

Original

Stark, A.; Oehring, M.; Pyczak, F.; Lippmann, T.; Lottermoser, L.; Schreyer, A.:
**The Transformation Mechanism of Beta Phase to Omega-Related
Phases in Nb-Rich Gamma-TiAl Alloys Studied by In Situ High-
Energy X-Ray Diffraction**
Materials Science Forum, Mechanical Stress Evaluation by Neutrons
and Synchrotron Radiation VI (2013)
Trans Tech Publications

DOI: [10.4028/www.scientific.net/MSF.772.85](https://doi.org/10.4028/www.scientific.net/MSF.772.85)

The transformation mechanism of β phase to ω -related phases in Nb-rich γ -TiAl alloys studied by *in situ* high-energy X-ray diffraction

Andreas Stark^a, Michael Oehring^b, Florian Pyczak^c, Thomas Lippmann^d,
Lars Lottermoser^e, Andreas Schreyer^f

Institute of Materials Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany

^aAndreas.Stark@hzg.de, ^bMichael.Oehring@hzg.de, ^cFlorian.Pyczak@hzg.de,
^dThomas.Lippmann@hzg.de, ^eLars.Lottermoser@hzg.de, ^fAndreas.Schreyer@hzg.de

Keywords titanium aluminides, phase transformation, omega phase, X-ray diffraction, synchrotron radiation

Abstract. In recent years intermetallic γ -TiAl based alloys with additional amounts of the ternary bcc β -Ti(Al,Nb) phase attracted increasing attention due to their improved workability at elevated temperatures. Depending on alloy composition and heat treatment the ductile high-temperature β phase can transform to several ordered phases at lower temperatures. However, currently available phase diagrams of these multiphase alloys are quite uncertain and the precipitation kinetics of some metastable phases is far from understood.

In the present study various transformation pathways of the third phase were observed *in situ* by means of high-energy X-ray diffraction using synchrotron radiation. A Ti-45Al-10Nb (at.%) specimen was subjected to a temperature ramp of repeated heating cycles (700 °C - 1100 °C) with subsequent quenching at different rates. Depending on the quenching rate reversible transformations of the B2-ordered β_0 phase to different ω -related phases were observed. The results indicate that the complete transformation from β_0 to hexagonal B8₂-ordered ω_0 consists of two steps which are both diffusion controlled but proceed with different velocities.

Introduction

Intermetallic γ -TiAl based alloys belong to the most promising light-weight structural materials for use in aerospace and automotive applications at temperatures in the range of 650 to 800°C [1,2]. Conventional titanium aluminides are two-phase alloys consisting of tetragonal γ -TiAl (L1₀ structure; P 4/m m m) and small amounts of hexagonal α_2 -Ti₃Al (D0₁₉ structure; P 6₃/m m c). Due to their low density (~4 g/cm³), their high yield and creep strength up to 800 °C and their good oxidation resistance they have the potential to partly replace the more dense Ni based superalloys (~8 g/cm³) for applications as compressor and turbine blades in industrial and aviation gas turbines.

Currently, 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 in order to improve the hot workability is to induce the formation of more ductile phases by adding ternary alloying elements. For instance, the body-centered cubic (bcc) β -Ti(Al) phase (A2 structure; I m $\bar{3}$ m) can act as a ductilizing phase in TiAl alloys because it provides a high number of independent slip systems. Several authors have reported that stabilizing the β phase by alloying elements such as Nb, Mo, Ta or V, can significantly improve the hot workability [3-5].

In spite of this progress, the exact pathway of phase transformations in β phase containing TiAl alloys is not fully understood up to now. The disordered bcc β phase can transform to ordered cubic β_0 -TiAl phase (B2 structure; P m $\bar{3}$ m) at lower temperatures. However, large discrepancies exist between calculated and experimental transition temperatures [6,7]. Moreover, β and/or β_0 can decompose to ordered hexagonal ω_0 -Ti₄Al₃Nb phase (B8₂ structure; P 6₃/m m c) in high-Nb containing TiAl alloys [8,9]. On the other hand the formation of an orthorhombic phase (B19 structure; P m m a) is reported in Al-lean and Nb-rich TiAl alloys [4].

Generally, it is assumed that ordered phases, such as β_0 and ω_0 , can be detrimental to ductility due to their low crystal symmetry. Otherwise ω_0 containing TiAl alloys show also good plastic

formability at 800 °C [8] and novel B19 containing TiAl alloys exhibited an excellent combination of strength and ductility also at room temperature [10]. 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.

Conventional *in situ* methods for measuring phase transformations such as calorimetry or dilatometry reach their limits with multiphase alloys, e.g. titanium aluminides, because signal changes or peaks can be caused by more than one transformation. But X-ray diffraction methods are able to distinguish between various phases by their specific diffraction pattern. Thus, we used in our study combination of a dilatometer and a heating stage for diffraction experiments, i.e. a commercial quenching dilatometer that was prepared to be installed in the high energy X-ray beam at the HZG beamlines at the Deutsches Elektronen-Synchrotron (DESY) [11].

Experimental Procedures

The phase transformations were studied in a powder-metallurgical Ti-45Al-10Nb (at.%) alloy. The powder metallurgical processing route ensures a good chemical homogeneity of the specimen material. Alloy powder was atomized in the PIGA-facility [12] at the Helmholtz-Zentrum Geesthacht (HZG) and subsequently hot-isostatically pressed for 2 h at 1250 °C and 200 MPa. The powder compact, shown in Fig. 1, has a globular almost equiaxed grain structure that mainly consists of γ grains and a few $(\alpha_2+\gamma)$ lamellar colonies with grain sizes of about 15 to 30 μm . At triple points between these grains, a Nb-rich third phase can be observed, which is clearly identified as B8₂-ordered ω_0 -Ti₄Al₃Nb phase by X-ray diffraction [8]. The phase composition as determined by microscopy and X-ray diffraction amounts to approximately 83 vol.% γ -TiAl, 8 vol.% α_2 -Ti₃Al and 9 vol.% ω_0 -Ti₄Al₃Nb [13]. Cylindrical specimens with a diameter of 4 mm and a length of 10 mm were prepared by spark erosion for the experiments.

High-energy X-ray diffraction experiments were carried out at the HZG beamline HARWI II at DESY. The *in situ* experiments were done in transmission geometry using a beam cross section of 1x1 mm². In order to penetrate the specimen, high-energy X-rays were used with a photon energy of 100 keV, corresponding to a wavelength of $\lambda = 0.124 \text{ \AA}$. The resulting Debye-Scherrer diffraction rings were recorded every 120 s on a Mar555 flat panel detector with an exposure time of 20 s. Conventional diffraction patterns were achieved by an azimuthal integration of the Debye-Scherrer rings.

A commercial dilatometer DIL 805A/D (Bähr-Thermoanalyse GmbH) with special modifications for high energy X-ray diffraction experiments was used for various heating and quenching cycles [11]. The temperature was controlled by an S-type thermocouple spot welded on the sample and could be controlled to $\pm 0.5 \text{ K}$ with respect to the nominal temperature even for the highest cooling rate. The samples were inductively heated and quenched by blowing the specimen with Ar. The experiments were performed in Ar atmosphere in order to prevent oxidation of the sample surface.

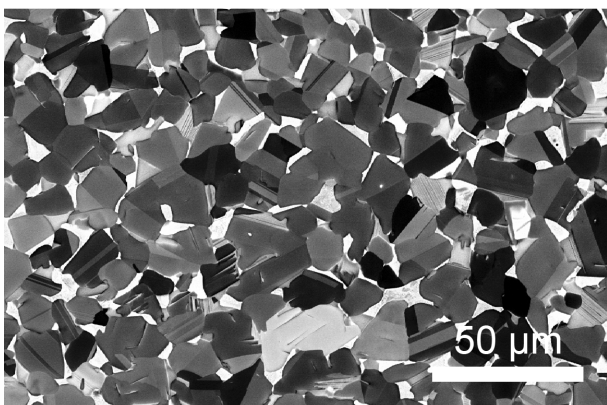


Fig. 1: Microstructure of the Ti-45Al-10Nb powder compact. Scanning electron microscope image taken in backscattered electron mode, i.e. γ grains appear in dark grey, $(\alpha_2+\gamma)$ lamellar colonies appear medium grey, and the Nb-rich third phase ω_0 appears almost white.

Results

Fig. 2 shows the temperature change together with the development of the diffraction pattern over time. Three heating/quenching cycles were performed in series. In each cycle the sample was heated up to 1100 °C and subsequently quenched to 700 °C with quenching rates of 10, 1000 and 100 K·min⁻¹, respectively. Reflections of γ and α_2 are permanently visible in the entire experimental temperature range, whereas the reflections of the third phase show significant alterations. However, due to the low detector frame rate and the in part high cooling rate it is not possible to determine exact transformation temperatures especially during some steps with rather high cooling rates.

At the beginning of the first cooling cycle (slow cooling with 10 K·min⁻¹) two additional reflections are visible besides γ and α_2 reflections. They can be attributed to β_0 reflections, namely 110 at $|q| = 2.76 \text{ \AA}^{-1}$ and 100 at $|q| = 1.95 \text{ \AA}^{-1}$. The presence of the superstructure reflection 100 is a clear evidence for the presence of B2-ordered β_0 phase. It is interesting to note that this weak reflection is not observable with laboratory X-ray sources in the same powder compact [8,13]. During further slow cooling the β_0 phase transforms to ω_0 at $780 \pm 20 \text{ °C}$. This is indicated by the formation of an additional reflection at $|q| = 1.58 \text{ \AA}^{-1}$. Now, all third phase reflections can be indexed as ω_0 reflections (Fig. 2). While reheating the specimen the ω_0 phase transforms back to β_0 indicated by the vanishing of the $10\bar{1}0$ reflection of ω_0 at approximately $870 \pm 40 \text{ °C}$.

After fast quenching with 1000 K·min⁻¹ again an ω -related phase is formed. However, besides the ω_0 reflections this time an additional weak reflection occurs at $|q| = 1.14 \text{ \AA}^{-1}$. It can be indexed as a superstructure reflection of a lower-symmetric (trigonal) intermediate structure between β_0 and ω_0 , namely the 0001 reflection of ω'' . During subsequent reheating this superstructure reflection vanishes at $790 \pm 40 \text{ °C}$ indicating the transformation of ω'' to ω_0 . After further heating at $870 \pm 40 \text{ °C}$, again the retransformation of ω_0 to β_0 takes place.

The intermediate phase ω'' is also formed during the third quenching sequence with an intermediate quenching rate of 100 K·min⁻¹, now at $680 \pm 200 \text{ °C}$. No further phase transformation occurs at lower temperatures up to the end of the experiment.

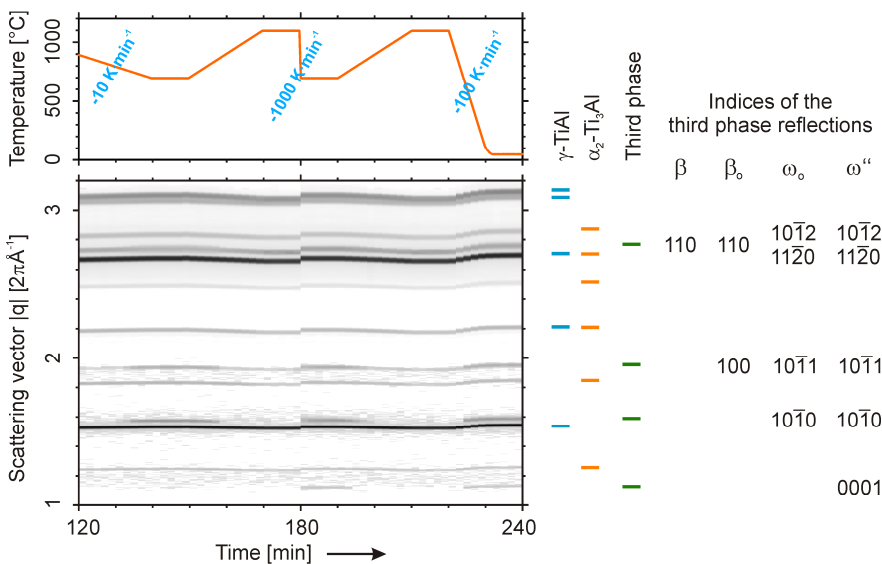


Fig. 2: Temperature ramp and development of the diffraction pattern with time. The pattern intensity is coded in greyscale; $|q| = 2\pi/d = 2\pi \cdot (2\sin\theta/\lambda)$. Gain and contrast of the weak superstructure reflections are increased for better visibility. The illustration starts in the first cooling cycle at $t = 120 \text{ min}$.

Discussion

Bendersky et al. [14] have studied the transformation of β_0 to an ω -related phase in alloys with a chemical composition near the stoichiometric composition of $\text{Ti}_4\text{Al}_3\text{Nb}$. They were the first who found that ordered ω_0 phase crystallizes in a hexagonal B8_2 structure. The structural correlation between β_0 and ω_0 is shown in Fig. 3a,c. Both phases have a crystallographic orientation relationship according to $\{111\}\beta_0 \parallel \{0001\}\omega_0$ and $\langle 1\bar{1}0 \rangle\beta_0 \parallel \langle 11\bar{2}0 \rangle\omega_0$. Three minor structural alterations are involved in the transformation of β_0 to ω_0 , which can be distinguished from each other by their specific forms in the X-ray diffraction pattern [13]:

(1) The so called “layer collapse”, i.e. every second and third former $\{111\}\beta_0$ layer merges into a double layer due to a small shift along the new $\langle 0001 \rangle_{\omega_0}$ direction.

(2) A small lattice deformation, i.e. the lattice is slightly compressed along the former $\langle 111 \rangle_{\beta_0}$ or the new $\langle 0001 \rangle_{\omega_0}$ direction and obversely stretched along $\langle 11\bar{2}0 \rangle_{\omega_0}$.

(3) 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.

The intermediate ω'' phase (Fig. 3b) occurs after quenching with rates $\geq 100 \text{ K} \cdot \text{min}^{-1}$. Presence and intensity of various superstructure reflections in the ω'' diffraction pattern reveal that during formation of the ω'' phase already double layers were formed and the heavy Nb atoms migrated to atomic sites located in the single layers. Bendersky et al. [14] observed a similar structure after water quenching. Obviously, the transformation of β_0 to ω'' is a relative fast process. The presence of the ω'' 0001 superstructure reflection proves that two alternating kinds of single layers are formed. This indicates that only Al(Nb) sites are involved in this transformation step. Nb atoms are transferred out of Al sites of the later double layers whereas Nb-rich Al(Nb) sites are formed in every second of the later single layers. Thus layers composed of almost unaltered Ti sites and layers of former Al(Nb) sites which now are enriched in Nb are formed (Fig. 3b). Hence, the transformation of β_0 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. This provides an obvious explanation for the fast formation of ω'' . 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 [14,15].

The ω'' 0001 reflection vanishes during reheating after rapid quenching indicating the transformation of ω'' to ω_0 . With increasing temperature the atoms start to migrate on and between the single layers by diffusion processes. As soon as the atomic sites in both kinds of single layers are equally occupied the ω'' 0001 reflection is extinct, the symmetry has changed and ω_0 is formed. This diffusion controlled transformation is obviously slower than the transformation of β_0 to ω'' because only two nearest atomic sites (sites 1a or 1b in Fig. 3b) are available for this rearrangement, compared to the six possibilities of the first transformation step.

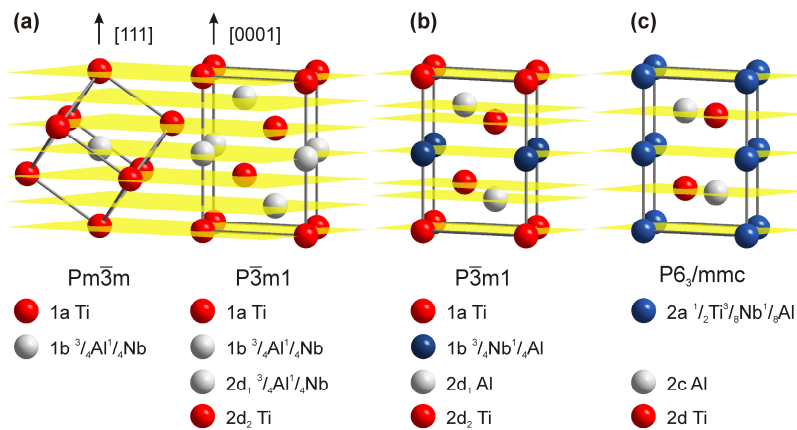


Fig. 3: Crystallographic structures and relationship of (a) β_0 , (b) ω'' , and (c) ω_0 . The unit cell of β_0 phase is displayed in cubic as well as in trigonal configuration. The Wyckoff positions of the individual atom sites and their ideal occupancies are given below the structures.

The complete transformation of β_0 to ω_0 requires both formation steps to be finished. In the case of slow cooling there is enough time available to finalize both steps. Thus ω'' actually is a metastable phase. However during fast quenching the second formation step is inhibited and the metastable ω'' will be conserved. The transformation $\omega'' \rightarrow \omega_0$ at re-heating after fast quenching and the reversibility of the $\beta_0 \leftrightarrow \omega_0$ transformation indicates on the other side that ω_0 is an equilibrium phase in this alloy at lower temperatures.

Recent experiments indicate that the transformation of β to ordered ω_0 in Nb-rich TiAl alloys requires the ordering transformation $\beta \rightarrow \beta_0$ as a primary step. A Ti-45Al-7.5Nb-1Mo-0.1B alloy that also has a three-phase composition was subjected to the same temperature ramp as discussed above. But during the whole experiment no phase transformation was observed [16]. However, the third phase in this alloy was disordered β phase. Additionally, a series of heating/cooling cycles between 1300 °C and 600 °C was done with the Ti-45Al-10Nb powder compact. The upper

temperature is above the ordering temperature of β , estimated at 1190 ± 10 °C. During fast quenching ($2000 \text{ K}\cdot\text{min}^{-1}$) the ordering transformation $\beta \rightarrow \beta_0$ was suppressed. In this case no transformation to ω -related phases was observed during slow reheating ($20 \text{ K}\cdot\text{min}^{-1}$). These results will be discussed in detail in a forthcoming paper.

Conclusion

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

The transformation of ternary phases was studied in a Ti-45Al-10Nb alloy by *in situ* high-energy X-ray diffraction during repeated heating/quenching cycles with different quenching rates between 10 and $1000 \text{ K}\cdot\text{min}^{-1}$.

The reversible transformation $\beta_0 \leftrightarrow \omega_0$ was observed *in situ*. This transformation consists of two diffusion controlled steps. The first transformation step $\beta_0 \rightarrow \omega''$ only needs atomic rearrangements over relative short distances which can occur significantly faster than the diffusion processes necessary for the second transformation step $\omega'' \rightarrow \omega_0$. By quenching with rates $\geq 100 \text{ K}\cdot\text{min}^{-1}$ the metastable intermediate ω'' -phase can be preserved at low temperatures.

This study demonstrates that the combination of synchrotron radiation and the quenching dilatometer is an excellent tool for the analysis of transformations in multiphase alloys and thus for advanced alloy design.

References

- [1] H. Kestler and H. Clemens, in: *Titanium and Titanium Alloys*, edited by C. Leyens and M. Peters, Wiley-VCH, Weinheim (2003) 351-392.
- [2] *Structural Aluminides for Elevated Temperature Applications*, edited by Y.-W. Kim, D. Morris, R. Yang and C. Leyens, TMS, Warrendale, PA (2008).
- [3] M. Takeyama and S. Kobayashi, *Intermetallics* 13 (2005) 993-999.
- [4] F. Appel, M. Oehring and J. D. H. Paul, *Adv. Eng. Mater.* 8 (2006) 371-376.
- [5] H. Clemens, W. Wallgram, S. Kremmer, V. Güther, A. Otto and A. Bartels, *Adv. Eng. Mater.* 10 (2008) 707-713.
- [6] V.T. Witusiewicz, A.A. Bondar, U. Hecht and T.Ya. Velikanova, *J. Alloys Comp.* 472 (2009) 133-161.
- [7] T. Schmoelzer, K.-D. Liss, G. A. Zickler, I. J. Watson, L. M. Droessler, W. Wallgram, T. Buslaps, A. Studer and H. Clemens, *Intermetallics* 18 (2010) 1544-1552.
- [8] A. Stark, A. Bartels, H. Clemens and F.-P. Schimansky, *Adv. Eng. Mater.* 10 (2008) 929-934.
- [9] S. Bystrzanowski, A. Bartels, A. Stark, R. Gerling, F.-P. Schimansky and H. Clemens, *Intermetallics* 18 (2010) 1046-1055.
- [10] F. Appel, J.D.H. Paul and M. Oehring, *Mater. Sci. Eng.: A* 510-511 (2009) 342-349.
- [11] P. Staron, T. Fischer, T. Lippmann, A. Stark, S. Daneshpour, D. Schnubel, E. Uhlmann, R. Gerstenberger, B. Camin, W. Reimers, E. Eidenberger, H. Clemens, N. Huber and A. Schreyer, *Adv. Eng. Mater.* 13 (2011) 658-663.
- [12] R. Gerling, H. Clemens, and F.-P. Schimansky, *Adv. Eng. Mater.* 6 (2004) 23-38.
- [13] A. Stark, *Textur- und Gefügeentwicklung bei der thermomechanischen Umformung Nb-reicher Gamma-TiAl-Basislegierungen*, Shaker Verlag, Aachen (2010).
- [14] L. Bendersky, W. Boettinger, B. Burton, F. Biancaniello and C. Shoemaker, *Acta Metall. Mater.* 38 (1990) 931-943.
- [15] M. Sanati, D. West and R. C. Albers, *J. Phys.: Condens. Matter.* 20 (2008) 465206.
- [16] A. Stark, M. Oehring, F. Pyczak and A. Schreyer, *Adv. Eng. Mater.* 13 (2011) 700-704.

Mechanical Stress Evaluation by Neutrons and Synchrotron Radiation VI

10.4028/www.scientific.net/MSF.772

The Transformation Mechanism of β Phase to ω -Related Phases in Nb-Rich γ -TiAl Alloys Studied by *In Situ* High-Energy X-Ray Diffraction

10.4028/www.scientific.net/MSF.772.85