Effect of Sintering Parameters on Microstructure and Properties of Mechanically Alloyed Copper-Tungsten Carbide Composite

Mahani Yusoff and Zuhailawati Hussain

***Abstract*—In this study, copper-tungsten carbide composite was produced by mechanical alloying and powder metallurgy. The effect sintering temperature and time (800 ℃ to 1000 ℃ and 1 to 3 h) on composite microstructure and properties were investigated. The results showed that WC is formed at lower temperature and the presence of WC favoured the enhancement of the properties of the composite. The increased both hardness and electrical conductivity has been observed with the increase sintering temperature.**

***Index Terms*—Copper-based composite, mechanical alloying, sintering.**

I. Introduction

Copper-based composite benefits from its excellent electrical properties, thermal conductivity and good resistance to oxidation are mostly utilized in electrical application [1]-[3]. Copper-based composite is as a promising material for electrical contact which is widely used in high voltage switches, circuit breakers, relays and welding electrodes. Carbide is frequently used as reinforcement material that is homogenously dispersed in copper matrix. The advantage is they can retard particle coarsening during annealing, in order to retain the strength of the composite. Tungsten carbide is a refractory metal with a high melting point (2777 ℃) [4], high hardness (1000 kg/mm^2) at elevated temperatures [5] excellent resistance to oxidation and a high thermal stability.

Copper-tungsten carbide composite electrical contact has been fabricated mostly by powder metallurgy through powder blending, compacting and sintering. Powder metallurgy able to disperse very fine reinforced particles into copper, leading to a better control of microstructure. Stobrawa and Rdzawski [3] have shown that fine separated tungsten carbide particles are embedded in copper matrix with the enhancement of composite density and hardness. On the other hand, powder metallurgy coupled with mechanical alloying imparts a large amount of interest among several researchers [6]-[8]. High energy milling can promote mechanical alloying, a process that causes severe mechanical plastic deformation of the entrapped powders due to ball-to-ball and ball-to-wall collisions, significantly enhancing the generation of dislocation. Solid state process is enhances by sintering in order to produce density-controlled materials by applying thermal energy. Solid state sintering occurs when the green compact is densified entirely in a solid state at particular sintering temperature. Many factors can be addressed to contribute composite sintering abilities. They include green density, constituent element, particle size, heating rate, sintering temperature, sintering time and sintering environment. Mechanical alloying mechanism is used to promote the diffusion process by producing nanostructured while sintering is expected to enhance the diffusion by forming a new phase. Solid state sintering for copper-based composite usually occurs at sintering temperature of 800 to 1000 ℃ [9]-[11]. Therefore, in the present work, the effects of sintering parameters on copper-tungsten carbide composite prepared by powder metallurgy and mechanical alloying were investigated. The properties of sintered composite were also discussed.

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II. Materials and Procedure

Elemental copper (Cu; 99.8% purity; average particle size 22.3 μm), tungsten (W; 99.9% purity; average particle size 11.4 μm) and graphite powders (C; 99.8% purity; average particle size 17.0 μm) were milled in a planetary ball mill (Fritsch Pulverisette 5) in an argon environment. The powder mixtures were milled for 40 h at 400 rpm speed with a ball-powder ratio of 10:1 with 10 mm ball. The powders were then compacted at compaction pressure of 300 MPa and sintered under argon atmosphere at sintering temperature of 800 ℃ to 1000 ℃ and holding time of 1 to 3 h. The characterization for microstructure and phase identification of sintered composite was scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Quantitative analysis was performed by Rietveld method. The density of composite was determined according to Archimedes' principle. Hardness of the sintered composite was characterized using Vicker's microhardness tester. The electrical conductivity determination was measured by four point probe.

III. Results and Discussion

Fig 1. shows the XRD patterns of sintered copper tungsten carbide composite milled at 40 h and sintered at different sintering temperature. No significant differences exist among patterns depending on the sintering temperature and holding time except the increased intensity of WC peaks and formation of $FeWO_4$ for sintering at 900 ℃, 3 h. Small WC peaks are detected at even lower temperature and its intensity is increased with increasing sintering temperature. After mechanical alloying for 40 h, each particle of as-milled Cu-W-C powder contains Cu, W, and graphite particles. During sintering, the Cu matrix in each particle sinters together by forming necking that creates Cu multi-networks [12]. Later, the process of carbide formation occurred in accordance to available embedded tungsten and graphite in Cu matrix. Therefore, WC was noted at even lower temperature. Nevertheless, W_2C formation was not affected by increasing sintering temperature since it can only be formed with sintering at 900 ℃; this feature is in contrast with Koc and Kodambaka’s [13] work. In general, high holding time is used to eliminate the impurities, but it is actually works with refined microstructure [14]. At sintering of 900 ℃ with 3 h temperature hold, in addition to Fe_3W_3C and Cu_2O phases, peak of $FeWO_4$ was identified. It could be that the entrapped gas gets evaporated during this sintering cycle. But, in the present case, some of them getting evaporated and some of them more preferably reacted with iron to form an oxide phase. The width of Cu peaks change with increasing sintering temperature from 900 to 1050 ℃. It is suggested that increasing sintering temperature has contributed towards stress releasing as well as grain growth of particles under sintering which is in accordance with the Hall-Petch principle [15].

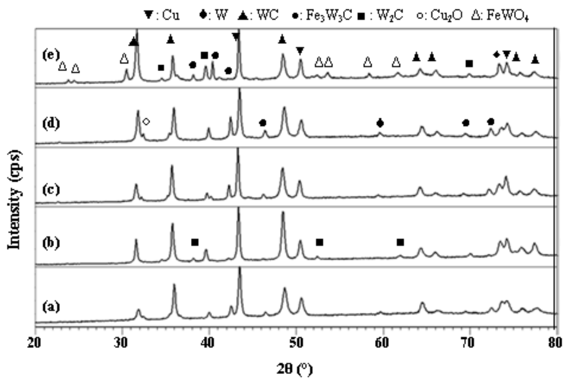


Fig. 1. XRD patterns of sintered compact sintered at (a) 800 ℃, 1 h (b) 900 ℃, 1 h (c) 1000 ℃, 1 h (d) 900 ℃, 2 h and (e) 900 ℃, 3 h

Fig. 2 shows the weight percentage of WC phase with sintering temperatures. W_2C formation was observed to not be influenced by increasing sintering temperature, it was also not included in this figure. The amount of WC increased with sintering temperature from 800 to 1000 ℃ while the reduction at 1050 ℃ is attributable to formation of Fe_3W_3C.

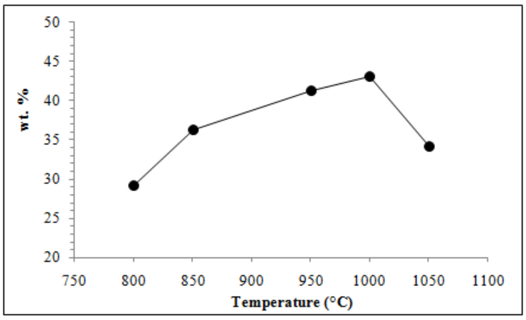
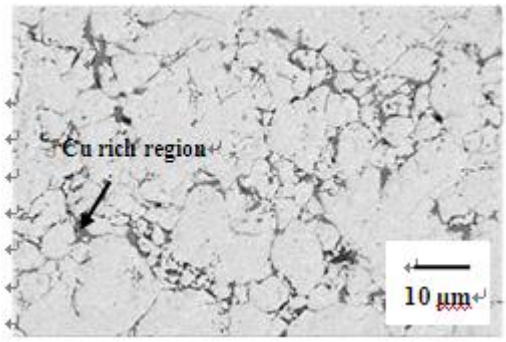
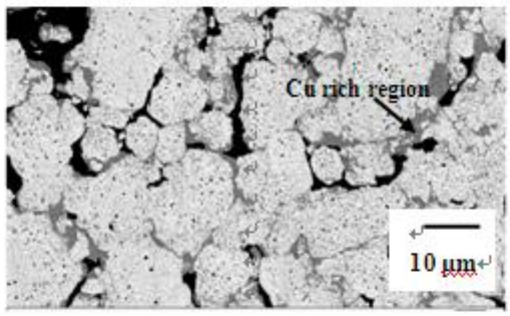


Fig. 2. WC weight percent (wt.%) of sintered compact with different sintering temperatures

The progress of microstructure with sintering temperature is illustrated in Fig. 3. The pores are seen to be located along the contact area and some of which located within the particles. The presence of carbide phases makes the particles moderately diffused as they act as barrier in the direction of grain boundary movement. Although grain features cannot be resolved under SEM resolution, it is can be suggested that the evolution of particle grain growth increased with increased sintering temperature. Owing much higher diffusion hence higher closed porosity is attained at increasing sintering temperature which refers to denser structure [16]. However, sintering at 1050 ℃ temperature has more distribution of pores within particles than that of composite sintering at 850 ℃. The reason is due to rapid grain growth at final sintering stage; as the pores has been moved away along the grain boundaries and they have been migrating from boundaries into the interior grain [17]. The appearance of these pores in interior grains had a crucial effect on the composite properties response.



(a)



(b)

Fig. 3. SEM images of sintered compact sintered at (a) 850 ℃ and (b) 1050 ℃ milled

Fig. 4 illustrates the effect of sintering temperature on sintered composite of copper-tungsten carbide composite. Sintered density was positively affected by sintering temperature from 850 to 950 ℃ but decreased with higher sintering temperature from 1000 to 1050 ℃. At 850 to 950 ℃, the possible explanation for the increment is a reduction of the amount pore which causes high dense structure. At higher sintering temperature, the decreased in sintered density may attribute to inadequate removal of the entrapped oxygen during sintering. For high dense structure, the open porosity on the surface of composite was close during sintering which prevented the entrapped oxygen inside to escape. After sintering, they are leaving within composite as porosity [18].

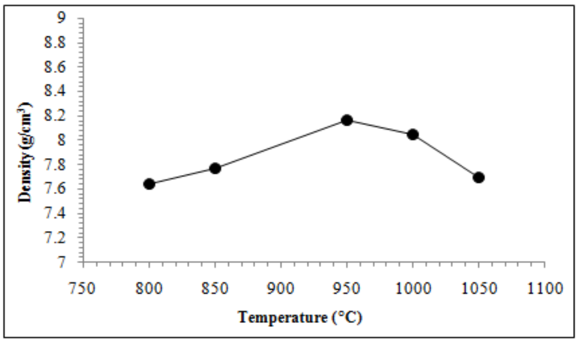


Fig. 4. Density of sintered compact with different compaction pressures

The hardness of sintered composite with different sintering temperature is shown in Fig. 5. An increased in hardness was observed in the composite sintered at 950°C. Such increment mainly relies on the increased of sintered density where this factor actually depend very much on sintering cycle. However, increasing in sintering temperature causes a reduction in composite hardness. This is due to the presence of Fe_3W_3C phase in which overcome strengthening effect provided by the precipitates WC to the composite at high temperature. Another reason for decreasing hardness is due to an increase of stress relaxation and Cu grain growth. When sintering temperature increase, crystallite growth was not too robust since deceleration of grain boundary movement due to WC and/or W_2C presence.

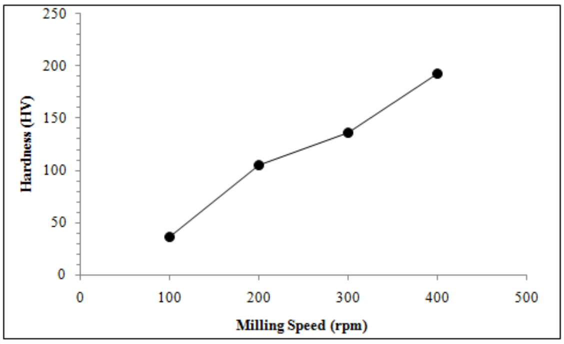


Fig. 5. Hardness of sintered compact with different sintering temperatures

Fig. 6 shows the electrical conductivity of composite with different sintering temperatures. It can be seen that electrical conductivity increased with increasing temperature from 800 to 950 ℃. The dominant contribution to this feature originates from pores elimination with increasing temperature. Since pores are non conductive, the charge carriers will face less pores on their way for higher sintering temperature and thereby lead to an increase of conductivity. Another possible contributing factor is the presence of high carbide amount that may also resist the electron movement.

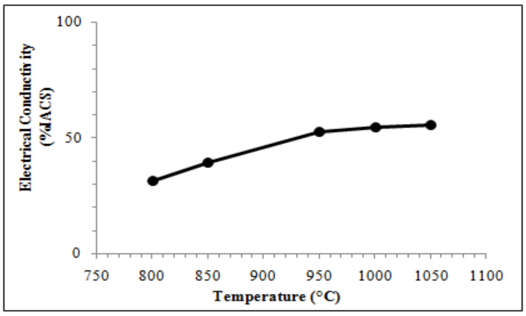


Fig. 6. Electrical conductivity of sintered composite with different sintering temperature

IV. Conclusion

In this work, microstructure and properties of the mechanically alloyed copper-tungsten carbide composite were investigated. WC phase was observed at lower sintering temperature. Increasing sintering temperature served to increased WC amount but the amount reduced to a certain extent. Large pores observed at higher temperature were not seen at lower temperature. Sintered density increased with increased sintering temperature. Reduction in densities after 950 ℃ was also observed which mainly influence by large number of porosities. Variation in hardness and electrical conductivity with increasing sintering temperature seems to follow variation in sintered density.

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