

CONSOLIDATION VIA HOT EXTRUSION OF Cu-NbC NANOCOMPOSITES

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Abstract. Powders of copper-based nanocomposites with nominal composition of 10 and 20 vol.% of NbC were prepared *in situ* from elemental powders with mechanical alloying in a planetary mill. Powder batches milled for 28.8 ks were vacuum encapsulated in copper cans and consolidated via hot extrusion at 873K. Microstructural characterization in both the as-milled powders and the extruded materials were performed using X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM). Mechanical properties were assessed with microhardness measurements. SEM observations of extruded Cu powders with 20 vol.% of NbC revealed prior particle boundaries and also Cu rich regions. Both extruded nanocomposites present a good densification without appreciable porosity. Microhardness values obtained for extruded Cu-10 vol.% of NbC powder are similar to those obtained in the as-milled condition. For Cu-20 vol.% of NbC a slight decrease in microhardness is observed after consolidation.

1. INTRODUCTION

Mechanical alloying (MA) has proved to be an important and effective method to synthesise a wide variety of alloys and compounds, namely, powders with extended solid solution, amorphous phases, intermetallic and metal matrix nanocomposites (MMnC) reinforced with nano-sized particles [1-7]. *In situ* formation of MMnC via MA produces a uniform distribution of nanoparticles in the metal matrix and also small particle size during the milling process. However, for almost all systems heat treatments or consolidation at high temperature are required to induce the precipitation of the reinforcing particles [2,8-13]. On the other hand, the consolidation of the powders into bulk parts, e.g. by sintering, involves the exposure of the material to high temperature. This exposure, even for short periods, leads in general to microstructural coarsening and to a decrease in mechanical properties. In this work, *in situ* Cu-NbC nanocomposites were

produced via MA without further heat treatment and consolidated by hot extrusion at 873K. The as-milled and as-consolidated nanocomposites were studied in terms of their structural evolution and mechanical properties. The hardening obtained in both nanocomposites was tentatively rationalised using the Orowan and Hall-Petch strengthening mechanisms.

2. EXPERIMENTAL

Cu powders with nominal compositions of 10 and 20 vol.% of NbC were synthesized via MA in a planetary mill for 28.8 ks according to described in the references [14,15]. The as-milled Cu-NbC powders were encapsulated in copper cans with an internal and external diameter of 8 and 16 mm, respectively; the cans were degassed and sealed in dynamical vacuum of about $\approx 10^{-5}$ mbar at 573K for 3.6 ks. The encapsulated powders were extruded with MoS₂ lubrication through a 45° conical die lo-

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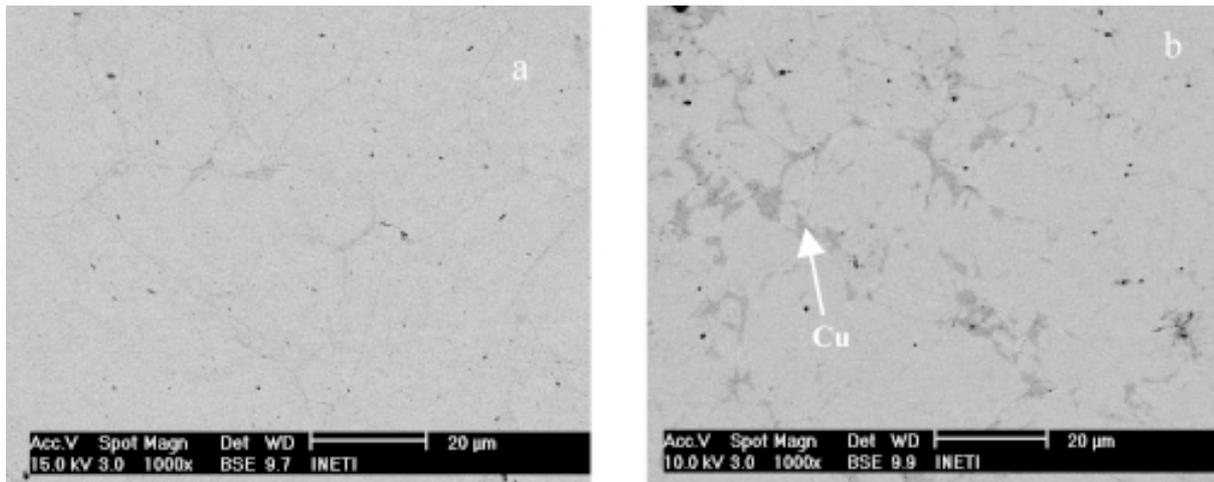


Fig. 1. Microstructure of the extruded Cu powders with (a) 10 and (b) 20 vol.% of NbC. Dark areas assigned with arrow are copper rich.

cally heated by induction. Isothermal extrusions were performed at 873K in a conventional INSTRON test machine, fitted with compression plates; the temperature was controlled with a thermocouple in direct contact with the die. The as-milled and as-extruded powder samples were characterized with SEM, TEM, and XRD. Mechanical properties of the nanocomposites were assessed by microhardness measurements. XRD experiments were performed with a RIGAKU Geigerflex diffractometer with $\text{CuK}\alpha$ radiation fitted with a graphite monochromator using $0.006^\circ (2\theta)$ per min for slow peak scan. Average crystallite size of Cu and NbC were determined for the most intense reflection, (111) in both cases, using the Scherrer equation, after correction for instrumental broadening. Samples for metallography and microhardness measurements from extruded and powder samples were mounted in conductive resin and polished using standard methods. Extruded samples for TEM observation were cut into discs of diameter 3 mm, followed by grinding to 50 μm of thickness and ion milling to electron transparency. The last operation was performed with a Gatan duo mill operating at an accelerating voltage of 4 kV with an incident angle of 12° until larger electron transparent areas were obtained. Microhardness tests in the as-milled and as-extruded samples were performed using Shimadzu HMV 2000 durometer with a load of 0.245 N (15 s).

3. RESULTS

Figs. 1a and 1b, obtained with SEM in backscattered mode, show the microstructure of copper powders with 10 and 20 vol.% of NbC extruded at 873K. As can be seen both extruded nanocomposites present good densification without significant porosity. However, in extruded Cu-20 vol.% of NbC samples powders prior particle boundaries, rich in Cu, can be seen. Figs. 2a and 2b show TEM bright field images of the Cu powders with 10 vol.% of NbC extruded at 873K. The microstructure of the nanocomposite consist of equiaxial and elongated copper grains with dimensions ranging from 20 to 80 nm and niobium nanocarbides with sizes of about 5 nm. These NbC nanoparticles, indicated by arrows in Fig. 2b, are crystalline and distributed within Cu grains and near to grain boundaries. Fig. 2b shows with more detail a twinned copper grain with NbC nanoparticles. The values of the average crystallite size of the copper matrix and NbC, estimated by the Scherrer equation and the equivalent yield stress, σ_v , calculated due to the relation $\sigma_v = H\sqrt{3}$, for both nanocomposites in the as-milled and as-extruded condition are presented in Table 1. The hardness observed in both nanocomposites for the as-milled and as-extruded condition can be explained either by the grain size strengthening – Hall-Petch (H-P) mechanism (Eq. (1)) and/or by a particle strength-

Table 1. Average crystallite size of the Cu matrix and NbC particles, microhardness values converted to equivalent yield stress, D_{γ} and the yield stress predicted by the Orowan and Hall-Petch strengthening mechanisms for the Cu-NbC nanocomposites in the as-milled and extruded conditions.

Sample id	XRD		TEM	Microhard. (MPa)	$\Delta\sigma_{\gamma}$ (MPa)	$\Delta\sigma_{\text{Orowan}}$ (MPa)	$\Delta\sigma_{\text{Hall-Petch}}$ (MPa)
	$\langle D_{\text{Cu}} \rangle$ (nm)	$\langle D_{\text{NbC}} \rangle$ (nm)	$\langle D_{\text{NbC}} \rangle$ (nm)				
Cu-10 vol.% NbC							
As-milled	19	4	-	2514 ± 111	675	968	1016
Extruded	19	4	5	2509 ± 69	673	968	1016
Cu-20 vol.% NbC							
As-milled	15	6	-	3568 ± 185	1026	1090	1143
Extruded	19	6	-	3038 ± 196	849	1090	1016

ening mechanism – Orowan mechanism (Eq. (2)) [16,17]. The H-P relationship is described by the expression

$$\sigma_{\text{HP}} = \sigma_0 + k_{\gamma} D^{-n}, \quad (1)$$

where, σ_{HP} is the yield stress of a material of crystallite size D , σ_0 the yield stress of matrix and k_{γ} the proportionality factor. The Orowan mechanism can be express by the following equation

$$\sigma_{\text{Orowan}} = \sigma_0 + \frac{M\alpha_1 Gb}{2\pi\phi} \left(\frac{6f}{\pi} \right)^{1/2} \ln \left(\frac{\phi}{b} \right), \quad (2)$$

where σ_{Orowan} is the Orowan stress for dislocations to bow completely around the particle, M the Taylor factor, G the shear modulus, b the Burgers vector of dislocation, f the particle size, ϕ the volume fraction of second phase particles, and α_1 a geometrical constant. In Table 1 the columns identified as $\Delta\sigma_{\text{Orowan}}$ and $\Delta\sigma_{\text{Hall-Petch}}$ correspond to yield stress predicted using both mechanisms the Orowan and H-P. The values of $\Delta\sigma_{\text{Orowan}} = \sigma - \sigma_{0(\text{Cu})}$ were obtained assuming a volume fraction of second phase particles, f , of 0.1 and 0.2, $M=3$, $b=0.25$ nm, $G_{\text{Cu}}=42.1$ GPa, $\sigma_{0(\text{Cu})}=163$ Mpa [17,18], and for ϕ the values determined, by XRD, for the average crystallite size of NbC. In the case of $\Delta\sigma_{\text{Hall-Petch}} = \sigma - \sigma_{0(\text{Cu})}$ the values were calculated using $n=1/2$, $k_{\gamma(\text{Cu})}=0.15$ MPa m^{-1/2} [17] and for $\langle D_{\text{Cu}} \rangle$ the average crystallite size of the Cu matrix obtained with the Scherrer equation. In the case of the extruded Cu-10 vol.% of NbC powders both values of $\langle D_{\text{NbC}} \rangle$ obtained from XRD data and TEM observation are similar.

4. DISCUSSION

The microstructure of the as-consolidated Cu powders with nominal compositions of 10 and 20 vol.% of NbC presented in Fig. 1 shows that in both cases the structure is composed of homogeneous large areas constituted by the Cu matrix and NbC nanoparticles (n-Cu and n-NbC) and powders prior particle boundaries rich in Cu, assigned with arrow. The latter feature, less evident for extruded Cu powders with 10 vol.% of NbC, can be associated with the exposure of the powders at high temperature during the encapsulation and consolidation process. Nevertheless, the matrix constituted by n-Cu and n-NbC nanoparticles appears uniform and no significant porosity is observed. The effect of rejection of Cu was previously observed by Takahashi *et al.* [9,13] in particle dispersion strengthened Cu-X (X=Al₂O₃, TaC, NbC, ZrC, TiC) alloys prepared via mechanical alloying and by Murphy *et al.* [19,20] in mechanically alloyed NbC-Cu cermets. According to Murphy *et al.* the Cu rejection phenomenon can be due to surface energy effects and/or to exudation of Cu from powders. However, to understand the origin of this phenomenon other experiments like extrusions at different conditions and heat treatments would be required. Results, obtained with Scherrer equation, of the average crystallite size of the Cu matrix and NbC nanoparticles in both the as-milled and as-consolidated nanocomposites show that no significant coarsening is observed after extrusion, Table 1. In particular, for NbC nanoparticles the values obtained via XRD are confirmed with TEM observations. An important observation is that the size of

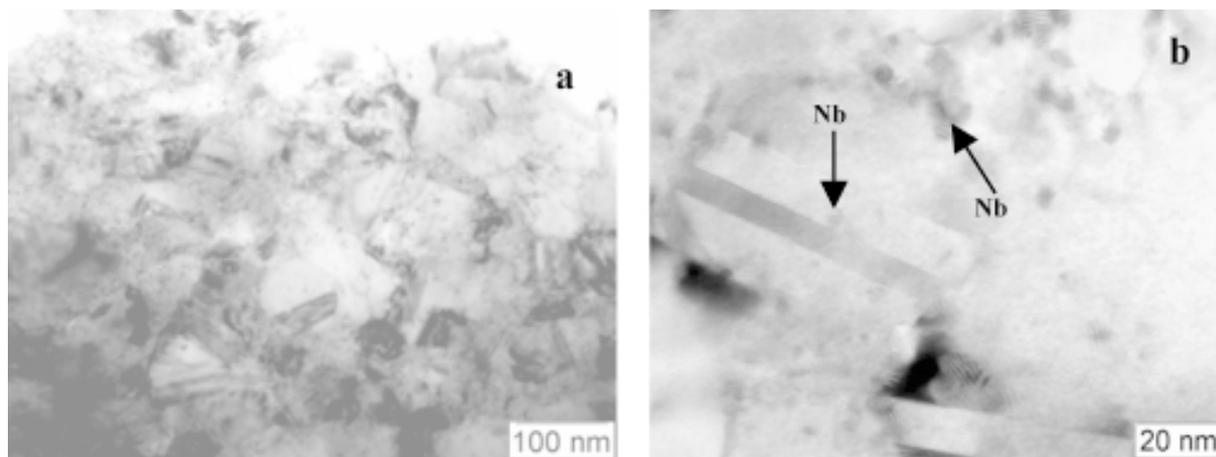


Fig. 2. TEM images of the Cu-10 vol.% of NbC nanocomposite extruded at 873K. Arrows indicate NbC nanoparticles.

NbC nanoparticles appears to be the same independently of their localization within Cu grains or at the grain boundaries, Fig. 2b. Bright field image reveals that the grain size of the Cu matrix is heterogeneous having grains with dimensions between 20 and 80 nm, significantly larger than that estimated with XRD, Fig. 2a and Table 1. The apparently “underestimated” Cu crystallite size, obtained from XRD data, can be explained by the possible existence of subgrains and/or by the amount of defects like twins and stacking faults. These features are resolved by XRD as different entities (coherency domains) and contribute individually to the average crystallite size. However, with TEM a grain having subgrains and/or twins or stacking faults can be regarded as unique entity depending of the tilting conditions; Fig. 2b is a good example of this evidence. Microhardness values, converted to equivalent yield stress, obtained for the as-milled and as-extruded Cu-10 vol.% of NbC powders are similar, Table 1. The results indicate that the as-milled nanostructure is thermally stable even considering that the temperature used to extrude the Cu-10NbC powders was about 0.64 of the absolute melting point of copper. In what concerns to Cu-20NbC nanocomposite a slight decrease of the equivalent yield stress is observed after powder extrusion owing to microstructure heterogeneities, in particular to softer Cu rich regions. Values of the equivalent yield stress obtained for both nanocomposites in the as-consolidated and

as-milled condition are below the values of yield stress predicted both by Orowan and Hall-Petch strengthening mechanisms. This indicates that although a significant proportion of potential strengthening was achieved in the both nanocomposites, the extrusion conditions were not optimized in terms of mechanical properties and thus in terms of performance.

5. CONCLUSIONS

Copper nanocomposites with 10 and 20 vol.% of NbC synthesised *in situ* via mechanical alloying without further heat treatment were hot extruded at 873K. A copper rich layer evidences the powder prior particle boundaries. Results obtained with XRD and TEM, from the as-extruded Cu with 10 and 20 vol.% of NbC powder, show no coarsening of NbC nanoparticles. This high thermal stability is reflected in the microhardness values of the Cu-10NbC powders that are maintained after hot extrusion. The slight decrease of microhardness in the case of extruded Cu-20NbC powders can be attributed to the presence of softer Cu rich zones. The equivalent yield stress obtained in both nanocomposites is slightly lower than that predicted both by Orowan and Hall-Petch strengthening mechanisms. This is an indication that the processing of both nanocomposites is not completely optimised in terms of mechanical properties.

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