COPPER ULTRAFINE POWDERS BY SONOELECTROCHEMICAL METHOD FOR ADDITIVE MANUFACTURING

V.N. Shut[1], S.Ye. Mozzharov[1], I. Yadroitsava[2*] & I. Yadroitsev[2]

[1]Institute of Technical Acoustics of the National Academy of Sciences of Belarus,
Vitebsk 210023, Belarus
lkm_ita@vitebsk.by

[2]Department of Mechanical and Mechatronic Engineering,
Central University of Technology, Free State (CUT), Bloemfontein 9300, South Africa
iyadroitsava@cut.ac.za

ABSTRACT

In this work, a short review on methods for the synthesis of ultrafine powders of micron- and submicron size is presented. A sonoelectrochemical method was used for the synthesis of Cu powder. It is shown that this technique quite simple, economical and environmentally friendly. Influence of parameters of the process on the particle size distribution and morphology of copper powder is studied. The resulting powder can be used for in-situ alloying in laser powder bed fusion and as an antibacterial filler in selective laser sintering process.

1. INTRODUCTION

The new industrial paradigm "Additive Manufacturing" (AM) combines a class of technologies that allow to create three-dimensional objects by sequentially adding material, usually layer by layer, as opposed to subtractive and formative manufacturing methodologies (casting, stamping) [1]. Additive manufacturing grows rapidly and requires new applications and advanced materials. Laser powder bed fusion (L-PBF) is an AM method that uses metal powders to produce parts. The high degree of freedom offered by L-PBF allows to create objects with unique geometry and complex internal structures, to apply topological optimization and consolidation of parts, combining many components into one functional part. By L-PBF, it is possible to create gradient structures both in terms of volumetric structures and from different materials. One of the promising directions in laser powder bed fusion is *in-situ* alloying, as a result of which additional opportunities to synthesize new materials from elemental powders. L-PBF *in-situ* alloying is used for reinforcing Al alloys, creation metal matrix composites (MMC) with unique mechanical properties [2,3] and for other functionalization of components.

Advanced implants with biocompatibility and antibacterial properties can be produced by L-PBF in-situ alloying [4,5]. Infection at a bone–implant interface is the most probable reason for implant failure directly after implantation [6]. Subsequently, utilization of materials with embedded antibacterial properties is advantageous as the antibacterial agent could act locally and permanently at the site of infection. For example, coating of the implant interface with materials that have antibacterial properties is a promising approach to prevent occurrence of the infection. Several metals like silver, zinc and copper have shown such antibacterial properties [7]. Therefore, alloying the base material with an antibacterial agent would increase the functionality and antibacterial performances of the implant.

The benefits of in situ alloying by L-PBF to produce new materials with unique properties were shown recently. Vrancken et al. [8] sintered Ti6Al4V-10% Mo alloy to stabilize the *β*-phase in the L-PBF alloy; a combination of excellent ductility and high strength in this alloy was reported. Sistiaga et al. [9] mechanically mixed 4% Si powder (-10 μm) and Al7075 alloy powder with an average particle size of 53 μm and produced dense crack-free parts. Vora et al. [10] demonstrated successful AlSi12 in situ alloy formation from elemental Al (-66 μm) and Si (-100 μm) powders. It was noted that *in situ* L-PBF alloying method could be potentially cost and time effective in developing new materials.

In our previous work, when the size of the refractory alloying 1.38% (wt%) Cu powder was comparable to the size of the base material powder (Ti6Al4V ELI powder had d_{50}~23 μm and pure copper had particles with d_{50}~22 μm), inhomogeneous areas were observed in *in-situ* alloyed material, although both Cu and Ti6Al4V particles were molten completely (Figure 1) [4]. It was shown that copper formed islands following solidification lines at the top surface. In the LPBF Ti6Al4V-1.38% Cu material, areas of increased copper concentration were associated with fusion boundaries in cross-sections. The enrichment of Cu varied depending on the region, between 1–5 wt % in areas with *a'*-martensitic microstructure and reached up to 20-35 wt % in areas with dendritic/cellular microstructure. Cu-rich areas influenced on tensile properties and fracture mechanism. It was found that nucleation of cracks at the surface occurred at regions with higher concentration of Cu. Thus, it is quite obvious that the size of the alloying powder should be significantly smaller than the size of the powder usually used in the L-PBF process.

To successful *in-situ* alloying, the molten pool should exist long enough to guarantee as good as possible mixing of the components. At the same time, the conditions should satisfy the operation window, that is required to manufacture high-quality 3D objects [11]. Submicron particles and ultrafine powders (~1 μm) are desirable to provide homogenous content of modified alloys. Nanoparticles have very poor flowability and requires special procedures for mixing and delivery, as well as handling [12].

Figure 1: Etched by Kroll's reagent cross-section of *in-situ* alloyed L-PBF Ti6Al4V ELI-1.38wt.%Cu sample. Dark colour shows Cu-rich areas (confirmed by SEM-EDS analysis). Data from [4].

Present work shows one of the possible methods for the production of ultrafine powders. Sonoelectrochemical method was used to produce ultrafine Cu powder, since copper is one of the natural elements of the human body and is not toxic in small quantities. In the powder preparation process, a current pulse is first passed through the cathode, which is accompanied by powder electrodeposition. Next, an ultrasound pulse is generated, during which the powder is removed from the cathode. The method is widely used to produce ultrafine powders of pure metals and alloys [13]. The characteristics of such powders are influenced not only by inherent parameters of the preparation of powders by electrolysis (current density, acidity, the nature and temperature of the electrolyte, the concentration of metal ions being discharged on the cathode, and others) [14,15] but also by parameters peculiar to the sonoelectrochemical process (current and ultrasound pulse durations and ultrasound pulse intensity). Therefore, the method is very flexible from the point view of controlling the properties of materials.

An ultrasound has a strong effect on electrochemical processes. In particular, it allows the current density to be raised considerably (for example, by 10 to 20 times in producing metallic coatings) [16–18]. It is, therefore, of great interest to examine the feasibility and understand general aspects of the preparation of fine powders at a higher current density (1 A/cm^2), which is expected to enhance the effectiveness of the process. The purpose of this study is to investigate the influence of parameters of the sonoelectrochemical process on the particle size distribution and morphology of copper powder.

2. MATERIALS AND METHODS

For the production of copper powders, two electrodes were used, one of which serves as both a cathode and an ultrasonicator. The anode was made of a 4 mm thick copper plate. The ultrasonic part of the system was built around a generator with an operating frequency of 22 kHz and electric power of 1 kW. A titanium concentrator with a working end face area of 1.3 cm^2 was used as an electrosonotrode. The system operates as follows: (1) a short current pulse is passed through the cathode, and this is accompanied by powder electrodeposition; (2) after the current pulse, ultrasound is turned on to remove the powder from the cathode; (3) everything is turned off and the system stabilizes.

Many electrolytes of various compositions have been proposed for copper electrodeposition. Electrolytes are usually divided into two groups - simple and complex. Among simple electrolytes, the most widespread are sulfuric acid electrolytes, the main components of which are $CuSO_4 \cdot 5H_2O$ and H_2SO_4, and this type of electrolyte (100 ml) was used in current experiments. Medical polyvinylpyrrolidone (FS 42-1194-98) with a molecular weight in the

range of 8000–35000 was chosen as an organic stabilizer. The powders were precipitated and washed using a centrifuge with a separation factor of 350.

Received powders were examined by high-resolution analytical scanning electron microscope (SEM) Tescan MIRA, which can be used for material characterization at the submicron scale. The particle size distribution (PSD) was done on ANALYSETTE 22 MicroTec Plus (Fritsch GmbH), which uses the principle of laser diffraction. X-ray structure analysis was performed on an X-ray diffractometer with FeKα radiation.

3. RESULTS AND DISCUSSION

Figure 2 shows the particle size distributions of copper powders prepared at various current densities (analysis on Fritsch equipment). The current pulse duration was 600 milliseconds. At cathode current densities of 1.15 A/cm^2, 750 mA/cm^2, and 450 mA/cm^2, the arithmetic mean particle size is about 2.6 μm, 820 nm, and 500 nm, respectively. A particle size of the powder increases with current density (Figure 2).

Figure 3 shows SEM images of copper powders prepared at two different current densities. It is clearly seen that the particle size is much smaller than indicated by the data of the laser diffractometer, which indicates the presence of a significant amount of agglomerates. However, electron microscopy data also confirm that particle size of the powder decreases with decreasing current density. It should be noted that the opposite trend was observed at low current densities in the range of 50–200 mA/cm^2 [19,20]. It is known that changes in current density can influence the particle size in two opposite ways [21]. Increasing the current density usually leads to the formation of finer particle deposits on the cathode. At higher current densities, more ions are discharged per unit area of the cathode. At fixed cation concentration in the electrolyte the growth rate of each of them decreases, and finer particle deposits result from this process [22,23]. At the same time, at a lower current density a decrease in particle size is possible due to the decrease in the total amount of material deposited on the cathode [24]. In present study, the latter factor seems to play a decisive role.
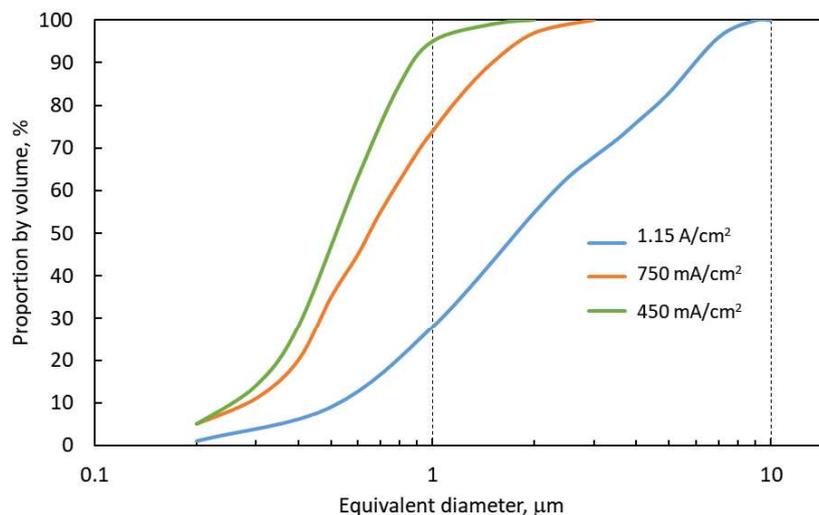

Figure 2: Particle size distributions of the copper powders prepared at various current densities. The current pulse duration is 600 ms.
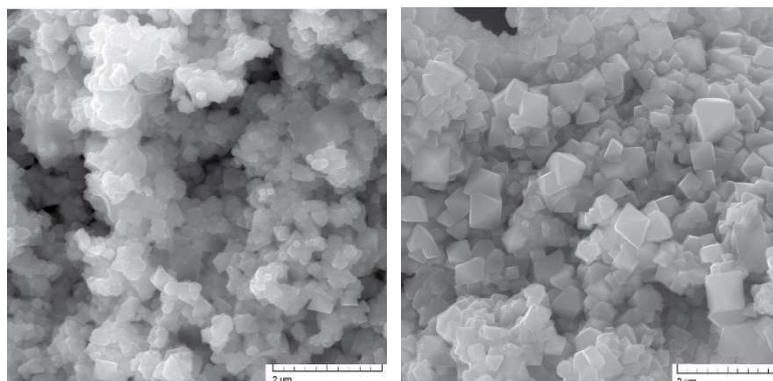
Figure 3: Morphology of the copper powders prepared at current densities of 450 mA/cm^2 (left) and 1.15 A/cm^2 (right).

Among the other parameters influencing the sonoelectrochemical process, it is worth noting the ultrasound pulse intensity, which should be high enough to remove all of the metal deposited on the electrode surface. At the same time, high ultrasound intensity leads to an excessive energy consumption and overheating of the electrolyte, which is extremely undesirable, since it leads to a change in the properties of the electrolyte and its degradation.

The SEM study made it possible to reveal some morphological features of the obtained powders. It is known that copper is deposited on the cathode in the form of dendrites [19]. Ultrasonic processing and centrifugation disintegrate most dendrites (with simultaneous agglomeration of particles). However, intact dendritic particles are still observed in some areas of the resulting product (Figure 4 left). Another noteworthy feature is that there are not only fine particles but also large particles with a size of several microns. One possible reason for this is that, in the presence of roughness and micro scratches on the surface of the sonotrode, not all of the particles are removed in one ultrasonication cycle, and some particles continue to grow during a few subsequent cycles. As a result, the final product may range widely in particle size (Figure 4 right).
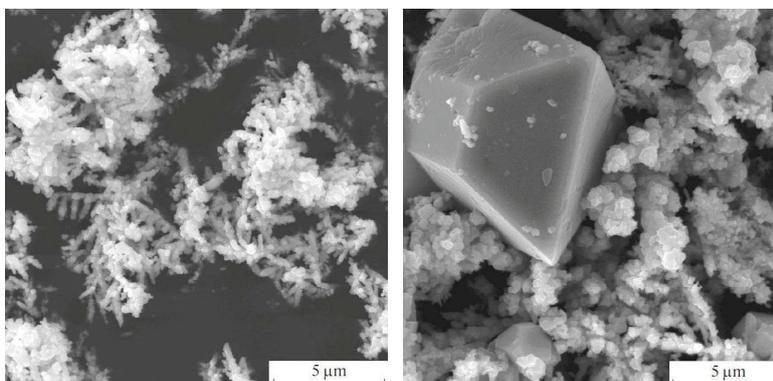

Figure 4: Dendrites in a copper powder (left) and SEM image of a copper powder containing a large particle (right).

Note that powders were obtained using solutions containing an organic stabiliser polyvinylpyrrolidone. This stabiliser ensures both a reduction in particle size and stability to oxidation, as evidenced by X-ray diffraction data. Figure 5 shows X-ray diffraction patterns of copper powders obtained from electrolytes containing the stabilizer and without it (two weeks after synthesis). Immediately after the process, the powders consist predominantly of copper, with a small amount of Cu_2O. The powders prepared with the use of the stabilizer

demonstrate a higher oxidation resistance over time (the amount of the copper oxide remains essentially unchanged).
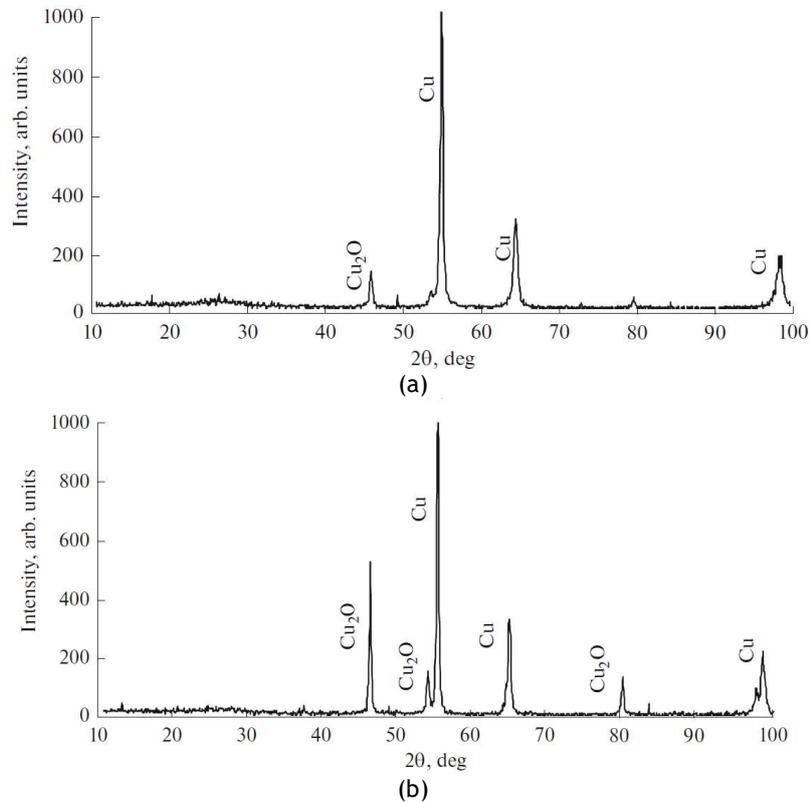

Figure 5: X-ray diffraction patterns of a copper powder prepared (a) with the stabilizer and (b) without stabilizer (two weeks after synthesis).

4. CONCLUSION

As it was shown in [4, 8-10, 25], *in-situ* L-PBF alloying is an efficient way to produce new materials by L-PBF; nevertheless, to manufacture a homogeneous alloy is a challenge. For efficient in-situ L-PBF alloying processes, not only process parameters (laser power, spot size, scanning speed, and so on) should be optimized, but also, material properties and powder size analysis must be performed to guarantee efficient melting and mixing of both materials.

In the present work, the parameters influencing the morphology and size of ultrafine copper powders obtained by the sonoelectrochemical method were studied. Investigations show that the sonoelectrochemical process is suitable for the synthesis of ultrafine copper powder. The cathode current density has been shown to have the most significant effect on the characteristics of the powders. Reducing the current density leads to a reduction in the particle size of the copper powders. The average particle size (weighted by volume) was d_{10}=520 nm, d_{50}=1.75 μm and d_{90}=6.0 μm at current density of 1.15 A/cm^2 and d_{10}=260 nm, d_{50}=520 nm and d_{90}=870 nm at current density of 450 mA/cm^2. The described method makes it possible to obtain copper powders with an average particle size of 100 nm to several microns. The received powder is planned to be tested for L-PBF *in-situ* alloying of advanced antibacterial additively manufactured materials.

5. ACKNOWLEDGEMENTS

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