Materials Letters 64 (2010) 2608–2611

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Investigation of phase transformations by in-situ neutron diffraction in a Co–Re-based high temperature alloy

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ARTICLE INFO

Article history:
Received 17 March 2010
Accepted 24 August 2010
Available online 6 September 2010

Keywords:
Superalloy
Carbide
Neutron diffraction
Phase transformation
In-situ measurement

ABSTRACT

In-situ neutron diffraction at high temperatures was used to investigate phase transformation in a Co–Re-based alloy. Stability of carbides and transformation of Co matrix from ε (hcp) to γ (fcc) phase were studied. The ε ⇄ γ phase transformation exhibited a large hysteresis with temperature. The alloy has a complex microstructure with $Cr_{23}C_6$, TaC and σ phase stable over a wide temperature range. The hysteresis is the result of composition interplay between Co-matrix and other phases, e.g. Cr-carbide and σ. TaC is stable at high temperatures up to 1300 °C.

1. Introduction

Development of high temperature material is mainly driven by gas turbine needs. Today, Ni-based superalloys are the dominant material class in the hot section of turbines, but they operate very close to their melting temperature. Demands for applications at higher temperatures are presently met partly through component cooling and application of thermal barrier coatings. However, this approach cannot be sustained indefinitely unless the base metal melting temperature is also significantly increased. Therefore, many efforts are being made world-wide for developing new alloy systems to supplement the Ni-base superalloys in the future [1]. Co–Re-based alloys are being developed at the Technische Universität Braunschweig, with this aim. The goal is to develop alloys for applications at +100 °C metal temperature above present day single crystal Ni-base superalloys [2].

The refractory metal Re with very high melting point (T_M – 3182 °C) dissolves readily in Co and is completely miscible. Therefore, very high melting temperatures can be achieved in Co–Re alloys. Further alloying additions (e.g. Cr, Si, Ta, C etc.) impart strength and oxidation resistance in Co–Re-based alloys [3–5]. Pure cobalt has two allotropic forms: hexagonal close packed (hcp) ε and face centered cubic (fcc) γ, and the high temperature γ structure is metastable at room temperature. Re addition stabilizes the low temperature ε structure and in Co–Re alloys hcp→fcc transformation occur on heating. In-situ neutron diffraction measurement was used for the first time, to map this phase transformation during heating and cooling.

2. Experimental method

An experimental Co–Re-base alloy, Co-17Re-23Cr-1.2Ta-2.6C alloy (in at. %) designated CoRe-2, was melted in a vacuum arc furnace and cast into square bars (12 mm × 12 mm and about 70 mm long). The cast bars were hipped for 3 h at 1400 °C under Argon pressure of 200 MPa and solution treated between 1350° and 1450 °C for a total of 15 h and argon quenched. The polycrystalline alloy has equiaxed grains with an average grain size of 120 μm.

In-situ neutron diffraction (ND) measurements were used to study the phase transformation and structural stability in the temperature range 1100° and 1300 °C. The Stress-Spec instrument at the FRM II, Garching, Germany, fitted with a 2 dimensional position sensitive detector was used for the measurements [6]. High temperature vacuum furnace was employed for the in situ heating and cooling. Temperature was quickly changed in 5 K steps between 1100° and 1300 °C and diffractograms were collected during 10 min hold time at each step. The neutron wavelength was 0.1636 nm. A 30 mm long cylindrical sample of 6 mm diameter was used for the experiment. At Stress-Spec the slit in front of the sample was 5 mm wide and 10 mm high. The diffractometer has the possibility to rotate sample in the

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doi:10.1016/j.matlet.2010.08.066

beam, however, this option – although tested – was not necessary to use for the CoRe-2 alloy to obtain a smooth powder pattern. Measurement was done in transmission mode.

3. Results and discussions

A typical microstructure of CoRe-2 alloy in heat treated condition is shown in Fig. 1. A complex microstructure develops in this carbide strengthened Co–Re alloy, with different phases (TaC and $Cr_{23}C_6$ carbides, Cr_2Re_3-type σ phase) being stable at various temperature ranges. While both types of carbides have fcc structure (Space Group no. 225), same like the high temperature γ Co phase, the σ phase has a tetragonal structure (Sp. Gp. no. 136) and the low temperature ε Co a hcp structure (Sp. Gp. no. 194). The topologically closed packed (tcp) σ phase (Strukturbericht Designation: $D8_b$ and Pearson Symbol: tP30) and $Cr_{23}C_6$ ($D8_4$ and cF116) structures are very complex and have large number of atoms in their unit cells. In comparison the Co allotropes, i.e. ε (A3 and hP2) and γ (A1 and cF4), and TaC (B1 and cF8) have simple unit cells.

In the standard heat treated CoRe-2 alloy, $Cr_{23}C_6$-type and TaC carbides are actually present in different length scales – as large grain boundary or globular carbides and as very fine structures [2,3]. Fig. 1 shows the thin $Cr_{23}C_6$ lamellae and the fine dispersion of TaC (size ~ 30 nm) embedded in ε Co matrix between the lamellae. It is an ideal morphology of the hardening precipitate phases for high temperature creep resistance. However, long term stability of the microstructure at high temperatures is also important for gas turbine applications.

The diffractograms were recorded at RT before and after the in-situ heating cycle (Fig. 2a) and during temperature increase (1100–1300 °C) and decrease (1300–1075 °C) with 5 K steps in a selected 2θ angular range from 42° to 56° (where large peaks of the interesting phases are present). It shows no preferred orientation in the polycrystalline material. The evolution of the different peaks with the increasing temperature can be seen in the 3D plot (Fig. 2b). It can be seen, that the Co matrix structure is hcp at low temperature (hcp peaks are indexed in Fig. 2a) and gradually transforms to fcc with increasing temperatures above 1225 °C. All the diffractograms were analyzed by FullProf program [7] using Rietveld method [8] and the resulting phase fractions were deduced from the integral intensity of the respective peaks.

The phase transformation: ε (hcp) ⇄ γ (fcc) Co exhibits a large hysteresis (Fig. 3a and b) of more than 100 K. The heating and cooling rates in the in-situ experiment do not play a role here, as measurements were done isothermally on holding for 10 min at different temperatures (no phase content evolution with hold time was observed). Similar plots from the minor phases $Cr_{23}C_6$, TaC and σ are also shown in Fig. 3(c–e). While $Cr_{23}C_6$ also show hysteresis, the effect is minimal in the case of TaC. In contrast, the fraction of σ phase in the microstructure is not reversible on cooling from 1300 °C. Fig. 3e clearly shows that the σ phase fraction (i.e. integral intensity) does not return to the original value on cooling – that is, some σ phase is stabilized to lower temperature at the expense of hcp Co matrix (see Fig. 3a and e).

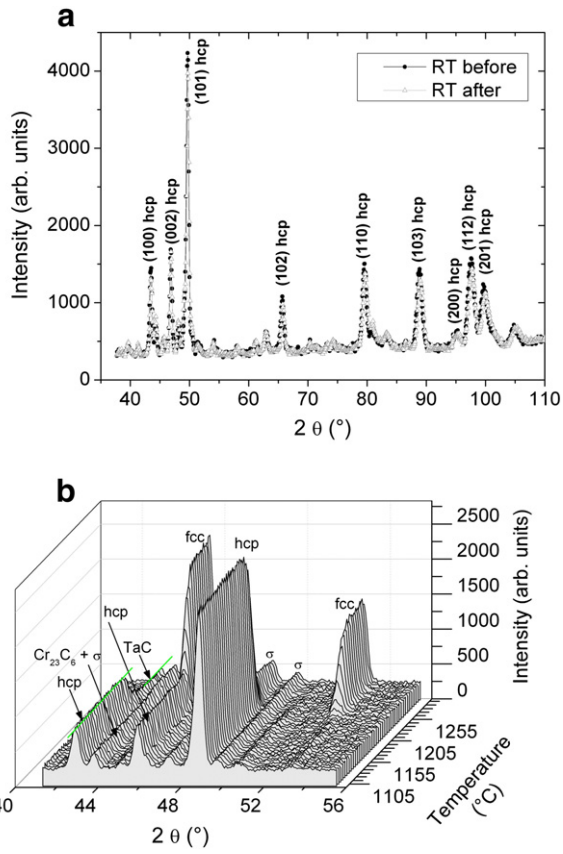

Fig. 2. a) Neutron diffraction patterns from CoRe-2 alloy before and after in-situ heating cycles show presence of Cr and Ta carbides and σ phase in Co matrix (only the hcp peaks are indexed), b) relative changes in peaks with increase in temperature (1100° to 1300 °C) in the 2θ range of 42° to 56° shows transformation from ε (hcp) to γ (fcc) Co phases.

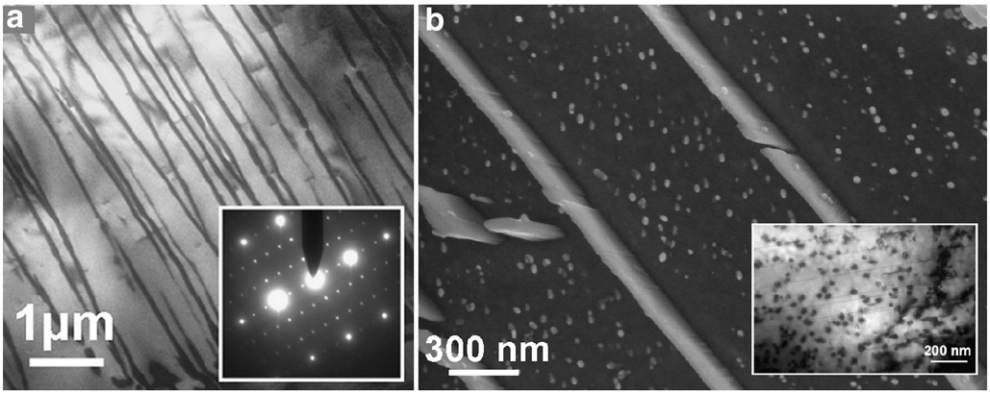

Fig. 1. Carbide morphologies in CoRe-2 alloy: a) Lamellar $Cr_{23}C_6$ type carbides. Inset: selected area diffraction pattern show presence of $Cr_{23}C_6$ phase, b) fine dispersion of TaC between Cr-carbide lamellae. Inset: TEM image of TaC precipitates. The carbides are embedded in ε Co matrix.