Kovove Mater. 51 2013 367–371
DOI: 10.4149/km_2013_6_367

Compaction and solid state sintering behavior of Cu-20wt.%ZnO powders

M. Ardestani*

Department of Materials Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received 1 November 2012, received in revised form 5 September 2013, accepted 30 September 2013

Abstract

In this research, compaction behavior and solid state sinterability of Cu-20wt.%ZnO powders were investigated. The compressibility of the powders was evaluated using Heckel and Panelli-Ambrosio equations. The powders were compacted uniaxially by 50, 100, 200 and 300 MPa at room temperature. The cold compacted powders were sintered at 850 and 1000 °C. The results showed that by increasing cold compaction pressure and sintering temperature the density of sintered compacts improved significantly. Additionally, it was found that the largest increase of density during sintering process was observed in the samples with relatively low green densities. The microstructural evaluation of the sintered samples by scanning electron microscopy (SEM) demonstrated that increasing the sintering temperature and cold compaction pressure resulted in decreasing the volume fraction of the pores and also their dimensions. However, it was confirmed that sintering temperature had more effective role on elimination of porosities rather than cold compaction pressure. The highest density was achieved for the samples which were compacted by 300 MPa and sintered at 1000 °C.

K e y w o r d s: metal matrix composites (MMC), powder consolidation, sintering

1. Introduction

Copper matrix composites are widely used in different industrial applications such as frictional break parts, contact electrode materials and spot welding [1–3]. In this kind of composites the second phase or the reinforcement can be a metal like tungsten or a ceramic compound such as tungsten carbide or alumina. Copper matrix composites are mainly produced by powder metallurgy (P/M) process which in many cases is more competitive than other fabrication processes like stamping, casting or machining. The P/M route which is applied for fabrication of copper matrix composites mainly includes mixing, cold compaction and sintering the starting powders. The cold compacted powders may be sintered in solid or liquid phase state. The solid state sintering is carried out below 1083 °C which is the melting point of copper. In this process, the main mechanism of densification and bonding the particles is atomic diffusion. However, in the liquid phase sintering, melting of copper and rearrangement of the reinforcement particles leads to relatively high densification [4–9].

Recently, a novel kind of Cu composites containing zinc oxide (ZnO) as the second phase were synthesized and characterized by Wang et al. [10]. The synthesis procedure included mixing, milling, cold compaction and sintering of Cu and ZnO powders. Cu-ZnO composites due to high hardness and high thermal stability of ZnO and excellent electrical conductivity of copper have a combination of the mentioned properties which are desired in electrical contact materials. However, like the other materials which are produced by powder metallurgy processes, the final density of sintered compacts influences significantly the properties of Cu-ZnO composites. Cold compaction magnitude and sintering temperature are effective parameters on the final density of the sintered compacts.

In the present study, compaction behavior of Cu-20wt.%ZnO powder mixtures was studied. Also, the effect of cold press magnitude and sintering temperature on the density of the solid state sintered powder

*Corresponding author: e-mail address: ardestani80@gmail.com

compacts were investigated. The compaction behavior of the powder mixtures was evaluated using Heckel and Panelli-Ambrosio equations [11]:

$$\ln\left(\frac{1}{1-D}\right) = KP + B, \tag{1}$$

$$\ln\left(\frac{1}{1-D}\right) = KP^{1/2} + B, \tag{2}$$

where D is the relative density, P is the compaction pressure and K and B are constants.

2. Experimental

Copper and zinc oxide powders were used as starting powders. The as-received powders were mixed and ground manually for 240 s using an agate mortar and pestle. The ground powders were uniaxially compacted by 50, 100, 200 and 300 MPa in a 13 mm diameter die. In order to compare the compaction behavior of the mixed powders with pure zinc oxide powder, ZnO powders were ground and compacted applying the above mentioned processes. Subsequently, Cu-ZnO compacts were sintered in a tube type electrical furnace in argon atmosphere at 850 and 1000 ℃ for 1.5 h. Green and sintered densities were determined from mass, diameter and thickness of the cold pressed and sintered compacts, respectively. The theoretical density of Cu-20wt.%ZnO composites was determined using the following formulae [12]:

$$\rho_{\mathrm{Cu-20wt.\%ZnO}} = \frac{\rho_{\mathrm{Cu}}\rho_{\mathrm{ZnO}}}{\rho_{\mathrm{Cu}}W_{\mathrm{ZnO}} + \rho_{\mathrm{ZnO}}W_{\mathrm{Cu}}}, \tag{3}$$

where ρ_{Cu} is density of copper, ρ_{ZnO} is density of zinc oxide, and W_{Cu} and W_{ZnO} are mass fractions of copper and zinc oxide, respectively.

The microstructures of the powders and the sintered samples were investigated by scanning electron microscopy (SEM-PHILIPS-XL30).

3. Results and discussion

Figure 1 shows the microstructure of Cu-ZnO powders at two magnifications. As it is shown, the particles have cubic, semi spherical and cylindrical shapes and are highly agglomerated. Also, the size of the particles is mainly below 2 µm. Figure 2 shows the effect of cold pressure magnitude on the relative density of the green compacts. As it can be seen, by increasing the uniaxial pressure, the density of the samples is increased. However, increasing the density of Cu-ZnO powder mixtures by pressure is higher than

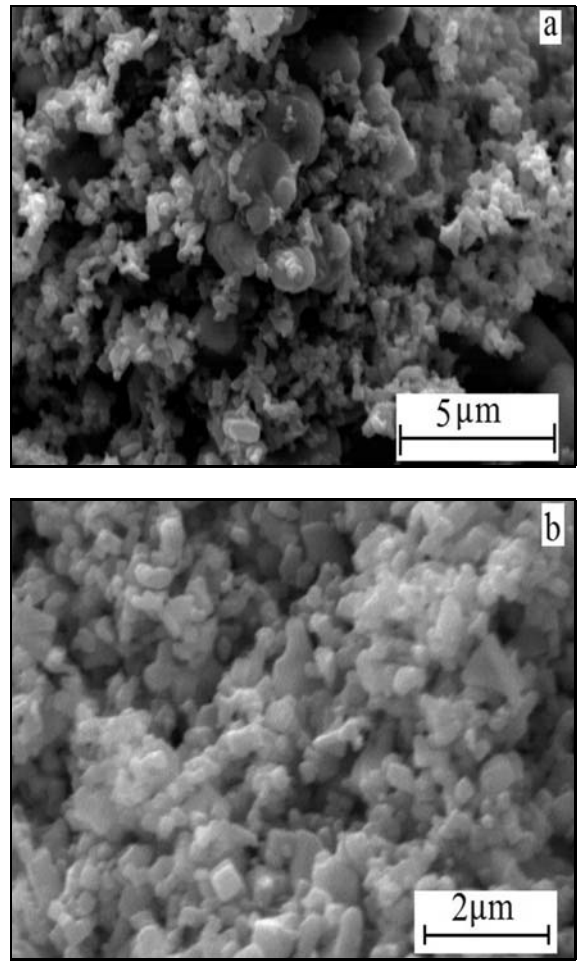

Fig. 1a, b. SEM image of Cu-ZnO powder mixtures.

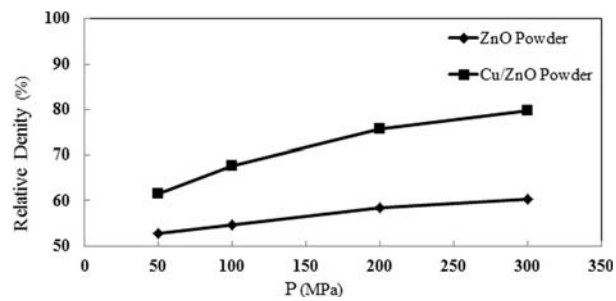

Fig. 2. The effect of uniaxial pressure on the relative density of Cu-ZnO and ZnO powders.

pure zinc oxide powders. This is due to existence of copper in the mixed powders which is a ductile phase and deforms during compaction. Plastic deformation of copper during cold compaction helps the densification of the composite powders.

The curves of Fig. 3a,b are related to Heckel and Panelli-Ambrosio equations. The amount of corresponding correlation coefficient (R^2) of each curve is

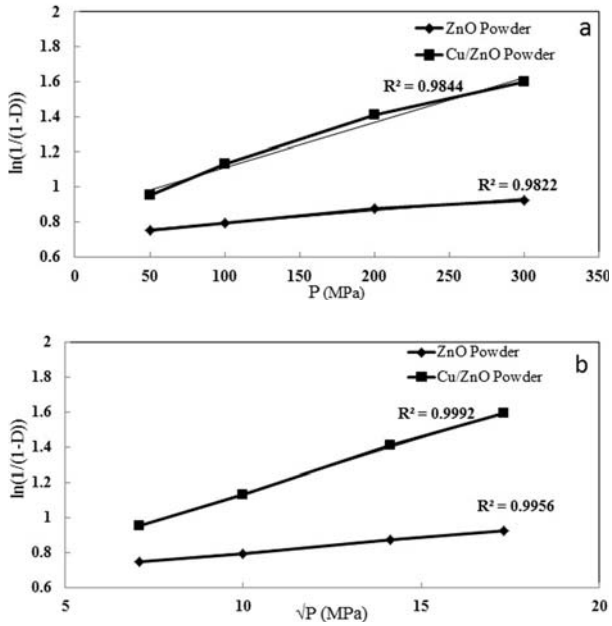

Fig. 3. (a) $\ln\left(\frac{1}{1-D}\right)$ versus uniaxial pressure compaction magnitude (P) (Heckel equation), (b) $\ln\left(\frac{1}{1-D}\right)$ versus the square root of uniaxial pressure compaction magnitude ($\sqrt{P}$) (Panelli-Ambrosio equation) for Cu-ZnO and ZnO powders. R^2 values represent the correlation coefficients.

given in this figure which shows higher accuracy of Panelli-Ambrosio rather than Heckel equation. Furthermore, the R^2 values of ZnO powder are lower than those of Cu-ZnO powder mixtures. This result is in good agreement with the result of Abdoli et al. [11] who investigated the compaction behavior of Al--AlN powder mixtures. They showed that the amount of correlation coefficient for the curve of $\ln\left(\frac{1}{1-D}\right)$ versus (P or $\sqrt{P}$) for Al-AlN mixture was higher than that of pure Al.

Figure 4 shows the relative densities of different sintered specimens. According to this figure, the samples which were cold compacted by 300 MPa and sintered at 1000 ℃ had the highest density among the sintered samples. Also, the lowest density was obtained for the samples which were cold pressed and sintered at 50 MPa and 850 ℃, respectively. The effect of cold press magnitude and sintering temperature on the relative density of sintered compacts is shown in Fig. 5. As it is shown in this figure, by increasing the cold compaction magnitude and sintering temperature, the final density of the sintered samples was increased. Increasing of the density was due to solid state sintering of the green compacts at 850 and 1000 ℃. During this process, dimensions of the interparticle pores were decreased. However, small pores might be eliminated during this procedure. Size reduction and elimination of the pores was due to diffusion of atoms from the bulk to the neck like region between the powder particles (Fig. 6). The driving force of this phenomenon was the higher concentration of voids upon the neck which was due to existence of a tensile force in this region. The magnitude of the mentioned force is calculated using the following formulae [13]:

$$\sigma = \gamma\left(\frac{1}{x} + \frac{1}{d}\right), \tag{4}$$

where γ is surface tension and x and d are the radii of surface curvatures (Fig. 6).

Figure 7 shows the difference between green and sintered densities for different samples. This figure shows that increasing of density for the samples which were sintered at 1000 ℃ was higher than for those which were sintered at 850 ℃. This observation was due to higher diffusion rate of atoms at higher tem-

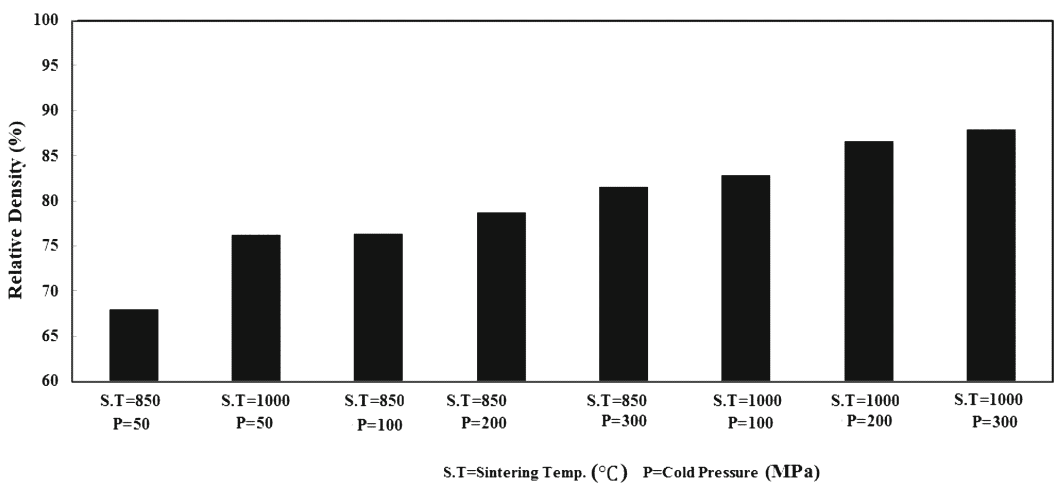

Fig. 4. Relative density of different specimens.

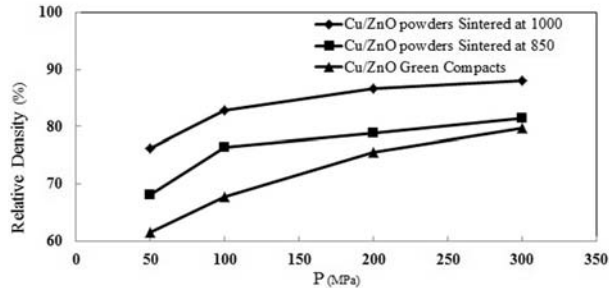

Fig. 5. Effect of cold press magnitude and sintering temperature on the relative density of sintered compacts.

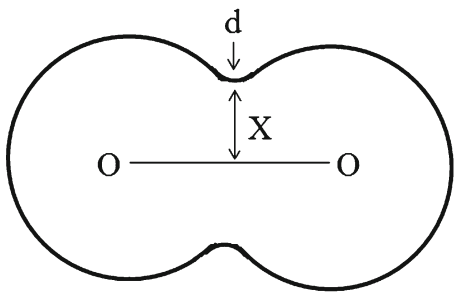

Fig. 6. Schematic illustration of solid state sintering between two spherical particles [13].

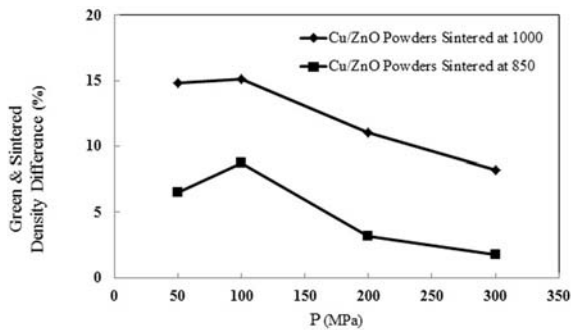

Fig. 7. Difference of green and sintered densities for different samples.

peratures which led to more densification. Also, as it can be seen in this figure, the samples which were compacted by relatively low uniaxial pressures (i.e. 50 and 100 MPa) before sintering showed higher densification during sintering process. In other words, reduction of porosities' volume in this group of samples was higher than that of other specimens. This phenomenon might be due to higher volume fraction of voids in the neck like regions of the mentioned samples which resulted in higher driving force for diffusion of atoms to the neck. More investigations should be done to confirm this finding and conclusion.

The microstructure of the densest samples which were compacted by 300 MPa and sintered at 1000 ℃ is

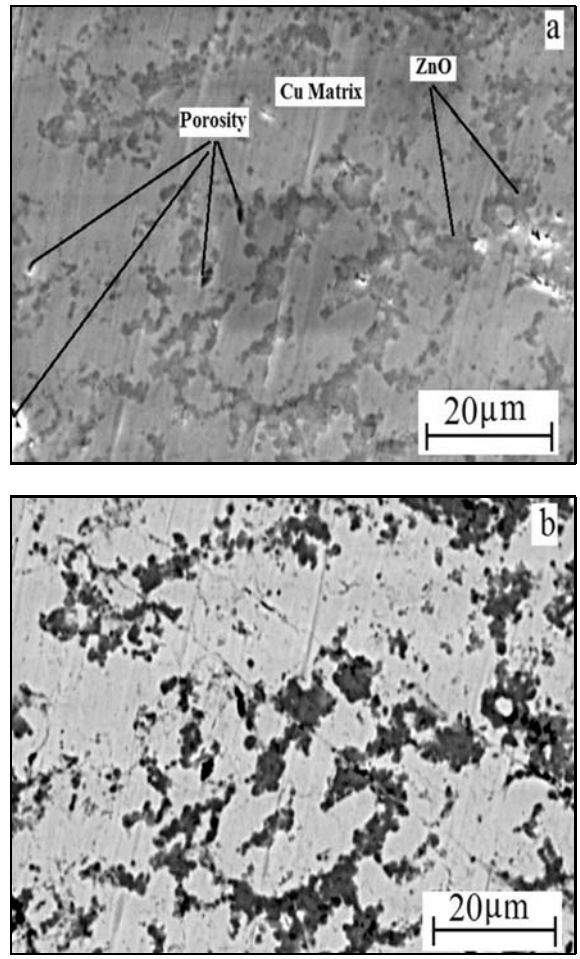

Fig. 8. (a) Secondary electron (SE) SEM image of the sample which was cold pressed by 300 MPa and sintered at 1000 ℃. (b) Back scattered electron (BSE) SEM image of (a). The Copper matrix is white, ZnO is gray and porosities are black.

shown in Fig. 8. Three distinct regions can be detected in the sintered structures: (1) Matrix phase which is copper, (2) Reinforcement which is ZnO, and (3) Porosities which are observed in Cu-ZnO interfaces and also ZnO phase. It seems that the applied cold compaction pressure and sintering temperature were suitable for densification of copper matrix phase. However, the mentioned conditions were not appropriate for consolidation of ZnO phase. The microstructures of two other samples which were compacted by low pressure and sintered at low temperature are shown in Fig. 9. The comparison of Figs. 8 and 9 indicates that increasing the compaction pressure and sintering temperature leads to decreasing the volume fraction and dimensions of porosities within the microstructure.

The obtained results confirm that both cold compaction pressure and sintering temperature are important parameters for densification of Cu-ZnO

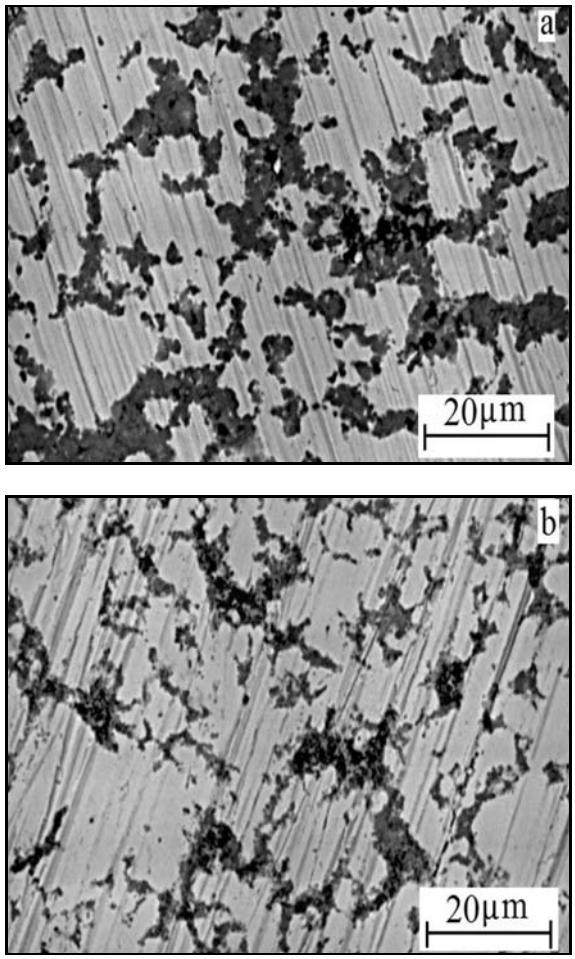

Fig. 9. Back scattered electron (BSE) SEM image of (a) sample which was cold pressed by 200 MPa and sintered at 1000 °C, (b) sample which was cold pressed by 300 MPa and sintered at 850 °C.

powder mixtures. However, the latter one is more effective and has a significant effect on consolidation of the specimens. Moreover, it seems that in order to synthetize dense structures with high relative densities, the samples should be repressed and resintered.

4. Conclusion

In this article, compressibility and solid state sintering behavior of Cu-20wt.%ZnO powders were investigated. Compaction behavior of Cu-20wt.%ZnO powders was studied using Heckel and Panelli-Ambrosio equations. The results showed higher accuracy of Panelli-Ambrosio rather than Heckel equation. Also, it was shown that compressibility of Cu-20wt.%ZnO was higher than of pure ZnO powder which was due to high ductility of copper.

The solid state sinterability of Cu-20wt.%ZnO is highly affected by cold compaction magnitude prior to sintering and also sintering temperature. However, the obtained results confirmed that the latter parameter was more effective than the first one. The microstructure investigations of the sintered specimens indicated that the pores were mainly existed in Cu-ZnO interfaces and also ZnO phase. The volume fraction porosities can be decreased by increasing the cold compaction pressure and sintering temperature.

References

[1] Lenel, F. V.: Powder Metallurgy: Principles and Applications. Metal Powder Industry 1980.
[2] Powder Metal Technologies and Applications. ASM Handbook, Vol. 7, 1998.
[3] Lassner, E., Schubert, W.: Tungsten. New York, Kluwer Academic Publishers 1999. doi:10.1007/978-1-4615-4907-9
[4] Zhao, N., Li, J., Yang, X.: J. Mater. Sci., *39*, 2004, p. 4829. doi:10.1023/B:JMSC.0000035321.65140.14
[5] Andic, Z., Korac, M., Tasic, M., Raic, K., Kamberovic, Z.: Kovove Mater., *44*, 2006, p. 145.
[6] Ardestani, M., Arabi, H., Rezaie, H. R., Razavizadeh, H.: Int. J. Refract. Met. Hard Mater., *27*, 2009, p. 796. doi:10.1016/j.ijrmhm.2009.01.001
[7] Ardestani, M., Rezaie, H. R., Arabi, H., Razavizadeh, H.: Int. J. Refract. Met. Hard Mater., *27*, 2009, p. 862. doi:10.1016/j.ijrmhm.2009.04.004
[8] Ardestani, M., Arabi, H., Razavizadeh, H., Rezaie, H. R., Mehrjoo, H.: Mater. Sci. Poland, *28*, 2010, p. 413.
[9] Upadhyaya, G. S.: Powder Metallurgy Technology. Cambridge International Science Publishing 2002.
[10] Wang, Q. Z., Cui, C. X., Lu, D. M., Bu, S. J.: J. Mater. Sci. Technol., *210*, 2010, p. 497. doi:10.1016/j.jmatprotec.2009.10.012
[11] Abdoli, H., Farnoush, H., Salahi, E., Pourazarang, K.: J. Mater. Sci. Eng., *486* (A), 2008, p. 580.
[12] Li, Z., Jia, C., He, Y., Chen, L.: J. Univ. Sci. Technol. Beijing, *13*, 2006, p. 338. doi:10.1016/S1005-8850(06)60070-4
[13] German, R. M.: Powder Metallurgy and Particulate Materials Processing. Princeton, Metal Powder Industries Federation 2005.