Synthesis and Characterization of Ag-8 %wt Cr$_2$O$_3$ Composites Prepared by Different Densification Processes

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Abstract:
A novel Ag-8 %wt Cr$_2$O$_3$ composite prepared via powder metallurgy route. Silver and chromium oxides were used as starting powders. The powder mixtures were mechanically milled by a SPEX high energy mill for 5 h. Based on the thermogravimetric analysis (TGA) and X-Ray Diffraction (XRD) results, the milled powders were calcined in an argon atmosphere at 550 °C. During calcination, the silver oxide decomposed into silver. The results showed that the Heckel equation was the preferred one for description the cold compressibility of the powders. The calcined powders were consolidated by Press-Sinter-Repress (PSR), Press-Sinter-Repress-Anneal (PSRA) and Spark Plasma Sintering (SPS) processes. The Field Emission Scanning Electron Microscope (FESEM) investigations showed a nearly dense microstructure of the sintered samples. However, the hardness of the pressed-sintered-repressed samples was 81 Vickers which was the highest among the processed specimen. Furthermore, the flexural strength of the PSR and SPS processed samples were 231 and 255 MPa, respectively which were too higher than that of the annealed specimens. The results confirmed the effect of microstructural parameters such as Cr$_2$O$_3$ particle size and processing route on the mechanical properties of the sintered composites.

Keywords: Silver Matrix Composite; Densification; Spark Plasma Sintering.

1. Introduction
The excellent physical and mechanical properties of Metal Matrix Composites (MMCs) like good electrical and thermal conductivity, high ductility and relatively high strength to weight ratio make them attractive in a variety of industrial areas such as aerospace, transportation, electronics and electric power transmission. Copper, aluminum, nickel, cobalt, magnesium, silver, (and their alloys and compounds) are the main nonferrous metals which are used as the matrix phase in MMCs. The reinforcement of MMCs may be particular or fibrous [1, 2].

Silver matrix composites (SMCs) are a group of MMCs which are widely used in electrical make-break contacts like air conditioner controls, aircraft switches, governor relays and wiping shoes in power transformers. In this group of composites, ceramic compounds such as oxides, carbides and also refractory metals have been used as reinforcement. CdO, SnO$_2$ WC, ZnO, CuO, W, and Mo are some of the constituents which have been used as the second phase in this kind of MMCs. However, in some kind of hybrid SMCs like Ag-Fe-Cu or Ag-W-C which are applied in complex composite contacts, two different constituents have been used as the reinforcement. The volume percent of silver and the kind of reinforcement(s) depend on the application of the contact material [3-5]. The conventional method for production of SMCs is powder metallurgy route. In this method, silver and the reinforcement

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powders are blended and then the powder mixtures solid state sintered below melting point of silver. For more densification, the sintered samples are repressed or extruded. The first process is called press-sinter-repress (PSR) and the latter one is called press-sinter-extrusion (PSE). The processed samples may be annealed after repressing or extruding [5]. However, the powder mixtures can be consolidated by other densification processes such as hot pressing or spark plasma sintering. SPS is a high efficiency, short time densification process which offers the possibility of producing fully dense bulk materials in relatively low temperatures [6-9].

It has been shown that the fine dispersion of the reinforcement within the matrix phase and high relative density or in other words low volume fraction of porosities lead to better performance of the contact material [10]. In order to have a fine dispersion of the second phase within the matrix phase and improve sinterability, the powder blends can be mechanically milled before sintering [11]. Other processes like chemical precipitation and hydrothermal processed have been applied for synthesizing composites with a fine dispersion of reinforcement within the matrix phase [12, 13].

In this research, a novel SMC containing 8 %wt Cr$_2$O$_3$ as reinforcement with a potential use as contact materials have been synthesized via PSR, PSRA, and SPS processes. Also, the microstructure and mechanical properties of the composites were investigated.

2. Experimental procedures

Silver and chromium oxide powders with above 99 % purity were used as starting materials (Ag$_2$O: Merck, Cr$_2$O$_3$: Sigma-Aldrich). Ag$_2$O-Cr$_2$O$_3$ powder mixture with a predetermined weight percent of each constituent was milled in a SPEX (Sampleprep 8000D) ball mill in a dry media. The milling process was performed in a zirconia container using a ball to powder ratio of 1:5 at 350 rpm for 5h. In order to determine the calcination temperature of the milled powders, the thermal behavior of the powders was investigated using thermogravimetric analysis (TGA) up to 850 °C with a heating rate of 10 °C/min in air and argon atmospheres (METTLER TOLEDO, USA). On the basis of TGA results, the milled powders were calcined at 550 and 700 °C in an argon atmosphere for 1 h. The powders were characterized by X-Ray Diffraction (XRD – Bruker AXS D8 Advance) analysis. The calcined powders were cold compacted under 200, 300, 350 and 450 MPa in 25 mm diameter cylindrical die. The powder compacts were sintered at 900 °C for 1 h in an argon atmosphere. The sintered samples were repressed by 900 MPa in room temperature. The repressed samples were annealed at 350 °C for 2 h. Also, the calcined powders were spark plasma sintered at 350 °C under 35 MPa pressure for 10 min in a graphitic die in a vacuum. The microstructure of the powders and the sintered samples were investigated by Field Emission Scanning Electron Microscopy (FESEM MIRA 3 TESCAN, Czech Republic) equipped with an Energy Dispersive Spectrometer (EDS). The densities of the sintered specimen were determined by Archimedes principle. The hardness of the samples was measured by a Vickers hardness tester. The three-point flexural test was used to determine the strength of the samples.

3. Results and Discussion

3.1. Mechanical Milling of Powder Mixtures

Fig. 1 (a, b) shows the FESEM image of the initial powders. As it is observed, the particle size of the silver oxide powders is too higher than that of chromium oxide. Also, the silver oxide particles are spherical while the chromium oxide ones do not have a regular shape. Fig. 2 shows the microstructure of the milled powders for 2.5 and 5 h. As it is observed, by mechanical milling the powder mixtures for 5 h, the size of the particles was
reduced to lower than 2 μm. Also, the milled powders are mainly spherical and the chromium and silver oxide particles cannot be distinguished. According to the observations, it can be declared that fragmentation and particle size reduction was the dominant phenomenon during mechanical milling and size increasing due to cold welding of the particles had not an effective role during the milling process. This observation and conclusion may be due to a brittle characteristic of oxide precursors (i.e. silver and chromium oxides) which were used in this research. Fig. 3 shows the elemental map analysis of silver and chromium of the milled powders. According to this figure, by increasing the milling time, a fine and homogenous dispersion of chromium and silver oxide can be obtained. It is worthy to note that the main purpose of mechanical milling of the powder mixtures was to obtain a homogenous and fine dispersion of the constituents.

![Fig. 1. FESEM image of the initial powders. (a) Silver oxide (b) Chromium Oxide.](image1)

![Fig. 2. Microstructure of the powders milled for (a) 2.5 (b) 5h.](image2)

However, the particle size of the powders has been reduced during milling too. The XRD patterns of the mixed and milled powders are shown in Fig. 4.
Fig. 3. Elemental map analysis of silver and chromium of the milled powders for (a) 2.5 h (b).

Fig. 4. XRD patterns of the mixed and the milled powders.

Fig. 5. Crystallite size and micro lattice strain of silver oxide as a function of milling time.
The effect of mechanical milling on the crystallite size and micro-lattice strain of the silver oxide are shown in Fig. 5. The crystallite size and micro strain of the silver oxide were determined by Debye-Scherrer’s (1&2) and Williamson Hall (3) equations [14, 15]:

\[ d = \frac{K\lambda}{\beta_s \cos \theta} \]  
\[ d = \frac{\beta}{4 \tan \theta} \]  
\[ \beta_s \cos \theta = \frac{K\lambda}{d} + 2\eta \sin \theta \]  

where \( d \) is the crystalline size, \( K \) shape factor (0.9), \( \lambda \) the wavelength 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 (FWHM) which can be determined by correcting the measured broadening (\( \beta_i \)) using the following relation:

\[ \beta_i^2 = \beta_e^2 - \beta_i^2 \]  

where \( \beta_i \) is the instrumental broadening corresponding to each diffraction peak.

As it can be seen, by increasing the milling time, the crystallite size and strain were decreased and increased, respectively. Increasing the lattice strain was due to the applied stress to the powder particles during mechanical milling. This result is in good agreement with the FESEM observations which confirmed the reduction of particle size during milling. According to Fig. 5, at the first stages of mechanical milling, the reduction in crystallite size is higher than that of the end of the process. Also, the increase of the lattice strain magnitude at the beginning of the mechanical milling process is too higher than the final stages. The latter finding implies that the rate of work hardening of the powder particles is not constant during the milling process.

3.2. Thermogravimetric Analysis and Calcination of the Milled Powders

![Fig. 6. TGA curves of the milled powders in air and argon atmospheres.](image)

Figs. 6 show the TGA curves of the milled powders in air and argon atmospheres. As it is seen, the corresponding TG curve in air shows three weight loss stages up to 850 °C.
Also, an increase of the weight sample can be detected in this curve. On the other hand, the other curve shows three weight loss stages without any increasing of the weight during heat treating. It seems that the weight loss stages correspond to thermal decomposition of silver oxide to silver. In order to determine the weight increasing stage during TGA of the samples in air atmosphere, the milled powders were calcined at 700 °C in a batch type furnace in air. This temperature is the onset temperature of the third weight loss stage of the TGA curve in air atmosphere. The XRD pattern of the calcined powders is shown in Fig. 7a. As it can be seen, the calcined powders at 700 °C contained Ag, Cr₂O₃ and Cr₃O₈. So, it can be confirmed that the weight loss stages are corresponded to thermal decomposition of silver oxide to silver. However, the weight increasing of the samples was due to formation of Cr₃O₈.

In order to determine the weight loss stages of the TGA curve in argon atmosphere, the milled powders were calcined at 550 °C in argon atmosphere. This temperature is the onset temperature of the third weight loss stage of the TGA curve in argon atmosphere. The XRD pattern of the calcined powders is shown in Fig. 7b. As it can be seen, the calcined powders contain Ag and Cr₂O₃. So, it can be declared that the weight loss stages are due to decomposition of Ag₂O to Ag. However, chromium oxide has not been converted to any other compound during calcination in argon. So, according to the results, it can be concluded that the Ag-Cr₂O₃ composites can be used only in contacts which work in vacuum or inert media like oil circuit breakers or vacuum switches.

![Fig. 7. XRD pattern of the calcined powders in (a) air (b) argon.](image-url)
According to TGA results, the calcination atmosphere and temperature were
determined as argon and 550 °C, respectively. It is worthy to note that higher calcination
temperatures may be due to further grain growth and pre-sintering of the powder particles
during calcination.

3.3. Densification of Calcined Powders

Fig. 8 shows the curve of relative green density versus cold compaction magnitude of
the calcined powders. As it is shown, by increasing the cold compaction pressure, the relative
density was increased. The cold compressibility of the powders was investigated using Heckel
(5), Panelli-Ambrosio (6) and Ge (7) equations [16, 17]:

\[
\ln\left(\frac{1}{1-D}\right) = KP + A \tag{5}
\]

\[
\ln\left(\frac{1}{1-D}\right) = KP^{1/2} + A \tag{6}
\]

\[
\log\left(\ln\left(\frac{1}{1-D}\right)\right) = K \log P + A \tag{7}
\]

Where \(D\) is the relative density, \(P\) is cold pressure, \(K\) is related to the plastic deformation
capacity of the powder particles and \(A\) represents the density without applied pressure or in
other words apparent density. The densification parameters \((A)\) and the correlation
coefficients \((R^2)\) corresponding to each equation are given in Tab. I.

![Fig. 8. Relative green density, relative sintered density and increase of density due to
sintering vs. cold compaction magnitude of the calcined powders.](image)

<table>
<thead>
<tr>
<th>Equation</th>
<th>Densification parameter</th>
<th>correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panelli-Ambrosio</td>
<td>0.5535</td>
<td>0.9005</td>
</tr>
<tr>
<td>Ge</td>
<td>0.4533</td>
<td>0.8879</td>
</tr>
<tr>
<td>Heckel</td>
<td>0.67</td>
<td>0.9071</td>
</tr>
</tbody>
</table>
The densification parameter values indicate that the plastic deformation capacity of the powders is high which is due to high volume of ductile phase i.e silver. Also, the correlation coefficients values confirm that the Heckel model provided the best fit scenario for the powders.

The relative sintered density vs. cold compaction magnitude for the solid state sintered samples is shown in Fig. 8. As it is shown, by increasing the compaction pressure, the relative sintered density has been increased. However, it can be declared that the magnitude of cold compaction prior to sintering had not a significant effect on densification and relative sintered density of the samples. The difference of relative green and sintered densities or in other words the increasing of relative density during solid-state sintering is shown in Fig. 8 too. As it is shown, the increase of relative sintered density during sintering was about 29 % for all of the samples. So, it can be concluded that the cold pressure magnitude prior to sintering, did not influence densification mechanisms during solid state sintering. By repressing the sintered samples under 900 MPa, the relative density of the sintered samples was increased to 91.65 % which was due to the plastic deformation of the samples and annihilation of porosities. During repressing the solid state sintered specimen, plastic deformation of the sintered bulks and also cold welding of the internal surfaces of porosities was led to the annihilation of porosities and increasing the relative density of the sintered samples. However, annealing the repressed samples did not effect on the relative density of the samples.

Fig. 9 shows the shrinkage curve of the powders as a function of temperature during spark plasma sintering. As it is shown, at about 350 °C, the samples did not show further shrinkage. On the basis of this observation, the samples were spark plasma sintered at 350 °C which is too lower than the solid state sintering temperature of the samples which were densified by PSR & PSRA processes. The relative density of the spark plasma sintered specimen was 93 % which was higher than that of the other samples.

The FESEM images of different samples are shown in Fig. 10. The silver matrix, chromium oxide particles, and porosities are shown by arrows in different samples. As it is observed, the sample with the lowest density (i.e. solid state sintered sample without repressing) contains the highest volume percent of porosities. It seems that the porosities are mainly observed at the interface of matrix/reinforcement and within the chromium oxide particles. This observation is due to the relatively low sintering temperature of the samples respect to the melting point of chromium oxide. As it is known, by increasing the melting temperature, the activation energy for atomic diffusion is increased [18]. So, at the low sintering temperature, the activation energy for atomic diffusion cannot be supplied sufficiently and as a result, the volume percent of porosities increases within the microstructure. However, by repressing the
solid state sintered samples, the volume fraction of the porosities has been decreased. Also, it seems that the size of the porosities has been decreased too.

Fig. 10. FESEM images of different sintered samples: (a) Solid state sintered (b) PSR (c) PSRA and (d) SPS specimen.

Fig. 11. Schematically illustration of Ag/Cr₂O₃ composite particles fragmentation within silver matrix during SPS process.

According to Fig. 10, the size and dispersion of chromium oxide particles within the matrix phase in the SPS processed samples differs from the other specimens. This observation can be explained by the fragmentation of Ag/Cr₂O₃ composite particles during the SPS process. The particles were formed through mechanical milling and subsequent calcination of the calcined particles. Fragmentation of the particles is due to applying uniaxial pressure to the powder particles and the plastic flow during spark plasma sintering. However, it seems that the fine dispersion of Ag and Cr₂O₃ and also local surface melting of powder particles during SPS [7]
have improved the fragmentation rate of the composite particles. Fig. 11 shows this phenomenon properly. Also, it can be declared that due to relatively low sintering duration and temperature of spark plasma respect to pressure-less sintering, the chromium oxide grains have not grown noticeably during densification.

Fig. 12a shows the interface region of Ag/Cr$_2$O$_3$ for the annealed samples. Also, the elemental line scan analysis of chromium, oxygen, and silver is shown in Fig. 12b. As it is observed, the line scan analysis reveals a transition layer at the interface of silver matrix chromium oxide particles. According to this figure, the weight percent of Ag at the interface is lower than the matrix. Also, the weight percent of chromium is not the same as chromium oxide particles. The formation of this layer was due to diffusion of Ag and Cr across the interface. However, it can be declared that formation of the intermediate region is mainly due to diffusion of silver and diffusion of chromium had not a significant rule on the formation of this layer. The reason for this declaration is the lower melting temperature of Ag than Cr which was led to relatively lower diffusion activation energy of this agent than Cr. It seems that by increasing the annealing duration, the width of the intermediate region would be increased.

**Fig. 12.** (a) Interface region of Ag/Cr$_2$O$_3$ for the annealed samples (b) Elemental line scan analysis of chromium, oxygen and silver.

The hardness and flexural strength of different samples are shown in Fig. 13. As it is shown, the hardness of the repressed samples was higher than that of the other ones which were due to work hardening of the samples during cold repressing. By repressing the solid state sintered samples, the density of dislocations was increased and strain hardening occurred. However, by annealing the repressed samples, the hardness of the samples was decreased. Furthermore, the hardness of the solid state sintered samples is the lowest one among the other specimen which is due to a high volume percent of porosities within the microstructure.

The flexural strength ($\sigma$) of the consolidated samples was determined using the following equation [1]:

$$\sigma = \frac{3F \ell}{2bh^2}$$

(8)

where $F$ is the load, $\ell$ is the span and $b$ and $h$ are the breadth and height of the specimen, respectively.
As it is shown in Fig. 13, the strength of the PSR and SPS processed samples were relatively higher than other samples which are due to the high relative density of these specimens. However, although the relative density of the PSRA processed samples was high, they showed relatively low flexural strength which might be due to the annealing process. This result shows that other than high relative density, work hardening of repressed samples and
fine chromium oxide particles were due to the high strength of PSR and SPS processed samples, respectively. The fractured surfaces of different samples are shown in Fig. 14. As it is observed, the size and morphology of the porosities are not similar in different samples. As expected, the volume fraction of porosities in the solid state sintered samples is higher than that of other ones. Also, the size of porosities in this group of samples is higher than other specimen and it seems that a network of porosities was formed in the microstructure. Moreover, the neckline regions can be observed between the powders particles in the fractured surface of the solid-state samples (Fig. 14a). It seems that by increasing the duration of the sintering, the neck like regions between the particles could grow and as a result, the size of the porosities would be decreased.

According to Fig. 14, the fracture mode of the repressed samples without annealing is brittle which is due to low ductility of these samples due to cold working. However, the fracture mode of the PSRA processed specimen is a mixed brittle-ductile one. The fractured surface of the spark plasma sintered sample is completely different from the other samples. The figure reveals the fine grain structure of the spark plasma sintered sample which is due to low temperature and duration of the densification process. Also, it seems that the fracture mode is completely ductile. The fine grain microstructure of the SPS processed samples was led to a high flexural strength of the SPS processed samples.

4. Conclusion

Ag-8 %wt Cr$_2$O$_3$ composites were prepared by press-sinter-repress, press-sinter-repress with subsequent annealing and spark plasma sintering processes. The FESEM image showed a homogenous dispersion of Cr$_2$O$_3$ within the silver matrix. The relative density of the processed samples was higher than 90 %. However, the hardness of the press-sinter-repressed samples was higher than other samples which were due to work hardening during cold repressing. Furthermore, the flexural strength of the annealed samples was too lower than the other specimen which implied that other than volume fraction of porosities, microstructural parameters such as size of the reinforcement has a significant effect on strength of the particle reinforced MMCs.

5. References


Садржај: Нови композит Ag- 8 %теж. Cr₂O₃ је припремљен металуршким путем. Сребро и хром-оксид су били почетни прахови. Смеше прахова су механички активирани у млину 5 сати. На основу анализе термогравиметрије и рендгена, лмевени прахови су калцинисани у атмосфери аргона на 550 °C. Током калцинације, оксид сребра је разложен. Резултати указују да Хекелова једначина најбоље описује процес консолидације прахова. Калцинисани прахови су синтеровани на више начина и то: пресовање-синтеровање-пресовање, пресовање-синтеровање-пресовање-очвршћавање и синтеровање у плазми. FESEM анализи указује на скоро потпуну густу микроструктуру синтерованих узорака. Ипак, тврдоћа узорка добијеног методом пресовање-синтеровање-пресовање је била највиша од свих осталих и износилаје 81 Викерс. Даље, отпорност на савијање узорака добијених том методом и синтеровањем у плазми износила је 231 и 255 MPa, што је много више од вредности добијених за узорке након очвршћавања. Резултати потврђују ефекат микроструктурних параметара као што су величина кристалита Cr₂O₃ и методе синтеровања на механичка својства синтерованих композита.

Кључне речи: композити; густине; синтеровање у плазми.

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