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Hardening in copper-based nanocomposites

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Abstract

Copper–iron carbide nanocomposites were prepared with mechanical alloying. Crystallite size measurements with X-ray diffraction (XRD) and transmission electron microscopy (TEM) observations of the nanocomposites are jointly reported. The measured hardening is rationalized in terms of combination of matrix hardening and load transfer to the reinforcing particles.

Keywords: Nanostructures; Metals; Mechanical alloying

1. Introduction

One of the major advantages of nanocrystalline materials is their enormous gain in mechanical strength over conventional materials. Hardness is an easily measurable property that has a strong correlation with tensile properties.

Previous research has shown that for small volume fractions of reinforcement, the hardening is essentially governed by the matrix grain size as determined by X-ray diffraction (XRD) [1]. For larger volumes of reinforcement, the hardening observed must also take into account the load transfer to the reinforcing particles. This is done using the rule for mixtures of composite materials [2].

In order to rationalize the observed hardening, it is essential to measure microstructural features such as grain size and particle size for the matrix and reinforcing phase, respectively. The Scherrer's equation is the most widely used procedure to analyse XRD data. New detailed transmission electron microscopy (TEM) observations in nanocomposites [3] revealed the existence of a high density of twins in the copper matrix, as well as stacking faults in the reinforcing phase. The existence of these defects contributes to a discrepancy between crystallite size determination with XRD and direct measurement of grain size with TEM. Recently, it was also demonstrated that nano-spaced twins play a major role in hardening of pure copper [4].

The aim of this paper is thus: (a) to jointly report and combine XRD and TEM measurements obtained from copper-based nanocomposites systems and (b) to rationalize the hardening observed in terms of the relevant hardening models, including the recently reported hardening due to nano-spaced twins. The relevance of the hardening models, of the several microstructural parameters obtained both with XRD and TEM, is also discussed.

2. Experimental procedure

The size and purity of raw elemental powders used are indicated in Table 1. These powders were mechanically alloyed in a Retsch PM400 planetary ball mill. The 250 ml stainless steel container was charged with a 20 g mixture of the elemental powders and 400 g of 10 mm diameter stainless steel balls. In order to prevent the oxidation of powders, the container was first evacuated and then filled with argon. The mill was operated at a rotating speed of 400 rpm. The milling time used was 50 h. The nominal composition of the synthesised powder is shown in Table 2.

After milling, the resultant powder batch was characterised by XRD using Cu Kα radiation, scanning electron microscopy (SEM) and microhardness measurements with a load of 25 g (0.196 N). The powders milled for 50 h were also annealed at 400 and 600 °C for 1 h in a tubular furnace under argon flow, to avoid powder oxidation. The annealed powders were characterised by the same techniques as the as-milled powders.

Crystallite size for the copper matrix was determined from XRD data. The crystallite size was estimated both with Scherrer's equation using the most intense low angle Bragg reflection, Cu(1 1 1) and with the Williamson–Hall method using Cu$\{1\,1\,1\}$ and Cu$\{2\,0\,0\}$.

The material annealed at 600 °C was also characterized by TEM using a Hitachi H-8100 instrument with a point resolution of 0.27 nm at 200 kV, equipped with energy dispersive spectroscopy (EDS). The samples for TEM were prepared by embedding the powder in an epoxy resin, followed by grinding, dimpling, and ion milling at 77 K to electron transparency.

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Table 1
Raw materials

	Copper	Iron	Carbon (synthetic graphite)
Size (μm)	$44 < d < 149$	44	22
Purity (wt.%)	99.9	99	99.5

Table 2
Nominal chemical composition

Fe (wt.%)	22.5
C (wt.%)	1.60
Cu (wt.%)	Bal.

3. Results and discussion

The XRD patterns obtained both for as-milled (for 50 h) and after annealing at 400 and 600 °C are shown in Fig. 1. The carbide structure evolves clearly, adopting the Fe_3C structure after annealing at 600 °C.

The microhardness results obtained both from as-milled powders (50 h) and annealed powders are shown in Fig. 2. The as-milled powders present a hardness value, 507 VHN, which represents a two-fold increase relative to that of nanostructured copper processed via MA, about 260 VHN [5]. Much of this increase is certainly due to the high volume fraction of carbide, about 30 vol.%. The decrease in hardness with increasing annealing temperature is probably due to the increase in crystallite size of both copper and carbide. However, with TEM it is observed that grain size is maintained in the nanocrystalline range upon annealing up to 600 °C (Fig. 3). Planar defects are also clearly visible.

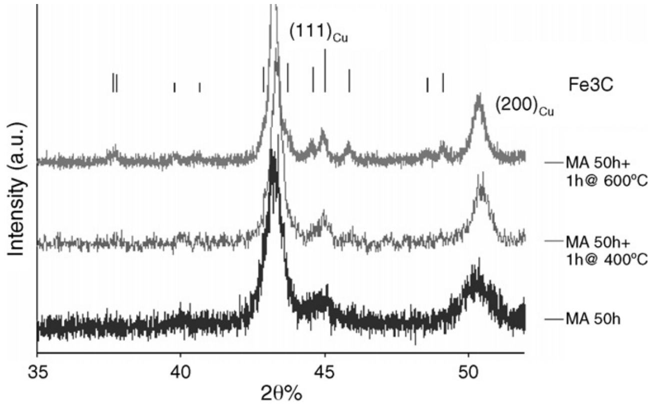

Fig. 1. XRD patterns of MA and annealed powders.

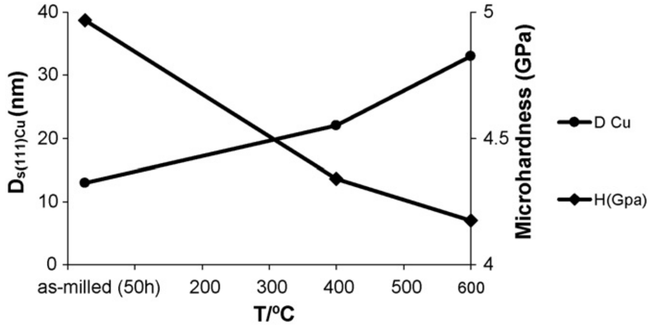

Fig. 2. Crystallite size and microhardness for as-milled and annealed powders.

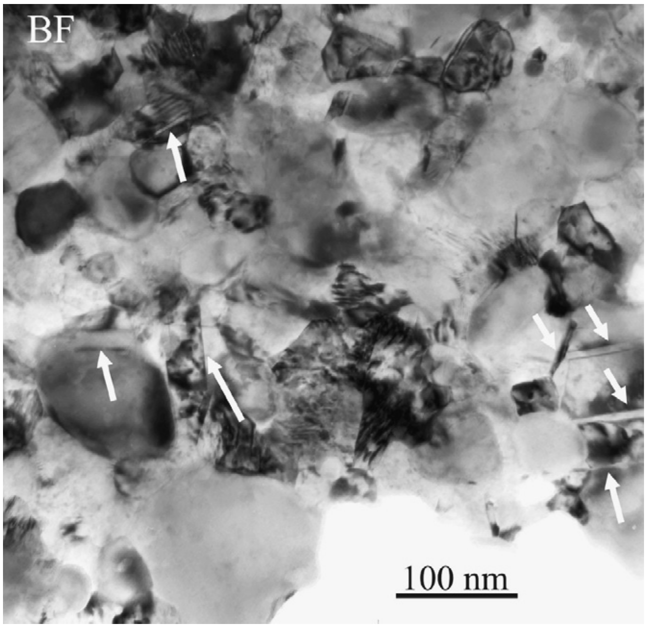

Fig. 3. TEM picture of powders annealed at 600 °C. The existence of planar defects is indicated.

The combined twin and stacking fault probability in the copper matrix, γ, was determined using a previously reported procedure [6–8]. This method is based on the shift produced by planar defects on families of XRD reflections. We adopted the same procedure reported by [8] for the reflections $\{1\,1\,1\}_{Cu}$ and $\{2\,0\,0\}_{Cu}$. These two crystallite sizes, $D\{1\,1\,1\}_{Cu}$ and $D\{2\,0\,0\}_{Cu,}$ were obtained through the Williamson–Hall method as it is necessary to discount the effect of strain [6]. The two crystallite sizes, obtained directly with XRD using the Williamson–Hall method, were then corrected using the probability information about planar defects to obtain a “true” grain size. These results are shown in Table 3. The “true” grain size is larger than that obtained with Scherrer’s equation with Cu(1 1 1) and the values obtained are comparable with the grain size determined by TEM. The planar defects probability is higher in the as-milled condition, decreasing with annealing.

The problem of modelling the hardening in nanocomposites is rather a difficult one. The main candidate for hardening in the nanocrystalline materials is the Hall–Petch model, Eq. (1), where D is the crystallite size, $k_H = 0.45\ \mathrm{MPa\ m}^{1/2}$ and $H_0 = 500$ MPa.

$$H_{HP} = H_0 + k_H D^{-1/2} \tag{1}$$

However, it is clear that when a high volume fraction of reinforcing phase is used, a significant load transfer from the matrix to the reinforcing particles must be considered. The rule of mixtures represents the upper limit for strengthening, i.e., the largest effect that can be obtained when the matrix and reinforcement

Table 3
Copper crystallite size determined by Scherrer's equation, Williamson–Hall plot and "true" grain size taking into account the planar defects

Sample	$D_S(1\,1\,1)$ (nm)	$D_{WH}\{1\,1\,1\}$ (nm)	$D_{WH}\{2\,0\,0\}$ (nm)	γ	$D_{\text{“true”}}$ (nm)
Milled for 50 h	13	23	16	0.0121	35
Annealed at 400 °C	22	39	28	0.0064	56
Annealed at 600 °C	33	47	38	0.0032	57

experience the same strain:

$$H_{\text{Comp}} = H_R \times f + H_M \times (1 - f) \quad (2)$$

where H_R and H_M are the reinforcement and matrix hardness, respectively and f is the volume fraction of reinforcement.

Replacing H_M with the Hall–Petch hardness H_{HP} in Eq. (2), and introducing a load transfer parameter δ, that takes into account the difference in stiffness between the matrix and the carbide, the misfit of the carbide particles and the difference in the expansion coefficients, we obtain,

$$H_{\text{Comp}} = \delta H_R \times f + (H_0 + k_H D^{-1/2}) \times (1 - f) \quad (3)$$

Previous research has shown that the twin boundaries can be as effective as grain boundaries in hardening [4]. The relevant distance for the Hall–Petch model is thus the crystallite size obtained directly with XRD, using for instance, the Scherrer's formula on a low angle reflection and not the "true" grain size, as a grain may include several planar defects.

In the current research, the volume fraction of reinforcing carbides expected from the nominal composition is about 30%, and that obtained from XRD using the Powder Cell software [9], is 35%. Taking the latter value as volume fraction, considering the rule of mixtures as a first approximation, as previously used [2], and ascribing a reasonable value to the hardness of cementite, 10 GPa, we can easily fit the experimental results using Eq. (3). A good fitting can be obtained by taking $\delta = 0.61$ (Fig. 4).

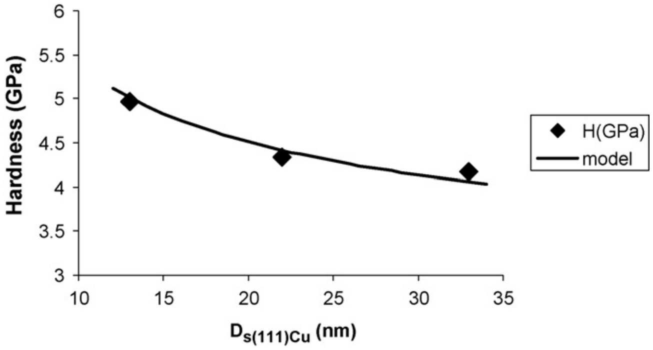

Fig. 4. Hardness vs. copper crystallite size.

It seems thus, that in this system the total hardness depends on the volume fraction and apparently not on the grain size of carbide phases. In contrast, crystal size seems to be very important for the other load-bearing phase, the copper matrix. The presence of planar defects in the matrix should be taken into account.

4. Conclusions

Planar defects have been identified in copper-based nanocomposites with high volume fraction of iron carbide. The crystallite size as measured with XRD, seems to be the relevant parameter to account for the matrix contribution to hardening.

The overall hardening observed can be rationalized considering some degree of load transfer from the matrix to the reinforcement, as in conventional particulate composites.

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