
Making movies in-situ at glowing temperatures up to 1300 °C through a microscope (false color image) and from two-dimensional X-ray diffraction (movie frames) reveal the lattice correlations, gradients and intermediate structures during phase transformations in titanium aluminide. A quenched, \(\alpha_2\)-rich \(\gamma\)-based TiAl first approaches its equilibrium by \(\alpha_2 \rightarrow \gamma\) on a heating ramp, disorders \(\alpha_2 \rightarrow \alpha\) and then evolves reversely \(\gamma \rightarrow \alpha\), which are morphologically different processes. More details can be found in the article by K.-D. Liss et al. on page 389.
Directional Atomic Rearrangements During Transformations Between the α- and γ-Phases in Titanium Aluminides**

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Phase transitions and their attendant atomic rearrangement processes in polycrystalline substances are most important for tailoring the physical properties of modern engineering materials. Multiphase alloys, such as γ-TiAl based intermetallics possess distinguished mechanical properties depending on their thermo-mechanical treatment history and thus their microstructure. Not surprisingly, both fundamental and industry-related research has been undertaken to find optimal process parameters. As these metallurgical investigations are often obtained off-situ, little is known about the kinetics of the phase transition, nor the path of atomic rearrangements. Here we report on novel, in-situ time resolved experiments which were conducted at elevated temperatures. The transition from α2-Ti3Al to γ-TiAl has been followed in both reciprocal and real space and is found to appear homogeneously over the bulk and to occur through an oriented rearrangement of atoms. At higher temperatures, the transition reverses and starts to grow slowly and stepwise from the grain boundaries into irregular shapes which impinge leading to grain refinement.

Usually, a phase transition can be monitored off the thermal equilibrium via dedicated experimental techniques such as Differential Scanning Calorimetry whilst metallurgical investigations such as microscopy and conventional diffraction methods employing 2-dimensional (2D) detectors have evolved. So far, those experiments were undertaken with accurately calibrated 2D detectors possessing read-out or scanning overhead times in the range of minutes. Some attention has been given to the development of time resolving setups, but mostly, 2D detectors have only been used in order to record a large solid angle to obtain good grain statistics for classical powder diffraction experiments. In these types of experiments it is common to spin the sample during acquisition for a better powder average, removing all the features of inter- and intra-grain relationships presented in this study. Complementary Laser Scanning Confocal Microscopy has been developed for highly time resolved high-temperature observations in real space.

Intermetallic titanium aluminides exhibit increasing technical importance for high-temperature applications in the automotive and aerospace industries. We have investigated the phase evolution of the composition Ti-45Al-7.5Nb (concentration in atomic %) which were previously tempered for 5 min at 1320°C and 1335°C and subsequently oil quenched in order to produce two samples of similar microstructure A and B, respectively, both resulting in 90 % α2-Ti3Al and 10 % massively transformed γ-TiAl phases in globular grains. When diffusion becomes important upon heating, such conditions far from thermodynamic equilibrium will first transform parts of the α2-phase into γ-phase (α2 → γ) until it reaches the eutectoid temperature...
$T_{eu}=1160^\circ$C at which $a_2$ disorders into $a$-phase ($a_2 \rightarrow a$) according to the phase diagram.\cite{13} Since $a$ is just the disordered phase of $a_2$, we work with a constant unit cell throughout the manuscript and mark all Miller indices in the $a_2$ notation. Above $T_{eu}$, the transformation ($\gamma \rightarrow a$) takes place and meets the $a$-transus at $T_a=1292^\circ$C (literature values from\cite{14}).

Snapshots in time at selected temperatures are given for the micrographs in Figure 1 and for the diffraction results in Figures 2 and 3. Above $600^\circ$C the first faint microstructures start to appear from the initially zero contrast of the polished surface of the sample whilst the diffraction patterns do not yet differ substantially from that obtained beforehand at room temperature: Randomly distributed Bragg reflections lying on barely occupied Debye-Scherrer rings testify to a relatively large grain size in comparison to the beam size. Incidentally a few grains in the sample match well or lie close to the Ewald condition revealing high intensity and thermal diffuse scattering.\cite{3}

Eventually an ultrafine lamellar microstructure appears homogeneously all over the bulk of the $a_2$-grains and can be resolved in the microscope, which further evolves to what is shown in Figure 1(c) at $850^\circ$C. It is known from literature\cite{15,16} that nanometer fine lamellae preferentially nucleate at grain boundaries. The qualitatively different behavior observed here relates to the fact that the annealing process is not gentle, instead it occurs on a relatively rapid heating ramp. Ultrafine lamellae may further nucleate on grain boundaries below the surface and then quickly grow into the entire grain towards the observed free surface. Note, some smaller grains do not transform at all, since they already consist of the massively transformed $\gamma$-phase. In reciprocal space, streaks evolve, Figure 2(b) and 3(c) starting around existing reflections of the $a_2$-grains and extending along a defined direction. When these streaks cross the position of a ring belonging to the $\gamma$-phase, intensity accumulates there. A movie created in real time from a sequence of experimental snapshots from the detector shows, that the intensity flows along the streak until the $a_2$-phase fades away leaving behind bright $\gamma$-reflections, see Figure 3(b–g).
The phase diagram reveals, that the transformation (\(\gamma \rightarrow \alpha\)) takes place above the eutectoid temperature, at which point the amount of \(\gamma\)-phase is maximal. The micrograph taken at 1100 °C indeed shows some new features which nucleate and develop at the grain boundaries. They evolve step-wise in a highly irregular shape as displayed for 1250 °C and their contrast becomes sharper until the alpha transus is reached.

Features in the surface relief as observed by the microscope will remain once they were formed and thus are still visible above the phase transitions, Figure 1(f), although we know from other studies that the system has already transformed into pure \(\alpha\). In reciprocal space, the correlated \(\alpha\)-reflection regains some intensity (3 h), which occurs by the reverse transformation in the bulk of the lamellar colonies, before almost all streaks disappear (3 i) and the morphology, particularly of the \(\alpha\)-rings changes to a less spiky but more continuous distribution stemming from a finer grain size (3 j-3 l).\(^{[19]}\) Yet the remaining matrix breaks up and the formerly sharp \(\gamma\)-reflections widen their mosaic spread up to 10 °. Even the massively transformed material is now affected by this transition and shows a very fine grained evolution of its microstructure.

Streaks in reciprocal space may occur on various occasions, such as gradients, truncation rods and diffuse scattering from phonons and here we may observe a superposition of all. Truncation rods, i.e. the peak broadening from the finite thickness of the lamellae play a role at the beginning of the phase transition, when extremely fine lamellae in the order of nanometers in thickness form. Next, the streaks take over a large fraction of intensity, which is comparable with the reflections of the pure phases, such that a considerable amount of the material must exist in gradual transition states. Gradients can exist in both, lattice parameter and orientation. A classical gradient crystal varies its lattice parameter from a start to an end value and thus a streak stemming from the lattice parameter distribution within this variation would be purely longitudinal, i.e. radial in the observed patterns and eventually be accompanied by an isotropic coarsening in the mosaic spread, due to compensation of misfits.\(^{[17,18]}\) The experimental streaks, however, are vectorial with a well defined and correlated radial and an angular or transverse component, expressed by a narrow but long streak. This gives evidence that a continuous distribution of lattice parameters exists, each linked through a well defined orientation angle to the original lattice orientation. Intermediate states exist in which the new lattice parameter grows gradually and coherently while the lattice mismatch is caught by corresponding, small angle grain boundaries. Last but not least, phonon softening\(^{[19]}\) may play a role in the rearrangement of atoms in martensitic and the suggested displacive phase transition.\(^{[15,20]}\) The dispersion relations would give raise to anisotropic thermal diffuse scattering, or streaks.\(^{[4,21]}\) Since this is a dynamic process, this third contribution should be considered for future evaluation of the mechanism.

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Fig. 3. Diffraction pattern from sample B evolving qualitatively on a temperature ramp (10 K/min), registered at ID15A with the image intensifier and the CCD camera. Sections of Debye Scherrer rings are shown with a common center well below each image. A legend is given in p) indexing from inside out \(\gamma\)-110, \(\alpha\)-200, \(\gamma\)-111 and \(\alpha\)-002 coinciding, \(\alpha\)-201 and the almost unresolved doublet \(\gamma\)-002/\(\gamma\)-200. Initially large \(\alpha\)-grains and few \(\gamma\)-spots a) exist; a faint streak forms around \(\alpha\)-201 and \(\gamma\)-002 b); which evolves in c), forming an opposite shoulder d) and extends to \(\alpha\)-002/\(\gamma\)-111 e). The \(\gamma\)-002/\(\gamma\)-200 intensity takes over in f) and the \(\alpha\)-201 peak almost fades away g) when the transformation reverses for a short time to feed intensity back h). The streak disappears completely i) and grain refinement occurs j) to l). Above the \(\alpha\)-transus m), no \(\gamma\)-rings are left and grain growth occurs rapidly until o).
The ($\gamma \rightarrow a$) transition at higher temperatures is more complicated. First, the mechanism may just reverse as observed in a short reverse flux along the faint streaks in reciprocal space which transforms the central bulk of the colonies. Another process nucleates at the grain boundaries: The higher, almost fcc symmetry of the $\gamma$-phase gives raise to 4 orientations of the nucleating, almost hcp $a$-phase. Therefore, the system starts from an unstable equilibrium and takes advantage from distortions and stresses at the grain boundaries. Nanometer-sized oriented $a$-lamellae form and then grow. Recrystallization processes as reported in[16] are necessary in order to grow the new directions throughout the ultrafine lamellar host structure and the irregular growth is due to the many allowed orientation relationships. Problems occur when the different domains intergrow into each other and impinge upon one another. Different domains do not necessarily match each other, thus many small-angle boundaries develop which finally leads to the observed grain refinement.

In conclusion, we have combined for the first time in-situ and in real-time both 2D diffraction and microscopy techniques to observe phase evolutions in a solid. There is unpublished evidence by further work of the authors, that similar transformations take place in many other material systems relevant for fundamental and applied research which has been overlooked in the past.

**Experimental**

Diffraction experiment: The synchrotron measurements were undertaken at the beamlines ID15A/B at the European Synchrotron Radiation Facility ESRF where in particular high energy X-rays are available for bulk study experiments.[22,24] A monochromator defines the incident beam to the sample which is scattered by a Debye-Scherrer ring registered by a 2D detector in the forward direction. For this experiment we set up fast detectors, first a commercial image intensifier tube coupled to the ESRF FReLoN CCD-camera in order to obtain data acquisition times between 0.3 s and 1 s.[23] which then was replaced by a THALES PIXYUM 4700 flatpanel pixel detector. The 2–4 mm thick sample was surrounded by a cylindrical furnace of 10 mm diameter which has been described elsewhere.[22,24]

Microscopy: A Laser Scanning Confocal Microscope has been set up with a high-temperature stage at the University of Wollongong.[10] The focal distance of such a device is large enough to obtain images from inside a mirror-furnace which can operate up to 1800 °C. Further the narrow band-width and the scan correction. For this experiment we set up fast detectors, first a commercial image intensifier tube coupled to the ESRF FReLoN CCD-camera in order to obtain data acquisition times between 0.3 s and 1 s.[23] which then was replaced by a THALES PIXYUM 4700 flatpanel pixel detector. The 2–4 mm thick sample was surrounded by a cylindrical furnace of 10 mm diameter which has been described elsewhere.[22,24]

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