pure metals. Electrical conductivity tests showed that compaction initially increased conductivity but decreased at higher pressures for pure metals, while the AgCu alloy maintained stable conductivity, suggesting different compaction behavior.

Cementation tests revealed that AgCu alloys were more efficient after 1 h in Pd(II) recovery than pure metals (most likely due to galvanic interactions), indicating that metal alloys may offer enhanced performance for cementation in industrial applications. Furthermore, in the case of AgCu alloy powders, since hydrogen is not produced during the cementation process, this technology can easily be scaled to meet industrial demands. Notably, experiments were conducted at 10 °C, which approximates the average yearly temperature in the US, UK, and Poland, demonstrating that similar results can be achieved without the need for additional heating, further simplifying the scalability and energy efficiency of this approach.

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