Effects of β -Dendrite Growth Velocity on $\beta \rightarrow \alpha$ Transformation of Hypoperitectic Ti–46Al–7Nb Alloy

Tan He · Rui Hu · Jun Wang · Jie-Ren Yang · Jin-Shan Li

Received: 21 January 2014/Revised: 3 June 2014/Published online: 21 November 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract Solidification characteristics of Ti–46Al–7Nb melts were studied by the electromagnetic levitation technique. A maximum melt undercooling up to 240 K has been achieved. When the undercooling is lower than the critical value $\Delta T^* = 205$ K, the alloy possesses typical hypoperitectic solidification characteristic which can be evidenced by a peritectic layer observed in the as-solidified microstructure. However, the Widmanstätten structure can be observed at large undercooling regime of $\Delta T \geq \Delta T^*$, where peritectic reaction cannot proceed and γ lamellar precipitation within α plates is suppressed. Based on the BCT dendrite growth model, the dendrite growth velocities were calculated as a function of undercooling. Theoretical analysis indicates that the growth mechanism of the primary β phase transforms from solutal-diffusion-controlled to thermal-diffusion-controlled in the undercooling range of 188–205 K, which can be attributed to the onset of solute trapping at the critical undercooling. Meanwhile, with increasing undercooling, the solute trapping effect becomes more dominant as a consequence.

KEY WORDS: TiAl alloy; Dendrite growth; Undercooling; Microstructure

1 Introduction

The high-Nb-containing hypoperitectic TiAl alloys have been paid significant attention recently due to their good oxidation resistance and good specific strength and modulus, especially at elevated temperature [1–3]. However, high Nb addition leads to the signification microsegregation which could greatly affect the mechanical properties of the alloys. The properties of as-cast materials are dependent on the solidification process. According to the hypoperitectic solidification characteristics, there is no residual liquid phase after the peritectic reaction occurs, leading to much more shrinkage porosities and cavities in the

solidified structure [4]. The above mentioned reason may cause the increase of embrittlement of cast alloy. Thus, it is of great importance to investigate the solidification behaviors of TiAl alloys.

Dendrite growth plays an important role in solidification behavior, which has a strong influence on the ultimate microstructure. The non-equilibrium solidification conditions governing the solidification of undercooled liquids lead to the dendritic growth [5]. Investigations on dendritic growth under rapid solidification condition contribute to relationship between the growth condition and the dendrite morphology [6–11]. Measurements of the growth velocity during solidification allow to identify the critical undercoolings for solute trapping [12, 13], disorder trapping [14], and microstructural transitions of coarse-grained dendritic to refined equiaxed grain [15, 16]. The rise of dendrite growth rate results in the transition to diffusionless solidification, and thus leads to the occurrence of the subsequent solidification path transformation. However, limited information on this topic was reported.

Available online at <http://link.springer.com/journal/40195>

T. He · R. Hu (✉) · J. Wang · J.-R. Yang · J.-S. Li
State Key Laboratory of Solidification Processing, Northwestern
Polytechnical University, Xi'an 710072, China
e-mail: rhu@nwpu.edu.cn

In the present paper, the non-equilibrium solidification behavior of the Ti–46Al–7Nb melts was investigated by the electromagnetic levitation (EML) technique. Since liquid γ -TiAl-based alloys are highly reactive with the majority of crucible materials, the EML containerless technique is very suitable for the investigation of rapid dendritic growth [17]. The purpose of this work is to investigate the influence of growth velocity of primary β dendrite on $\beta \rightarrow \alpha$ phase transformation in Ti–46Al–7Nb alloys and to reveal the mechanism of microstructure evolution.

2 Experimental

Ternary master alloy with a nominal composition of Ti–46Al–7Nb (at%) were prepared by arc-melting under a Ti-gettered argon atmosphere. About 150 g alloy was re-melted for five times, and then was homogenized in a vacuum furnace at 1,273 K for 80 h in order to ensure the compositional homogenization. The as-cast ingot was cut into ~ 1.2 g segments for the undercooling experiment.

The undercooling experiments were performed in an EML facility. The vacuum chamber of the EML facility was evacuated to 10^{-4} Pa and then filled with high-purity Ar gas. The sample was melted by induction heating and further overheated to about 100 K above its liquidus. After keeping for about 1 min, the sample was cooled by a gas stream of He. The temperature–time curves during melting and cooling process were recorded by a two-color pyrometer with a precision of 5 K and a response time of 10 ms. The recalescence behavior was studied after spontaneous nucleation or triggering with a substrate at various undercooling levels. Melt drops of well-defined undercooling level were quenched onto the substrate.

The specimens were cut, mechanically polished, and etched using Kroll's reagent for metallurgical observation. X-ray diffraction (XRD, DX-2700) with $\text{CuK}\alpha$ as a radiation was performed to identify their phase constitution. The microstructures were characterized by scanning electron microscopy (SEM, JSM-6460LV) under back-scattered electron imaging mode, and energy dispersive spectrum (EDS) was used to identify local phase compositions.

3 Results and Discussion

Figure 1 shows the calculated section of the TiAl–7.5Nb phase diagram [18], which can approximately depict the phase composition of Ti–46Al–7Nb alloy. It can be seen that the solidification path of the Ti–46Al–7Nb alloy locates in the hypoperitectic area. Before the solid-state

Fig. 1 Section of the phase diagram of TiAl–7.5Nb calculated with ThermoCalc and MatCalc [18]

phase transformations occur, the equilibrium solidification microstructure consists of a residual primary β phase and peritectic phase α , which shows typical characteristics of the peritectic reaction. After solidification, the growth of fine γ plates from α phase occurs. Therefore, the final microstructure of α_2/γ lamellar is observed. Differing from the equilibrium solidification microstructure, the evolution of solidification microstructure under non-equilibrium conditions shows some interesting morphology as undercooling increases. This analysis will be described in the following section.

3.1 Microstructural Characteristics

Temperature–time characteristics of primary recalescence events of undercooled Ti–46Al–7Nb alloys are shown in Fig. 2. The maximum undercooling of 240 K for Ti–46Al–

Fig. 2 Temperature-time characteristics of primary recalescence events of undercooled Ti–46Al–7Nb alloys with different undercoolings

Fig. 3 SEM back-scattered electron images showing the microstructures of Ti-46Al-7Nb alloy with different undercoolings (arrows indicate the zones for solute concentration measurements): **a** $\Delta T = 10$ K; **b** $\Delta T = 54$ K; **c** $\Delta T = 94$ K; **d** $\Delta T = 188$ K; **e** $\Delta T = 205$ K; **f** $\Delta T = 226$ K; **g** $\Delta T = 240$ K

7Nb alloy can be achieved. Figure 3 shows the microstructure of Ti-46Al-7Nb alloys with different undercoolings examined by SEM. When the undercooling is equal to 10 K, the primary dendrite is β phase. After that, the peritectic reaction of α phase occurs at dendrite edges of primary β phase. As the reaction proceeds, α phase would separate β phase from the liquid phase gradually. The peritectic α phase envelopes the primary β phase firstly by nucleation and then the dissolution of primary β and growth of peritectic α happen near the triple-junctions. Once the peritectic reaction is complete, the peritectic α phase can be thickened by the direct precipitation from the liquid and from β phase during the peritectic transformation. Then the $\alpha \rightarrow \gamma$ transformation is seen in the interdendritic regions. EDS analysis shown in Fig. 7 exhibited that Al content rise to about 53.5 at%. This transformation, which has been reported by Jung *et al.* [19], also is observed in Ti-46Al alloy. Subsequently, the γ lamellae are precipitated from the α phase. Both dendrite core and dendrite edge transform into a lamellar structure, consisting of alternating α_2 and γ plates. The formation of lamellar colonies has a negligible influence on the as-solidified morphologies, as shown in Fig. 3a. For the sample with an undercooling of 54 K, the overall cross-section is occupied by equiaxed dendrites and presented higher branches which are different from the aforementioned coarse dendrites, as shown in Fig. 3b. At a medium undercooling, i.e., $\Delta T = 94$ K, coarse and well-developed dendrite can be found as shown in Fig. 3c. Once the undercooling exceeds approximately 188 K (Fig. 3d), the developed directional fine dendrites can be observed by dendrite morphology in shrinkage cavities due to the key role of thermal undercooling. In other words, the β dendritic began to transform from solute-diffusion-controlled growth to thermal-

diffusion-controlled growth. Well-developed directional fine dendrite can be obtained because the severe solute trapping weakens the effect of solute diffusion during the dendrite growth. As the undercooling $\Delta T < 205$ K, it showed peritectic solidification characteristics, which can be confirmed from Al-rich segregations resulted from the peritectic solidification reaction [20, 21]. For $\Delta T \geq 205$ K, the solute trapping effect becomes more significant, and the peritectic reaction is suppressed. A sole solidification of β phase is formed and equiaxed β grain is obtained. It has been also found that the microstructure for the Ti-46Al-5Mo button, as shown in Fig. 4a and b, was essentially equiaxed and solidified as the β phase [21]. The final microstructure is developed during the subsequent solid-state transformations, and α phase plates with orientations according to the Burgers relationship are precipitated from the β phase. Subsequently, γ lamellar precipitated within the α phase plates has been suppressed, and the microstructure is characterized by Widmanstätten structure similar to near α or ($\alpha + \beta$) Ti alloys. The β phase always forms as the primary phase at $\Delta T \geq 205$ K, because the β /liquid interfacial energy is less than the α /liquid interfacial energy [22]. Anderson *et al.* [23] also found that the primary solidification phase is β phase in all TiAl alloys containing less than 49.6 at% Al in TiAl alloy, regardless of bulk undercooling. With the increase of undercooling, the peritectic reaction is found to be suppressed. A remarkable morphological transition from typical hypoperitectic solidification to a sole solidification of the β phase occurs, which is also coincident with previous work on the undercooled Fe-Ni alloy reported by Chen *et al.* [24].

In order to identify the phase constitution, XRD spectra taken from the samples solidified at different undercoolings

Fig. 4 XRD patterns of samples solidified under different undercoolings

are shown in Fig. 4. Samples corresponding to low undercoolings exhibit α_2 and γ phases. The diffraction intensity of the $\gamma(111)/\alpha_2(002)$ peaks dramatically increases in the sample solidified at a undercooling of 188 K. It can be also found that the relative content of α_2 and γ phase does not significantly change from the microstructures. Thus, the strongest diffraction peak on the XRD spectra is ascribed to preferred orientation growth of dendrite. That partly explains the directional fine dendrites formed at $\Delta T = 188$ K. However, samples solidified at undercoolings above 205 K contain predominantly α_2 phase. The content of B2 phases cannot be detected by the XRD analysis.

3.2 Dendrite Growth of Primary β Phase

Rapid growth of β dendrite is the dominating solidification behavior during rapid solidification of Ti–46Al–7Nb alloy. Experimental results showed that the primary β dendrites evolve from re-melted dendrite to equiaxed grain with the increasing of the undercooling. To explore the kinetic mechanism of rapid growth of β dendritic, the developed Boettinger–Coriell–Trivedi (BCT) model [25] has been proven to be the most successful model for undercooled dendrite growth. In the current work, BCT model was applied to calculate the growth velocity of β phase. According to the BCT model, undercooling ΔT can be expressed as follows:

$$\begin{aligned} \Delta T &= \Delta T_t + \Delta T_c + \Delta T_r + \Delta T_k \\ &= \frac{\Delta H_f}{C_p} I_v(P_t) + mC_0 \left[1 - \frac{m'/m}{1 - (1-k)I_v(P_c)} \right] + \frac{2\Gamma}{R} + \frac{V}{\mu}, \end{aligned} \quad (1)$$

$$k = \frac{k_0 + a_0 V/D}{1 + a_0 V/D}, \quad (2)$$

$$m' = m \left[1 + \frac{k_0 - k[1 - \ln(k/k_0)]}{1 - k_0} \right], \quad (3)$$

$$\mu = \frac{\Delta H_f V_0}{R_g T_L^2}, \quad (4)$$

$$R = \frac{\sigma / (\Delta S \sigma^*)}{\frac{P_t \Delta H_f}{C_p} \xi_t + \frac{2m' P_c C_0 (k-1)}{1 - (1-k)I_v(P_c)} \xi_c}, \quad (5)$$

$$\xi_c = 1 + \frac{2k}{1 - 2k - \sqrt{1 + \frac{1}{\sigma^* P_c^2}}}, \quad (6)$$

$$\xi_t = 1 - \frac{1}{\sqrt{1 + \frac{1}{\sigma^* P_t^2}}}, \quad (7)$$

where ΔT_t is the thermal undercooling; ΔT_c is the solutal undercooling; ΔT_r is the curvature undercooling; ΔT_k is the kinetic undercooling; Γ is the Gibbs–Thomson coefficient; $P_t = VR/2\alpha_1$ is the thermal Peclet number; α_1 is the thermal diffusivity in liquid; $P_c = VR/2D$ is the solute Peclet number; $I_v(P_c) = P_c \exp(P_c) E_1(P_c)$ is the Ivantsov function of solute Peclet number; m' is the actual liquidus slope under non-equilibrium conditions; m is the slope of the liquidus line; k is the actual solute partition coefficient; k_0 is the equilibrium solute partition coefficient; μ is the actual kinetic coefficient; R is the radius at the dendrite tip; σ is the interface energy; ΔS is the entropy of fusion; $\sigma^* = 1/(4\pi)^2$, σ^* is a stability constant; ΔH_f is the heat of fusion; C_p is the specific heat of the undercooled melt, V_0 is the velocity of sound in the liquid, and R_g is the gas constant; T_L is the liquidus temperature of the alloy; ξ_c is the solute stability function; ξ_t is the thermal stability function; D is the atomic diffusive coefficient; a_0 is the atomic distance; C_0 is the alloy composition.

According to Kim et al. [26], 1 at% of Nb addition to Ti–Al binary alloy is known to shift the phase boundaries to the Al-rich side by 0.3%. The alloy composition of Ti–46Al–7Nb approximately corresponds to the binary Ti–48Al alloy. In the present model, the melting temperature of Ti–46Al–7Nb alloy is 1,868 K, which was obtained by experiments. The latent heat of fusion in Ti–Al–Nb alloy is from Ref. [27]; the specific heat capacity and thermal diffusivity of liquid Ti–Al–Nb ternary alloy are from Ref. [28]; the diffusion coefficient and thermal-diffusion coefficient in Ti–Al alloy are from Ref. [29]; the equilibrium partition coefficient and slope of liquidus line of Ti–Al–Nb alloy are from Ref. [30]; the Sound speed is fitting parameter, which is 3,000 m/s in the paper; the Gibbs–Thomson coefficient is from Ref. [31]. The parameters for the calculation of dendrite growth in Ti–46Al–7Nb alloy are summarized in Table 1.

Table 1 Parameters of Ti–46Al–7Nb alloy used for calculations

Parameter	Value and unit	Ref.
Liquid temperature, T_m	1,868 K	Exp.
Latent heat of fusion, ΔH_f	14.23 kJ/mol	[27]
Specific heat capacity, C_p	32.72 J/(mol K)	[28]
Diffusion coefficient, D_l	3.5×10^{-9} (m ² /s)	[29]
Equilibrium partition coefficient, k_0	0.63	[30]
Thermal-diffusion coefficient, α	0.71	[29]
Speed of sound, V_0	3,000 (m/s)	Constant
Slope of the liquidus line, m	−9.14 (K/at%)	[30]
Interfacial energy, σ	0.216 (J/m ²)	[31]
Thermal diffusivity in liquid, α_l	4.9×10^{-6} (m ² /s)	[28]

Fig. 5 Partial undercoolings versus bulk undercooling of Ti–46Al–7Nb alloy

Figure 5 illustrates the variations of four partial undercoolings to the total bulk undercooling. Figure 6 shows the relationship between growth velocities of the dendrites of β phase versus the undercooling. This microstructure transition is more evidently reflected in Fig. 5. Apparently the solute undercooling ΔT_c plays an important role if bulk undercooling $\Delta T \leq 188$ K, and the β dendrite velocities rise slowly, as shown in Fig. 6. As undercooling increases in the range 188–205 K, the contribution of the solute undercooling decreases and thermal diffusion happens gradually. Thus, a transition from solute diffusion to thermal diffusion-controlled growth happens. In other words, dendritic growth is controlled by mixed mechanism of thermal diffusion and solute diffusion [32]. Once undercooling exceeds approximately 205 K, the dendrite growth velocity ascends sharply with undercooling, which is attributed to

Fig. 6 Calculated growth velocities of β dendrite versus the undercooling **Fig. 7** Solute concentrations in the interdendritic zone of Ti–46Al–7Nb alloys versus undercooling

the kinetic feature of thermal-diffusion-controlled growth. The regime is defined by a critical undercooling ΔT^* and a solidification velocity V_D , as shown in Fig. 6. The complete solute trapping occurs. The transition point can explain that the microstructure transforms from typical hypoperitectic solidification characteristic to a sole solidification of the β phase. The critical undercooling between the experimental and calculated result is somewhat deviation. Because the approximate value of physical parameters can result in higher value of the calculated one. At the largest undercooling, $\Delta T = 240$ K, the refined equiaxed grain is observed. Obviously, the experimental data are in well agreement with the calculated results. The curvature undercooling and kinetic undercooling are less important under the present experimental conditions.

To analyze the solute trapping effect in the rapid dendritic growth process, EDS is applied to investigate the solute redistribution in the interdendritic liquid. Figure 7 shows the relationship between the solute concentrations at the interdendritic zone and undercooling. The solute trapping effect becomes more significant, and almost segregationless solidification is achieved at high undercooling.

4 Conclusion

The high undercooling and rapid solidification of Ti–46Al–7Nb ternary alloy were achieved by EML containerless process. The relationship between the dendritic growth velocity of primary phase and undercooling was determined by the sharp interface model of local non-equilibrium solidification. The β dendritic transforms from solutal-diffusion-controlled growth to thermal-diffusion-controlled growth as the undercooling varies in the region of 188–205 K. However, as the undercooling exceeds 205 K, the complete solute trapping occurs and the hypoperitectic solidification characteristic of Ti–46Al–7Nb alloy disappears. The microstructure of investigated Ti–46Al–7Nb alloy confirms the tendency of reduced microsegregation with increasing undercooling.

Acknowledgments This work was financially supported by the National Basic Research Program of China (No. 2011CB610404) and the “111 Project” of Northwestern Polytechnical University (No. B08040).

References

- [1] J.P. Lin, L.L. Zhao, G.Y. Li, L.Q. Zhang, X.P. Song, F. Ye, G.L. Chen, *Intermetallics* **19**, 131 (2011)
- [2] W.J. Zhang, G.L. Chen, F. Apple, T.G. Nieh, S.C. Deevi, *Mater. Sci. Eng.* **315**, 250 (2001)
- [3] X.J. Xu, J.P. Lin, Z.K. Teng, Y.L. Wang, G.L. Chen, *Mater. Lett.* **61**, 369 (2007)
- [4] L. Huang, P.K. Liaw, C.T. Liu, Y. Liu, J.S. Huang, *Trans. Nonferrous Met. Soc. China* **21**, 2192 (2011)
- [5] D.M. Herlach, *Mater. Sci. Eng. R* **12**, 177 (1994)
- [6] P.R. Algosio, W.H. Hofmeister, R.J. Bayuzick, *Acta Mater.* **51**, 4307 (2003)
- [7] W.L. Wang, Y.J. Lu, H.Y. Qin, B. Wei, *Sci. China G.* **52**, 720 (2009)
- [8] H.P. Wang, W.J. Yao, B. Wei, *Appl. Phys. Lett.* **89**, 201905 (2006)
- [9] W.J. Yao, B. Wei, *Sci. China E* **46**, 549 (2003)
- [10] W.J. Yao, X.L. Niu, L. Zhou, N. Wang, J. Lee, *Acta Metall. Sin. (Engl. Lett.)* **26**, 523 (2013)
- [11] H. Hartmann, P.K. Galenko, D. Holland-Moritz, M. Kolbe, D.M. Herlach, *J. Appl. Phys.* **103**, 073509 (2008)
- [12] J. Chang, H.P. Wang, K. Zhou, B. Wei, *J. Appl. Phys. A* **109**, 139 (2012)
- [13] Y. Ruan, F.P. Dai, *Intermetallics* **25**, 80 (2012)
- [14] M. Barth, B. Wei, D.M. Herlach, *Phys. Rev. B* **51**, 3422 (1995)
- [15] M. Schwarz, A. Karma, K. Eckler, D.M. Herlach, *Phys. Rev. Lett.* **73**, 1380 (1994)
- [16] W.L. Wang, H.Y. Qin, Z.C. Xia, B. Wei, *Chin. Sci. Bull.* **57**, 1073 (2012)
- [17] F.H. Froes, C. Suryanarayana, D. Elizer, *J. Mater. Sci.* **27**, 5113 (1992)
- [18] H.F. Chladil, H. Clemens, H. Leitner, *Adv. Eng. Mater.* **12**, 1131 (2005)
- [19] J.Y. Jung, J.K. Park, C.H. Chun, *Intermetallics* **7**, 1033 (1999)
- [20] E. Schwaighofer, B. Rashkova, H. Clemens, A. Stark, S. Mayer, *Intermetallics* **46**, 173 (2014)
- [21] D.R. Johnson, K. Chihara, H. Inui, M. Yamaguchi, *Acta Mater.* **18**, 6529 (1998)
- [22] O. Shuleshova, W. Loser, D. Holland-Moritz, D.M. Herlach, J. Eckert, *J. Mater. Sci.* **47**, 4497 (2012)
- [23] C.D. Anderson, W.H. Hofmeister, R.J. Bayuzick, *Metall. Trans. A* **23**, 2699 (1992)
- [24] Y.Z. Chen, F. Liu, G.C. Yang, N. Liu, C.L. Yang, Y.H. Zhou, *Scr. Mater.* **57**, 779 (2007)
- [25] W.J. Boettinger, S.R. Coriell, R. Trivedi, in *Rapid Solidification Processing: Principles and Technologies IV*, ed. by R. Mehrabian, P.A. Parish (Claitor's Publishing Division, Baton Rouge, 1988), pp. 13–25
- [26] J.H. Kim, S.W. Kim, H.N. Lee, M.H. Oh, H. Inui, D.M. Wee, *Intermetallics* **13**, 1038 (2005)
- [27] I. Egry, R. Brooks, D. Holland-Moritz, R. Novakovic, T. Matsushita, E. Ricci, S. Seetharaman, R. Wunderlich, D. Jarvis, *Int. J. Thermophys.* **28**, 1026 (2007)
- [28] K. Zhou, H.P. Wang, B. Wei, *Philos. Mag. Lett.* **93**, 138 (2013)
- [29] K. Zhou, H.P. Wang, J. Chang, B. Wei, *Philos. Mag. Lett.* **90**, 455 (2010)
- [30] V.T. Witusiewicz, A.A. Bondar, U. Hecht, T. Ya, Velikanova, *J. Alloys Compd.* **472**, 133 (2009)
- [31] F. Spaepen, R.B. Meyer, *Scr. Mater.* **10**, 257 (1976)
- [32] F. Liu, H.F. Wang, S.J. Song, K. Zhang, G.C. Yang, Y.H. Zhou, *Prog. Phys.* **32**, 1 (2012)