Jurnal Teknologi

Full paper

# The Effect of Ball Milling Process on Sintering and Densification Enhancement of W-Bronze Composites

Kahtan Sadiq Mohammed[a]*, Azmi Rahmat[a], Khairel Rafezi Ahmad[a]

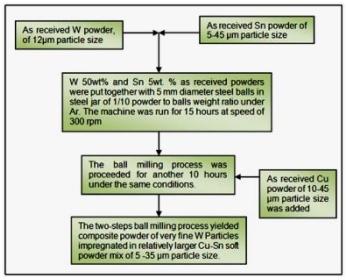
[a]*Universiti Malaysia Perlis, School of Materials Engineering-Taman Muhibah-Jejawi-Arau 02600 Perlis, Malaysia*

*Corresponding author: kahtan@unimap.edu.my

**Article history**

Received : 28 March 2012
Received in revised form : 22 May 2012
Accepted : 30 October 2012

**Graphical abstract**




**Abstract**

**T**he miscibility of W in Sn and Cu is extremely poor. The wettability of W by those two elements is limited. To tackle this problem, two step ball milling process of the W–bronze elemental powders was proposed in this study. The softness of Sn in the first step was exploited to modify the surface morphology of the W particles. In the second step Cu was added to the ball milled mixture. To achieve this goal, two different sets of W50wt. %–pre mix bronze compacts of ball milled and of as received powders were utilized. Sintering process was performed at 1150°C. The two–step ball milled powders yielded sintered compacts of fine polygonal and homogeneous W network skeletal dispersed in bronze matrix. Sintered compacts of about 95% theoretical density were produced by this technique.

*Keywords*: Metal matrix composites; mechanical alloying; sintering; microstructure; scanning electron microscopy

**Abstract**

Kebolehcampuran W ke dalam Sn dan Cu adalah sangat terhad. Kebolehbasahan W oleh kedua-dua unsure juga adalah terhad. Untuk mengatasi ini, proses dua-langkah pengisaran bebola serbuk-serbuk unsur-unsur gangsa dan W telah dicadangkan dalam kajian ini. Sifat lembut Sn telah dieksploitasi dalam langkah pertama untuk mengubahsuai morfologi permukaan partikel W. Dalam langkah kedua, Cu telah ditambah kepada campuran bebola terkisar. Untuk mencapai matlamat ini, dua set berbeza kompak W50% berat – pracampur gangsa bebola terkisar dan serbuk sebagaimana diterima telah digunakan. Proses persinteran telah dilakukan pad 1150° C. Proses dua-langkah pengisaran bebola menghasilkan kompak tersinter yang mempunyai poligon halus dan rangkaian rangka W terserak dalam matriks gangsa. Kompak tersinter dengan ketumpatan teori lebih kurang 95% dapat dihasilkan melalui teknik ini.

*Kata kunci*: Metal matrix composites; mechanical alloying; sintering; microstructure; scanning electron microscopy



## 1.0 INTRODUCTION

W–bronze MMCs are used in various applications. Characterized by their high strength, adequate fracture toughness, high hardness, high density and high wear resistance, it makes them very useful in military and industrial applications [1, 2]. W is immiscible in Cu and Sn and vice versa. Copper heat of mixing with W is positive i.e. 35.5 kJ/mol and the energy of formation of W–Sn solid solution is positive as well i.e. 20 kJ/mol [1, 2]. Mechanical alloying (MA) is a rapidly developing technology that is capable of producing a wide range of dispersion strengthened, energetic and fine powders called composite particles [2].

There are many factors influence the liquid phase sintering and densification of W–bronze composites. Those include; W particle size, W particle shape, and solid–liquid density difference, dispersion of W particles, green compact pressure, wettability, sintering time and sintering temperature [3, 4, 5 and 6].

Denser structures of W–bronze systems can be attained by using finer elemental powders, incorporating sintering activators and sintering at higher temperatures [7, 8, and 9]. Tungsten volume fraction as low as 17%, is sufficient to prevent slumping and retain the shape of the sintered compact [4].

In this investigation, the effects of MA of the elemental powder mixtures by the two–step ball milling (BM) process on the densification of W50wt. %–pre mix bronze composite were studied. Density measurements, X–ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive X–ray spectroscopy (EDS) were used to evaluate the effectiveness of MA on the sintered compacts densification.

Finally, the results of Vickers micro hardness, residual porosity, W–base grain size and W grain distribution were interrelated.

## 2.0 EXPERIMENTAL

The two–step BM W50wt. %–pre mix bronze powder was prepared according to the procedure specified in Figure1.

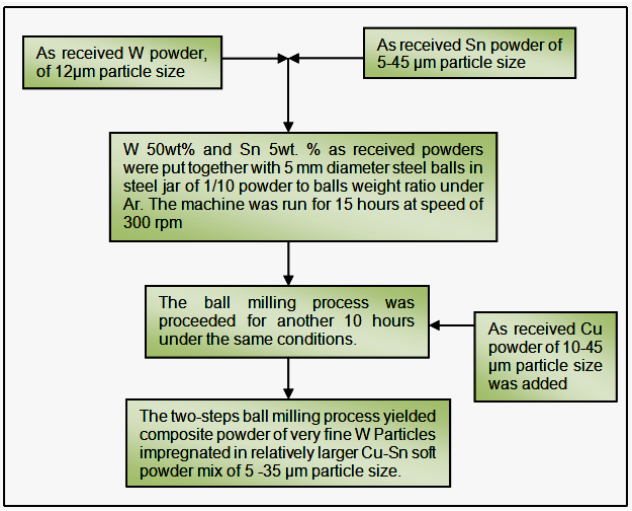



**Figure 1** The flow chart of the two–step ball milling process used for the preparation of the W50wt%-pre mix bronze powder.

Small amounts of the powder mix from each preparation stage were spared for testing. Powder mixture charges of 4 grams each were die pressed at 360 MPa to yield disc-like green compacts of 13 mm diameter and approximately 4 mm thickness. The sintering process was conducted at 1150°C for 3 hours under dry $H_2/N_2$ gas. The sintered compacts density was evaluated by direct sample dimensions measurement and by water displacement (Archimedes) method. Post sintering, the sintered compacts were prepared according to the conventional metallographic procedure. The effects of BM and MA on sintering mechanisms and consequently on sintered compacts microstructure were examined using optical microscopes, XRD analysis, SEM and EDS.

The densification degree of the sintered compacts were evaluated according to the following formula

$$\psi = \rho_s - \rho_G / \rho_T - \rho_G \qquad (1)$$

Where; $\psi$ is the densification degree pct; $\rho_s$, $\rho_G$ and $\rho_T$ are sintered density, green density and the theoretical density in g/cm$^3$ respectively [10].

## 3.0 RESULTS AND DISCUSSION

The modification of the W surface morphology during the BM process was realized by adding very thin Sn layer to the W particles surface. In the first step and by repetitive collision and impaction of the W and Sn particles with the milling media most of the extremely soft Sn particles were plastically deformed and formed very thin plate like particles while the tungsten particles mainly fractured to smaller sizes. With the continuation of the process, more small hard tungsten particles got embedded in the soft thin plate–like Sn particles, or got coated and smeared with a very thin film of Sn element as shown in Figure 2.

In the second step and by the addition of Cu elemental powder, very similar action took place. The free W un–embedded particles either embedded in Cu or in Sn particles or broke again and again to small and smaller sizes as shown in Figures 3

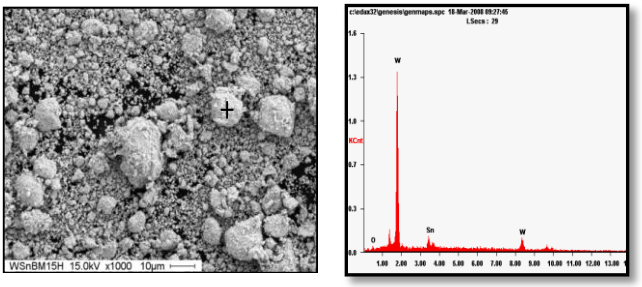



**Figure 2** SEM image of the W50wt. %-Sn mixture after the first step of the "two–step BM process"

The final outcome of the two–step ball milling process was composite particles of W–Sn–Cu with very fine polygonal W grains dispersed and embedded in Cu–Sn matrix. Additionally, some other relatively large, loose and detached W particles can be seen in the powder mixture as well. Due to the ball milling action, W slightly deformed and Cu heavily deformed but both of them maintain their crystalinity while the Sn phase, and only after few hours of the ball milling process, it entirely lost its crystalline structure.

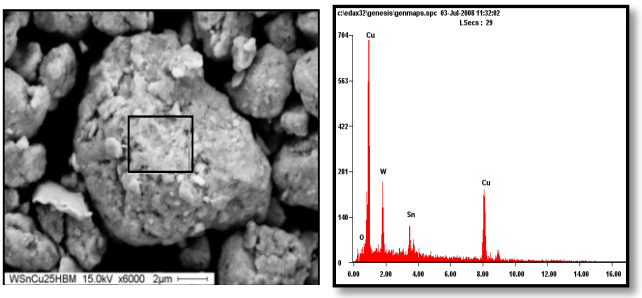



**Figure 3** SEM image of the final product of the W50wt. %-pre-mix bronze powder mixture.

In sintering, the dispersion of very fine W particles within the Cu–Sn matrix brought about by the two–step ball milling process has led to a very narrow W–W spacing and consequently to a higher capillary force [3, 11]. Incorporating high Cu-Sn (bronze) liquid phase volume fraction of 70% and adequate capillary force have led to rapid pore closure followed by rapid densification [12, 13]. The W network skeletal was strong enough to retain compact shape and prevent any distortion. The sintered compacts of the non BM powders gave much lower hardness and sintered density as opposed to those compacts of BM powder as shown in Table 1.

During sintering, the densification process occurred simultaneously at two levels, within the W–Cu–Sn composite particles and in the compact bulk. The fine W particles and the availability of Cu-Sn liquid phase enhance the densification process within the composite particles. The liquid phase covered these particles and connected them together; capillary force brought them in intimate contacts [2, 7]. The SEM image in

Figure 4 (a) shows agglomerates of very fine W grains in chain clusters among relatively large W particles. The low viscosity bronze melt drifted some relatively large, isolated and uncoupled W grains and to a less extent some W loop-like fine aggregates to the solid/liquid transition zone at the compact periphery as shown by the SEM image in Figure 4 (b).

For the sintered compacts of the two–step BM powders and due to inadequate wetting of the W particles by the bronze matrix, the excess bronze liquid phase exuded to the surrounding.

The interaction between gravity and capillary forces has led to this exudation phenomenon and resulted in sintered compacts of high dense W rich cores covered by thin layers of almost pure bronze.

The low magnification optical graph in Figure 5 (a) depicts the outer features of these sintered compacts. The optical graph in Figure5 (b) shows a conventional sintered compact of as received powder.

The SEM and the low magnification optical images of W50wt%-pre-mix bronze sintered compacts of BM powder in Figure 6 (a) and Figure 6 (b) depict the microstructure and the sintered compacts outer shell feature respectively. .

In some military applications such as small and medium caliber kinetic projectiles, it is very desirable to have a high dense W-rich core covered by a relatively thin and soft shell. This sort of microstructure can cope with the external and internal ballistic requirements. The high dense core serves small size and drag force reduction while the soft shell promotes anti wear resistance of the barrel internal surface at high rate of firing and rubbing action. This type of structure is preferable in electronic applications as well, specifically for power supply heat sinkers fabrication whereas the high W volume fraction core results in low coefficient of thermal expansion (CTE) matching that of electronic parts. While the Cu covering shell serves as an efficient heat dissipative and electrical conductive path. Proper material selection and pre–designed ball milling procedures coupled with controlled sintering parameters can yield the desired compact microstructure [14].

**Table 1** The specifications of the two sintered compact sets

| Compositions | Milling time (hours) | Green density %T.D | Sintering conditions | Sintered density %T.D | Microhardness (Hv) | Densification % |
|---|---|---|---|---|---|---|
| W50wt.%-pre-mix bronze Two-steps | 25 | 71 | conventional | 95 | 197 | 45 |
| W50wt.%-pre-mix bronze | as received | 80 | conventional | 82 | 90 | 4.5 |

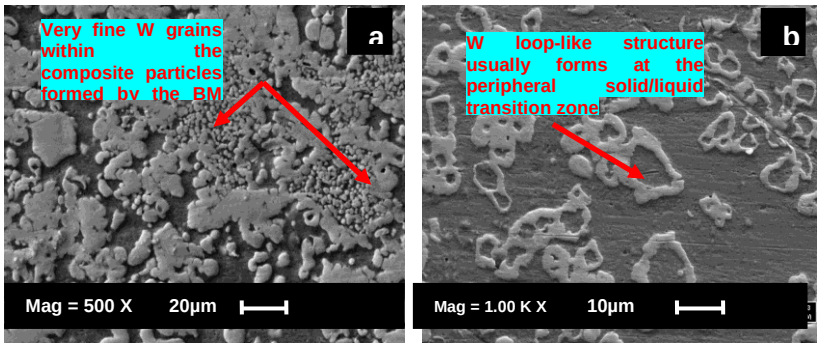



**Figure 4** SEM images of W50wt. %-pre-mix bronze sintered compacts of BM powder (a) sintered compact of agglomerates of very fine W grains in chain clusters among relatively large W particles (b) a typical loop-like structure of tungsten grains appeared at the extreme solid/liquid transition zone adjacent to the compact periphery

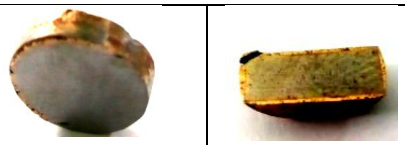
| Composition | Sintered compacts |
|---|---|
| **(a)** W50wt.%-pre mix bronze of two-steps BM powders |  |
| **(b)** W50wt. %-pre mix bronze of as received powders. |  |

**Figure 5** Low magnification (X2) optical graphs of the two sintered compact sets. The sintered compacts of the two-step BM powder in (a) showed the higher relative sintered density and Hv hardness values as opposed to compacts of as received powder in (b), they were covered by thin shells of pure bronze

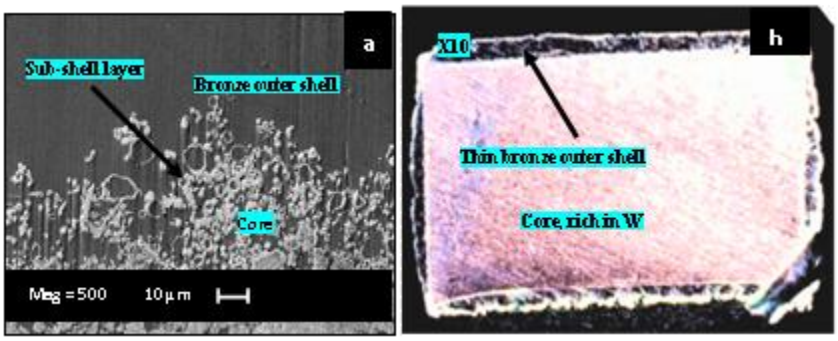



**Figure 6** The SEM image in (a) depicts three distinguished zones in the microstructure of W50wt%-pre-mix bronze sintered compact of two-step BM powder, thin pure bronze outer layer, sub layer of large W grains and high dense W-rich core (b) optical graph of a vertical cross sectional area of a similar sintered compact reveals a high dense W rich-bronze core covered by an almost pure thin shell of bronze

## ■4.0 CONCLUSION

The two-step ball milling process of the W50wt. %-pre mix bronze elemental powders yielded MA mixture with good fineness and dispersion of W particles in Cu-Sn mix. Compacts of this composition were liquid phase sintered at temperature above the bronze melting temperature with bronze liquid phase volume fraction of ≈70% without distortion. The interaction between gravity and capillary forces has led to exudation of the excess bronze melt and resulted in a high dense W rich core sintered compacts covered by thin bronze layers.

## Acknowledgement

This work is supported under the Tin Technology UK (ITR) and Malaysian Smelting Corporation, grant No. 650079. The authors gratefully acknowledge the support provided by ITR, MSC.

## References

[1] Xia, Z. Shen, J. Shen, Y. Li, Z. 2006. W-Sn solid solution synthesized by mechanical alloying at room temperature. *J. alloys compd*. 10: 1-5.

[2] Raghu, T. Sundaresan, Ramakrishnan, R. Mohan, T. 2001. Synthesis of nanocrystalline copper–tungsten alloys by mechanical alloying. *Mater. Sci. Eng*. A (304–306): 438–441.

[3] da Gosta F., da Silva, A., Gomes, U. 2003.The influence of dispersion technique on the characteristics of the W-Cu powders and on the sintering behavior. *Powd. techno*. 1346:123-132.

[4] Johnson, J., German, R. 2005. Densification and distortion of liquid phase sintered W-Cu. *Sintering*: 291-294.

[5] Ryu, S., Kim, Y., Moon, I. 2002. Dilatometric analysis on the sintering behavior of nanocrystalline W-Cu prepared by mechanical alloying. *J. Alloys Compd*. 335; 233-240.

[6] Li, Z., Jia, C., He, Y., Chen, L., 2006. Kinetic characteristics of liquid phase sintering of mechanically activated W-15wt%Cu powder. *J. of Univ. Sci. and Techno*. Beijing. 13(4): 338-345.

[7] German, R. 1997. Supersolidus liquid-phase sintering of prealloyed powders. *Metall Mater. Trans*. A 28A: 1553-1567.

[8] Elliot, K. 2004. Composite material containing tungsten and bronze. Free patent on line. www.freepatentsonline.com/EP1436436.html assignee, international. Non-toxic composites publication.

[9] Johnson, J., German, R. 1993. Phase equilibria effects on the enhanced liquid phase sintering of tungsten-copper. *Metall. Trans.* A 24a 11: 2369-2377.

[10] German, R. 1992. Powder Metallurgy Science, (second edition), *The Pennsylvania State University*: 281: 455

[11] Boonyongmaneerat, Y. 2007 Mechanical properties of partially sintered material. *Mater. Sci. Engin.* A 452-453: 773-780.

[12] Johnson, J. Bresovesky, J. German, R. 2005. Effect of liquid content on distortion and rearrangement densification of liquid-phase-sintered W-Cu. *Metall. Mater. Trans* A. 36A: 1557-1565.

[13] Kahtan, S., Azmi, R., Ismail, A. 2009. The effects of Fe additions on the liquid phase sintering of W–bronze composites. *J. Alloys Compd.* 482: 447-454.

[14] Upadhyaya. A., German, R. 2001. Gravitational effects during liquid phase sintering, *Mater. Chem. phys.* (67): 25-31