The effect of the amount of process control agent on the properties of Cu25W composite powder

S. Biyik[1] & M. Aydin[2]
[1]*Department of Metallurgical and Materials Engineering,*
Karadeniz Technical University, Turkey
[2]*Department of Mechanical Engineering,*
Karadeniz Technical University, Turkey

Abstract

This study is based upon the optimization of production parameters of Cu25W electrical contact material. Commercial elemental copper (Cu) and tungsten (W) powders were synthesized to produce Cu25W composite powder by mechanical alloying technique at various amounts of stearic acid via using a planetary type ball mill. The effect of amount of stearic acid on production of Cu25W composite powder was evaluated. In order to achieve true alloying among powder particles, it is necessary to establish a balance between cold welding and fracturing. Hence, different types of process control agents (PCA) were used to reduce excessive cold welding. Here, the effect of various amounts of stearic acid, namely 0, 0.5, 1, 2 and 3 wt.% on morphology and some properties of Cu25W composite powder were studied. The microstructural evolution of the milled powders was characterized by using scanning electron microscopy. The test results showed that the morphology and particle size distribution of the milled powders were changed considerably depending upon the variable amount of PCA. In addition, holding the same milling duration, different microhardness values were obtained for various amounts of PCA.
Keywords: composite powders, copper matrix composites, electrical contact materials, mechanical alloying, process control agent, tungsten.

1   Introduction

Mechanical alloying (MA) is a very effective powder processing technique to synthesize a wide variety of equilibrium and non-equilibrium alloy phases, and

composites. It is possible to obtain fine and homogeneous dispersion of brittle phase in the ductile matrix by using this technique (Soni [1]). MA involves loading the blended elemental or prealloyed powder particles along with the grinding medium in a vial and subjecting them to heavy deformation (Suryanarayana [2]). In addition, this process includes repeated cold welding, fracturing and rewelding of powder particles in a high-energy ball mill, resulting in the formation of alloy phases. Cold welding and fracturing are the main events occurred during this process.

Depending upon the nature of the powder being milled (ductile or brittle), utilizing some surface additives called process control agent (PCA) are necessary to establish a balance between cold welding and fracturing. These agents are added to the powder mixture during milling, especially when the powder mix involves a substantial fraction of a ductile component (Suryanarayana [3]). The non-use of the PCA may result in excessive cold welding of powder particles among themselves and/or to the milling container and the grinding medium, and this causes formation of larger particles. In addition, the powder yield could also be lower if the powder gets stuck to the inner walls of the milling container due to increase in cold welding and true alloying may also not occur. Furthermore, the quantity of PCA used and the type of powder milled determine the final size, shape, and purity of the powder particles and there is no universal PCA. However, excessive amounts of PCA may lead to inhibition of cold welding and hence prevents the formation of new materials even though fine particle size may be obtained (Lu and Lai [4]). Therefore, the type and amount of PCA should be carefully optimized with respect to milling duration. A wide range of PCAs in the form of solid, liquid or gaseous have been used in practice and they are mostly organic compounds used approximately 1–5 wt.% of the total powder charge. These surface-active agents inhibit agglomeration and lower the surface tension of the solid material via absorbing on the surface of the powder particles. Several PCAs, such as stearic acid, hexane, methanol, ethanol, and polyethylene glycol are often used in MA experiments (Suryanarayana [5]).

The methodology used in this study is based upon the optimization of the production of electrical contact materials. Contact material has a major influence on the performance of relays, contactors and other switching devices affecting maximum inrush current, maximum switching current, contact resistance together with contact reliability and electrical life. A majority of contact applications in the electrical industry utilize silver-type composite contact materials [6–11]. These include powder metal combinations which offer combinations of metals ordinarily cannot be achieved by alloying (ASM [12]). On the other hand, commercially pure copper has high electrical and thermal conductivities and this, together with its ease of fabrication, and its low cost and plentiful supply compared with precious metals, makes it an obvious choice as a contact material (Turner and Turner [13]). However, copper has also some drawbacks such as poor resistance to oxidation and corrosion (ASM [14]). Refractory metals, such as tungsten and molybdenum, which have high melting and boiling points, and excellent resistance to arc erosion are frequently used in

combination with silver or copper in applications involving severe arcing and welding.

Copper can be used in contact applications either as the pure metal (applications where arcing and welding are not severe), or in the form of alloys or compounds made by powder metallurgy. Hence, different types of copper-based composite electrical contact materials have been developed in order to meet the requirements for various applications [15, 16]. Copper-based electrical contact materials are used in a variety of applications, such as arcing contacts in oil switches, current carrying contacts, vacuum interrupter, oil-circuit breakers, arcing tips, contactors, vacuum switches, automotive starters, instruments, fuel pumps, welding machines, industrial truck motors, automotive heaters, antenna motors and generators, etc. (ASM [12]). Much work has previously been done in production and evaluation of copper-based contact materials in terms of electrical performance [17–20].

In this study, the effect of amount of PCA on some properties of Cu25W composite powder was investigated. This work may also be called as a pre-study for manufacturing electrical contacts.

2   Experimental details

In this study, copper was used as the matrix material and tungsten as the reinforcement. As starting materials, elemental copper having particle size of 44 µm and purity of 99% and tungsten having average particle size of 12 µm and purity of 99.9% powders were used for ball milling experiments. Both copper and tungsten powders were supplied by Alfa Aesar Corporation.

The morphology of the starting powders was investigated by means of scanning electron microscopy (SEM) on a Zeiss Evo LS 10 model (Fig. 1). Particle size distribution of the starting copper powder was analyzed using Malvern Instruments Laser Diffractometer Mastersizer 2000 (Fig. 2).
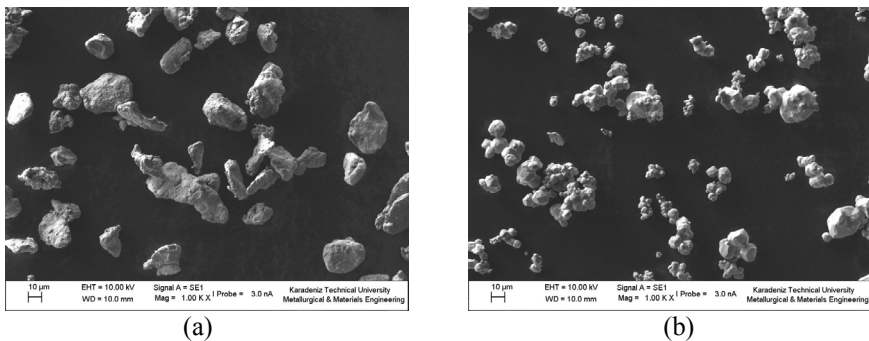

(a)   (b)

Figure 1:   Morphology   of   as-received   powders: (a)   Copper   powder;
(b) Tungsten powder.

d(0.1):   17.248   um   d(0.5):   28.897   um   d(0.9):   49.064   um
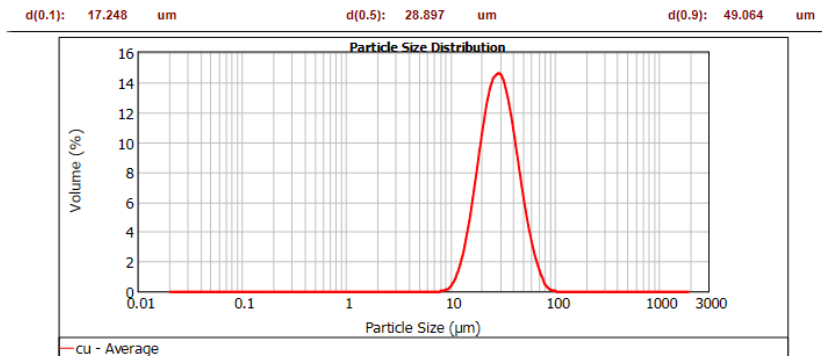

Figure 2:   Particle size distribution curve of starting Cu powder.

Planetary type ball mill, Fritsch Pulverisette 6, was used to carry out milling experiments (Fig. 3(a)). Both the milling container and the grinding balls (Fig. 3(b)) are made of tungsten carbide (WC). The diameter of the balls is 10 mm.

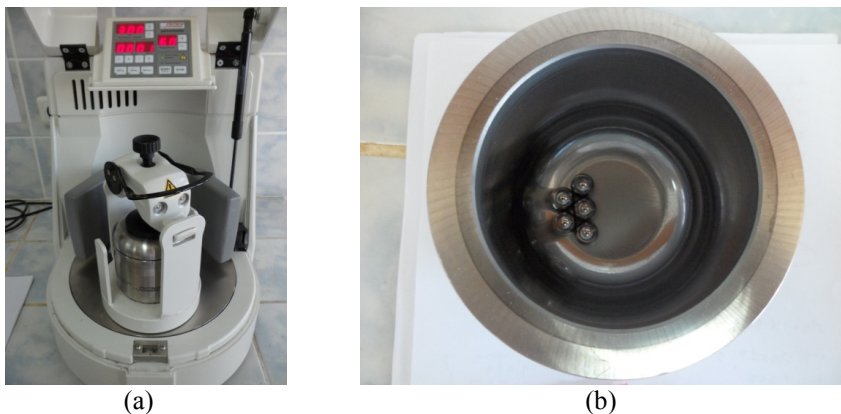(a)   (b)

Figure 3:   Equipment used for MA experiments, (a) planetary type ball mill; (b) WC vial and balls.

Tungsten powders were added to copper powders in the amount of 25 wt.%. The chemical composition of the composite powder, namely the percentages of both matrix and reinforcement was kept constant in this order for each experiment. The milling was carried out at the speed of 300 rpm and ball-to-powder weight ratio (BPR) of 10:1. Stearic acid was used as a process control agent. The powders were ball milled under the aforementioned test conditions by adding various amounts of stearic acid, namely 0, 0.5, 1, 2 and 3 wt.%. The whole experiment may be subdivided into five separate experiments due to the differences of the amounts of PCA. In this regard, the starting powders ball-

milled separately up to 25 hours of milling duration. For each test having different amount of stearic acid, the fresh powder charge was installed into the vial. In addition, to prevent overheating of the grinding medium, the milling process was interrupted at least 30 minutes after certain milling durations until the room temperature is ensured. All milling conditions for the whole experiment were given in Table 1. After each test duration listed on the table, the powder samples were withdrawn for particle size measurements. The variation of average particle sizes (d_{50}) with milling duration was also investigated using SEM.

Table 1:   Milling parameters used to investigate the effect of PCA on the particle size and morphology.

Type of Mill	Fritsch Pulverisette 6 Planetary Ball Mill
Milling Container	Tungsten Carbide (WC)
Grinding Medium	WC balls ($\Phi = 10$ mm)
Amount of PCA (wt.%)	0, 0.5, 1, 2, 3
Milling Energy/Speed (rpm)	300
Milling Time (h)	0.5, 1, 4, 7, 10, 13, 16, 20, 25
Ball-to-Powder Weight Ratio (BPR)	10:1
Milling Atmosphere	Air
Chamber Temperature (°C)	Room Temperature
Chamber Capacity (ml)	225

The optimization of the production of Cu25W composite powder was achieved by comparing these separate experiments. Utilizing the ideal test values of these experiments, some physical properties of the green compacts were investigated with the increasing milling time. For this aim, the powders were deoxidized by using reduction furnace at the temperature of 500°C for 15 minutes in a hydrogen atmosphere prior to compaction process. The composite powders were then processed to bulk solid pieces by conventional powder metallurgy route. The powders were consolidated in the form of green compacts of approximately a diameter of 6 mm and a thickness of 2 mm by hydraulic press under the pressure level of 100 bars in a single action steel die. And then, the contact surfaces were grinded by using sand paper with the grit size of 800. The hardness measurements were carried out using a Microvickers hardness tester by applying load of 4.904 N and loading period of 15 seconds. The hardness of the samples in all conditions was taken as the average of five measurements.

3   Results and discussion

3.1   Particle size evaluation and morphology of milled powder

The initial morphologies of both Cu and W powders are shown in Fig. 1(a) and (b), respectively. It can be seen from the figure that copper powders have

irregular shape while tungsten powders have angular shape from a morphological point of view. To simplify and better understand the observations, the whole experiment was sub-divided into five process codes as seen in Table 2.

Table 2:   The amounts of stearic acid with respect to the codes of process.

Process Code	Amount of PCA (wt.%)
Process 1	0
Process 2	0.5
Process 3	1
Process 4	2
Process 5	3

The shapes of the particles and regarding morphologies with the increasing milling duration were presented in Table 3 and Fig. 4, respectively. Fig. 4 shows the SEM images of the powders having a stearic acid of 2 and 3 wt.% and milled for different milling durations, namely 0.5, 2, 3 and 4 h. It is clear from the figure that powder particles had undergone morphological changes with the increasing milling duration. In the initial stages of milling, the ductile copper particles get flattened by the ball-powder-ball collisions. After a milling time of 0.5 h, the particles having 2 wt.% of PCA were partly deformed plastically by MA (Fig. 4(a)). However, with the increasing amount of PCA up to 3 wt.%, plastic deformation decreased and the powders were exhibited less change in morphology. Therefore, the powder particles still remain irregular as seen in Fig. 4(b). On contrary, lesser amounts of stearic acid caused severe deformation between the powder particles. Thereby, distinctive flake morphology is seen earlier in compositions having lesser amounts of PCA, namely 0, 0.5 and 1 wt.%. It can be seen from the Fig. 4(c) and (d) that exact flake morphology is achieved after a milling duration of 2 h though flattening is more dominant in P4 process (Fig. 4(c().

Table 3:   The shapes of the particles with the increasing milling duration.

	Process	Milling time (h)					
		0.5	2	4	10	16	25
Particle shape	P1	Irregular + Flake	Flake	Flake	Flake + Irregular	Flake + Irregular	Semi Equiaxial
	P2	Irregular + Flake	Flake	Flake	Flake	Flake	Flake
	P3	Irregular + Flake	Flake	Flake	Flake	Flake	Flake
	P4	Irregular	Flake	Flake + Irregular	Flake + Semi Equiaxial	Semi Equiaxial	Equiaxial
	P5	Irregular + Flake	Flake	Flake	Flake + Irregular	Flake + Semi Equiaxial	Semi Equiaxial

2% PCA   3% PCA

(a)   (b)

(c)   (d)

(e)   (f)

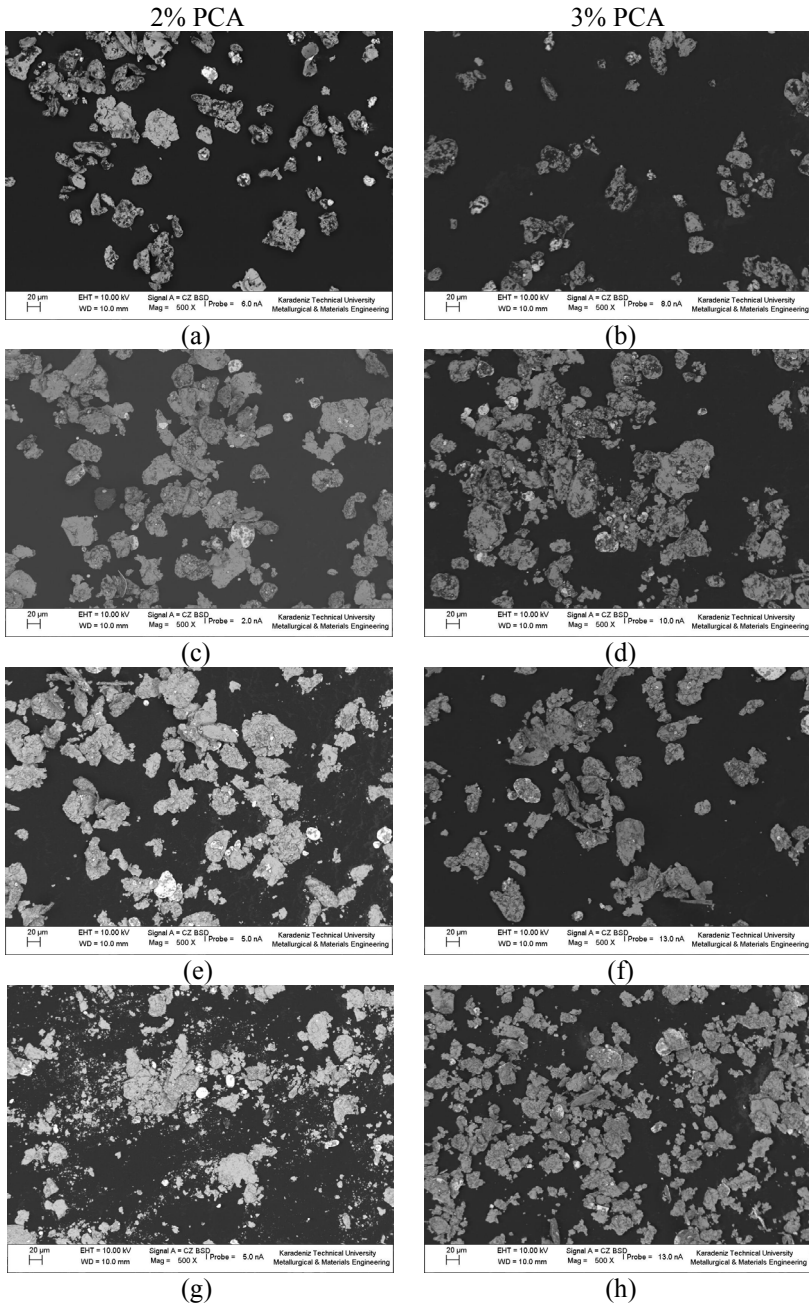(g)   (h)

Figure 4:   Morphologies of the composite powders having different amounts of
            PCA after being milled for different milling durations: (a)–(b) 0.5 h,
            (c)–(d) 2 h, (e)–(f) 3 h, (g)–(h) 4 h.

The milling duration of 3 hours is critical for P4 process as fracturing partly begins in this period while fracturing event occurs at the later stages of MA for P5 process. Here, it could be seen that the amounts more than 2 wt.% of stearic acid decreased the ball-to-powder collisions and reduced the efficiency. The effects of PCA are more apparent at the later stages of milling experiments. Fig. 5 shows the SEM images of the powders having a stearic acid of 1, 2 and 3 wt.% and milled for 16 and 25 h. It can be seen from the Fig. 5(a) that deformation and flattening of the soft copper matrix are dominant to fracturing. Hence, the flake powders are in majority in P3 process.

16 h   25 h

(a)   (b)

(c)   (d)

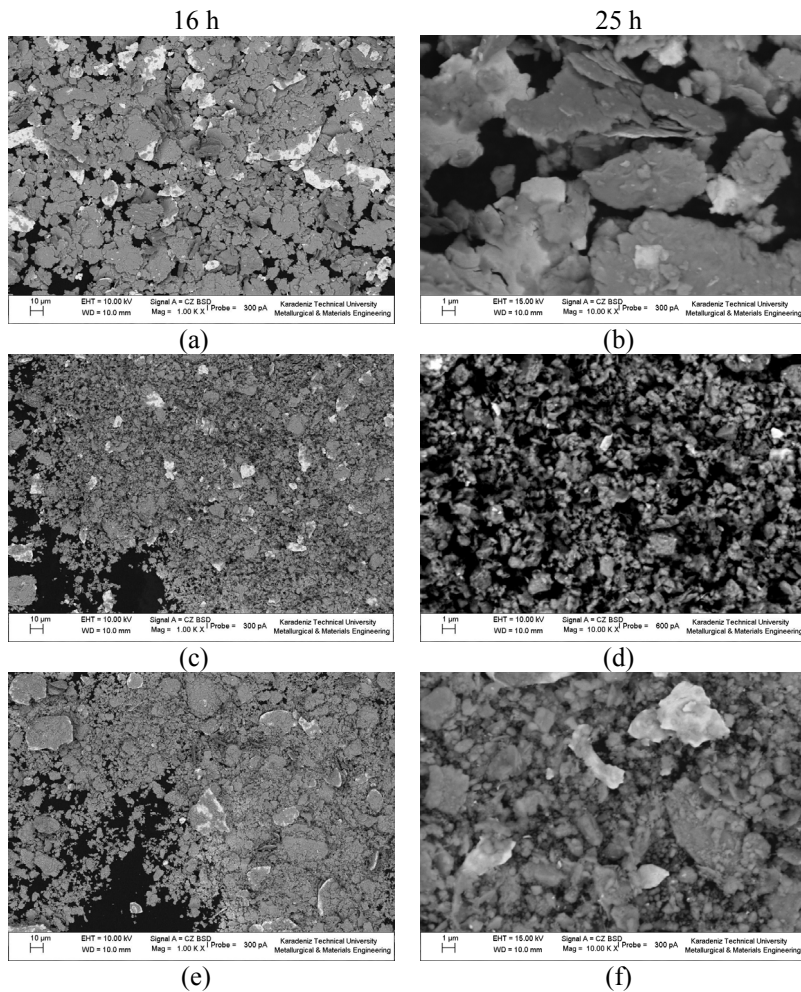(e)   (f)

Figure 5: Morphologies of the composite powders having different amounts of PCA after milled for different milling durations: (a)–(b) 1% PCA, (c)–(d) 2% PCA, (e)–(f) 3% PCA.

Grain refinement of both copper matrix and tungsten reinforcement occurred and more homogeneous distribution of the brittle tungsten phase is observed in P4 process (Fig. 5(c). The microstructure has semi-equiaxial shape in P4 process after a milling duration of 16 h. However, broad size distribution of powders was observed in P5 process (Fig. 5(e)) as a consequence of the aforementioned procedure. As can be seen in Fig. 5, fracturing effectiveness decreased beyond the critical point. Excess amounts of stearic acid blocks the tungsten particles to be processed and they remain coarser and flake like in the microstructure as seen in Fig. 5(e). With further milling, the work hardening of powders becomes dominant and structural embrittlement comes out. Brittle tungsten powder particles get fragmented into smaller particles and refined in size. Therefore, the improvement in fracturing efficiency is achieved and the later stages of milling process which supported by regarding SEM image prove this explanation (Fig. 5(d)). Comparing Fig. 5(c) and (d), the morphology was found to change from semi-equiaxial to equiaxial. On the other hand, at very small particle sizes, the brittle tungsten powder particles behave in a ductile fashion. This situation makes further reduction in size more difficult or even impossible. Therefore, the limit of comminution of harder tungsten reinforcement in the softer copper matrix is achieved. During milling of copper and tungsten powders, it has also been observed that some of the copper particles get fragmented and get embedded in the relatively coarse tungsten particles as seen in Fig. 5(f).

The effects of the amount of PCA and milling time on the average particle size of the Cu25W composite powders was shown in Fig. 6. The curve in this figure was obtained by recording mastersizer results for each powder charge.
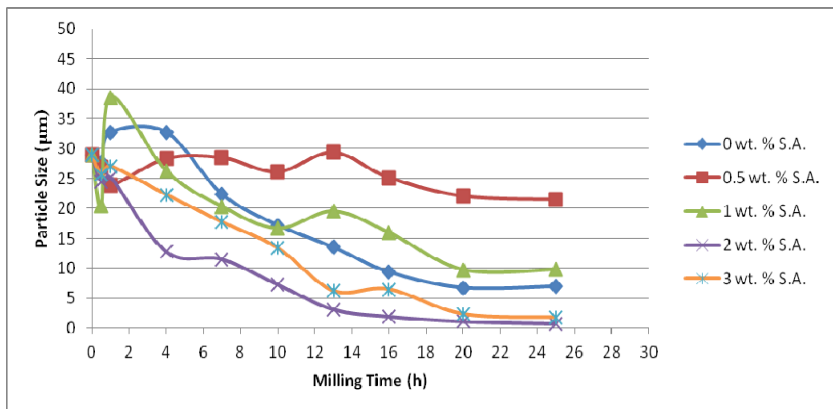

Figure 6:   Particle size vs. milling time graph for different amounts of PCA.

The analysis report containing average particle sizes for all specimens are presented in Table 4. The powders having a stearic acid of 0, 0.5 and 1 wt.% (P1, P2 and P3 processes) were exposed to severe deformation and cold welding rather than fracturing. This leads to particle coarsening as compared to initial size (28.897 microns) and range between 32.743 and 38.544 microns which

apparently seen in Table 4. On the other hand, the balance between cold welding and fracturing is achieved at the powders having a stearic acid of 2 wt.% and the minimum particle size, namely 0.726 microns is obtained in P4 process at the milling duration of 25 h. In P5 process, excessive amount of PCA caused coarsening of tungsten particles and thereby, the final particle size (1.775 microns) is bigger than that in P4 process.

Table 4:   The average particle sizes of the composite powders having different amounts of PCA.

	Process	Milling time (h)					
		0.5	1	4	10	16	25
Particle size (d_{50}, μm)	P1	27.771	32.743	32.76	17.225	9.366	6.964
	P2	26.911	23.869	28.296	26.096	25.13	21.462
	P3	20.49	38.544	26.239	16.646	15.947	9.792
	P4	24.401	25.19	12.765	7.29	1.933	0.726
	P5	25.679	27.038	22.286	13.394	6.463	1.775

After evaluation of the final particle sizes and morphologies, the optimum amount of stearic acid for copper-tungsten system was determined as 2 wt.%. In addition, the same amount of PCA produced the best result for homogeneous dispersion of tungsten particles in copper matrix.

3.2 Microhardness

The change of microhardness of green compacts consisting milled powders as a function of milling duration and PCA content is given in Fig. 7. In this figure, the hardness increases with the increasing milling time in general as the particle size tends to reduce and the real contact area between powder particles increases. This results in stronger compact. The maximum value of microhardness, namely 240 HV is obtained in the green compacts having a stearic acid of 2 wt.% (P4 process) after milled for 25 h.
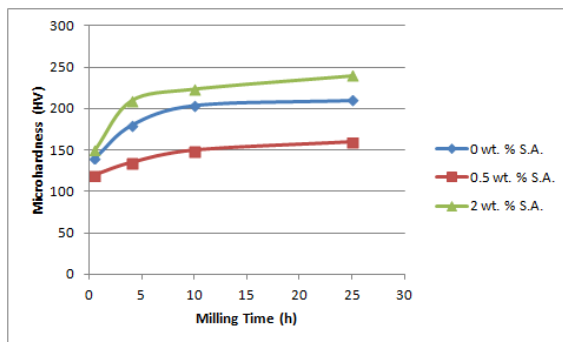

Figure 7:   Microhardness vs. milling time graph for different amounts of PCA.

4   Conclusions

The following conclusions can be drawn for this investigation:
1. Particle sizes were decreased with the increasing milling duration. The minimum particle size (0.726 microns) is obtained in the powders having a stearic acid of 2 wt.% after milled for 25 h.
2. Cold welding is dominant to fracturing in the powders having lesser amounts of stearic acid, especially a content of 0.5 and 1 wt.%. Therefore, flake morphology is observed in these powders even after milled for 25 h.
3. Optimum PCA content was determined as 2 wt.%.
4. The microhardness values increased with the increasing milling duration and the maximum value was achieved in the powders having a stearic acid of 2 wt.% after milled for 25 h.
5. Further milling caused very small and brittle tungsten powder particles to behave in a ductile fashion and the powders got enormously stuck to the inner walls of the grinding chamber.

Acknowledgement

References

[1] Soni, P.R., Mechanical Alloying: Fundamentals and Applications, Cambridge International Science, 1999.
[2] Suryanarayana, C., Mechanical Alloying and Milling, CRC Press, 2004.
[3] Suryanarayana, C., Non-equilibrium Processing of Materials, Pergamon Press, 1999.
[4] Lu, L. & Lai, M. O., Mechanical Alloying and Milling, Springer, 1997.
[5] Suryanarayana, C., Mechanical Alloying and Milling, Progress in Materials Science, 46, pp. 1-184, 2001.
[6] Borkowski, P., Walczuk, E., Wojcik-Grzybek, D., Frydman, K. & Zasada, D., Electrical Properties of Ag-C Contact Materials Containing Different Allotropes of Carbon, Proceedings of the 56th IEEE Holm Conference on Electrical Contacts (HOLM), pp. 1-9, 2010.
[7] Biyik, S. & Arslan, F., Investigation of Properties of Silver - Boric Oxide Based Contact Materials Produced by Powder Metallurgy, 6th International Powder Metallurgy Conference & Exhibition, Ankara, Turkey, pp. 671-678, 2011.
[8] Leung, C. & Streicher, E., Material transfer in dynamic welding of Ag and Ag/SnO$_2$ contact material, Proceedings of the 48th IEEE Holm Conference on Electrical Contacts, pp. 21-28, 2002.

[9]   Biyik, S., Toz Metalurjisi Yontemiyle Gumus-Bor Oksit Esasli Kontak Malzemesi Uretimi ve Ozelliklerinin Incelenmesi, M.Sc. Thesis, Karadeniz Technical University, Trabzon, 2008.

[10] Walczuk, E., Borkowski, P., Ksiezarek, S., Missol, W., Rdzawski, Z. & Durst, K., Evaluation of Basic Electrical Parameters of Silver-Based Contact Materials of Different Chemical Composition and Manufacturing Technology, Proceedings of the 56th IEEE Holm Conference on Electrical Contacts (HOLM), pp. 1-8, 2010.

[11] Biyik, S. & Aydin, M., Investigation of the Compaction Behaviour of Ag8ZnO Composite Produced by Mechanical Alloying, International Porous and Powder Materials Symposium and Exhibition, Izmir, Turkey, pp. 145-149, 2013.

[12] ASM Handbook: Volume 2: Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, 1990.

[13] Turner, H. W. & Turner C., Copper in Electrical Contacts, CDA Publication 23, 1997.

[14] ASM Handbook: Volume 7: Powder Metal Technologies and Applications, 1998.

[15] Zhao, L., Li, Z. & Zhou, Y., Arc erosion characteristics of nanocrystalline CuCr contact material, 1st International Conference on Electric Power Equipment - Switching Technology (ICEPE-ST), pp. 594-597, 2011.

[16] Miao, B., Xie, J., He, J., Liu, G., Wang, W. & Wang, X., Effects of trace Te on the anti-welding property of Cu-30CrTe alloy contact material, 25th International Symposium on Discharges and Electrical Insulation in Vacuum (ISDEIV), pp. 189-192, 2012.

[17] Cui, Y.S., Wang, Y., Shao, W.Z., Zhen, L. & Ivanov, V.V., Microstructure Analysis and the Effect of Cr Additive on Electrical Performance of (Cp-Nb)/Cu-Cd Electrical Contact Materials, Proceedings of the 52nd IEEE Holm Conference on Electrical Contacts, pp. 136-142, 2006.

[18] Wang, Y. & Ding, B., The preparation and the properties of microcrystalline and nanocrystalline CuCr contact materials, IEEE Transactions on Components and Packaging Technologies, pp. 467-472, 1999.

[19] Gentsch, D. & Gorlt, K., Welding behavior of vacuum interrupters equipped with CuCr contact material caused by making and breaking operations under short circuit current interruption, 25th International Symposium on Discharges and Electrical Insulation in Vacuum (ISDEIV), pp. 213-216, 2012.

[20] Godechot, X., Ernst, U., Dalmazio, L., Kantas, S., Hairour, M. & Fadat, N., Late breakdown phenomena investigation with various kinds of contact material, 24th International Symposium on Discharges and Electrical Insulation in Vacuum (ISDEIV), pp. 206-209, 2010.