RAPID SOLIDIFICATION AND HEAT-TREATMENT OF THE Ti$_{92}$B$_8$ EUTECTIC ALLOY$^1$

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Abstract
In this work the Ti$_{92}$B$_8$ alloy was processed via rapid solidification (splat-cooling) and then heat-treated at 700°C and 1000°C. A careful microstructural characterization has shown that after rapid solidification a very fine two-phase microstructure is produced with no significant saturation of B in $\alpha$/$\beta$ Ti. There was no indication of amorphous formation in the rapidly solidified splats. Both $\alpha$Ti and TiB are observed in the microstructures of the splats after heat-treatment at 700°C and 1000°C, confirming the stability of the $\alpha$Ti+TiB two-phase region in this temperature range.

Key words: Rapid solidification; Splat-cooling; Eutectic alloy; Ti-B system.

SOLIDIFICAÇÃO RÁPIDA E TRATAMENTO TÉRMICO DA LIGA EUTÉTICA Ti$_{92}$B$_8$

Resumo
Neste trabalho a liga Ti$_{92}$B$_8$ foi produzida via solidificação rápida (splat-cooling) e em seguida tratada termicamente a 700°C e 1000°C. Uma cuidadosa caracterização microestrutural mostrou que após a solidificação rápida uma fina microestrutura bifásica foi produzida, sem indicação de importante saturação de B em $\alpha$/$\beta$ Ti. Não foi encontrado nenhum indício de formação de material amorfo nas amostras solidificadas rapidamente. Foram identificadas as fases $\alpha$Ti e TiB nas microestruturas das amostras produzidas via solidificação rápida após os tratamentos térmicos a 700°C e 1000°C, confirmando a estabilidade do campo bifásico $\alpha$Ti+TiB neste intervalo de temperatura.

Palavras-chave: Solidificação rápida; Splat-cooling; Liga eutética; Sistema Ti-B

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INTRODUCTION

Due to their low density, high mechanical strength and good corrosion resistance, Ti and Ti alloys are suitable for several important structural applications in the aerospace industry for service in the 700-1000°C temperature range.[1]

The currently accepted Ti-B phase diagram[2] shows in its Ti-rich region the following stable solid phases: α-Ti solid solution- hcp (at room temperature), β-Ti solid solution– bcc (885°C - 1670°C) and TiB. An eutectic reaction (L ⇔ β-Ti + TiB) occurs at 1540°C for ~ 8 at.% B and a peritectoid reaction (β-Ti + TiB ⇔ α-Ti) at 885°C.

As part of a work, which aims to evaluate the phase equilibria in the Ti-rich region of the Ti-Si-B system in the 700-1000°C temperature range, it was the objective of this investigation to evaluate the phase equilibria in the Ti-rich region of the Ti-B system in this temperature range. The equilibrium experiments were carried out using samples produced via rapid solidification to allow the attainment of equilibrium conditions. In addition, the microstructure of the rapidly solidified samples also became an interest of this investigation.

The rapid solidification technique used was the splat-cooling method where cooling rates of ~ 10^6 K.s^{-1} are reached. Due to the significant undercooling, the solidification conditions lead to a fine-grained microstructure, which assists the attainment of equilibrium in a shorter time. Others possible effects of a rapid solidification process include: solid solution extension, retainment of high-temperature phases, formation of metastable crystalline phases, and formation of amorphous alloys.[5-8] However, all these effects in the microstructure are not only associated to high cooling rates, but they can also depend on the alloy composition, the ratio between the melting temperature and the glass transition temperature, the ratio of the atomic sizes of components and the crystalline structures of the components.[7]

Tavadze[8] studied Ti-B (Ti-rich) alloys prepared by rapid solidification (cooling rate ~ 10^6 K.s^{-1}) and observed an extension of the B solubility in Ti and the appearance of an amorphous phase through X-ray diffraction (XRD), however, no details about the method of alloy production was given. Sastry[10] shows that the Ti-1.0B and Ti-1.0C alloys produced via rapid solidification present a large volume fraction of fine dispersoids which increase the yield strength. Other works[11,12] suggest that the solubility of B in both α- and β-Ti may reach values beyond 10 at. % due to rapid solidification.

EXPERIMENTAL PROCEDURE

Initially, an ingot (~ 6g) of the Ti_{92}B_{8} (at. %) alloy was produced from commercially pure Ti foil (min. 99.3 wt%) and B pieces (min. 99.5 wt%) via arc-melting under a gettered argon atmosphere on a water-cooled copper crucible. Five melting steps were carried out to ensure chemical homogeneity. Samples of ~ 0.1 g were then taken from the ingot and arc-melted just to produce a near spherical shape suitable for levitation in the rapid solidification apparatus. Nine rapidly quenched splats of the Ti_{92}B_{8} alloy were produced under argon in a Splat-Cooling System from Edmund Bühler GmbH. The steps of levitation, melting and splat-formation were easily accomplished with this alloy composition. Part of the splats were encapsulated under argon in quartz tubes with Ti getter and then heat-treated at 700°C for 120 h and at 1000°C for 48 h. At the end of the experiments the capsules were removed from the furnace and air-cooled. Microstructural characterization of the materials was
performed via X-ray diffraction (XRD) and Scanning electron microscopy (SEM), Conventional and Field-Emission Gun (FEG) using Back Scattered Electrons Detector. The XRD experiments were performed using a Shimadzu model XRD6000 diffractometer at room temperature, using Ni-filtered CuKα (\(\lambda = 1.5418 \text{ Å}\)) radiation. The arc-melted spherical samples were evaluated in powder form while the splats and heat-treated splats in bulk form (incident X-ray beam in one of the faces). The phases present in the materials were identified by means of comparisons of the experimental diffractograms with simulated diffractograms of the phases using the PowderCell program\[^{13}\] and crystallographic data.\[^{14}\] Evaluation of possible solid solution extension was investigated with the refinement of the crystalline structures via the Rietveld method\[^{15}\] using the FullProf program.\[^{16}\]

Vickers Microhardness of the produced material was measured using 100 gf load for 30 s, using a MICROMET 2004 Buehler instrument. All the measurements were concentrated in the central region of the samples.

Some evaluation about absorption of penetrating X-rays in the splats were considered in accordance with equation (1),\[^{17}\] where \(I = \text{intensity}, \mu = \text{linear absorption coefficient}, \mu_m = \mu_P = \text{mass absorption coefficient for each chemical element}, \rho = \text{specific mass of the chemical element} \text{ and } t = \text{thickness of X-rays penetration}. \) The mass absorption coefficient of the compounds was calculated with the use of equation (2), where \(w = \text{mass fraction} \) :

\[
I = I_0 \cdot \exp(-\mu_t) = I_0 \cdot \exp\left[-\left(\frac{\mu}{\rho}\right)\cdot t\right] \tag{1}
\]

\[
\frac{\mu}{\rho} = w_1\left(\frac{\mu}{\rho}\right)_1 + w_2\left(\frac{\mu}{\rho}\right)_2 + ... \tag{2}
\]

For the SEM experiments a LEO 1450VP SEM and a Philips FEG-SEM were used. The arc-melted spherical samples were prepared following standard metallographic procedures: hot mounting in resin, grinding in the sequence #220 - #1000 (SiC sand paper); polishing with colloidal silica suspension (OP-S, Struers). For the splats and the heat-treated splats, cross-sections were observed. They were mounted in cold resin (Epofix Kit, Struers) and prepared by the same metallographic procedures cited above. None of the samples were etched.

RESULTS

The X-ray diffractogram of the arc-melted (sphere) Ti_{92}B_{8} alloy is shown in Figure 1-a and indicates the presence of \(\alpha\)Ti and TiB. Figure 2-a shows a SEM (BSE) micrograph of this material where a typical eutectic microstructure is observed, constituted of a \(\alpha\)Ti (light regions) matrix and TiB particles (dark regions), based on the XRD data and the average atomic number dependence of the SEM image (BSE mode). The TiB particles seem to present a needle-like shape, with higher dimensions such as \(\sim 30 \mu\text{m} \text{ long by } \sim 2 \mu\text{m} \text{ wide}. \) The lattice parameters of the \(\alpha\)Ti phase (Table 1) are close to the literature values for pure \(\alpha\)Ti, a result which does not indicate a large supersaturation of B in \(\alpha\)Ti after conventional arc melting.
Figure 1 – X-ray diffractograms from the Ti₉₂B₈ alloy: (a) sphere – powder form; (b) splat - bulk; (c) splat heat-treated at 700°C for 120 h - bulk; (d) splat heat-treated at 1000°C for 48 h - bulk.

Table 1 – Unit cell parameters of the αTi phase present in the different materials from Rietveld refinement method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure αTi (Literature [15])</td>
<td>2.9503</td>
<td>4.6810</td>
</tr>
<tr>
<td>Sphere</td>
<td>2.950 ± 0.002</td>
<td>4.681 ± 0.006</td>
</tr>
<tr>
<td>Splat after rapid solidification</td>
<td>2.952 ± 0.004</td>
<td>4.681 ± 0.001</td>
</tr>
<tr>
<td>Splat heat-treated at 700°C for 120 h</td>
<td>2.946 ± 0.001</td>
<td>4.696 ± 0.002</td>
</tr>
<tr>
<td>Splat heat-treated at 1000°C for 48 h</td>
<td>2.937 ± 0.003</td>
<td>4.674 ± 0.006</td>
</tr>
</tbody>
</table>
The thicknesses of the produced splats were in the range of 53 to 69 μm. Figure 1-b shows an X-ray diffractogram of a splat, which indicates the presence of αTi and possibly some βTi orientated in the [110] direction. The result also suggests a slight orientation of the αTi phase in the direction of the c crystallographic axis. The presence of βTi indicates an incomplete βTi → αTi (at 885 °C for pure Ti) transformation due to the high cooling rate achieved in the splat-cooling process. [4, 5,7] Based on our previous observation, the βTi phase should be present only at the regions close to the surface of the splat. In addition, due to possible texture effects and the limited X-rays penetration in the splats, the quantity of the αTi and βTi phases present in the samples cannot be inferred from this diffractogram. The calculated depth of X-rays penetration in the splats for 99% of absorption is almost twice higher than for 90% absorption. According to the calculated values, the scattering of X-rays is just superficial (3 to 10 μm), since the thickness of the splats is ~ 60 μm. The diffractogram in Figure 1-b also shows peaks with the full-width-at-half maximum (FWHM) larger than those in the Figure 1-a, suggesting the presence of finer grains in the microstructure of the splats, as expected. No indication of borides was noted in this diffractogram, suggesting a supersaturation of B in (α/β)Ti. However, the lattice parameter of the αTi phase in the splat (Table 1) does not suggest a significant extension of B solid solubility in the αTi phase due to rapid solidification. Figure 2-b shows a SEM (BSE) micrograph from the cross-section of
one splat where the lack of contrast suggests either a very fine boride precipitation or a single-phase microstructure, the latter indicating the formation of a supersaturated solid solution of B in $\alpha$Ti. In order to evaluate this aspect, SEM-FEG (BSE) analyses were carried out and showed a chemical composition contrast as indicated in Figure 3, where the lighter regions are associated to $\alpha$Ti of dimensions smaller than 100 nm. The dark regions in the same figure are associated to a B-rich phase (Ti-poor), however, the nature of this phase could not be determined so far. This type of microstructure was found in the whole cross-section of the splats. Nevertheless, these results indicates that an important quantity of B is not dissolved in the $\alpha$Ti phase and it agrees with the results from the refinement of the $\alpha$Ti lattice parameters which did not suggest a significant extension of B solubility in $\alpha$Ti, and in this way disagrees with the data from the literature.$^{[8,11,12]}$

Figure 3 – Cross-section of the Ti$_{92}$B$_8$ alloy after rapid solidification. Image from SEM-FEG (BSE).

Figure 1-c shows the X-ray diffractogram of a splat heat-treated at 700°C for 120 h. In all splats heat-treated in this condition only the phases $\alpha$Ti and TiB were identified. The peaks of TiB present low values of intensity and there are no reflections of $\beta$Ti, indicating the occurrence of the allotropic transformation $\beta$Ti $\rightarrow$ $\alpha$Ti during the heat treatment. Comparing the diffractogram of Figure 1-c with the simulated powder diffractogram of the $\alpha$Ti phase, it could be observed in the splat a slight orientation in the direction of the c crystallographic axis. The Rietveld refinement of the $\alpha$Ti phase indicated a small change in the a and c parameters associated to the B presence in the $\alpha$Ti lattice. The Figure 2-c shows a SEM (BSE) micrograph from the cross-section of this splat, the lighter region corresponds to $\alpha$Ti and the dark regions to TiB, with dimensions of $\sim$ 1 or 2 $\mu$m. It can be observed a higher amount of TiB in the central part of the splat’s cross-section, which leads to a finer grain size of the $\alpha$Ti phase in this region due to grain boundary pinning effects.

Figure 1-d shows the diffractogram of a splat heat-treated at 1000°C for 48 h. As in the previous case, in all splats heat-treated in this condition only the $\alpha$Ti and TiB phases were observed. Again, the TiB peaks appear with low intensity. The peaks belonging to $\alpha$Ti phase in this diffractogram are narrower (FWHM) than those in the diffractogram of the sphere (Figure 1-a) as well as those in the diffractogram of the splat (Figure 1-b), indicating the presence of larger $\alpha$Ti grains in the heat-treated splat. No reflections of the $\beta$Ti are observed, however, according to the Ti-B phase diagram$^{[2]}$ during heat-treatment at 1000°C a $\beta$Ti+TiB microstructure should be present in the whole sample. After removal of the sample from the furnace, followed
by air cooling, the $\beta$Ti phase should have transformed to $\alpha$Ti. No significant preferential orientation is observed concerning to the $\alpha$Ti peaks in the diffractogram of Figure 1-d. Also in this case, the lattice parameters of the $\alpha$Ti phase (Table 1) are slightly different from those of the pure $\alpha$Ti phase. Figure 2-d shows a SEM (BSE) micrograph of this splat’s cross section. A two-phase microstructure is observed where the dark regions are associated to TiB, confirmed by WDS analyzes (at.% Ti = 52 ± 2 and at.% B = 48 ± 2), and the light regions to $\alpha$Ti. The TiB particles present much larger dimensions than in the previous case, which is clearly associated to the higher temperature and longer time of this heat treatment. The trend for TiB to grow in needle-shape is clearly seen. Moreover, these results from heat-treated (700°C, 1000°C) Ti$_{92}$B$_8$ alloy confirms the stability of the Ti$(\alpha/\beta)$ + TiB two-phase region in the Ti-rich region of the Ti-B system in the 700°C-1000°C temperature range.

Table 2 shows microhardness values from the sphere, splats and heat-treated splats. The highest hardness value of the splat is likely due to its very fine-grained microstructure compared to the others.

Table 2 – Vickers microhardness values of different materials produced in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vickers microhardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>255 ± 12</td>
</tr>
<tr>
<td>Splat after rapid solidification</td>
<td>443 ± 79</td>
</tr>
<tr>
<td>Splat heat-treated at 700°C for 120 h</td>
<td>373 ± 11</td>
</tr>
<tr>
<td>Splat heat-treated at 1000°C for 48 h</td>
<td>392 ± 28</td>
</tr>
</tbody>
</table>

SUMMARY

The results of rapid solidification of the Ti$_{92}$B$_8$ eutectic alloy appointed to a fine and crystalline microstructure. It was not observed the formation of amorphous materials in any of the produced splats. The XRD data of the rapidly solidified splats shows essentially the presence of $\alpha$Ti, and possibly some $\beta$Ti in the microstructures. It was not observed an important extension of the B solubility in $\alpha$Ti. SEM-FEG (BSE) images of the rapidly solidified splats showed microsegregation of a B-rich phase around the $\alpha$Ti grains. A two-phase microstructures formed by the $\alpha$Ti and TiB phases were formed after heat-treatment of the rapidly solidified splats, confirming the stability of these phases in the 700°C to 1000°C temperature range of the Ti-B system.

Acknowledgments

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REFERENCES