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Non-monotonic variation of the grain size in Cu nanopowders subjected to ball milling

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Abstract

Ball milling (BM) a Cu nanopowder resulted in an increase of the average grain size from 8 to 52 nm, followed by a gradual decrease to 19 nm. In contrast, the grain size of coarse-grained Cu decreased monotonically from 290 nm to 19 nm. Fitting a model to the kinetic curves indicates that the two processes have similar activated volumes during collisions. It also reveals that particles over 100 nm are formed when nanoparticles are compressed during a collision for the first time.

Keywords: Ball milling; Metals and alloys; Microstructure; Kinetics.

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1. Introduction

Processing coarse-grained materials by BM typically induces the formation of nanocrystalline structures resulting from the competition between grain growth and grain refinement [1,2]. Vice versa, a monotonic grain growth occurs for ultra-fine-grained powders subjected to BM [3], due to a predominance of grain coalescence processes.

Starting from such evidence, we investigated the variation of grain size while milling nanocrystalline Cu powder with 8-nm grains. BM of commercial Cu powder was performed for comparison. Experimental findings indicate that the mean grain size increases to 52 nm initially and decreases back to 20 nm after additional milling. A model is proposed to explain the observed behavior and estimate some processing parameters.

2. Experimental outline

Cu nanopowders were prepared as described in the literature [4]. Equal volumes of two solutions were mixed at room temperature. One contained 40 mM hydrazine as the reducing agent. The other contained 1 mM $CuCl_2$, 10 mM cetyl-trimethyl-ammonium bromide as capping agent and NH_3 to adjust the pH to 10.

UV/Vis absorption spectra obtained using a Bruker TENSOR 27 FTIR spectrophotometer exhibit broad absorbance around 577 nm due to surface plasmon resonance effects marking the formation of Cu nanoparticles [4,5]. Transmission electron microscopy (TEM) was performed using a FEI-TECNAI instrument on nanoparticles dried at room temperature under flowing Ar. A TEM micrograph and the particle size distribution are shown in Figs. 1a and 1b respectively. Dry powder was monodisperse with a mean particle size around 7 nm.

BM was performed using a SPEX Mixer/Mill 8000 with a hardened steel reactor and a single stainless-steel ball of 12 g. A powder batch of 2 cm^3 was used to assure inelastic collisions between ball and reactor. Under such conditions, the collision velocity and frequency equalled 4.1 m s^{-1} and 36.6 Hz respectively, and the variation of grain size was recorded as a function of the number of collisions [6].

For comparison, 99.99% pure Cu powder was subjected to BM under the same conditions. Prior to BM, it was sieved to select particle sizes between 5 and 15 μm, and annealed at 500 °C under Ar for 10 h to induce grain growth and annihilate lattice defects.

XRD patterns were collected using a Rigaku Miniflex II diffractometer and Cu K_α radiation. Representative data are shown in Fig. 1c. The mean grain size was estimated from XRD patterns using the Rietveld method [7].

3. Results and discussion

The average grain size, L, of Cu nanopowder is shown in Fig. 2 as a function of the number of collisions, n. Starting from about 8 nm, L increases, reaches a maximum of 52 nm after 3.9×10^6 collisions approximately, and, then, decreases to about 19 nm. This non-monotonic behavior is quite unexpected and calls for explanation. Conversely, the grain size of coarse-grained Cu decreases monotonically, as also shown in Fig. 2. Also in this case, the final grain size is approximately 19 nm.

The kinetics of microstructural evolution can be described by a model developed earlier [8]. It captures the main features of BM, provides kinetic equations that can be fitted to experimental points, assigns physical meaning to fitted parameters, and provides consistent description for microstructural evolution. The model assumes that (i) any portion of the powder is impacted with the same probability regardless of its prior history, (ii) each collision traps only a small amount of powder, (iii) only in a small sub-volume V^* of trapped powder are mechanical stresses large enough to change grain size.

The volume fraction of powder processed during each collision is $k = V^*/V$, where V is the volume of powder inside the reactor. k also measures the probability that a change of grain size occurs in a given volume V^* during a single collision. It is a small number, typically of the order of 10^{-6}. The mean number of hits in n collisions is $n\,k$. Thus, the probability of being hit i times in n collisions is given by the Poisson distribution:

$$\chi_i(n) = \frac{(k\,n)^i}{i!} e^{-k\,n} . \tag{1}$$

If the average grain size in a volume element that was hit i times is L_i, the average grain size of the entire sample, L, can be expressed as the weighted average

$$L = \sum_{i=0}^{\infty} \chi_i(n) L_i . \tag{2}$$

Let's assume that the first impact on a volume element reduces the grain size from the initial value L_0 to the final value L_f and further collisions do not change the mean grain size in that volume element. These assumptions lead to the expression

$$L = L_0\, e^{-k\,n} + L_f\,(1 - e^{-k\,n}) . \tag{3}$$

Eq. 3 fits the data for coarse-grained Cu shown in Fig. 2 perfectly, providing an estimate of $2.5 \times 10^{-7} \pm 0.1 \times 10^{-7}$ for k and the values 287 ± 3.4 and 18.8 ± 2.1 nm for L_0 and L_f respectively. The same assumptions were used successfully in earlier works [2,9,10].

To fit the non-monotonic variation of grain size undergone by Cu nanopowder, it is assumed that the first time a volume element is involved in a collision, its average grain size changes from L_0 to L_1. A second collision results in a further change to L_f and further collisions do not change the average grain size in that volume element. Under such circumstances

$$L = L_0\, e^{-kn} + L_1\, k\, n\, e^{-kn} + L_f\, (1 - e^{-kn} - k\, n\, e^{-kn}). \tag{4}$$

As seen in Fig. 2, this equation fits the data satisfactorily. The fitted values are $k = 2.4 \times 10^{-7} \pm 0.2 \times 10^{-7}$, $L_0 = 7.8 \pm 0.6$ nm, $L_1 = 121.3 \pm 1.3$ nm and $L_f = 19.0 \pm 0.7$ nm. This suggests that large grains, around 120 nm, form abruptly when a volume of pristine Cu nanopowder is compressed for the first time.

The product of k and the total volume V of powder provides an estimate of V^* equal to about 5×10^{-4} $mm^3 \approx (80\ \mu m)^3$. This represents the volume of powder that reaches the critical loading conditions necessary to activate grain growth or grain refinement. The identical k values for coarse- and nano-grained powders suggest that grain coalescence and fracture require similar loading conditions.

Although non-thermal processes may also play some role, the abrupt formation of large grains when pristine Cu nanopowder is compressed for the first time is probably a thermal process. In a nanopowder, surface energy gives an important contribution to the total energy. Assuming that the Cu powder consists of spherical particles 8 nm in diameter, the total surface area of 1 mol of Cu is 5340 m^2. Using 1.8 J m^{-2} for the free surface energy of Cu [11], the total surface energy is 9.6 kJ. If pairs of neighbouring free surfaces are pressed together into a single grain boundary and the grain boundary energy is about 28% of the free surface energy [11], the compression of 1 mol of 8-nm Cu particles into a nanocrystalline agglomerate releases about 8.3 kJ of energy, or 62% of the enthalpy of fusion, comparable with the 39% of the enthalpy of fusion released during grain growth by ball-milled nanocrystalline systems with 20-nm grains [3]. The additional contribution of mechanical energy from the collision makes local melting and thermally activated grain rotation and coalescence possible.

The formation of large grains in Cu nanopowder hit the first time is somewhat surprising. Therefore, ball drop experiments were performed to obtain independent evidence. Experiments were carried out in a mechanochemical reactor described in detail elsewhere [12]. It consists of a stainless steel cylindrical chamber with rounded-bottom base and a spring-loaded launching device that can drop a 12-g stainless steel ball to the bottom with 4.1 m s^{-1} collision velocity, measured by laser beams. It is the same collision velocity characterizing BM experiments in the SPEX mill. The target was 1 g of Cu nanopowder, sufficient to produce perfectly inelastic collisions.

TEM was used to investigate the powder after the ball drop. Compared to the TEM image of the smallest particles of commercial Cu powder, shown in Fig. 3a, the TEM micrographs reported in Figs.

3b and 3c demonstrate that the ball drop results in the formation of Cu particles with large grains. The rounded edges suggest that partial melting could have contributed to the particle formation. The grain size is somewhat smaller than the 120 nm predicted by the model on a strictly phenomenological basis, but clearly larger than 52 nm, the maximum of the average grain size.

Therefore, it is reasonable to conclude that the first step of BM a Cu nanopowder is immediate and induces substantial grain growth by thermally assisted processes.

Acknowledgements

References

1. D. L. Zhang, Processing of advanced materials using high-energy mechanical milling, Prog. Mater. Sci. 49 (2004) 537-560.

2. S. Garroni, S. Soru, S. Enzo, F. Delogu, Reduction of grain size in metals and metal mixtures processed by ball milling, Scripta Mater. 88 (2014) 9-12.

3. S. Mørup, J. Z. Jiang, F. Bødker, A. Horsewell, Crystal growth and the steady-state grain size during high-energy ball-milling, Europhys. Lett. 56 (2001) 441-446.

4. S.-H. Wu, D.-H. Chen, Synthesis of high-concentration Cu nanoparticles in aqueous CTAB solutions, J. Colloid Interf. Sci. 273 (2004) 165-169.

5. M. A. Garcia, Surface plasmons in metallic nanoparticles: fundamentals and applications, J. Phys. D: Appl. Phys. 44 (2011) 283001.

6. F. Delogu, L. Schiffini, G. Cocco, The invariant laws of the amorphization processes by mechanical alloying - I. Experimental findings, Phil. Mag. A 81 (2001) 1917-1937.

7. P. Scardi, L. Lutterotti, P. Maistrelli, Experimental determination of the instrumental broadening in the Bragg-Brentano geometry, Powder Diffr. 9 (1994) 180-186.

8. F. Delogu, L. Takacs, Mechanochemistry of Ti-C powder mixtures, Acta Mater. 80 (2014) 435-444.

9. E. Musu, G. Mura, G. Ligios, F. Delogu, Formation of metastable solid solutions by mechanical alloying of immiscible Ag and Bi, J. Alloys Compd. 576 (2013) 80-85.

10. F. Delogu, Mechanical processing of Fe powders, J. Mater. Sci. 47 (2012) 4757-4762.

11. S. N. Zhevnenko, Surface Free Energy of Copper-Based Solid Solutions, J. Phys. Chem. C 119 (2015) 2566-2571.

12. F. Delogu, Stability of elastically deformed massive and nanometer-sized Pd hydrides, J. Phys. Chem. C 115 (2011) 21230-21235.

Figure captions

Fig. 1. (a) TEM micrograph of Cu nanoparticles and (b) particle size distribution. (c) XRD patterns of Cu nanopowders subjected to 0, 4 and 20 h of BM (0, 5.2×10^6 and 26.3×10^6 collisions). Best-fitted Rietveld profiles are shown.

Fig. 2. The average grain size, L, as a function of the number of collisions, n, for coarse- (open black squares) and nano-grained Cu (open red circles). Detail is given in the inset. The vertical dotted line indicates the maximum. Best-fitted curves are shown.

Fig. 3. TEM micrographs of (a) a particle of commercial fine Cu powder, (b) particles formed during a ball-drop experiment with Cu nanopowder, and (c) magnified view of one of the particles.
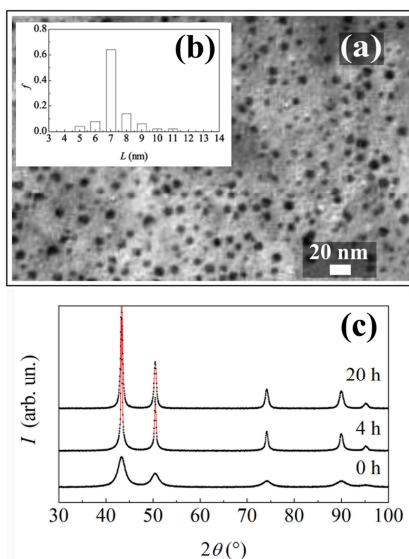
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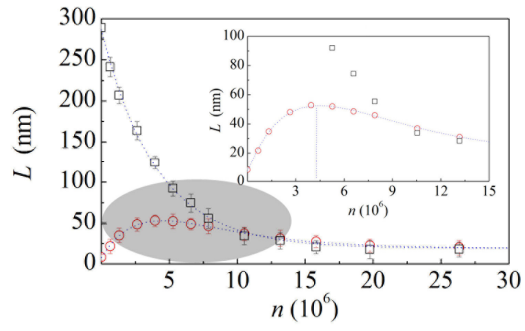
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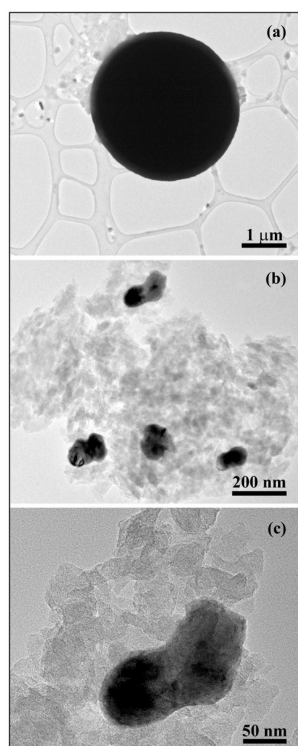
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Highlights

- Cu nanopowders were subjected to ball milling;
- Mean grain size increased up to a maximum and then decreased;
- Particles over 100 nm form when nanoparticles are impacted for the first time;
- The non-monotonic grain size variation was described by a kinetic model.

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