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In situ small-angle X-ray scattering study of the perovskite-type carbide precipitation behavior in a carbon-containing intermetallic TiAl alloy using synchrotron radiation

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Abstract

Intermetallic γ-TiAl based alloys of the latest generation, e.g. TNM alloys with a nominal composition of Ti–43.5Al–4Nb–1Mo–0.1B (in at.%), exhibit the potential to be used in modern high-performance combustion engines due to their low density, high strength and creep resistance as well as their good oxidation properties at elevated temperatures. Alloying with C can further improve the high-temperature performance by both solid solution hardening and/or carbide formation. In this study, starting from a supersaturated TNM–1C alloy the precipitation behavior and thermal stability of perovskite-type carbides Ti_3AlC during isothermal annealing and ensuing re-heating to 1200 °C are quantified by means of an in situ small-angle X-ray scattering experiment using synchrotron radiation. Complementarily, the formed hierarchical structures on the nano-scale, i.e. p-type carbide precipitates within ultra-fine γ-lamellae of the α_2/γ-colonies, were investigated by means of monochromatic high-energy X-ray diffraction in combination with scanning and transmission electron microscopy. Additionally, an explanation of an obtained diffraction phenomenon is given, i.e. streak formation that is caused by the very small lamellar spacing of the γ-phase within the α_2/γ-colonies. It was also found that the geometrically well-defined nanostructure allows a correlation between the γ-lath thickness and a characteristic dimension of p-type carbides.

Keywords: Intermetallics; Titanium aluminides; Carbon; Precipitation hardening; X-ray synchrotron radiation

1. Introduction

In the last two decades γ-TiAl based alloys have been implemented for application as turbine blades and turbocharger wheels in modern high-performance combustion engines due to their attractive properties, e.g. low density of $\sim 4\ g\ cm^{-3}$ combined with enhanced high-temperature (HT) strength and creep resistivity up to 750 °C as well as their good oxidation behavior [1–3]. A further step to improve the HT capability of advanced intermetallic γ-TiAl based alloys, such as TNM alloys with a nominal composition of Ti–43.5Al–4Nb–1Mo–0.1B, is alloying with carbon [4–7]. Note that all compositions are stated in at.%. Thereby, C can act as an efficient solid solution strengthener [8] or form needle-shaped precipitates of perovskite-type Ti_3AlC carbides which are finely dispersed in the γ-phase [6,7,9].

As a powerful tool for studying phase transformations and the precipitation behavior of minor phases from a supersaturated matrix, e.g. p-type carbides, high-energy

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X-ray diffraction (HEXRD) can be applied. Furthermore, in situ performed small-angle X-ray scattering (SAXS) can give a deeper insight into the precipitation kinetics and thermal stability when p-type carbides are arranged continuously in the γ-matrix. Additionally, complementary information can be gained from transmission electron microscopy (TEM), i.e. size, orientation and morphology of p-type carbides, which is needed for the evaluation and validation of SAXS measurements. Moreover, the size of γ-lamellae within the α_2/γ-colonies is suggested to contribute to the appearance of the HEXRD pattern, i.e. streaking, but the mechanism behind this has not been clarified yet [10].

Aging at low temperatures, e.g. at 750 °C, of a supersaturated TiAl material leads to the formation of an ultra-fine hierarchical structure, i.e. fine γ-lamellae with a typical thickness of 10–100 nm wherein p-type carbides are finely precipitated [7]. The formed nanostructure depends on the specific orientation relationships between the constituting phases. Thus, the extremely small characteristic dimensions of these microstructural constituents can lead to a broadening of the HEXRD reflections. Therein, the peak broadening can be quantified by means of the so-called Scherrer equation [11,12]:

$$L = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \tag{1}$$

where L is the crystallite size; K represents the shape factor, taking values between 0.62 and 2.08 [12,13]; λ is the wavelength; β the full width at half maximum (FWHM); and θ denotes the Bragg angle of the center of the considered diffraction peak.

The SAXS measurements are evaluated by means of the two-phase model according to the small-angle neutron scattering (SANS) experiments as reported in Ref. [9]. Thus, the macroscopic differential scattering cross-section $d\Sigma/d\Omega$ is given as, e.g. [14]:

$$\frac{d\Sigma}{d\Omega}(q) = (\Delta\eta)^2 \int_0^\infty n(R) \cdot V(R)^2 \cdot F(q,R)^2 \cdot dR \tag{2}$$

Here, $\Delta\eta$ is the difference of the scattering length densities (SLDDs) of the matrix and the precipitates, $n(R)$ relates to the number density of precipitated particles with a size between R and $R + dR$, $V(R)$ is the precipitation volume and $F(q,R)$ corresponds to the form factor, wherein the absolute value of the scattering vector is defined as $q = 4\pi/\lambda \sin\theta$.

2. Material and experimental

The material for the current study was produced by GfE Metalle und Materialien GmbH, Germany, as described in Ref. [7] and has a chemical composition of Ti–43.35Al–4.06Nb–1.02Mo–0.11B–1.02C. Subsequent to ingot metallurgy, the TNM–1C material was hot-isostatically pressed (HIP) at 1200 °C for 4 h followed by furnace cooling (FC). The material exhibits a polycrystalline and fine-grained microstructure due to the precipitation of coarse-grained h-type carbides Ti_2AlC during the solid state phase transformations subsequent to peritectic solidification as reported in Ref. [7]. Especially the fine-grained microstructure is a necessary precondition for reliable examination by means of monochromatic X-ray radiation.

The precipitation kinetics, size evolution and thermal stability of p-type carbides were studied by means of an in situ SAXS experiment conducted at the HZG-operated beamline HEMS, using the experimental hutches P07-EH 3 and EH 4, at the Petra III storage ring of the synchrotron facility DESY in Hamburg, Germany. A sketch of the experimental setup is shown in Fig. 1. A cylindrical sample with a diameter of 5 mm and a length of 10 mm length was inductively heated in an adapted quenching and deformation dilatometer DIL 805 A/D of Bähr Thermoanalyse, Germany, according to the temperature–time (T–t) evolution given in Fig. 2. The monochromatic X-ray beam had a size of $0.8 \times 0.8\ mm^2$ and a wavelength of 0.12398 Å. The scattering data were recorded by employing a mar345 image plate detector from Marresearch, Germany, with a sample-to-detector distance of 11.654 m and an exposure time of 40 s. Due to the detector characteristics, the in situ SAXS measurements could be performed with a frame rate of 20 images h^{-1}. Slits made of pure tungsten minimized undesired scattering from the slits and thus ensured a low background. Data evaluation was performed by means of the program Fit2D with respect to azimuthal integration [15,16] followed by a fitting procedure of the derived scattering curves with the program SANSFit based on a least-square method iteration as conducted in Ref. [9]. The sample-to-detector distance of the SAXS measurements was calibrated by means of an Ag-Behenate standard, while the macroscopic scattering cross-section was calibrated by means of the known precipitated volume fraction of p-type carbides after annealing at 750 °C for 4 h, which was determined by Rietveld analysis of the diffraction data. Due to the maximum content of p-type carbides of <5 vol.%, effects arising from interparticle interference are expected to be negligible. The p-type precipitates were modeled as prolate ellipsoids of revolution with axes of $2R$, $2\mu R$, where R is the radius of the elongated particle with a size aspect ratio $\mu = 7$ [9]. The particles are suggested to be randomly oriented within the polycrystalline sample obeying a lognormal size distribution [9]. According to the two-phase model in Eq. (2) the scattering contrast primary depends on the difference of the chemical compositions of the γ-phase matrix and the precipitated p-type carbide particles. The SLDD, which corresponds to the scattering contrast, can be calculated according to $\eta_m - \eta_p$, where η_m and η_p are the scattering length densities (SLDs) of matrix and particles, respectively. Generally, η is given as the phase-specific quotient of the coherent scattering length b_c and the mean volume per atom v_a. For TNM alloys the SLDD between the γ-phase and the p-type carbide Ti_3AlC was determined to be $(1.27 \pm 0.03) \times 10^{11}\ cm^{-2}$ using phase