



# *Article* **Microstructure, Mechanical Properties, and Corrosion Resistance of Ag–Cu Alloys with La2O<sup>3</sup> Fabricated by Selective Laser Melting**

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**Abstract:** Ag and its alloys, when prepared by a selective laser melting (SLM) process, have a low density and poor overall performance due to their high reflectivity when the most commonly used laser ( $\lambda = 1060$  nm) is used, and they have exorbitant thermal conductivity. These characteristics lead to the insufficient melting of the powders and severely limit the applications of additive manufactured silver alloys. To improve the absorption of the laser, as well as for better mechanical properties and higher resistance to sulfidation, Ag–Cu alloys with different  $La<sub>2</sub>O<sub>3</sub>$  contents were prepared in this work using the SLM process, via the mechanical mixing of  $La<sub>2</sub>O<sub>3</sub>$  nanoparticles with Ag–Cu alloy powders. A series of analyses and tests were conducted to study the effects of  $\rm La_2O_3$  in Ag–Cu alloys on their density, microstructure, mechanical properties, and corrosion resistance. The results revealed that the addition of  $La_2O_3$  particles to Ag–Cu alloy powders improved the laser absorptivity and reduced defects during the SLM process, leading to a significant rise from 7.76 g/cm $^3$  to 9.16 g/cm $^3$ in the density of the Ag–Cu alloys. The phase composition of the Ag–Cu alloys prepared by SLM was Silver-3C. La<sub>2</sub>O<sub>3</sub> addition had no influence on the phase composition, but refined the grains of the Ag–Cu alloys by inhibiting the growth of columnar grains during the SLM process. No remarkable preferred orientation existed in all the samples prepared with or without  $\rm La_2O_3.$  An upwards trend was achieved in the hardness of the Ag–Cu alloy by increasing the contents of  $\rm La_2O_3$  from 0 to 1.2%, and the average hardness was enhanced significantly, from 0.97 GPa to 2.88 GPa when the alloy contained  $1.2\%$  La<sub>2</sub>O<sub>3</sub> due to the reduced pore defects and the refined grains resulting from the effects of the La<sub>2</sub>O<sub>3</sub>. EIS and PD tests of the samples in 1% Na<sub>2</sub>S solution proved that La<sub>2</sub>O<sub>3</sub> addition improved the corrosion resistance of the Ag–Cu alloys practically and efficaciously. The samples containing  $La_2O_3$  exhibited higher impedance values and lower corrosion current densities.

**Keywords:** Ag alloy;  $\text{La}_2\text{O}_3$ ; selective laser melting; electron back scatter diffraction

# **1. Introduction**

As a type of common noble metal, silver has been used in ornaments and coins for hundreds of years, and is still popular in jewelry and electrical contact materials [\[1,](#page-11-0)[2\]](#page-11-1). Pure silver exhibits low strength and hardness [\[3\]](#page-11-2), making it prone to scratches and wear scars on its surface. The inferior mechanical properties of silver can downgrade its luster and decorative function in jewelry, and also limits its application in electrical contacts [\[4](#page-11-3)[,5\]](#page-12-0). Alloying is a simple and effective method for improving the performance of pure metals  $[6,7]$  $[6,7]$ . Among the numerous available alloys  $[8-10]$  $[8-10]$ , Ag–Cu alloys  $[11,12]$  $[11,12]$ are a commonly used silver alloy for electrical contacts and decoration purposes, due to its improved mechanical performance, good electrical and thermal conductivity, and moderate



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cost. However, the introduction of the Cu element reduces the Ag's chemical stability, such that the Ag–Cu alloy is more likely to react with the element sulfur to generate black sulfides, in comparison to pure silver [\[13\]](#page-12-7). The existence of sulfides can also negatively affect the functionality of silver jewelry and the conductivity of electrical components [\[14\]](#page-12-8). Additionally, due to the alloy's two-phase structure at room temperature, micro-batteries generated at the phase interface in the corrosion medium would accelerate the corrosion behavior of the Ag–Cu alloy [\[15\]](#page-12-9). Thus, it is necessary to further optimize the composition of the Ag–Cu alloy by combining the two components' excellent mechanical properties and corrosion resistance, including sulfidation resistance [\[16,](#page-12-10)[17\]](#page-12-11).

Development trends in the customization of jewelry, as well as in the miniaturization and complexity of electrical components, have attracted increasing attention from researchers [\[18,](#page-12-12)[19\]](#page-12-13). While many metallic products produced by additive manufacturing have been extensively applied in many fields [\[20](#page-12-14)[–22\]](#page-12-15), there are only a few research studies on the preparation of silver or its alloys by laser powder bed fusion technology. Most reports have remained stuck on the preliminary exploration of process parameters [\[4,](#page-11-3)[18\]](#page-12-12). Besides the high cost of silver powder, the more important reason for this is that the high reflectivity to the lasers used ( $\lambda = 1060$  nm) and the exorbitant thermal conductivity [\[23,](#page-12-16)[24\]](#page-12-17) of silver leads to insufficient melting of the powders during laser scanning. As such, the silver products produced by additive manufacturing usually have a low density and poor overall performance. To reduce defects and improve the density of the finished product, two feasible solutions have been proposed by researchers. The first one focuses on the laser equipment and process parameters; a shorter-wavelength laser, higher laser power, and smaller laser-focused spots can be used to increase the absorption and energy density of the laser, which make the powder melt better [\[25](#page-12-18)[–27\]](#page-12-19). The other method concerns the powders; it has been proven by some studies that adding alloying elements or mixing particles or fibers with other powders could reduce the reflectivity of silver effectively [\[26](#page-12-20)[,28](#page-12-21)[,29\]](#page-12-22).

Inspired by previous works,  $\text{La}_2\text{O}_3$  nanoparticles were mixed in Ag–Cu alloy powders in this work.  $La_2O_3$  is a kind of rare earth oxide (REO) often-used in the preparation of steel [\[30\]](#page-12-23), glass [\[31\]](#page-12-24), and ceramics [\[32\]](#page-12-25). REO was used in this work mainly based on the following three considerations: Firstly, rare earth ions are able to absorb laser rays over a wide wavelength range because of their special 4 f electronic configuration [\[33,](#page-12-26)[34\]](#page-13-0), which is able to increase the laser absorptivity when added into Ag–Cu alloy powders. Secondly, rare earth elements have often been applied in metallurgical fields because of their significant effects on refining the grain, purifying the grain boundary, and microalloying [\[35–](#page-13-1)[37\]](#page-13-2), etc. This is a feasible method for improving the mechanical properties of Ag–Cu alloys. Finally, rare earth elements are helpful for decreasing the generation of sulfide in silver alloys according to some research studies [\[14](#page-12-8)[,38\]](#page-13-3). For the above reasons, Ag–Cu alloys with different contents of  $La_2O_3$  were prepared by a selective laser melting (SLM) process in this work. Then, to verify the effects of the content of  $La_2O_3$  in selective-laser-melted silver alloys on their phase compositions, microstructures, mechanical properties, and corrosion resistance in  $Na<sub>2</sub>S$  solution, a series of studies were conducted in detail.

### **2. Materials and Methods**

# *2.1. Preparation of Ag–Cu Alloys with Different La2O<sup>3</sup> Contents by SLM*

The digital model of the Ag–Cu alloy was designed in a conical shape using Magics software (v20.03); the detailed dimensions of the sample are shown in Figure [1.](#page-2-0) The Ag– Cu alloy powders used in this work were supplied by Legor Group, and the chemical compositions of the powders analyzed by an X-ray fluorescence spectrometer are listed in Table [1.](#page-2-1) The different contents (mass fraction of 0, 0.4%, 0.8% and 1.2%) of  $La_2O_3$ particles, with a purity of more than  $99\%$  and a diameter of less than 1  $\mu$ m, were uniformly mechanically admixed in Ag–Cu alloy powders by a drum mixer (shown in Figure [2\)](#page-2-2). A Sisma Mysint 100 SLM system with a Nd: YAG fiber laser (that the wavelength was 1060 nm) was employed for the preparation of the designed samples. The parameters applied in the present work were dependent on the author's previous work, as shown in Table [2.](#page-2-3)



**Figure 1.** The specific sizes of the Ag–Cu alloy sample model: (**a**) isometric view and (**b**) front view.

<span id="page-2-0"></span>with a purity of more than 99% and a diameter of less than 1  $\mu$  mechanisms were uniformly mechanisms were uniformly

<span id="page-2-1"></span>**Table 1.** Chemical compositions of the Ag–Cu powders used in this work.

Element						
Mass fraction $(\% )$	5.626	ገ.893	0.431	1.242	138	Bal.

<span id="page-2-2"></span>

Figure 2. The SEM images of the Ag-Cu alloy powders mixed with a content of (a) 0, (b) 0.4%, 0.8%, and (**d**) 1.2% La2O<sup>3</sup> particles. (**c**) 0.8%, and (**d**) 1.2% La2O<sup>3</sup> particles.

<span id="page-2-3"></span>**Table 2.** SLM process parameters used for preparing the Ag–Cu alloy samples.



# *2.2. Characterizations*

After the samples were prepared by the SLM process, the samples were cut into flat pieces with the thickness of 2 mm along the dashed line, as shown in Figure [1,](#page-2-0) for further investigation into the differences between the XY and Z planes, separately. An X-ray diffraction (XRD, Bruker D8 Advance, Bruker Corporation, Billerica, MA, USA) system was employed to identify the phase compositions of the Ag–Cu alloy samples prepared by SLM using a Cu Kα radiation source in θ/2θ scanning mode; scanning ranged from 20 $^{\circ}$  to 90 $^{\circ}$  at a rate of 5 $^{\circ}$ /min. The densities of the samples with different La<sub>2</sub>O<sub>3</sub> contents were measured by a DX-300 density tester, and the average density of three samples of the same content was calculated to ensure accuracy. The mixed powders and defects after the preparation of the samples with different  $La_2O_3$  contents were observed by a Hitachi S3400 N scanning electron microscope (SEM). The distribution mapping of Ag and La in the Ag–Cu alloy prepared by SLM was corroborated with an electron probe micro analyzer (EPMA, JXA-iHP200F). Moreover, the details of the samples concerning their microstructure and preferred orientation were analyzed by a Thermo Scientific Apreo 2 SEM equipped with electron back scatter diffraction (EBSD). Before being analyzed by EBSD, the samples were ion beam-polished to meet the requirements.

# *2.3. Mechanical Properties*

An Agilent Nano Indenter with a diamond Berkovich tip was used to measure the hardness of the samples with varying  $La<sub>2</sub>O<sub>3</sub>$  contents. The tests were carried out under the conditions of a maximum load of 30 g, a loading/unloading rate of 30 mN/s, a peak holding time of 10 s, and a Poisson's ratio of 0.36, respectively. To ensure the accuracy of the resultant data, at least 5 individual indentation tests were conducted for every sample.

# *2.4. Corrosion Behavior in Na2S Solution*

The existence of sulfides in silver and its alloys negatively affects its conductivity and decorative performance. The corrosion resistance performance of selective laser-melted samples with different  $La_2O_3$  contents in 1% (mass fraction) Na<sub>2</sub>S solution was evaluated using a PARSTAT 4000 electrochemical workstation with a standard three-electrode system. During the test, a platinum plate (the size of  $10 \times 10 \times 0.2$  mm) and samples with an exposure area of 1 cm<sup>2</sup> served as the counter electrode and the working electrode, respectively. A saturated calomel electrode was chosen as the reference electrode. An electrochemical impedance spectroscopy (EIS) test and potentiodynamic (PD) polarization were conducted on the samples to assess the impact of adding  $La_2O_3$  on the corrosion resistance. The measurements of EIS and PD for all the samples were conducted after achieving a stable open circuit potential (OCP). The EIS tests were carried out by applying an amplitude of 10 mV at the OCP and scanning frequencies from 100,000 to 0.01 Hz. The PD polarization analysis was executed from −0.3V to +0.3V vs. OCP using a scan rate of 1 mv/s.

### **3. Results and Discussion**

# *3.1. The Effect of La2O<sup>3</sup> Contents on the Densities and Phase Compositions of Ag–Cu Samples Prepared by SLM*

Conical Ag–Cu alloy samples with different  $La_2O_3$  contents were successfully prepared using the SLM process. As shown in Figure [3a](#page-4-0), the sizes of the prepared samples were consistent with the designed model. The samples presented a gray metallic luster and seemed to be relatively rough. From Figure [3b](#page-4-0)–e, various amounts of pore defects in the Ag–Cu alloy, caused by insufficient melting of the powders, could be seen in the XY plane. Furthermore, it is noteworthy that as the  $La<sub>2</sub>O<sub>3</sub>$  content increased from 0 to 1.2%, there was a decline in the number of defects observed in the images. The results of the density measurements for the samples with different  $La_2O_3$  contents, as listed in Table [3,](#page-4-1) also support this viewpoint; this indicates that the addition and mixture of  $La_2O_3$  nano-particles to Ag–Cu alloy powders plays a positive role in improving laser absorption during the



<span id="page-4-0"></span>SLM process, leading to a significant increase in the density of the Ag–Cu alloys, rising from 7.76 g/cm<sup>3</sup> to 9.16 g/cm<sup>3</sup>.

**Figure 3.** (**a**) Photos of the Ag–Cu alloys prepared by the SLM process, and the SEM images of the **Figure 3.** (**a**) Photos of the Ag–Cu alloys prepared by the SLM process, and the SEM images of the samples with  $\text{La}_2\text{O}_3$  contents of (**b**) 0, (**c**) 0.4%, (**d**) 0.8%, and (**e**) 1.2%.

<span id="page-4-1"></span>**Table 3.** The densities of the Ag–Cu samples with different La2O<sup>3</sup> contents. **Table 3.** The densities of the Ag–Cu samples with different  $La_2O_3$  contents.



were executed on both the XY and Z planes of the Ag–Cu alloys prepared using SLM with different  $La_2O_3$  contents. The results are shown in Figure 4. Firstly, the phase composition of all the samples as-prepared was Silver-3C, and no diffraction peak of any other phase was observed. Secondly, the relative intensities of the diffraction peaks changed after the addition of La<sub>2</sub>O<sub>3</sub>. The intensities of the (222) crystal plane of the samples with La<sub>2</sub>O<sub>3</sub> showed a significant increase in both the XY and Z planes, compared to the patterns of the samples without  $La<sub>2</sub>O<sub>3</sub>$  addition and the data from the powder diffraction files (PDF) provided by the International Centre for Diffraction Data (ICDD), shown at the bottom in To identify the phase compositions and to analyze the grain orientation, XRD tests Figure [4.](#page-5-0) The (222) planes are parallel to the (111) planes, but the interplanar distance is different. The notable rise in the relative intensities of the (222) plane could be attributed to the distortion caused by La atoms diffused into the Ag lattices. Although the relative diffraction intensities of the (111) and (222) planes were higher than those of the PDF data, further research was necessary to confirm whether a preferred orientation existed in the selective laser-melted Ag–Cu alloys.

<span id="page-5-0"></span>

**Figure 4.** XRD patterns of SLMed Ag–Cu alloys with different La<sub>2</sub>O<sub>3</sub> contents in the (**a**) XY and Z plane. (**b**) Z plane.

# *3.2. The Effect of La2O<sup>3</sup> Content on the Microstructure of Ag–Cu Samples Prepared by SLM*

*3.2. The Effect of La2O3 Content on the Microstructure of Ag–Cu Samples Prepared by SLM* contents fabricated by SLM, EBSD technology was employed to analyze their grain size, morphologies, and orientation. As shown in Figure 5, the grain size and morphology [w](#page-6-0)ere apparently influenced by the addition of La<sub>2</sub>O<sub>3</sub>. In the sample without La<sub>2</sub>O<sub>3</sub>, a number of large columnar grains were visible. The columnar grains were oriented parallel to the sample of language of la building direction, and there were also nainerous line equiaxed grains observed. These line<br>equiaxed grains were able to form at the border of the melting pool, where the cooling rate was higher than that in the middle area of the melting pool. With a slower cooling rate, the grains could grow larger in the direction of the temperature gradient. When  $0.\overline{4}\%$  La<sub>2</sub>O<sub>3</sub> was added, both the number and the length of the columnar grains decreased notably, while the ratio of equiaxed grains was enhanced. As the  $La_2O_3$  content reached 0.8% and 1.2%, the microstructures were dominated by equiaxed grains. The transition of grain  $\sim$ morphology indicated that the addition of  $La_2O_3$  could inhibit the growth of columnar<br>grains during the SI M process To investigate the microstructure characteristics of Ag–Cu alloys with varying  $\rm La_2O_3$ building direction, and there were also numerous fine equiaxed grains observed. These fine grains during the SLM process.

The average grain sizes of the Ag–Cu alloys with different  $La_2O_3$  contents, as calculated based [on](#page-6-0) the observations in Figure 5, are presented in Figure 6. The average grains size of the Ag–Cu alloys without  $La_2O_3$  was 2.41  $\mu$ m, which was larger than that of the samples containing  $La_2O_3$ . As the contents of  $La_2O_3$  increased from 0.4% to 0.8% and 1.2%, the corresponding grain size values decreased to 1.90  $\mu$ m, 1.91  $\mu$ m, and 1.36  $\mu$ m, now assume the average grains size of the averals with 0.4% and 0.8% Le  $\Omega$  average with size of the Alexander Schultz with  $0.8\%$  La<sub>2</sub>O<sub>3</sub> had a higher distribution of smaller grains compared close, but the sample with  $0.8\%$  La<sub>2</sub>O<sub>3</sub> had a higher distribution of smaller grains compared to the sample with 0.4% La<sub>2</sub>O<sub>3</sub>. Based on the aforementioned results, the addition of La<sub>2</sub>O<sub>3</sub> could refine the grains of Ag–Cu alloys prepared by SLM. respectively. The average grain sizes of the sample with  $0.4\%$  and  $0.8\%$  La<sub>2</sub>O<sub>3</sub> were quite

As mentioned previously, to confirm the presence of a preferred orientation in the selective laser melted Ag–Cu alloys and to investigate the effect of  $La<sub>2</sub>O<sub>3</sub>$  on grain orientation, pole figures of Ag–Cu alloys with different  $La_2O_3$  contents were obtained using<br>EBSD technology. These nole figures are presented in Figure 7. The information presented in Figure [7](#page-7-0) shows that no significant preferred orientation existed in either the samples EBSD technology. These pole figures are presented in Figure [7.](#page-7-0) The information presented prepared with or those without  $La<sub>2</sub>O<sub>3</sub>$ . This again shows that the notable rise in the relative intensities of the (222) plane in Figure [4](#page-5-0) was caused by La atoms entering into the Ag lattices, rather than the preferred orientations being generated after  $La<sub>2</sub>O<sub>3</sub>$  was added. These results might also be caused by the fact that the chosen area for magnification was too small to accurately represent the entire sample. However, due to the exceptionally small grain sizes of the sample caused by the high cooling rate of the process and the excellent

<span id="page-6-0"></span>

thermal conductivity of Ag–Cu alloys, a higher magnification had to be chosen in order to reveal the details of their morphology.

<span id="page-6-1"></span>**Figure 5.** EBSD maps of SLMed Ag–Cu alloys with a La<sub>2</sub>O<sub>3</sub> content of (**a**) 0, (**b**) 0.4%, (**c**) 0.8%, and (**d**) 1.2%, scale: 10 µm. (**d**) 1.2%, scale: 10 µm. (**d**) 1.2%, scale: 10 µm.







<span id="page-7-0"></span>

**Figure 7.** Pole figures of the Ag–Cu alloys prepared by SLM with a La<sub>2</sub>O<sub>3</sub> content of (a) 0, (b) 0.4%, (**c**) 0.8%, and (**d**) 1.2%.

The elemental mappings of Ag and La in the as-prepared Ag–Cu alloys were assayed using EPMA technology in this study. The sample containing  $1.2\%$  La<sub>2</sub>O<sub>3</sub>, which had the highest  $La_2O_3$  content among all the samples, was chosen to determine whether the element of La concentrated at grain boundaries or within grains. As shown in Figure [8a](#page-8-0), a number of fine and dense equiaxed grains and cellular grains were observed in the selected area, which was similar to the morphology shown in Figure [5d](#page-6-0). The distribution of Ag was very uniform in Figure [8b](#page-8-0), but La was barely present in some areas marked in Figure [8c](#page-8-0). The specific areas appeared to be narrow sheets, resembling grain boundaries more. At this point, we have a comprehensive understanding of how the  $La_2O_3$  content affects the microstructure of Ag–Cu samples produced through SLM.

### *3.3. The Effect of La2O<sup>3</sup> Content on the Mechanical Properties of Ag–Cu Samples Prepared by SLM*

To evaluate the mechanical properties of the Ag–Cu alloys with different  $La<sub>2</sub>O<sub>3</sub>$ contents, the nano-indentation technique was used to measure the hardness of all the samples. The results are presented in Figure [9.](#page-8-1) As shown in Figure [9a](#page-8-1), when a maximum load of 300 mN was applied on the samples using the tip, the indentation depths of the samples with  $La_2O_3$  were found to be lower than that of the sample without  $La_2O_3$ . With an increase in La<sub>2</sub>O<sub>3</sub> content from 0 to 1.2%, the indentation depths declined gradually at the max load. The residual indentation depth followed the same law during unloading, indicating that the deformation of the samples decreased as the  $La_2O_3$  content decreased from 1.2% to 0.8%, 0.4%, and 0. The average hardness of the Ag–Cu alloys with different  $La<sub>2</sub>O<sub>3</sub>$  contents, as depicted in Figure [9b](#page-8-1), provided more direct results. The upward trend of the hardness was prominent with increasing  $La<sub>2</sub>O<sub>3</sub>$  contents. The average hardness of Ag–Cu samples prepared by SLM without  $La_2O_3$  was 0.97 GPa; it raised to 2.10 GPa, 2.27 GPa, and 2.88 GPa when 0.4%, 0.8%, and 1.2%  $La_2O_3$  was mixed into the powders,



<span id="page-8-0"></span>respectively. The enhancement in the hardness of the Ag–Cu alloys was mostly due to reduced pore defects and the more refined grains created by the effects of  $La<sub>2</sub>O<sub>3</sub>$ .

<span id="page-8-1"></span>**Figure 8.** (a) The morphology, and elemental distribution of (**b**) Ag and (**c**) La in the sample with  $1.2\%$  La<sub>2</sub>O<sub>3</sub>.



 $\mathbf{F}^*$  and  $\mathbf{F}^*$  and  $\mathbf{F}^*$  and  $\mathbf{F}^*$  was mixed into the power mixed into the **Figure 9.** (a) The load and unload curves and (b) average hardness of Ag–Cu alloys with different  $La<sub>2</sub>O<sub>3</sub>$  contents prepared by SLM.

# 3.4. The Effect of La<sub>2</sub>O<sub>3</sub> Content on the Corrosion Resistance of Ag–Cu Samples Prepared by SLM<br>in 1% Na<sub>2</sub>S Solution *in 1% Na2S Solution*

Through the above explanation, the addition of La<sub>2</sub>O<sub>3</sub> improved the density and hardness of the Ag–Cu samples, which conformed to the first two assumptions of this work. The following content would focus on the corrosion resistance of the Ag–Cu alloy samples containing  $\rm La_2O_3$  in sulfide solution. The EIS spectra of the Ag–Cu alloys with different

 $La<sub>2</sub>O<sub>3</sub>$  contents in 1% Na<sub>2</sub>S solution are presented in Figure [10,](#page-9-0) The values obtained from the plots, fitted using ZSimp software (v3.30), are provided in Table [4.](#page-10-0) According to Figure [10a](#page-9-0), the fittings of the equivalent circuit diagram given in Figure [10d](#page-9-0) to the EIS plots of all the samples were appropriate. The Bode phase angle plots (in Figure [10b](#page-9-0)) of all the samples presented three valleys, indicating the existence of three time constants in the frequency range. These time constants corresponded to three resistances and two constant phase elements (CPE) connected in parallel. In the equivalent circuit,  $R_1$  represented the solution resistance, while  $R_2$  and  $R_3$  expressed the resistance of the passive film (or the corrosion product layer) and the resistance of the Ag–Cu alloy substrate, respectively. The values listed in Table [4](#page-10-0) showed that the resistances of the Ag–Cu alloys containing  $La<sub>2</sub>O<sub>3</sub>$ were enhanced compared to the samples without  $La<sub>2</sub>O<sub>3</sub>$ . Furthermore, as the amount of  $La<sub>2</sub>O<sub>3</sub>$  increased, the resistance value of the sample continued to grow. This observation was consistent with the trends shown in Figure [10c](#page-9-0). The impedance values of the Ag–Cu alloys with La<sub>2</sub>O<sub>3</sub> contained improved significantly from ~102  $\Omega$ /cm<sup>2</sup> (the sample without La<sub>2</sub>O<sub>3</sub>) to ~383  $\Omega$ /cm<sup>2</sup> (0.4% La<sub>2</sub>O<sub>3</sub> content), ~1090  $\Omega$ /cm<sup>2</sup> (0.8% La<sub>2</sub>O<sub>3</sub> content), and ~4145  $\Omega$ /cm<sup>2</sup> (1.2% La<sub>2</sub>O<sub>3</sub> content). Higher total impedance values (R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>) indicate greater corrosion resistance.

<span id="page-9-0"></span>

**Figure 10.** Ag–Cu alloys with different La2O<sup>3</sup> contents in 1% Na2S solution—(**a**) EIS Nyquist dia-(b) EIS Bode phase angle plot, (c) EIS Bode impedance plot, and (d) equivalent circuit diagram used<br>to fit the EIS grastic to fit the EIS spectra. **Figure 10.** Ag–Cu alloys with different  $La_2O_3$  contents in  $1\%$  Na<sub>2</sub>S solution—(**a**) EIS Nyquist diagram,

$La_2O_3$ Content (wt%)	$R_1$ $(\Omega/cm^2)$	CPE $(10^{-4} \text{ F} \cdot \text{cm}^2)$	$n_1$	R <sub>2</sub> $(\Omega/cm^2)$	<b>CPE</b> $(10^{-3} \text{ F} \cdot \text{cm}^2)$	n <sub>2</sub>	$R_3$ $(\Omega/cm^2)$
	$7.77 + 0.73$	$1.82 + 0.25$	$0.82 + 0.05$	$7.74 + 1.02$	$2.32 + 0.03$	$0.38 + 0.01$	$86.91 + 6.65$
$0.4\%$	$9.90 + 2.87$	$0.22 + 0.03$	$0.68 + 0.03$	$23.44 + 3.36$	$1.46 + 0.05$	$0.81 + 0.05$	$0.35 + 0.08 \times 10^3$
0.8%	$9.57 + 1.43$	$5.39 + 0.83$	$0.71 + 0.02$	$39.50 \pm 5.56$	$3.36 + 0.18$	$0.73 + 0.02$	$1.04 \pm 0.21 \times 10^3$
1.2%	$7.25 + 1.69$	$6.54 + 0.99$	$0.75 + 0.06$	$47.54 + 9.31$	$1.64 + 0.41$	$0.77 + 0.01$	$4.09 + 0.30 \times 10^3$

<span id="page-10-0"></span>**Table 4.** EIS resistance values of Ag–Cu alloys with different  $La_2O_3$  contents in 1% Na<sub>2</sub>S solution.

The PD curves of the Ag–Cu alloys with different  $La_2O_3$  contents in 1% Na<sub>2</sub>S solution are presented in Figure [11,](#page-10-1) The values of the corrosion current densities  $(I_{\rm corr})$  and corrosion potentials (*E<sub>corr</sub>*) extracted from the curves are listed in Table [5.](#page-10-2) The corrosion potentials of all the samples were similar numerically. Higher corrosion potentials represent a lower corrosion tendency. Thus, in terms of corrosion tendency only, all the samples were very close. While comparing the curve of the sample without  $La_2O_3$ , it was observed that the curves of all the samples with  $La_2O_3$  shifted to the left by varying degrees; this shift resulted in a decrease in their corrosion current densities. It was suggested that the corrosion rate of the Ag–Cu alloys slowed down after  $La_2O_3$  was added. A reasonable explanation for this is provided by previous work [\[4\]](#page-11-3), indicating that there is a higher occurrence of preferential corrosion within the interior grain than along the grain boundary in Ag–Cu alloys. As the  $La<sub>2</sub>O<sub>3</sub>$  content grew, the grain sizes decreased, as shown in Figure [6;](#page-6-1) this shows that the quantity of grain boundaries increased. Thus, the corrosion rate of the Ag–Cu alloys slowed down after the addition of  $La<sub>2</sub>O<sub>3</sub>$ . The values in Table [5](#page-10-2) also support the view that as the  $La<sub>2</sub>O<sub>3</sub>$  content increased from 0 to 1.2%, the corrosion current densities decreased gradually; 1.2% La<sub>2</sub>O<sub>3</sub>-containing Ag–Cu alloys achieved the minimum corrosion current density of 9.62 µA·cm<sup>-2</sup>, which significantly declined from 126.35 µA·cm<sup>-2</sup> in the sample without La<sub>2</sub>O<sub>3</sub>. Through EIS and PD tests of the samples in  $1\%$  Na<sub>2</sub>S solution, the practical and efficacious effects of La<sub>2</sub>O<sub>3</sub> addition on the corrosion resistance of Ag–Cu alloys prepared by SLM, in particular their resistance to sulfidation, was demonstrated.

<span id="page-10-1"></span>

**Figure 11.** Potentiodynamic polarization curves of Ag–Cu alloys with different La<sub>2</sub>O<sub>3</sub> contents in 1% Na2S solution. Na2S solution.

<span id="page-10-2"></span>**Table 5.** Corrosion current density and corrosion potential of Ag–Cu alloys with different La<sub>2</sub>O<sub>3</sub> contents in 1% Na2S solution. contents in 1% Na2S solution.

La <sub>2</sub> O <sub>3</sub> Content $(wt\%)$		$0.4^{\circ}$	0.8	1.2
$E_{corr}$ (V)	$-0.87 + 0.015$	$-0.88 + 0.040$	$-0.89 \pm 0.045$	$-0.87 + 0.055$
$i_{corr}$ (µA·cm <sup>-2</sup> )	$126.35 + 17.33$	$40.80 + 2.16$	$11.23 + 2.68$	$9.62 + 0.89$

# **4. Conclusions**

In this work, to improve the laser absorptivity and to acquire better mechanical properties and higher resistance to sulfidation, Ag–Cu alloys with different  $La_2O_3$  contents were prepared using the SLM process, via mechanical mixing of  $La<sub>2</sub>O<sub>3</sub>$  particles with Ag– Cu alloys powders. Then, the phase compositions and microstructures of the Ag–Cu alloys with different  $La<sub>2</sub>O<sub>3</sub>$  contents were analyzed. Additionally, their mechanical properties and corrosion resistance in 1% Na2S solution were evaluated. The main conclusions of this work can be summarized as follows:

- 1. The addition and mixture of  $La<sub>2</sub>O<sub>3</sub>$  nano-particles to Ag–Cu alloy powders plays a positive role in improving laser absorptivity and reducing defects during the SLM process, leading to a significant increase in the density of Ag–Cu alloys, rising from 7.76 g/cm<sup>3</sup> to 9.16 g/cm<sup>3</sup>.
- 2. The phase composition of Ag–Cu alloys, as prepared by SLM, was found to be Silver-3C. The presence of  $La_2O_3$  had no influence on this composition, but refined the grains of the Ag–Cu alloys by inhibiting the growth of columnar grains during the SLM process. No particular preferred orientation was observed in either the samples prepared with or without  $La<sub>2</sub>O<sub>3</sub>$ .
- 3. There was an upwards trend in the hardness of the Ag–Cu alloys as the  $La<sub>2</sub>O<sub>3</sub>$  content was increased from 0 to 1.2% (mass fraction). The average hardness significantly increased from 0.97 GPa to 2.88 GPa when  $1.2\%$  La<sub>2</sub>O<sub>3</sub> was added, which was also higher than the ~1.11 GPa hardness of the sample with a similar chemical composition prepared by the powder metallurgy method, reported by a previous study [\[39\]](#page-13-4). This enhancement in hardness was mostly due to a reduction in pore defects and the refined grains caused by the effects of adding  $La<sub>2</sub>O<sub>3</sub>$ .
- 4. EIS and PD tests of the samples in 1% Na<sub>2</sub>S solution proved that the addition of La<sub>2</sub>O<sub>3</sub> improved the corrosion resistance of Ag–Cu alloys prepared by SLM practically and efficaciously. This improvement was evident in the form of higher impedance values and lower corrosion current densities.

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