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In Situ Observation of Various Phase Transformation Paths in Nb-Rich TiAl Alloys during Quenching with Different Rates

In situ observation of various phase transformation paths in Nb-rich TiAl alloys during quenching with different rates**

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Abstract

In recent years intermetallic γ-TiAl based alloys with additional amounts of the ternary β phase have attracted attention due to their improved hot workability. Depending on alloy composition and heat treatment the ternary β phase can transform to different ternary phases at lower temperatures. A few of them are assumed to be detrimental to ductility. However, the current phase diagrams of these multiphase materials are often quite uncertain. Thus, the possible transformations of third phases in the temperature range between 700 and 1100 °C are studied by means of in situ high-energy x-ray diffraction (HEXRD). Depending on quenching rate reversible transformations of β_o to different ω related phases are observed, indicating a stepwise diffusion controlled transformation mechanism of B2-ordered β_o to $B8_2$-ordered ω_o. Apparently, the addition of Mo can hinder this transformation.

Intermetallic γ-TiAl based alloys are a class of novel, light-weight structural materials with attractive mechanical properties for advanced high-temperature applications. Due to their low density (4 g/cm^3), their high yield and creep strength up to 800 °C and their good oxidation resistance they have the potential to replace the heavier Ni based superalloys (8 g/cm^3) in industrial and in aviation gas turbines as well as in automobile engines.[1] Conventional titanium aluminide alloys consist of tetragonal γ-TiAl (L1$_0$ structure; P 4/m m m) and small amounts of hexagonal α$_2$-Ti$_3$Al (D0$_{19}$ structure; P 6$_3$/m m c). Through special heat treatments various microstructures can be established in these two phase alloys to optimize their mechanical properties.[2]

The most restricting factor for a broad industrial implementation of titanium aluminides is their low ductility that also limits their workability. A promising design strategy to overcome the brittleness and to improve the hot workability is to induce the formation of more ductile phases by adding ternary alloying elements. The body-centred cubic (bcc) high-temperature β-Ti(Al) phase (A2 structure; I m $\overline{3}$ m) can act as a ductilizing phase in TiAl alloys because it provides a high number of independent slip systems. In recent years several authors have reported that stabilizing the β phase by alloying elements such as Nb, Mo, Ta or V, significantly improves the hot workability.[3,4,5] Additionally, novel types of microstructures can be achieved exploiting the ternary solid state transformations. [3,4]

In spite of this progress, the exact pathway of phase transformations and thus the evolution of microstructures in β phase containing TiAl alloys are not fully understood up to now. At lower temperatures, the disordered bcc β phase can transform to ordered cubic β$_o$-TiAl phase (B2 structure; P m $\overline{3}$ m). However, calculated and experimental transition temperatures show large discrepancies.[6,7] In high-Nb containing TiAl alloys β and/or β$_o$ can decompose to

ordered hexagonal ω_o-Ti$_4$Al$_3$Nb phase (B8$_2$ structure; P 6$_3$/m m c).[8,9] The formation of an orthorhombic phase (B19 structure; P m m a) is reported in Al-lean and Nb-rich TiAl alloys and is interpreted as a transition structure between the cubic β and/or β$_o$ and the orthorhombic O-Ti$_2$AlNb phase (C m c m).[4] The crystallographic data of all phases mentioned above and relevant for this work are listed in **table 1**.

Ordered phases, such as β$_o$ and ω_o, are often assumed to be detrimental to ductility due to their low crystal symmetry. Otherwise the orthorhombic O phase is known to be relatively ductile and even ω_o containing TiAl alloys show good plastic formability at 800 °C.[8] Thus, with respect to alloy design and processing, it is of high importance to know which kind of additional phase will be formed and which further phase transformations occur during processing and service.

Table 1. Relevant phases and their structures.

Phase	Space group	Structure	Wyckoff symbols of atom sites
γ-TiAl	P 4/m m m	L1$_0$	1a (Al); 1c (Al); 2e (Ti)
α$_2$-Ti$_3$Al	P 6$_3$/m m c	D0$_{19}$	2d (Al); 6h (Ti)
β-Ti(Al,Nb)	I m $\bar{3}$ m	A2	1a (Ti,Al,Nb)
β$_o$-TiAl(Nb)	P m $\bar{3}$ m	B2	1a (Ti); 1b (Al,Nb)
ω_o-Ti$_4$Al$_3$Nb	P 6$_3$/m m c	B8$_2$	2a (Ti,Nb,Al); 2c (Al); 2d (Ti)
ω''-Ti$_4$Al$_3$Nb	P $\bar{3}$ m 1		1a (Ti); 1b (Nb,Al) 2d$_1$ (Al); 2d$_2$ (Ti)
B19	P m m a	B19	2e (Ti); 2f (Al)
O-Ti$_2$AlNb	C m c m	A$_2$BC	4c$_1$ (Al); 4c$_2$ (Nb,Ti); 8g (Ti,Nb)

Experimental

Phase transformations are studied in two Nb-rich TiAl alloys with a basic composition of Ti-45Al-xX (all alloy compositions within the text are given in atomic percent; X = β-stabilising element): Ti-45Al-***10Nb*** (TiAl-10Nb) and Ti-45Al-***7.5Nb-1Mo***-0.1B (TiAl-7.5Nb-1Mo). In TiAl-7.5Nb-1Mo Nb is partly replaced by Mo that is known as a two times stronger β-stabilisator compared to Nb with respect to the α phase.[10] TiAl-10Nb was produced from

powder, atomized in the PIGA-facility at the GKSS Research Centre, filled in Ti cans, degassed and subsequently hot-isostatically pressed for 2 h at 1250 °C and 200 MPa. TiAl-7.5Nb-1Mo was fabricated by arc melting under an Ar inert gas atmosphere. A button with a mass of 30 g was remelted ten times to ensure a good chemical homogeneity. Cylindrical specimens with a diameter of 4 mm and a length of 10 mm were prepared by spark erosion for the experiments.

The *in situ* high-energy x-ray diffraction (HEXRD) experiments were carried out at the GKSS beamline HARWI II at Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany, in transmission geometry. In order to penetrate the specimen, high-energy x-rays with a photon energy of 100 keV, corresponding to a wavelength of $\lambda = 0.12398$ Å, and a beam cross section of 1 x 1 mm^2 were used. The resulting Debye-Scherrer diffraction rings were continuously recorded on a Mar555 flat panel detector with a frame rate of 120 s and an exposure time of 20 s. Conventional diffraction patterns were achieved by an azimuthal integration of the Debye-Scherrer rings.

A dilatometer DIL 805A/D (Bähr-Thermoanalyse GmbH) that is especially modified for working at the beamline HARWI II was used for heating and quenching.[11] The samples were inductively heated. Quenching was achieved by blowing the specimen with water cooled Ar. During the experiments the temperature was controlled by an S-type thermocouple spot welded on the sample. In order to prevent oxidation of the sample surface the experiments were performed in Ar atmosphere. The cylindrical samples were heated up to 1100 °C and subsequently quenched to 700 °C three times in a row with quenching rates of 10, 1000 and 100 K·min^{-1}, respectively (see temperature ramp in figure 2).

Microstructure

As shown in **figure 1a** TiAl-10Nb, the powder compact, has a globular almost equiaxed grain structure that mainly consists of γ-grains and a few lamellar ($\alpha_2+\gamma$) colonies with grain sizes of about 15 to 30 μm. At triple points between these grains, a Nb-rich third phase can be observed. This is probably the $B8_2$-ordered ω_o-Ti_4Al_3Nb phase which is clearly identified in x-ray diffraction (XRD). TiAl-7.5Nb-1Mo (figure 1b) has a typical as-cast microstructure consisting of dendritic elongated lamellar ($\alpha_2+\gamma$) colonies up to about 100 μm in length. Between these colonies and at triple points a (Nb,Mo)-rich phase can be observed that is identified as β-phase by XRD. However, the presence of β_o cannot totally be ruled out, as discussed later. Although the microstructure of both alloys varies due to the different production processes, they have a similar phase composition showing a significant amount of the third phase, of about 5 to 10 vol.-%.
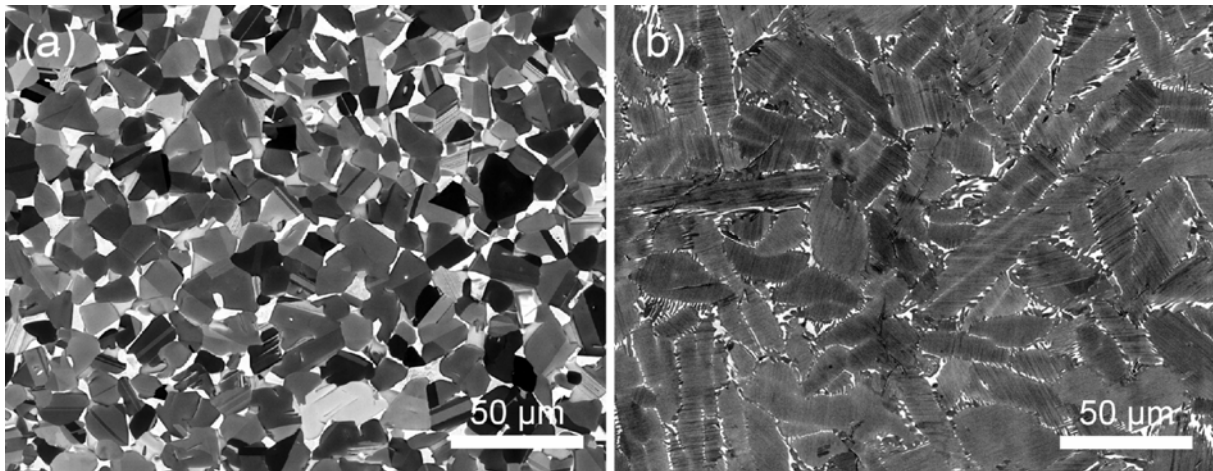

Fig. 1. Microstructure of (a) Ti-45Al-10Nb and (b) Ti-45Al-7.5Nb-1Mo-0.1B. Scanning electron microscope (SEM) images taken in backscattered electron (BSE) mode, i.e. γ-grains appear in dark grey, ($\alpha_2+\gamma$) lamellar colonies appear medium grey, and the Nb-rich third phase appears almost white.

***In situ* high-energy x-ray diffraction**

Figure 2 shows the temporal development of the diffraction pattern during the experiments starting in the first cooling cycle. Due to the effect of thermal expansion the reflections shift to smaller scattering vectors |q| during heating and to larger vectors during cooling. In the entire temperature range observed here the γ and α_2 reflections are visible in both alloys. However, the reflections of the third phase (**table 2**) show significant alterations.
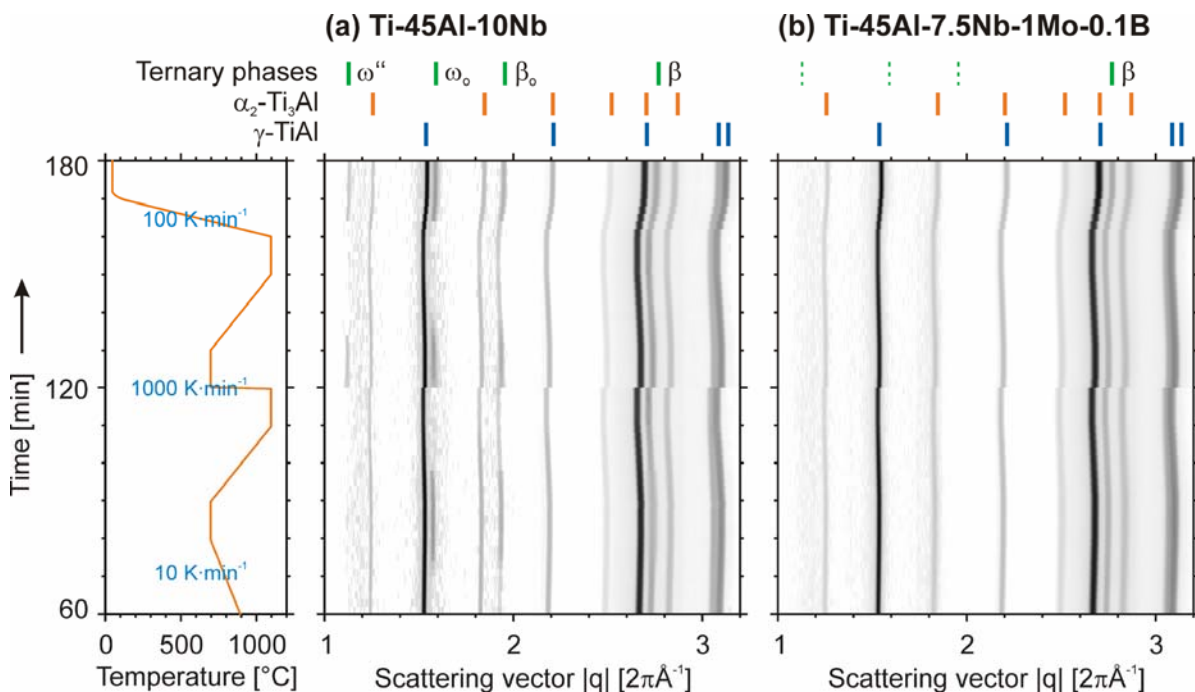

Fig. 2. Development of the diffraction pattern with temperature and time. The illustration starts in the first cooling cycle at t = 60 min. The pattern intensity is coded in greyscale; $|q| = 2\pi/d = 2\pi\cdot(2\sin\theta/\lambda)$. Gain and contrast of the weak superstructure reflections are increased. The characteristic reflection of each ternary phase is exclusively labelled in the diagram above; their additionally visible reflections are listed in table 2.

In TiAl-10Nb (figure 2a) two additional reflections are visible besides γ and α_2 reflections at the beginning of the first cooling cycle. They can be attributed to the β_o phase: 110 at |q| =

2.76 Å^{-1} and 100 at 1.95 Å^{-1}. The presence of the superstructure reflection 100 is a clear evidence for the presence of the ordered β_o phase with B2 structure. It is interesting to note that this weak reflection is not observable with laboratory x-ray sources in the same powder compact.[8] During slow cooling with 10 K·min^{-1} at T $\approx 780 \pm 20$ °C (t = 72 min) an additional reflection appears at |q| = 1.58 Å^{-1}, indicating the transformation of β_o to ω_o. All reflections besides those of the γ and the α_2 phase now can be indexed as ω_o reflections (see table 2): $10\overline{1}2$ and $11\overline{2}0$, respectively, at about 2.76 Å^{-1}, $10\overline{1}1$ at 1.95 Å^{-1}, and $10\overline{1}0$ at 1.58 Å^{-1}. So it is assumed that the β_o phase has fully or partly transformed to ω_o during this cooling step. While reheating the specimen ω_o transforms back to β_o at approximately T $\approx 870 \pm 40$ °C (t = 98 min) indicated by the vanishing of the $10\overline{1}0$ reflection of the ω_o phase at |q| = 1.58 Å^{-1}.

Table 2. Reflections of the third phases (indices and scattering vector |q|).

β	β_o	ω_o	ω''	|q|
110	110	$10\overline{1}2$ $11\overline{2}0$	$10\overline{1}2$ $11\overline{2}0$	2,76
	100	$10\overline{1}1$	$10\overline{1}1$	1,95
		$10\overline{1}0$	$10\overline{1}0$	1,58
			0001	1,14

After fast quenching with 1000 K·min^{-1} the β_o phase has transformed again to an ω related phase. However, besides the ω_o reflections this time a further additional weak reflection occurs at |q| = 1.14 Å^{-1}. It can be indexed as a superstructure reflection of a lower symmetric (trigonal) intermediate structure between β_o and ω_o, namely the 0001 reflection of ω''. Due to the high cooling rate and the low frame rate it is not possible to exactly determine the temperature of this transformation from β_o to ω''. During subsequent reheating this superstructure reflection vanishes at T $\approx 790 \pm 40$ °C (t = 134 min) indicating the

transformation of ω'' to ω_o. After further heating at $T \approx 870 \pm 40\,°C$ ($t = 138$ min), the retransformation of ω_o to β_o takes place.

During the third quenching sequence with a medium quenching rate of 100 K·min⁻¹ the intermediate phase ω'' is formed again, at $T \approx 680 \pm 200\,°C$ ($t = 164$ min). At lower temperatures up to the end of the experiment no further phase transformation occurs.

TiAl-7.5Nb-1Mo, in figure 2b, also shows reflections of three phases at t = 60 min. But in contrast to TiAl-10Nb only one further reflection, at $|q| = 2.76$ Å⁻¹, now is visible besides γ and α_2 reflections. This strongly points to the presence of disordered β (A2 structure) being the third phase in TiAl-7.5Nb-1Mo. However, ordered β_o (B2 structure) cannot totally be ruled out. Especially in Nb-rich TiAl alloys β and β_o are hardly distinguishable by XRD methods. The heavy Nb and Mo atoms prefer the Al atom sites in the ordered B2 structure of β_o.[12] These mixed Al(Nb,Mo) sites and the Ti sites show almost no electron density difference leading to very weak β_o superstructure reflections in x-ray diffractograms. During the whole experiment, neither at quenching nor at heating, did the β phase show any tendency to transform to another third phase in TiAl-7.5Nb-1Mo, which is again in contrast to TiAl-10Nb.

Transformation mechanisms

The transformation of β_o to an ω related phase was studied first by Bendersky et al. in alloys with a chemical composition near the stoichiometric composition of Ti_4Al_3Nb.[13] They found that the ordered ω_o phase crystallizes in a $B8_2$ structure. **Figure 3** shows the structural correlation between β_o and ω_o. Both phases have a crystallographic orientation relationship according to $\{111\}\beta_o \parallel \{0001\}\omega_o$ and $<1\bar{1}0>\beta_o \parallel <11\bar{2}0>\omega_o$. The transformation of β_o to ω_o can be described by several minor structural alterations:

(1) The so called "layer collapse", i.e. every second and third former $\{111\}\beta_o$ layer merges into a double layer due to a small shift along the new $<0001>\omega_o$ direction.

(2) A change of the site occupancies, i.e. the heavy Nb atoms move into the single layers. Thus, the double layers are almost exclusively occupied by Al or Ti on their respective sites (see figure 3b,c).

(3) A small lattice deformation, i.e. the lattice is slightly compressed along the former $<111>\beta_o$ axis, i.e. the new $<0001>\omega_o$ axis, and obversely stretched along $<11\overline{2}0>\omega_o$.

Each of these alterations can be identified and distinguished from each other by its specific separate form in the diffraction pattern.[14]
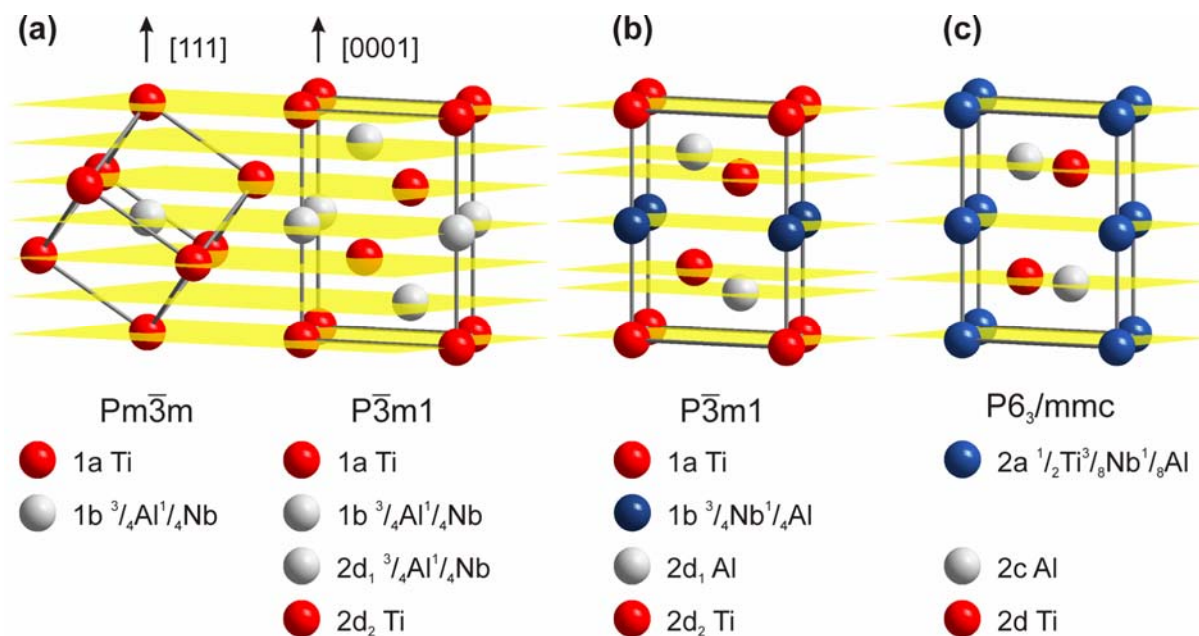

Fig. 3. Structural relationship between the phases (a) β_o, (b) ω'', and (c) ω_o. β_o is displayed in cubic as well as in trigonal configuration. Wyckoff positions and occupancies of the individual atom sites are given below the structures.

After quenching with rates of $100 \text{ K} \cdot \text{min}^{-1}$ and faster the intermediate ω'' phase occurs. The presence and intensity of various superstructure reflections in the diffraction pattern reveal that already double layers were formed and the heavy Nb atoms migrated to atomic sites located in the single layers during formation of the ω'' phase. Bendersky et al. also observed a similar structure after water quenching.[13] Obviously, the transformation of β_o to ω'' is a

relative fast process. Probably, as a first step a rearrangement of Al and Nb atoms on the Al(Nb) sites of the β_o phase takes place. Thus, Nb atoms are transferred out of Al sites of the later double layers whereas Nb-rich Al(Nb) sites are formed in the every second of the later single layers (figure 3a,b). It is suggested that the driving force for this rearrangement is to maximize the number of Al-Ti interactions which are stronger than Al-Nb and Ti-Nb interactions.[13,15] In fact, the amount of pure Al-Ti near neighbour configurations increases within the double layers. Parallel with this ordering, the collapse of the {111} planes takes place. Thereby the Al-Ti distances are slightly reduced in the double layers which additionally stabilizes the Al-Ti bonds. Hence, the transformation of β_o to ω'' simply requires a short-distance exchange of Al and Nb atoms between Al(Nb) sites and one of their six nearest Al(Nb) sites and this provides an obvious explanation for the fast formation of ω''.

The presence of the ω'' 0001 superstructure reflection provides a further argument that only Al(Nb) sites are involved in the first transformation step. Thus two alternating kinds of single layers are formed: layers composed of almost unaltered Ti sites and layers of former Al(Nb) sites which now are enriched in Nb (see figure 3b).

During reheating after rapid quenching with 1000 K·min^{-1}, the ω'' 0001 reflection vanishes indicating the transformation of ω'' to ω_o. At these elevated temperatures the atoms can migrate on and between the single layers by diffusion processes. Hence they distribute more and more homogeneously on the two different kinds of atomic sites in the single layers (sites 1a and 1b in figure 3b). As soon as the atomic sites in both kinds of single layers are equally occupied (site 2a in figure 3c) the symmetry has changed. Thus, the differences in scattering behaviour between the two kinds of single layers and in conjunction the 0001 reflection are extinct. The diffusion controlled transformation of ω'' to ω_o is obviously slower than the transformation of β_o to ω''. This is because only two nearest atomic sites are available in the

two adjacent single layers for this rearrangement (sites 1a or 1b in figure 3b), compared to the six possibilities of the first transformation step.

For a complete transformation of β_o to ω_o both formation steps have to be finished. During slow cooling with 10 K·min^{-1} β_o fully transforms to ω_o. In this case the specimen runs through the temperature ramp slowly enough to finalize both steps. Thus ω'' actually is a metastable phase. However during fast quenching the specimen does not stay long enough in the temperature range necessary for full homogenization. Hence this formation step is inhibited and the metastable ω'' will be conserved.

Both transformation steps are fully ($\omega'' \rightarrow \omega_o$) or at least partially ($\beta_o \rightarrow \omega''$) diffusion controlled processes. This is a significant difference to the transformation of disordered β to disordered ω (C32 structure; P 6/m m m) as it is known from Ti or Zr alloys which solely is a displacive transformation mechanism.[16,17] However, it is quite possible that pure displacive fluctuations will promote and/or accelerate the β_o to ω'' transformation step. Temporarily such fluctuations may form incompletely collapsed double layers. Thereby, the distances between sites involved in the rearrangement are reduced and this facilitates the diffusion.

Surprisingly, the third phase in TiAl-7.5Nb-1Mo, i.e. β or β_o, did not show any tendency to decompose at lower temperatures. It can be speculated, that Mo actually stabilises the disordered β phase (or ordered β_o if present). Singh et al. [18] solely observed β_o in an as cast Ti-37.5Al-12.5Mo alloy whereas Bendersky et al. [13] clearly identify that β_o completely transformed to ω'' in as cast Ti-37.5Al-12.5Nb. As indicated by the present study, obviously, even a small substitution of Nb by Mo seems to stabilise β or β_o, against decomposition. The stabilization can be either a thermodynamic effect, i.e. β or β_o is a stable phase down to room temperature in this alloy composition, or a kinetic effect, i.e. Mo drastically slows down one

step in the transformation pathway from β to ω''. However, this question cannot be further clarified based on the current results. In order to deepen the knowledge on interaction of various alloying elements during ternary phase formation in TiAl alloys further experiments are planned.

Conclusions

Ternary β phase improves the processing behaviour of γ-TiAl based alloys at elevated temperatures, but it can transform to various ternary phases at lower temperatures. A few of them are assumed to embrittle the material. Thus, the exact transformation pathways depending on alloy composition and heat treatment are of major interest for alloy design and processing.

The transformation of ternary phases in Nb-rich γ-TiAl based alloys was studied by *in situ* high-energy x-ray diffraction (HEXRD). Two alloys, Ti-45Al-10Nb and Ti-45Al-7.5Nb-1Mo-0.1B, were subjected to a temperature ramp of repeated heating cycles with subsequent quenching at different rates.

A reversible transformation $\beta_o \leftrightarrow \omega_o$ is observed *in situ* in Ti-45Al-10Nb. At high quenching rates (≥ 100 K·min^{-1}) the metastable intermediate ω''-phase can be preserved. The complete transformation $\beta_o \rightarrow \omega_o$ consists of two steps which are both diffusion controlled. But the transformation step between β_o and ω'' only needs rearrangement over relative short distances which can occur significantly faster than the diffusion processes necessary for the $\omega'' \rightarrow \omega_o$ transformation.

Otherwise, no transformation of β or β_o is observed in Ti-45Al-7.5Nb-1Mo-0.1B. Obviously, even a small amount of Mo stabilises β or β_o against transformation.

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