

As-cast structure refinement of Ti-46Al alloy by hafnium and boron additions

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Abstract: The influence of Hf and B on the solidification structure of cast Ti-46Al alloys was investigated. The results show that the coupling effect of Hf and B changes the solidification structure morphology and strongly refines the grain size. When the Hf+B contents were increased from 0 + 0.0 to 3 + 0.2, 5 + 0.6 and 7 + 1.0 (in at. %), the solidification structure morphology changed from coarse columnar dendrite to fine columnar dendrite, then to equiaxed dendrite, and further to fine near granular grain whilst the average grain size decreased to 20 μm . It is concluded that the columnar dendrite refinement is due to the effect of Hf and B on the decrease of Al diffusion coefficient in the melt. The fine near granular grain formation is attributed to the combined constitutional supercooling formed by Al and B segregation that is strengthened by Hf and B additions at the solid/liquid interface during solidification, and the TiB_2 precipitates acting as heterogeneous nuclei.

Key words: Hf; B; Ti-46Al alloy; microstructure; diffusion coefficient; heterogeneous nuclei

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A great deal of research work on TiAl-based alloys has been performed over the past four decades and several different alloys and processing techniques have been developed^[1, 2]. Although thermo-mechanical process and heat treatment can improve the microstructure and properties, near-net-shape process, such as casting, often tends to be chosen for component production in order to utilize a minimum material cost and also to address the limited ductility of TiAl alloys. Therefore, cast TiAl-based alloys have been intensively studied over several decades^[3]. The addition of a strong beta-stabilizer and boron into TiAl-based alloys are more often used as effective methods in refining the coarse structure formed during solidification. Improved hot workability, room temperature tensile strength and ductility of the alloys have thus far been achieved in this way. For example, Cheng^[4] studied the association of transition metals (Nb, Zr, and Ta) with Ti-44Al alloy. Lapin^[5] studied the creep behavior of cast Ti-45.2Al-2W-0.6Si-0.7B alloy. Hu^[6, 7] reported studies on cast Ti-48Al-2Cr-2Nb-1B and Ti-44Al-4Nb-4Hf-0.1Si-1B alloys. Johnson and co-workers^[8] reported research on the microstructure control of Ti-Al-Mo-B alloys. However, no paper was found in the literature concerning the study on Ti-Al-Hf-B alloys until now. Therefore, the aim of this work is to investigate the coupling effect of Hf and B additions on the solidification structure of cast Ti-46Al alloy. The solidification structure is discussed and the resulting coupling effect of Hf

and B additions is related to the mechanisms of columnar dendrite refinement and fine near granular grain formation.

1 Experimental procedure

The experimental alloys are Ti-46Al, Ti-46Al-3Hf-0.2B, Ti-46Al-5Hf-0.6B and Ti-46Al-7Hf-1.0B (in at. %). B was added in the form of Al-5Ti-B (wt. %). The alloys were produced as small buttons (25g) by arc-melting in an argon atmosphere. The buttons were re-melted at least three times to ensure homogeneity of composition and were vertically cut along their axis of symmetry by electrical discharge machining (EDM). In all samples a region in the lower part close to the axis of symmetry was studied. Microstructural analyses were performed using optical microscopy (OM), scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectrometry.

2 Results

2.1 As-cast macrostructure

Figure 1 shows the as-cast structures of the experimental alloys. It is clearly seen from Fig. 1 (a) and (b) that the solidification structure morphologies of Ti-46Al and Ti-46Al-3Hf-0.2B are typical columnar dendrites. On increasing the Hf+B addition from 0 + 0.0 to 3 + 0.2, the average columnar dendrite spacing decreases from 1,000 μm to 500 μm . A further increase of Hf+B content produces equiaxed dendrites, as shown in Fig. 1 (c). Figure 1 (d) shows that this equiaxed dendrite is further developed to fine near granular grain (hereafter called FNGG) with average grain size of 20 μm . The whole section of the sample is composed of the FNGG.

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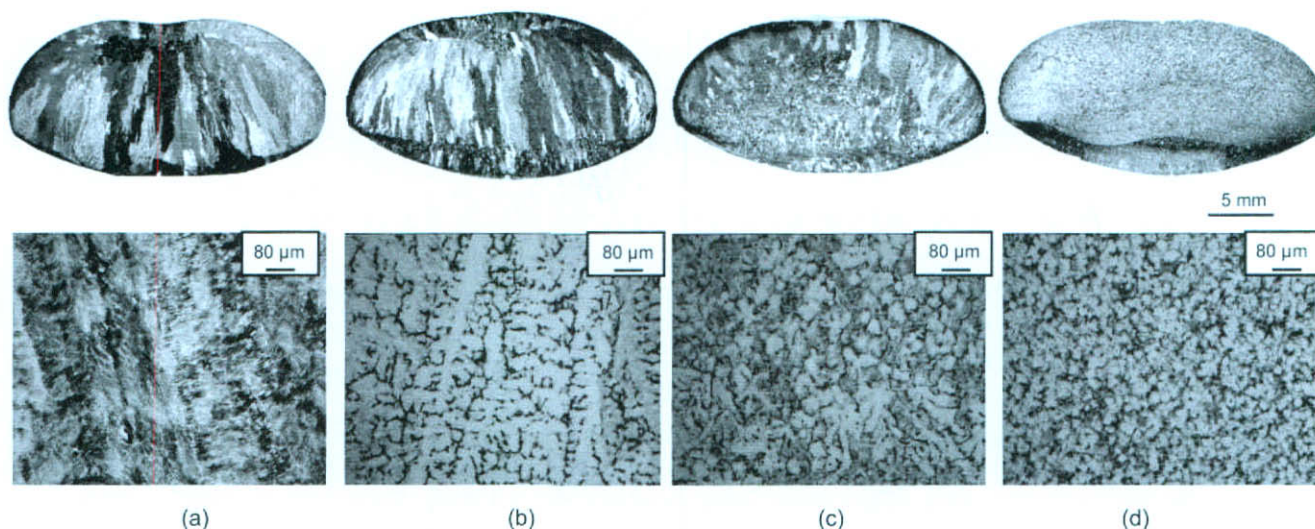


Fig. 1 Image showing the solidification structure morphologies of Ti-46Al (a), Ti-46Al-3Hf-0.2B (b), Ti-46Al-5Hf-0.6B (c), and Ti-46Al-7Hf-1.0B (d)

2.2 As-cast microstructure

Figure 2 is the representative microstructures of the selected alloys. The microstructure of Ti-46Al alloy, as shown in Fig. 2 (a), is coarse near lamellar, mainly consisting of α_2/γ

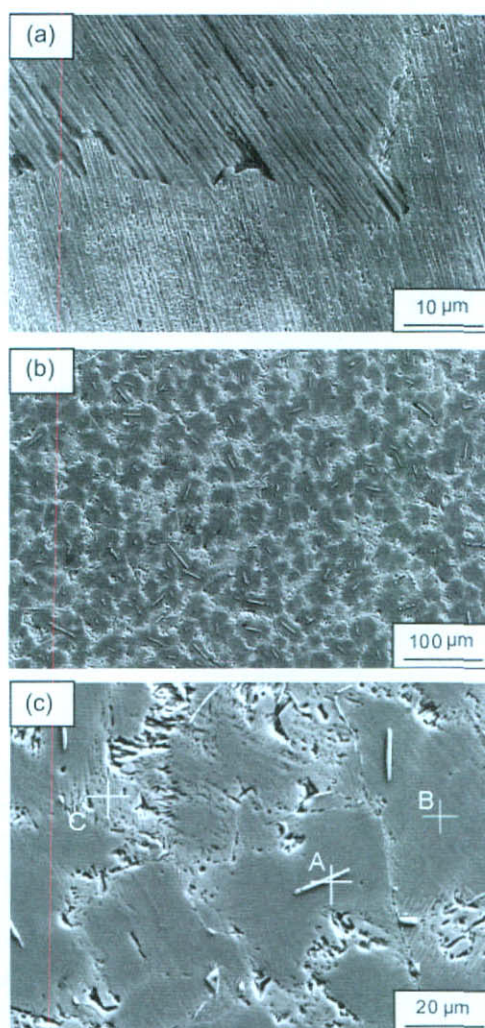


Fig. 2 Microstructure of Ti-46Al (a), Ti-46Al-7Hf-1.0B (b) and (c)

and a small amount of dark blocky γ on the lamellar colony boundaries. It is worth noting here that the microstructure of Ti-46Al-7Hf-1B alloy, as shown in Fig. 2 (b) and (c), is also near lamellar, but has fine near granular morphology and there are many randomly oriented borides in it. However, Fig. 2 (c), the close-up view, shows that there exist coarse structures at the triple junction of FNGGs. Some shrinking cavities are seen in this region.

According to the projected view of Ti-Al-B liquidus surface determined by Hyman et al.^[9], as shown in Fig. 3, the borides in Ti-46Al-7Hf-1.0B alloy are TiB_2 , rather than TiB or Ti_3B_4 . Most of TiB_2 distribute inside the FNGGs with long or short needle-like shapes. A small amount of TiB_2 with ribbon-like shape exists at the boundaries of the FNGGs, and some blocky γ also appeared there.

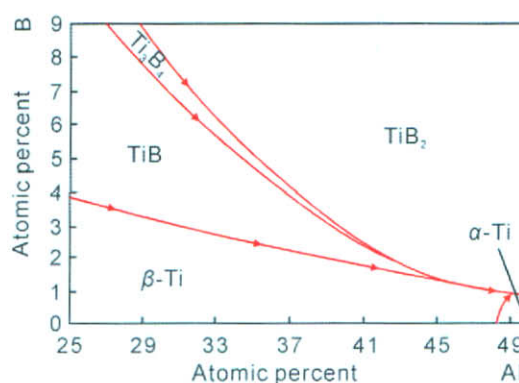


Fig. 3 Projected view of the Ti-Al-B liquidus surface

SEM-EDS analyses were conducted on TiB_2 , FNGG and coarse structure as indicated in Fig. 2 (c) by marks A, B and C, respectively. The results, compared with the nominal composition of the alloy, show that TiB_2 is richer in Ti, leaner in Al and equal in Hf; the FNGG is richer in Ti (49.24 at. %) and leaner in Al (44.08 at. %) and Hf; the coarse structure is richer in Al (50.58 at. %) and Hf and leaner in Ti (31.72 at. %).

3 Discussions

As shown above in section 2, the solidification structure of Ti-46Al alloy changes from coarse columnar dendrite to fine columnar dendrite, then to equiaxed dendrite, and further to FNGG due to the addition of Hf and B into the Ti-46Al alloy. Compared with the results of our previous study^[10], it is clearly known that the coupling effect of Hf and B can change the solidification structure morphology and refine the grain size strongly. The FNGG appear only under the coupling effect of Hf and B. The mechanisms of columnar dendrite refinement and FNGG formation are discussed below.

3.1 Columnar dendrite refinement

For columnar dendrite spacing, Kurz et al.^[11] have given an equation as:

$$\lambda = 4\pi \left(\frac{D\Gamma}{V\Delta T_0} \right)^{1/2} \quad (1)$$

Where D is the diffusion coefficient of solute in melt, Γ is the Gibbs-Thomson coefficient, V is the tip velocity and ΔT_0 is the liquidus-solidus temperature interval. The current work is confined just to a discussion of the effect of Hf and B on the factor D in order to explain the columnar dendrite refinement mechanism.

In our previous study^[10], it has been shown that one reason for Hf refining columnar spacing in cast Ti-46Al alloy is that the addition of Hf into Ti-46Al alloy increases the melt viscosity, due to the inverse relation between viscosity and diffusion coefficient, leading to a decrease of Al diffusion coefficient in the melt. Consequently, the columnar dendrite spacing is refined as indicated in equation (1).

On the other hand, the effect of B on Al diffusion coefficient in Ti-46Al melt can be discussed qualitatively using Arrhenius equation. Taking into account both the effects of atom diameter and activation energy, the Arrhenius equation is given by:^[12]

$$D_{ab}^j = D_0^j (d_b/d_a) \exp(-Q_0^j/RT) \quad (2)$$

Where D_{ab}^j is diffusion coefficient of solute a in melt b ; D_0^j is the frequency factor of melt b ; and d_b and d_a are the atomic diameters of b and a ; Q_0^j is the activation energy of solvent b on diffusion of solute a , R is gas constant, and T is temperature in Kelvin. When B is added to Ti-46Al alloy, some micro-regions richer in B will form in the melt, and this makes it possible for solute Al to diffuse through these regions. In this case, as indicated in equation (2), the diffusion coefficient of solute Al in these regions will decrease compared with B-free melt due to the much smaller atomic diameter of B than the atomic diameter of Ti. Hence, it can be deduced that the presence of B decreases the Al diffusion coefficient in Ti-46Al melt, thereby assisting the process of columnar dendrite refinement mechanism.

3.2 FNGG formation

It is well established that the precondition for FNGG formation is when the maximum constitutional supercooling is stronger

than the minimum heterogeneous nucleation supercooling in melt. Important studies conducted by Chalmers and co-workers^[13] have shown that the constitutional supercooling occurs when:

$$G_L/v < \frac{m_L C_0}{D_L} \cdot \frac{1-k_0}{k_0} \quad (3)$$

Where G_L is the temperature gradient, v is the rate of solidification, m_L is the slope of the liquid line, C_0 is the overall solute concentration, D_L is diffusion coefficient of solute in melt, and k_0 is the solute distribution coefficient. As mentioned above, both Hf and B can decrease the Al diffusion coefficient in the melt. According to equation (3), the constitutional supercooling caused by Al segregation at the solid/liquid interface during solidification becomes stronger with the increase of Hf and B content. In addition, there also exists an additional constitutional supercooling caused by B segregation since the solid solubility limit of B in β phase is very small^[4,7]. Consequently, the combined constitutional supercooling in Ti-46Al-7Hf-1B melt is stronger apparently, compared with that of B-free alloys. In the meantime, as shown in Fig. 3, TiB₂ will precipitate firstly from the melt during solidification when B > 1.0 at. %. The prior TiB₂ can act as heterogeneous nuclei as indicated by most TiB₂ needle-shape orientation coexisting parallel to the lamellar orientation shown in Fig. 2 (c), therefore reducing the degree of β nucleation supercooling. Hence, addition of 7Hf and 1B into Ti-46Al alloy is found to promote the increase of constitutional supercooling and demote the heterogeneous nucleation supercooling. Also, the presence of large amount of TiB₂ in the melt increases the nucleation rate of β precipitates and the strong constitutional supercooling impact on the growth of β grain. As a result, FNGG is achieved in cast Ti-46Al-7Hf-1B alloy. This assertion is consistent with the experimental results shown in Figs. 2(b) and (c) and the EDS analyses.

4 Conclusions

- (1) Addition of 7Hf and 1B into cast Ti-46Al alloy results in the formation of FNGG. The average grain size of the FNGG is 20 μm .
- (2) Formation of the FNGG is attributed to the strong combined constitutional supercooling formed by Al and B segregation that is strengthened by Hf and B additions at the solid/liquid interface during solidification, and the prior TiB₂ precipitates acting as heterogeneous nuclei.

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