Tr. Doğa ve Fen Derg. − Tr. J. Nature Sci. 2017 Vol. 6 No.1

Türk Doğa ve Fen Dergisi
Turkish Journal of Nature and Science
http://www.bingol.edu.tr/dergiler/turk-doga-ve-fen-dergisi.aspx

Production of WCu electrical contact material via conventional powder metallurgy method: Characterization, mechanical and electrical properties

Ali Erçetin*[1], Kubilay Aslantaş[2]

Abstract

In this study, the effects of increase of sintering temperature and Cu amount on microstructure, mechanical and electrical properties of WCu electrical contact materials fabricated via conventional powder metallurgy (P/M) method were investigated. The powders obtained by adding copper at different ratios into the tungsten powders were cold pressed in a mold under 60 MPa pressure. Samples were sintered at 1000 ^{o}C and 1100 ^{o}C using three different compositions (W-%10wtCu, W-%20wtCu- and W-%30wtCu). Microstructures of the samples were investigated by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) analysis. Mechanical properties were determined by measuring hardness values and electrical properties were determined by measuring electrical resistivity. When the effect of the copper ratio on the microstructure, mechanical and electrical properties is analyzed, the reduction in the amount of copper has a positive effect on the hardness, while the electrical conductivity is adversely affected. In addition, the application of the sintering temperature above the melting temperature of copper has been effective in increasing the hardness and electrical conductivity values.

Keywords: Powder metallurgy; tungsten-copper; microstructure; hardness, electrical resistivity

WCu elektrik kontak malzemesinin konvansiyonel toz metalurjisi yöntemiyle üretimi: Karakterizasyon, mekanik ve elektriksel özellikler

Özet

Bu çalışmada, geleneksel toz metalürjisi (T/M) yöntemiyle üretilen WCu elektrik kontak malzemelerinin mikroyapı, mekanik ve elektriksel özelliklerine bakır miktarı ve sinterleme sıcaklığı artışının etkileri incelenmiştir. Tungsten tozu içerisine farklı oranlarda bakır ilavesi yapılarak elde edilen tozlar bir kalıp içerisinde 60 MPa basınç altında soğuk preslenmiştir. Üç farklı kompozisyon (WCu 90/10, WCu 80/20 ve WCu 70/30) kullanılarak numuneler 1000 ^{o}C ve 1100 ^{o}C sıcaklıklarında sinterlenmiştir. Taramalı elektron mikroskobu (SEM), enerji dağılımlı x-ışını spektroskopisi (EDX) ve x ışını kırınımı (XRD) analizleri ile numunelerin mikroyapıları incelenmiştir. Sertlik ölçümleri yapılarak mekanik özelliklerin belirlenmesi, elektriksel öz direnç ölçümleri yapılarak da elektriksel özelliklerin belirlenmesi sağlanmıştır. Bakır oranının mikroyapı, mekanik ve elektriksel özelliklerine etkisi analiz edildiğinde, bakır miktarındaki azalma sertliğe olumlu etki ederken, elektriksel iletkenliği olumsuz etkilemiştir. Ayrıca sinterleme sıcaklığının bakırın ergime sıcaklığının üzerinde uygulanması sertlik ve elektriksel iletkenlik değerlerinin yüksek çıkmasında etkili olmuştur.

Anahtar Kelimeler: Toz metalürjisi; tungsten-bakır; mikroyapı; sertlik; elektriksel öz direnç

1. Introduction

Tungsten-copper (WCu) composites are used in many applications such as moving or stationary current-cutting electrical contact materials [1-4], heat sinks and electrodes due to its low thermal expansion coefficient, high thermal conductivity and high electrical conductivity properties [5-8]. Especially electrical contact materials are forced in the mechanical and electrical direction during the opening and closing of the current. The high melting temperature, thermal and electrical conductivity of these materials is important to ensure integrity during operation [1-4].

Due to the high melting temperature of tungsten, high thermal and electrical conductivity of copper necessitate the use of these materials together. However, it has been proved that WCu composites are difficult to produce because W and Cu are not completely mixed in both solid and liquid phases. This is why powder metallurgy is the most effective way to produce WCu composites [8, 9]. Criteria such as mechanical alloying, mixing method and duration, pressing pressure and duration, sintering temperature, sintering time, applied heat

[1] Bingol University, Faculty of Engineering and Architecture, Mechanical Engineering, 12000 Bingol, Turkey
[2] Afyon Kocatepe University, Faculty of Technology, Mechanical Engineering, Afyonkarahisar, Turkey
*Sorumlu yazar E-posta: aliercetin@bingol.edu.tr

treatment are quite effective in the change of electrical, thermal conductivity and mechanical properties of materials produced through powder metallurgy method [5, 6, 10, 12]. The density changes and hardness values were positively affected by increasing the sintering temperature [13, 14]. Addition of alloying elements of Cu, Ag, Ni, Co also caused serious changes in mechanical, electrical, thermal and corrosion properties of materials [12-16].

From studies on tungsten-copper composites, W-Cu composites were prepared by mechanical alloying and the effect of the ball agitation time on density of the tungsten-copper composite was studied. In addition, the effects of Ni, Fe, Pd and Zn alloys on the thermal and electrical properties of W-Cu composites were investigated [17]. The prepared W-Cu composite blends were sintered in liquid phase at high temperature above the melting temperature of copper and more dense WCu composites were obtained [18]. Wettability between copper and tungsten was improved by the addition of Pd, Ni, Co, Fe and Zn to W-Cu composites [19-22]. While producing tungsten and copper (WCu) based composites, the effect of condensation in composite depending on sintering under high pressure was investigated on microstructure and micro hardness. The effect of the tungsten (W) particle size on the sintering density is also investigated [23]. In another study, it was generally stated that composites made of tungsten powders coated with Cu exhibited higher density, hardness, compressive strength and electrical conductivity than composites made from elemental powders [16].

The purpose of this study is to improve the mechanical and electrical properties of the WCu electrical contact materials used in many applications through P/M method.

2. Material and Method

WCu based mixtures were sintered at 1000 ^{o}C and 1100 ^{o}C temperatures in 3 different composites and 6 samples were produced. The weight percent (%) compositions of the WCu based metal powder mixtures are given in Table 1. Powder mixtures prepared homogeneously in a container with a mechanical stirrer were pressed into a rectangular prism at a pressure of 60 MPa in a mold having a length of 40 mm and a width of 8 mm. Sintering processes of the raw samples prepared by pressing were carried out in a pure (99% pure) argon atmosphere tube furnace. Sintering was applied to the pressed samples at a temperature of 1000 ^{o}C and 1100 ^{o}C for 1.5 hours and the samples were allowed to cool in a tube furnace. During the sintering, the argon gas applied in the tube furnace was sent with a flow rate of 3 L / min. After the sintering process, the metallographic analysis of the samples were carried out using LEO 1430 VP SEM device. During SEM analysis, the surfaces were cleaned with alcohol to obtain a better microstructure images. In order to determine the elemental distributions and percentage ratios, EDX analysis were performed on the sample surfaces using a Röntec EDX instrument connected to a SEM microscope. Inspections were carried out on the Shimadzu LabX XRD device to determine the phases in our WCu-based composite materials. Qualitative analysis was performed by comparison with ICDD cards. Hardness measurements were also made on the specimens prepared for microstructure studies.

The average of the hardness values obtained from 5 different regions on each sample was used. The hardness tests were performed with the Shimadzu HMV 2L brand Vickers hardness tester. The hardness of the surface layers of the samples was measured under a load of 4.903 N in a micro vickers hardness (HV0.5) device. In addition, the electrical resistivity values of the samples were measured with a dielectric spectrometer.

3. Results and Discussion

3.1. SEM Analysis

SEM images (5 kx) of WCu composite samples are given in Figure 1. Partially porous structures are found in samples sintered at 1000 ^{o}C. Full wetting of the tungsten grains can't be achieved due to the absence of the Cu matrix in the liquid phase at a 1000 ^{o}C sintering temperature. As a result, the formation of the neck between the granules was not seen at this temperature. The amount of pores in the SEM image taken from the WCu-3 sample appears to be less than the WCu-1 sample. This can be explained by the fact that WCU-3 has a higher copper content.

Samples with the same composition (WCu-4, WCu-5 and WCu-6) with the increase of sintering temperature to 1100 oC have been reduced to have no porous structure. When SEM images of the sintered samples are analyzed at this temperature, it is understood that the copper forms a liquid phase. The resulting liquid Cu phase allowed complete diffusion of the surface of the W powders and provided formation of necks between the tungsten grains. Neck formations are more evident in samples sintered at 1100 ^{o}C, where the copper ratio is increased. Thus, the metallic binding between grains in the microstructure has been increased. This is thought to have a positive effect on mechanical properties (Figure 5). During the sintering of the samples at 1100 ^{o}C, the blanks in the microstructure were filled with liquid Cu and the pores decreased in the microstructure. Thereby, a more dense structure was obtained with the W grains on the sample surface.

Table 1. Chemical composition of WCu samples.

Sample Name	**Composition**	**Sintering Temperature (^{o}C)**	**(%wt) W**	**Cu**
WCu-1	%90W%10Cu	1000	90	10
WCu-2	%80W%20Cu	1000	80	20
WCu-3	%70W%30Cu	1000	70	30
WCu-4	%90W%10Cu	1100	90	10
WCu-5	%80W%20Cu	1100	80	20
WCu-6	%70W%30Cu	1100	70	30

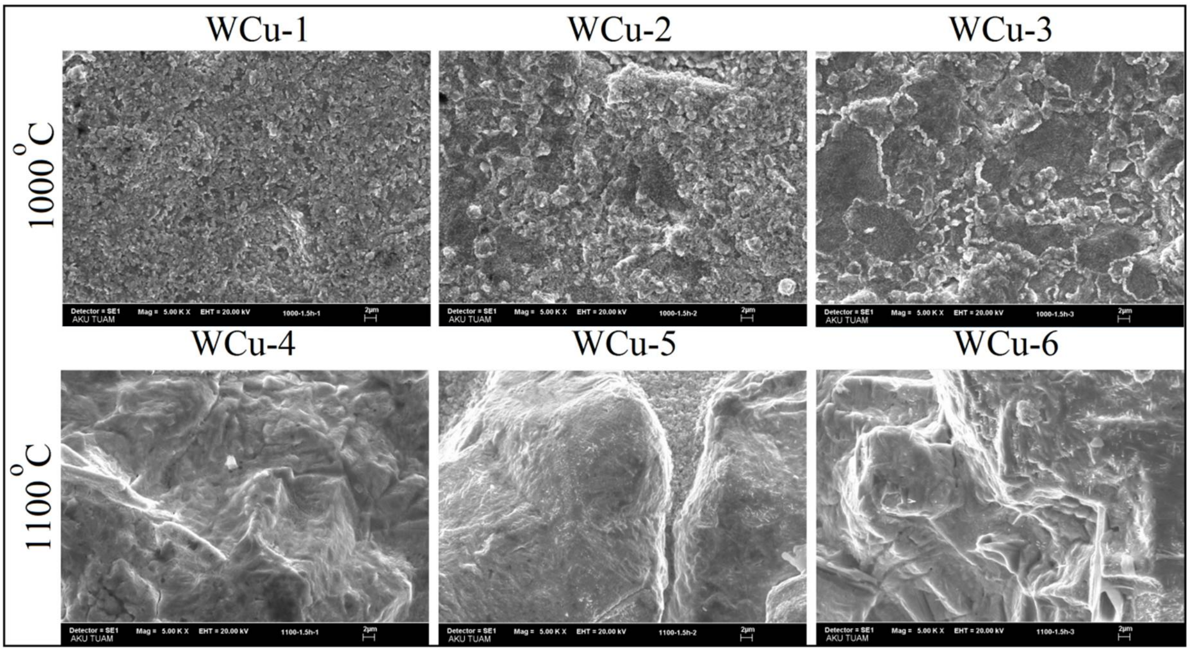

Figure 1. SEM images of WCu electrical contact materials

3.2. EDX Analysis

Figure 2 shows the EDX images and elemental analysis of WCu samples sintered under pure argon gas atmosphere in conventional tube furnace. In the composite samples sintered at 1000 oC (WCu-1, WCu-2 and WCu-3), a heterogeneous pore structure of the Cu matrix was formed. Depending on this situation, the amount of Cu on the surface of the composite specimens increased. As can be seen from the EDX analysis curve, the peak intensities of the amount of Cu element at this sintering temperature are higher than the peak intensities of element W. Therefore, samples sintered at low temperature have a softer structure than samples sintered at higher temperature. The hardness values obtained also support this.

As the sintering temperature increased to 1100 ^{o}C, the copper could converted into liquid phase, full wetting of the tungsten grains was provided and neck formation occurred between grains. EDX analysis of sintered samples (WCu-4, WCu-5 and WCu-6) at 1100 ^{o}C with the same compositions shows that the tungsten peak intensities are higher than copper. This is thought to be effective in increasing mechanical properties.

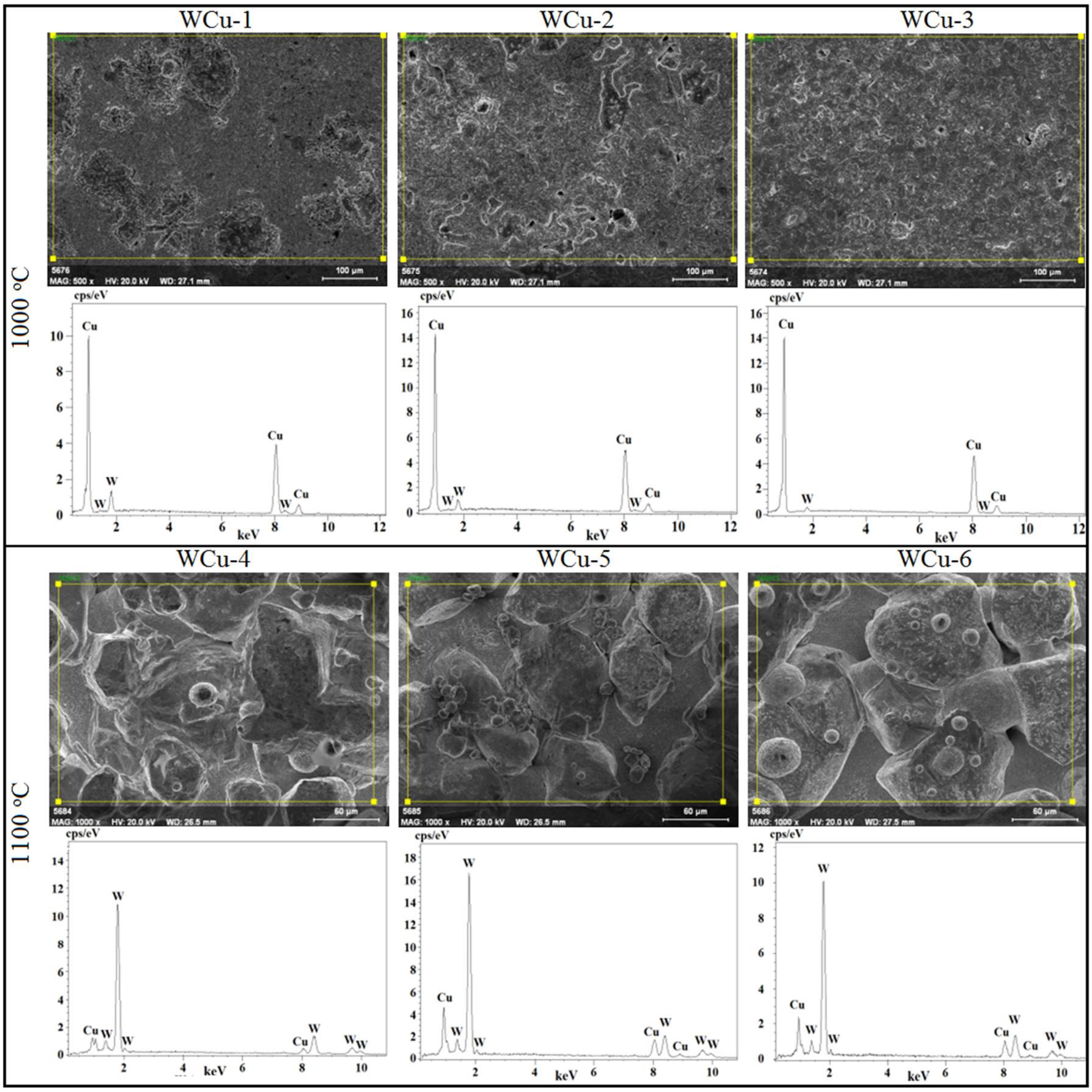

Figure 2. EDX images of WCu electrical contact materials

3.3. XRD Analysis

X-ray diffraction analysis results of WCu-1, WCu-2 and WCu-3 composites sintered at 1000 °C are given in Figure 3. Only W and Cu peaks were formed in XRD patterns of WCu-1, WCu-2 and WCu-3 composite samples. The highest peak intensity in the XRD pattern of all three composite samples was W peaks. While the W peak intensity is the highest and the Cu peak intensity is the lowest in the XRD pattern of the WCu-1 composite, XRD pattern of the WCu-2 composite showed a decrease in the W peak intensity and an increase in the Cu peak intensity. The lowest W peak intensities and the highest Cu peak intensities are seen in the XRD pattern of the WCu-3 composite, but the W peak intensities are higher than the Cu peak intensities. In the composite samples of XRD patterns in which W peak intensity falls and Cu peak intensity increases, the micro vickers hardness values decrease (Figure 5). It is seen that the micro vickers hardness values are increased in the composite samples of the XRD patterns in which W peak intensity increases and Cu peak intensity decreases (Figure 5).

Figure 4 shows XRD patterns of WCu-4, WCu-5 and WCu-6 composites sintered at 1100 °C. Only W and Cu peaks were formed in these XRD patterns of these composite samples, too. The highest peak intensity in the XRD pattern of all three composite samples was W peaks. XRD of WCu-4 composites showed the highest W peak intensity and the lowest Cu peak intensity, whereas the XRD graph of the WCu-5 composite showed a decrease in W peak intensity and an increase in Cu peak intensity. W peak intensities were higher for all three compositions than Cu peak intensities, although the lowest W peak intensities and highest Cu peak intensities were seen on the XRD patterns of the WCu-6 composite. Generally higher hardness values were obtained from samples with reduced Cu peak intensities.

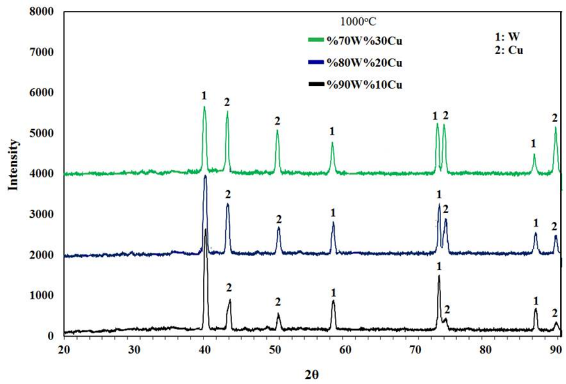

Figure 3. XRD patterns of WCu-1, WCu-2 and WCu-3 samples sintered at 1000 ^{o}C temperature

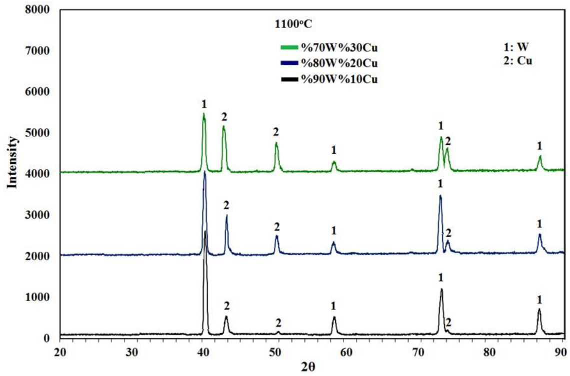

Figure 4. XRD patterns of WCu-4, WCu-5 and WCu-6 samples sintered at 1100 ^{o}C temperature

3.4. Micro Vickers Hardness Analysis

Micro-vickers hardness values of WCu electrical contact materials sintered at both temperatures are given in Figure 5. The values obtained indicate that the increase in the Cu content leads to a decrease in hardness values. However, the hardness values increased with the increase in the sintering temperature. This is due to the fact that, at high temperature, Cu forms a liquid phase to wet the W particles better, and thus a more dense structure, as indicated in the SEM review.

Generally, as the Cu content increases in the samples, the porous structures decrease and improve in the microstructure was seen. However, the increase of Cu amount has led to a decrease in hardness values. In another study supporting this prediction, they obtained the lowest hardness value in the W-%40wt Cu composite with the highest Cu content [13].

The highest hardness value was obtained from the WCU-4 sample. This value is around 355 HV. This is because of the presence of high-strength W metal powders and sintering at higher temperatures. Contrary to this, the micro vickers hardness value of WCu-3 composite sample is the lowest with 230 HV. In a study by Ibrahim et al. [16], the hardness values were only obtained in the range of 220-250 HV, although the sintering temperature was up to 1250 ° C.

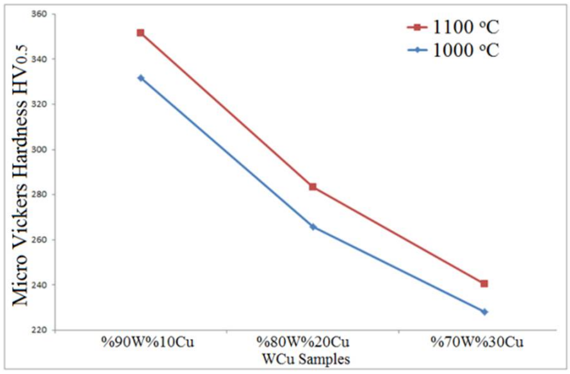

Figure 5. Micro vickers hardness values of WCu samples sintered at 1000 ^{o}C and 1100 ^{o}C temperatures.

3.5. Electrical Resistivity Analysis

Electrical resistivity values of WCu electrical contact materials sintered at 1000 ^{o}C ve 1100 ^{o}C temperatures are shown in Figure 6. The lowest electrical resistivity value was obtained from WCu-6 samples sintered at 1100 ^{o}C temperature while the highest electrical resistivity value in WCu samples was obtained from WCu-1 sample sintered at 1000 ^{o}C. As the electrical resistivity value decreases, electrical conductivity increases. It shows that the increase in copper ratio and sintering temperature increases the electrical conductivity. As a result of sintering at 1000 ^{o}C, W particles were completely prevented from touching each other because of that Cu matrix couldn't convert into liquid phase. Conduction of electrons between atoms became more difficult. Compared to the samples sintered at 1000 ^{o}C, the Cu matrix was able to convert to liquid phase at the sintering temperature of 1100 ^{o}C. Thus, the contact surfaces of the grains increased with each other, and accordingly, the electrical conductivity of the samples sintered at high temperature was higher. A study on the W-20% Cu and W-30% Cu composites is similar to our experimental results and supports the results obtained by decreasing the electrical resistivity values in composites with increased Cu content [16].

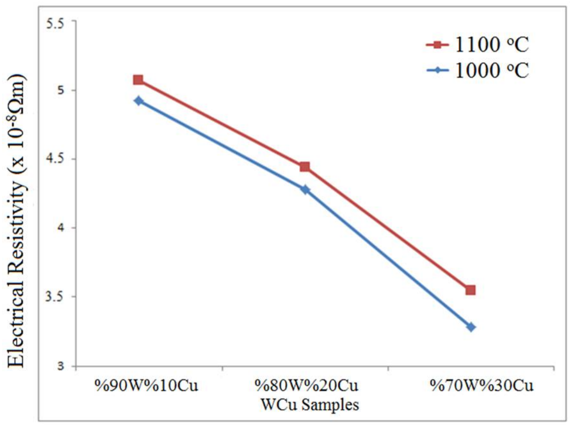

Figure 6. Electrical resistivity values of WCu electrical contact materials sintered at 1000 ^{o}C ve 1100 ^{o}C temperatures

4. Conclusions

Generally, the increase in sintering temperature has a positive effect on the increase of mechanical and electrical properties. In the samples having the same content in the W + Cu system, the hardness values of the samples sintered at

1100 °C are higher than the samples sintered at 1000 °C. In addition, as the Cu ratio and sintering temperature increased, the pores in microstructure decreased and development in microstructure were seen in samples produced according to the W+Cu system. However, the increase in the Cu content led to a decrease in hardness values. Pressing pressure can be increased to reduce porosity in samples which have low copper content.

The increase in copper ratio positively affected the increase in electrical conductivity. However, the electrical resistivity values of the samples sintered at 1100 °C were lower than the electrical resistivity values of the samples sintered at 1000 °C. Namely, WCu electrical contact materials with low electrical resistivity values are found to be more conductive.

In future studies, alloying elements such as Ni, Co can be added to increase the mechanical properties of high-copper-content materials. In order to improve the electrical properties of materials with high tungsten content, it is also possible to add silver with better electrical conductivity than copper.

Acknowledgement

This research was supported by grants from the Support Program for Afyon Kocatepe University Scientific and Technological Research Projects, Project No: 14.FEN.BİL.39. SEM images were supported by Bingol University Center Laboratory.

References

[1] Bloor, D., Brook, R.J., Flemings, M.C. and Mahajan, S. The Encyclopedia of Materials, Permagon Pres, Oxford, 1999.

[2] Güler, Ö. and Evin, E. The investigation of contact performance of oxide reinforced copper composite via mechanical alloying, *Journal of Materials Processing Technology*, 209(3), 1286-1290, 2009.

[3] Güler, Ö. Investigation of electrical properties of oxide reinforced copper composite produced by mechanical alloying, (Master Thesis), Fırat University, Elazığ, Turkey, 2006.

[4] Gök, M.G., Kaplan, M. The production of electrical contact material by means of powder metallurgy and investigation its contact performance, 6th International Advanced Technologies Symposium (IATS'11), 294-298, Elazığ, Turkey, 2011.

[5] Kim, D-G, Kim, G-S, Suk, M-J, Oh, S-T, Kim, Y-D. Effect of heating rate on microstructural homogeneity of sintered W-15 wt.% Cu nanocomposite fabricated from W–CuO powder mixture, *Scr. Mater.*, 51, 677–681, 2004. doi:10.1016/j.scriptamat.2004.06.014.

[6] Kim, J, Ryu, S, Kim, Y, Moon, I. Densification behavior of mechanically alloyed W–Cu composite powders by the double rearrangement process, *Scr. Mater.*, 39, 669–676, 1998.

[7] Liu, B.B., Xie, J.X., Qu, X.H. Fabrication of W–Cu functionally graded materials with high density by particle size adjustment and solid state hot press, *Compos. Sci. Technol.*, 68(6), 1539–1547, 2008. doi:10.1016/j.compscitech.2007.10.023.

[8] Chen, P, Shen, Q, Luo, G, Wang, C, Li, M, Zhang, L, Li, X and Zhu, B. Effect of interface modification by Cu-coated W powders on the microstructure evolution and properties improvement for Cu–W composites, *Surface & Coatings Technology,* 288, 8-14, 2016. doi:10.1016/j.surfcoat.2016.01.014.

[9] Bhalla, A.K., Williams, J.D. Comparative assessment of explosive and other methods of compaction in the production of tungsten–copper composite, *Powder Metall.*, 1, 31–37, 1976. doi:10.1179/pom.1976.19.1.31.

[10] Li, S.B., Xie, J.X. Processing and microstructure of functionally graded W/Cu composites fabricated by multi-billet extrusion using mechanically alloyed powders, *Compos. Sci. Technol.*, 66(13), 2329-2336, 2006. doi:10.1016/j.compscitech.2005.11.034.

[11] Ihn, T.H., Lee, S.W., Joo, S.K. Effect of transition metal addition on liquid phase sintering of W–Cu, *Powder Metall.*, 37(4), 283-288, 1994. **doi:**10.1179/pom.1994.37.4.283.

[12] Luo, S.D., Yi, J.H., Guo, Y.L., Peng, Y.D., Li, L.Y., Ran, J.M. Microwave sintering W-Cu composites: Analyses of densification and microstructural homogenization, *Journal of Alloys and Compounds*, 473, L5-L9, 2009. doi:10.1016/j.jallcom.2008.05.038.

[13] Ardestani, M., Rezaie, H.R., Arabi, H., Razavizadeh, H. The effect of sintering temperature on densification of nanoscale dispersed W-20-40%wt Cu composite powders, *Int. Journal of Refractory Metals & Hard Materials*, 27, 862-867, 2009. doi:10.1016/j.ijrmhm.2009.04.004.

[14] Erçetin A. Manufacturing, characterization and micro machinability of W+Cu+(X) electrode utilized in resistance welding through powder metallurgy method, (Master Thesis), Afyon Kocatepe University, Afyonkarahisar, Turkey, 2015.

[15] Findik, F., Uzun, H. Microstructure, hardness and electrical properties of silver-based refractory contact materials, *Materials and Design*, 24, 489-492, 2003. doi:10.1016/S0261-3069(03)00125-0.

[16] Ibrahim, A., Abdallah, M., Mostafa, S.F., Hegazy, A.A. An experimental investigation on the W-Cu composites, *Materials and Design*, 30, 1398–1403, 2009. doi:10.1016/j.matdes.2008.06.068.

[17] Kecskes, L.J., Klotz, B.R., Cho, K.C., Dowding, R.J., Trexler, M.D., Densification and structural change of mechanically alloyed W–Cu composites, *Metall. Mater. Trans. A*, 32A, 2885–2893, 2001. doi:10.1007/s11661-001-1039-0.

[18] Yang, X., Liang, S., Wang, X., Xiao, P., Fan, Z., Effect of WC and CeO_2 on microstructure and properties of W–Cu electrical contact material, *Int. J. Refract. Met. Hard Mater.*, 28(2), 305–311, 2010. doi:10.1016/j.ijrmhm.2009.11.009.

[19] Chen, P., Luo, G., Li, M., Shen, Q., Zhang, L. Effects of Zn additions on the solid-state sintering of W–Cu composites, *Mater. Des.*, 36, 108–112, 2012. doi:10.1016/j.matdes.2011.10.006.

[20] Chen, P., Luo, G., Shen, Q., Li, M., Zhang, L. Thermal and electrical properties of W–Cu composites produced by activated sintering, *Mater. Des*., 46, 101–105, 2013. doi:10.1016/j.matdes.2012.09.034.

[21] Johnson, J.L., German, R.M. Chemically activated liquid phase sintering of tungsten–copper, *Int. J. Powder Metall.*, 30, 91–102, 1994.

[22] Johnson, J.L., German, R.M. Phase equilibria effects in enhanced liquid phase sintering of tungsten–copper, *Metall. Mater. Trans. A*, 24, 2369–2377, 1993. doi:10.1007/BF02646516.

[23] Zhou, Z.J., Kwon, Y.S. Fabrication of W–Cu composite by resistance sintering under ultra-high pressure, *Journal of Materials Processing Technology*, 168(1), 107–111, 2005. doi:10.1016/j.jmatprotec.2004.11.008.