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An investigation of the ordered DO_{19} phase formation in the Ti–Al system

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For the Ti-rich, Ti–Al system, the α–β and α–α_2 phase boundaries have been obtained through differential thermal analysis for alloy compositions ranging from 10.2 to 25.2 at% Al (6 to 16 wt% Al). It has been shown that in the above mentioned composition range, a metastable disordered α-phase can be quenched in. This metastable α then transforms to the ordered α_2 (DO_{19}) phase upon heating and/or isothermal ageing. It has also been observed that the kinetics of this ordering phenomenon is composition dependent.

1. Introduction

The nature of the phase diagram of titanium rich Ti–Al system, has long been a subject of considerable controversy, [1–8]. In Ti–Al alloys, which exhibit an increase in solid solubility with increasing temperature, it is possible to produce a supersaturated α solid solution, which will subsequently undergo decomposition during ageing. Several eutectoid alloys exhibit extensive solid solubility and in these, the alpha precipitates an intermetallic compound on ageing below the eutectoid temperature. In alloys between titanium and group III or group IV elements, (notably aluminium, gallium, indium, tin and lead), a significant amount of supersaturation can be achieved. There is a general agreement that in Ti–Al system a phase exists at or near Ti_3Al composition with an ordered DO_{19} structure. Several other phases, in this composition range, have also been proposed in the past. Ence and Margolin, [1] have proposed Ti_2Al and Ti_3Al phases at compositions up to 25 at % aluminium. From these studies as well as from our present experiments, it can be concluded that α_2 phase (Ti_3Al) can exist over a wide range of composition and temperature.

X-ray diffraction, optical microscopy, and physical properties such as electrical resistivity are commonly used for establishing phase equilibria. X-ray diffraction results however, are often inconclusive due to the low intensity of superlattice reflections in the Ti–Al system. Optical microscopy on the other hand cannot be used for an absolute verification of structures, since microstructural modifications can result from hydrogen contamination, thermomechanical history of the sample etc. Similarly, electrical resistance is an indirect technique, although it is very sensitive to phase changes. In our present study, a differential thermal analysis (DTA) technique has been used to investigate some aspects of the ordered α_2-phase formation in the titanium aluminium alloys, ranging in composition from 10.2 to 25.2 at % Al.

Fig. 1a shows the phase diagram proposed by Crossley [2] and Fig. 1b shows the diagram proposed by Blackburn [3], for the Ti–Al alloys. Crossley's diagram shows that the Ti_3Al phase exists only as a stoichiometric line compound, whereas Blackburn's diagram indicates that the single phase α_2 exists over a wide range of composition. He also indicates a region of alloy composition in which anomalous antiphase boundary (APB) contrast is observed. According to Blackburn [3], the anomalous phase contrast may be due to a thin layer of disordered material. Shull *et al.* [4] studied $\alpha_2 \rightarrow \alpha$ transition using DSC/DTA techniques. Fig. 2 shows the DSC profile of a Ti–15 at % Al, and Ti–6Al–2V–1Ta–0.8Mo samples. There are two endothermic responses on heating, one centred at about 825° C corresponding to $\alpha_2 \rightarrow \alpha$ transformation and the other at about 1140° C corresponding to $\alpha \rightarrow \beta$ transformation.

2. Experimental procedure

Samples for this study were obtained by vacuum arc melting (courtesy of RMI company) in the form of buttons. Chemical composition of samples, used in our experiments, are as follows: (a) Ti–6Al (10.2 at % Al), (b) Ti–8Al (13.4 at % Al), (c) Ti–10Al (16.5 at % Al), (d) Ti–12Al (19.3 at % Al), (e) Ti–14Al (22.5 at % Al), (f) Ti–16Al (25.2 at % Al). Samples (approximately 12 mm × 12 mm × 20 mm) were vacuum encapsulated in quartz tubes and then annealed at 1200° C for 1 h and water quenched. Some quenched samples were subsequently aged at various temperatures. Quenched as well as aged samples (approximately 70 to 80 mg) were used for the DTA experiments. Dry argon gas was passed through the furnace tube of the DTA to maintain an inert atmosphere.

3. Results and discussions

Fig. 3 shows a typical DTA trace for a Ti–16Al (25.2 at %) alloy which was heated to 1200° C and water quenched. In this figure we observe one exothermic and two endothermic events during the heating cycle. There is nothing in the existing phase diagram of Ti–Al system, which suggests such an exothermic reaction in the observed temperature range of 600 to

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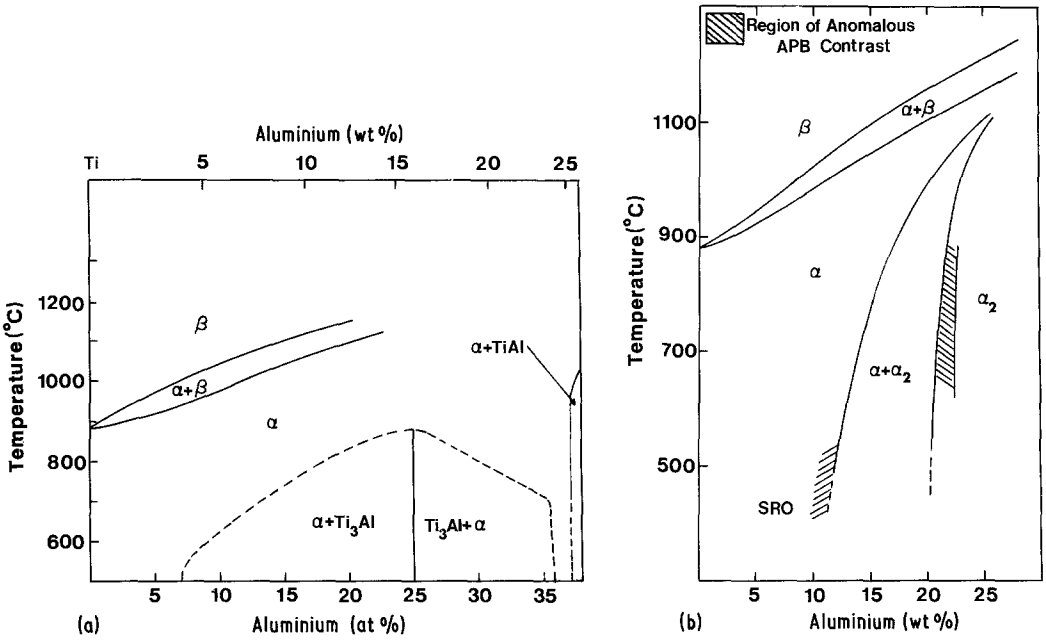

Figure 1 (a) Phase diagram of the titanium rich end of the Ti–Al system after Crossley [2]; (b) phase diagram of the titanium rich end of the Ti–Al system after Blackburn [3].

800° C for this alloy composition. We believe that this event (which starts at about 617° C) is due to the formation of α_2 (DO_{19}) from the quenched-in α(hcp) phase. The first endothermic peak corresponds to the transformation for the ordered α_2 back to the disordered α and the second endothermic peak corresponds to the transformation of α to β(bcc). Similar behaviour has also been observed in Ti–14Al (22.5 at % Al) and Ti–12Al (19.3 at % Al) samples. This can be seen in Fig. 4, which is a composite DTA pattern of a series of alloys starting from Ti–6Al (10.2 at % Al) through Ti–16Al (25.2 at % Al). All of these samples (Fig. 4) were initially annealed at 1200° C or 1 h and water quenched to room temperature. It can be seen from Fig. 4 that there is a shift of the $\alpha \rightarrow \alpha_2$ transformation temperature to higher values with increasing aluminium content. Similarly, the temperature for $\alpha_2 \rightarrow \alpha$ transformation increases with increasing aluminium content. These reactions are not observed for alloys with lower aluminium contents i.e. Ti–6Al (10.2 at % Al), Ti–8Al (13.4 at % Al) and Ti–10Al (16.5 at % Al).

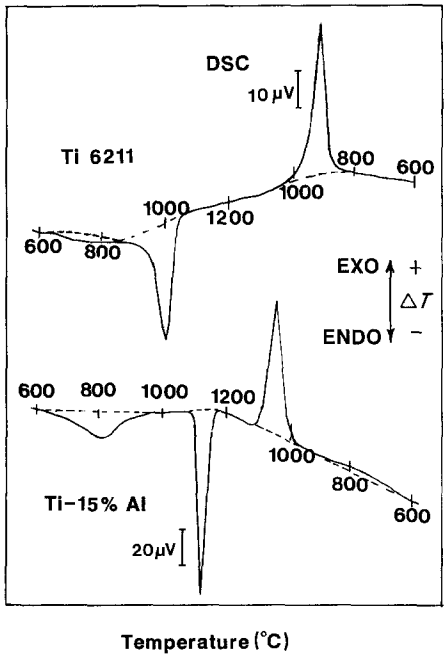

Figure 2 DSC data obtained on aged Ti–15 at % Al and as-received Ti 6211 samples. Heating and cooling rate 29.9° C min^{-1} (after Shull *et al.* [4]).

Fig. 5 illustrates the effect of ageing on the Ti–16Al (25.2 at % Al) alloy. Samples were initially quenched from 1200° C and then aged at various temperatures for a fixed time and cooled to the ambient temperature. Subsequently DTA measurements were conducted. A sample, aged at 800° C, and then subjected to a DTA analysis did not reveal the initial exothermic peak. We believe that ageing at 800° C completed the $\alpha \rightarrow \alpha_2$ transformation and thus no further calorimetric effects were observed. Ageing at 500° C for 6 h, however, reveals the initial exothermic peak as shown in Fig. 5. This will imply that 500° C is not high enough a temperature for reordering of the metastable α-phase quenched in from 1200° C i.e: this reaction kinetics is extremely sluggish at about 500° C.

Based on the above mentioned experimentation, and prior work by other authors, a Ti–Al phase diagram up to 25.2 at % Al can be plotted as shown in Fig. 6. Phase boundaries, as determined from DTA experiments are indicated by full circles on this diagram. The dotted lines (marked 1 and 2) in this diagram delineate the region within which the quenched in α-phase is converted to the equilibrium ordered α_2-phase.

From our proposed phase diagram, we note that in quenched samples we can have various amounts of metastable α-phase depending on the quenching rate and alloy composition. The amount of α_2-phase formed during quenching from 1200° C will also depend on the alloy composition and cooling rate. It appears that the kinetics of reordering of the quenched phase is

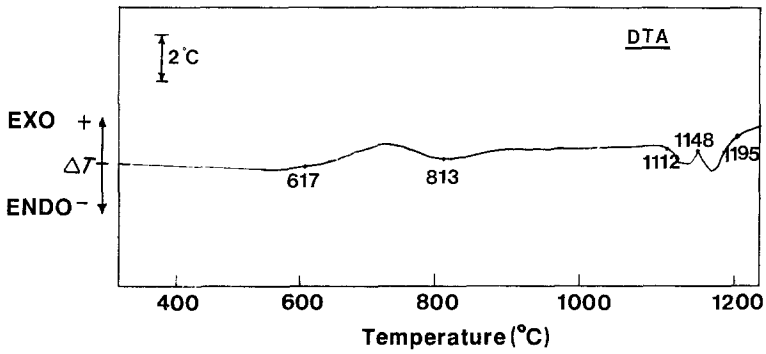

Figure 3 DTA data obtained from an as quenched (from 1200° C) Ti–25.2 at % Al (Ti–16 wt % Al) sample. Heating rate 20° C min^{-1}.

faster in Ti–19.3 at % Al alloy than in Ti–25.2 at % Al alloy. In the absence of a detailed morphological and microscopic (TEM) analysis, an explanation for this observed relative stability of the quenched α-phase cannot be provided. Preliminary X-ray diffraction studies on Ti–25.2 at % Al sample, support the results obtained by DSC/DTA studies. For example, a Ti–25.2 at % Al sample upon quenching from 1200° C, does not show any superlattice reflection. But when this quenched sample is aged at 1000° C for 4 h, superlattice reflections corresponding to the DO_{19} structure are observed. It must be pointed out that except for the $(1\,0\,\bar{1}\,1)$ α_2 line other superlattice reflections are extremely weak. Further X-ray and electron diffraction studies and electron microscopic observations of antiphase domains are being conducted to understand the ordering phenomenon more comprehensively.

4. Conclusions

For the Ti–Al system, we have obtained the α–β and α–α_2 phase boundaries through a DTA analysis for alloy compositions ranging from 10.2 to 25.2 at % Al. In this range, our proposed diagram is very similar to that proposed by Blackburn [3] rather than the one proposed by Crossley [2]. We have also shown that in the above mentioned composition range, a metastable (disordered) α-phase can be quenched in. This metastable α then transforms to the ordered α_2 DO_{19} phase upon heating and/or isothermal ageing. The kinetics of this ordering process is composition dependent and the ordering kinetics is more sluggish for higher aluminium content alloys. Further detailed TEM work is in progress to understand the mechanism(s) involved in the $\alpha \rightarrow \alpha_2$ phase change in quenched alloys.

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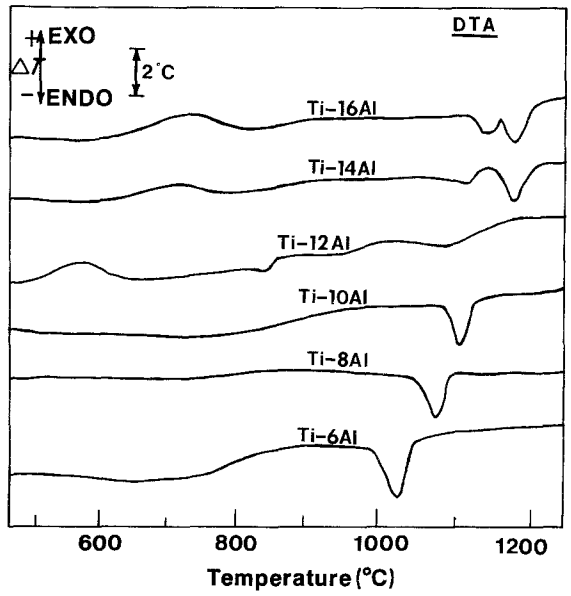

Figure 4 Series of DTA data obtained from as quenched (from 1200° C) samples starting from Ti–16 wt % Al to Ti–6 wt % Al. Heating rate 20° C min^{-1}.

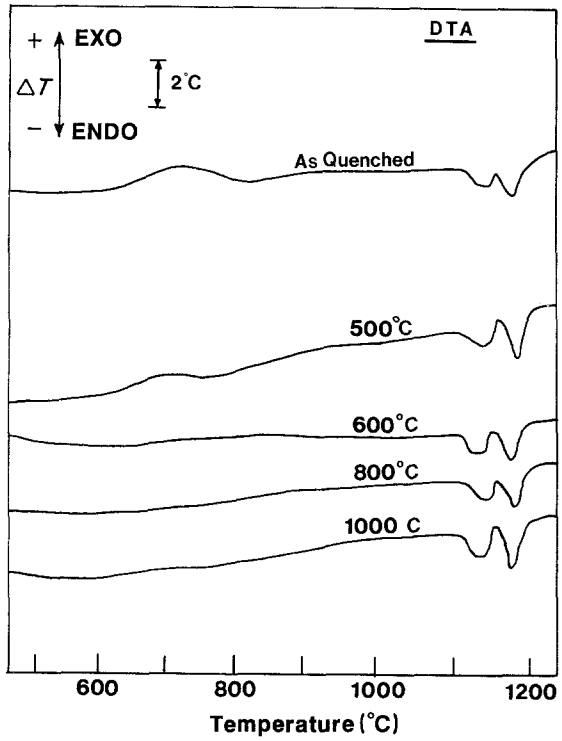

Figure 5 Series of DTA obtained from Ti–16 wt % Al (Ti–25.2 at % Al) samples which are either quenched from 1200° C or quenched and aged at the various temperatures indicated. Heating rate 20° C min^{-1}.

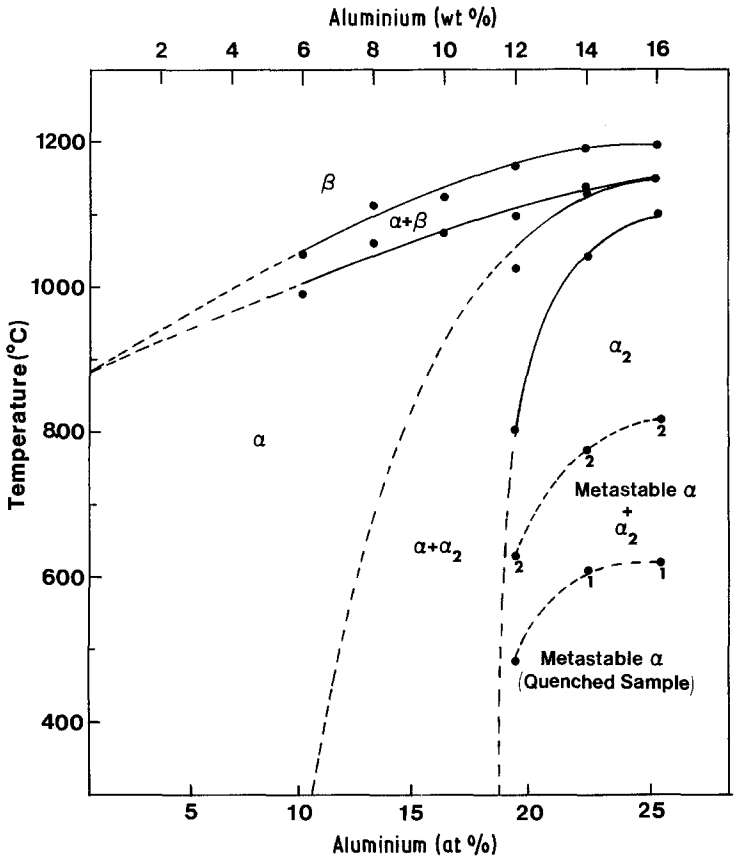

Figure 6 Proposed phase diagram of the titanium rich end of the Ti–Al system. The full circles indicate the experimentally obtained phase boundaries. (Please see text.)

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