Phase transition and ordering behavior of ternary Ti–Al–Mo alloys using in-situ neutron diffraction

Dedicated to Prof. F. D. Fischer on the occasion of his 70th birthday

1. Introduction

Intermetallic γ-TiAl based alloys are of increasing technological importance for high-temperature applications in automotive and aerospace industries [1]. Their advantage is mainly seen in low density combined with high specific yield strength and stiffness, good creep properties up to high temperatures and good oxidation resistance. Current γ-TiAl based alloys are examples of complex multi-phase materials. Knowledge of the constituent phases and their transition temperatures form the basis for performing heat treatments which are utilized for the optimization of mechanical properties. Thus, for the cost-effective production of parts by hot working as well as subsequent heat treatments, the influence of alloying elements on volume fraction and thermodynamic stability of the phases present at given temperatures has to be fully understood. Depending on the composition several phases are present in TiAl alloys. While conventional TiAl alloys are stabilized in the ($\alpha_2 + \gamma$) phase field region, novel alloying concepts include the disordered ductile β-phase obtained by adding strongly β-stabilizing elements, such as Mo and Nb [2, 3]. This can be utilized to such an extent that the formation of $\alpha_2/\beta_0$-phase is completely suppressed and only $\beta/\gamma$- and $\gamma$-phases occur. From a crystallographic point of view, the hcp based $\alpha$-Ti structure orders in a eutectoid reaction. The ordered variant is designated $\alpha_2$-Ti3Al (DO19 structure) while $\alpha$ refers to the disordered phase (A3 structure). In contrast to $\alpha/\alpha_2$, the $\gamma$-TiAl phase (L10 structure) exhibits atomic order up to its dissolution temperature. Less densely packed are the ordered $\beta_0$ and disordered β-phase which exhibit B2 and A2 structure, respectively.

In the present work we have studied two alloy variants of so-called β/γ-alloys in which the $\beta/\gamma$-phase was stabilized by adding 3% and 7% Mo, respectively (all concentrations are given in at.% henceforth) while the nominal Al concentration was kept constant at 44%. The goal of this study was to determine the temperatures at which atomic ordering and disordering occur by means of in-situ neutron diffraction and to correlate the determined results to those obtained by a recent investigation using in-situ high-energy synchrotron X-ray diffraction [4]. In addition, the validity of a Ti–Al–Mo ternary phase diagram, which was constructed from experimental data published in the literature, is reviewed.

2. Experimental

Two Mo containing TiAl alloys were used for this study, which were nominally similar to the ones used in previous experiments [4]. Their compositions, in at.%, were Ti-44.46Al-3.26Mo-0.12B (referred to as 3M) and Ti-43.7Al-6.86Mo-0.09B (7M). Details regarding the sample preparation and composition determination have been reported [4]. Boron was added to refine the microstructure during solidification by boride formation [5]. Due to the small volume fraction of borides, however, an appreciable influence on phase fractions, transformation or order and disorder temperatures, is not expected.
In-situ heating experiments were conducted on the WOMBAT diffractometer at the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, NSW, Australia [6]. The instrument was used in medium resolution set-up with a take-off angle at the monochromator of 2θm = 10°, wave number k = 3.767 Å⁻¹ and wavelength λ = 2π/k = 1.668 Å. A focused Ge-511 monochromator was used. An ILL-type high temperature vacuum furnace of AS-Scientific, Abington, United Kingdom, was used for heating the specimen. It consists of a heating element and Nb heat shields while the specimen is suspended from a top-loading sample stick by a V wire. Although radial collimators were employed, background from the Nb elements is not completely excluded. The geometrical shape of the multi-walled, cylindrical container results in a positional offset of the Nb pattern on the detector, which results in the four diffraction lines appearing in the range of 2.6 Å⁻¹ to 3.0 Å⁻¹. Temperature measurements were performed with a C-type thermocouple, located approximately 20 mm above the upper edge of the sample. The temperatures recorded by the thermocouple were consistently 55 °C too high as compared to differential scanning calorimetric measurements [4]. We attribute this inconsistency to the fact that the temperature was not measured directly on the sample. Temperatures reported herein have been adjusted by subtraction of this offset.

The samples were heated from room temperature up to 1350 °C and cooled back to room temperature (RT). A 20 K min⁻¹ ramp rate was used from RT to 1000 °C after which the heating rate was lowered to 2 K min⁻¹. Similarly, during cooling, a –2 K min⁻¹ ramp was applied from 1350 °C to 1000 °C and –20 K min⁻¹ from 1000 °C to RT. Since the furnace did not incorporate an active cooling device, the desired cooling rate could not be maintained at temperatures below ~500 °C. Diffraction patterns were measured continuously in 60 s integration intervals by the position sensitive area detector covering ~120° × 20° during heating and cooling. After making the necessary geometric corrections, the diffraction patterns were azimuthally integrated in order to get intensity versus Q = 2k sin(θ) plots for each collected pattern.

3. Results and Discussions

Figure 1 shows a section through the Ti–Al–Mo ternary phase diagram for a constant Al concentration of 44 at.%, which was constructed from experimental data published in the literature [7–10]. The Mo contents for the investigated alloys, 3M and 7M, are indicated by vertical lines. In addition, the data obtained from a recent in-situ high energy X-ray diffraction study are included [4]. Figure 2 shows the microstructure of alloy 3M obtained by scanning electron microscopy using back-scattered electron mode. The microstructure consists of some lamellar (γ + α₂)-colonies. Additionally, globular γ grains are present most of which are embedded in the ordered β₀-phase. Energy dispersive X-ray spectroscopy provided clear evidence that the β/β₀-phase exhibits higher Mo contents than the α/α₂ phase. From this observation it is assumed that the β-stabilizing element has segregated to β/α₂-interface boundaries during the β → α reaction which took place after solidification via the β-phase (see Fig. 1) as well as during subsequent hot-isostatic pressing (HIP), which was applied to close residual casting porosity [4]. The microstructure of alloy 7M shows former β-grains intersected by elongated γ-grains, which were formed during the solid state phase transformations following solidification (see Ref. [4]). Additionally, a small fraction of globular α₂-grains was detected, which is considered a remnant of the HIP process and has not dissolved during subsequent cooling to room temperature. Furthermore, it was found that the β₀-phase fraction of alloy 7M at room temperature is significantly higher than that of alloy 3M. Concerning the evolution of the microstructure during solidification, HIP, short- and long-term aging treatments, further investigations are underway and will be published in a forthcoming paper.
Fig. 3. Neutron diffraction patterns (a) as-recorded by the 2D detector, (b) integrated to a conventional powder diffraction pattern and as a function of time during heating-cooling cycles for alloys (c) 3M and (d) 7M. The intensity of the grayscale represents the detected intensity.
Figure 3a shows the neutron diffraction patterns, as recorded on the 2D detector. The integrated intensity against the modulus of the scattering vector or momentum transfer $Q$ is shown in 3b. In Fig. 3c and d, the integrated intensity is shown in grayscale as a function of time and the scattering vector $Q$. On the right-hand side of the graphs, the sample temperature is shown as a function of time, using the same time axis as the grayscale plots, while the temperature is indicated on the abscissa. Each one of the vertical lines in the grayscale plots corresponds to a Bragg peak of a particular phase. The position of each Bragg peak and the corresponding indices, as calculated using lattice parameters from Rietveld fits, are indicated by position markers. The slopes of the lines in Fig. 3 stem from the expansion and contraction of the lattice during heating and cooling, respectively. Abrupt changes in slope at $2 \times 10^3$ s and $22 \times 10^3$ s, however, correspond to the change in heating/cooling rate at 1000 °C.

Disappearance of the lines can be related either to a phase transformation of disordering character or to the dissolution of an ordered phase. In particular for TiAl alloys, neutron scattering is complementary to the X-ray diffraction technique as the contrast produced by the oppositely signed neutron scattering lengths of Ti and Al atoms distinguishes the neutron diffraction pattern uniquely from X-ray patterns. The strength of a reflection is given by its structure factor, which is a coherent superposition of the scattering amplitudes of all atoms in the lattice. Scattering amplitudes, in turn, are described by the scattering lengths of the individual atoms in a crystallographic unit cell. For X-rays, the atomic scattering length is the scattering length or classical turn, are described by the scattering lengths of the individual phases. Scattering amplitudes, in which is a coherent superposition of the scattering amplitudes Ti and Al, have been tabulated in Refs. [11, 12]. The coherent scattering lengths $b_i$ for bound atoms has to be utilized in the present situation of a solid material. Contrary to X-rays, neutron scattering lengths are negative for some isotopes. The elements Ti and Al have opposite signs of neutron scattering lengths, i.e., $b_{\text{Ti}} = -3.370 \text{ fm}$ and $b_{\text{Al}} = 3.449 \text{ fm}$, respectively [11]. Mo has a neutron scattering length of $b_{\text{Mo}} = 6.715 \text{ fm}$. In disordered phases, i.e. $\alpha$ and $\beta$, the probability to find one kind of atom on a specific crystal site is given by the respective concentration. Therefore, the average scattering length of the respective phases has to be used. For alloy 3M, energy dispersive X-ray spectroscopy yields a chemical composition of Ti–46.57(±0.5)Al–3.02(±0.3)Mo for the $\alpha$-phase and Ti–43.23(±0.5)Al–5.44(±0.3)Mo for the $\beta$-phase leading to average scattering lengths of 0.110 fm and 0.126 fm, correspondingly. For 7M, the measured compositions and mean scattering lengths are Ti–47.44(±0.5)Al–5.25(±0.3)Mo and 0.397 fm for $\alpha$-phase respectively Ti–47.36(±0.5)Al–8.15(±0.3)Mo and 0.486 fm for $\beta$-phase. All values are small as compared to the scattering lengths of the atomic species alone. Thus, Bragg diffraction from the disordered phases does not take place or is of minimal residual value which disappears in the intensity distribution of other scattering effects such as thermal diffuse scattering. On the other hand, when the structures are ordered, such as in $\alpha_0$, $\beta_0$, and $\gamma$, the intensity of a reflection is given by its structure factor $F$, which is a coherent superposition of the scattering lengths.

Generally, the fundamental reflections have structure factors which add up the scattering lengths of the individual atoms in the unit cell, such as $F(b_0-110) = b_{\alpha}(A) + b_{\beta}(B)$ for atoms $A$ and $B$. In the X-ray case, where all scattering lengths are of positive sign, this would lead to the strongest reflections as the cross-sections are proportional to $|F|^2$. Superstructure reflections, however, typically contain the differences of the individual site contributions in their structure factor, such as $F(b_0-100) = b_{\alpha}(A) - b_{\beta}(B)$. For a disordered phase ($A = B$) this leads to vanishing intensity by the structural symmetry and not by the kind of atoms. If order occurs, however, $A$ and $B$ are different species, i.e., Ti and Al, then the difference leads to a large absolute number in neutron scattering, while relatively small in the case of X-ray diffraction. Therefore, neutron diffraction is an ideal means to study order and disorder in the Ti–Al system. Alloying with Mo may alter this behavior, but the sensitivity for order remains very high. In the present case, order occurs in the $\alpha_0$, $\beta_0$ and $\gamma$ phases, while $\alpha$ and $\beta$ are disordered and thus not seen in the diffraction pattern (Fig. 3).

Figure 3 reveals that both alloys are dominated by the two ordered $\beta_0$ and $\gamma$ phases at room temperature. This conclusion is in agreement with the phase diagram (Fig. 1), as Mo tends to stabilize the $\beta_0/\beta$-phase in these alloys. For alloy 3M the $\alpha_2/\alpha$-peaks are weak at room temperature (Fig. 3c). It follows from the phase diagram that a significant fraction of ordered $\alpha_2$-phase is present only below 1200 °C, an observation that has been confirmed by recent in-situ X-ray diffraction [4]. Additionally, the X-ray investigations have shown that $\alpha_2$ is completely suppressed at room temperature in alloy 7M, in agreement with our neutron data, but contradicts the phase diagram shown in Fig. 1, which predicts the presence of an $\alpha_2$-phase at low temperatures. Some of the individual peaks in Fig. 3 were further analyzed in order to quantify the amount of each type of phases present. The integrated intensities of some $\alpha_2/\alpha$, $\beta_0/\beta$ and $\gamma$-phase peaks are plotted in Fig. 4. For X-rays, the diffraction signature of an order/disorder reaction, e.g. $\beta_0 \leftrightarrow \beta$, is the loss in intensity and eventually the disappearance of superlattice peaks without dramatic change in intensity of the fundamental peaks. In the case of neutron diffraction, however, the fundamental peaks of disordered phases in TiAl alloys are very low in intensity due to their small mean scattering length (close to zero). The disappearance of the neutron diffraction peaks in these alloys therefore represents either a disordering or a dissolving event. From the initial peak intensities it is inferred that alloy 3M contains a relatively high amount of $\gamma$-phase, while in alloy 7M the fraction of $\beta_0$-phase is higher, which is attributed to the increased Mo content. Quantitatively, this behavior was proven by in-situ high energy X-ray diffraction [4]. The loss of intensity of the $\gamma$-phase peak upon heating represents the dissolution of the $\gamma$-phase in alloys 3M and 7M (Fig. 4a and d). Vanishing of the $\beta_0$ (Fig. 4b and c) and the $\alpha_2$-phase reflections in alloy 3M (Fig. 4c) potentially correspond to either dissolution or disordering. However, from the phase diagram as well as from
in-situ high energy X-ray diffraction it is evident that both phases $\beta_0$ and $\alpha_2$ disorder into $\beta$ and $\alpha$, respectively. The dissolution and disordering temperatures derived from Fig. 4 have been summarized in Table 1.

From Table 1 it is concluded that in alloy 3M, $\alpha_2$ is the first phase to disorder at 1205 °C, followed by $\beta_0$ at 1240 °C. After increasing the temperature by 15 °C the $\gamma$-phase dissolves at 1255 °C. Both, $\beta_0$ and $\gamma$, show hysteresis in the heating/cooling cycle with this effect being more pronounced for the $\gamma$-phase (Fig. 4). During cooling, the $\beta$-phase orders $\sim$ 15 °C below the temperature where it was found to disorder upon heating. For the $\gamma$-phase a temperature difference of $\sim$ 50 °C between dissolution and formation temperature was found. It is interesting to note that ordering of $\alpha$ to $\alpha_2$ does not show any significant undercooling (Fig. 4c). It can be derived from the peak intensities in Fig. 4a and b that in alloy 3M the phase fraction of $\beta_0$ and $\gamma$-phase present after the full heating/cooling cycle is lower than in the initial state. Consequently, the amount of $\alpha_2$-phase increases significantly implying that some $\beta_0$ and $\gamma$-phase have transformed into $\alpha_2$-phase during continuous heating and subsequent cooling. However, the observed behavior might be related to the fact that the HIP starting material was not in chemical equilibrium.

In alloy 7M, the $\alpha_2$-phase could not be characterized since it either does not exist or the volume fraction was below the detection limit. In-situ high energy X-ray diffraction experiments [4] as well as recent isothermal short and long-term heat-treatment studies have shown that $\alpha_2$-phase is thermodynamically unstable at temperatures below $\sim$ 1200 °C. Disordering of the $\beta_0$-phase and dissolution of the $\gamma$-phase during heating were found to occur at the same temperature (1265 °C). In this case, the $\beta_0$-phase did not show any pronounced undercooling whereas the $\gamma$-phase showed significantly smaller undercooling ($\sim$ 25 °C) compared to alloy 3M.

Since Mo is a strong $\beta$/$\beta_0$ stabilizer in TiAl alloys, alloy 7M contains more $\beta_0$-phase and exhibits an increased disordering temperature compared to alloy 3M (Table 1). The strong hysteresis in the $\gamma$-phase and the decrease in the amount of $\beta_0$ and $\gamma$-phase at the end of a heating/cooling cycle is probably related to diffusion-controlled redistribution of the different chemical elements (Ti, Al, Mo) among the phases as well as nucleation and growth processes (e.g. $\gamma$-phase) [13].

A striking fact of the experimental data is that no undercooling is observed for the $\alpha$$\rightarrow$$\alpha_2$ ordering reaction, whereas a pronounced difference between $\gamma$ dissolution and formation temperatures is evident. This observation probably means that the short range diffusion processes by which ordering of $\alpha_2$ is facilitated are short range and fast, which leads to a small dependence of the ordering temperature on cooling rate. Consistent with observations from previous experiments is the finding that $\gamma$-phase forms upon cooling only after the $\alpha$$\rightarrow$$\alpha_2$ transformation has occurred. The near close packed $\gamma$-lattice differs from $\alpha$ and $\alpha_2$ by a change in stacking sequence along the hexagonal c-axis and the decoration of the atoms, i.e. chemical order. In contrast to the other phases present, $\gamma$-phase has never been observed in a disordered state, which would be of cubic fcc structure [14]. It is speculated, that the ordered $\alpha_2$ phase serves as a heterogeneous nucleation site for the formation of $\gamma$-phase. This is underlined by the structural relationship of $\alpha_2$ and $\gamma$, which is also apparent in the well known Blackburn relationship [15] and by the fact, that $\alpha_2$ and $\gamma$ always appear together [16].

The results obtained during continuous heating (Table 1) are shown in the cross-sections of the phase diagram in Fig. 1, along with data derived from in-situ X-ray diffraction [4]. The results from the different diffraction methods...
Table 1. Phase dissolution/formation and disorder/order temperatures observed in alloys 3M and 7M. Data evaluated from results shown in Fig. 4.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(T_\text{dissolving upon heating})</th>
<th>(T_\text{dissolving upon cooling})</th>
<th>(T_\text{transforming upon heating})</th>
<th>(T_\text{transforming upon cooling})</th>
<th>(T_\text{ordering upon heating})</th>
<th>(T_\text{ordering upon cooling})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M</td>
<td>1255°C</td>
<td>1205°C</td>
<td>1240°C</td>
<td>1265°C</td>
<td>1225°C</td>
<td>1265°C</td>
</tr>
<tr>
<td>7M</td>
<td>1265°C</td>
<td>1240°C</td>
<td>1265°C</td>
<td>1265°C</td>
<td>1285°C</td>
<td>1265°C</td>
</tr>
</tbody>
</table>

are in good agreement. However, both the neutron and X-ray diffraction data indicate that the phase diagram does not describe the phase transition temperatures correctly. Whereas the phase diagram predicts the dissolution of the \(\gamma\)-phase correctly for both alloys, the temperature of the \(\alpha_2 \to \alpha\) transition is underestimated. This means that the surface which separates the \((\alpha_2 + \beta + \gamma)\)-phase field region from the \((\alpha + \beta + \gamma)\)-phase field region is at too low a temperature. Furthermore, from this study it is evident that the alloy with the higher Mo concentration (7M) does not contain the ordered \(\alpha_2\)-phase but high energy X-ray diffraction studies have clearly shown the onset of \(\alpha\)-phase formation at \(\sim 1220^\circ\mathrm{C}\) [4]. This observation implies that the line separating the \((\alpha_2 + \beta + \gamma)\) and \((\beta + \gamma)\) phase field regions must be shifted to lower Mo contents and the region where the \(\alpha\)-phase appears and \(\gamma\)-phase disappears requires revision. This topic will be treated in a forthcoming paper. The order/disorder temperature of the \(\beta/\beta_0\)-phase is not included in the original phase diagram as shown in Fig. 1. From the neutron data it is apparent that the reaction \(\beta_0 \leftrightarrow \beta\) takes place in the lower temperature range of the \((\alpha + \beta)\)-phase field region, after the \(\gamma\)-phase dissolved.

4. Conclusions

The in-situ neutron diffraction studies conducted are complementary to in-situ high energy X-ray diffraction experiments performed in an earlier study [4]. In Ti–Al based systems, neutrons are particularly sensitive to order-disorder in the site occupancy of the underlying crystallographic point lattices, which themselves are well determined by X-rays. From neutron diffraction experiments, the order transition temperatures for \(\alpha/\alpha_2\) and \(\beta/\beta_0\) phases as well as dissolution and formation temperatures of \(\gamma\)-phase have been determined accurately. The results are consistent with the previously performed X-ray studies and significantly differ from the phase diagram established from published data.

Upon heating, the transition sequence for alloy 3M is \(\alpha_2 \to \alpha, \beta_0 \to \beta\) which is followed by the dissolution of \(\gamma\). No \(\alpha/\alpha_2\)-phase was observed in alloy 7M during the neutron diffraction experiments and \(\beta_0 \to \beta\) disorders simultaneously with the dissolution of \(\gamma\).

Upon cooling alloy 3M, the first phase transformation \(\beta \to \beta_0\) occurs followed by the ordering reaction \(\alpha \to \alpha_2\), which is speculated to facilitate the nucleation of \(\gamma\) approximately 50°C below its dissolution temperature. In alloy 7M the ordering reaction \(\beta \to \beta_0\) occurs before \(\gamma\) nucleates. The temperature of the \(\beta \to \beta_0\) reaction increases with increasing Mo content.

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