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Effect of Milling Speed on the Synthesis of In-Situ Cu-25 Vol. % WC Nanocomposite by Mechanical Alloying

Nurulhuda Bashirom[a*], Nurzatil Ismah Mohd Arif[a]

[a]*School of Materials Engineering, Universiti Malaysia Perlis, Taman Muhibbah, 02600 Arau, Perlis, Malaysia*

*Corresponding author: hudabashirom@unimap.edu.my

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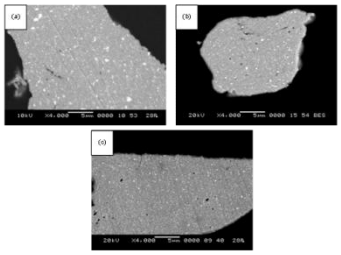
Graphical abstract



Abstract

This paper presents a study on the effect of milling speed on the synthesis of Cu-WC nanocomposites by mechanical alloying (MA). The Cu-WC nanocomposite with nominal composition of 25 vol.% of WC was produced in-situ via MA from elemental powders of copper (Cu), tungsten (W), and graphite (C). These powders were milled in the high-energy "Pulverisette 6" planetary ball mill according to composition Cu-34.90 wt% W-2.28 wt% C. The powders were milled in different milling speed; 400 rpm, 500 rpm, and 600 rpm. The milling process was conducted under argon atmosphere by using a stainless steel vial and 10 mm diameter of stainless steel balls, with ball-to-powder weight ratio (BPR) 10:1. The as-milled powders were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD result showed the formation of W_2C phase after milling for 400 rpm and as the speed increased, the peak was broadened. No WC phase was detected after milling. Increasing the milling speed resulted in smaller crystallite size of Cu and proven to be in nanosized. Based on SEM result, higher milling speed leads to the refinement of hard W particles in the Cu matrix. Up to the 600 rpm, the unreacted W particles still existed in the matrix showing 20 hours milling time was not sufficient to completely dissolve the W.

Keywords: Mechanical alloying, Cu, WC, in-situ, milling speed, nanocomposite

Abstrak

Kertas ini membentangkan kajian kesan kelajuan pengisaran terhadap sintesis nanokomposit Cu-WC melalui pengaloian mekanikal (MA). Nanokomposit Cu-WC dengan komposisi 25 vol.% WC dihasilkan secara in-situ melalui MA daripada serbuk-serbuk elemen kuprum (Cu), tungsten (W), dan grafit (C). Serbuk-serbuk ini dikisar di dalam penggiling bebola planet "Pulverisette 6" bertenaga tinggi berdasarkan komposisi Cu-34.90 wt% W-2.28 wt% C. Serbuk-serbuk ini dikisar dalam kelajuan kisaran yang berbeza; 400 rpm, 500 rpm, dan 600 rpm. Proses pengisaran dilakukan dalam persekitaran argon dengan menggunakan bekas keluli nirkarat dan bebola keluli nirkarat bergarispusat 10 mm, dengan nisbah bebola-terhadap-serbuk (BPR) 10:1. Serbuk yang telah dikisar dicirikan dengan Pembelauan Sinar-X (XRD) dan Mikroskop Imbasan Elektron (SEM). Keputusan XRD menunjukkan bahawa fasa W_2C dibentuk setelah dikisar pada kelajuan 400 rpm dan dengan peningkatan kelajuan kisaran, puncak dilebarkan. Tiada puncak WC dikenalpasti selepas pengisaran. Peningkatan kelajuan kisaran menyebabkan pengecilan saiz kristaliniti Cu dan terbukti dalam saiz nano. Berdasarkan keputusan SEM, kelajuan kisaran yang lebih tinggi menyebabkan penghalusan partikel keras W di dalam matrik Cu. Sehingga 600 rpm, fasa W yang belum bertindak masih wujud di dalam matrik menunjukkan tempoh pengisaran 20 jam tidak mencukupi untuk melarutkan W sepenuhnya.

Kata kunci: Pengaloian mekanikal, Cu, WC, in-situ, kelajuan pengisaran, nanokomposit

1.0 INTRODUCTION

Copper is the most common metal used in electrical industries which is known to have an outstanding electrical and thermal conductivity as well as high mechanical properties. However, its strength is relatively low at elevated temperature although provide excellent strength levels at low and intermediate temperatures [1]. To improve this, led to the production of dispersion strengthened copper-based composites with hard particles, as they commonly offer unique combination of high strength and hardness of hard particles and excellent electrical conductivity of copper at high temperature [2]. Carbides and oxides frequently used as reinforcement that are homogeneously dispersed in the copper matrix. A transition metal carbide, tungsten carbide (WC) which

has superior hardness, abrasive wear strength and high melting point, promises to meet requirements of a good reinforcement material [3].

The in-situ technique is used to overcome the limitations observed in ex-situ technique in the preparation of MMCs such as poor wettability between the reinforcements and the matrix, and also the limited scale of reinforcing phase. In addition, fine and thermodynamically stable ceramic reinforcement phases are formed. The in-situ technique basically involves the synthesis of reinforcement phase in matrix phase by chemical reactions between elements or between element and compound during the composite fabrication. For the conventional ex-situ technique, the reinforcing phases are prepared separately prior to the composite fabrication [4].

Mechanical alloying (MA) is found to be a suitable method to produce in-situ MMCs [5]. It is completely a solid-state processing technique that can be used to synthesis the novel alloys which is not possible to be produced by other method. MA is a dry, high energy milling process and has been employed to manufacture variety of commercially advanced materials including the nanocrystalline materials that has grain size less than 100 nm with excellent physical and mechanical properties [6,7]. The process consists of repeated welding-fracturing-welding of a mixture of powder particles in a high energy ball mill [6]. The process causes severe mechanical plastic deformation and intense cold working of the entrapped powders due to ball-to-ball and ball-to-wall collisions, significantly enhancing the generation of dislocation which leads to formation of nanocrystalline materials due to the reduction of crystallite size that can reached to nanosized particle [3].

The properties and structure of mechanically alloyed composite is highly dependent on the milling parameter such as milling time, ball-to-powder weight ratio (BPR), milling media and milling speed. Varying the collision velocity by changing the milling speed may influence the kinetic energy between powder and milling media in the planetary ball mill. Faster rotation of ball mill transfers more impact energy to the powders throughout collision process and therefore influences the phase formation and properties of composite. Lower milling speed may direct to incomplete phase formation, thus the required properties cannot be achieved [5].

The main interest in this work was to synthesize the hard WC particles into a Cu matrix from the elemental powders of W and C by mechanical alloying, resulting in an in-situ nanostructured Cu-WC composites. The phase identification and morphology of as-milled powders as a function of milling speed were made through XRD and SEM analysis.

■2.0 MATERIALS AND METHODS

Copper powder (99.8% pure, <42 μm), tungsten powder (99.9% pure, <6 μm), and graphite powder (99.8% pure, <21 μm) were used as raw materials. The mixture of Cu, W, and graphite powders with composition of Cu-34.90 wt% W-2.28 wt% C which corresponding to nominal composition of Cu-25 vol.% WC was milled in a high energy Planetary Mono Mill "Pulverisette 6" for 20 hours. The N-heptane was added into the powder mixture to reduce the effect of excessive cold welding that may leads to agglomeration. The milling was conducted at rotational speed of 400 rpm, 500 rpm and 600 rpm to investigate the effect of milling speed on the formation of WC reinforcing phase in the Cu matrix. 10 mm diameter of stainless steel ball was used with BPR ratio 10:1. The as-milled powder was characterized by XRD and SEM. The crystallite size and internal strain of Cu were evaluated using Williamson-Hall method as shown in Eq.1 [8].

$$B_r \cos\theta = \frac{0.89\lambda}{D} + 2\eta \sin\theta \quad (1)$$

where θ is the Bragg angle, D is the average crystallite size, B_r is the line broadening, λ is the X-ray wavelength and η is the lattice strain.

■3.0 RESULTS AND DISCUSSION

3.1 Identification of WC Phase in Cu-W-C Powder

The XRD patterns of as-milled powder Cu-25 vol.% WC for different milling speed; 400 rpm, 500 rpm and 600 rpm are shown in Figure 1. Two strongest XRD reflections were detected on Cu and W peaks. Since the atomic weight of W (183.84 g/mol) is higher than Cu (63.55 g/mol), it tends to give the higher intensity of reflection than Cu as according to Huang, *et al*.(1996), the X-ray atomic scattering factor of an element is directly proportional to its atomic weight. If the element has higher atomic/molecular weight, it has tendency to give higher intensity of reflections due to its high scattering factor [9], even though W has significantly lower volume fraction than Cu. The W peaks were detected up to 600 rpm, indicating it was not completely dissolved in the Cu matrix to react with graphite to form WC. It is in good agreement with SEM result shown in Figure 4, whereby the W particles were still existed in the Cu matrix even it had been milled to the fastest rotation of 600 rpm. This scenario indicating 20 hours milling time was not sufficient to promote the full chemical reaction between W and C to form WC. The graphite peak was not detected in all milling speed because it had been diminished with increasing milling speed as it was dissolved into the Cu lattice as a solid solution [3].

According to Figure 1, the intensity of W reflections was gradually decreased with higher milling speed indicating the increased reaction of W to achieve solid solution. W and Cu peaks were getting broadened suggesting higher milling speed facilitated the gradual deformation of the powder, and indirectly modifying the crystallite size and lattice strain of the powder mixture [3].

The metastable hexagonal phase, W_2C was formed after milling at 400 rpm, 500 rpm, and 600 rpm, but at low intensity peak. This result was in contrast with the finding of Yusoff, *et al*., whereby the W_2C and WC phases only can be formed and precipitated after sintering at 900°C for an hour [3]. After milling up to 60 hours at 400 rpm, they only can observed the elemental starting powders of Cu, W and graphite. The formation of metastable W_2C phase was suspected due to low temperatures obviously found during early hours of milling [10]. In addition, the W_2C phase was observed in the compositions with higher carbon content which milled at low speed and BPR ratio, as well as in carbon-deficient composition milled for shorter period [11]. It was suggesting the appropriate amount of carbon and the optimization of milling parameters plays a crucial role in the successful production of WC phase. In this work, the extended milling time would be beneficial to provide the enough energy to overcome the activation energy for the conversion of W_2C to WC phase. Bolokang *et al*. proposed that longer milling time is required to provide enough energy to drive the reaction between C and W_2C to form WC [3, 11]. When the milling process took longer period, the temperature inside the vial significantly increased which caused the rate of alloying to increase as well. This in turn helps the formation of new phase, in this case, WC phase [3]. No powder contamination observed due to excessive wear of milling tools such as grinding medium and container that may be resulted due to increased milling speed.

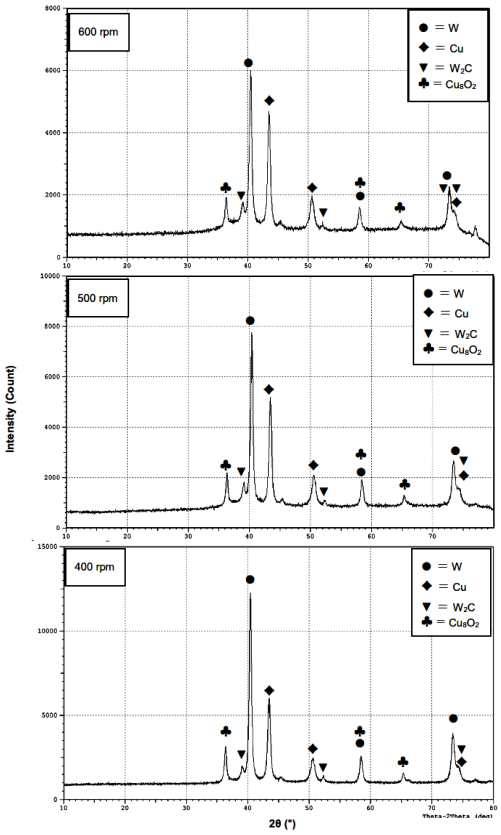


Figure 1 XRD patterns of as-milled Cu-W-C nanocomposite powder with different milling speed

3.2 Crystallite Size and Lattice Strain Measurement

The measurements of crystallite size and lattice strain of copper as a function of milling speed are shown in Figure 2 and Figure 3. Cu peaks were broadened as milling speed increased. The broadening of XRD peaks arises mainly due to three factors which are instrumental effects, crystallite size and internal strain [12]. With increasing milling speed, the crystallite size decreases. Simultaneously, the lattice strain increases due to the generation of dislocations and other crystal defects. The high densities of dislocations are needed to achieve a supersaturated solid solution [8]. Both of these effects are shown in Figure 2 and Figure 3. Consequently, the amount of peak broadening increases with milling speed.

Based on Figure 2, the copper crystallite size decreased gradually from 41 nm to 38 nm with increasing milling speed, suggesting the formation of nanostructured copper composite (with grain size < 100 nm). The faster the mill rotates, the higher will be the energy input into the powder. This is because the kinetic energy of the grinding medium ($E = ½ mv^2$, where m is the mass and v is the relative velocity of the grinding medium) is imparted to the powder being milled [13]. The higher energy transferred to the powder with increased ball impact energy resulted in greater fracturing of the powder than that caused by cold welding at lower milling intensity, thus resulted to decreased crystallite size of copper with increased milling speed [5, 14]. Besides that, the addition of a second element to a pure metal increases the metal strength and hardness also indirectly resulting in a smaller final crystallite size obtained by milling [15]. MA has been known as one of the "top-down" approach in which the bulk material with conventional coarse grain sizes is reduced in its grain size until it reaches nanometer dimensions. The grain sizes with nanometer dimensions have been observed in almost all mechanical alloyed pure metals, intermetallics, and alloys. Thus, it appears that synthesis of nanostructures by MA is a ubiquitous phenomenon and nanostructures could be produced by MA in every material [13].

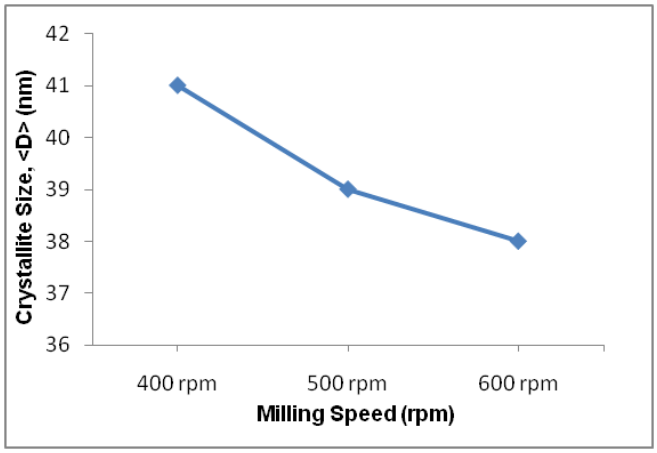


Figure 2 Crystallite size of copper with different milling speed

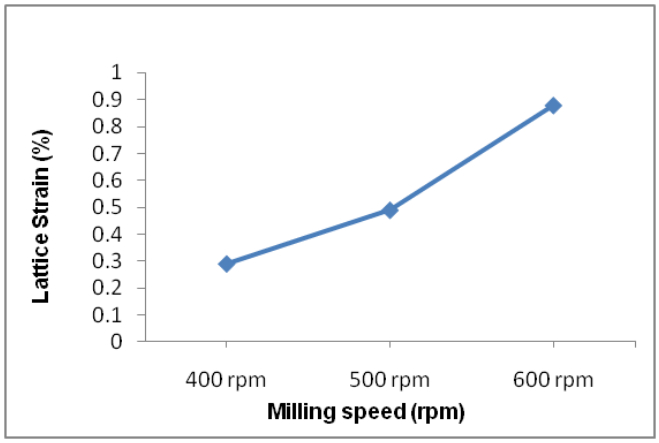


Figure 3 Lattice strain of copper with different milling speed

3.3 Microstructure Evolution

The microstructure evolution of as-milled powder Cu-25 vol.% WC with various milling speed are shown in Figure 4. Two distinctive phases observed, in which white region (labeled as X) and grey region (labeled as Y), respectively (Figure 5). From the EDX result shown in Figure 5 (a) and (b), the white region represents W particles while the grey region represents Cu particles. Generally, the higher atomic number of W will show brighter region relative to regions of low atomic number (in this case is Cu) under back scattered electron (BSE) mode.

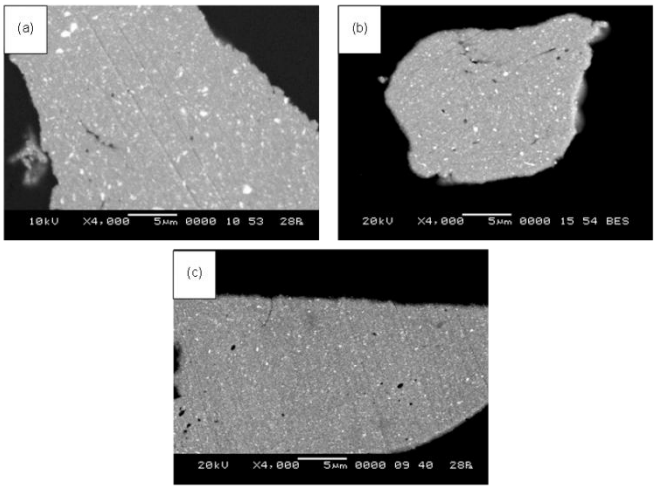


Figure 4 The microstructure evolution of as-milled powder after milling at rotational speed (a) 400 rpm, (b) 500 rpm and (c) 600 rpm

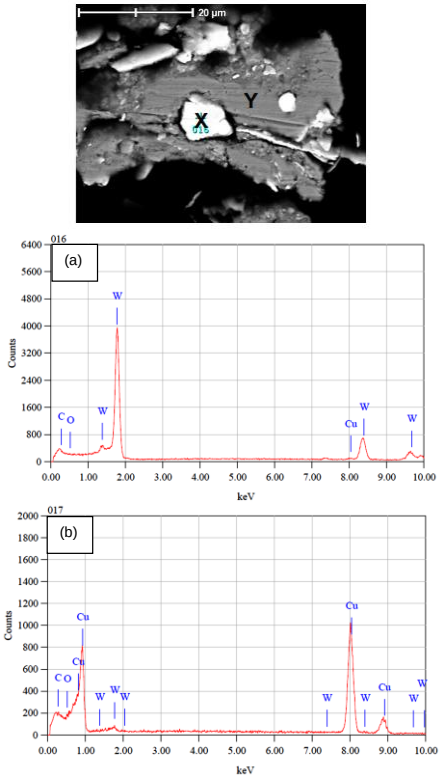


Figure 5 Corresponding EDX analysis on (a) X region and (b) Y region

The homogeneous distribution of W particles in copper matrix was observed in Figure 4 (a), (b) and (c). The unreacted W particles still existed in the matrix in good agreement with XRD result shown in Figure 1. The W particles were refined gradually with rising milling speed. Even at higher milling speed, there was still unreacted W particles observed in the matrix due to its properties which is very hard and dense element. Longer milling time is needed to completely dissolve the W.

During MA, the powder particles are repeatedly deformed, cold welded and fractured by the collision of balls. The collisions caused the impact force to be higher and therefore led to finer powder particle. For ductile-brittle components of Cu-W-C system, the ductile particles (Cu) were plastically deformed and cold-welded and at the same time, the brittle particles (W and C) were embedded into Cu and experienced fragmentation due to the powder entrapment between ball-to-ball and ball-to-inside wall of vial during the milling process [16]. The repeated cold welding (with plastic deformation and agglomeration) and fracturing (reduction in size) throughout milling process eventually produced refined and homogenized microstructure with increasing milling speed. The rising temperature in the vial caused by faster rotation of milling promotes to homogenization due to the high rate of alloying in the powders [16].

4.0 CONCLUSION

The metastable hexagonal W_2C phase was formed without additional heat treatment facilitated by high kinetic energy exerted from the collisions of ball-powder-ball. No WC phase was detected after milling indicates 20 hours milling time was not sufficient to overcome the activation energy for the full reaction of W with C and conversion of W_2C to WC phase. The copper peaks were broadened as milling speed increased due to the refinement of Cu-W-C particles. Cu crystallite size decreased but lattice strain increased with increasing milling speed. The higher milling speed shows the homogeneous microstructure of in-situ Cu-25 vol.% WC where there was still some unreacted W phase observed even after milling at the fastest rotation of 600 rpm

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