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Pathways of phase transformation in β-phase-stabilized σ/γ-TiAl alloys subjected to two-step heat treatments

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ABSTRACT

In order to increase the maximum service temperature of intermetallic TiAl materials novel alloy and microstructure concepts are required. Thus, this study focuses on so-called σ/γ-TiAl materials alloyed with β-stabilizing elements Cr and Mo. These alloys in principle show improved mechanical capabilities, but their microstructure control necessitates judicious design of composition and heat treatment parameters. In this work the effects of the alloying elements Cr and Mo are elucidated. The presence of these elements retards the formation of γ- and σ-phases due to diffusional redistribution required, thereby, allowing for the formation of a fine-grained matrix with an embedded particle structure.

Intermetallic titanium aluminides with a σ/γ-microstructure as introduced by Ebrahimi et al. [1–3] have been suggested to outperform conventional γ-TiAl based alloys in terms of high temperature capabilities as evidenced by high temperature compression testing [4]. To this end, the existence of the intermetallic σ-phase ($D8_b$-Nb_2Al [5]) in the Ti-Al-Nb ternary alloy system is exploited [6]. The resulting microstructure ideally consists of a fine-grained γ-matrix with fine, homogeneously dispersed σ-phase particles. Thereby, a technological prerequisite is the formation of sub-micron-sized, disconnected σ-precipitates and a fine-grained γ-matrix [3,7]. Both requirements arise so as to avoid brittle fracture behavior, i.e. (i) prevention of precipitate fracture or interface delamination and (ii) facilitation of ductile deformation by the fine-grained γ-matrix providing for reduced stress accumulation at grain boundaries [4,8]. To meet these demands, two-step heat treatments in combination with alloying with β-stabilizing elements have been proposed [9,10]. The addition of β-stabilizing elements yields manifold effects on the microstructural evolution: (i) An enlargement of the high temperature β single phase region is obtained, while keeping the Nb content to a minimum, which in turn yields a desirable low volume fraction of disconnected σ-phase particles at room and service temperature [11–13]; (ii) The kinetics of Widmanstätten γ-phase formation is sufficiently retarded, which is needed as the preferential formation of Widmanstätten γ-laths leads to an inhomogeneous particle structure and premature brittle failure at ambient temperatures [8,13]; (iii) The preservation of a sufficient amount of β_o-phase upon quenching is of utmost importance and allows for the adjustment of a homogeneous and ultra-fine precipitate structure following the annealing sequence [10,14].

This study aims at extending the understanding of the microstructure formation in Ti-Al-Nb-Cr-Mo titanium aluminide alloys, since this fundamental knowledge is required to exercise control over the microstructure formation and the concomitant property profile. For this purpose, thermal, structural as well as microstructural analyses are conducted and combined with information from atom probe tomography and *ab initio* calculations. The results gained allow for novel insights into transformation pathways and alloying element effects during heat treatment of an intermetallic β-stabilized σ/γ-TiAl alloy.

Alloy buttons of Ø ≈ 75 mm and a mass of ≈ 150 g with the chemical composition given in Table 1 were produced by GfE Metalle und Materialien GmbH, Nuremberg, Germany. Subsequent furnace heat treatments (RHF 1600, Carbolite) were carried out under atmospheric conditions, whereby temperature was accurately controlled using three separate type-S thermocouples. For this purpose, specimens were cut to dimensions of approximately $5 \times 5 \times 15$ mm^3. The heat treatments were conducted by inserting the specimens into the preheated furnace and all cooling steps were performed by quenching either in water or in air directly from the hot zone.

In order to identify transformation sequences and to adjust heat treatment parameters, differential scanning calorimetry (DSC, LabSYS Evolution, Setaram Instrumentation) was performed on quenched sample material in Ar-atmosphere using a heating rate of 15 °C/min, 100 µl alumina crucibles and a sample quantity of ≈ 60 mg.

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Table 1
Chemical analysis including standard error of the investigated σ/γ-TiAl alloys determined by X-ray fluorescence spectroscopy.

	Ti	Al	Nb	Cr	Mo
m.%	bal.	26.06 ± 0.22	29.37 ± 0.23	5.62 ± 0.12	3.15 ± 0.09
at.%	bal.	44.50 ± 0.38	14.56 ± 0.11	4.98 ± 0.11	1.51 ± 0.04

The hardness of the different material conditions was determined by Vickers HV10 measurements (M4C 025 G3M, Emco-Test). Values given correspond to the arithmetic mean of at least five different indents and the error given is the standard deviation of the mean.

Microstructural analysis was conducted by scanning electron microscopy (SEM, EVO 50, Zeiss and Versa 3D DualBeam™, FEI) in backscattered electron (BSE) mode. Specimens were mounted into conductive resin, ground using SiC abrasive papers, polished with 3 μm diamond suspension and mechano-chemically polished using colloidal silica. The Olympus Stream Motion 1.9 software was used for quantitative image analysis.

Additional structural analysis was carried out by X-ray diffraction (XRD, D8 Advance, Bruker AXS) using Cu-K_α-radiation.

Atom probe tomography (APT, LEAP™ 3000X HR, Cameca Instruments Inc.) was performed using laser pulsing mode at 60 K, 250 kHz pulse repetition rate and 0.4 nJ pulse energy. The Cameca IVAS™ 3.6.8 software was used for data analysis. Needle-shaped APT specimens were prepared using a classic electrolytic etching procedure described in Ref. [15].

First principles calculations based on density functional theory (DFT) [16,17] were utilized to analyze the effects of alloying elements on phase stability. We used a plane-wave Vienna Ab initio Simulation Package (VASP) [18,19] with projector augmented wave method-capable pseudopotentials [20] describing the electron-ion interactions. Quantum mechanical electron-electron interactions were treated within the generalized gradient approximation (GGA) [21]. The γ-phase was modeled using $4 \times 4 \times 2$ supercells (64 atoms), based on a $\sqrt{2}/2 \times \sqrt{2}/2 \times 1$ unit cell containing one Al and one Ti atom. The β_o-phase was modeled using $3 \times 3 \times 3$ supercells (54 atoms) based on the B2 unit cell. Finally, the unit cell of the σ-phase, containing 30 atoms, was enlarged to a $1 \times 1 \times 2$ supercell (60 atoms). In all cases, we aimed at a similar number of atoms in the supercells, while keeping their shape close to cubic (equivalent distance to periodic-boundary images in all directions). Disorder induced by alloying was considered utilizing special quasi-random structures (SQS) [22] using a software developed in-house [23]. There, the short-range order parameters were optimized up to the 7th nearest neighbor distance. The reciprocal space was sampled using a Monkhort-Pack mesh with a k-point spacing of ≈ 0.12 Å^{-1}. The plane wave cut-off energy was set to 500 eV, and structural optimizations were finished when the total energy (per supercell) was changing by less than 0.1 meV. All structures were fully optimized with respect to volume, cell shape and atomic positions.

According to Ref. [5], the σ-phases lattice is subdivided into two Al sublattices and three Nb dissimilar sublattices, which were treated individually and the alloying elements were distributed according to the evaluated lattice site preference. The two sublattices of γ- and β_o-phases were populated according to each alloying elements' preferred substitution [24]. The stability of the phases and the elemental phase preference was assessed using their energies of formation, E_f^η, according to Eq. (1):

$$E^{\eta}_{f,Ti_nAl_mNb_iCr_jMo_k} = E^{\eta}_{Ti_nAl_mNb_iCr_jMo_k} - \frac{1}{n+m+i+j+k}(nE_{Ti} + mE_{Al} + iE_{Nb} + jE_{Cr} + kE_{Mo}), \quad (1)$$

whereby, the difference between the total energy per atom of the newly formed compound η and the total energies of the individual components in their stable crystal lattices is calculated. Changes of energies of formation, $\Delta E_f^\eta = E_{f,X}^\eta - E_f^\eta$, express the energy differences between phases after incorporation of either one Cr or Mo atom (denoted by the index X) and Cr- and Mo-free compounds.

Initially, the material was solution heat treated (SHT) at 1400 °C for 30 min followed by water quenching, referred to as condition A. In order to identify phase transition temperatures and to define the annealing parameters, material of this condition was reheated in the DSC evidencing two pronounced exothermal peaks at $T_{P1} \approx 620$ °C and $T_{P2} \approx 750$ °C. T_{P1} and T_{P2} are according to Bean et al. [14] associated with the formation of γ- and σ-phases, respectively. Thus, for further investigations two different material conditions were chosen: 700 °C for 30 min (condition B) and 950 °C for 120 min (condition C).

Fig. 1 depicts SEM micrographs after the SHT. Upon quenching (Fig. 1(a) and (b)) the microstructure displays a coarse grain structure corresponding to the prior β-grains present during SHT. At room temperature the ordered counterpart of the β-phase, the β_o-phase, is present as revealed by XRD. The former grain boundaries are decorated by Widmanstätten γ-phase (γ_W) (Fig. 1(a)) [14], whereas the grains' interior is percolated by lath-like structures, Fig. 1(b), closely resembling the martensitic structures reported in Ref. [25]. XRD measurements of the quenched material condition revealed the nature of this phase as the hexagonal α_2'-phase in accord to its known occurrence in the Ti-Al-Nb system as indicated in Refs. [6,26]. All microstructural analyses reported in the following sections were restricted to the grains' interior as the microstructure formation differs somewhat in the presence of course γ-scale (see e.g. Refs. [10,13,14]). The considerable hardness of 622 ± 4 HV10 of this microstructure is related to the β_o-phases high hardness, which stems from restricted dislocation mobility within the B2-ordered structure at ambient temperature [27,28].

Annealing the material at 700 °C for 30 min allows analyzing the early stages of phase transformation (Fig. 1(c), condition B). A very fine γ-phase structure is formed directly from the retained β_o-phase. At the γ-platelets' boundaries a bright contrast is visible indicating the pile-up of heavy elements and the concomitant early stages of σ-phase precipitation. Apparently, the extended isothermal annealing procedure allows the material to transform even below T_{P2}. The α_2'-laths decompose by forming the γ-phase (see enlarged section of the SEM micrograph), which is in agreement with earlier reports by Cheng and Loretto [29] and Zhang et al. [30]. Thereby, stacking faults prevailing in the martensitic α_2'-laths were suggested to act as nuclei of the newly forming γ-grains [30]. The lower hardness of the condition B of 519 ± 8 HV10 is related to the fact that the overall hardness is dominated by the comparably soft preponderant γ-phase.

Annealing at 950 °C for 120 min (Fig. 1(d)) yields the formation of a very fine particle structure possessing a Vickers hardness of 522 ± 4 HV10. Equal hardness values as in condition B can be explained as deformation is again mainly carried by the relatively soft γ-phase. In Fig. 1(d) the bright particulates correspond to σ-phase exhibiting a facetted morphology, while the matrix consists of γ-phase. Also, an intermediate gray phase is visible, which was identified by XRD as the β_o-phase. In the inset of Fig. 1(d) the phases are labeled for clarity. Apparently, the transformation of the SHT condition upon heating to a σ/γ-microstructure is incomplete, due to the presence of strong β-stabilizing elements. This observation suggests that the $\sigma + \gamma + \beta_o$ three-phase region present in the Ti-Al-Nb system [6] is extended to lower temperatures due to the addition of Cr and Mo. Quantitative phase analysis of the condition C yields $f_{\beta_o,C} \approx 6.4\%$ and $f_{\sigma,C} \approx 6.9\%$. The latter value is distinctly lower than reported in Refs. [9,10], where apparently all microstructural constituents with a bright contrast were attributed to the σ-phase fraction ignoring the presence of β_o-phase. It should be mentioned that a pronounced spatial adjacency of β_o- and σ-particles is observed. A quantitative grain size analysis of SEM images of the