

MICROSTRUCTURE AND ELECTRON MICROPROBE STUDY OF OXIDE LAYERS OBTAINED ON ZIRCALOY-4 BY OXIDATION AT HIGH TEMPERATURE

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Abstract: *The paper presents the results of analyses carried out for oxide films formed during isothermal oxidation of Zy-4. The oxidation process was done in dry air at 600 - 1050°C having a constant duration of 60 min. According to the oxidizing temperature, the structure, compactness and adherence of the oxide layers vary from the black, compact, adhering oxide to white – yellowish oxide having pores and fissures. The oxide films were analyzed by optical microscopy, scanning electronic microscopy, microprobe and mass spectroscopy of secondary ions. The variation profiles of the concentration was held by the main elements in the black oxide layer as well as white oxide layers, and their deterioration process was analyzed in keeping with the oxidation temperature.*

Keywords: Zircaloy – 4, Oxidation.

INTRODUCTION

The oxidation of zirconium alloys at high temperatures in air results in the formation of two types of oxides: a black, compact, adherent oxide and a white oxide showing a defective structure that deteriorates even more as the temperature increased. [1], [4], [5]

The process of oxygen diffusion in the metal under the oxide layer at temperatures above the phase transformation points of the alloy leads to the formation of a stabilized solid solution enriched in oxygen.

A study by scanning electron microscopy, by microprobe analysis and by SIMS has been carried out in this paper on the oxide films obtained at the surface of Zy – 4 isothermal oxidation in a temperature range of 600 – 1050°C.

MATERIALS AND METHODS

Zircaloy – 4 samples, having the chemical composition: 1,58% Sn, 0,22% Fe, 0,10% Cr, 50 ppm Cu, 1200 ppm O₂, and a microstructure consisting of equiaxed grains, have been oxidized isothermally for 60 min in a dry air at a series of temperatures stepped up by 50°C in the temperature range 600 - 1050°C. The oxide layers have been studied by optical microscopy, scanning electron microscopy (SEM), SIMS and by quantitative energy dispersive microprobe analysis (EDAX).

EXPERIMENTAL RESULTS AND DISCUSSION

Optical and scanning electron micrographs show a different structure for the samples oxidized below 750°C and above this temperature. Oxidation below 750°C ends with formation of a black, compact, adherent film (Fig.1a). At 750°C a new layer of white oxide begins to appear. As one can see in the micrograph in (Fig.1b), this white oxide layer comprises two phases: a grayish – white phase and a yellow phase located predominantly in the vicinity of the oxide – metal interface.

By comparison with the black oxide layer, the white oxide layer is less compact: pores and cracks exist in the oxide white layer (Fig.2), the cracks being mostly parallel to the oxide/gas interface but also perpendicular in the vicinity of the oxide/metal interface (Fig.3). The number of pores and cracks proved to be temperature dependent. It was observed that increasing temperature resulted not only in the increase of the white oxide layer thickness but also in a further deterioration of the compactness of this layer.

The structure of the metal is equiaxed up to transition level (Fig.1a) after which an oxide layer of a solid

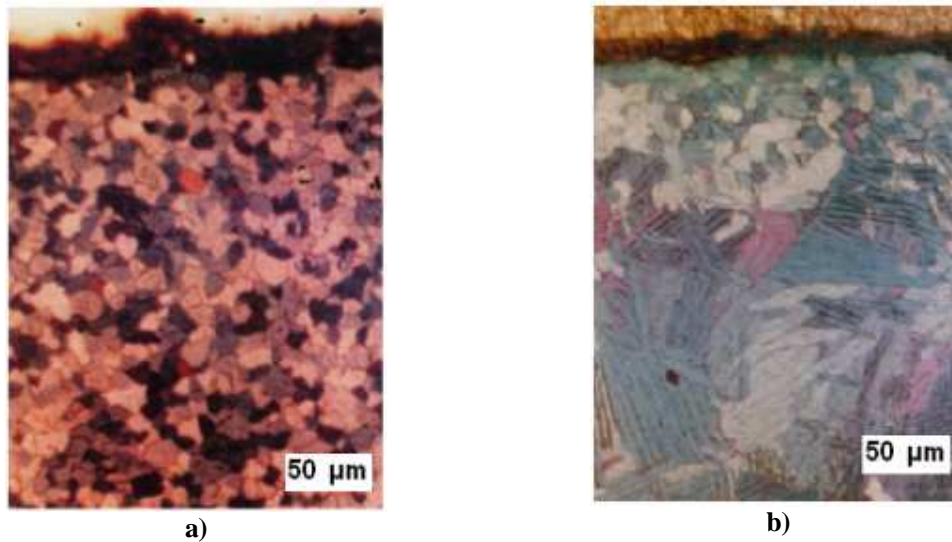


Figure 1 Micrograph for a zircaloy-4 sample isothermally oxidized for 60 min (a) At 600°C, black oxide; (b) at 1050°C, white oxide

stabilized solution α is formed by oxygen dissolution (Fig1b), while the core has a needle – like structure formed on the initial β grains. In both situations the increase of oxidation temperature causes an increase of grain size. The deterioration process of the grain boundary by oxygen diffusion was observed in the metal.

MICROCHEMISTRY OF THE OXIDE LAYERS

To confirm the distribution of different component elements existing in the oxide layers, a profiling was carried out by SIMS and by X – ray microprobe analysis. The SIMS analysis allowed determination of concentration profiles only for thin oxide layers whose thickness was less than penetration depth.

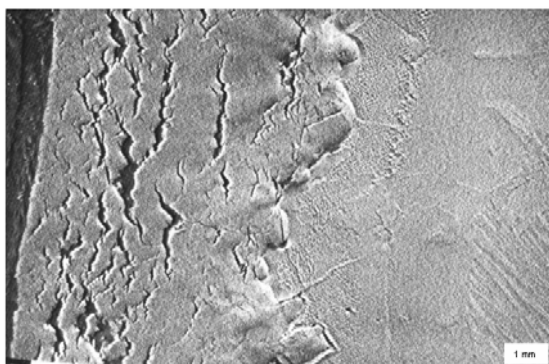


Figure 2 SEM Micrograph for a zircaloy-4 sample isothermally oxidized for 60m min at 1050°C in dry air

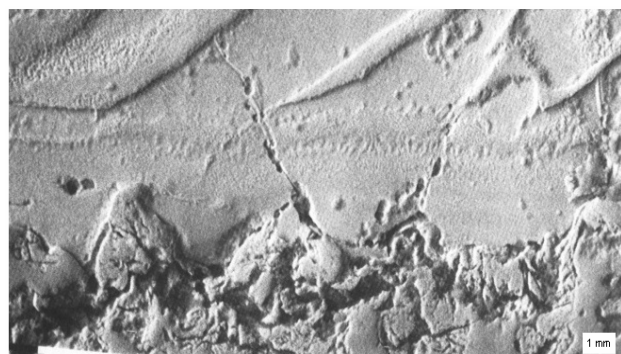


Figure 3 SEM Micrograph for an oxide-metal interface for the sample oxidized at 1050°C

So we have succeeded in carrying out this profiling by SIMS only for the black oxide layer. Figure 4 for the sample oxidized at 600°C comprised only the black oxide layer. For samples oxidized at higher temperature with white oxide layers, we have not succeeded in obtaining information by SIMS on the microchemistry of the white layer because this layer was thick and too deeply located from the samples surface.

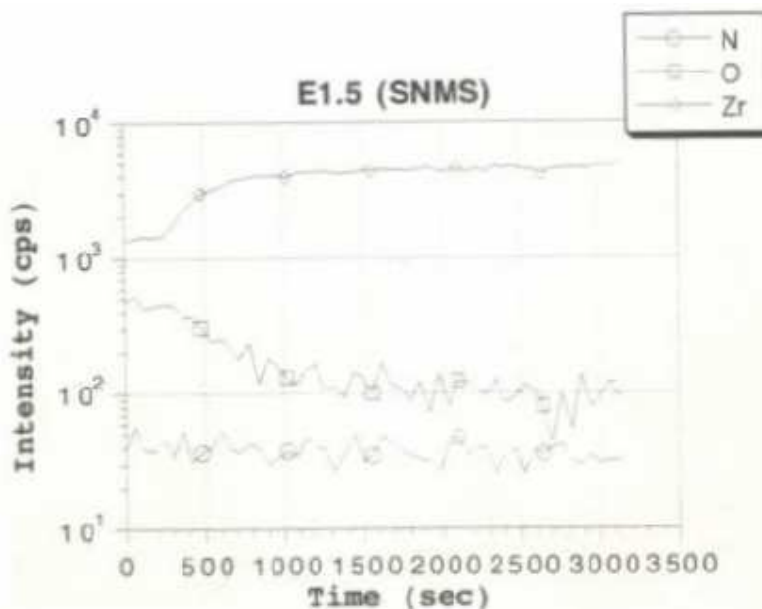


Figure 4 Profiles for oxygen and zirconium for the sample oxidized at 600 °C (black oxide layer 8 μm thick)

Interesting information on the white oxide layer microchemistry and the solid solution underlying layer were obtained by profiling the distribution of the component elements by X – ray microprobe analysis. Figure 6 shows the concentration profiles for the main metallic elements (Zr and Sn) and for two non – metallic elements (O₂ and N₂) assumed to have penetrated by diffusion in the sample oxidized at the highest temperature (1050°C).

The oxygen content in the white oxide layer seems to be constant, while a decrease is noticed in the underlying metal layer. This decrease is typical for a diffusion layer and so we can infer that a layer of stabilized solid solution has been formed by the dissolution of oxygen in metallic zirconium.

A very interesting effect was noticed concerning the penetration of nitrogen from the heating atmosphere into oxide layer. The nitrogen profile in Fig.6 shows increased nitrogen content in the vicinity of the oxide – metal interface, more specifically in the region where the oxide layer has yellow color and where a new phase is sometimes seen. We consider that the penetration of nitrogen by diffusion in the depth of white oxide layer is favored by defective microstructure of this layer that comprises a temperature increasing area fraction of pores and cracks. The nitrogen enriched region in Fig.6 may correspond to a reaction diffusion process that results in the formation of the stable compound ZrN.

It is interesting to mention that the micrograph in Fig.1b for a sample oxidized under the same conditions with the same conditions with the sample in Fig.6 shows clearly the existence of a thin layer of a new hard yellow phase located just in the region of nitrogen enrichment, namely at the interface between α Zr solid solution (clearly seen in Fig.6) may be a consequence of the diffusion barrier provided by the ZrN compound located at the oxide – metal interface and also as a consequence of the slow diffusion rate of nitrogen in the metallic phase.

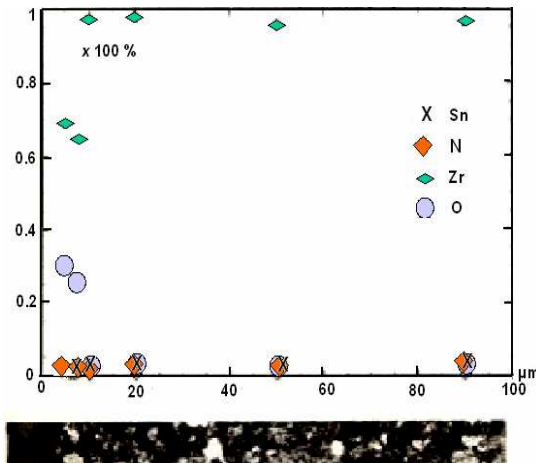


Figure 5 X-ray microprobe concentration profiles for the sample comprising black oxide formed at 600°C

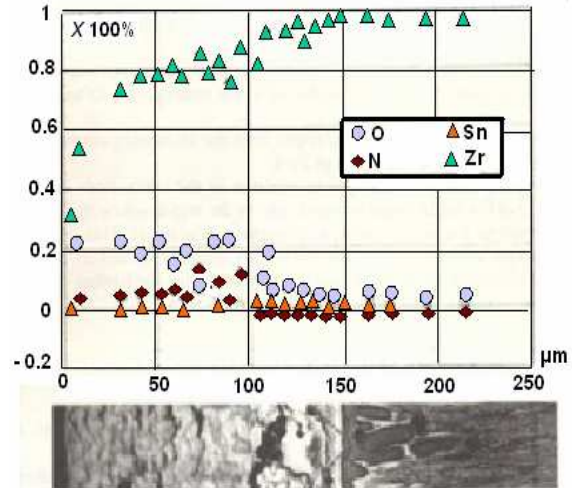


Figure 6 X-ray microprobe concentration profiles for the sample comprising white oxide formed at 1050°C

CONCLUSIONS

The optical and electron microscopy study and the microscope profiling carried out in this paper have shown that the oxide layers formed on Zy – 4 by isothermal oxidation in dry air in the temperature range 600 - 1050°C show the following characteristic features:

1. up to 750°C a single layer of black oxide is formed that looks compact and adherent;
2. at 750°C a new inner layer of white oxide begins to appear;
3. the white oxide layer is less compact than the black oxide layer, comprising an area fraction of pores and cracks that increases with the oxidation temperature;
4. the white oxide layer seems to comprise two phases: a grayish – white phase and a yellow phase located predominantly in the vicinity of the oxide – metal interface;
5. the oxygen content in the white oxide layer is approximately constant, but a typical diffusion decrease is manifested in the underlying α Zr solid solution layer;
6. a penetration by diffusion of nitrogen from the air heating atmosphere was observed during the oxidation of Zy – 4;
7. a nitrogen enrichment was put in evidence in the white oxide layer in the vicinity of the oxide – metal interface, just in the region where the oxide layer has a yellow colour and seems to comprise a new phase. This nitrogen – rich phase was presumed to be stable ZrN compound, and its presence at the oxide – metal interface proved to be a barrier for the further diffusion of nitrogen into underlying metal.

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