JOURNAL OF MATERIALS SCIENCE **38** (2003) 3995–4002

Order-disorder transformation of the body centered cubic phase in the Ti-Al-*X* (*X* = Ta, Nb, or Mo) system

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The ordering of the bcc phase present in the Ti-Al-*X* (*X* = Ta, Nb, or Mo) system is investigated in this paper. There is a ternary phase of ordered bcc (B2) structure near the composition Ti-25Al-25*X*. All compositions mentioned in this paper are in atomic percent, unless mentioned otherwise. The phase reactions in Ti-33Al-17Ta alloy are examined in detail following solidification and solid-state processing treatments. It can be found from the differential thermal analysis (DTA) that the B2 phase in this alloy is stable up to 1205°C, where it experiences a solid-state order to disorder transformation. The rate of this ordering reaction is so high that it cannot be arrested by rapid solidification processing (RSP). The presence of thermal antiphase boundaries (APBs) in the microstructure confirms the solid-state ordering of the B2 phase from the disordered bcc phase. Ordering reactions involving the bcc phase in the Ti-Al-Nb and Ti-Al-Mo systems are also studied because of their similarity with the Ti-Al-Ta system. It can be found that they are also solid-state ordering reactions. In the Ti-25Al-25Nb alloy the B2 phase is ordered up to 1141°C; whereas in the Ti-25Al-25Mo alloy the B2 phase is ordered up to 1418°C.

1. Introduction

The high temperature structural materials for aerospace applications must have high strength and a reasonable ductility both at elevated and room temperatures along with sufficient oxidation and corrosion resistance. It is apparent that all these requirements may not be met by single monolithic component. On the basis of phase diagrams it is possible to select a combination of phases, which possesses the desirable properties. For intermetallic alloys the phase diagrams of relevance are at least of ternary order. Among all the intermetallics, the titanium aluminides showed most potential for high temperature structural applications. In binary Ti-Al system, an alloy with a two-phase microstructure consisting of α_2-Ti_3Al (DO_{19}) and γ-TiAl (Ll_0) phases offers more attractive mechanical properties than any single-phase alloy. On the basis of this knowledge, quite a few studies have been done to develop multiphase microstructures in the Ti-Al-*X* (where *X* is the third alloying element) systems. It was suggested that the presence of bcc or bcc related phase in the microstructure could have significant effect on the mechanical properties of these ternary alloys [1]. In the Ti-Al-*X* system, a multiphase microstructure consisting of bcc and other intermetallic phase(s) can possibly be developed for high temperature applications. It is often found that the bcc phase in many alloys is present in the ordered form. Since the size of the antiphase domains (APDs) has significant effect on the ductility of the intermetallic phases [2, 3], it is quite important to study the ordering mechanism of the bcc (B2) phase in the Ti-Al-*X* system.

Alloys or composites based on the Ti-Al-Ta system are potential candidates for high temperature applications. Although good progress has been made in clarifying the binary equilibrium diagrams for the aluminides, especially in the case of the Ti-Al system [4–6], there are still some questions that remain to be resolved. For example, in the Ta-Al system previous work [7] reported the existence of only two intermetallic phases (Ta_2Al, σ (D8) and $TaAl_3$, η (DO_{22})). However, several studies indicated the presence of other intermetallic phases with the compositions near TaAl [8], $TaAl_2$ [8], and Ta_2Al_3 [9]. The information on the ternary Ti-Al-Ta system is quite limited. In 1996, Raman [10] proposed an isothermal section at 1000°C revealing an extensive solubility of the β (bcc), σ, α_2 (DO_{19}), and γ ($L1_0$), and a complete solubility of the η binary phases within the ternary system. In 1983, Sridharan and Nowotny [11] reported an isothermal section at 1100°C confirming the extensive solubility into the ternary system of the various binary phases. They also reported the complete miscibility between $TaAl_3$ and $TiAl_3$, but did not consider a third intermetallic in the Ta-Al system between Ta_2Al and $TaAl_3$. In both ternary phase equilibrium studies [10, 11], no evidence was reported for the development of specific ternary phases. Das *et al.* [12]

reported the existence of a ternary phase of ordered bcc (B2) structure near the composition Ti-25Al-25Ta.

Intermetallics based on the Ti-Al-Nb system received most attention among all ternary titanium aluminides. Bendersky *et al.* [1] and Perepezko *et al.* [13] reported the existence of an ordered bcc phase (B2) near the composition Ti-25Al-25Nb. It was suggested that the presence of bcc or bcc related phases in the microstructure might had significant effect on the mechanical properties of theses ternary alloys [1]. The authors did not observe any antiphase boundary (APB) in the B2 phase. It was possible that the APBs might had annealed out during slow cooling, but very slow coarsening rate of the APDs questioned that possibility [1]. Although their results did not show any evidence for a disordering reaction of the B2 phase before the onset of melting, they concluded that the solid-state B2 ordering was an open question.

It was reported that as little as 5% addition of Mo to γ-TiAl ($L1_0$) caused the formation of a lamellar microstructure consisting of ordered bcc (B2) and γ ($L1_0$) phases upon suitable heat treatment [14]. Such a lamellar microstructure may offer attractive properties. Mo was chosen as an alloying element because a review of literature suggested that a two-phase microstructure consisting of bcc and γ phases was possible in the Ti-Al-Mo system. The early work in the Ti-Al-Mo system focussed on the Ti-rich corner of the ternary diagram [15, 16]. Both these studies reported the existence of a two-phase field consisting of β and γ phases. The existence of an ordered bcc (B2) type structure in the Ti-Al-Mo system was first identified by Bohm and Lohberg [17]. Two extensive investigations discussed earlier [15, 16] did not indicate whether the β-phase was ordered in the $\beta + \gamma$ alloys. The TEM investigation by Banerjee *et al.* [18] did not reveal any B2 ordering. These authors believed that the B2 ordered region did not extend to the β compositions in the $\beta + \gamma$ two-phase alloys investigated. However, it was possible that the high oxygen level (0.4 wt%) in the alloys investigated might have resulted in disordered β as opposed to ordered B2 [18].

The study of B2 phase is important because alloys based on the two-phase microstructure consisting of B2 and α_2 or γ may offer attractive properties. The Ti-Al-Mo and Ti-Al-Nb systems are similar to the Ti-Al-Ta systems. Therefore, the ordering reactions involving the bcc phase of the Ti-Al-Nb and Ti-Al-Mo systems are also studied.

2. Experimental procedure

The alloys used in this study were prepared in a non-consumable electric arc furnace using a water-cooled copper hearth. The nominal compositions (in atomic percent) of the alloys are reported in this paper. A controlled atmosphere vertical furnace was designed in such a way where rapid quenching was performed by momentarily opening a gate at the bottom of the furnace, and then dropping the sample in the quenching medium (brine solution). The heat treatment was carried out in a protective atmosphere of flowing argon, which was subjected to pass through a Ti-getter furnace to remove oxygen. Moreover, the samples were coated with Y_2O_3 to minimize the chance of oxidation. The rapid solidification processing (RSP) of the alloys was carried out using an Edmund Buhler two-piston splat-quenching system. In this process a small piece of the alloy was melted inside a levitation coil, and was allowed to drop by cutting the power to the levitation coil off. The falling bright alloy droplet triggered an "electric eye" mechanism, which in turn allowed two copper anvils coming from opposite directions to strike the molten droplet at the same time with a very high velocity. A cooling rate of 10^5 to 10^6 K/s can be achieved in this process [19]. The differential thermal analysis (DTA) experiments were carried out using both Al_2O_3 standard and crucible. The Al_2O_3 crucibles were coated with Y_2O_3 to minimize any chance of reaction between the crucible and the sample. The transmission electron microscopy (TEM) samples were prepared either by twin jet electropolishing at 50 V and −40°C using an electrolyte of 8 vol% H_2SO_4 in methanol or by ion milling at 5 kV and 0.5 mA. The TEM work was carried out either in a JEOL 200CX microscope operating at 200 kV or in a Philips CM 30 microscope operating at 300 kV.

3. Results and discussion

3.1. Ti-Al-Ta system

The initial phase equilibria work, involving both diffusion couple study and bulk alloy sample study, definitely indicates the presence of a ternary phase near the composition Ti-25Al-25Ta [12]. An alloy of composition Ti-33Al-17Ta was prepared by non-consumable electric arc melting technique. Although the microstructure consists mainly of the ternary phase, there is some α_2 (DO_{19}) phase present in the microstructure. This is due to alloy composition lying very close to the ternary phase boundary; therefore, it is causing the formation of α_2 during non-equilibrium cooling. The presence of α_2, especially near the surface

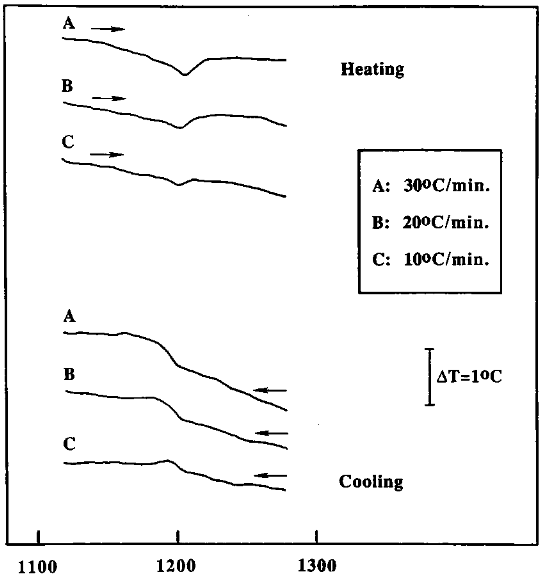

Figure 1 A set of DTA scans for the Ti-33Al-17Ta alloy showing the effect of heating and cooling rates on the order-disorder transformation temperature of the B2 phase.

of the sample, may also be due to oxygen contamination. In order to understand the phase reactions in this alloy, it was subjected to heating up to 1540°C followed by cooling in a DTA, as shown in Fig. 1. The endothermic peak near 1205°C of Fig. 1 is due to the B2/bcc order-disorder transformation [20]. To study this transformation the samples were annealed at both 1100°C and 1300°C followed by quenching in brine solution. These temperatures are below and above the transformation point near 1205°C, respectively. Fig. 2 shows a typical trasmission electron micrographs of this alloy subjected to quenching from 1100°C along with selected area electron diffraction patterns (SADPs) obtained from the ternary phase. The ternary phase is indicated as B2 in the micrographs. The second phase, α_2, is also present in the sample. Several diffraction patterns were obtained with the incident electron beam parallel to all the major low index zone axes of the ternary phase. The $\langle 001\rangle$ and $\langle 011\rangle$ diffraction patterns are only shown in Fig. 2. These diffraction patterns contain superlattice spots as indicated by arrows. From the subsequent analysis it is clear that the crystal structure of the ternary phase is ordered bcc (B2). Fig. 3 shows the transmission electron micrograph of the ternary phase present in the alloy quenched from 1300°C along with a SADP obtained from the ternary phase. The superlattice spots in the diffraction pattern are indicated by arrows. From subsequent analysis it is clear that this diffraction pattern is also from an ordered bcc (B2) phase. As mentioned before, the DTA analysis suggests that the B2/bcc order-disorder transformation is taking place near 1205°C. But the diffraction pattern (Fig. 3) is also from the B2 phase, although the sample was quenched from the disordered bcc phase field. This implies that the rate of this ordering reaction is so high that quenching by dropping the sample from a vertical furnace into brine solution cannot arrest this transformation. The presence of the thermal APB in the B2 phase quenched from 1300°C is evident in Fig. 3. Indeed, this confirms that the bcc to B2 ordering is taking place around 1205°C as a solid-state transformation. Thermal APBs only form during solid-state ordering reaction [20–22]. This is due to the fact that each antiphase domain (APD) corresponds to a distinct nucleus of ordered phase. On the contrary, when an ordered phase forms directly from the melt, it does not contain APBs. This can be explained by the fact that each nucleus of ordered phase grows into a complete grain.

The B2 ordering transformation is probably of second-order type. The main difference between first-order and second-order transformations is that there is no evolution or absorption of latent heat in the latter.

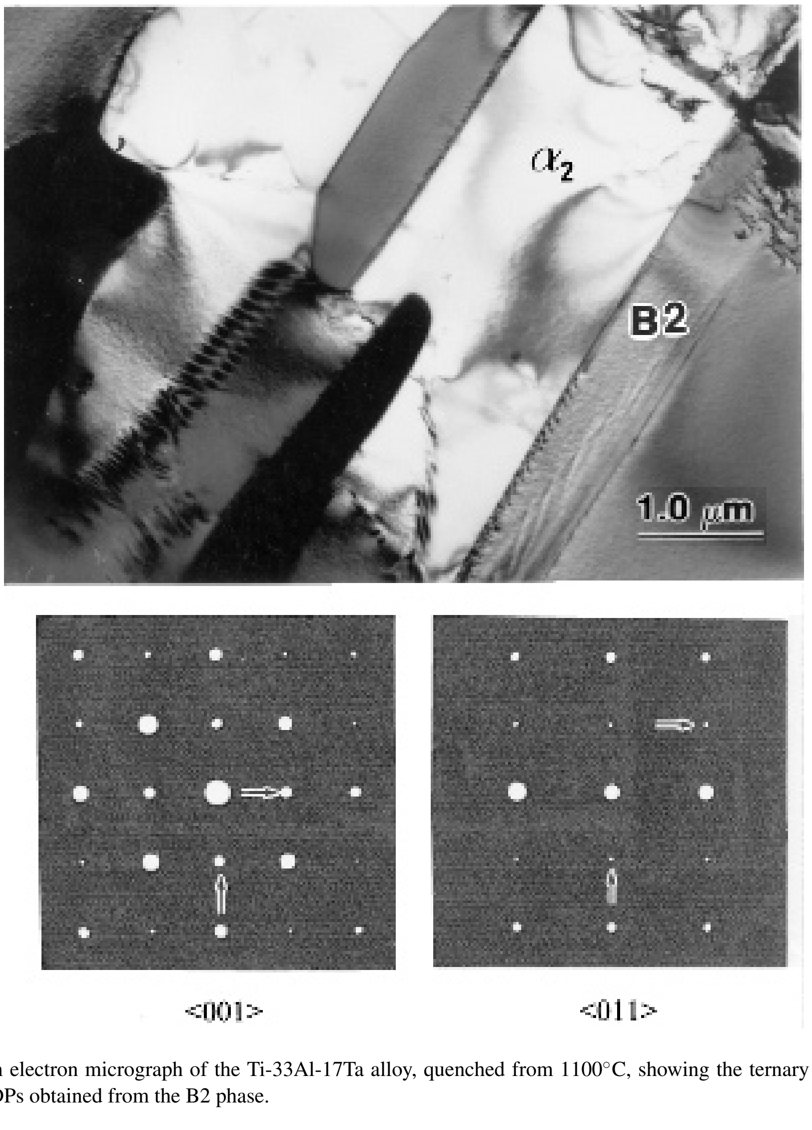

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Figure 2 The transmission electron micrograph of the Ti-33Al-17Ta alloy, quenched from 1100°C, showing the ternary phase (B2) and a second phase (α_2) along with SADPs obtained from the B2 phase.

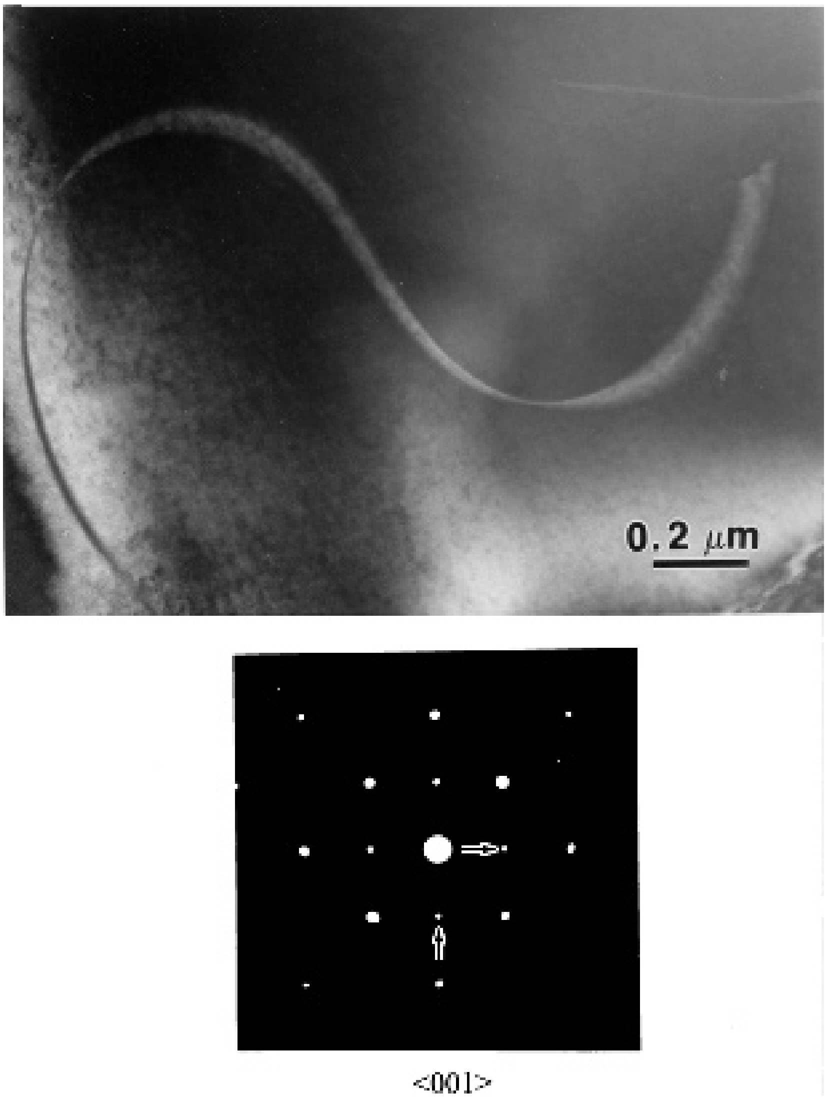

Figure 3 The transmission electron micrograph of the ternary phase (B2) in the Ti-33Al-17Ta alloy, quenched from 1300°C, showing the thermal APB along with a SADP obtained from the B2 phase.

It is well known that the second-order transformations are not rate limited by nucleation; therefore, they do not show any transformation temperature hysteresis due to the change in heating or cooling rate. This simply means that if the heating or cooling rate is changed, the second-order transformation will always take place more or less at the same temperature range; therefore, significant under cooling or superheating will not develop at the transformation point. The second-order transformation never takes place at a constant temperature, instead it occurs over a range of temperature [23]. The DTA peak of this transformation for the Ti-33Al-17Ta alloy is present near 1205°C. Fig. 1 presents the DTA results showing the effect of heating and cooling rates on the temperature of order-disorder transformation of the bcc phase present in Ti-33Al-17Ta alloy. It is clear that there is no significant thermal hysteresis for this transformation around 1205°C. Similar experiment was conducted for the B2 phase of Ti-27Al-33Ta alloy, and similar observation was made (Fig. 4).

It is also known that for the first-order, order-disorder transformation there is always a two-phase region below the ordering temperature for non-stoichiometric compositions [23]. In that case the disordered phase

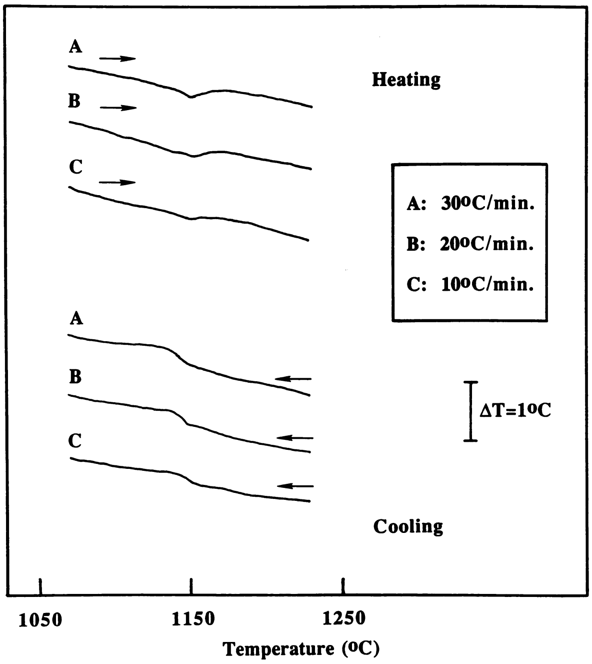

Figure 4 A set of DTA scans for the Ti-27Al-23Ta alloy showing the effect of heating and cooling rates on the order-disorder transformation temperature of the B2 phase.

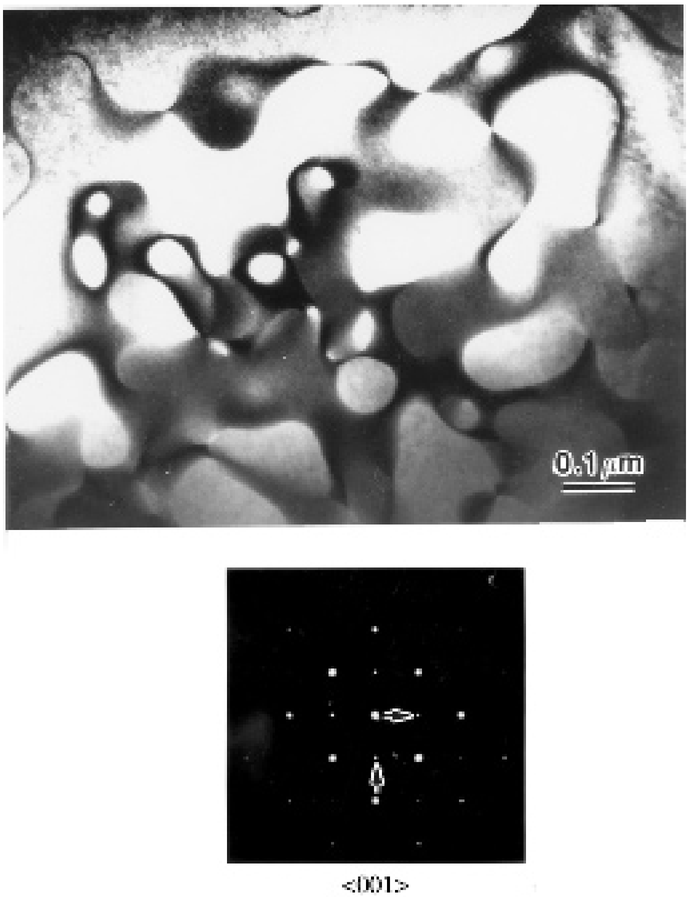

Figure 5 The transmission electron micrograph of the ternary phase (B2) present in the rapidly solidified (splat-quenched) Ti-33Al-17Ta alloy showing thermal APBs along with a SADP obtained from the B2 phase.

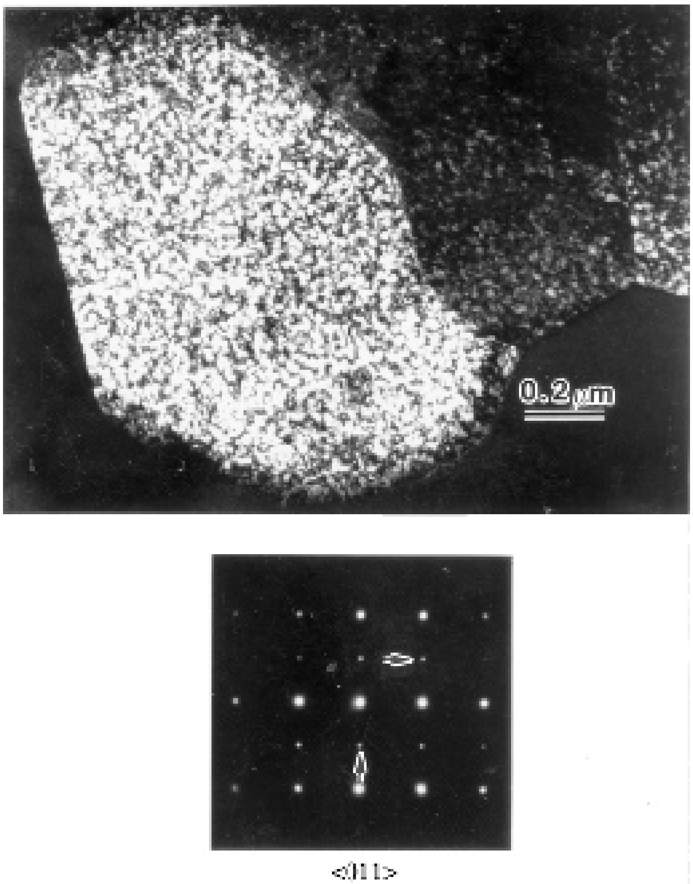

Figure 6 The transmission electron micrograph of the ternary phase (B2) present in the rapidly solidified (splat-quenched) Ti-25Al-25Nb alloy showing thermal APBs along with a SADP obtained from the B2 phase.

transforms upon change in temperature to a mixture of ordered precipitates and disordered matrix of different composition. But for the second-order, order-disorder transformation this two-phase structure never exists. The present alloy composition of interest is not perfectly stoichiometric, and no disordered bcc phase is observed in the quenched microstructure. In another study it was reported that only the ordered bcc (B2) phase was present below the ordering point in the Ti-33Al-20Ta alloy [24]. These results are in agreement with the above-mentioned point. Therefore, this is probably a second-order transformation.

The profile of the DTA peak may also suggest the order of the transformation. For a "true" second order transformation (e.g., the Curie point of $NiFe_2O_4$) the DTA peak is asymmetric, but for a "nearly" second-order transformation (e.g., the ferroelectric transformation of $BaTiO_3$), where latent heat is small but non-zero, the DTA peak is symmetrical [25, 26]. The DTA peak for order-disorder transformation of the bcc phase is found to be asymmetric in this study, and thereby suggesting a second-order transformation.

Attempts were made to arrest B2 ordering by RSP. The transmission electron micrograph of the splat-quenched Ti-33Al-17Ta alloy is shown in Fig. 5 along with a diffraction pattern obtained from the ternary (B2) phase. The diffraction pattern contains superlattice spots as indicated by arrows. From subsequent analysis it is clear that this diffraction pattern is also from an ordered bcc (B2) phase. The cooling rate (10^5 to 10^6 K/s) associated with the splat-quenching technique is not even high enough to arrest the ordering reaction taking place near 1205°C. The presence of thermal APBs in Fig. 5 suggests that the ordering reaction is indeed taking place in the solid-state. It is also clear that these APBs are significantly smaller than those present in the sample quenched from 1300°C, as shown in Fig. 3. The size difference of the APBs associated with these two processing conditions agrees with the cooling rate difference between these two processing conditions. During splat-quenching, the APBs did not get enough time to grow due to a very high cooling rate associated with this processing technique; therefore, they are quite small in size. For the sample quenched from 1300°C into brine solution, the APBs grew in size quite a bit due to relatively slow cooling rate associated with this quenching technique. But for the sample annealed at and quenched from 1100°C, most of the APBs were annealed out completely. This is due to fact that the sample was annealed at a temperature where the bcc phase was already ordered; therefore, the APBs had enough time to grow, and eventually to get annealed out.

The presence of thermal APBs suggests that the ordering of the B2 phase is indeed taking place as a solid-state transformation from the disordered bcc phase. The rate of this ordering reaction is so high that the transformation can not be arrested even by splat quenching. The absence of significant thermal hysteresis for the order/disorder transformation, as obtained in the DTA experiment, along with the absence of any disordered bcc phase suggest that the B2 ordering is probably of second-order type.

3.2. Ti-Al-Nb system

Bendersky *et al.* [1] and Perepezko *et al.* [13] reported the existence of a ternary phase (B2) near the composition Ti-25Al-25Nb. Bendersky *et al.* [1] did not observe any thermal APBs in the B2 phase, and suggested that the B2 phase might be ordered up to the melting point. From the prior knowledge of the Ti-Al-Ta system, it can be speculated that the growth rate of APDs in the B2 phase of the Ti-Al-Nb system may also be very high. Therefore, they might be annealed out

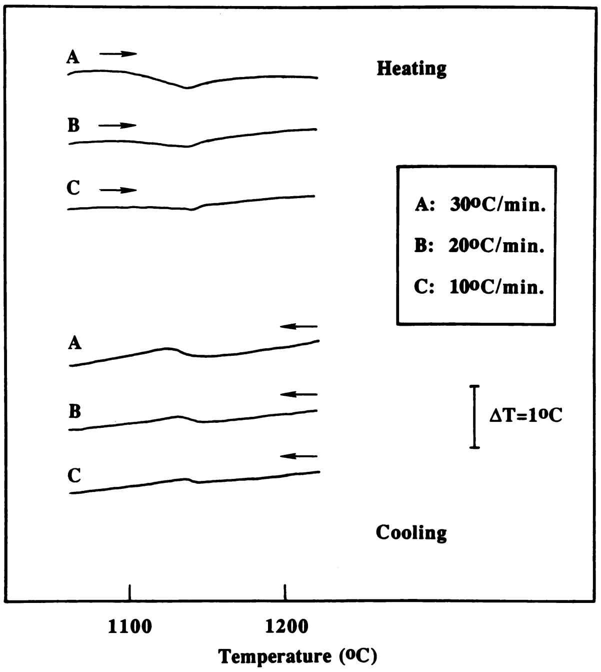

Figure 7 A set of DTA scans for the Ti-25Al-25Nb alloy showing the effect of heating and cooling rates on the order-disorder transformation temperature of the B2 phase.

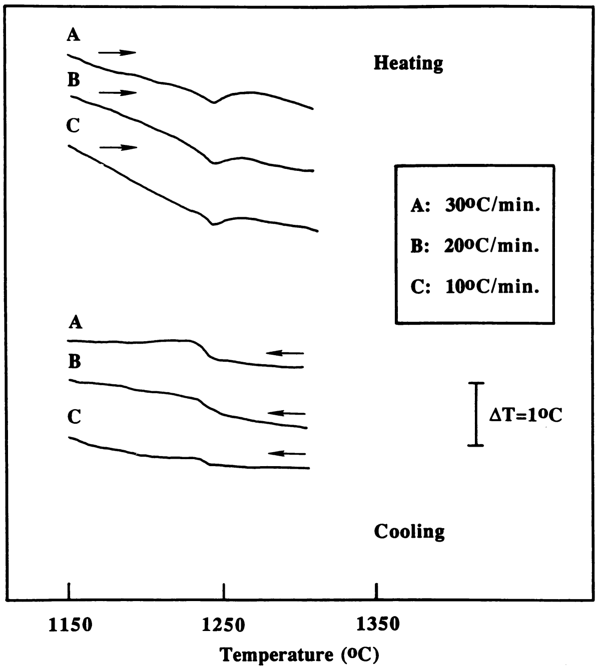

Figure 8 A set of DTA scans for the Ti-33Al-17Nb alloy showing the effect of heating and cooling rates on the order-disorder transformation temperature of the B2 phase.

during conventional quenching treatment. Therefore, small samples of the Ti-25Al-25Nb alloy were rapidly solidified using the splat-quenching technique. Fig. 6 shows a dark-field transmission electron micrograph of the B2 phase along with a SADP obtained from this phase. Very fine thermal APBs are clearly visible in this dark-field micrograph. The diffraction pattern contains superlattice spots as indicated by arrows.

Fig. 7 presents a set of DTA scan for the Ti-25Al-25Nb alloy showing the effect of heating and cooling rates on the ordering temperature of the B2 phase. It is quite clear from this figure that there is no significant thermal hysteresis observed for this ordering reaction around 1140°C. Similar experiment was conducted for the B2 phase of the Ti-33Al-17Nb alloy, and similar observation was made (Fig. 8). The present alloy compositions of interest are not perfectly stoichiometric, and no disordered bcc phase is observed in the quenched microstructures.

3.3. Ti-Al-Mo system

The existence of an ordered bcc (B2) phase in the Ti-Al-Mo system was first identified by Bohm and Lohberg [17]. Two extensive investigations discussed earlier [15, 16] did not indicate whether β-phase in the $\beta + \gamma$ alloys was ordered or not. The TEM investigation by Banerjee *et al.* [18] did not reveal any B2 ordering. These authors believed that the B2 ordered region did not extend to the β compositions in the $\beta + \gamma$ two-phase alloys investigated. However, it was possible that the high oxygen level (0.4 wt%) in the alloys investigated might had resulted in disordered B2 [18]. From the prior experience with the Ti-Al-Ta and Ti-Al-Nb systems, it was assumed that B2 phase could be found in an alloy with the composition Ti-25Al-25Mo. Due to the similarly with the fist two systems discussed, it can be speculated that the growth rate of the APBs in the B2 phase of the Ti-Al-Mo system would also be very high. Therefore, they might get annealed out during conventional quenching. Samples of an alloy with a composition near Ti-25Al-25Mo were rapidly solidified using the splat-quenching technique. Fig. 9 shows a dark-field transmission electron micrograph along with a micro diffraction pattern of the B2 phase present in this alloy.

Fig. 10 presents a set of DTA scans for the alloy Ti-25Al-25Mo showing the effect of heating and

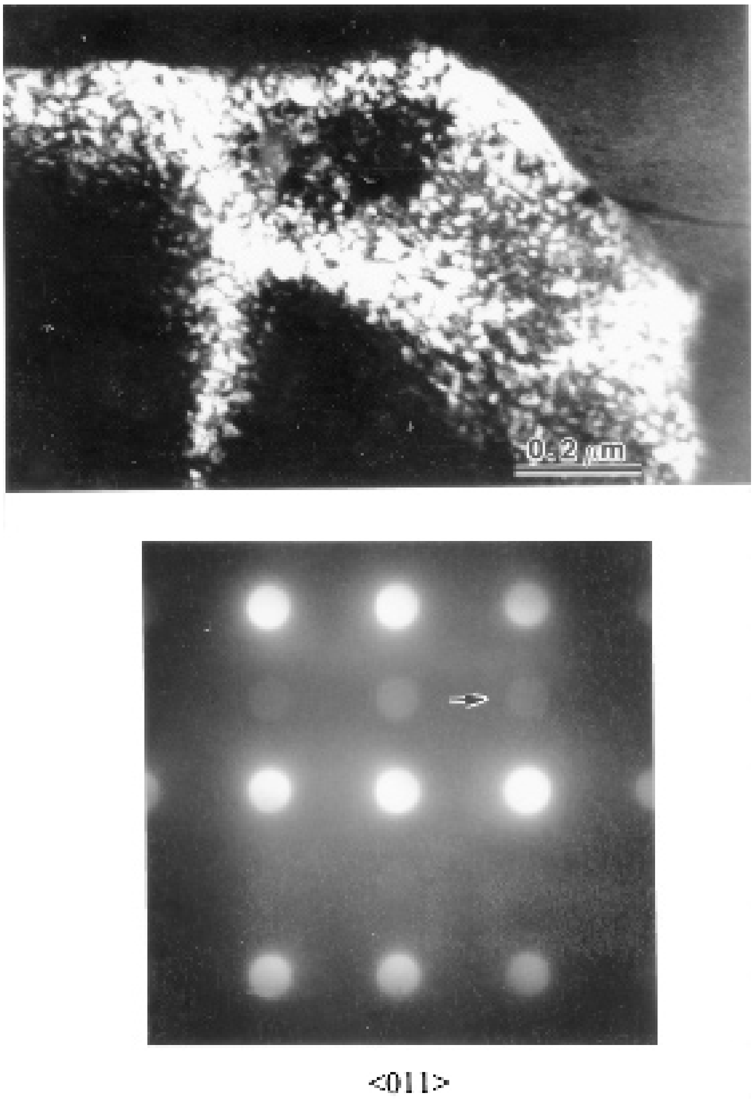

Figure 9 The transmission electron micrograph of the ternary phase (B2) present in the rapidly solidified (splat-quenched) Ti-25Al-25Mo alloy showing thermal APBs along with a micro-diffraction pattern.

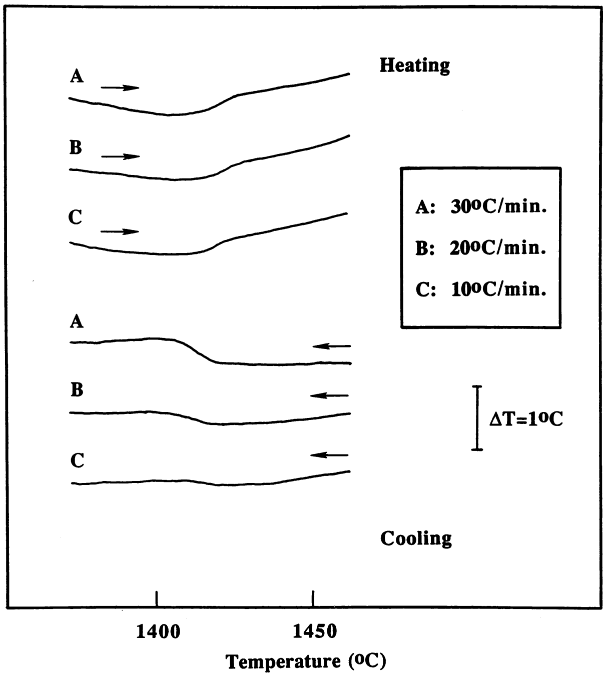

Figure 10 A set of DTA scans for the Ti-25Al-25Mo alloy showing the effect of heating and cooling rates on the order-disorder transformation temperature of the B2 phase.

cooling rates on the ordering temperature of the B2 phase. It is quite clear from this figure that there is no significant thermal hysteresis observed for this ordering reaction around 1418°C.

4. Summary

The ordering of the B2 phase present in the Ti-Al-*X* system has been studied. The presence of thermal APBs suggests that the ordering of the B2 phase in these three systems is indeed taking place as a solid-state transformation from the disordered bcc phase. The rate of this solid-state ordering reaction is so high that even splat quenching can not arrest the transformation. The present alloy compositions of interest are not perfectly stoichiometric, and no disordered bcc precipitate is observed below the ordering temperature in any alloy reported here. The absence of any significant thermal hysteresis for the order-disorder transformation, as obtained in the DTA experiment, suggests that the B2 ordering is probably of second-order type.

Acknowledgement

The authors would like to thank Professor J. H. Perepezko of University of Wisconsin-Madison for his help during the course of this research.

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Received 11 November 2002
and accepted 9 July 2003