

Synthesis and consolidation of copper/chromium oxide nanocomposite powders via pressureless and spark plasma sintering

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Copper/chromium oxide (75%wt) nanocomposite powders were synthesized via chemical precipitation process. The process was included chemical precipitation of Cr-Cu containing precipitates, calcination and reduction of the precipitates. Based on thermogravimetric analysis of the precipitates, the optimum calcination temperature was determined as 700 °C. The synthesized powders were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The observations revealed that the powder particles were agglomerated and their shape was mainly spherical. The powders were densified via spark plasma and pressureless sintering at 1000 °C and 1100 °C, respectively. The microstructural evaluation of the spark plasma sintered samples confirmed a near dense structure with a fine dispersion of the constituents. However, the microstructure of the pressureless sintered specimen showed a large number of pores between the powder particles. The relative density and micro-hardness of the spark plasma sintered samples were 95.8% and 1600 HV, respectively.

Key words: Nanocomposite, Thermogravimetric analysis, Sintering.

Introduction

Metal/metal oxide particle reinforced composites are widely used in electrical components such as pressure and temperature controls, low voltage circuit breakers, light switches and relays. Generally, in this group of composites, silver and copper are used as the matrix phase while tin, aluminum, copper, zinc, chromium and cadmium oxides are applied as the reinforcement [1-5]. These kinds of metal matrix composites are mainly produced via powder metallurgy routes like press-sinter, press-sinter-repress, press-sinter-extrusion, hot press and spark plasma sintering of copper (silver)/metal oxide powder mixtures. However, it has been shown that fine dispersion of the constituents within the microstructure of powder mixtures was led to enhanced sinterability and properties of the produced composite [6]. Several methods such as chemical and mechanical milling processes were applied to synthesis the powders with fine and homogenous dispersion of the constituents. However, during the milling process the powders could be contaminated which may be due to decreasing the properties of the synthesized composite [7, 8].

In this research, chemical synthesis of copper/chromium oxide (75%wt) nanocomposite powders was investigated. Also, the densification of the synthesized powders by liquid phase and spark plasma sintering processes were investigated.

Experimental

Copper nitrate, chromium nitrate and ammonium carbonate were used as precursors. The initial precipitates were synthesized by adding ammonium carbonate to copper and chromium nitrate solution drop by drop. The synthesized powders were dried, calcined and reduced by hydrogen at 50 °C, 700 °C and 1000 °C, respectively. The thermogravimetric and differential thermogravimetric (TG and DTG) analysis of the precipitates were carried out up to 1000 °C with a heating rate of 10 °C · min⁻¹ in air atmosphere. The powders were characterized by X-ray diffraction (XRD). The synthesized powders were cold pressed by 300 MPa and sintered at 1100 °C in hydrogen atmosphere for 2 hrs. Also, the synthesized powders were spark plasma sintered at 1000 °C in vacuum. The microstructure of the powders and sintered samples were evaluated by scanning electron microscope (SEM). The hardness of the samples was determined by a micro hardness tester.

Results and Discussion

Fig. 1 shows the XRD pattern of the initial precipitates. The precipitates consist of $\text{Cu}_2\text{CO}_3(\text{OH})_2$ and $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ compounds. A typical SEM image of the precipitates is shown in Fig. 2. It is seen that the powder particles are mainly spherical and their dimension is about 100 nm and also, can be declared that the powder particles have been agglomerated due to high specific area.

The TG and DTG analysis curves of the Cu-Cr

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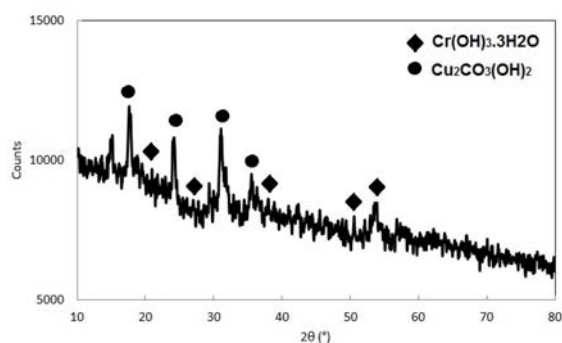


Fig. 1. XRD pattern of the initial precipitates.

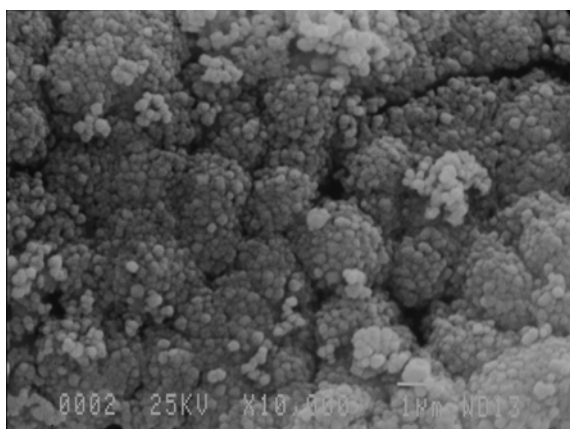
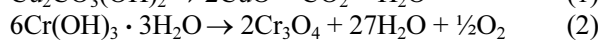
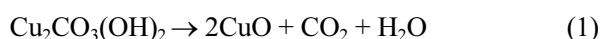
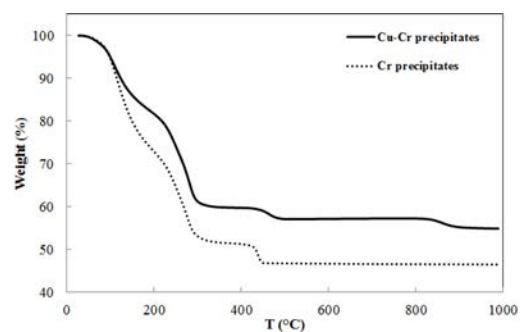


Fig. 2. SEM image of the initial precipitates.

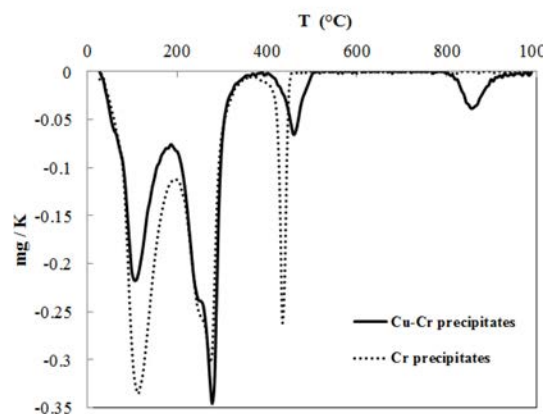
containing precipitates are shown in Fig. 3. For better investigation, the result of similar analysis on copper free precipitates which were synthesized by the same synthesize method is shown in Fig. 3. A comparison between the two TG curves shows that the overall weight loss stages up to 700 °C are similar which implies that evaporation of volatile compounds such as H₂O for both chromium and copper precipitates occurs in the same temperature ranges. However, the Cu-Cr containing TG curve shows an additional weight loss stage at about 900 °C. It can be concluded that this weight loss step is not corresponded to chromium containing precipitates and is related to copper compounds. The XRD pattern of the Cu-Cr calcined precipitates at 700 °C is shown in Fig. 4, showing that the calcined precipitates consist of CuO and Cr₃O₄ oxides. So, based on the obtained results and also literature [9], the fourth weight loss stage of Cu-Cr TG curve is related to decomposition of CuO to Cu₂O which is a weight losing reaction. The proposed calcination reactions are as below:



The TG curve of the Cr-Cu containing precipitates shows about 57% weight loss at 700 °C which is about 3% lower than theoretical calculations. The difference between the experimental data and theoretical values



a



b

Fig. 3. (a) TG and (b) DTG analysis curves of the Cu-Cr and Cu free precipitates.

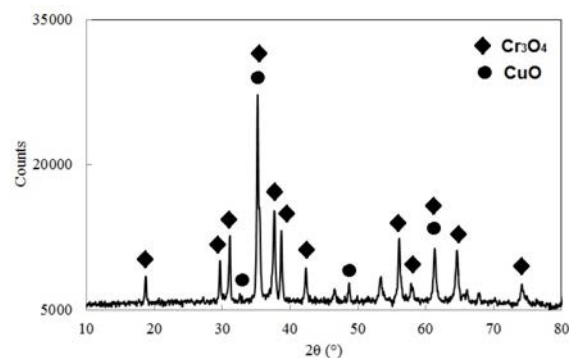


Fig. 4. XRD pattern of Cu-Cr calcined precipitates at 700 °C.

may be due to evaporation of physically adsorbed water which has not been evaporated during drying the initial precipitates. However, the theoretical weight loss percent of copper free precipitates is 54% which is in good agreement with theoretical value.

The SEM image of the calcined powders is shown Fig. 5. The calcined particles were agglomerated and their dimension is below 100 nm. However, the relatively high calcining temperature of the powders was due to pre-sintering of the powders. Furthermore, the existence of submicron pores within the microstructure is due to evaporation of the volatile compounds during calcination.

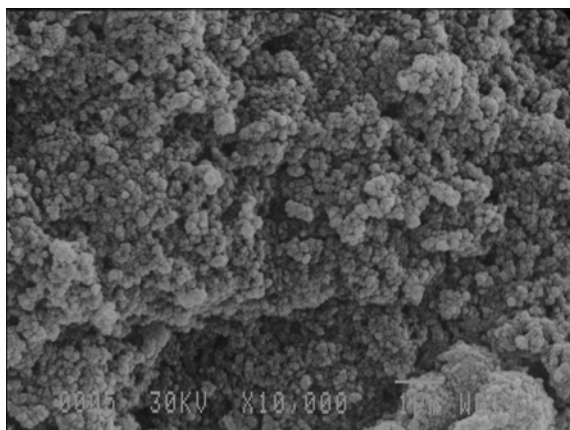


Fig. 5. SEM image of the calcined powders.

The XRD pattern of the reduced powders at 1000 °C is shown in Fig. 6. Based on the obtained results, copper oxide has been reduced to copper while Cr_3O_4 has been reduced to Cr_2O_3 during reduction. Fig. 7 shows the SEM image of the pressureless sintered samples at 1100 °C which is higher than melting temperature of copper. In other words, the samples were sintered at liquid phase. The relative density of the pressureless sintered samples was 52% which implies that the samples have not been densified during pressureless sintering. This conclusion is in good agreement with microstructural observation of the sintered samples which shows a porous microstructure. As it known, the liquid phase sintering process includes three stages after the liquid forms [5]: rearrangement, solution-reprecipitation and final-stage sintering. However, due to non-solubility of Cr_2O_3 in molten copper the second stage of the sintering sequence did not have an effective role on densification during sintering the powders. So, it can be declared that the first stage of liquid phase sintering was the main mechanism for densification of the powder compacts. However, regarding the relative density of the sintered samples and also microstructural observations it can be concluded that the Cr_2O_3 particles have not been rearranged by the liquid copper properly. This finding differs from W-Cu sintering results which were synthesized via similar routes and densified by similar conditions (i.e. sintering temperature and volume percent of liquid phase) [10, 11]. In the case of W-Cu composite powders, liquid phase sintering was led to relatively high relative sintered density. It is worthy to note that like Cr_2O_3 , tungsten has no solubility in molten copper and the rearrangement of the solid phase by the liquid is the dominant mechanism for densification of powder compact during sintering. It seems that the reason of this matter is the higher melting temperature of tungsten than chromium oxide. By increasing the melting temperature, the activation energy for diffusion of atoms is increased and as a result formation of neck like zone between solid-solid particles (i.e. W-W or Cr_2O_3 - Cr_2O_3 particles) needs

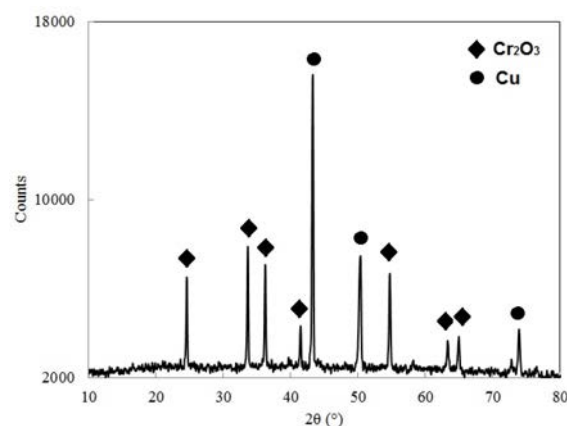


Fig. 6. XRD pattern of the reduced powders at 1000 °C.

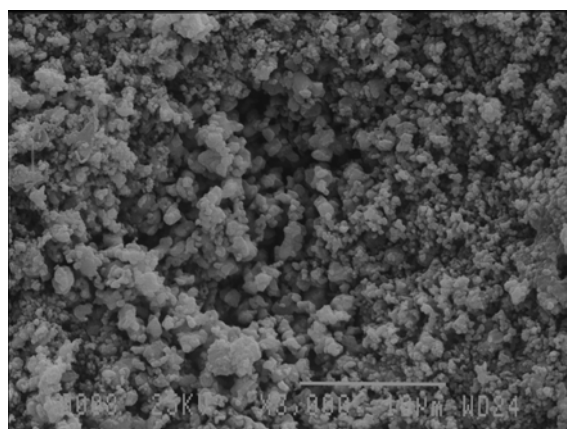


Fig. 7. SEM image of the pressureless sintered samples at 1100 °C.

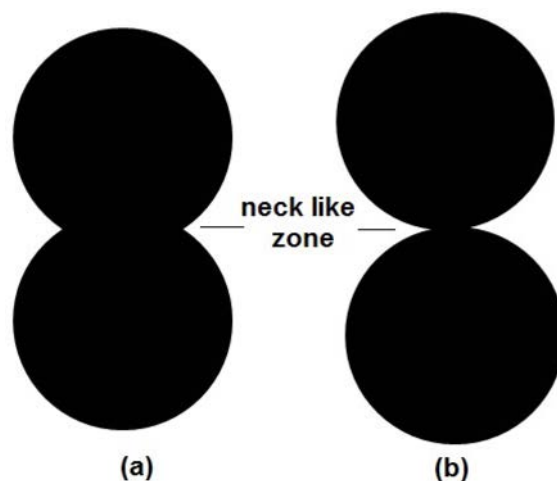


Fig. 8. Schematic representation of the neck like zone which forms between solid particles during sintering: (a) Solid particle with relatively low melting temperature. (b) Solid particle with relatively high melting temperature.

more time. In other words, the neck region which forms during sintering between the tungsten particles is weaker than chromium oxide (Fig. 8). So, the rearrangement of tungsten particles by liquid copper would be facile due to fragmentation of the neck like region between the solid particles.

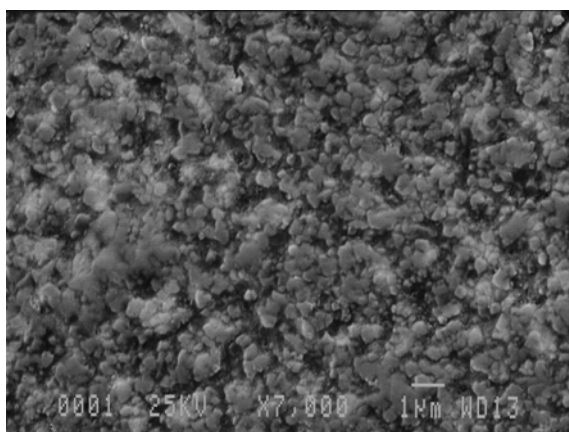
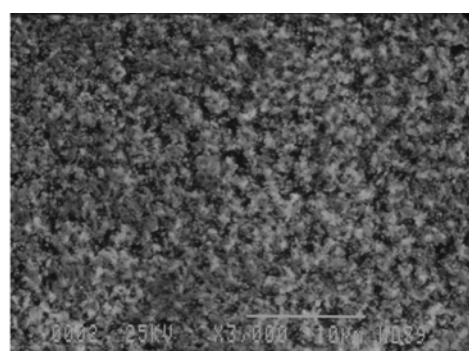
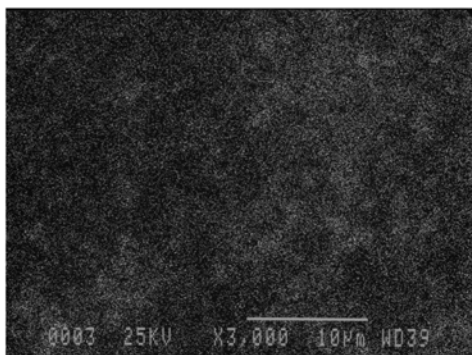


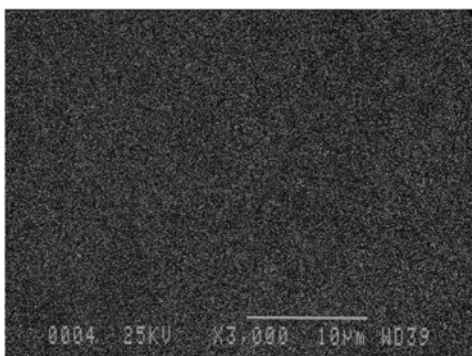
Fig. 9. Typical microstructure of the spark plasma sintered samples.



a



b



c

Fig. 10. (a) Microstructure image of the spark plasma sintered samples. (b) copper map analysis of "a" and (c) chromium map analysis of "a".

The relative density of the spark plasma sintered samples was 95.8% which shows a proper densification of powder compacts during sintering. A typical microstructure of the spark plasma sintered samples is shown in Fig. 9. As it can be observed, the microstructure is near dense with no detectable porosities. Fig. 10 shows another microstructure image of the sintered samples with the corresponding copper and chromium map analysis. The ultra-fine dispersion of copper and chromium oxide is obvious in the elemental map analysis which implies that the applied chemical synthesis route is a useful process for synthesizing the nanocomposite powders with fine dispersion of the constituents. The micro hardness of the spark plasma sintered samples was 1600 HV. According to the obtained results, it can be concluded that the preferred process for densification of powder compacts is spark plasma sintering.

Conclusions

Copper/chromium oxide nanocomposite powders were synthesized via a chemical process. The synthesizing process was included precipitation, calcination and reduction stages. The thermogravimetric analysis of the initial precipitates showed four weight loss stages up to 1000 °C. The synthesized powders were liquid phase and spark plasma sintered at 1000 and 1100 °C, respectively. The results showed that the latter sintering process was the preferred procedure for consolidation of the powders. The spark plasma sintered samples showed a near dense microstructure with fine dispersion of the constituents. The relative density and micro-hardness of the spark plasma sintered samples were 95.8% and 1600 HV, respectively.

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