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Chemical synthesis and densification of a novel Ag/Cr₂O₃-AgCrO₂ nanocomposite powder

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Abstract: Ag/Cr₂O₃-AgCrO₂ nanocomposite powders were chemically synthesized using a chemical precipitation method. The synthesis method stages included precipitation and calcination. The initial precipitates contained Cr(OH)₃·3H₂O and Ag₂CO₃ compounds. Calcination of the initial precipitates led to thermal decomposition of the precipitates and evaporation of volatile compounds such as H₂O and CO₂. The calcined precipitates contained silver, chromium oxide, and silver-chromia. The crystallite size of Ag₂CO₃ and Ag were determined as 18.9 and 45 nm, respectively. The scanning electron microscopy investigations showed that the particle size of the initial precipitates was lower than 100 nm. The calcined powders were sintered at 550°C in air atmosphere. The sintered samples were cold-repressed under 300 and 550 MPa. It was found that by increasing the repressing compaction magnitudes, the density and hardness of the sintered samples were increased. The scanning electron microscopy evaluation of the densified samples showed nearly dense microstructure.

Keywords: nanocomposite; powder; sintering.

1 Introduction

Metal matrix composites (MMCs) are a group of materials that have been widely used in various industrial fields such as aerospace, transportation, electronics, electric power transmission, sporting goods, and wear-resistant materials. These kinds of materials mainly consist of two chemically and/or physically distinct phases in which a particulate or fibrous reinforcement is dispersed in an appropriate manner in a matrix phase to give properties not obtainable with/or any one of the phases individually [1].

Silver matrix composites are a group of MMCs that are widely used in various kinds of electrical contacts such as snap switches, motor controllers, thermostat controls, and relays. WC, ZnO, CuO, and SnO₂ are widely used as reinforcements in silver matrix composites. This group of MMCs is synthesized by different powder metallurgy processes such as press-sinter, press-sinter-repress, and press-sinter-extrusion of the Ag/reinforcement powder mixtures. The properties of the silver matrix composites, such as hardness, depend on different factors such as the distribution of reinforcement within the matrix and the density of the synthesized powders [6, 7].

Recently, it has been shown that the sinterability of composite powders is higher than that of the powder mixtures [8]. Coprecipitation is one of the processes that is applied to synthesis composite powders with fine and relatively homogenous dispersion of the constituents. The process includes precipitation, calcination, and in some cases reduction of the calcined precipitates [9, 10].

In this research, a novel silver-chromium containing nanocomposite powders were synthesized using a coprecipitation method. Also, the sinterability of the synthesized powders was investigated.

2 Materials and methods

Silver and chromium nitrates were used as precursors. A total of 42.48 g silver nitrate (AgNO₃) and 23.07 g chromium nitrate (Cr(NO)₃·9H₂O) were used to synthesize Ag/20%wt Cr₂O₃-AgCrO₂ nanocomposite powders. The initial precipitates were synthesized by adding ammonium carbonate to silver and chromium nitrates solution mixture. The precipitates were filtered, washed, and dried at 100°C. The thermal behavior of the precipices was studied by thermogravimetric (TG) and differential thermogravimetric (DTG) analysis up to 800°C with a 10°C/min heating rate in air atmosphere. The precipitates were calcined at 550°C for 1.5 h in air atmosphere. The initial precipitates and the calcined powders were characterized by X-ray diffraction.
(XRD) method. The calcined powders were cold-pressed in a 20 mm diameter die under 300 MPa. The cold-pressed compacts were sintered at 550°C and repressed under 300 MPa. The repressed samples were annealed and repressed at 450°C and 550 MPa, respectively. The microstructure of the powders and the densified specimen were investigated by scanning electron microscopy (SEM). The hardness of the samples was determined by a Vickers microhardness tester.

3 Results and discussion

Figure 1 shows the XRD pattern of the initial precipitates. According to the pattern, the precipitates were Cr(OH)$_3$·3H$_2$O and Ag$_2$CO$_3$ compounds. The microstructure of precipitates is shown in Figure 2. The figure shows that the particles were spherical and have been agglomerated due to relatively small particle size. However, according to this figure, it can be declared that the size of the particles is less than 100 nm.

Figure 3 shows the TG and DTG curves of the initial precipitates. The DTG curve shows two peaks at 200°C and 681°C, which correspond to two distinct weight loss stages in the TG curve between 100°C to 280°C and 550°C to 700°C, respectively. The weight loss of the initial powders during heat treatment is due to the evaporation of volatile compounds such as water and carbon dioxide. According to the thermal analysis curves, it can be declared that calcination of the initial precipitates at 550°C led to complete thermal decomposition of the precipitates and evaporation of volatile compounds. This temperature is approximately the onset of the second weight loss stage of the TG curve. The XRD pattern of the calcined powders at 550°C is shown in Figure 4. On the basis of the obtained results, the calcined powders contained Ag, Cr$_2$O$_3$, and AgCrO$_2$. The thermal decomposition of Cr(OH)$_3$·3H$_2$O, and Ag$_2$CO$_3$ during calcination are

$$2\text{Cr(OH)}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 9\text{H}_2\text{O}$$ (1)

$$\text{Ag}_2\text{CO}_3 \rightarrow \text{Ag}_2\text{O} + \text{CO}_2 \uparrow \rightarrow 2\text{Ag} + \frac{1}{2}\text{O}_2$$ (2)

Also, the proposed reaction for formation of AgCrO$_2$ is

$$2\text{Cr(OH)}_3 \cdot 3\text{H}_2\text{O} + \text{Ag}_2\text{CO}_3 \rightarrow 2\text{AgCrO}_2 + \text{CO}_2 \uparrow + 9\text{H}_2\text{O} \uparrow$$ (3)

A similar reaction between chromium hydrate compound and silver nitrate has been previously reported by Zied [11]. Also, Sofie et al. [12] proposed a reaction between AgO and Cr$_2$O$_3$ that led to AgCrO$_2$ formation. However, it seems that the AgCrO$_2$ compound was formed at the interface regions of Cr(OH)$_3$·3H$_2$O and Ag$_2$CO$_3$ compounds during calcination.

The crystallite size and microstrain of Ag$_2$CO$_3$ and Ag were determined by Debye-Scherrer’s formulae [13]:
where $d$ is the crystalline size, $K$ the shape factor (0.9), $\lambda$ the wave length of CuK$_\alpha$ radiation (0.15404 nm), $\theta$ the Bragg angle, $\eta$ the lattice strain, and $\beta_s$ the sample broadening related to full-width at half-maximum, which can be determined by correcting the measured broadening ($\beta_e$) using the following relation:

$$\beta_i^2 = \beta_e^2 - \beta_s^2$$

(6)

The lattice strain and crystallite size of Ag$_2$CO$_3$ and Ag are given in Table 1. The results show that by calcination or, in other words, by heating the precipitates, the crystallite size and lattice strain were increased and decreased, respectively. Also, the derived crystallite sizes are in good agreement with SEM observations.

The SEM image of the calcined powders is shown in Figure 5 in two magnifications. The image was obtained in the secondary electron mode. The particles are mainly semispherical and their size is less than 10 μm. As can be observed, during calcination, due to relatively high calcination temperature, the powder particles have been presintered. The neck-like regions, which are generally formed during solid-state sintering, are observed between the powder particles. These regions were formed due to atomic diffusion during heat treating the particles. The driving force of this phenomenon is the reduction of particles’ surface area during sintering. In some cases, the neck-like regions have grown and the individual particles have sintered and become one particle. A typical example of these regions is shown in Figure 5. The higher calcination temperatures or the longer calcination duration may be due to further sintering of the powder particles. The density and microhardness of the sintered and repressed samples are given in Table 2.
specimens are given in Table 2. As it is seen, by increasing the pressure magnitude, the density and hardness of the samples were increased, which is due to the decreasing volume fraction of porosity within the structure of the samples. During repressing the sintered specimens, plastic deformation and cold welding leads to annihilation of the porosities. However, it seems that higher repressing cold compaction magnitude or hot repressing of the sintered samples maybe due to more densification of the samples.
The microstructure of the repressed samples at less than 550 MPa and the corresponding silver and chromium map analysis is shown in Figure 6. Figure 6A was obtained in the secondary electron mode. Also, Figure 6B and C shows the elemental map analysis of silver and chromium in Figure 6A, respectively. According to Figure 6, there are three distinct regions within the microstructure of the sintered samples: a region with fine dispersion of chromium compounds, a region with relatively lower chromium volume fraction and microstructural porosities region. However, it was observed that silver has a fine and relatively homogenous dispersion throughout the microstructure. Figure 7 shows the microstructure and correspondence elemental map analysis of chromium and silver in higher magnification. Regarding the map analysis (Figure 7B and C), it can be declared that the big spherical regions are silver. Also, the fine spherical dispersed particles in Figure 7A are chromium oxides and silver/chromia, which are dispersed in silver matrix. To have a more homogeneous microstructure or in other words to eliminate the chromium-depleted regions, the initial precipitation process may be modified. More investigations should be done in this regard.

4 Conclusion

A novel silver-chromium-containing composite was synthesized using a chemical precipitation process. The synthesis method included precipitation and calcination processes. The initial precipitates were silver carbonate and chromium hydrate. Calcination of the precipitates led to thermal decomposition of precipitates and formation of Ag, Cr₂O₃, and AgCrO₂. The synthesized powders were densified by sintering and subsequent cold-pressing of the sintered samples. The results showed that by increasing the pressing magnitude, the density and hardness of the samples were increased. The SEM investigations on the densified samples showed a relatively homogenous and dense microstructure.

References