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In-Situ High Energy X-Ray Diffraction Study and Quantitative Phase Analysis in the α+γ Phase Field of Titanium Aluminides

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Quantitative atomic structure and phase analysis in the titanium aluminide intermetallic system of composition Ti-45Al-7.5Nb-0.5C (at %) has been conducted in-situ by use of high-energy X-ray diffraction from a synchrotron and evaluated using the Rietveld method, implementing a model for atomic order in the α-phase which describes the order to disorder transition $\alpha_2 \rightarrow \alpha$ at the eutectoid temperature. The order parameter exhibits unexpected behavior and is entangled with the competition of different kinetic processes.

Keywords: *titanium aluminides; intermetallic compounds; order-disorder phenomena; phase transformation kinetics; synchrotron radiation;*

The properties of intermetallic γ-based TiAl alloys render them very desirable for high temperature applications in the automotive and aerospace industries [1]. Understanding of the alloy's phase constituents and behavior over transition temperatures is important for optimizing the mechanical properties of the material. In classical physical metallurgy, micro structural and atomic arrangements from heat treated samples are studied ex-situ after being quenched from a high temperature state, whilst temperatures of phase transitions and reactions are often obtained from differential scanning calorimetric measurements. Although in-situ diffraction studies have been reported earlier [2, 3], very little is known about the observed details behind phase transitions. With the introduction of high-energy X-ray diffraction, however, information can be gathered in real time and in-situ from the bulk of a material [4, 5, 6, 7]. Such data sets are extremely rich in information and now shed light upon the characteristic phase evolution occurring some distance from the transition temperature. The present study follows the competition between phases within the α+γ two-phase field, figure (1), of a high niobium containing titanium aluminide alloy, which is one of the most important interplays in the processing of these intermetallic materials. The multitude of microstructures in this phase field ranging from globular, duplex to lamellar [1], highlights the need for quantitative in-situ information, both at and far from the thermodynamic equilibrium which has been investigated in this work.

The investigated Ti-45Al-7.5Nb-0.5C sample (composition in atomic %) is part of a series [8] of different high Nb containing γ-TiAl based alloys which have been produced using a powder metallurgical approach, guaranteeing a homogeneous chemical distribution of the constituting elements. Pre-alloyed powder of the alloy was produced by means of gas atomization in the PIGA-facility (Plasma Melting Induction Guiding Gas Atomization) at the GKSS Research Center [9]. Powder of particle size < 180 μm was placed into a titanium can, which then was degassed, welded and subsequently hot-isostatically pressed (HIP) at 200 MPa for 2 hours at 1553 K. Chemical analyses indicates that the composition of both the alloy powder and the HIP material, match the nominal compositions within the experimental error. After HIP, the content of oxygen and nitrogen was analyzed to be 450 mass-ppm and 50 mass-ppm, respectively. During HIP a duplex microstructure is formed which consists of globular γ-TiAl / α_2-Ti_3Al grains. The average grain size is about 15 μm [10].

High-energy X-rays employing a 2-dimensional detector have been used to conduct diffraction studies at the ID15B beamline at the ESRF in Grenoble [4, 5]. A furnace was used to control the temperature with an input of helium flow to reduce oxidation [8]. The Ti-45Al-7.5Nb-0.5C sample in as HIP condition was ramped from room temperature up to 1375 K at 5 K / min before the ramp was lowered down to 2 K / min. Once the temperature reached 1675 K, it was left to hover for 5 minutes and was then subsequently cooled down to room temperature at 5 K / min. Although the sample was in direct contact with a regular type-S thermocouple, temperature readings on the ramp were not particularly accurate and required re-calibration to the α-transus temperature of the Ti-45Al-7.5Nb-0.5C alloy obtained via differential scanning calorimetry on a sample from the same batch [8].

The X-ray energy, wave number, detector distance and pixel size of the beamline were calibrated to 89.05 keV, 45.12 $Å^{-1}$, 1146 mm, and 0.150 mm, respectively. The software package *dataRring* was developed at ANSTO [11] on the SCILAB platform [12] to reduce the 2-dimensional diffraction patterns into one-dimensional diffractograms with a regular 2θ scaling as necessary to be converted into GSAS format for quantitative phase analysis [13, 14].

Batch Rietveld refinement was conducted in the α+γ phase field upon heating to the alpha transus temperature T_α = 1565 K, using a model that describes the co-existence of both phases, namely hexagonal α_2/α-Ti_3Al and tetragonal γ-TiAl.

The hexagonal phase was modeled as α_2 throughout the entire temperature range, taking into account atomic disorder within the unit cell itself. It treats the α_2 and α phases as a single phase (space group $P6_3/mmc$, a ~ 5.8 Å, c ~ 4.7 Å), with the α phase being a fully disordered state of the α_2 phase. There is also a constraint on the total site occupancy ratio which is set to 1. The model does not treat chemical disorder which is introduced by the deviation from stoichiometry. There is a continuous exchange of atoms between the γ- and the α-phase depending on the position in the phase diagram and thus a change of the composition of the α -phase takes place as temperature varies. This additional parameter was not included in the Rietveld model and thus chemical disorder will have to be added to the results obtained from the fit, which has not been further considered here. We can interpret the site occupancies being 100 % for maximal order as the chemical composition of the phase will allow.

Further, the Nb atoms were treated as sitting statistically distributed on the Ti sites and both kinds of atoms could not be distinguished in the model. Without any doubt, the Nb content influences all evaluated data as there are phase fraction, lattice parameters and the eutectoid temperature T_{eu}. Also it is known, that the carbon content stabilizes and leads to a higher c/a ratio of the α_2-phase [8], but we did not aim to specify these influences in the present work, which would need comparable data without these elements.

Figures (2a and 2b) show the integrated intensity values of the γ-001 and α_2-101 reflections as a function of temperature for both heating and cooling. Upon heating, the α_2-phase drops considerably at the $\alpha_2 \rightarrow \alpha$ transition which occurs at T_{eu} = 1476 K, while the γ-001 intensity drop has a kink in its slope and decreases continuously until T_{α} = 1565 K. In contrast, the nucleation of the γ-phase is delayed upon cooling and appears at 1518 K resulting in an undercooling of -47 K. Undercooling effects of this transition were observed at numerous occasions [15] and stem from the small difference in the Gibbs free energy of both phases at T_{α}. It increases at lower temperatures driving the probability for nucleation and then the growth of the appearing γ-phase. The α_2-101 reflection however, reappears at a higher temperature 1539 K, which is +63 K earlier than expected at T_{eu}, which itself was obtained from the heating part and complementary differential scanning calorimetry measurements. It shows a change in the slope at T_{eu}.
With the actual sets of data, an explanation for the early observation of ordering of α to α_2 can only be speculative and may be related to changes in local chemistry and α_2 stabilizing oxygen content which was taken up during the experiment. Comparison of the behavior of the intensities also shows that the phase fractions γ / α are higher on heating than on cooling. However, for this paper, the following quantitative analysis will concentrate on the heating section only.

The quantitative Rietveld results are presented in figures (2c, d, e, f) for the γ and α phase fractions, the c/a ratio of lattice parameters and site occupancies of the α_2-phase as well as for the c/a ratio of the γ-phase respectively.

It can be seen from figure (2c) that the system starts with a phase fraction of 78% γ and 22% α_2 composition which increases to 81% γ at 1280 K, before the γ transforms into α and vanishes at T_{α}. We attribute this initial raise in γ to a residual, non-equilibrium state of the phase composition in the starting material. Although furnace cooling is used after the HIP process, a higher α_2 phase fraction is retained at room temperature in contrast to the expected values for thermodynamic equilibrium for which an infinite small cooling rate is required. Around 1050 K a small raise in γ-fraction can be seen from figure (2c). It is assumed that at this temperature the constituting atoms become mobile enough to undergo the phase transition $\alpha_2 \rightarrow \gamma$ [16]. At higher temperatures, the $\gamma \rightarrow \alpha_2$ transition prevails and takes off rapidly at 1460 K.

The qualitative behavior of the c/a ratio in the α_2-phase is similar, namely starting with a relative high value of 0.8062 which increases above 1050 K to peak with a value of 0.8073 at 1205 K, before continuing to decrease to 0.8033 towards T_α where the phase undergoes an order → disorder transition. The change in composition in the α_2-phase dominates the behavior of the c/a ratio. The system starts with a small over-saturation of the α_2-phase due to the production history (HIP and cooling). The mobility of atoms becomes high enough above 1050 K that the concentrations of (Ti, Nb) and Al try to reach the equilibrium. c/a starts to increase accordingly due to an increase of the Ti-content in the α_2-phase and a small decrease of the phase fraction. Around 1200 K the equilibrium of phases and phase composition is reached and the process of increasing chemical disorder can be followed upon further heating which is combined with a steady decrease of the Ti-content in the α_2-phase resulting in the observed linear decrease of c/a. It is observed, that a linear extrapolation of the c/a decrease up to T_α meets again the c/a-ratio of the disordered α-phase.

The site occupancy curves from figure (2e) represent the average amount of disorder of the chemical disorder within the site occupancies of the Ti and Al atoms for the α_2-phase, with both curves for one type of site having a total site occupancy of 100 %. Due to the slow cooling rate during sample manufacture, the material initially starts off in near thermodynamic equilibrium with a fairly low amount of atomic disorder. The order in the α_2 phase at room temperature is high with 94.1% of Al atoms on Al lattice sites and 97.9% of Ti (+Nb) atoms on Ti lattice sites. Thus 5.9% of Ti (+Nb) and 2.1% of Al atoms can be said to be in an atomically disordered state. The Ti : Al ratio of the disordered part evaluates to 2.8 : 1 which is close to the expected stochiometric value of 3 : 1 for Ti_3Al.

However, as the temperature approaches T_α, the amount of disorder slowly increases until the phase transition is reached, at which there is a sudden jump in the occupancies of the atoms, defining the phase transition at T_{eu}. After the phase transition, the amount of Ti atoms sitting on both Ti and Al sites tend towards ~75 % and the amount of Al atoms sitting on both Al and Ti sites tend towards ~25 %, again following closely to the initial stoichiometric ratio of Ti_3Al.

A closer inspection of the occupancy behavior over the whole heating ramp reveals a tendency towards 100 % order at 1300 K. This is consistent with the behavior of the phase fraction and c/a ratio of the α_2-phase, where disorder, initially frozen into the system during the production process, disappears and atoms become mobile. However, the temperatures at which these behaviors peak differ; first occurring for the c/a ratio, then the phase fraction followed by the site occupancy. Through this, it seems that the c/a ratio is not solely determined by atomic order, but is further biased by another process which decreases it linearly with increasing temperature between 1250 K and 1440 K. It is noted that the ratio loses this linearity just before T_{eu} is reached, though the final point at T_{α} lies again on the extrapolated straight line.

The c/a behavior of the γ–phase is shown in figure (2f) as a function of temperature. It first decreases continuously until the onset of the $\alpha_2\rightarrow\alpha$ disorder transition at 1460 K and then increases again rapidly with the ongoing transition from $\gamma\rightarrow\alpha$, reaching its maximum value at T_{α}. The face centered tetragonal structure of the γ-phase distinguishes the crystallographic **c** direction by alternating layers of Ti and Al atoms from **a** staggered by planes each containing both atom types. Thus, if the lattice was fully disordered, there would not be a distinction between the directions and the lattice would be cubic. In a thought experiment, the lattice can be described by a cubic and a tetragonal component, which is related to the order of the phase. The observed behavior is then related to the chemical disorder, which is given in thermodynamic equilibrium by the phase line between the ($\alpha_{(2)}$+γ) and the γ phase fields [17]. As such the observed behavior of $c/a|_{\gamma}$ can be interpreted as follows: $c/a|_{\gamma}$ shows up to 900 K a small linear decrease, which describes the anisotropy of thermal expansion of the γ phase. In this temperature range $c/a|_{\alpha}$ is nearly constant. Above this temperature, the rate of decrease of the $c/a|_{\gamma}$ is more than linear until T_{eu} is reached. This is predominantly caused by the decrease of the Al-content in the γ phase and the induced chemical disorder. In accordance with the phase diagram [17] the lowest possible Al-content in the γ-phase is reached at T_{eu} and, therefore, the lowest $c/a|_{\gamma}$-ratio. Both values increase again at higher temperatures. The smaller slope of the respective phase line is consistent to the faster evolution above with respect to below T_{eu}.

Phase compositions and crystallographic lattice parameters in the $\alpha_{(2)}$+γ phase field of titanium aluminides depend on order and disorder within the atomic structure and on the initial deviation from the thermodynamic equilibrium during manufacture. The resulting phenomena manifest themselves as anomalies in behavior with respect to temperature. The study reveals a series of new results, such as the $\alpha_2\rightarrow\alpha$ transition and its corresponding precursor behaviors and aftereffects, which can be extrapolated to the α-transus temperature. During the decrease in temperature, undercooling occurs and the appearance of the γ phase is delayed, whilst the α-phase orders earlier than expected, which may be related to the interplay of the atomic structures and changes in local chemistry of the phases.

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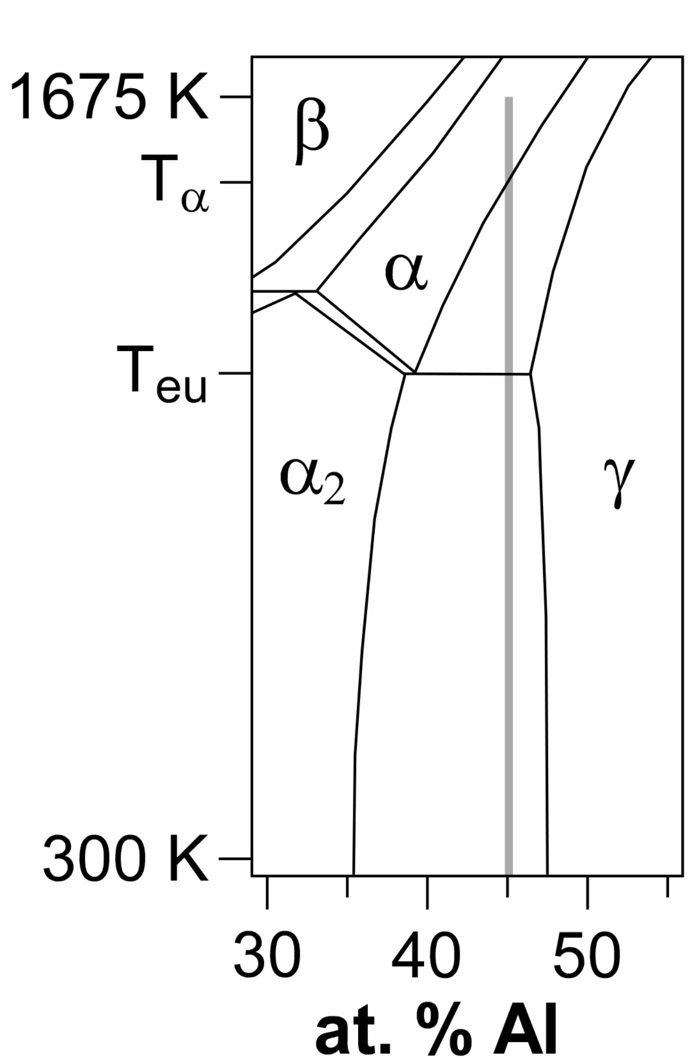

Figure 1:
Quasi-binary phase diagram based on Ti-Al from [17] showing the relevant region of interest. The scale to the left is not drawn linearly and indicates only schematically the heating range and transition markers for the used composition represented by the vertical gray line. It should be noted that alloying additions such as Nb and C have a marked influence on the shape of the phase diagram, see e.g. [8].

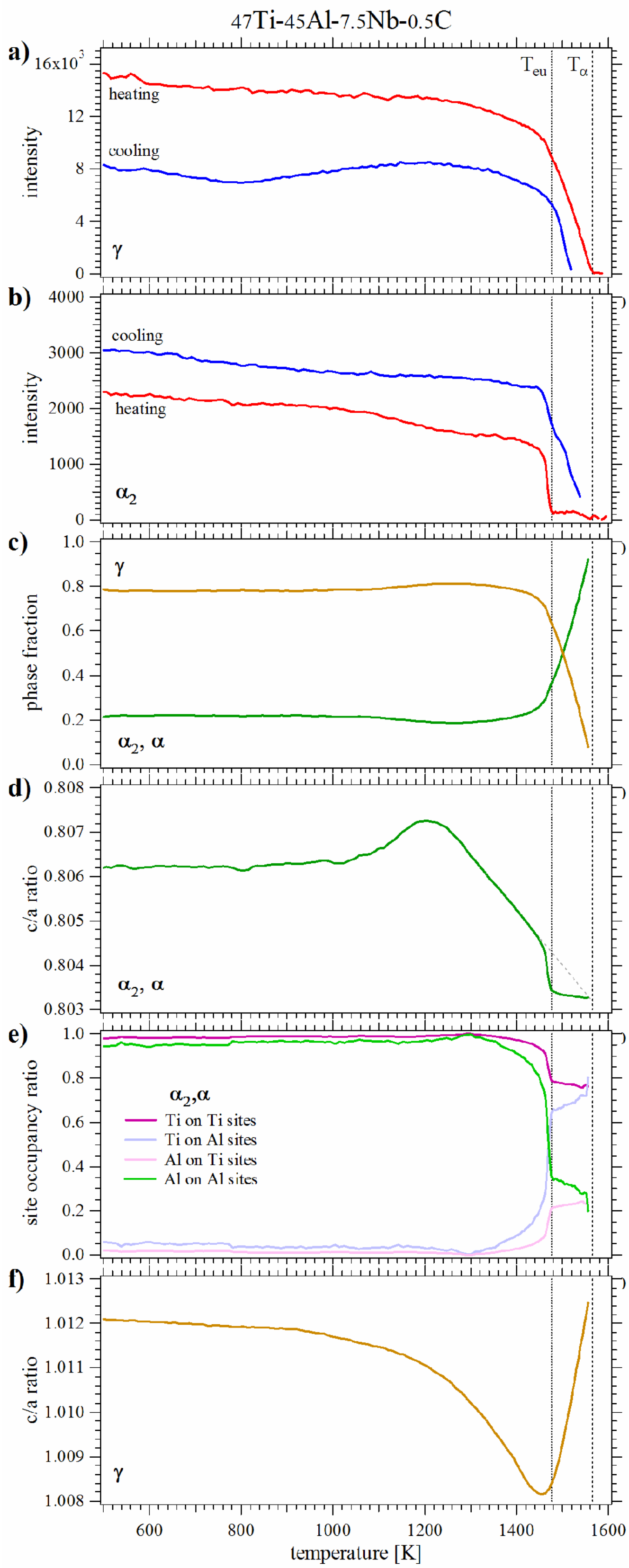

Figure 2:

Temperature dependencies of reflections and Rietveld results. a) peak intensity of the γ-001 reflection upon heating (upper) and cooling (lower curve); b) α_2-101 reflection upon heating (lower) and cooling (upper curve); c) γ / α phase fractions; d) ratio c / a and e) site occupancies in the α_2-phase; f) c / a of the γ-phase. A starting material Ti-45Al-7.5Nb-0.5C with duplex microstructure was used. The dotted lines indicate T_{eu} and T_{α}.

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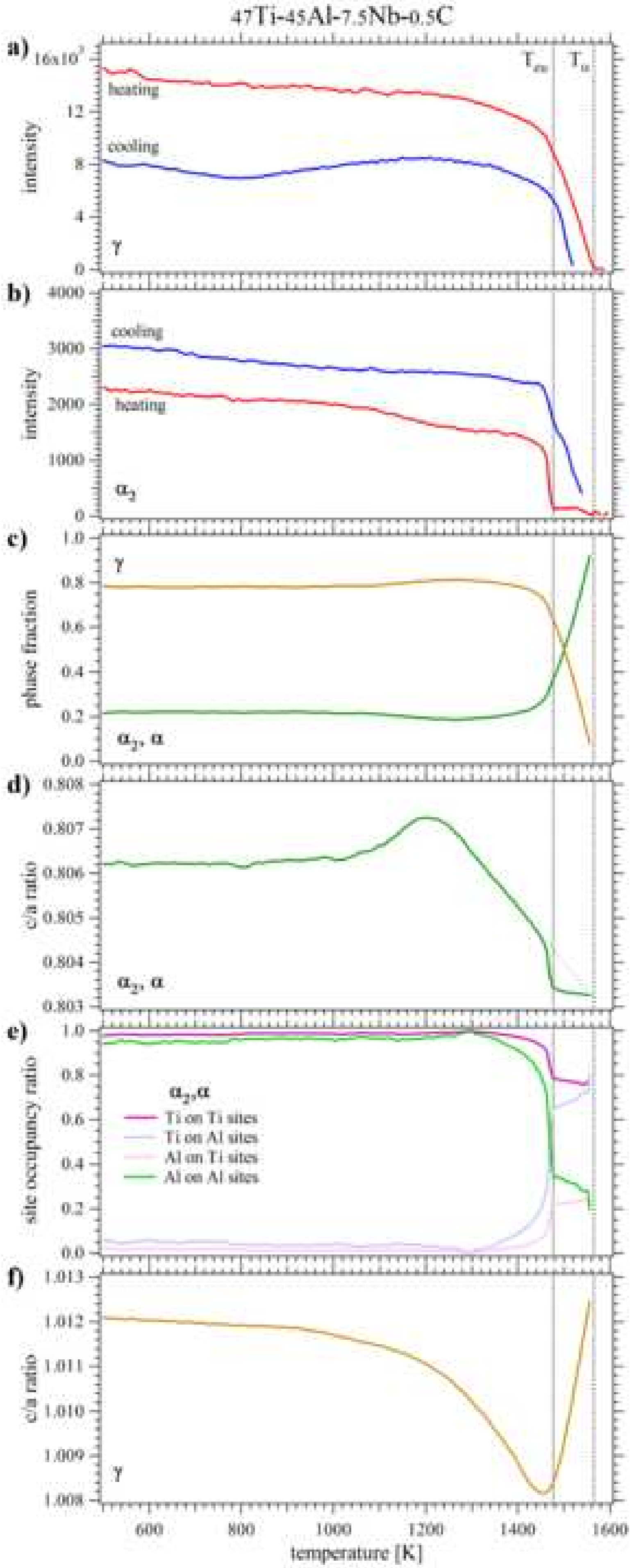

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