Sinterability and Characterization of Ag/Al₂O₃ Metal and Ceramic Matrix Composites Processed by Mechanical Milling

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Abstract:
In this research, the sinterability of Ag/Al₂O₃ milled powders with 10 and 90 wt%Ag were investigated. The powders were consolidated by two different processes including conventional and spark plasma sintering. The conventionally sintered composites with 90 wt%Ag were further densified by cold pressing and subsequent annealing at 700 °C. The microstructural evaluations confirmed a fine dispersion of the constituents within the microstructure of the spark plasma sintered composites. Moreover, the results showed that the relative density, hardness, and flexural strength of the spark plasma sintered samples were much higher than those of the other samples. The hardness and flexural strength of Ag/10 wt%Al₂O₃ spark plasma sintered samples at 650 °C were 146 HV and 264 MPa, respectively. However, unlike the composite with 90 wt%Ag, the applied sintering temperatures have not led to the synthesis of an Ag/90 wt% Al₂O₃ composite with the desired properties.

Keywords: Spark Plasma Sintering; Ag/Al₂O₃ Composites; Mechanical Milling; Densification; Microstructure.

1. Introduction
Silver containing composites (SCCs) are widely used in various industrial components like high voltage circuit breakers, motor governors, relays, and cutting tools. In these kinds of materials, silver can be as used as the matrix or the reinforcement phase. Various metals and compounds such as SnO₂, ZnO, MoS₂, WC, Cr₂O₃, CdO, TiB₂, W, Ni, Mo, Fe, and Al₂O₃ have been used in SCCs as the reinforcement or matrix phase [1-7]. In SCCs, the existence of a metal such as silver which has the highest electrical conductivity among metals improves the electrical and thermal conductivity of the composite. On the other hand, the reinforcing particles enhance the hardness and wear resistance of the composite. However, nowadays some of the introduced compounds are not the preferred ones for use as reinforcement in SCCs. For example, because of the toxicity of cadmium, using CdO has been restricted in SCCs and other pollution-free composites like Ag-SnO₂ have been gradually replaced Ag-CdO composites in industrial applications [8].

Casting and particularly powder metallurgy are the two applied processes for producing both kinds of the above-mentioned silver-containing composites [9-11]. However, processes like hot extrusion have been applied for the fabrication of Ag/MeO composites with desired properties by some of the researchers [12, 13].

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In the powder metallurgy processes, the composites are mainly produced by sintering or in the other words densification of Ag and the reinforcement powder mixtures. However, it has been shown that the fine dispersion of the constituents enhances the sinterability of powder mixtures significantly [14]. Hydrothermal processes, mechanical milling, chemical routes, and hot mechano-chemical processing are some of the applied methods for the synthesis of Ag containing powder mixtures with a fine dispersion of the composite components. In the mentioned processes Ag and the reinforcement powders or their oxides or nitrides such as Ag2O, ZnO, and AgNO3 have been used as starting materials for the synthesis of composite powders [15-21]. The conventional methods for densification of Ag containing powders are hot press (HP), pressureless, and spark plasma sintering (SPS) processes [22-24]. SPS is a rapid and low-temperature densification method that has been used for the consolidation of metallic, ceramic, and composite powders [25, 26]. Like other sintering processes, various parameters such as the SPS temperature and the weight percentage of the reinforcement have a significant influence on the final properties of the synthesized composite [27]. Several investigations were conducted on the synthesis and characterization of silver containing composites. However, there are a few investigations about the simultaneous effect of the Ag volume percent and the applied sintering process on the sinterability, microstructure, and properties of Ag/MeO composites.

In this research, mechanical milling and densification of Ag/10wt% Al2O3 and Ag/90wt% Al2O3 powder mixtures were investigated. The composites were prepared by SPS and pressureless sintering processes. To prevent the silver evaporation, the sintering behavior of the powder compacts was conducted on relatively low temperatures.

2. Materials and Experimental Procedures

High purity Silver Oxide (Ag2O) and Alumina (Al2O3) powders were used as starting materials in this research. The Ag2O and Al2O3 powders with > 99.0 % purity were supplied by IRAN SHIMI and Fluka (06285) Co., respectively. The morphology of the starting powder particles is shown in Fig. 1. As observed, the Ag2O particles have been agglomerated and their size is mainly below 2 μm. On the other hand, the size of the agglomerated Al2O3 particles is mainly below 5 μm and their shape is mainly worm-like. However, some plate-like Al2O3 particles could be observed in the micrograph too. The size of the Al2O3 agglomerates is about 100 μm. Two different Ag2O-Al2O3 powder mixtures with the aim of production of Ag/10wt% Al2O3 and Ag/90wt% Al2O3 powders were prepared in a tubular powder mixer. The powder mixtures were milled in a planetary ball mill in a dry media in the air atmosphere. The milling process was performed using a ball to powder weight ratio of 10:1 at 250 rpm for 16 h. The balls and containers were made of Zirconia. To determine the Ag2O decomposition temperature, the thermal behavior of the milled powders was evaluated by simultaneous thermal analysis (STA Q600-TA) up to 700 °C with a heating rate of 10 Kmin⁻¹ in an argon atmosphere. According to the thermal analysis results, the milled powders were heat-treated at 365 °C for 90 min in a tubular furnace in an Argon atmosphere.

The heat-treated powders were consolidated by two different methods. In the first processes, the heat-treated powders were cold pressed under 400 MPa in a 30 mm cylindrical die. The cold-pressed samples with 10 and 90 wt% Ag were sintered in a tubular furnace at 1150 and 800°C, respectively. The sintering was carried out in an argon atmosphere with a heating rate of 10 Kmin⁻¹ for 90 min. Subsequently, the Ag/10wt% Al2O3 sintered samples were cold-pressed by 200, 300, 400, 500 and 700 MPa for more densification. The cold-pressed samples were annealed at 700 °C in an argon atmosphere for 1h.

The second applied densification process of the composite powders was SPS. The powders with 90 wt%Ag were SPSed at 400, 550 and 650 °C. Also, the powders with 10 wt%Ag were SPSed at 700, 800 and 900 °C. The SPS processes were carried out in a vacuum
with a heating rate of 10 Kmin\(^{-1}\) for 10 min. The morphologic and microstructural evaluations of the powders and sintered samples were carried out by field emission scanning electron microscopy (FESEM MIRA 3 TESCAN, Czech Republic) equipped by energy dispersive spectrometer. The phase of the milled and heat-treated powders was identified by X-ray diffraction analysis (Philips XRD PW1730) with a Cu\(\alpha\) (1.5404 Å) radiation source over the 2\(\theta\) range 20-80° in reflection geometry. The densities of the sintered specimen were determined by the Archimedes principle. The hardness of the samples was measured by a Wilson Wolpert Vickers hardness tester using 1 kgf load for 20s. The three-point flexural test was used to determine the strength of the samples. The flexural strength (\(\sigma\)) of the SPSed samples was determined using the following equation [28]:

\[
\sigma = \frac{3FL}{2bh^2}
\]  

(1)

where \(F\) is the load, \(l\) is the span and \(b\) and \(h\) are the breadth and height of the specimen, respectively.

Fig. 1. FESEM micrograph of the starting powders: (a) Ag\(_2\)O (b) Al\(_2\)O\(_3\).

3. Results and Discussion

3.1. Mechanical Milling and Thermal Behavior of the Powder mixtures

Fig. 2. FESEM micrograph and elemental map analysis of the milled powders for 16 h (a) Al\(_2\)O\(_3\) rich powders (b) Ag\(_2\)O rich powders.
Fig. 2 shows the FESEM micrograph and corresponding elemental map analysis of the milled powders for 16 h. As it is observed, the mechanical milling has led to a reduction of particle size for both groups of the samples. The brittleness of the oxide particles (i.e. Ag$_2$O and Al$_2$O$_3$) was improved the particle size reduction of the powder mixtures during mechanical milling. However, according to the map analysis, the dispersion of the constituents within the microstructure of the powders with higher wt% of Al$_2$O$_3$ (Al$_2$O$_3$ rich samples) is more homogenous than that of the other sample which might be due to higher vol% of the hard phase (i.e. alumina) in this group of the samples. The reduction of powder particle size enhances the driving force of the sintering process by increasing the specific surface of the powder particles. Furthermore, the homogenous dispersion of the elements in the microstructure of the powder would lead to the synthesis of a sintered microstructure with fine and homogenous dispersion of the constituents.

Fig. 3 shows the STA (TG/DTA) curves of the milled powders. The TG curve shows a 7% weight loss up to about 410°C. However, above this temperature, no further weight loss can be detected. According to the TG curve, the weight loss process includes two stages: The first stage is from room temperature to about 300 °C and the second one is in the range of 300 to 410 °C. It can be said that the weight loss of the sample is because of the thermal decomposition of Ag$_2$O to Ag. However, the theoretical calculation shows about 6% weight-losses which is about 1% lower than that of the experimental value. According to the results, it can be concluded that the difference of the experimental weight-loss value and that of the theoretical one, is due to the evaporation of the physically absorbed water of the powder particles. So, it can be concluded that the first stage of the weight loss process which has been occurred at relatively low temperatures, is related to the evaporation of the physically absorbed water and the second one which has been accompanied by a DTA peak at about 365 °C, is corresponded to thermal decomposition of Ag$_2$O to Ag. However, according to the thermal analysis results, the milled samples were heat-treated at 365 °C. The XRD patterns of the heat-treated samples are shown in Fig. 4. According to the patterns, the powders have consisted of Ag and Al$_2$O$_3$ which implies the thermal decomposition of Ag$_2$O to Ag.

Fig. 3. TG/DTA curves of the milled powders.
3.2. Microstructure and mechanical properties of the sintered samples

The relative densities of Ag/10wt% Al₂O₃ and Ag/90wt% Al₂O₃ pressureless sintered samples were 70 and 64 %, respectively. According to the sintering temperatures (800 and 1150 °C), the Ag/10wt% Al₂O₃ and Ag/90wt% Al₂O₃ samples were sintered at the solid and liquid states, respectively. However, in both groups of samples, a high volume of porosities exists within the microstructure of the sintered specimen. Noteworthy that higher sintering temperature leads to evaporation of silver [29] which is not the desired phenomenon.

The mechanism of densification is not similar in the solid and liquid states. In the solid-state, atomic diffusion is responsible for the densification of powder compacts during the sintering process. On the other hand, the rearrangement of the solid particle by the molten phase is the main phenomenon that leads to densification at the liquid state for the powders with negligible mutual solubility like Ag and Al₂O₃ [30]. The fine dispersion of Ag within the microstructure due to mechanical milling might be led to increasing the capillary forces and as a result better rearrangement of Al₂O₃ particles. However, it seems that in the current investigation, the relatively low volume percent of the liquid phase (i.e. molten Ag) has not led to an effective rearrangement of the solid particles (i.e. Al₂O₃). So, the relative sintered density of the synthesized composites is not so high.

Fig. 5 shows the relative density of Ag/10wt% Al₂O₃ composites as a function of cold-pressed magnitude. As it is observed, by increasing the cold press pressure, the relative density of the samples was increased. However, it can be stated that increasing the cold press pressure from 500 to 700 MPa, has no significant effect on further densification of the sintered composites which might be due to the high percentage of work hardening of the cold-pressed sample. As known, by increasing the work hardening in a cold-worked sample, the necessarily applied load for densification is increased. However, higher cold press pressures maybe led to the failure of the work-hardened sample. To increase the ductility of the work-hardened samples, the cold-pressed by 500 MPa samples were annealed at 700 °C. The
relative density of the annealed sample was 84% which is higher than that of the cold-pressed samples. It seems that annealing the cold-pressed sample has led to further sintering of the samples at solid-state and decreasing the volume percent of the porosities. This phenomenon is due to the diffusion of the atoms at the solid-state and eliminating the microstructural porosities. Higher annealing temperatures or longer annealing time might be led to more densification.

Fig. 5. The relative density of Ag/10wt% Al₂O₃ composites vs. cold press magnitude.

Fig. 6 shows the relative density of the SPSed samples as a function of sintering temperature. As it is shown, by increasing the sintering temperature, the relative density of the sintered samples was increased. However, the relative density of the sample with relatively higher weight Ag percent is much higher than that of the other sample. As known, various phenomena such as creep and plastic flow are responsible for the densification of the powder compacts during the sintering process [22, 31]. The mentioned mechanisms are accelerated by increasing the SPS temperature. Furthermore, by elevating the process temperature, better necks are formed between the powder particles due to the higher diffusion coefficient of the atoms. However, it can be stated that by increasing the volume percent of the constituents with relatively lower melting temperature, the densification of the powder compacts is enhanced. According to results, unlike the Ag/10wt% Al₂O₃ composites, the relative density of the Ag/90wt% Al₂O₃ sintered samples is not the desired value. Commonly, the conventional sintering of Al₂O₃ rich Ag/Al₂O₃ composites is conducted at higher temperatures which are about 600 °C higher than the applied SPS sintering temperature in the current research [15, 29]. It seems that for the synthesis of an Al₂O₃ rich composite with higher relative density at relatively low sintering temperatures, the other SPS parameters such as the applied pressure during the sintering process and the time of SPS should be optimized in further investigations.

Fig. 6. The relative density of the SPSed samples as a function of sintering temperature.
Fig. 7 (a, b) shows the FESEM micrograph (BSE Mode) and elemental map analysis of the SPSed and annealed samples with 90 wt% Ag. According to the map analysis, the bright continuous phase stands for Ag and the black regions represent the homogenous and fine dispersed Al₂O₃ particles within the Ag matrix. The bright view of Ag rich regions is due to a higher density of silver respect to alumina which scatters a higher quantity of the backscattered electrons. The homogeneity of the reinforcement within the matrix phase leads to the synthesis of a composite with the uniform property. However, it can be stated that some of the black regions stand for the microstructural porosities. According to the FESEM micrographs, the size of the Al₂O₃ particles in the SPSed samples is lower than that of the annealed sample. This might be due to the effect of densification mechanisms like the plastic flow on the size of the reinforcement particles during SPS. A model has been proposed in this regard in other work [26]. Fig. 7c shows the FESEM micrograph and elemental map analysis of the Ag/90wt% Al₂O₃ SPSed samples. According to the microstructural images, in this group of composites, the Ag particles which their size is mainly below 10 µm are dispersed within the Al₂O₃ matrix phase. In other words, a ceramic matrix composite (CMC) has been formed. Unlike the samples with high weight percent of Ag, the porosities are more obvious in this group of samples. Furthermore, some neck like regions can be detected between the Al₂O₃ particles. However, the desired integrity of the matrix phase could not be observed in the corresponding microstructural images in this group of composites.

Fig. 8 show the hardness of the SPSed, cold worked and annealed samples. As it is seen, the hardness of the annealed Ag/10wt% Al₂O₃ sample is higher than that of the cold-worked one which seems to be due to higher relative density or in other words lower volume fraction of the annealed samples. The notable point is that although the relative density of the annealed samples is about 3 % higher than that of the cold-worked ones; the difference of the
hardness between these groups of samples is about 30 Vickers. In other words, a 3% increase in the relative density value has led to a more than 35% increase in the hardness value. However, according to the results, the hardness of the SPSed samples is higher than the pressureless sintered ones. Other than the higher relative density, the higher hardness of the SPSed samples compared with the annealed ones might be due to the lower size of Al₂O₃ particles as the reinforcement in this group of the specimen (Fig. 7a, b). Fig. 9 shows the typical curves of the flexural strength (stress versus strain) for the SPSed samples which had the highest relative densities among the processed composites. The strength of the samples with 10 and 90 wt% Ag are 94 and 264 MPa, respectively. According to the results, the strength of Ag/10wt% Al₂O₃ composites is much higher than that of the Ag/90wt% Al₂O₃. In other words, the strength of the composite with a higher vol% of the high strength phase (i.e. alumina) is about one-third of the other sample which implies the detrimental effect of porosities on the mechanical properties of the CMCs.

![Hardness comparison](image1)

**Fig. 8.** Hardness of different samples.

![Flexural strength curves](image2)

**Fig. 9.** Typical curves of flexural strength for the SPSed samples.

Fig. 10 (a, b) shows the fractured surface of the sintered samples in BSE mode. As it is seen, the fractured surfaces of the samples show different features. According to Fig. 10a, the outstanding point in the microstructure of Ag/90wt% Al₂O₃ samples is the bridging phenomenon in the alumina matrix that occurred in the presence of silver particles. Silver ductile particles capable of plastic deformation well above the ceramic matrix, by placing in the crack growth pathway, spend part of their energy on the local plastic strain and increase
the toughness of the alumina matrix. In other parts of the microstructure, in addition to their proper bonding to alumina, silver particles, due to their ductility, do not participate in the brittle fracture mechanism and improve the mechanical properties of alumina. On the other hand, the microscopic images of specimens containing 90% silver show a relatively sintered microstructure with good integrity. In this group of the samples, the grain size is smaller in comparison with the former and the formation of effective bonds between the particles at the applied temperature and pressure during the SPS process reduces the porosity and increases the strength of the sample. Besides, in this case, the main fracture mechanism of the specimen is a ductile fracture. In the fracture surface image of this sample, the crack growth path, unlike the alumina sample, was not straight and the crack did not pass through the grains (intragranular). The rough surface in the fracture surface image indicates the growth of cracks in the inter-granular path and led to removing particles from the matrix.

Fig. 10. Fractured surface of (a) Ag/90wt% Al₂O₃ samples. A bridging phenomenon in alumina matrix which occurred in the presence of silver particles (Dotted line) and well sintered silver grains to the alumina particles (red arrows) (b) Ag/10wt% Al₂O₃ samples. The crack growth path is shown by a dotted circle.
4. Conclusion

Ag/10wt% Al₂O₃ and Ag/90wt% Al₂O₃ composites were synthesized by mechanical milling, heat treating and sintering of Ag₂O/Al₂O₃ powder mixtures. The heat-treated powders were consolidated by conventional and spark plasma sintering processes at relatively low temperatures. The microscopic evaluations confirmed a homogenous and fine dispersed of the second phase within the matrix of the SPSed samples. Moreover, the relative density and mechanical properties of the SPSed samples including hardness and flexural strength were much higher than those of the conventional processed ones. The results confirmed that the SPS process is a preferred densification process for the synthesis of Ag/10wt% Al₂O₃ composite. However, according to the achievements of this research, the applied SPS parameters and especially the sintering temperature did not result in the synthesis of an Ag/90wt% Al₂O₃ composite with dense microstructure and desired mechanical properties.

5. References

1. A. C. Krzemień, L. Burzyńska, M. Galanty, Powder Metall. 52 (2009) 49.
2. ASM Handbook Committee, Powder Metal Technologies and Applications (ASM Handbook Vol. 7). ASM International: USA, (1998).
3. X. Wang, H. Yang, M. Chen, J. Zou, S. Liang, Powder Tech. 256 (2014) 20.
4. F. Y. Chen, Y. Feng, H. Shao, B. Li, G. Qian, Y. F. Liu, X. B. Zhang, Powder Metall. 56 (2013) 397.
5. M. Ardestani, Int. J. Mater. Res.106 (2015) 1294
6. N. Mansourirad, M. Ardestani, M. Reza Afshar, Sci Sintering, 50 (2018) 323.
7. A. K. Dutta, A. B. Chattopadhyaya, K. K. Ray, J. Mater. Sci. Lett. 20 (2001) 917.
8. X. M. Liu, S. L. Wu, P. K. Chu, C. Y. Chung, J. Zheng, S. L. Li, Mater. Chem. Phys. 98 (2006) 477.
9. Z. Guan, I. Hwang, X. Li , Procedia Manuf. 26 (2018) 146.
10. P. Jaimeewong, P. Ngernchuaklin, O. Khamman, T. Dechakpt, Ferroelectr. 457 (2013) 153
11. I. Turcan, V. Lukacs, L. Curecheriu, L. Padurariu , C. E. Ciomaga, M. Airimioaei, G. Stoian, N. Lupu, L. Mitoseriu, J. Eur. Ceram. Soc. 38 (2018) 5420.
12. C. Xu, D. Yi, C. Wu, H. Liu, W. Li, Mater. Sci. Eng. A 538 (2012) 202.
13. W. Wasserbach, W. Skrotzki, Materialia 5 (2019). Article 100175
14. F. A.Costa, A. G. P. Silva, U. U. Gomes, Powder Technol. 134 (2003) 123.
15. E. R.Rangel, A. P. Fuente, J. A. R. Garcia, I. E. Guel, R. M. Sánchez, Can. Metall. Q. 56 (2017) 332.
16. L. Zhang, J. Xiao, K. Zhou, Tribol. Trans. 55 (2012) 473.
17. M. Ardestani, Materiali in tehnologije/Mater Tech. 50 (2016) 281.
18. D. Guzman, C. Aguilar, P. Rojas, J. M. Criado, M. J. Dianez, R. Espinoza, A. Guzman, C. Martinez, Trans. Nonferrous Met. Soc. China 29 (2019) 365.
19. T. Yang, Z. Du, Y. Gu, J. Cent. South Univ. Technol. 14 (2007) 176.
20. M. Ardestani, F. Karpasand, Sci Eng Compos Mater 25 (2018) 739.
21. M. Ardestani, M. Zakeri, M. J. Nayyeri, M.R. Babollhavaejie, Mater. Sci. Poland 32 (2014) 121.
22. H. Desplats, H. E. Brisson, P. Rogeon, P. Carre, A. Bonhomme, Rare Met. 38, (2019) 35.
23. X. Chen, C. Jia, X. Liu, Rare Met.29 (2010) 366.
24. Z. Lin , S.Liu , X. Sun, M. Xie, J. Li, X. Li, Y. Chen, J. Chen, D. Huo, M. Zhang, Q. Zhu, M. Liu, J. Alloy Compd. 588 (2014) 30.
25. E. Rahimi, M. Ardestani, M.M. Goudarzi, A. Abbasi, Mater. Chem. Phys.223 (2019) 805.
26. A. Heydarian, S.A. Sajjadi, F. Kern, M. Johnsson, Mater. Sci Tech.35 (2019)1204.
27. S. Sovizi, M.E. Seraji, Sci. Sintering 51 (2019) 135.
28. K. K.Chawla, Composite Materials Science and Engineering, Springer, (2012).
29. A. K. Dutta, A.B. Chattopadhyaya, K. K. Ray, J. Mater. Sci. Lett.19 (2000) 1501.
30. R. M. German, Powder Metallurgy and Particulate Materials Processing, Princeton, Metal Powder Industries Federation, (2005).
31. M. Naghikhani, M. Ardestani, M. M. Goudarzi, Met. Mater. Int. (In Press doi.org/10.1007/s12540-019-00564-0).
32. S. Memari, M. Ardestani, A. Abbasi, Arch. Civ. Mech. Eng. 18 (2018) 1013.

Сажетак: У овом раду, испитивано је синтеровање Ag/Al₂O₃ млевених прахова са 10 и 90 wt.%Ag. Прахови су синтеровани употребом два различита процеса, конвенционалним и синтеровањем у плазми. Конвенционално синтеровани композити са 90 wt.%Ag су додатно третирани хладним пресовањем и загревањем на 700 °C. Микроструктура је доказала фино дисперговане конституенте унутар композита који је синтерован у плазми. Даље, резултати указују да су релативна густина, тврдоћа и отпорност на савијање много већи код узорака добијених синтеровањем у плазми. Тврдоћа и отпорност на савијање Ag/10wt.% Al₂O₃ узорка синтерованог у плазми на 650 °C су 146 HV и 264 MPa, истим редом. Ипак, за разлику од композита са 90 wt.%Ag, температуре синтеровања нису довеле до синтезе Ag/90wt.% Al₂O₃ композита са жељеним својствима.

Кључне речи синтеровање у плазми; Ag/Al₂O₃ композити; механичко млевење; згушњавање; микроструктура.

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