INFLUENCE OF SELECTIVE LEACHING PARAMETERS ON PROPERTIES OF SILVER NANOPARTICLES

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Abstract

Metallic nanoparticles are considered as very prospective material due to unique properties and wide range of possible applications. In this work, our attention was focused on preparation of silver nanoparticles by selective leaching of aluminium matrix under various conditions. As an initial material, rapidly solidified binary aluminium alloy AlAg30 (wt. %) prepared by melt-spinning technique was used. Leaching process was carried out in the sodium hydroxide solution and as a result, nanocrystalline silver in the form of very fine powder was obtained. The influence of production conditions such as dissolving temperature, concentration of sodium hydroxide and using ultrasound bath on the morphology, phase composition and dimensions of nanoparticles was studied. The prepared product was investigated by means of transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD). The size of nanoparticles was determined by image analysis of TEM micrographs and from diffraction patterns. It was found that particle size is strongly dependent on leaching temperature and concentration of sodium hydroxide significantly affects the phase composition of the product.

Keywords:
Metallic nanoparticles, silver, selective leaching

1. INTRODUCTION

Metallic nanoparticles and nanocrystalline metals are very popular subjects of various studies due to their unusual properties. Since the grain sizes are small (typically less than 100 nm), a significant volume fraction of microstructure consists of interfaces, especially grain boundaries. That is the reason why nanocrystalline metals exhibit higher hardness and strength in comparison to their coarse-grained counterparts. In addition, metallic nanoparticles are usually characterized by catalytic activity or gas absorption capability. Some of them also exhibit magnetic properties [1–3]. Metallic nanoparticles and nanocrystalline bulk metals are currently used in different areas. High hardness and strength are important for advanced structural and functional applications. Other properties such as magnetic or optical behavior are utilized in electronics or biomedicine. High specific surface of metallic nanoparticles is used in catalysis or in environmental purification processes [2,4–6]. Silver nanoparticles show antibacterial properties. This ability is frequently used in medicine and dental works [7]. In other studies it was mentioned that silver nanoparticles can be used as superior disinfectant for wastewaters containing infectious microorganisms [6,8], but residual nanoparticles in the treated water may adversely affect human health. Silver nanoparticles can be embedded onto various surfaces leading to significant reduction of their leakage into environment. These surfaces can be consequently utilized for medical instruments and devices, water treatment or food processing [7]. There are various methods how nanocrystalline metals and metallic nanoparticles can be produced. They include wide range of vapor, liquid and solid state processing routes [9]. The most common of them are inert gas condensation, intensive plastic deformation, precipitation from liquids or rapid solidification. Another promising technique is selective leaching when one component of an alloy is dissolved and the second one remains in solid state in the form of fine powder [10].
2. EXPERIMENTAL

Aluminium alloy with 30 % (wt.) of silver (AlAg30) was prepared by conventional melting of appropriate amount of pure metals in the induction furnace under the protective argon atmosphere followed by casting into brass mold. Prepared ingot was re-melted and processed by melt-spinning technique. This method consists in ejecting the molten alloy onto fast rotating copper wheel. As a result, rapidly solidified (RS) ribbons were obtained. These ribbons were used as the initial material for selective dissolving because rapid solidification ensures fine microstructure of the ribbon. Fine microstructure is very advantageous for obtaining nano-size-grained powders. Experiments were carried out for 3 hours at different temperatures (0 °C, 40 °C, 80°C) and using sodium hydroxide solution with different concentrations (20 wt. %, 30 wt. %). Dissolving at the temperature of 40 °C was further supported by stirring in ultrasound bath (ult.). Aluminium matrix dissolves according to following reaction:

$$2 \text{Al} - \text{Ag} + 2 \text{NaOH} + 6 \text{H}_2\text{O} \rightarrow 2 \text{Na}[\text{Al(OH)}_4] + 3 \text{H}_2 + \text{Ag}.$$  (1)

Silver is insoluble in the sodium hydroxide solution and it remains in the form of very fine powder. Prepared powder was decanted and rinsed by distilled water and by isopropyl alcohol (g.r.) respectively. The isopropyl alcohol was consequently evaporated.

For examination of the powder various analytical and microscopic techniques including X-ray diffraction analysis (XRD, PANalytical X’Pert Pro, Cu anode) and transmission electron microscopy (TEM Jeol JEM 3010, W cathode) were used. The particle size of the powder was measured by image analysis using Image J software and these results were also compared to the size estimated from XRD peak broadening.

3. RESULTS AND DISCUSSION

In this work, silver nanoparticles were produced by selective leaching method. In Fig.1 are TEM micrographs revealing microstructure of rapidly solidified ribbon made of AlAg30 alloy prepared by melt-spinning technique. There is evident fine microstructure mainly formed of rectangular and nearly regular shaped grains of solid solution of silver in fcc-aluminium reaching sizes of around 200-300 nm (Fig. 1a). In addition, there are visible small particles of intermetallic phases situated at the grain boundaries (Fig. 1b). By using XRD phase analysis, these particles were identified as Ag2Al intermetallic phase.

![Fig. 1: TEM micrographs of rapidly solidified ribbon. a) Fine structure of the ribbon. b) Detailed image of the ribbon with particles of Ag2Al intermetallic phase located at the grain boundaries.](image)

In Fig. 2 are shown TEM micrographs revealing that the powder residue is composed of clusters having a size of few micrometers (a, c, e, g). In addition, each cluster is formed of many fine spherical and/or vermicular-shaped particles. By using the ultrasound bath, better dispersion of individual particles was
assumed. But this expectation was not confirmed as evident from Figs. 2g and h showing agglomerated nanoparticles. Detailed views of nanoparticles are shown in the right column of TEM micrographs (Figs. 2b, d, f, h).
By using XRD analysis it was found that the phase composition of the nanocrystalline powder is dependent on sodium hydroxide concentration. By using 20 % (wt.) sodium hydroxide solution, final powder product was composed of silver and small amount of Ag$_2$Al intermetallic phase. By using 30 % (wt.) sodium hydroxide solution, presence of Ag$_2$Al intermetallic phase was not detected in the powder (Fig. 3). Ag$_2$Al intermetallic phase is nobler than aluminium and it is more resistant to 20 % sodium hydroxide solution. However, by using 30 % sodium hydroxide solution even Ag$_2$Al intermetallic phase was dissolved.

Except of phase composition, dependence of the particle size on dissolving conditions was investigated. For determination of this parameter, two methods were used. By image analysis of TEM micrographs it was found that decreasing temperature of leaching reduces the particle size. Comparison of the size of particles obtained under various conditions of dissolving is summarized in the Fig. 5. It can be seen that the smallest particles were prepared at the temperature of 0 °C and almost 50 % of them reached a size between 20-30 nm. In contrast, the largest particles were obtained by dissolving at the temperature of 80 °C in the 20 % sodium hydroxide solution. Higher temperature is probably responsible for coarsening of particles because most of them reached a size of about 60-70 nm.
The average particle size was also estimated from XRD peak broadening (Fig. 4) using the Scherrer calculator [10]. Results of this method show approximately twice lower values of the particle size in comparison to image analysis. The source of this difference is probably presence of sub grains in particles. Grain boundaries are also necessary to be taken account. They contain more lattice defects and considering the particle size, they make up large section of the grain. These results are shown in the Fig. 6. Nevertheless, particle sizes determined by two mentioned methods show the same dependence on the dissolving conditions.

4. CONCLUSION

In this work, selective leaching method was successfully used for preparing of silver nanoparticles. Processes were carried out under various conditions and it was found that leaching temperature has a significant effect on the particle size when higher temperature causes coarsening of the prepared particles. Phase composition of the product depends on concentration of sodium hydroxide solution. By using 30 % solution, pure silver powder without presence of Ag₂Al intermetallic phase was obtained.

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6. REFERENCES


