

On the Sinterability of Commercial-Purity Niobium

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Abstract. Niobium and niobium-base materials are currently used in several technological applications. High-vacuum sintering is a suitable technique to obtain commercial-purity niobium with a homogeneous fine-grained microstructure. High-vacuum sintering tests were carried out in the range 1000-2000°C using a fine niobium powder ($d_p \approx 10 \mu\text{m}$) in order to investigate the microstructural evolution. Sintering parameters such as density, linear shrinkage and porosity were evaluated. In addition to diffusion-controlled mass transport towards sintering necks, oxygen degassing also takes place due to the volatilization of niobium suboxides (NbO and NbO₂) depending on its initial content. At higher sintering temperatures, e.g. $T_s > 1800^\circ\text{C}$, grain growth becomes the predominant mechanism and the pore-boundary interaction plays an important role during further densification. The higher mobility of high angle boundaries results in pore trapping inside the grains whereas sub-boundaries appear to be more susceptible to pore pinning because of their lower mobility.

Introduction

Niobium has very interesting properties like high melting point, very-low ductile-to-brittle transition temperature (DBTT), good fabricability, and a moderate-to-high elastic modulus [1]. Representative examples of pure and low-alloyed niobium applications include the manufacture of thermal shields, evaporation boats and components for sodium-vapour lamps [2]. Niobium is also very ductile and can be easily deformed at room temperature to very large strains without intermediary annealing.

Niobium ingots processed by electron beam melting (EBM) or vacuum arc remelting (VAR) are typically coarse-grained materials. Further processing of such ingots demands special operations to break up this coarse structure. Moreover, costly vacuum annealing is necessary to get a homogeneous fine-grained microstructure. This homogeneous fine-grained microstructure is required, for instance, in applications where deep-drawing operations are required.

Powder metallurgy is a suitable technique to get fine-grained niobium [3]. Niobium must be sintered in vacuum at high temperatures to degas oxygen and nitrogen by means of well-known mechanisms [4]. On the other hand, at high temperatures boundary mobility increases and grain growth takes place intensely. As a consequence, a high volume fraction of isolated pores remains in the microstructure hindering further densification. These aspects will be focussed in this paper with emphasis to the specimens sintered above 1800°C.

Experimental

The niobium powder used in this work was obtained from the hydride-dehydride process (HDH). Table 1 shows the main physical properties of the niobium powder used in this work. Table 2 presents its chemical composition and their main contaminants.

Table 1 - Main physical properties of the Nb-powder.

Characteristic	Nb
Melting Point (°C) ¹	2468
Tap Density (kg/m ³) ¹	3840
BET (m ² /g)	0.61
Average particle diameter (µm)	6.71

Table 2 - Chemical composition of the Nb-powder.

Impurity content (wt-ppm)						
Nb	O	N	Al	Fe	Cu	Si
bal.	6200	380	30	40	10	30

For the sintering experiments, Nb powder was cold isostatic pressed (CIP) for three minutes at 200 MPa. The typical green compacts dimensions were 6.8 mm diameter and 20 mm length. High-vacuum sintering was carried out in a tubular electrical resistance furnace at temperatures ranging from 1000°C to 2000°C ($P < 10^{-5}$ mbar). Niobium pipes (13mm diameter and 160mm length) were used as heating elements to avoid contamination. Additional information concerning the experimental set-up is found elsewhere [3]. Standard metallographic techniques were used to prepare the samples before etching with a 3%HF-2%HNO₃-glycerin (in vol-%) solution to reveal the grain boundaries and the pore-grain boundary morphology. The porosity was evaluated by means of density measurements. Dilatometry was carried out in a Netzsch model 402-E/7 equipment at 10°C/min. Grain size was determined using quantitative metallography (Quantimet-520, Cambridge Instruments). Oxygen and nitrogen contents were determined using an equipment Leco model TC-136. Back-scattered electron images (BSE) and secondary electron images (SEI) were obtained in a JEOL JSM-6400 scanning electron microscope (SEM) operating at 10 kV.

Results

The niobium powder obtained via HDH consists of angular-shaped particles. This morphology results from cleavage of brittle niobium hydride (NbH_{1.89}) particles during ball-milling. Further dehydrating leads to minor changes in the particle morphology.

The general aspects concerning the microstructural evolution of pure niobium during sintering have been reported previously [3]. In addition to diffusion-controlled mass transport towards sintering necks, oxygen degassing also takes place due to the volatilization of niobium suboxides (NbO and NbO₂) depending on its initial content [4]. Nitrogen degassing takes place via diffusion of N-atoms towards metal's surface followed by recombination and further desorption in vacuum [4]. Fig.1 shows the decrease of oxygen content as a function of time for two distinct temperatures. As expected, degassing reactions are more effective at higher temperatures owing to their exponentially

dependence on temperature. After sintering at 2000°C for 3 hours, oxygen content in niobium is about 500 wt-ppm. Because of the detrimental effects of oxygen in niobium, mainly in ductility, these contents should be even lowered.

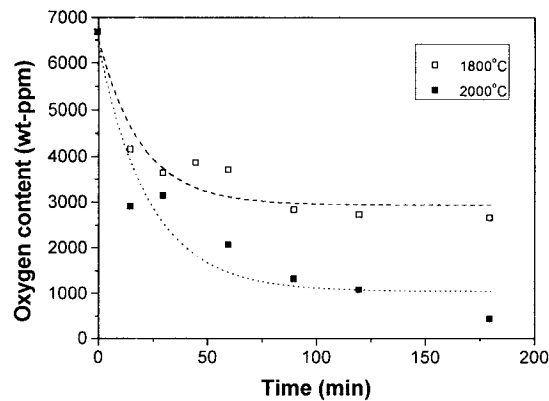


Figure 1 – Oxygen degassing for niobium showing oxygen content versus sintering time at 1800 and 2000°C.

By using different techniques like density and linear shrinkage measurements, one can verify that the densification of niobium speeds up at about 1300°C, as shown in Figs. 2a and 2b, respectively. With increasing temperature, the classical features of pore closure and grain growth take place. An interesting aspect to note is that even after sintering at 2000°C for 1 hour a few interconnected pores remain in the microstructure.

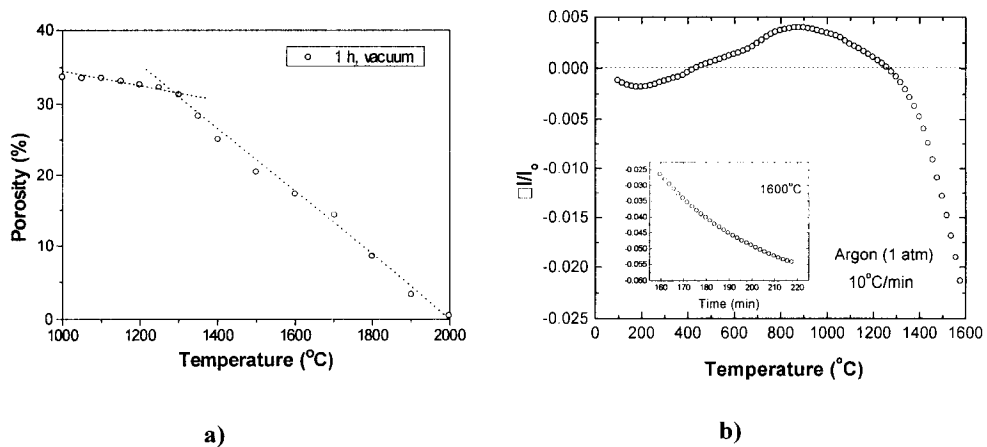


Figure 2 – Densification behavior of niobium determined indirectly by two distinct techniques: a) porosity versus temperature and b) linear shrinkage versus temperature.

Figs. 3a and 3b show the microstructure of the specimens sintered at, respectively, 1900 and 2000°C. In both cases, it consists of an equiaxed grain structure containing nearly spherical pores. Isolated (spherical) and a minority of interconnected pores can be found in the whole extension of the specimens. Both grain size and volume fraction of isolated pores increase with increasing temperature. Grain size varies with temperature according to the curve displayed in Fig.4. After sintering at 1100°C for 1 hour, grain size is about 13 μm , a value close to the initial particle size. At 1900°C, grain size is about 74 μm while at 2000°C this value nearly doubles ($\approx 120 \mu\text{m}$). Abnormal grain growth is observed to occur predominantly in the specimen sintered at 2000°C.

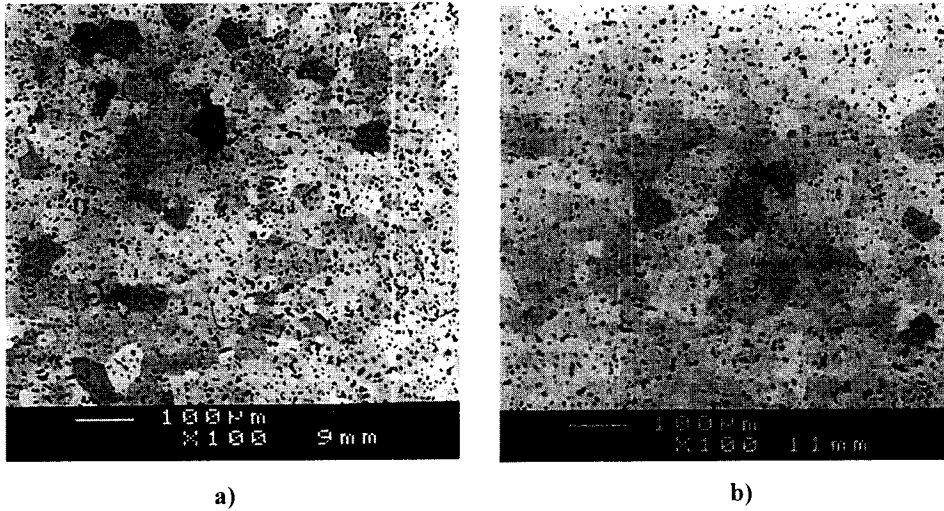


Figure 3 – SEM micrograph showing the microstructure of niobium sintered at: a) 1900°C and b) 2000°C (BSE).

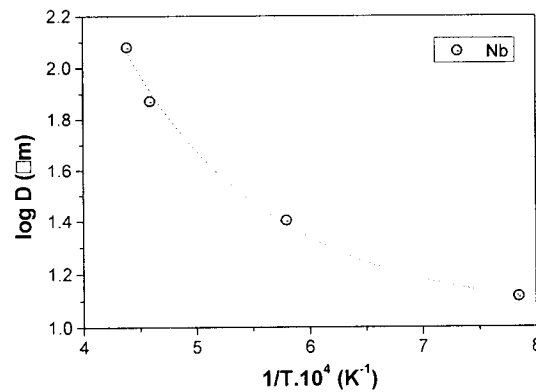


Figure 4 – Final grain size as a function of reciprocal sintering temperature in niobium.

Discussion

When niobium is sintered at high temperatures, e.g. above 1800°C, the mobility of grain boundaries increases and leads to boundary breakaway resulting in pore trapping inside grains. In contrast, sub-boundaries appear to be more susceptible to pore pinning because of their lower mobility. One could speculate about the origin of these low angle boundaries in the microstructure after sintering at high temperatures. In our experiments, low angle boundaries were determined using electron backscattered diffraction (EBSD). The results concerning this investigation will be reported in a forthcoming paper. One possible explanation could be provided by the grain coalescence theory formulated by Nielsen [5]. When grain growth takes place the smallest grains are preferentially consumed. Grain coarsening is driven by the reduction in the grain boundary area. Let us suppose a hypothetical situation where two grains A and B with similar orientations get in close vicinity while grain C disappears. This mechanism results in the formation of a low angle boundary. The sequence of events is shown in Figure 5a to 5d. This mechanism is not expected to occur intensely in materials with a random distribution of orientations (absence of texture), however, with increasing temperature abnormal grain growth may occur in some extent.

Texture changes are commonly associated with grain growth [6]. When abnormal grain growth takes place, few grains distributed elsewhere become much larger than the average grain size. Changes in texture tend to become more pronounced when abnormal grain growth occurs [7]. In that sense, sintering might give rise to texture-free materials if grain growth (mainly abnormal growth) is prevented. This behavior is commonly reported for other sintered materials, e.g. stainless steel [8], and contributes to minimize the differences in terms of grain orientation easing the coalescence of grains. In a porous material, besides the mechanisms above described, one has to take into account the effects of pore pinning to understand the microstructural evolution during sintering at high temperatures. In this case, low and high angle boundaries pinned by pores are hypothetically included in this model, as shown in Figs.5d and 5e. Fig.6 shows a grain which exhibits abnormal growth in niobium sintered at 2000°C for 1 hour. In this representative figure, pores can be seen pinning a low angle boundary formed in the center of this grain (see arrow). Owing to the low misorientation, the contrast is less intense. Pore pinning is also observed in some parts of the grain boundaries. At this stage, isolated pores are majoritary in the microstructure.

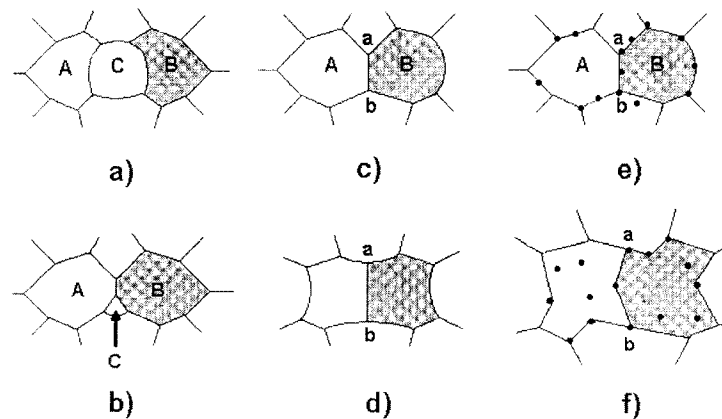


Figure 5 – a) to d): Mechanism for geometric coalescence of grains proposed by Nielsen [5]; e) and f): extended to a material containing pores. The segment **ab** represents a low angle boundary.

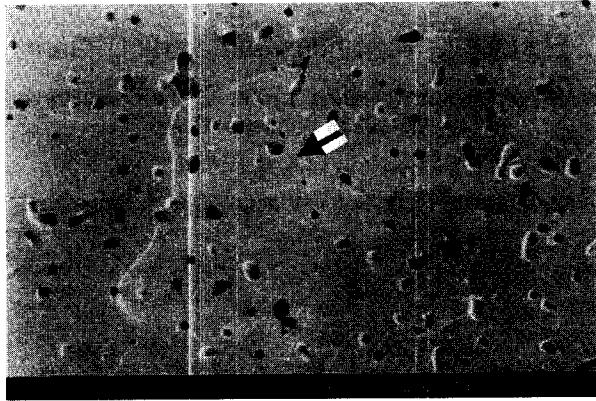


Figure 6 – SEM micrograph showing a grain exhibiting abnormal growth in niobium sintered in vacuum at 2000°C for 1 hour (SEI).

The texture changes associated with grain growth are not easily explained yet. The current understanding of the fundamentals of grain growth are still rather unknown owing to the intrinsic orientation-dependence of grain-boundary energies and respective mobilities. This feature becomes more complicated when the concurrent action of retarding forces to grain growth such as pore and solute pinning are taken into account. To calculate this pinning force, one has to know the dependence of the grain boundary energy with regard to the grain boundary structure. In niobium, the relatively large amounts of oxygen play also an important role increasing solute-pinning effects contributing to diminish boundary mobility.

Conclusions

Niobium sintered at temperatures above 1800°C exhibits intensive grain growth. Abnormal grain growth takes place above 1900°C. New sintering cycles have to be investigated in order to minimize grain boundary breakaway to enhance further densification as well as allowing the decrease of interstitial impurities in niobium. A close inspection in the microstructure reveals that low angle boundaries are more susceptible to pore pinning due to their lower mobility. One simple model to explain the presence of low angle boundaries in the microstructure was proposed.

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