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

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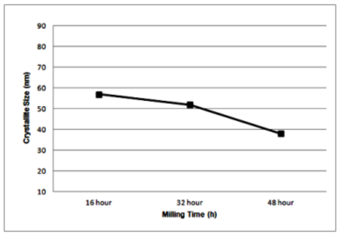
Graphical abstract



Abstract

This paper presents a study on the effect of milling time on the synthesis of Cu-WC nanocomposites by mechanical alloying (MA). The Cu-WC nanocomposite with a 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 the composition Cu-34.90 wt.% W-2.28 wt.% C. The powders were milled in the different milling times; 16 hours, 32 hours, and 48 hours at rotational speed of 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 indicated the formation of WC after milling for 32 hours, and the peak broadening was observed at higher milling time. From SEM observations, the particle size of Cu-25 vol.% WC composites was gradually refined with increasing milling time until the homogenous microstructure was obtained at 48 hours of milling, even though there were still some unreacted W particles existed in the matrix. Increasing milling time resulted in smaller crystallite size and higher lattice strain of Cu. The overall result demonstrates that the longer milling time can be used to achieve WC reinforced copper matrix nanocomposite.

Keywords: Mechanical alloying; Cu; WC; in-situ; milling time; nanocomposite

Abstrak

Kertas ini membentangkan kajian kesan tempoh 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 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.%. Serbuk-serbuk tersebut dikisar dalam tempoh pengisaran yang berbeza; 16 jam, 32 jam, dan 48 jam pada kelajuan putaran 600 rpm. Proses pengisaran dilakukan dalam persekitaran argon dengan menggunakan bekas keluli nirkarat dan bebola keluli nirkarat bergarispusat 10 mm, dengan nisbah bebola-kepada-berat serbuk (BPR) 10:1. Serbuk-serbuk yang selesai dikisar dicirikan dengan Pembelauan Sinar-X (XRD) dan Mikroskop Imbasan Elektron (SEM). Keputusan XRD menunjukkan pembentukan fasa WC selepas pengisaran selama 32 jam, dan pelebaran puncak diperhatikan pada tempoh pengisaran yang lebih tinggi. Melalui pemerhatian SEM, saiz partikel komposit Cu-25 vol.% WC dihaluskan secara beransur-ansur dengan peningkatan tempoh pengisaran sehingga mikrostruktur seragam diperolehi pada kisaran 48 jam, walaupun masih terdapat partikel W yang belum bertindak balas di dalam matrik. Peningkatan tempoh pengisaran menyebabkan pengecilan saiz kristaliniti dan peningkatan terikan kekisi kuprum. Keputusan akhir menunjukkan tempoh pengisaran yang panjang boleh digunakan untuk mencapai nanokomposit kuprum diperkuat WC.

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

■1.0 INTRODUCTION

Copper and its alloys have high electrical and thermal conductivity and found widespread applications, such as resistance welding electrodes, high voltage switches, motor commutators, continuous casting moulds and many more. Within this group of materials particular attention is being drawn to those of a nanometric size of copper matrix grains [1]. Investigations had been carried out so far on the relationship between milling durations and the copper grains size according to Hall-Petch dependence, in which the grain size decreases with longer milling time [2]. Nanostructured copper composites which combine the high conductivity of copper and the excellent mechanical and physical properties of its extremely fine grained nanocrystalline structure are suitable candidates for use in high performance electrical applications. Carbide and oxide particles frequently used as reinforcement materials that are homogenously dispersed in the copper matrix. Tungsten carbide (WC), transition metal carbide known for its high hardness, high elastic modulus and high wear resistance, promises to meet the requirements as a good reinforcement material [3].

Mechanical alloying (MA) is a unique process for fabrication of several alloys and advanced materials at room temperature. Fundamentally, the term milling may be referred to as the breaking down of relatively coarse materials to the ultimate fineness. Over the past three decades, ball milling has evolved from being a standard technique in mineral dressing and powder metallurgy, used primarily for particle size reduction, to its present an important method for the preparation of either materials with enhanced physical and mechanical properties or indeed, new phases or new engineering materials [4]. The MA process using ball milling technique [5], has received much attention as a powerful tool for fabrication of several advanced materials, including equilibrium, nonequilibrium such as amorphous, quasicrystals, nanocrystalline and composite materials [6,7,8]. In addition, it has been employed for reducing some metallic oxides by milling the oxide powders with metallic reducing agents at room temperature [9,10,11]. In fact, MA is a unique process in that a solid state reaction takes place between the fresh powder surfaces of the reactant materials at room temperature [12] and the process that cause severe mechanical plastic deformation of the entrapped powders due to ball-to-ball and ball-to-wall collisions, significantly enhancing the generation of dislocation. Powder fracturing during MA introduces defects into the powder and generates new clean surfaces that are beneficial for atomic diffusion. This process has been developed to synthesize reinforcement directly in the metal matrix composite fabrication using chemical reaction between the raw materials. A metal matrix composite fabricated through in-situ processing has finer powder particles [3].

The milling time is one of the most important parameters in milling of powders. Normally the time is chosen to achieve a steady state between fracturing and cold welding of powder particles to facilitate alloying. The times required vary depending on the type of milling used, mill settings, intensity of milling, BPR ratio, and temperature of milling. The necessary times have to be decided for each combination of the above parameters and for the particular powder system under consideration [13].

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 time were characterized via 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. 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" at rotational speed of 600 rpm. The N-heptane was added into the powder mixture to reduce the effect of excessive cold welding that may lead to agglomeration. The milling process was performed at the different duration; 16 hours, 32 hours, and 48 hours in order to investigate the effect of milling time on the formation of WC 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 technique. The crystallite size and lattice strain of Cu were measured using Williamson-Hall method as shown in Eq. 1 [14]. Williamson-Hall method considered that the peak broadening is caused by crystallite size and lattice strain [13].

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

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 pattern of as-milled powder Cu-25 vol.% WC for the different milling times; 16 h, 32 h, and 48 h are shown in Figure 1. At 16 h milling time, the metastable hexagonal phase W_2C was detected with low intensity peaks. According to Chrysanthou and Erbaccio [15], the formation of metastable W_2C phase was suspected due to low temperatures obviously found during early hours of milling. 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 [16]. After milling for 32 h, it can be seen the intensity of W_2C phase was reduced to permit the reaction with graphite to form the stable phase, WC. The formation of WC was indicated from the existence of low intensity WC peaks diffracted at position 31.512° (001), 35.642° (100), 65.758° (002), and 75.480° (200). The result was in contrast with the findings of Yusoff, et al. [3], whereby the W_2C and WC phases only can be formed and precipitated after sintering at 900°C for an hour [3]. Thus, this indicates the WC phase is possible to be formed after milling without heat treatment.

The broadening of XRD peaks can be observed at 32 h and 48 h of milling, corresponding to crystallite size and lattice strain. This result is in good agreement with crystallite size and lattice strain results shown in Figures 2 and 3. The Cu and W peaks were shifted to lower diffraction angle suggesting the presence of stacking faults [13]. The heavy deformation introduced into the particles during milling is manifested by the presence of this defect structure, which enhances the diffusivity of the solute elements into the matrix [13]. The decreased intensity of W peaks is correlated with the formation of W_2C and WC phases upon extended milling. No graphite peaks were detected in all XRD pattern due to its low scattering factor [17, 18]. It tends to be diminished with extended milling time and dissolved into the Cu lattice as a solid solution [3].

The W peaks still can be observed after milling up to 48 h. This indicates the incomplete reaction of W to form WC. It suggesting the longer milling time is needed to promote the full reaction of W with C, and W_2C with C to form WC.

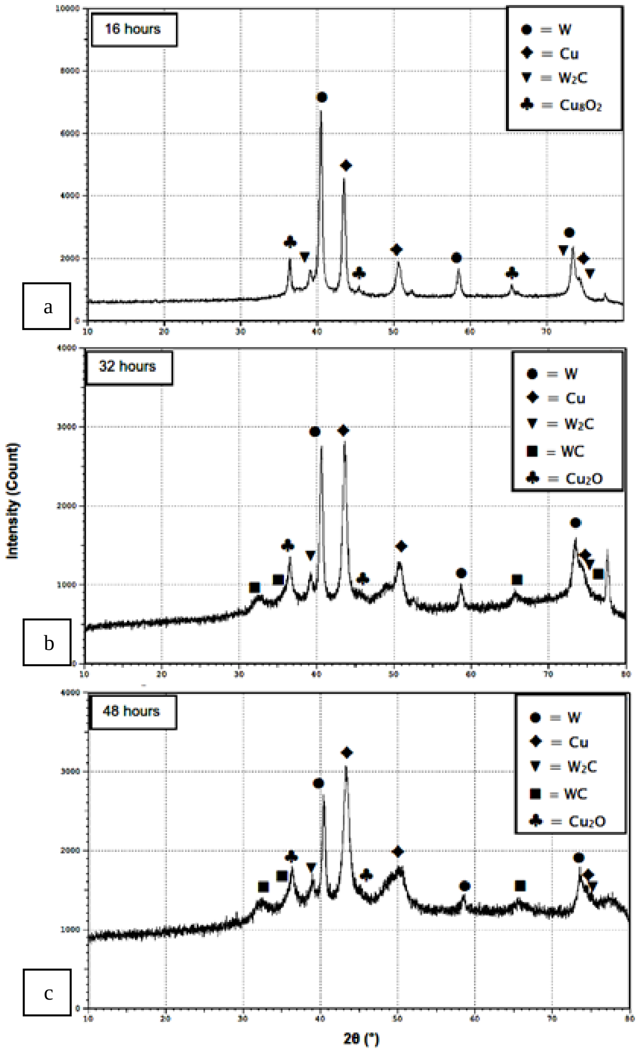


Figure 1 XRD pattern of as-milled Cu-W-C in-situ powder after (a) 16 h, (b) 32 h and (c) 48 h milling time

3.2 Crystallite Size and Lattice Strain Measurement

The concept of X-Ray line broadening related to crystallite size is widely accepted in the research of mechanically alloyed powder particles [19]. Figure 2 shows the reduction of Cu crystallite size with higher milling time, corresponding to peak broadening observed at Figure 1. The Cu crystallite size was decreased with longer milling time due to the repeated fracturing and rewelding of a mixture of powder particles in a highly energetic ball mill and created an accumulation of dislocations that are proved by the result of lattice strain shown in Figure 3. Prolonged milling introduced a high density of defects into the powders, hence increasing its lattice strain [20]. The high densities of dislocations are needed to achieve a supersaturated solid solution [21], whereby the presence of defects structure enhances the diffusivity of solute element into the matrix [13].

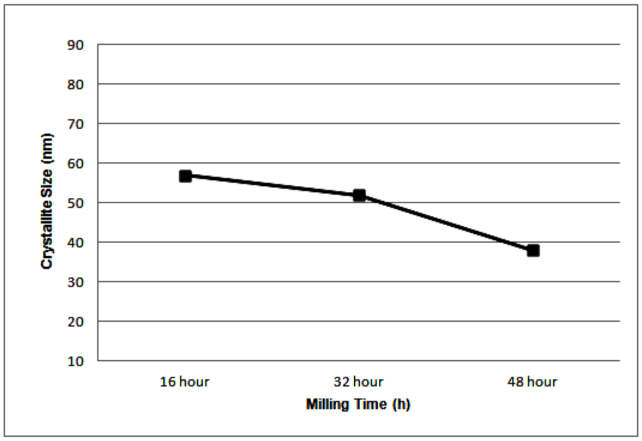


Figure 2 Crystallite size of copper with different milling time

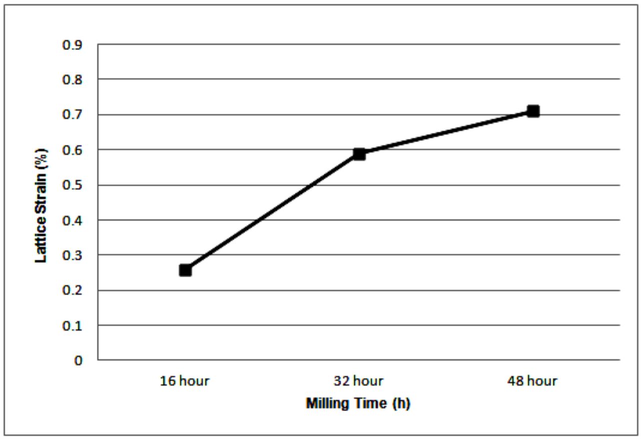


Figure 3 Lattice strain of copper with different milling time

3.3 Microstructure Evolution

From the SEM observation shown in Figure 4, the powder particle size of as-milled Cu-25 vol.% WC decreases exponentially with milling time. Under 1000X magnification, the evolution of particle size can be observed clearly. The refinement and homogenized microstructure of powder particles were due to the competing events of cold welding (plastic deformation and agglomeration) and fracturing (size reduction) throughout the milling period. The rate of refinement of particle/grain/crystallite size with milling time can be increased with increasing milling energy, BPR ratio, and lower temperature [13].

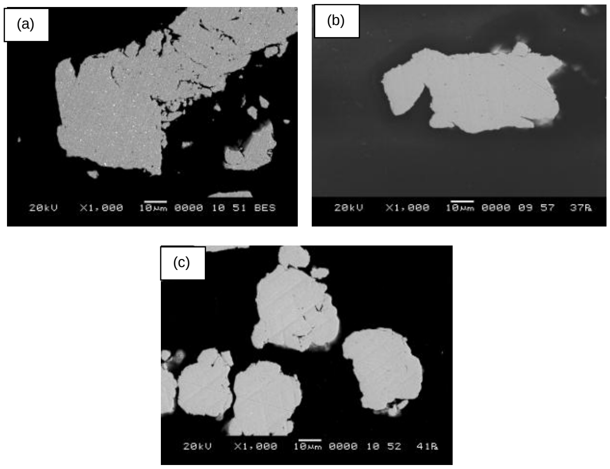
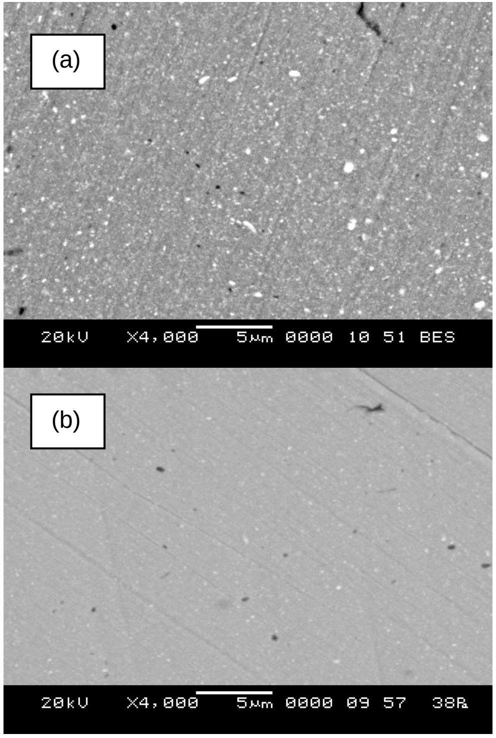


Figure 4 The microstructure evolution of as-milled powder after milling at (a) 16 h, (b) 32 h and (c) 48 h at 1000X magnification.

Figure 5 shows the microstructure of as-milled powder Cu-25 vol.% WC at higher magnification (4000X). From the EDX result shown in Figure 6 (a) and (b), the white region represents W particles while the grey region represents Cu particles. The uniform distribution of undissolved W particles in the Cu matrix can be seen clearly in Figure 5 (a), and these W hard particles were refined further and embedded in the matrix with extended milling duration. During milling, the more brittle constituents such as W and C particles tend to become occluded by ductile Cu and trapped in the composite. Due to repeated cold welding and fracturing events, the homogenized microstructure can be obtained [13].



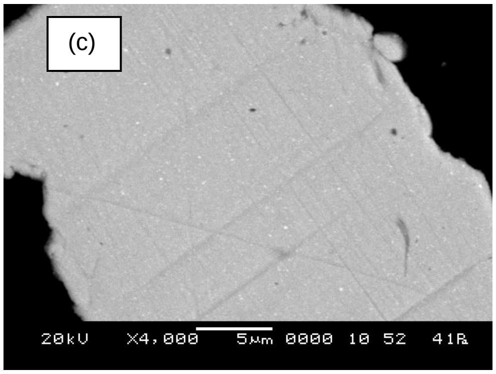


Figure 5 The microstructure evolution of as-milled powder after milling at (a) 16 h, (b) 32 h and (c) 48 h at 4000X magnification.

No interface layer of matrix-reinforcement can be seen from the microstructure at high magnification. The interface is atomically abrupt and free from any interfacial phase, suggesting the direct contact on an atomic scale is established between in-situ reinforcement and the metal matrix [22].

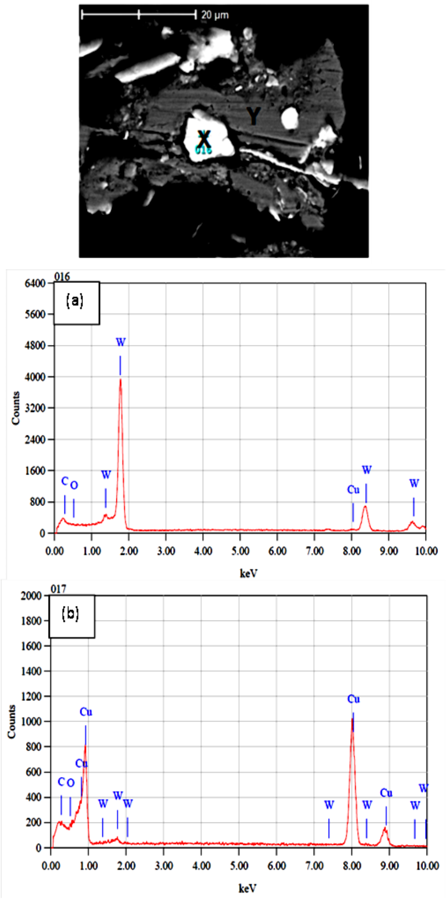


Figure 6 Corresponding EDX analysis on (a) X region and (b) Y region

4.0 CONCLUSION

The WC reinforcement phase was successfully formed by mechanical alloying without heat treatment, but at low intensity of XRD diffraction. Smaller crystallite size and higher lattice strain were observed at higher milling time. The refinement and homogeneous microstructure of in-situ powder Cu-25 vol.% WC was also achieved with prolonged milling time. The longer milling time is required to enhance the formation of WC in the Cu matrix.

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