

**Experiment title:**

Characterisation of the oxide layers on bond coats of thermal barrier coatings

**Experiment****number:**

ME – 393

**Beamline:**

BM 20

**Date of experiment:**

from: 10/07/02 to: 16/07/02

**Date of report:**

25.11.2002

**Shifts:****Local contact(s):**

N. Schell, A. Bauer

*Received at ESRF:***Names and affiliations of applicants** (\* indicates experimentalists):

W. Reimers, A. Pyzalla, B. Camin\*, S. Dieter\*, H. Freydank\*

TU Berlin

Sek. BH 18

Ernst-Reuter-Platz 1

D – 10587 Berlin

Germany

Tel. ++49 / (0)30-8062-3095, Fax: ++49 / (0)30-8062-3195

**Report:**

Thermal barrier coatings bonded by an NiCoCrAlY-alloy on an Ni-base-superalloy as well as intermetallics on  $\gamma$ -TiAl-base have met considerable interest as potential materials for high-temperature applications. Because of the good high-temperature-strength and strength-to-weight ratio of  $\gamma$ -TiAl, investigations focus on this new class of lightweight materials. Improving the oxidation resistance, which is the major drawback of TiAl at high temperatures, additions of further elements like Ag were tested that favour the formation of highly protective aluminium surface scales. The characterisation of the oxide scales in the early stages of oxidation by in-situ heating experiments includes analyses of phase and stress development which can be responsible for the initiation of cracks in the protection layer.

In previous experiments it was proven, that phase and residual stress analyses using synchrotron radiation offer numerous advantages compared to conventional X-ray diffraction. Among these advantages is the high intensity of the synchrotron X-ray which permits measurements at short measurement times, that are necessary carrying out in-situ experiments detecting phase changes. Due to the high intensity and parallelism of the synchrotron beam, the resolution of the very close situated peaks of the Ti-Al-O System is possible which could not be achieved using conventional X-ray radiation.

In-situ experiments were accomplished using a furnace (Fig. 1) with halogen lamps for heating up to 800°C in air. The measurements were carry out in theta-2theta modus with an energy of 6930,3 eV (corresponds to the wavelength of Co K $\alpha$ -radiation) by using a szintillation detector. A range of 2theta between 40° and 53° was chosen, because in that range peaks with a high intensity of all phases of bulk material and oxides were expected.

The typical surface morphology of a oxide scale of a Ti-50Al-2Ag sample after 8h in-situ heating at 800°C is shown in Fig. 2.

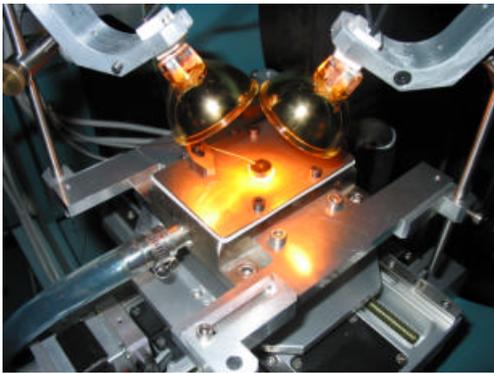


Fig. 1 furnace for in situ heating

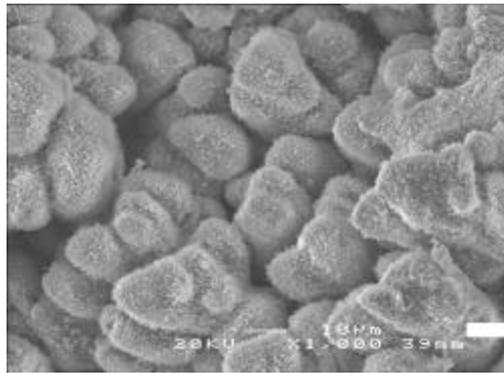


Fig. 2 SEM image, surface oxid scale, situ 800°C, 8h

Fig. 3 shows the spectra obtained in an in-situ heating experiment at 800°C of a Ti-50Al-2Ag sample after adjusting the heating temperature as well as after appr. 3h and 8h annealing time. In the initial state there is one peak of very high intensity of 111  $\gamma$ -TiAl (not all shown) and a smaller one of 002 Ti<sub>3</sub>Al. After 3h annealing several peaks of  $\gamma$ -TiAl, Ti<sub>3</sub>Al, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and a cubic Ti<sub>5</sub>Al<sub>3</sub>O<sub>2</sub> phase (called Z-Phase [1]) were found. After 8h annealing there are Ti<sub>3</sub>Al, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Z-Phase only.

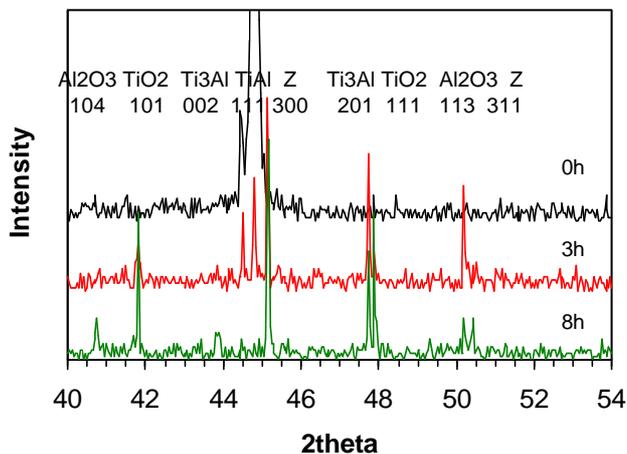


Fig. 3 in situ Spectra of Ti-50Al-2Ag at several times

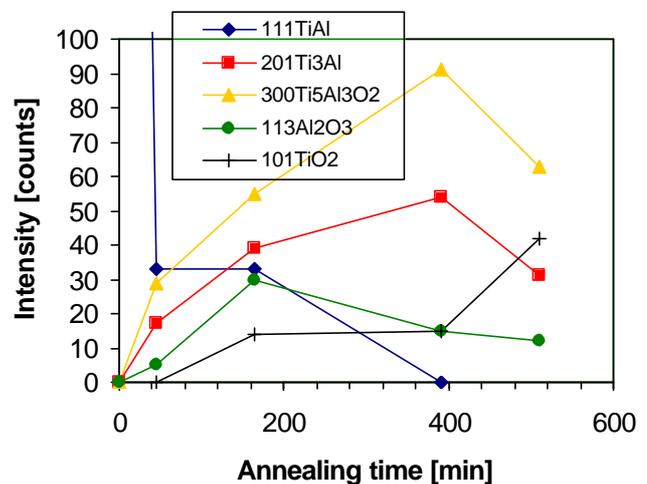


Fig. 4 Development of several peak intensities

In Fig. 4 the development of the peak intensities in dependence on the annealing time of the same sample is shown. Whereas the peak intensity of the TiAl substrate decreases rapidly after a short oxidation time, oxide peaks appear and increase after further heating. A mixed scale of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> instead of a dense Al<sub>2</sub>O<sub>3</sub> scale as reported by [2] was found. The increasing of the Ti<sub>3</sub>Al peak might be related to the formation of a Ti<sub>3</sub>Al sublayer because of outward Al diffusion [3] during the oxidation as found in Ti-46.5Al-4(Cr,Nb;Ta,B) [2]. The Z-phase might have formed due to the reaction of Ti<sub>3</sub>Al with O and /or Al<sub>2</sub>O<sub>3</sub> in following equation:  $2\text{Al}_2\text{O}_3 + 5\text{Ti}_3\text{Al} \rightarrow 3\text{Ti}_5\text{Al}_3\text{O}_2$  [3]. This might be the reason for the same distribution of intensity of Ti<sub>3</sub>Al and Z-phase (Fig. 4). However, the exact procedure of the formation of the Z-phase by reaction of oxygen with Al and Ti<sub>3</sub>Al is unclear at the moment, this reaction plays an important role in the formation of a dense Al<sub>2</sub>O<sub>3</sub> layer on the surface of the alloy.

In-situ stress analyses were carried out using the  $\sin^2 \psi$ -method and tilting to 4 different  $\psi$  angles. For the calculation of the residual stresses from the strain distribution, the knowledge of diffraction elastic constants is essentially. The analysis of the data and the determination of these constants is still in progress.

[1] V. Shemet, et al, Intermetallics, 5, (1997), p. 271-280

[2] L. Niewolak, et al., Structural Intermetallics 2001, TMS, 2001, p. 535-540

[3] M. R. Yang, S.K. Wu, Oxid. Met., 54, (2000), p. 473-490

