On the solidification microstructure of copper-rich niobium alloys

J. L. FIHEY, P. NGUYEN-DUY, R. ROBERGE

IREQ, Institut de recherche de l'Hydro-Québec, Varennes, Québec, Canada

The microstructure of copper-rich niobium alloys has been studied as a function of cooling rate. The main alloy composition investigated was Cu−7 wt % Nb. The cooling rate was varied from $40°$ C sec^{-1} to approximately $7 \times 10^{4}°$ C sec^{-1}. The microstructure as observed in the scanning electron microscope changes from well-dispersed niobium spheres for fast-cooling to an heterogeneous distribution of niobium "flowers" for slow-cooling.

1. Introduction

A very large number of elements, alloys and compounds are superconductors [1]. However, it is now generally accepted that the interesting superconductors, i.e. the materials with a high critical temperature (> 16 K) and with a good critical current density, are intrinsically brittle. One solution to the problem of fabrication of a brittle material is to use composite techniques.

A recent approach [2, 3] for manufacturing a natural composite is showing some promise [4]. These composites are copper-rich alloys prepared by either arc melting or induction heating. Fig. 1 shows a typical microstructure in the as-cast condition. A dispersion of niobium "flowers", approximately $10 \mu m$ in size and several microns apart, can be observed. The object of this paper is to report on the origin and formation of these flowers by observing the solidification microstructure as a function of cooling rates.
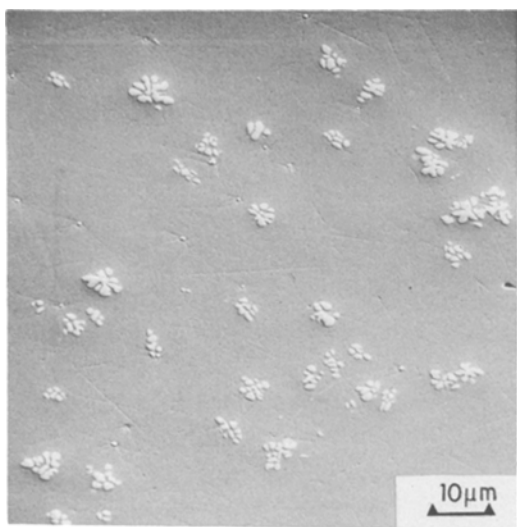

Figure 1 Typical microstructure of copper-rich niobium alloys. A dispersion of Nb flowers in a sea of nearly pure copper.
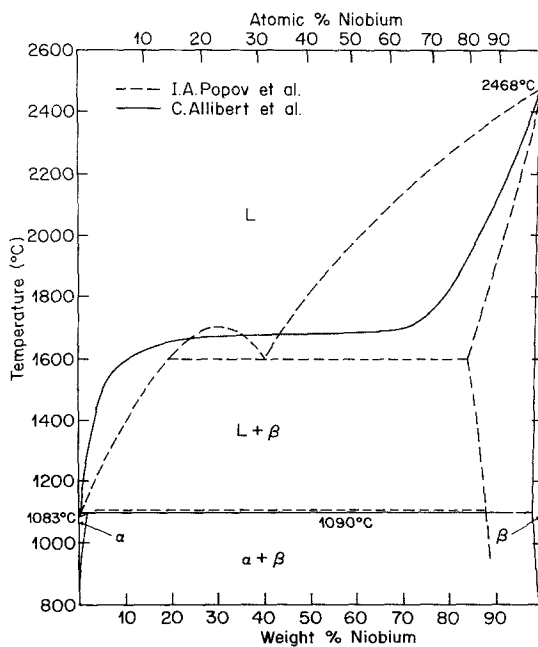

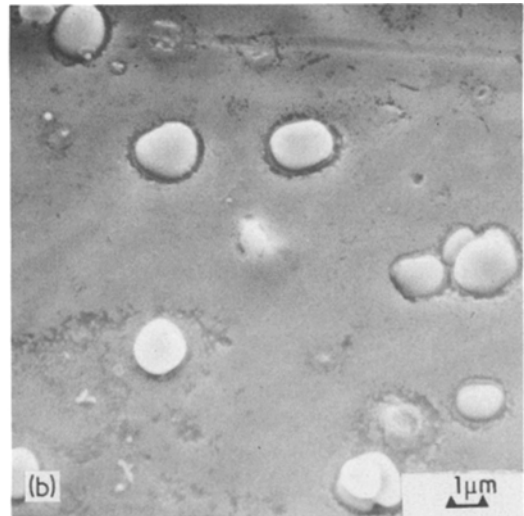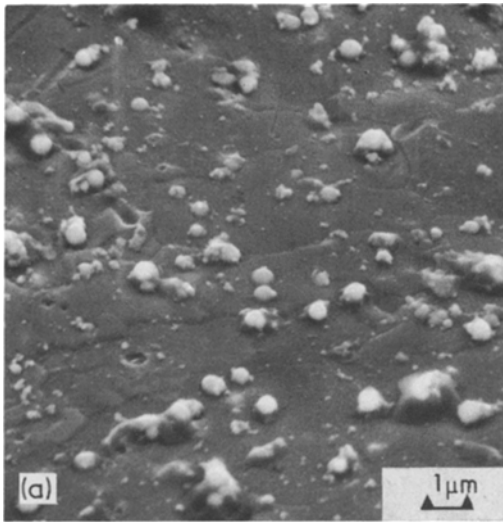*Figure 2* Cu−Nb equilibrium phase diagrams.

Figure 3 Typical microstructures of a Cu–7 wt % Nb alloy after various cooling rates: (a) quenched at 7×10^4 ° C sec $^{-1}$; (b) water-quenched 1800° C sec $^{-1}$; (c) water-quenched 1200° C sec^{-1}; (d) cooled in argon 40° C sec^{-1}.

2. Copper—niobium phase diagram

The two main references for the Cu–Nb diagram (Fig. 2) are Popov and Shirjaeva [5] and Allibert *et al.* [6]. There is an obvious discrepancy in the high temperature region of the diagram. It is generally accepted that the phase diagram of Allibert *et al.* is more accurate. Their phase diagram indicates a very limited solubility of the elements. At the peritectic temperature, 1090° C, the maximum solubility of Nb in copper is 1.5 wt % and the maximum solubility of Cu in niobium is 2.0 wt %. The broad plateau at slightly above 1700° C is a clear indication that phase separation will occur in this system [7].

The microstructure of a Cu–7 wt % Nb alloy is, from the equilibrium phase diagram, composed of β plus copper containing small Nb precipitates. The β-phase can be expected to be totally agglomerated if enough time is spent in the liquid–solid region. Since equilibrium solidification cannot be achieved experimentally the microstructure may be strongly dependent on the actual cooling rate.

3. Experimental techniques

A number of Cu–7 wt % Nb alloys were prepared from a melt at 1800° C and subjected to a range of cooling rate. A few alloys containing 1 to 6 wt % Nb were also prepared. The range of cooling rate covered is approximately three orders of magnitude. The cooling techniques used were: (1) natural
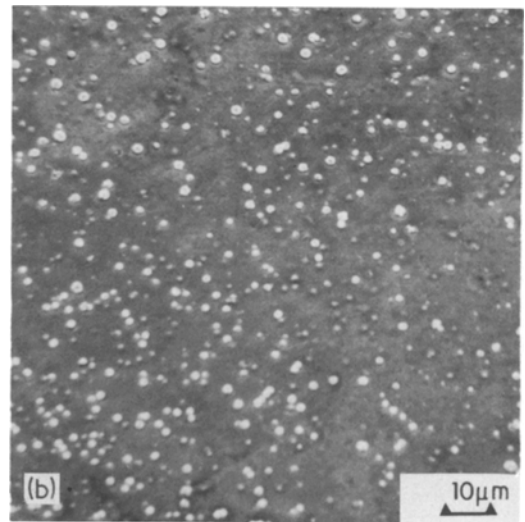
cooling in argon (40° C sec^{-1}), (2) water quenching (300 to 6000° C sec^{-1}), (3) quenching onto a metallic substrate (10^4 to 10^{5} ° C sec^{-1}).

The details of the estimation of the various cooling rates are given in the Appendix. After polishing and etching in a phosphoric acid–propanol solution, the specimens were observed in the scanning electron microscope in order to obtain an indication of the spatial distribution of the niobium.

4. Results and discussion

In Fig. 3, typical microstructures of the Cu–7 wt % Nb solidified at various cooling rates are shown: (a) quenched at 7×10^4 ° C sec^{-1} onto a metallic substrate, (b) water-quenched 1800° C sec^{-1}, (c)
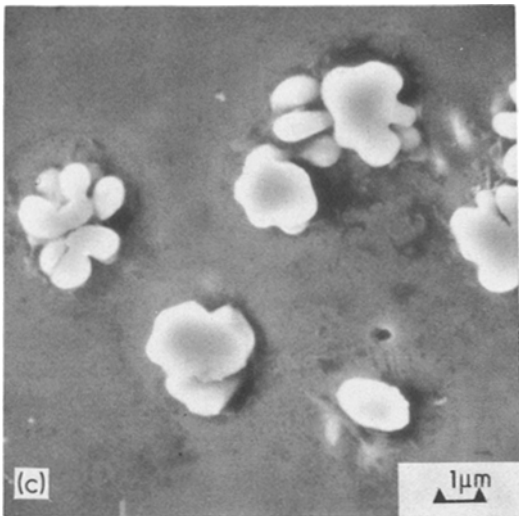
a precipitate as well as its relative volume, i.e. the average volume of a precipitate (v) divided by the volume of the total niobium in the sample (V) are plotted against cooling rate on a log–log graph. The open circles represent the niobium spheres while the closed circles are for the niobium "flowers". For the spheres a straight line with a slope of minus one indicates an inverse relationship between cooling rate and volume of the precipitate. For the "flowers" a straight line with a slope of between -2 and -3 is observed. It should be noted that the measurement on the "petals" forming the "flowers" is difficult since the approximation to a sphere is rapidly lost for slow cooling rates.

An explanation for the observed inverse relationship between sphere size and cooling rate is
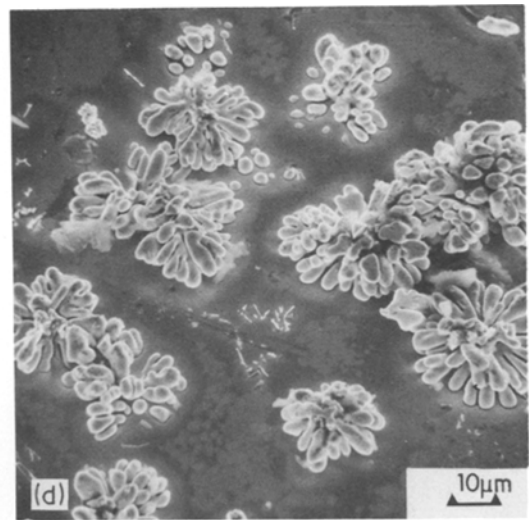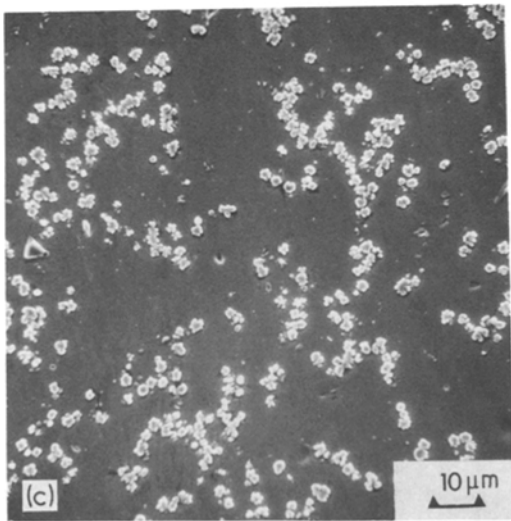

Figure 3 Continued.

water-quenched $1200°\,\mathrm{C\,sec^{-1}}$, (d) slowly cooled in argon at $40°\,\mathrm{C\,sec^{-1}}$. A number of important facts can be deduced from these micrographs:

(1) Niobium could not be preserved in solution in the copper matrix within the range of cooling rates covered in this study. This was confirmed by precise lattice parameter measurements.

(2) The niobium precipitates are most spherical for the highest cooling rate. At slow-cooling rate the niobium appears as "flowers".

(3) By comparing Fig. 3b, c and d (same magnification) it is seen that the homogeneity of the Nb distribution is greatly improved by fast cooling.

The qualitative ideas previously described are represented graphically in Fig. 4. The diameter of

that there is coarsening of the particles. A simple equation for the size of the particles as a function of time for a coarsening reaction is given by:

$$R^m - R_0^m = k(t - t_0)$$

where R is the radius of particle at time t, R_0 the radius of particle initially formed, t_0 the reaction time for a particle of R_0, and $t =$ time. Unfortunately the exponent m cannot be obtained rigorously unless the value of $(t_0 - R_0^m/k)$ is known. However, this term can be neglected for measurements at reaction times greater than t_0. A plot of $\log R$ versus $\log t$ can be used to evaluate m. In order to obtain an estimate for the reaction time, the hypothesis that coarsening is the result of the
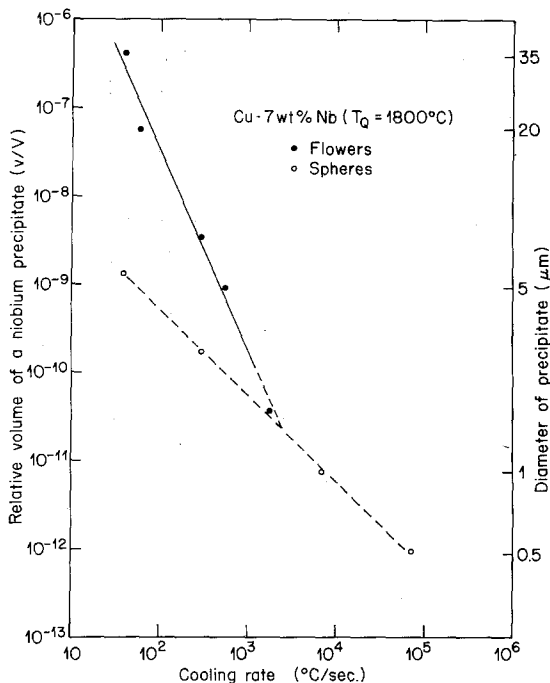
Figure 4 Relative volume and diameter of a niobium precipitate as a function of cooling rate.

time spent in the temperature range 1530 to 1100° C is used. In Fig. 5, the results are represented graphically. A value of $m = 3.08$ support the idea that coarsening is responsible for the growth of the niobium spheres.

A closer examination of the microstructure in Fig. 3a shows the presence of two different size distributions; the large spheres and also niobium on a much smaller scale. This small scale dispersion of niobium becomes more evident if we examine

microstructures of compositions less than 7 wt% Nb. Fig. 6 shows the microstructure of Cu–4.3 wt%Nb quenched from the liquid state onto a stainless steel substrate. A very fine dispersion of niobium is observed with no large spheres. This composition 4.3 wt%Nb represents approximately the transition between the very fine precipitation (Fig. 6) and the larger spheres plus very fine precipitates (Fig. 3a). This composition is situated close to the knee in the liquidus curve in the Cu–Nb phase diagram.

Based on these results we can visualise the process of solidification of Cu–7 wt%Nb alloys as follows. When the alloy traverses the liquidus (the plateau region at 1600° C), niobium is rejected from the liquid. The size and shape of the niobium is greatly influenced by the cooling rates in the range of 1600 to 1100° C. The larger spheres following the slower cooling rates may be the result of the coarsening of the smaller spheres which have a large size distribution. On the other hand, the "flowers" are the result of the connectivity of spheres of comparable sizes.

5. Conclusions

The microstructure of as-cast copper 7 wt% niobium alloys has been studied as a function of cooling rates. The niobium shape, size and distribution are all strongly influenced by the cooling rate. Fast cooling rates, greater than 2×10^3° C sec^{-1}, lead to an homogeneous microstructure of niobium spheres in a copper matrix. Slower cooling rates give rise to the appearance of niobium "flowers". Therefore, it is expected that variations in cooling techniques will lead to important struc-
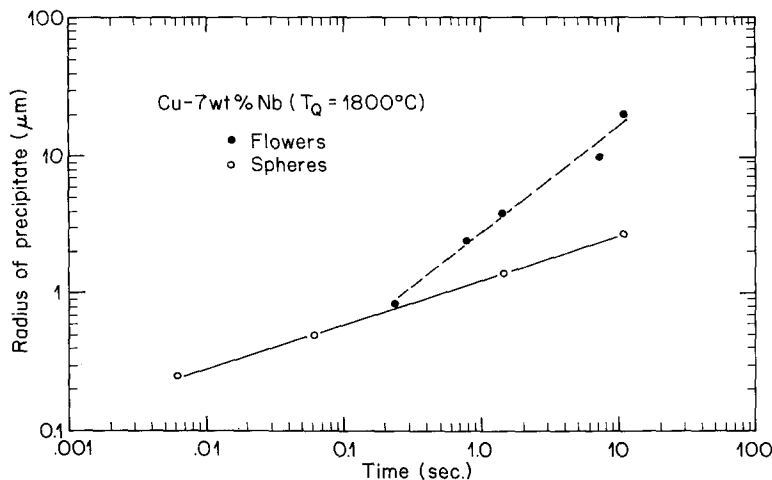

Figure 5 Radius of niobium precipitate as a function of the time spent in the temperature range 1530 to 1100° C.
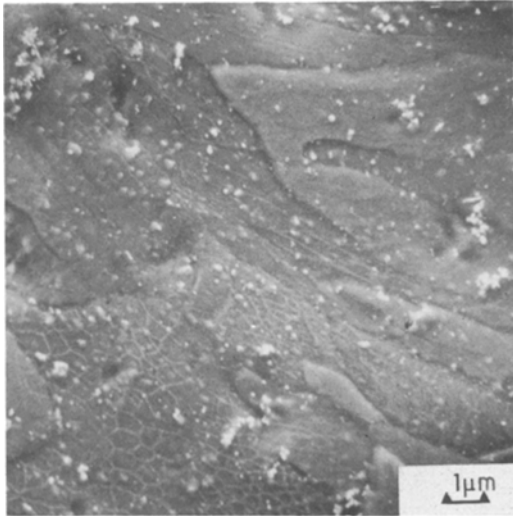
Figure 6 Microstructure of a Cu–4.3 wt % Nb alloy quenched from the liquid state onto a metallic substrate. Very fine dispersion of niobium.

ture modifications which in turn greatly influence the mechanical and electrical properties of these alloys.

Appendix. Outlines of the techniques used to evaluate the cooling rates

(1) Cooling in argon. The temperature of the graphite crucible was followed using an optical pyrometer in the range of temperature 1600 to 1090° C.

(2) Water quenching. The specimens were quenched directly from the liquid (1800° C) into water at 20° C. As soon as the alloy entered the water it is surrounded by a water vapour blanket. We assumed an average temperature of 950° C for the water vapour and 60° C for the water. The heat transfer coefficient h was estimated using the Sparrow and Cess [8] analytical solution.

To calculate the cooling rate it is known [9] that, if

$$\frac{hd}{k} \leqslant 0.1, \qquad (A1)$$

where h is the heat transfer coefficient (estimated at 0.024 cal cm$^{-2\,°}$ C^{-1} sec^{-1}), k is the thermal conductivity of the alloy ($\sim$ constant = 0.90 cal

TABLE AI Calculated cooling rates for a liquid alloy quenched from 1800° C in water at 20° C.

Diameter (cm)	0.8	0.5	0.19	0.07
h (cal cm$^{-2\,°}$ C^{-1} sec^{-1})	0.024	0.027	0.034	0.041
dT/dt (° C sec^{-1})	300	550	1800	5700

cm$^{-1\,°}$ C^{-1} sec^{-1}) and d is the diameter of the specimen, then the cooling is Newtonian. For a sample of 0.8 cm diameter, hd/k is 0.021. Therefore, we are clearly justified in assuming an exponential cooling rate. The results of the estimations are given in Table AI.

(3) Quenching on a metallic substrate. The alloy is projected from 1800° C against a stainless steel drum. For a specimen of 22 μm thick the heat transfer coefficient is estimated at 0.11 cal cm$^{-2\,°}$ C^{-1} sec^{-1}. Again assuming a Newtonian regime the cooling rate between 1600 and 1090° C is estimated at $7 \times 10^{4\,°}$ C sec^{-1}.

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