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Studies by X-ray Absorption Spectrometry (XAS) of the Local Order at the Zironium Threshold in an α-AL_2O_3 Layer Developed by Oxidation at High Temperature on an Alloy $FeCr_{22}Al_5$

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Abstract: In this work, we present X-ray absorption spectrometry (XAS) results concerning the local environment of the zirconium dopant at the two interfaces of a layer of α-alumina developed by oxidation on a Zr-pre-implanted $FeCr_{22}Al_5$ alloy.

Keywords: XAS, α-alumina, Zr-doped, oxidation, $FeCr_{22}Al_5$ alloy.

1 Introduction

α-alumina is one of the best protective layers for high temperature alloys: it acts as a diffusion barrier against the environment. This layer is of great interest in the field of superalloys which are widely used industrially in all cases where the conditions are extreme [1, 2, 3]: high temperature and corrosive gas. But this stoichiometric oxide has transport and adhesion properties controlled by the impurities or dopants incorporated therein, these dopants come from the underlying substrate on which the alumina layer is developed. The dopants tend to segregate at the metal/oxide interfaces and alumina grain boundaries [4, 5, 6]. During the growth of the oxide layers, the segregation kinetics of the dopants at the grain boundaries are accelerated by the dragging of these dopants by the mobility of the grain boundaries, which affects the physicochemical properties of these interfaces. Furthermore, it is well known that the addition of zirconium (≈ 0.05% by weight) is beneficial in the trapping of sulfur in refractory alloys.

In this work, we present X-ray absorption spectrometry (XAS) analyzes [7, 8] of the real local environment of the zirconium dopant at the interfaces of a layer of alumina Developed by oxidation on a Zr-pre-implanted $FeCr_{22}Al_5$ alloy. Given the small amounts of material analyzed and the large dilution by doping oxide layers, standard laboratory techniques (X-ray spectrometry or electrons) are unsuitable for this study. X-ray scattering gives no information on the local order around dopants.

2 Program of the Study

In order to study the effects of Zr dopants, we implanted zirconium in $FeCr_{22}Al_5$ samples of dimensions 70*30*2 mm^3. The $FeCr_{22}Al_5$ alloy is supplied by the company Ape ram Imply. The average dose of implanted zirconium is $5 * 10^{15}$ $atom.cm^{-2}$. This dose was chosen to have about 300 ppm of ZrO^2 in the α-alumina layer, this concentration represents the solubility limit of ZrO^2 in α-Al_2O_3 [6]. The zirconium implantations in $FeCr_{22}Al_5$ alloys were carried out by Ms. O. Kaitasov at CSNSM, UMR 8609 Bât. 108 UFR ORSAY in collaboration with J. C. Pivin. The experimental conditions of implantation are: Energy of the ions Zr = 100 k.eV, the average depth of implantation is R_P = 230 Å with an average width of the implanted zone of ΔR_P = 99 Å. The implanted FeCr22Al5 samples are then oxidized at 1300 ° C for 12 hours in air. From the weight gain, the density of α-alumina (≅ 3.98 $g.cm^{-3}$) and the total surface of a sample we deduce the average thickness of the oxide layer

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developed on the alloy: it is of the order of 5 µm.

3 XAS Experimental Techniques

The XAS analyzes were performed in collaboration with R. Cortès at LURE-Université Paris-Sud [4, 5, 6].
Two detection modes were used: secondary electrons detection and X-ray fluorescence detection.

- To analyze the Zr dopants near the outer surface of the α-alumina layer, we worked, at room temperature, by secondary electron detection at the K threshold of Zr, the threshold energy is E_K = 17977 eV , Fig-1.
- To analyze the Zr dopant near the internal Metal / Oxide interface, we worked in X-ray fluorescence mode at the K threshold of Zr, Fig-2.

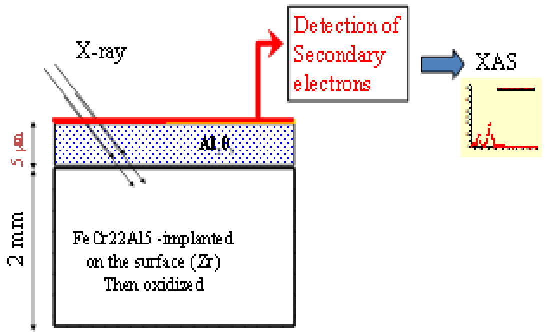

Fig.1: Principle of XAS measurements at the K-threshold of zirconium at the external interface by secondary electron detection.

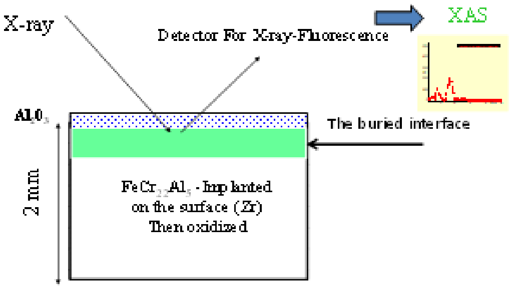

Fig.2: Principle of XAS measurements at the K-threshold of zirconium at the internal interface by X-ray fluorescence.

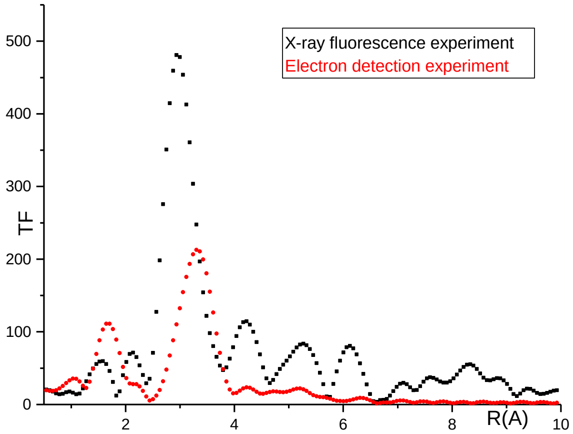

Fig.3: Fourier-transform magnitude spectrum (uncorrected for the phase shift), obtained by electron detection and X-ray fluorescence at the K-threshold of zirconium.

4 XAS Experimental Results

The Fourier transforms, FT, of the signal XAS [4, 5, 6, 7, 8], obtained with the two types of experiments are shown in Fig-3.
The signal XAS is expressed by the relation (1), the parameters that appear in the explanations (1) and (2) reported on the reference, [4, 5, 6, 7, 8].

$$\chi(k) := \frac{N f(k,\pi)\, e^{\left(2\frac{R}{\lambda(k)}\right)}\, e^{(-2\sigma^2 k^2)} \sin(2kRJ + 2\delta j(k) + \phi(k))}{kR^2} \tag{1}$$

Where, $k = \sqrt{(E - E_0)2m\hbar^2}$ is the photoelectron wave vector (Eo is the reference energy for the edge), N_j is the number of atoms in the jth shell located at the average distance R_J, λ(k) is the electron mean path, $f_J(k,\pi)$ is the backscattering amplitude, σ_J Debye-Waller factor, and $\arg[f_J(k,\pi)]$ and δ are the phase shifts of the J_{th} shell and the absorbing atom, respectively. The chemical transferability of the phase shifts is well established, at least when the chemical state and the local environment are similar. We can use theoretical values for the atomic phase shifts given by Teo and Lee" [7, 8] or determine them by an experimental fitting procedure.
To extract χ(k) from the experimental absorption coefficient, µ, the data are analyzed following standardized procedures. First,

μx resulting from the K edge is obtained by removing the background due to the other edges and the other elements using a polynomial fit. $\chi(k)$ k) is obtained by :

$$\chi(k) = \frac{\mu x - \mu_0 x}{\mu_0 x} \qquad (2)$$

Where $\mu_0 x$ is the smooth background and x the sample thickness.

From $\chi(k)$ a radial structure function FT(R) can be derived. The positions of the peaks in FT(R) are shifted compared to the true distances, as a result of the contribution of the scattering phase which depends on k [4, 7, 8]. Next, we select a shell using a smooth window and then back-Fourier-transform to k space yielding partial XAS spectra (due to one shell) which can be fitted with equation (1).

The Fourier transform (FT) of the XAS signal is represented by the expression (3), [4].

$$FT := \int_{kmin}^{kmax} \mathrm{w}(k)\, k^2\, \chi(k)\, \mathrm{e}^{(2\, i\, kr)}\, dk \qquad (3)$$

The abscissa axis on the FT, Fig.-3, represents the distance in angstrom between the central atom Zr and its close neighbors, and the ordinate axis represents the intensity of the different peaks, the peak area is proportional to the number of neighbors.

The first peak on the FT mainly represents the first close neighbors of zirconium which are oxygen ions, Zr-O, and the second most intense peak mainly represents the second neighbors of the zirconium type, Zr-Zr. It can be seen that the local environment around the Zr dopant is not the same at the two interfaces of the oxide layer. To specify these environments at the two interfaces, we carried out XAS experiments at the K-threshold of zirconium on two standard samples [4, 5, 6]: on the one hand on tetragonal zirconia ZrO_2 and on the other hand on α-zirconium metal, Fig-4- 5.

From Figure-4 we can deduce that, at the external interface of oxide layer, the zirconium has a local environment similar to that of zirconium in tetragonal zirconia. Being metastable at room temperature, these zirconia particles are then stabilized at room temperature because of the large contribution of free surface energy [5]. The difference in peak intensities is due to the small size of the particles [6].

From Figure-5 at the internal interface the local environment around zirconium is similar to that of α-zirconium metal.

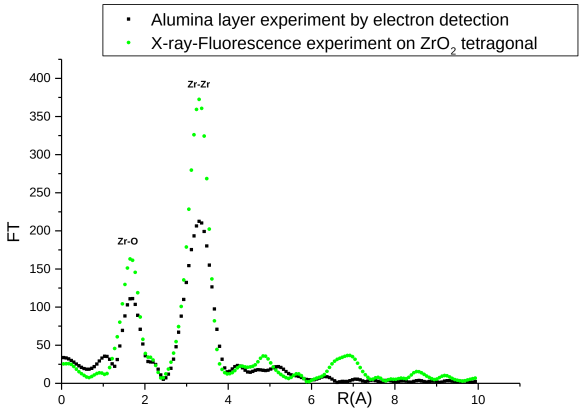

Fig.4: Fourier-transform magnitude spectrum (uncorrected for the phase shift) obtained at the K-threshold of Zr by electron detections on the alumina layer and by X-ray fluorescence on the tetragonal ZrO2 standard sample.

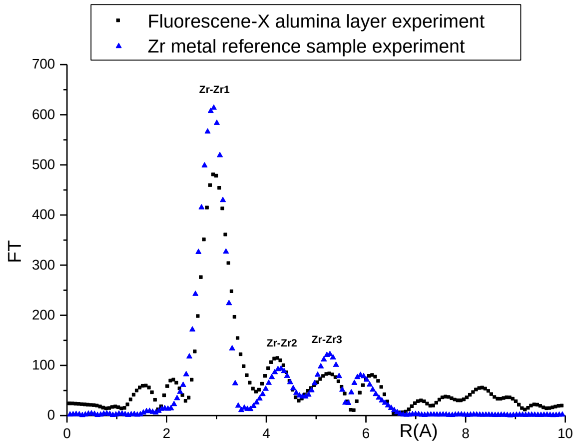

Fig.5: Fourier-transform magnitude spectrum (uncorrected for the phase shift) , obtained at the K-threshold of Zr by X-ray fluorescence on the one hand on the alumina layer and on the other hand on the Zr-α metal standard sample.

5 Conclusions

XAS experiments on $FeCr_{22}Al_5$ samples implanted in zirconium and oxidized show that zirconium is in two chemical states: near the outer Air/Oxide interface, most of the zirconium is oxidized in the form of tetragonal ZrO_2 particles. The zirconium near the internal Oxide/ alloy interface is in the form of Zr-α metal precipitates.

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