Microstructure Characterization and Thermal Stability of Nanocrystalline Cu Powders Processed via Cryomilling

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Nanocrystalline Cu powders with a grain size of about 32 nm have been successfully synthesized using cryomilling technique. The effect of cryomilling time on the particle size, grain size, and structure of cryomilled Cu powders were investigated. The thermal stability of cryomilled Cu powders was studied and the study described the enthalpy change due to grain growth and stress relaxation of cryomilled Cu particles by annealing. The stress relaxation process associated with reordering of the grain boundaries was found to occur at 280°C. The grain growth process was found at 330°C and the thermal release of the grain growth was detected by differential scanning calorimetry analysis.

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1. Introduction

Nanostructured materials, characterized by a microstructural length scale of 1 to 100 nm, have received considerable scientific attention and technological interest because the small grain size can result in notable improvements in mechanical, magnetic, optical and other physical properties.^{1,2} Cryomilling, originally developed to process nanophase dispersion strengthened aluminum alloys, is a high/low energy mechanical milling technique, by which elemental and/or prealloyed powders are milled in cryogenic media, e.g., liquid nitrogen, liquid argon, etc., to form a slurry.^{3,4} Nanocrystalline materials produced by cryomilling have the advantage of smaller crystallite sizes, more homogeneous microstructure and also higher thermal stability compared to other techniques. Extensive studies have been performed on the evolution of the microstructure by cryomilling of single-phase powders and atomized powders.^{5–8} The evolution of microstructure is coupled to the mechanical properties of the powders. Understanding of the microstructure evolution is therefore critical to the understanding of the alloy behavior.⁹ Thermal stability is another facet of the alloy under service. Understanding the thermal stability of the cryomilled powders is important for their potential application. Recently, the enhanced grain stability of cryomilled powders was reported in diverse alloy systems, such as pure Al,¹⁰ pure Ni,¹¹ TiAl,¹² and PdZr.¹³

Previous studies have failed to detect the thermal effect of the grain growth owing to the limited accuracy of the calorimeter.^{14,15} In present study, we detected the thermal release of the grain growth based on differential scanning calorimetry (DSC) analysis. The object of this study was to investigate the microstructure evolution and thermal stability of Cu powders produced by cryomilling.

2. Experimental Procedure

The starting powder used for this work was a commercial

water-atomized Copper (99.81 mass% purity) powder. The copper powder particles have spherical-like shape and in the size range from 5 to 50 μm. The milling of Cu powders was conducted at the rate of 200 rpm for 12 h under a liquid nitrogen environment. The temperature in the vial was between –160 and –193°C. The stainless steel balls of 6.4 mm in diameter were used as the grinding media, and the ball-to-powder weight ratio was 30 : 1. The process details on the cryomilling can be found elsewhere in the literature.¹⁶

The morphology observation of the powders were conducted using a ZEISS SUPRA55 scanning electron microscope (SEM). Particle size distribution was conducted using a SEISHIN LMS-30 laser scattering with ethanol as the scattering media. Microstructure analysis of the as-milled powder was performed using a Hitachi H-800 and JEM-2010 high resolution transmission electron microscope (HRTEM) with an acceleration voltage of 200 kV. The TEM sample of powders was prepared using the carbon grid method.¹⁷ X-ray diffraction (XRD) analysis was performed in the 2θ range of 10 to 100° using Cu Kα (λ = 0.15406 nm) radiation in a Rigaku DMAX-RB 12KW diffractometer equipped with a graphite monochromator. After the component of Kα₂ was corrected, the peak data, e.g. the full width at half maximum, of diffraction peaks were measured using a software package in the diffractometer. In the present study, fully annealed pure copper powders were selected as standard samples for the determination of instrumental broadening. The calculation of grain size and microstrain based on the XRD data was conducted by the Integral Breadth method, assuming a Cauchy–Gaussian profile of the reflection,¹⁸

$$\frac{(\delta 2\theta)^2}{\tan^2 \theta_0} = \frac{K\lambda}{L} \left(\frac{\delta 2\theta}{\tan \theta_0 \sin \theta_0} \right) + 16e^2 \quad (1)$$

in which K is a constant taken as 1, where θ_0 is the position of the analyzed peak maximum, λ the X-ray wave length, L is the crystallite size, e is the maximum strain, and $\delta 2\theta = B(1 - b^2/B^2)$, b and B are the breadths in radians of the same peak in the reference and experimental patterns, respectively. Any available orders of a given reflection may be used to construct a linear plot of $(\delta 2\theta)^2/\tan^2 \theta_0$ against

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Fig. 1 SEM morphology of the starting Cu powders (a) and as-cryomilled Cu powders (b).

$(\delta 2\theta)/(\tan \theta_0 \sin \theta_0)$. From the slope, λ/L and ordinate intercept $16e^2$, the crystallite size, L , and strain, e , may be determined.

To verify the thermal stability of the cryomilled powders, samples sealed in quartz tube were isothermally annealed in a box furnace at 280 and 330°C for 30 min and were characterized for grain size.

Thermal analysis was performed with a differential scanning calorimeter (DSC Q2000, TA Instruments, Inc.). The DSC samples (approx. 20.26 mg) were run in Al pans with tightly-fitted inverted lids at constant heating rates in a flowing N_2 atmosphere.

3. Results and Discussion

Figures 1(a) and 1(b) showed atomized Cu powders and cryomilled Cu powders, respectively. These images indicated that the starting Cu powders had spherical shape with a size of approximately 24 μm, however, cryomilling for 12 h generated irregularly shaped Cu particles/agglomerates with a size of approximately 7 μm. It was generally acknowledged that cryomilling could result in micron-sized powder particles/agglomerates attributing to the continuous flattening, welding and fracturing of the powder particles during the cryomilling process.⁴⁾

Figure 2 displayed XRD patterns of the starting and cryomilled powders. The initially sharp diffraction peaks of fcc Cu phase became significantly broadened after the cryomilling due to the refinement of grain size and the introduction of lattice strain. The calculation of grain sizes based on the XRD data was conducted by the Integral Breadth method, and the grain size values was between 20 to 55 nm. The formation of nanostructure by cryomilling was demonstrated in many previous studies.^{5,8,19)}

The average grain size and mean microstrain measured from the X-ray diffraction line broadening during the cryomilling process was illustrated in Fig. 3. The average grain size and mean microstrain of the 12 h milled powders were 24 nm and 0.41%, respectively.

To obtain further information about the microstructure of the cryomilled powders, the as-cryomilled powders were investigated by TEM. Figures 4(a) and 4(b) show a bright-

Fig. 2 XRD patterns of cryomilled Cu powders for different milling times.

Fig. 3 The mean grain size and microstrain of the 12 h cryomilled Cu samples.

field image and the corresponding selected area electron diffraction (SAED) pattern, respectively. Typical grains observed were equiaxed-like and the average grain size was 32 nm, being consistent with the results from our XRD measurements. As shown in Fig. 4(b), the SAED pattern of the Cu grains shows a ring pattern, indicating that the individual grains are separated by high-angle grain boundaries and have a random orientation with neighboring grains.

Fig. 4 Bright-field TEM image (a) and SAED pattern (b) of the 12 h cryomilled Cu powder, revealing a nanocrystalline grain structure in the powder. (c) The distribution of grains measured from the bright field images.

The average grain size shown in Fig. 4(c) is about 32 nm. It is interesting that the TEM bright-field image for the milled Cu powders shows ultrafine particles with a size less than 5 nm [as indicated by the arrows in Fig. 4(a)] as well as Cu nano-grains. From the SAED pattern, these fine particles were identified as Cu₂O. It should be pointed out that it was difficult to produce bright-field images exclusively from the reflections from the oxide particles because of the close spacing of the ring patterns.

The formation of these fine oxide particles was considered as a result of interaction between Cu and O from the surrounding environment under the energetic milling conditions. During cryomilling, the microstructural evolution followed the well-known stages of a mechanical alloying process: flattening, fracturing, and welding of constituent materials.^{3,4)} The large amount of surface area of the freshly cryomilled powders resulted in extremely high reactivity. Furthermore, the high surface area associated with the cryomilled powders was likely to enhance chemical reactions that occur during cryomilling.¹¹⁾

Figure 5 showed the XRD pattern of the as-cryomilled Cu in comparison with those of the as-annealed Cu powders. As can be clearly seen, the intensity of Cu peaks in XRD patterns increased and narrowed sharply after annealing for one hour. The strain prior to annealing was 0.41%. At heat treatment temperature above 330°C, strain could not be detected utilizing the integral breadth technique. The lack of strain at temperatures above 330°C made clearly that a restructuring of the grain boundaries or a grain growing

Fig. 5 X-ray diffraction patterns of as-milled powders annealed for 30 min at 280 and 330°C.

process of highly unstable grains, which led to a more stable structure above 330°C.²⁰⁾ In addition, the reflection from Cu₂O was still existed after annealing for one hour, which may indicate Cu₂O could be thermally stable.

The thermal effect observed in the cryomilled nc Cu was very different from that in the conventional coarse-grained Cu. A comparison of DSC signals between the nc Cu and the conventional coarse-grained polycrystalline Cu was shown in Fig. 6. For the conventional Cu samples, no clear exothermic reaction was observed. For the cryomilled nc Cu samples, two clear exothermic reaction was observed. The exothermic

Fig. 6 DSC curves of the cryomilled and conventional Cu powders at a heating rate of $10^{\circ}\text{C min}^{-1}$.

reactions for the cryomilled samples may be attributed to the microstrain release process and the grain growth process as well, which was confirmed by XRD results shown in Fig. 4. After annealing at 280°C , the microstrain could not be detected using the integral breadth technique. The lower temperature peak was at about 280°C , the higher temperature peak was at about 330°C . The exothermic heat associated with the lower temperature (at about 330°C) peak was calculated from the area under the peak. The stored enthalpy increased to a maximum of 5.96 J/g . The first exothermic peak was perhaps the easiest to explain. There has been much discussion that nanostructured materials undergo three processes, namely, recovery, recrystallization, and grain growth during heating. This dramatic decrease in the strain combined with the relatively little increase in grain growth for the first exothermic peak (37 to 44 nm) indicated that this first exothermic peak can be associated with the stress relaxation and reordering of the grain boundaries. Some literatures^{20,21} found that the exothermic peak at a lower temperature which they attributed to energy released when randomly oriented grain boundaries were transformed to ordered grain boundaries and with the advent of a recovery process in which the grain boundaries became more clearly delineated and the dislocation density within the grains was reduced.

The second DSC peak at a higher temperature may be due to dislocations removed in the larger grains during the annealing process. The enthalpy release of the higher exothermic peak has been determined to be approximately 6.40 J/g .

Isothermal annealing treatment of the as-milled powder at 280 and 330°C showed that the as-milled disordered structure became ordered and strain relaxation after annealing at 280°C by the level of lattice strain decreased from about 0.41% (as-milled) to 0.27% after annealing at 280°C . Considering the sluggish grain growth by annealing at 330°C , the majority of the heat release below 280°C was supposed to be produced by reordering and strain release processes. The isothermal annealing treatment showed three kinds of structural evolution: reordering, strain relaxation and grain growth. The reordering and strain relaxation processes were completed during the first exothermic peak. The sluggish grain

growth has been attributed to both intrinsic and extrinsic sources. Intrinsic factors, such as random orientation of neighboring grains or reorientation of random atoms in disordered grain boundaries, may incubate the grain growth until some mechanisms operates to favor grain growth.²²⁾

4. Conclusions

Nanocrystalline Cu powders was synthesized using cryogenic mechanical milling at liquid nitrogen temperature. The average particle size initially decreased from the original 24 to $7\text{ }\mu\text{m}$ after 12 h of milling. The microstructure of the powders was consisted of irregular grains with average grain size of about 32 nm. The cryomilled powder demonstrated good thermal stability below 330°C . The Cu_2O scale presented an obstruction to the grain boundary migration. The thermal effect of the grain growth has been detected by DSC analysis.

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