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Study of early stages of Cu–NbC nanocomposite synthesis

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Abstract

Cu–NbC nanocomposites with nominal compositions of 5, 10 and 20 vol.% of NbC were produced in situ via MA from elemental powders. The powders were milled for 1, 2, 4, 8, 16 and 32 h. The as-milled powders were characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction results showed that the niobium carbide phase is formed in the early stages of milling and that the time necessary to complete the reaction ranges from 1 to about 8 h of milling.

Keywords: High-energy ball milling; Metals; Nanostructures

1. Introduction

Copper nanocomposites reinforced with ceramic particles can be produced by several methods, such as internal oxidation and mechanical alloying (MA). In almost all of the reported experiments MA alone is not able to produce directly the reinforcing phase, without additional and appropriate heat treatment at relatively high temperatures [1–4]. Results reported by Biseli et al. [2] showed that the in situ production of TiB_2 particle reinforced copper nanocomposites via MA is only achieved after a suitable heat treatment. They reported that the reaction between Ti and B does not occur readily during milling, but instead takes place during annealing, for short periods at temperatures of 873–1073 K, although the mechanism of in situ formation of TiB_2 was not very clear. Takahashi [1] has synthesised copper alloys reinforced with NbC and TaC particles by MA. The in situ formation of the carbide phases was not observed in the as-milled powder but only after appropriate heat treatment in the temperature range 873–1323 K. Recently, Marques et al. [5] have produced in-situ copper-niobium carbide (Cu–NbC) nanocomposites via mechanical alloying without additional heat treatment. The authors observed that relatively short milling time (less than 20 h) is sufficient to form NbC nanoparticles in a copper matrix. The aim of this research is to study the early stages of synthesis of Cu–NbC nanocomposites via mechanical alloying.

2. Experimental procedure

The starting materials used in the milling experiments were Cu (99.9% purity; particle size $44\,\mu m < d < 149\,\mu m$), Nb (99% purity; average particle size 65 μm) and synthetic graphite (99.9995% purity; average particle size 74 μm), used as carbon source. Details of the milling operation are reported in Ref. [5]. Different powder batches were produced with nominal compositions of 5, 10 and 20 vol.% NbC. For nominal composition of Cu–10, 20 vol.% NbC the milling was carried out for 1, 2, 4 8, 16 and 32 h and up to 8 h for Cu–5 vol.% NbC. In all experiments two steps were used; initially the Cu and carbon powders were milled for 4 h, then niobium was added and the milling proceeded for the required time. Milling time is considered after Nb addition. For each milling time and nominal composition, the phase identification of the as-milled powders was performed by XRD using Cu Kα radiation. From XRD data the average crystallite size $\langle D \rangle$ of the copper matrix and, when possible, that of the NbC phase were assessed using the Scherrer's equation with the most intense Cu and NbC reflections, (1 1 1) in both cases. The matrix lattice parameter was determined from the peak shift of the copper reflections; (2 2 2), (3 3 1) and (4 2 0) Cu reflections were used. To follow the niobium carbide synthesis reaction the ratio between the NbC and Cu integral peak intensities, I_{NbC}/I_{Cu}, was estimated. This procedure was only possible for Cu powders with 10 and 20 vol.% NbC, in which the NbC reflections are well defined. After milling, samples were mounted in conductive resin, metallographically prepared and characterised by SEM/EDS.

3. Results

Fig. 1 shows the XRD pattern of the as-milled Cu–20 vol.% NbC powder for different milling times and also a spectrum of the Cu powder used as starting material. As can be seen, the niobium carbide phase starts to form after 1 h of milling. From 1 up to 8 h of milling time the peak intensity of niobium carbide phase becomes more intense and well defined, showing

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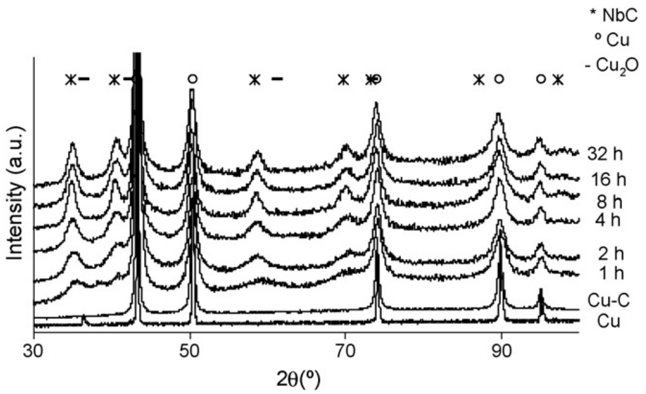

Fig. 1. XRD patterns for Cu–20 vol.% of NbC MA-powders for different milling times.

an increase of NbC volume fraction. After this milling time no further features are seen. The relative intensity of NbC and Cu peaks for Cu powders milled with 10 and 20 vol.% of NbC for different milling times is shown in Fig. 2(a). Similar representation for Cu powders with 5 vol.% of NbC was not possible to draw because the reflections of the niobium carbide phase are poorly defined. This figure is very illustrative because it shows clearly the evolution of the synthesis reaction of NbC; for example, for Cu powders with 20 vol.% of NbC NbC is forming between about 1 h and 8 h of milling time. For Cu powders milled with 10 vol.% of NbC the niobium carbide phase seems to form between 1 and 4 h of milling time. Fig. 2(b) shows the average crystallite size for Cu and NbC phases as a function of milling time, evaluated by Scherrer's equation using (1 1 1) reflections, after correction for instrumental broadening. It can be observed that $\langle D_{\mathrm{NbC}} \rangle$ increases slightly up to about 8 h of milling time and after this point it remains almost constant. Results of Cu average crystallite size show that after 1 h and up to 32 h of milling $\langle D_{\mathrm{Cu}} \rangle$ reaches a stable value below 30 nm for all nominal compositions and systematically decreases with NbC volume fraction.

The change in the Cu lattice parameter, in as-milled powders for all nominal compositions, for different milling times is shown in Fig. 3(a). It can be seen that the Cu lattice parameter for 10 and 20 vol.% of NbC milled up to 32 h shows a similar trend; however, for 32 h of milling the lattice parameter of the two composites is very different. This difference can be due to an increase of the Fe content due to contamination from the milling media. For Cu powder milled with 5 vol.% of NbC the Cu lattice parameter has no significant evolution for different milling times. Fig. 3(b) shows the Fe content for different milling times for as-milled Cu powders with 5, 10 and 20 vol.% of NbC. Standardless chemical analyses were performed by EDS at relatively low magnification in particle powder surfaces of as-polished samples. As shown in this figure the Fe content increases for different milling times and seems to follow the same tendency as the Cu lattice parameter. Fig. 4(a) shows a SEM picture, taken at relative low magnification, of Cu powder with 20 vol.% of NbC milled for 1 h. The small bright particles, labelled with Nb, with dimensions around 400 nm are unreacted niobium, as can be confirmed by the corresponding EDS point chemical analysis results shown

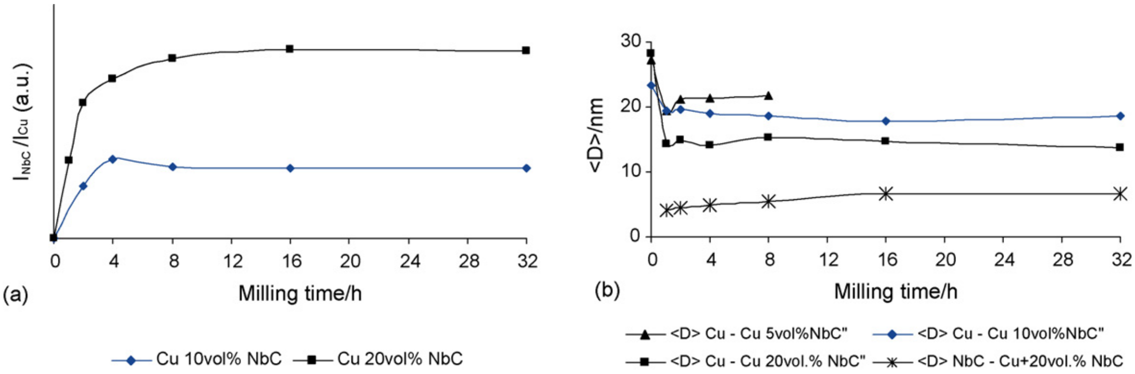

Fig. 2. (a) Evolution of the ratio of the integral peak intensity of NbC (1 1 1) to Cu (1 1 1) and (b) average crystallite size of Cu and NbC phases vs. milling time. NbC crystallite size is only presented for Cu–20 vol.% of NbC powders.

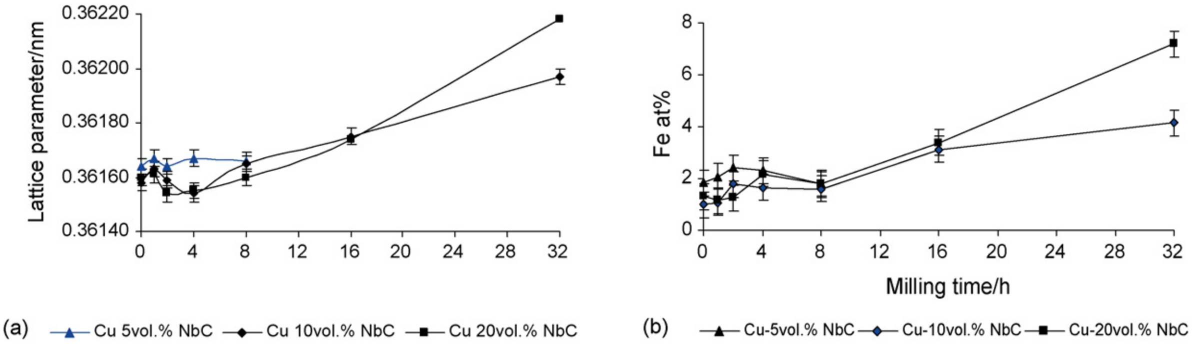

Fig. 3. (a) Cu lattice parameter and (b) Fe content vs. milling time for as-milled Cu powders with 5, 10 and 20 vol.% of NbC.

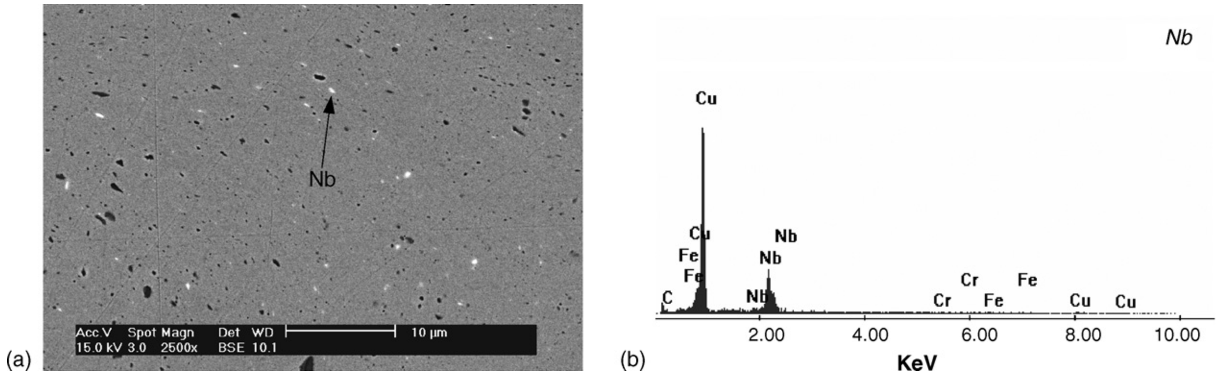

Fig. 4. (a) SEM image of the as-milled Cu powder with 20 vol.% of NbC milled for 1 h and (b) EDS point chemical analysis of the small bright particle labelled Nb.

in Fig. 4(b). Small dark particles are also observed. These are probably contamination arising from the milling media and some porosity.

4. Discussion

Results presented in Fig. 1 show that the niobium carbide synthesis in the copper matrix takes place in the early stages of milling. Indeed, after 1 h of milling almost all of the NbC reflections are detected, suggesting, that a significant volume fraction of NbC is already formed. In fact, at this time only a small amount of unreacted niobium particles still remain, as revealed in Fig. 4(a) for Cu–20 vol.% of NbC powders milled for 1 h. After this time and up to about 8 h of milling, the peak intensities tend to be higher and well defined, but after this point no further features are detected. This is also confirmed by the ratio of integral peak intensity of NbC (1 1 1) to Cu (1 1 1) $I_{\mathrm{NbC}}/I_{\mathrm{Cu}}$, which shows that the volume fraction of NbC formed reaches a maximum at this stage of milling, Fig. 2(a). This short period of time for NbC formation can be attributed to the previous dispersion of carbon in the Cu matrix. The evolution of the average crystallite size of NbC, $\langle D_{\mathrm{NbC}}\rangle$, for Cu–20 vol.% of NbC powders for different milling times is presented in Fig. 2(b). The value of $\langle D_{\mathrm{NbC}}\rangle$ is less than 10 nm for all milling times, indicating that after the maximum volume fraction of NbC has formed, typically after 8 h, further milling does not induce any change in NbC crystallite size. Cu matrix average crystallite size, $\langle D_{\mathrm{Cu}}\rangle$, for Cu powders with 5, 10 and 20 vol.% of NbC for different milling times is also showed in Fig. 2(b). It is interesting to note that the variation of $\langle D_{\mathrm{Cu}}\rangle$ for different milling times for all nominal compositions is very similar, reaching a constant value after 1 h of milling only and the systematic decreasing with NbC content. No further reduction in crystallite size is achieved with longer milling, indicating that fracture/cold welding processes typical of MA for reduction of powder particles to nanometer size, is highly efficient. It has been suggested that the final grain size achievable by MA for pure metals is determined by the minimum grain size that can sustain a dislocation pile-up within a grain and by the rate of recovery during the MA process [6]. In general, the addition of a second element to a pure metal increases its strength and hardness resulting in a smaller final grain size obtained by milling [7]. In the present research the addition of Nb and carbon powders and, therefore, the content of NbC are the reason for the decrease in Cu grain size with the increase of NbC content. The obtained values of final grain sizes for Cu and NbC are comparable to the grain sizes reported for mechanically alloyed Cu powders with NbC [8]. Fig. 3(a) shows the changes in Cu lattice parameter for different milling times for all nominal compositions. As mentioned previously, before the addition of Nb, Cu powders were milled with graphite powders for 4 h. This procedure was used for two reasons. The first was to eliminate traces of oxygen present in Cu elemental powders, as can be seen in Fig. 1 from XRD spectra collected from Cu elemental powders and Cu–C milled for 4 h. The second was to promote a prior carbon dispersion in copper matrix and, therefore, to enhance the formation of the niobium carbide. As a result of the pre-alloying, a large amount of defects, internal strain and probably iron contamination were introduced in the powders, what results in an increase of the Cu lattice parameter from 0.36148 nm for pure copper to about 0.36158 nm for pre-alloyed powders. For Cu powders with 10 and 20 vol.% of NbC milled up to 1 h, the lattice parameter increases slowly from 0.36158 nm (corresponding to pre-alloyed Cu–C powders) to about 0.36163 nm; this increase can be due to defects, internal strain and also to the beginning of NbC formation. The results show that, at this stage, a large proportion of the NbC phase is already formed, which can be in the form of small clusters with dimensions of a few nanometres. These clusters are in quantity sufficient to be detected but are also small enough to strain the Cu lattice. This conclusion needs further analysis by TEM to confirm the existence of NbC clusters. From 8 to 32 h of milling the Cu lattice parameter increases continuously, reaching a maximum value of 0.36197 nm for Cu–10 vol.% of NbC and 0.361218 nm for Cu–20 vol.% of NbC powders milled for 32 h. The main reason for this behaviour is the increase of Fe content in the copper matrix. In fact, the Cu lattice parameter as well as the iron content appear to follow a similar trend for different milling times, particularly after 8 h of milling, Fig. 3(b). The increase of Fe content with milling time is not surprising because it is a well known problem in MA, that long periods of milling lead to an increase of contamination due to wear of the container and balls [9]. On the other hand, as reported in Ref. [10], the copper lattice expands when iron atoms are dissolved in copper matrix having a linear trend with increasing iron content. According to these authors [10] the Cu lattice parameter is about 0.36164 nm for 2.7 at.% of Fe, a value that is close to that obtained for all Cu powders milled for 8 h (0.36165 nm). Therefore, Fe contamination seems to be the main reason for the increase in copper lattice parameter for long periods of milling. Contamination content can also contribute to line broadening. However, in this research the average crystallite sizes of the Cu matrix and NbC phase were determined using the Scherrer's equation where this contribution was not take into account. It is important to note that a milling time between 1 and 8 h seems to be sufficient to reach a maximum value the NbC volume fraction for both Cu powders with 10 and 20 vol.% of NbC. This is an important conclusion because it provides technical information about the evolution of the reaction, and prevents further contamination by milling media.

5. Conclusions

This research proved that is possible to synthesise in situ Cu–NbC nanocomposites via mechanical alloying at room temperature without additional heat-treatment. The NbC phase starts to form in the early stages of milling, typically after 1 h, probably due to previous carbon dispersion in the copper matrix. The maximum volume fraction of niobium carbide in copper matrix is achieved after 8 h of milling. Further milling leads to an increase of Fe contamination only.

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