Sintering of P/M Nb-TiB₂ alloys

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ABSTRACT

In this paper, we have investigated the possibility of using TiB₂ particles to promote reinforcement strengthening in niobium. Niobium obtained from the HDH process and TiB₂, both in the powdered form, were mixed, cold pressed and sintered in high vacuum in temperatures ranging from 1300 to 1900°C for 4 hours. In this paper we present and discuss the results concerning the microstructural evolution during high-vacuum sintering of niobium with additions of TiB₂ up to 2 wt-%. Aspects related to phase stability and chemical composition of the resulting alloys will be discussed. Results show that dissolution of TiB₂ particles becomes significant above 1400°C. After sintering at 1900°C, the smaller TiB₂ particles are fully dissolved whereas the larger ones are partially dissolved. Dissolution of TiB₂ particles occurs with the formation of Nb-Ti solid solution and NbB phases.

INTRODUCTION

Niobium is a metal with very interesting properties such as high melting point, very-low ductile-to-brittle transition temperature, and a moderate-to-high elastic modulus [1]. Due to its low strength at room temperature (≈ 200 MPa), unnaloyed niobium has a limited range of applications which include the manufacture of thermal shields, evaporation boats and components for sodium-vapour lamps [2].

Powder metallurgy is a suitable technique to get fine-grained niobium. Niobium must be sintered at high temperatures in vacuum to decrease oxygen and nitrogen contents by means of well-known degassing reactions [3] and promote high densification.

TiB₂ has been investigated as a suitable agent to promote dispersion hardening in niobium by means of melting and further aging of B-containing alloys [4]. In addition to the enhancement of the mechanical properties of the matrix, mainly at high temperatures (creep strength), dispersoids are also very effective to retard grain growth during sintering.

Another possibility to promote strengthening in niobium could be the use of particle reinforcements. Dispersion and reinforcement strengthening mechanisms differ in terms of particle size and interparticle spacing [5]. While dispersoids exert a pinning effect on dislocations, reinforcements cause strengthening because they impede plastic flow of the softer matrix material. In consequence, chemical stability, or at least a slow reaction kinetics, and a high shear modulus are desired characteristics for a reinforcement material. TiB₂ has a high melting point (3225°C ± 20°C) as well as a very negative free energy of formation. The aim of this paper is to investigate the behavior of titanium diboride particles during sintering of niobium in terms of its stability at high sintering temperatures, a necessary condition to the processing of PM-niobium.
EXPERIMENTAL

The niobium powder 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. TiB₂ was obtained by means of double arc melting of elemental Ti pieces and B as crystalline powder (Alfa Aesar) followed by crushing and sieving to obtain a ~200 mesh powder. Both niobium and TiB₂ powders are formed by particles with angular morphology.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>2468</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>8.57</td>
</tr>
<tr>
<td>BET (m²/g)</td>
<td>0.61</td>
</tr>
<tr>
<td>Average particle diameter (µm)</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 2 - Chemical composition of the niobium powder.

<table>
<thead>
<tr>
<th>Impurity content (wt-ppm)</th>
<th>Nb</th>
<th>O</th>
<th>N</th>
<th>Al</th>
<th>Fe</th>
<th>Cu</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>bal.</td>
<td>6200</td>
<td>380</td>
<td>30</td>
<td>40</td>
<td>10</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

For the sintering experiments, Nb and TiB₂ powders were mixed and cold pressed for three minutes at 500 MPa. TiB₂ contents were 0.5, 1.0 and 2.0 wt-%. The dimensions of the green compacts were about 12 mm in diameter and 5 mm in height. High-vacuum sintering was carried out in a tubular resistive furnace (P < 10⁻⁵ mbar) at temperatures ranging from 1300°C to 1900°C for 4 h. 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. Secondary (SE) and back-scattered electron images (BSE) were obtained in a LEO 1450-VP electron microscope (SEM) operating at 15 kV. WDS analyses were carried out in a Stereoscan 440 equipment operating at 12 kV.

RESULTS

The green density of the Nb-TiB₂ alloys was about 64%. There were no major differences in the green density as a function of the TiB₂ initial contents. The preliminary results have pointed out that increasing TiB₂ additions to niobium caused a slight decrease of the densification during sintering. Fig. 1 shows the plots of the logarithm of shrinkage versus the reciprocal of the sintering temperature for niobium containing TiB₂ additions ranging from 0.5 to 2 wt-%. For temperatures ranging from 1300°C to 1900°C, the behavior of the shrinkage for all samples seems to be very similar, reaching values around 20% at 1900°C for Nb-0.5TiB₂. Many papers report the effects of the additions of oxide particles on the reduction of the sintering rates in metallic systems, e.g. Al₂O₃ in iron [6]. In these cases, densification is inhibited by the second phase. A similar behavior is observed in the Nb-TiB₂ specimens investigated in this paper. In the specimens sintered at 1900°C, pores are predominantly spherical whereas at lower sintering temperatures, interconnected pores are found in every part of the microstructure.
Microstructural characterization of the sintered specimens using SEM reveals that TiB₂ particles are found homogeneously distributed in the niobium matrix, as shown in Figs. 2a and 2b. Because of the initial TiB₂ powder wide size distribution, fine and coarse particles are present in the microstructure. The final porosity in the specimens sintered at 1900°C for 4 hours is lower than 5% for all the additions.

Two representative specimens containing 2-wt%TiB₂ were selected for the WDS analyses (elemental mapping), i.e. 1300 and 1900°C. In the specimens sintered at 1300°C/4h, results showed that the larger TiB₂ particles did not dissolve and no interfacial reaction-zones could be resolved. The chemical composition of these particles determined by WDS is about 69 at-%B and 31 at-%Ti (Fig. 3a) indicating that the particle composition remains unchanged (TiB₂). Matrix consists predominantly of niobium. It can be also seen in Fig. 3a the presence of much finer B-rich regions indicating that probably very fine TiB₂ particles could be dissolved at this temperature.

At intermediary temperatures, 1500 and 1700°C, dissolution of TiB₂ particles becomes more pronounced as well as the reaction layer around large particles, as shown, respectively, in Figs. 3b and 3c. An enlarged view of the microstructure of the specimen sintered at 1700°C for 4 hours reveals the presence of interconnected pores and a slight composition contrast provided by the SEM-BSE. This contrast probably comes from the dissolution of smaller TiB₂ particles.

The behavior of TiB₂ particles during sintering at the highest temperature investigated is quite different from that one observed at 1300°C. The finer TiB₂ particles were fully dissolved in the niobium matrix. Fig. 2b shows darker areas in the matrix indicating the presence of lighter elements such as Ti and B as well as isolated NbB particles. Surrounding the larger particles, a wide interfacial reaction zone is present. These reaction zones were investigated in detail using WDS analysis. In the specimens sintered at 1900°C, these reaction zones consist predominantly of NbB with a small amount of dissolved Ti (< 5 at-%). WDS-analyses also reveal that the Ti content in the niobium matrix surrounding the larger particles after sintering at 1900°C/4h is about 2 at-% (Fig. 3d). Boron content in the solid-solution phase is not significant. Smaller plate-like TiB₂ particles were found throughout the matrix in the specimens sintered at 1900°C. These particles have probably grown in regions containing small particles that have dissolved at 1900°C. A similar behavior is found in the Ti-TiB₂ system, where the thermodynamically favored interfacial reaction occurs, as shown in Eq. 1 [7].

$$\text{Ti} + \text{TiB}_2 \rightarrow 2 \text{TiB} \quad (1)$$

![Figure 1](image.png)

**Figure 1** – Shrinkage behavior of Nb-TiB₂ specimens sintered in high vacuum for 4 hours between 1300 and 1900°C.
Figure 2 – Scanning electron micrographs showing the microstructure of Nb-2wt%TiB₂ compacts sintered for 4 hours at a) 1300°C, b) 1500°C, c) 1700°C, and b) 1900°C. SEM, BSE. Note the reaction zone around TiB₂ particles (black particles) in the specimen sintered at 1900°C for 4 h. Circles mark isolated plate-like NbB particles. Arrows show the presence of the reaction layer.

DISCUSSION

The investigation of the nature and kinetics of interfacial reactions is essential to avoid detrimental effects in the mechanical properties of metal matrix composites (MMC) under service conditions or during their fabrication [8]. The interfacial reaction observed at high temperatures occurs because niobium displaces Ti from the TiB₂ phase, leading to the formation of a NbB layer around TiB₂ particles and titanium diffusing to the niobium matrix to form the BCC-(Nb,Ti) solid solution. The reaction kinetics depends on the diffusion of Ti atoms through the NbB layer. NbB has an orthorhombic structure similar to CrB [9]. Depending on the mechanism of NbB growth during the interfacial reaction, pores might be formed in the center of the former TiB₂ particles, mainly within the larger ones. These pores remain in the microstructure preventing further densification.

In terms of phase stability, the results have indicated that at 1900°C the overall composition of these alloys are in the BCC-(Nb,Ti) plus NbB two-phase field. The boron content in this BCC-(Nb,Ti) solid solution should be low as expected from the low solubility of boron in both Nb and Ti [9]. The microstructure observed in the specimens sintered at 1900°C is not to be thermodynamically stable. The BCC-(Nb,Ti) plus NbB two-phase microstructure is not formed due to kinetics constraints.

Based on these results, it is possible to conclude that TiB₂ particles are not suitable agents to promote reinforcement strengthening in niobium, in the case of the conventional sintering route adopted in this work. It would be worth to evaluate the microstructure and mechanical properties of a BCC-(Nb,Ti) plus NbB composite, using finer TiB₂ particles to reinforce niobium.
Figure 3 – SE-images of sintered specimens of Nb-2wt%TiB₂ and the corresponding WDS elemental mappings of Ti, Nb and B, respectively, for Nb containing 2 wt%TiB₂ after high-vacuum sintering at: a) 1300°C/4h; b) 1900°C/4h.
CONCLUSIONS

From the results presented in this paper, the following conclusions can be drawn:

The densification of niobium during sintering is slightly reduced with increasing TiB₂ additions. The reaction of TiB₂ with niobium takes place in a significant manner in temperatures above 1400°C leading to the formation of a reaction layer consisting of NbB surrounded by a BCC-(Nb-Ti) solid solution. At 1300°C for 4 hours, the reaction zone cannot be resolved at SEM. One could suggest the necessity of using a much finer TiB₂ powder in order to get full dissolution of particles and carry out further aging treatment to promote precipitation of NbB throughout the material.

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References