Science of Sintering, **48** (2016) 71-79

doi: 10.2298/SOS1601071H

UDK 692.533.1; 622.785

Cold compaction behavior and Pressureless Sinterability of Ball Milled WC and WC/Cu Powders

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Abstract:

In this research, cold compaction behavior and pressureless sinterability of WC, WC-10%wtCu and WC-30%wtCu powders were investigated. WC and WC/Cu powders were milled in a planetary ball mill for 20h. The milled powders were cold compacted at 100, 200, 300 and 400 MPa pressures. The compressibility behavior of the powders was evaluated using the Heckel, Panelli-Ambrosio and Ge models. The results showed that the Panelli-Ambrosio was the preferred equation for description the cold compaction behavior of the milled WC and WC-30%wtCu powders. Also, the most accurate model for describing the compressibility of WC-10%wtCu powders was the Heckel equation. The cold compacts were sintered at 1400°C. It was found that by increasing the cold compaction pressure of powder compacts before sintering, the sinterability of WC-30%wtCu powder compacts was enhanced. However, the cold compaction magnitude was not affected significantly on the sinterability of WC and WC-10%wtCu powders. The microstructural investigations of the sintered samples by Scanning Electron Microscopy (SEM) confirmed the presence of porosities at the interface of copper- tungsten carbide phases.

Keywords: *WC-Cu composites; Compressibility Behavior; Sintering*

1. Introduction

Generally, the composite materials which are used in electrical industries are made of an excellent thermal and electrical conductive matrix phase like silver or copper and a wear resistant hard reinforcement such as tungsten or tungsten carbide. These kinds of composites are used as oil switches and wiping shoes in power transformers, vacuum interrupters and reclosing devices [1,2]. The conventional synthesis method for this group of metal matrix composites is infiltration of the hard phase porous perform with liquid copper or silver. Unfortunately, infiltration does not result in a homogeneous microstructure and is not a net shape process [3,4]. Another technique which is applied as the production process is included mixing, cold compaction and sintering the starting powders. The sintering temperature of the cold compacts depends on the volume fraction and melting temperature of the constituent with lower melting point. In some cases, in order to obtain a nearly dense structure, the produced compacts may be repressed after sintering [5]. Recently, it was shown that the sinterability of the powders was enhanced significantly by using composite powders instead of the mixture ones [6]. Several methods like such as ball milling [7,8], thermochemical [9]

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sol gel [10] and chemical precipitation [11-13] has been applied for synthesizing fine dispersed composite powders such as W/Cu [14,15], W/Ag[16], Ag/ZnO[17] WC/Cu[18] and Cu/Al_2O_3[19]. The effect of sintering temperature on densification of the composite powders has been investigated by many researchers. However, compressibility behavior and the effect of cold compaction pressure on the sintered density of the powder compacts have not been investigated properly.

In this study, the Heckel, Panelli-Ambrosio and Ge equations were used for evaluation the cold compaction behavior of ball milled WC and Cu/WC powders. Also, the effect of cold compaction pressure or in other words green density magnitude on the final sintered density and sinterability of the powders was investigated.

2. Materials and Methods

Tungsten carbide (Alfa Aesar-United States) and copper (Merck-Germany) powders were used as starting powders. The morphology of the as received powders is shown in fig.1. WC, WC-10%wtCu and WC-30%wtCu powder batches were milled in a planetary ball mill at the milling speed of 400rpm for 20h in argon atmosphere. The ball to powder weight ratio was 15:1. The milling vessels and balls were made of tungsten carbide. The milled powders were cold pressed at 100,200,300 and 400 MPa in a 13mm diameter cylindrical die. The powder compacts were sintered at 1400^{o}C in a tube type furnace in argon atmosphere. The microstructure of the milled powders and sintered samples were investigated by Scanning Electron Microscopy (SEM).

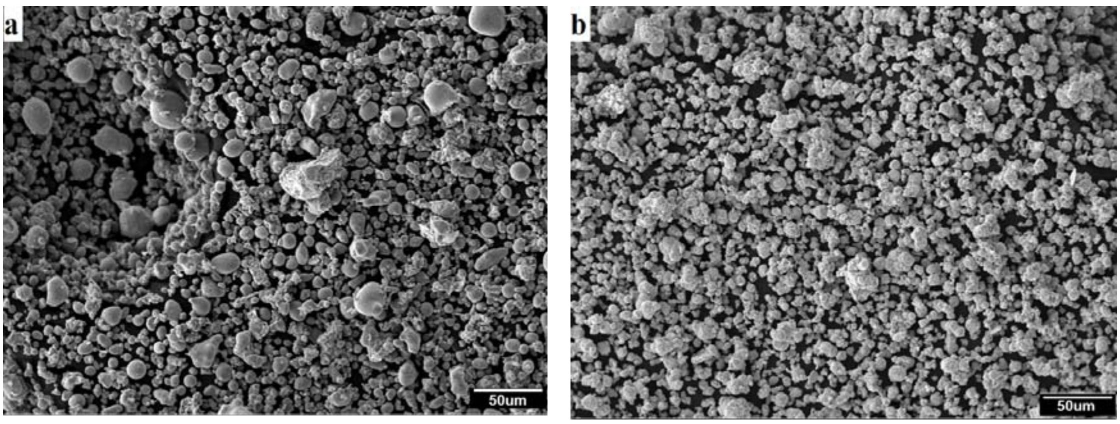

Fig.1. SEM image of the as received powders (a) Copper (b) Tungsten Carbide.

3. Results and Discussion

Fig.2 shows the microstructure of the milled powders. As it can be observed, mechanical milling was due to size reduction and agglomeration of powder particles. However, it seems that increasing the copper content in the powders' composition, was due to higher agglomeration of the powder particles during milling. This observation may be due to cold welding of the powder particles in presence of copper.

Fig.3 shows the effect of cold compaction pressure on the relative green density for different samples. As it is shown, by increasing cold compaction pressure, the relative densities of the powders were increased. However, the slope of corresponding curve for WC-30%wtCu powders is higher than that of other samples. This observation was due to high ductility of copper which was deformed during cold pressing and led to densification and elimination of the structural pores.

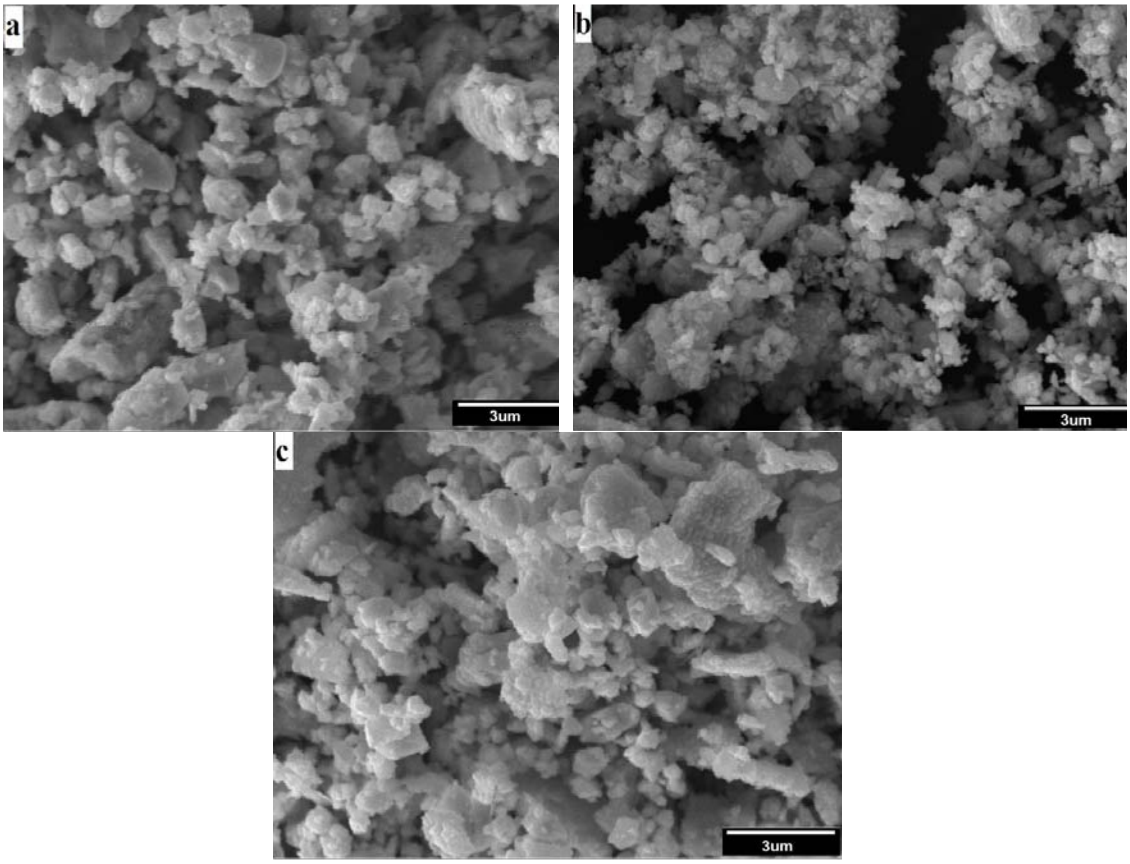

Fig.2 SEM image of the as milled powders (a) WC (b) WC-10%wtCu (c) WC-30%wtCu

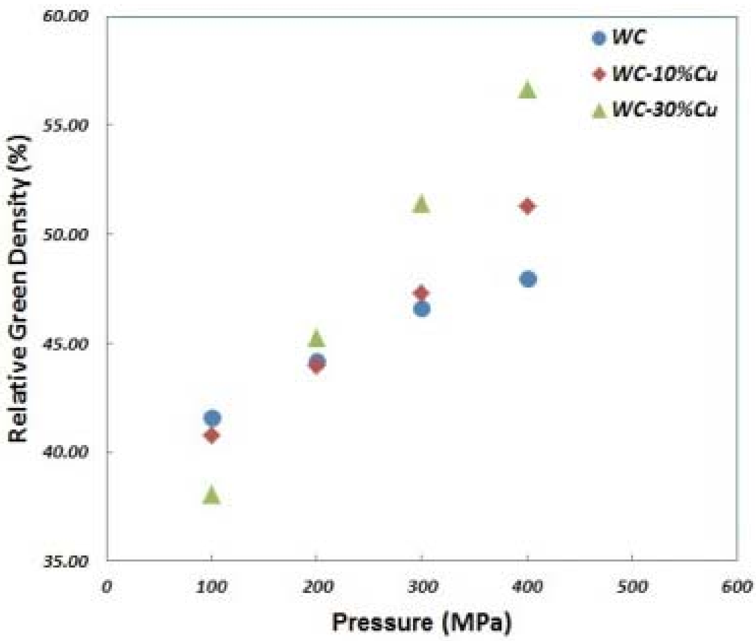

Fig. 3. The effect of cold compaction pressure on the relative green density for different samples.

As mentioned above, in order to analyze the compressibility of the milled powders, the Heckel (1), Panelli-Ambrosio (2) and Ge (3) equations were used [20, 21]:

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

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

$$\log\left(\left(\frac{1}{1-D}\right)\right) = K \ln P + F \tag{3}$$

Where D is the relative density, P is cold pressure and K, B, C and F are constants.

The curves of figs.4, 5&6 are related to the Heckel, Panelli-Ambrosio and Ge equations. The values of correlation coefficient (R^2) for different curves are given in table1. Based on the R^2 values, it can be declared that the Panelli-Ambrosio model provided the best fit scenario for WC and WC-30%wtCu powders. Furthermore, the compaction data of WC-10%wtCu powders was best fitted to the Heckel equation.

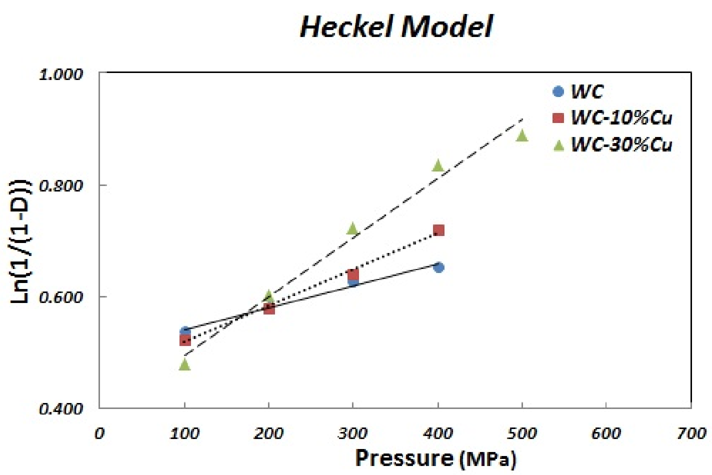

Fig. 4. $\ln\left(\frac{1}{1-D}\right)$ versus uniaxial pressure compaction magnitude (P) for different samples (The Heckel equation).

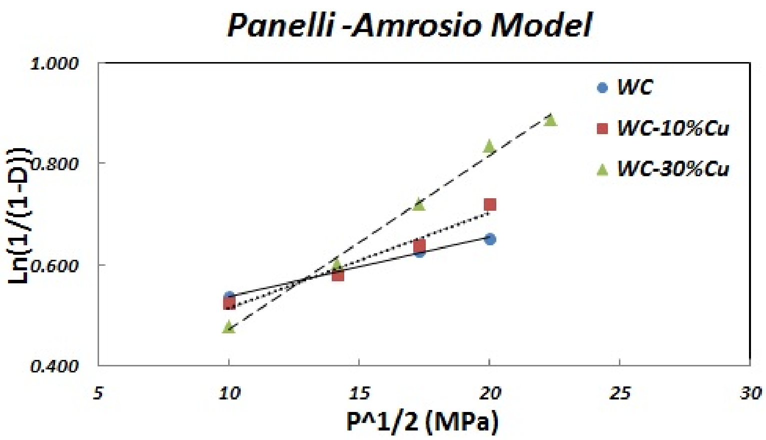

Fig. 5. $\ln\left(\frac{1}{1-D}\right)$ versus the square root of uniaxial pressure compaction magnitude P ½ for different samples (The Panelli-Ambrosio equation).

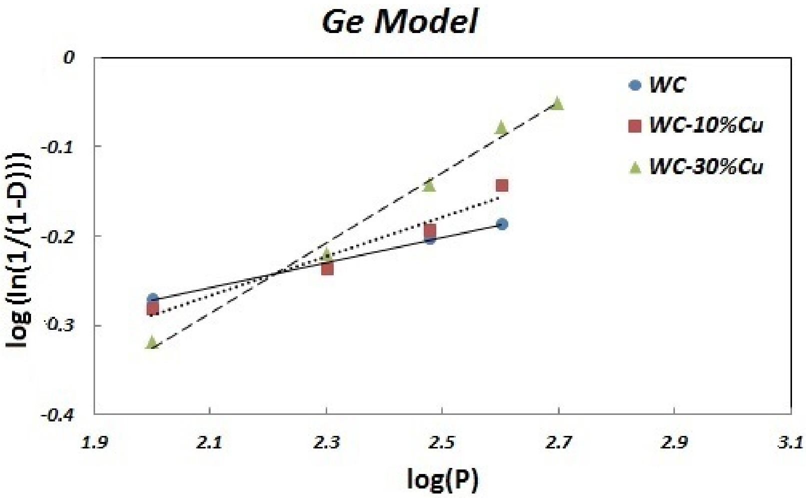

Fig. 6. $\log\left(\ln\left(\frac{1}{1-D}\right)\right)$ versus uniaxial pressure compaction magnitude log (P) for different samples (The Ge equation).

Tab. I. The values of correlation coefficient R^2 for the fitted models.

Powder Composition	Heckel	Panelli-Ambrosio	Ge
WC	0.9863	0.9949	0.9878
WC-10%wtCu	0.9932	0.9686	0.9488
WC-30%wtCu	0.9838	0.9945	0.9933

Fig.7 shows the effect of cold compaction pressure magnitude on the relative density of the sintered samples at 1400°C. According to the obtained results, WC-30%wtCu samples had the highest density among the sintered specimens. The densification of WC/Cu powders was due to formation of molten copper as the liquid phase during sintering process. As it is known, densification during liquid phase sintering (LPS) commonly occurs in three stages: rearrangement, solution-reprecipitation and final stage sintering [5]. However, due to non-solubility of WC in molten copper, the second stage of liquid phase sintering had not an effective role on densification and the rearrangement of tungsten carbide particles by the molten copper was the dominant mechanism for consolidation of WC/Cu powder compacts. Also, the fine dispersion of the constituent within the microstructure of the powder compacts had a positive effect on the rearrangement of the solid particles during liquid phase sintering. The sintering mechanism of WC powders was different from the composite ones. Elimination of structural pores and densification in this group of samples was due to atomic diffusion at the solid state. However, due to high melting point of tungsten carbide and relatively low sintering temperature of the powder compacts, the required energy for atomic diffusion could not be supplied sufficiently. So, the atomic diffusion did not have the expected role on densification and increasing the density of powder compacts during sintering process.

According to the literature [22, 23], during liquid phase sintering, if the volume fraction of the liquid phase does not exceed a definite value, the densification mechanisms of LPS cannot operate properly. However, it seems that the negative effect of this phenomenon on rearrangement is higher than that of the two other stages of LPS. Furthermore, the molten phase may act as a barrier for atomic diffusion between the solid phase particles which is due to deterioration of overall densification during sintering. So, it can be concluded that the low volume percent of the molten copper at the sintering temperature had a negative effect on densification of WC-10%wtCu composite powders. However, the high volume percent of the liquid phase was led to a high sintered density of WC-30%wtCu composite powders.

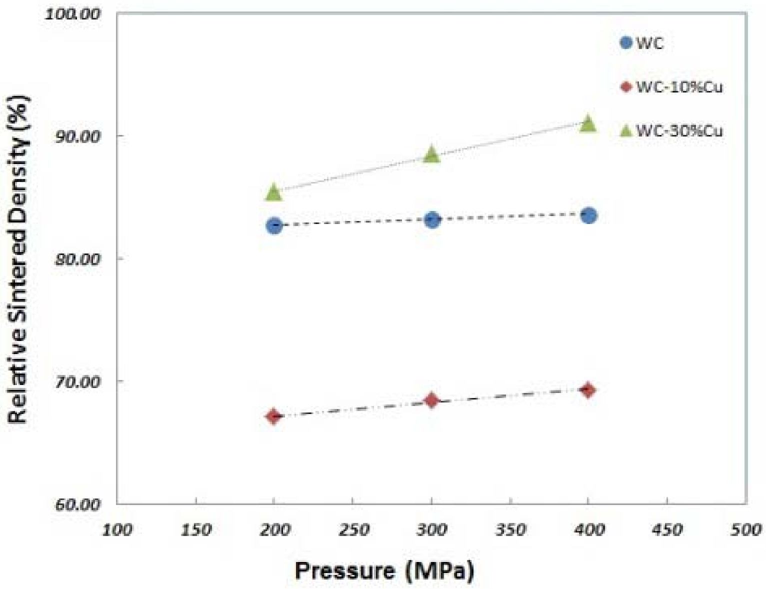

Fig. 7. The effect of cold compaction pressure magnitude on the relative density of the sintered samples at 1400°C.

Sinterability φ of the WC and WC/Cu powder compacts is determined by the following equation [20]:

$$\varphi = \frac{d_s - d_g}{d_{th} - d_g}$$

Where d_{th} , d_g and d_s are theoretical, green and sintered densities, respectively.

Fig.8 shows the sinterabilty of different samples versus cold compaction pressure. As it is shown, the sinterabilty of WC-30%wtCu composite powders was increased by elevating the pressure. However, cold compaction magnitude did not have a significant influence on sinterability of WC-10%wtCu powders. Based on the obtained results, it can be concluded that increasing the magnitude of cold compaction prior to sintering effects significantly on rearrangement of solid particles for the samples with relatively high volume fraction of liquid phase. On the other hand, it can be declared that increasing the compaction pressure had not a sensible effect on sinterability of WC powders at the solid state. The microstructure of the sintered WC powders is shown in fig.9. The black regions are tungsten carbide and the white ones are the particle boundaries. Some of the microstructural porosities are shown by arrows in this figure. As it can be observed, the distribution of the porosities is relatively homogenous within the microstructure. A typical microstructure of the sintered WC/Cu powders is shown in fig.10. The white, gray and black regions are tungsten carbide, copper and porosity regions, respectively. According to this figure, the porosities mainly exist at the interface of copper and tungsten carbide phases and also within the tungsten carbide regions. It seems that for further densification, the powder compacts may be sintered at higher temperatures. However, a finer distribution of the composite powder constituents may be due to decreasing the volume percent of porosities and increasing the relative density of the sintered compacts.

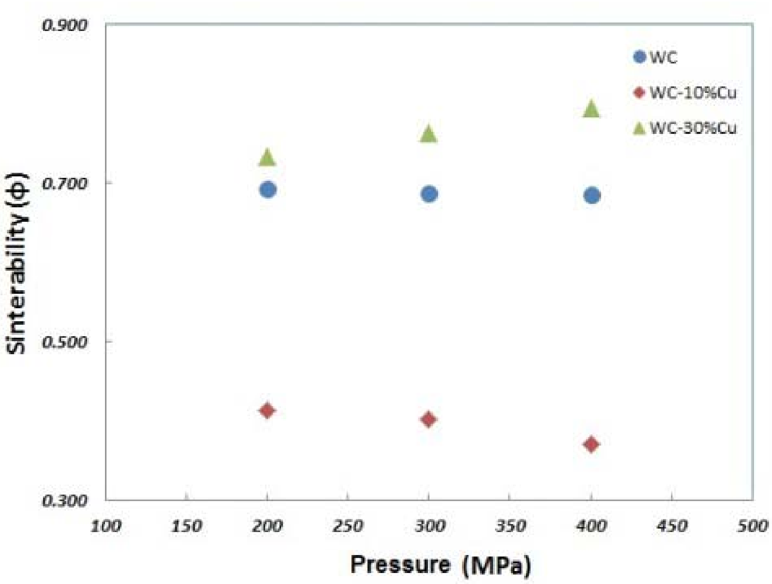

Fig. 8. Sinterability φ of different samples versus cold compaction pressure.

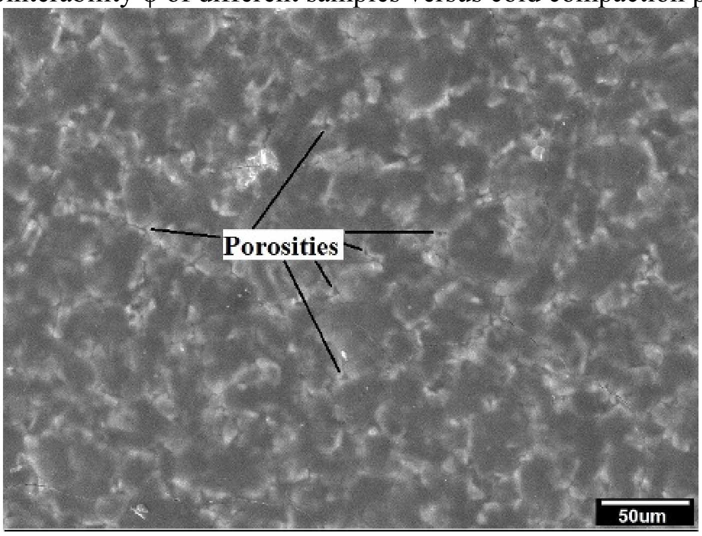

Fig. 9. SEM image of WC sintered samples.

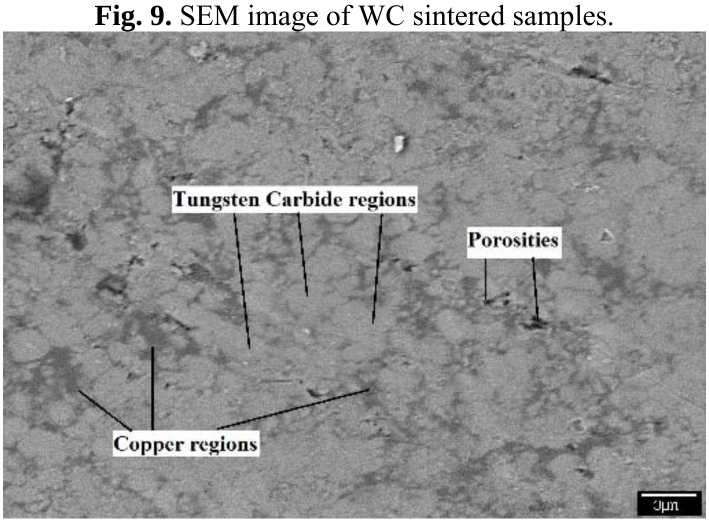

Fig. 10. SEM image of WC/Cu composites. The white, gray and black regions are tungsten carbide, copper and porosity regions, respectively.

4. Conclusion

In this study, cold compaction behavior of ball milled WC, WC-10%wtCu and WC-30%wtCu powders were investigated. Also the effect of cold compaction magnitude on sinterability of the milled powders was studied. It was shown that the most accurate model for description the cold compaction behavior of the milled WC and WC-30%wtCu powders was Panelli-Ambrosio. Also, the Heckel was the most precise equation for describing the compressibility of WC-30%wtCu powders. Furthermore, the results showed that the magnitude of cold compaction had no significant effect on sinterability of WC and WC-10%wtCu powders. However, it was confirmed that by increasing the compaction pressure the sinterability of WC-30%wtCu powders were enhanced.

5. References

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Садржај: *У овом раду, хладно компактирање и синтеровање без притиска WC, WC-10%wtCu и WC-30%wtCu прахова је испитивано. WC и WC/Cu прахови су млевени у планетарном млину 20 сати. Млевени прахови су компактирани при 100, 200, 300 и 400 MPa. Компресибилност прахова испитавана је користећи Heckel, Panelli-Ambrosio и Ge моделе. Резултати су показали да Panelli-Ambrosio најбоље описује понашање млевених WC и WC-30%wtCu прахова. Такође, најтачнији модел за описивање компресибилности WC-10%wtCu праха је Heckel-ова једначина. Прахови су синтеровани на 1400^{o}C. Показано је да се са повећањем притиска пресовања, синтерабилност WC-30%wtCu праха побољшава. Ипак, магнитуда пресовања не утиче значајно на синтерабилност WC и WC-10%wtCu праха. СЕМ испитивања синтерованих узорака указују на појаву порозности у бакат-тунгстен карбидној фази.*
Кључне речи: *WC-Cu композити; понашање током пресовања; синтеровање*