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Fabrication of Nanostructured Cu matrix Nanocomposites by High Energy Mechanical Milling and Spark Plasma Sintering

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A B S T R A C T

Spark plasma sintering (SPS) is a sintering process that is capable of sintering work hardened powders in short times. This technique was used to fabricate bulk Cu and Cu-SiC nanocomposites. Pure Cu and mixed powders of Cu including 4 vol. % of SiC nanoparticles were mechanically alloyed for 25 h and then sintered at 750 °C under vacuum condition by SPS method. Microstructures of the materials were characterized using optical and scanning electron microscopes and x-ray diffraction patterns, and mechanical properties were evaluated by micro-hardness tests. The results showed density values of 8.69 and 8.30 g/cm^3 and hardness values over 105 and 128 Hv for Cu and its nanocomposite respectively. The addition of nanoparticles retarded Cu matrix grain growth during SPS process and resulted in higher hardness of nanocomposite compared to non-reinforced copper.

1. INTRODUCTION

Copper is an industrial metal and widely used as an alloy or pure metal. This metal has unique properties e.g. high electrical and thermal conductivity, inherent corrosion resistivity, anti-bacterial effect, excellent capability of being alloyed, suitable appearance and is easy to produce [1]. Technological improvements in recent decades depend on using improved materials such as metals, alloys, composites and other structural materials and most of them contain copper. Copper matrix composites are one of the most important and technical materials with extensive applications in structures, heat management, aerospace and automobiles. Copper matrix composites with different nano and micro reinforcements have been produced in recent decade. Through different reinforcements, particles like alumina, tungsten, titanium and silicon carbides and fibers like carbon fibers, tungsten fibers and carbon nanotubes are more attracted. Recently using nano particles of silicon carbide due to their high thermal conductivity, semiconductor behavior, high hardness and low cost have been considered for the copper reinforcement in heat exchanger and resistant welding electrode manufacturing [2 and 3]. An issue in using nanoparticles in metal matrix is the lack of uniform distribution in fabrication methods based on melting and casting. Therefore, in order to make these composites high energy solid state milling method is used to achieve composite powders [4]. Mechanical alloying of copper along with SiC nanoparticles recently has been performed. Of the features of milled powders are high work hardening and nano-metric grains that lead to considerable hardness of powders. Because of the extreme work hardening, milled powders include formability problems and achieving bulk materials with high density through forming of powders with simple methods is difficult [5].So different methods have been used for this purpose such as forming of Cu-SiC composite powders using hot press that lead to bulk composite densities close to theoretical density with significant strength [2]. In a recent work, consolidation of mechanically milled Cu- SiC with different SiC nanoparticles by hot pressing under 150 MPa at 700 °C has been performed. It has been ascertained that the strength of the fabricated nanocomposite increases by adding SiC nanoparticles to nanostructured Cu up to 4 vol.% and then decreases at higher amounts of the nanoparticles (i.e. 6 vol.%) [2]. SPS is a kind of rapid sintering process that is capable of sintering different

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work hardened powders. This method is based on electron discharge phenomenon and providing instant spark plasma with very high temperature in a fraction of second at a local small region of powder particles [6]. The method has been used for the manufacture of several copper matrix composites [7 and 8]. Zhang et al. [7] have considered and optimized the effect of SPS parameters including pressure, temperature and holding time to investigate the sintering process of bulk copper. They could produced large-size ultrafine-grained copper with an average grain size less than 2.2 μm and a relative density greater than 96% be prepared by the SPS process with initial pressure of 1MPa, holding pressure of 50MPa, sintering temperature of 750 ◦C, holding time of 6 minutes and heating rate of 80 ◦C/min. According to their work, when the sintering temperature is under 750 ◦C, the grain growth is slow and limited, while sintering temperatures exceeding 750 ◦C result in the grains growing significantly. Also, with an increase in the initial pressure and decrease of the holding pressure, the bulk density decreases. In another research, the effect of SPS consolidation parameters on submicron Cu and Cu- 0.25 wt. % CNT composites has been studied [8]. They could obtain optimum relative density and hardness of 95.0 and 1.07 GPa for Cu, and 99.2 and 1.30 GPa for the composite, respectively. Sintering of mechanically milled Cu and Cu-SiC powder via SPS process and the microstructural evolution due to this process have not been reported until now. Therefore, in this study fabrication of Cu-SiC nanocomposites by mechanical alloying and spark plasma process as well as microstructure and hardness of produced materials were investigated.

2. EXPERIMENTAL PROCEDURE

In the present study, Cu powder with dendrite morphology and particle sizes lower than 20 μm (purity of 99.7%, Merck Co., Germany) and SiC nanoparticles with average size of 40 nm (purity more than 99%, Nabond Co., China) were used. Monolithic Cu and mixtures of Cu powders (as matrix) and 4 vol. % of SiC nanoparticles (as reinforcement) were mechanically alloyed in a high energy planetary ball mill (Retsch model-Germany) for 25 h. The ratio of ball to powder was 10:1 and ball diameters of 16mm and 10 mm (equal numbers) and rotational speed of 300 rpm were used. The balls and container that used were made of stainless steel. Ball milled powders were formed by SPS process at 750 ˚C under the pressure of 70 MPa for 10 minuts. The microstructure was studied by field emission scanning electron microscope (Mira 3-XMU) and X-ray diffraction method (D8 advanced Bruker). To determine instrumental broadening, annealed Cu powder was used as standard sample. Sample densities were determined by Archimedes method (ASTM B962 – 15 [9]) and the related hardness evaluated by micro hardness test (ASTM E384 - 11e1 [10]) using an Olympus micro-hardness tester (FM-700) (FM-700) with a load of 10 g applied for 15 s.

3. RESULT AND DISCUSSION

Cu powder and Cu matrix nanocomposite including 4 vol.% of SiC nanoparticles were mechanically alloyed for 25h. Figure 1. shows the morphology of nanocomposite powder after different ball milling times. During mechanical alloying, at the initial stages, Cu particles are flattened due to impact of milling medium (Figure 1 (a)). With increasing the milling time, cold welding process become severe and particle sizes increase (Figure 1 (b)). At longer times, amount of work hardening increases and leads to initiation of particle's fracture (Figure 1 (c)). With more increasing in ball milling time, cold welding process and fracture of particles reach a balance and the ratio of particle's fracture in cold welding increases in completely work hardened particles, leading to decreasing in particles size. Finally after 25 h milling, most of the particles become semi spheroids, but some particles are observed in flat morphology (Figure 1 (d)). This mechanism has been reported in several researches for reinforced metal powders [11-13]. In addition, due to repeated impacts from milling medium during milling, nano reinforcements are distributed homogenously and embedded to the copper particles. Figures 2. shows SEM micrograph of a composite powder milled for 25 h and the distribution of the nanoparticles on surface of a particle (distribution map of Si, C and Cu elements).

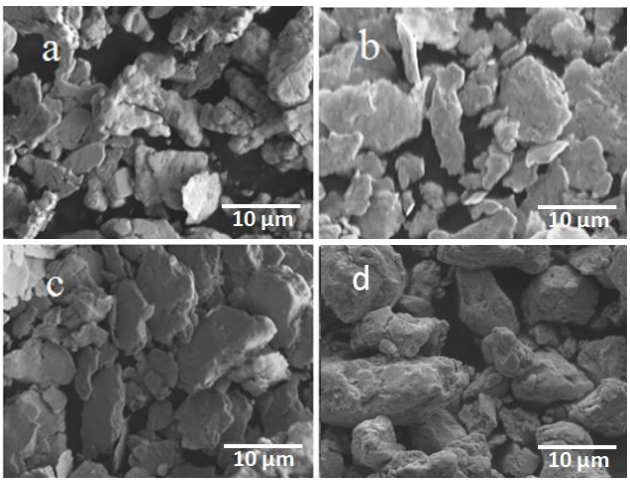

Figure 1. Morphological changes during milling process after (a) 1 h, (b) 5 h, (c) 15 h and (d) 25 h.

This Figure shows that the distribution of the nanoparticles on the surface is homogenous. Figure 2(f) shows the EDS analysis of indicated region on surface of a particle shown in Figure 2(b). Figure 3 shows the

XRD patterns of 25 h - ball milled Cu and Cu-SiC powders.

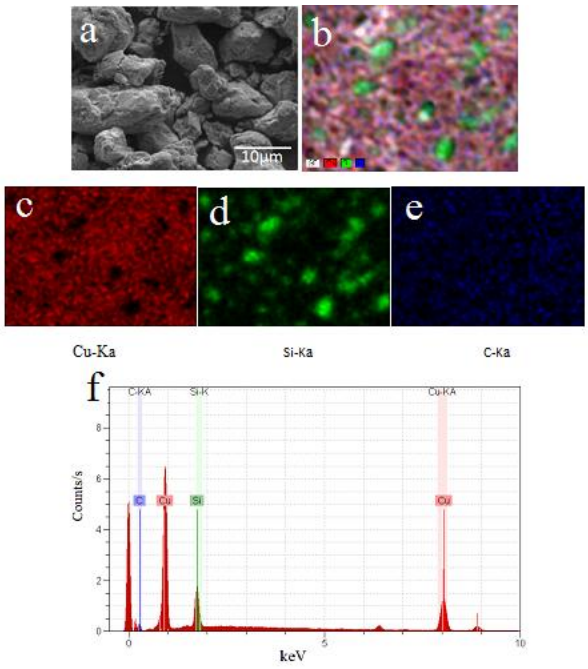

Figure 2. (a) Cu-SiC nanocomposite morphology after 25 h ball milling, (b) surface of a particle, and distribution map of (c) Si, (d) C and (e) Cu on the surface of particle (indicated in part (b) of the figure) , and (e) chemical analysis of the determined area.

In these patterns, the observed four peaks belong to copper. Due to small volume fraction and sizes of nano-metric SiC particles, there is no characteristic peak of SiC in the pattern.

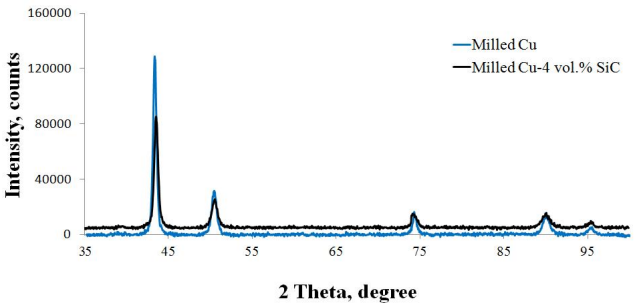

Figure 3. X-ray diffraction patterns of Cu and Cu-SiC after 25 h ball milling.

XRD pattern of the samples show peaks broadening and decreasing of peaks intensities due to ball milling that it is more evident for composite samples. The observed broadening of peaks is due to the increase of lattice strain and grain refinement in Cu matrix.
Grain size and amount of lattice micro-strains were determined equal to 25 nm and 0.35 % for pure Cu and 15 nm and 0.37 % for the nanocomposite respectively using Williamson-Hall method [14 and 15].
Adding nanoparticles to Cu matrix leads to decreasing in Cu grain size and small increasing in lattice strain. Figures 4. shows a typical bright- field TEM micrograph of the nanocomposite microstructure that indicates average grain size of 17nm in which is slightly different from those obtained by x-ray diffraction.
Condensation of the ball milled powders (for 25 h) using SPS process was performed at 750 ˚C and 70 MPa pressure to achieve density close to theoretical density of the powders. Figure 5 shows optical micrographs of bulk Cu and Cu-SiC samples.

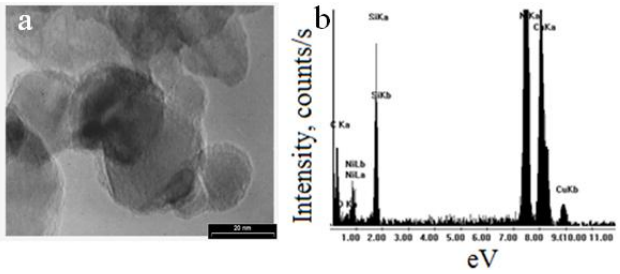

Figure 4. (a) Bright- field TEM micrograph of Cu-SiC nanocomposite, and (b) Chemical analysis of point A in micrograph shown in part (a).

This figure shows that even though the bulk nanocomposite material has slightly much porosity than the bulk Cu, little porosity is observed both materials and they have reached to densities close to theoretical densities. The relative density of the bulk Cu and nanocomposite materials were measured 97% and 95%, respectively.

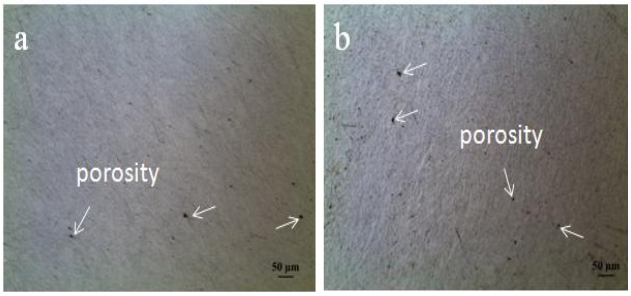

Figure 5 Optical microscope micrographs of bulk (a) Cu and (b) Cu-SiC nanocomposite, provided by spark plasma sintering.

The lower density of the nanocomposite material in comparison to monolithic Cu can be attributed to the effect of SiC nanoparticles on work hardening of the milled powders during mechanical milling and deformation capability of the powders during hot consolidation. The presence of SiC nanoparticles in

copper matrix enhances the work hardening and decreases deformation capability of the powders [11]. Figure 6 (a) shows secondary electron

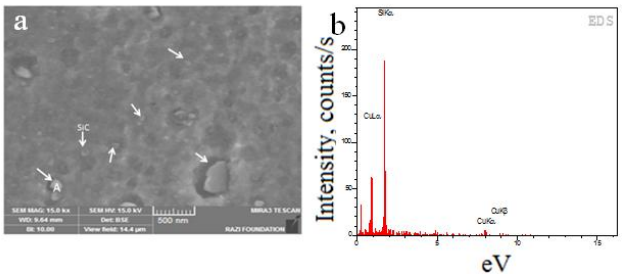

Figure 6. (a) SE-SEM micrograph of nanocomposite sample after severe etching (in 62.5ml Ammonia+ 125ml Hydrogen peroxide+62.5ml DI water solution) that shows distribution of nanoparticles and (b) Chemical analysis of point A in micrograph of part (a). Cu and (b) Cu-SiC nanocomposite, provided by spark plasma sintering.

SEM micrograph of the severe etched nanocomposite that uniform distribution of nanoparticles in its microstructure is observed. Some SiC nanoparticles in this figure have been shown by arrows. Also, a typical EDS analysis of a particle (point A) in micrograph of part (a)) on the etched surface is shown in Figure 6 (b). Microstructure of formed samples by SPS process were evaluated using XRD as well as Williamson-Hall method and grain size of the matrix phase (Cu) were determined in both samples.

TABLE 1. Density, grain size and hardness values of bulk samples prepared by SPS process**.**

material	Cu	Cu reinforced with SiC
Grain size of matrix phase nm	145	83
density g/cm^3	8.69	8.30
Vickers microhardness HV	105	128

Table 1 shows the values obtained for Cu and its composite. After sintering, Cu and the nanocomposite reach grain size of 145 nm and 83 nm respectively. Pure Cu sample experiences more grain growth compared to the nanocomposite during SPS process. Immobile dispersed particles cause decreasing in driving force for the movement of grain boundaries. Many researches have shown that increasing Zener drag force, drastically changes the rate of grains growth and its feature from normal state to abnormal state [16]. The presence of SiC nanoparticles increases the thermal stability of nanocrystalline Cu
trough grain boundaries drag by Zener effect. Grain refinement is one of the most important methods to increase the strength of materials. The effect of grain sizes on yield strength and hardness is expressed by Hall-Petch equation [2]. In this case, strengthening depends on dislocation pinning at grain boundaries. Dislocation pinning at grain boundaries causes stress concentration at the neighboring grains and leads to sliding effect at the vicinity of the grain. Small grains relative to their sizes cause small accumulation of dislocations, hence produce lower stress concentrations. Regarding that adding nanoparticles to Cu matrix caused grain refinement, it can be stated that Hall-Petch mechanism is one of the main strengthening mechanisms in addition to direct strengthening effect of reinforcement by Orowan mechanism and generated dislocations due to thermal mismatch between reinforcement and matrix phase. Table1 shows that by adding nanoparticles to Cu in the prepared Cu-SiC composite by SPS method, hardness value reaches 128Hv from 105HV. The microhardness values of the produced Cu and Cu- SiC bulk materials by SPS are respectively ~200% and 175% higher than the hardness value reported for Cu with micron-size grains (60 Hv) in literature [17]. This strengthening due to nano reinforcements have also been reported for other metal matrix composites and Cu-SiC composites produced by hot press process [3 and 18-20].

4. CONCLUSION

- Nanostructured Cu and Cu-SiC nanocomposite with high relative density were successfully produced using high energy mechanical milling as well as spark plasma sintering process (SPS) at 750 ˚C.
- Adding nanoparticles improved the stability of Cu matrix microstructure during sintering process.
- The prepared nanostructured Cu and Cu-SiC nanocomposite showed hardness values of 105Hv and 128Hv respectively. High hardness value of the nanocomposite attributed to the fine grains of Cu matrix and direct strengthening effect of nanoparticles.

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