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The influence of thermal shock at high temperature on Zy-4 alloy

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Abstract. Zy-4 alloy is a basic material in the construction of the current generation nuclear reactors. Due to the diffusion processes and the chemical reactions that take place, the corrosion in air at high temperatures of the zircaloy-4 alloy determines the appearance of new phases and constituents and the stabilization of the alpha phase at high temperatures, above the allotropic transformation temperature. The paper presents the structural transformations that take place in the alloy following the oxidation under thermal shocks applied in the range 600-1500 ° C, in correlation with the chemical composition, hardness and thermal transfer properties.

Keywords: thermal shocks, corrosion, structural transformations, hardness, diffusivity.

1. Introduction

High corrosion resistance, high hardness, good ductility, good thermal transfer properties and low absorption capacity of thermal neutrons, properties that recommend it for use in nuclear energy characterize the zirconium. Zirconium-based alloys used in nuclear energy have the chemical composition made up mainly of Zirconium with low percentages of Sn, Nb, Fe, Ni and other metals, alloying elements that have the role of

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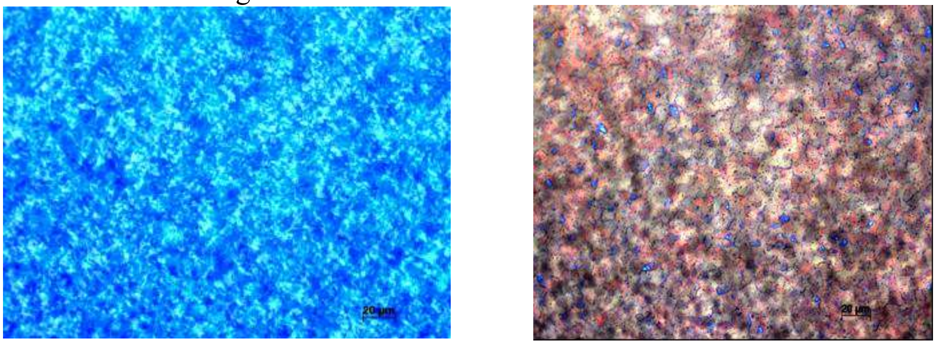
improving the mechanical properties and corrosion resistance. Under allotropic temperature, their microstructure is formed of polyhedral fine grains of solid solution α, with dimensions of 3-7 µm [3,4,7,8]. Allotropic transformation α-> ß occurs with the formation of needles and platelets structures, with large grains of solid beta solution. This structure is not reversible upon cooling and it is kept up to ambient temperature. The corrosion processes have as a main result the formation of a corrosion layer and they are accompanied by diffusion processes of elements (O, H, N) in metal, under the corrosion layer, processes whose magnitude is determined by temperature and duration. At low temperatures, the oxide layer formed is hypo stoichiometric hypo, of dark color, compact and adherent, with protective properties. As temperature increases it also causes a rise in the oxygen content in the layer, the transition to the stoichiometry and hyper- stoichiometry and the appearance of the degradation processes of the corrosion layers formed. [10, 11, 12].

In reactors of third generation, which operate at present and are expected to operate until the 2040s, zirconium alloys are used in the execution of the fuel element sheath. The current research on materials for new generation reactors will be the basis for their development, choice and use in new nuclear reactors. In the case of CANDU reactors the operating temperature of the Zy-4 sheath in contact with the cooling agent is 350°C. Sudden fluctuations in temperature or even accidents may occur during operation [5,6]. The research carried out has proposed to study the structural transformations that take place in zircaloy-4 during corrosion in air, under thermal shocks, depending on the temperature and the duration of the shock and to determine their influence on some characteristics of the material.

2. Experimental materials and techniques

The research was carried out on cylindrical samples of Zy-4 alloy, with 10 mm diameter, with the composition within the standard limits (Sn-1.31%, Fe-0.20%, Cr-0.11%, Zr balance) and the structure in the delivery state. (fig.1.) The microstructure shows polyhedral grains whose average size is 4.6 µm to 6.5 µm cross section and longitudinal section (fig.1.). The hardness in the cross section is 228 HV and 258 HV in the log-section.



a. *b.*

Fig. 1. The microstructure of the zircaloy-4 alloy in the delivery state,
a - in cross-section; b - in longitudinal section.

The thermal shock tests had been performed with the help of solar energy, in the PROMES laboratory by means of, the Odeillo solar furnace, France (Fig. 2), in the temperature range 600-1500°C. The samples were subjected to 3 shocks and 6 successive thermal shocks with durations of 30 and 60s (fig. 3). The samples had been characterized by micro-hardness determinations and, after mechanical preparation and attack with 45% HNO_3, 45% H_2O and 10% HF solution, were analyzed on the surface and in section by optical microscopy, scanning electron microscopy and EDX.

The thermal diffusivity had been determined by the flash method [18-21] with a FlashLine TM3000 system (+ 0.5 ° C) with an accuracy of + 4%. The results were compared with those obtained during experiments performed at Ecole de Mines de Nancy by isothermal oxidation in air in the oven for one hour [10.11], and with data provided by the literature.

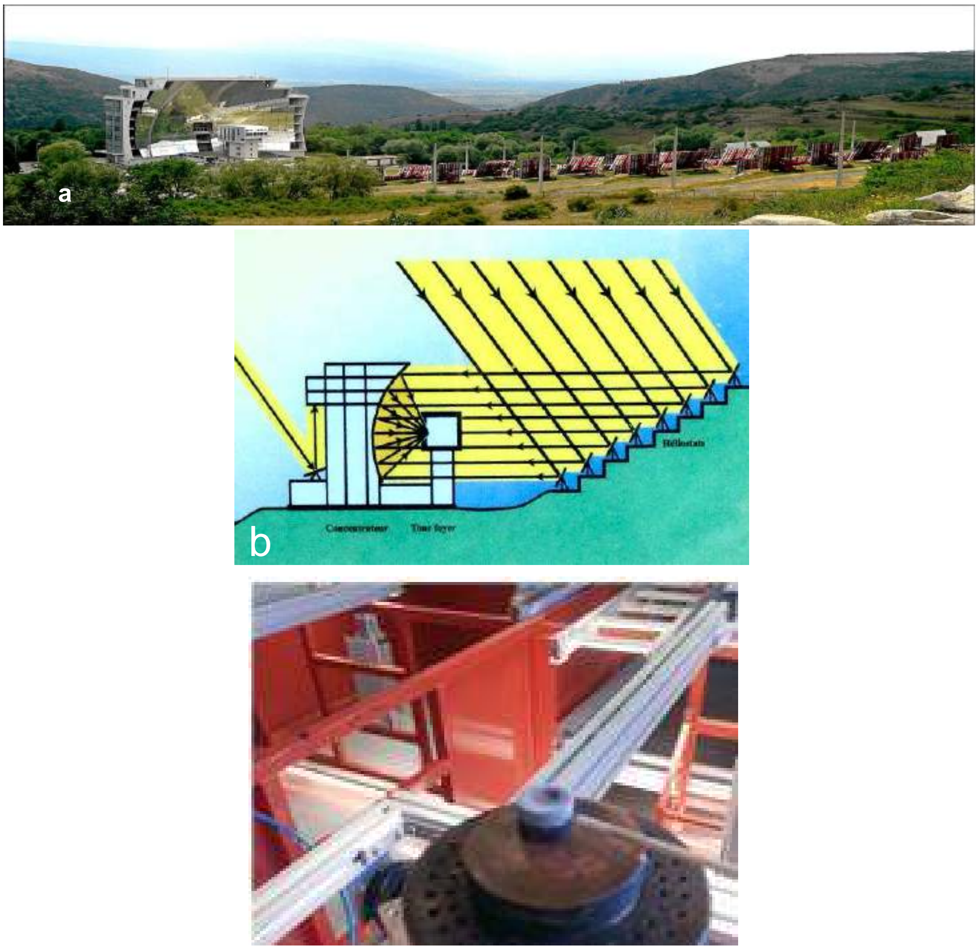


Fig. 2. The Odeillo solar furnace from-Font Romeu Laboratory:
a. France: general presentation; b. working principle; c. sample handling system.

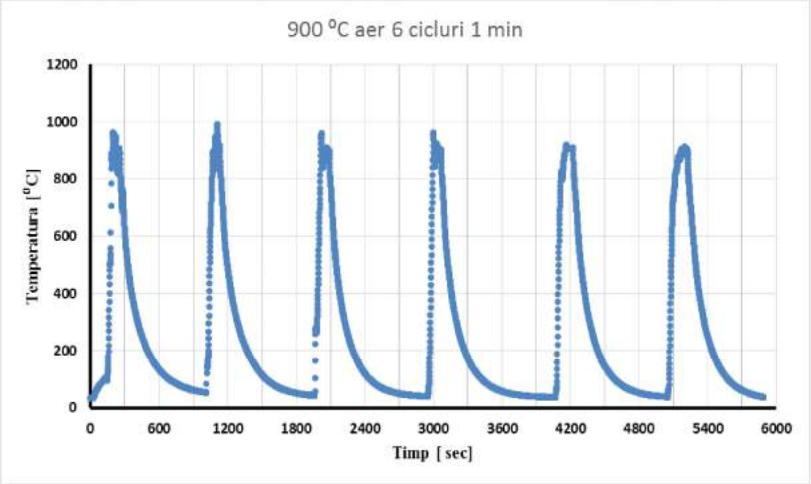
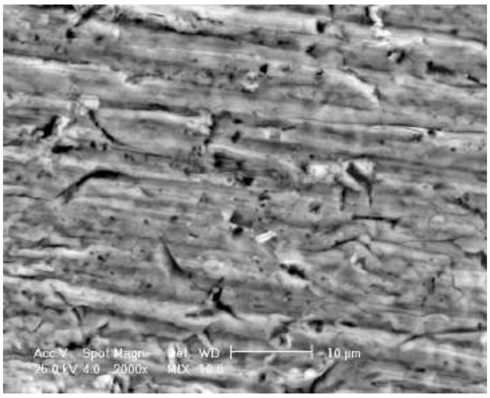


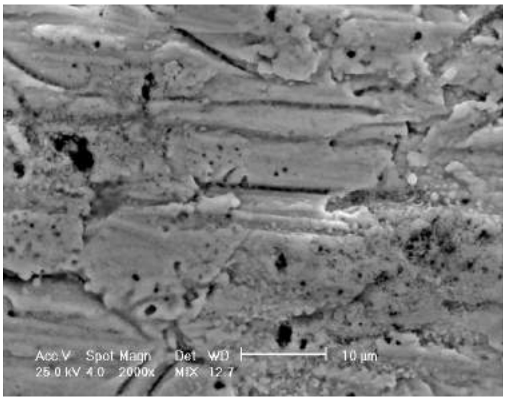
Fig. 3. Treatment at 900 ° C with 6 cycles of thermal shock of 60s.

Considering the importance of the morphology and the adhesion of the layers formed at the surface of the samples on the behavior of the alloy to the corrosive action, the layers had been characterized microstructurally in the surface and in the section.

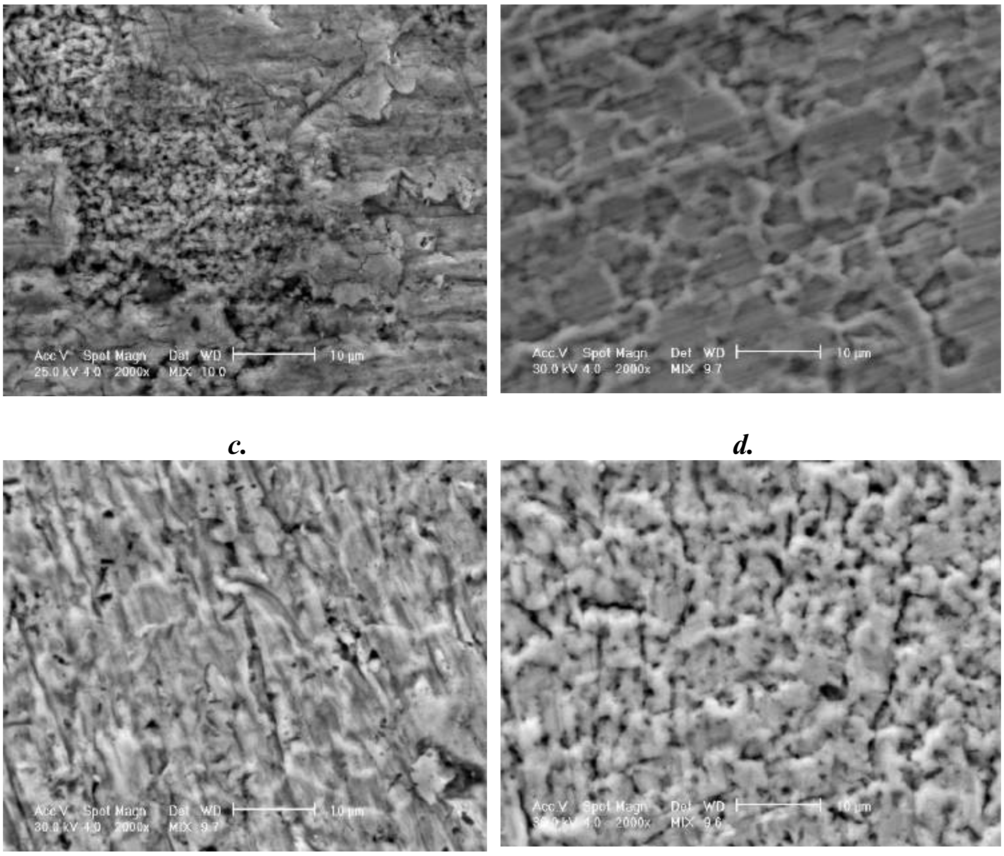
The microscopic analysis on the surface shows the increase of the thickness of the oxide layers with the increase of the temperature and of the number of applied thermal shocks (fig. 4.a-c). The increase in thickness and volume during the transformation determines the degradation of the layers by the appearance of the pores and cracks. At rapid cooling of samples at high temperatures, the cracks determine the occurrence of the processes of oxide layer exfoliation, but at the same time the surface is recoated with an oxide layer that remains relatively even during the remaining test period. (fig.4.d) process that explains the external appearance of the oxide layers formed at temperatures above 1400 ° C (Fig. 4.e, f).



a.



b.



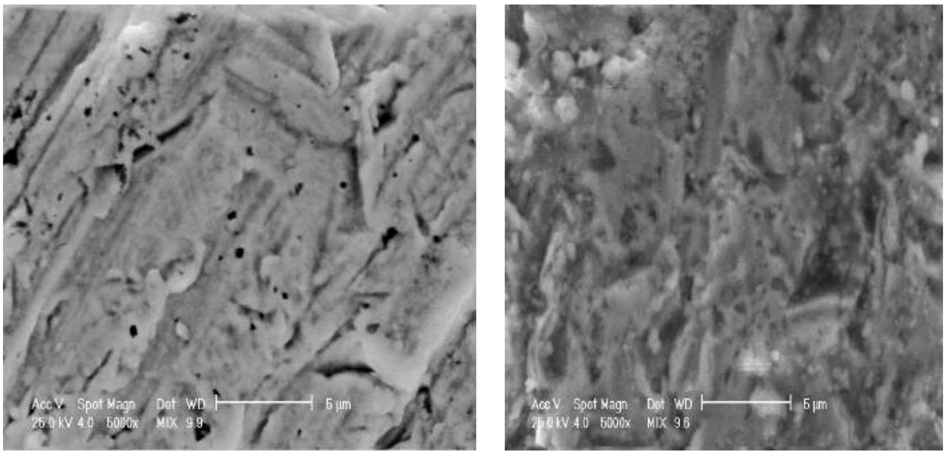
c. ***d.***

e. ***f.***

Fig. 4. Surface microstructure of oxide layers formed at different temperatures for a single thermal shock of 30s: a-1000°C, b-1200°C, c-1300°C, d-1450°C, e-1500°C and f-1600°C.

For the same thermal shock temperature, the characterization of the samples highlighted an important intensification of the degradation processes with an increase of applied thermal shocks number (fig. 5).

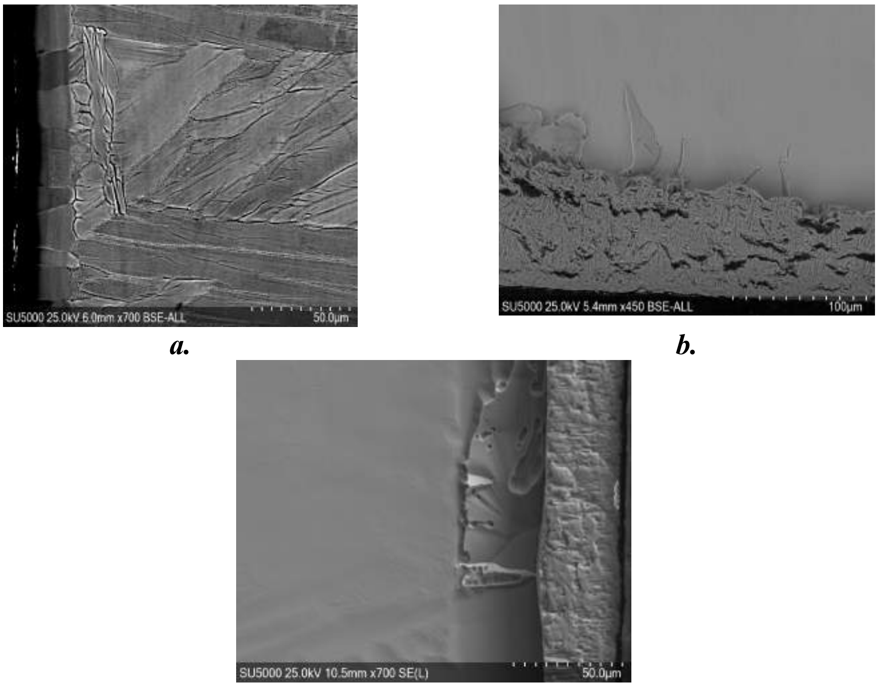
The microstructural analyzes in the section have highlighted the microstructure of the layers, their defects and compactness, as well as the quality of the metal-oxide interface (fig. 6). The oxide layers show cracks with a more pronounced thickness in a parallel direction with the metal-oxide interface (fig. 6, b.), a solid alpha solution layer is formed under the oxide layer, stabilized by the dissolution of oxygen in the metal. (fig. 6, a, c). Unlike the long-lasting isotherm oxidized samples [10-13], in which the growth of the alpha solid solution layer is columnar and its thickness is uneven, the samples treated by thermal shocks show layers of stabilized solution with uniform thickness, which can be explained by the holding time at elevated temperatures, which favors the oxygen diffusion.



a. ***b.***

Fig. 5. Surface structure of oxide layers formed on samples subjected to shocks lasting 30s at 1000 °C: a. 3 cycles, b. 6 thermal cycles.

The samples treated at higher temperature then of the allotropic transformation temperature, show under the layer of alpha solid stabilized solution, a structure with large needles and plaques (fig. 6, a).



a. ***b.***

c.

Fig. 6. The microstructure of samples subjected to thermal shocks in the air at 1000°C a-oxide: a stabilized alpha solution and the microstructure in needles and plaques formed after a shock of 30s, b, c-oxide layer formed at 3 and 6 thermal shocks lasting 30s.

The short duration of holding at high temperatures allowed the highlighting of some structural areas in which the allotropic transformation is incomplete, in which the polyhedral alpha phase coexists with the beta phase in needles and plaques. (fig. 7).

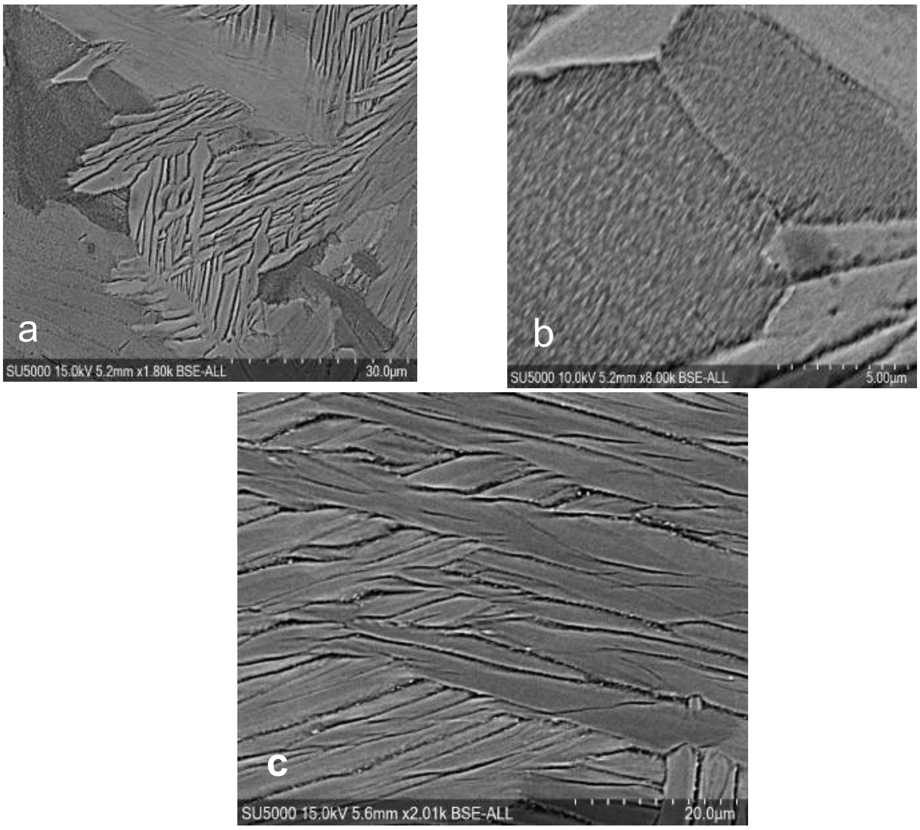
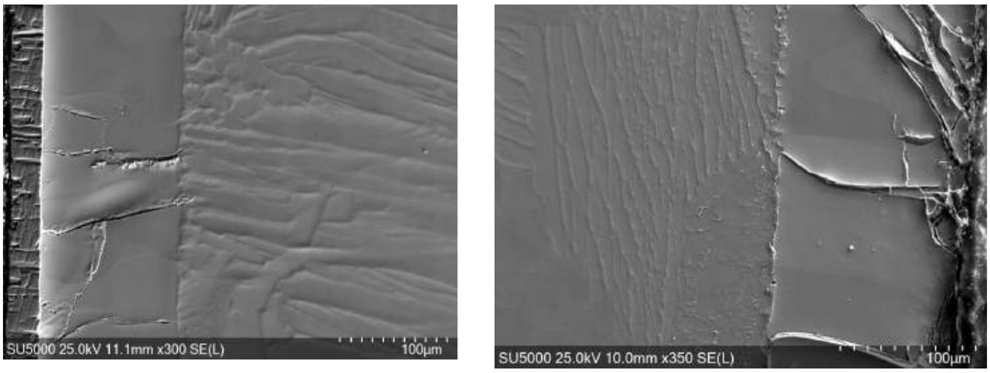


Fig. 7. The α->β transformation in samples subjected to heat shock at 900 °C with a duration of 30 s (a, b) and duration of 60s (c).

At the metal-oxide interface, cracks develop mainly perpendicular to the interface, which advance into the α solid solution layer stabilized towards the core with structure in needles and plaques (fig. 8). The phenomenon favors the penetration of oxygen into the metal and the corrosion process.

For the same treatment temperature and the same duration of applied shocks, the increase of the number of thermal shocks applied increases the thickness of the layers of oxide and α stabilized solid solution, and intensifies the processes of degradation through pores and cracks in the oxide layers and the cracking of the metal matrix.



a. **b.**

Fig. 8. Degradation of the solid alpha layers under the oxide layer:
a-1200°C, 3 cycles of 30s, b-1600°C, a 30s shock.

The EDS analysis reveals the variation of the chemical composition, mainly of the oxygen concentration per sample section.

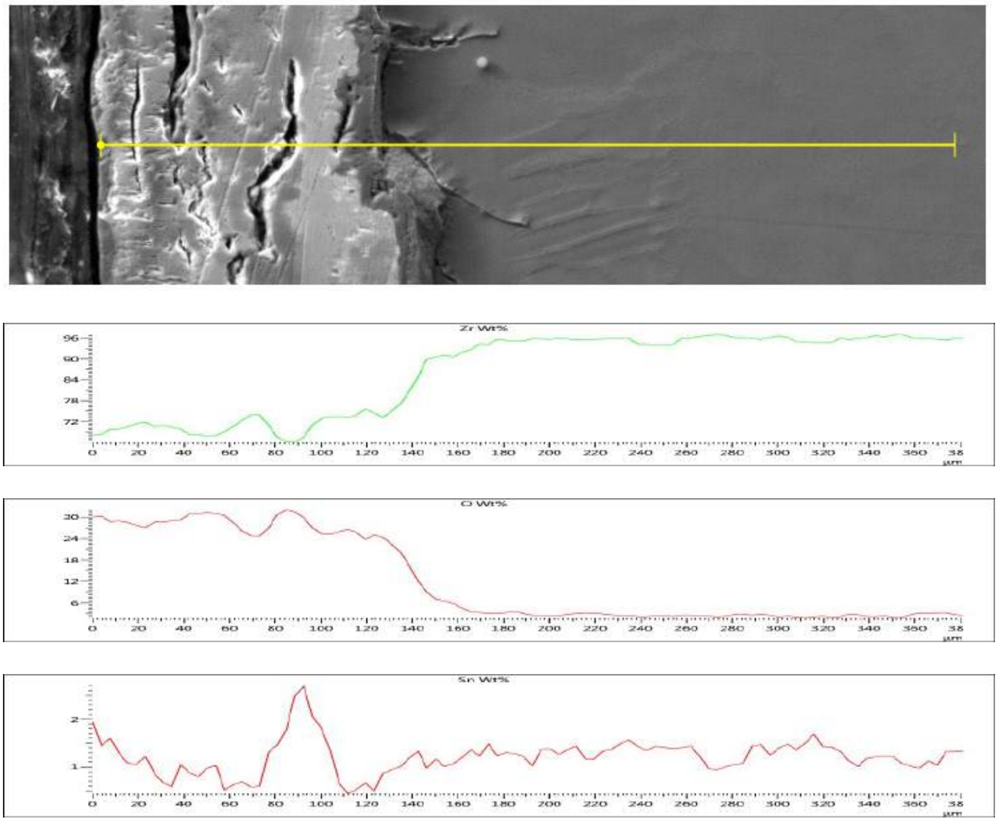


Fig. 9. The EDS analysis for the sample subjected to 6 thermal shock cycles of 30s duration at 900°C.

This analysis correlated well with the presence of degradation processes, the transfer of oxygen under the oxide layer and the appearance of the alpha solid solution layer (fig.9). The penetration of oxygen to the metal through heavily degraded areas is even more evident for the sample treated at 1600°C (fig. 10).

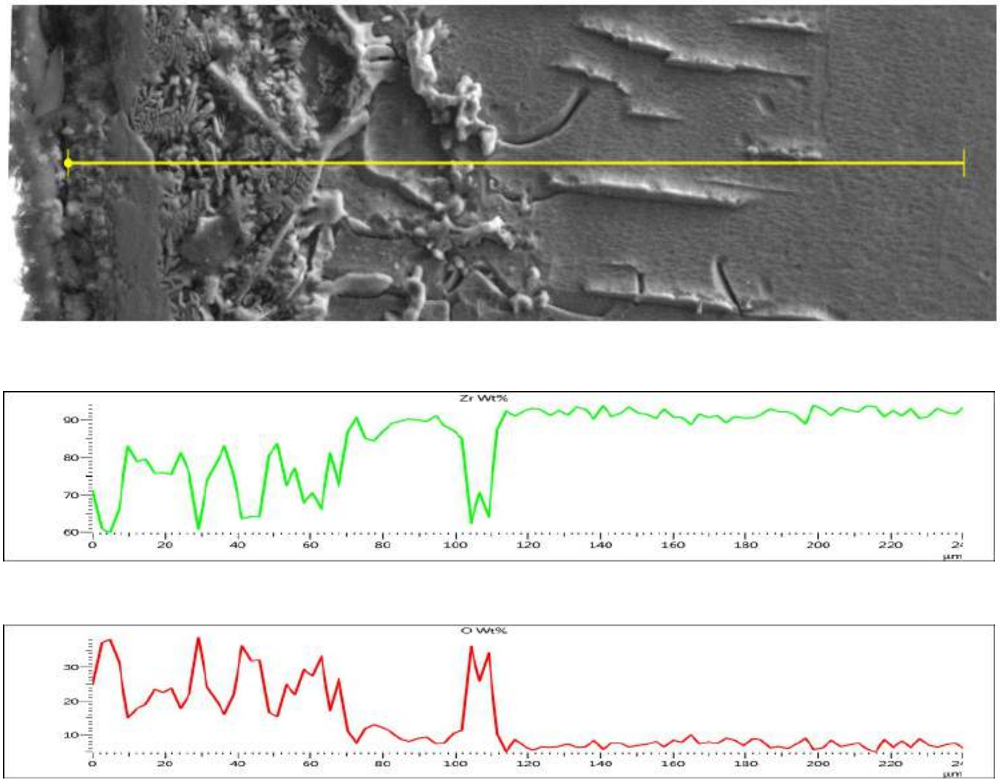


Fig. 10. The EDS analysis for the sample subjected to a 30s heat shock at 1600°C.

Micro-durability of samples. Dissolving the oxygen in the metal and forming the stabilized alpha solution causes the increase of the hardness of the metal matrix. Previous research have shown that the hardness profile in the section is similar to that of oxygen concentration [12,13]. The hardness profile in the section for samples subjected to 3 cycles of thermal shocks with a duration of 30s, in the range 600-1500°C, is shown in fig. 11.

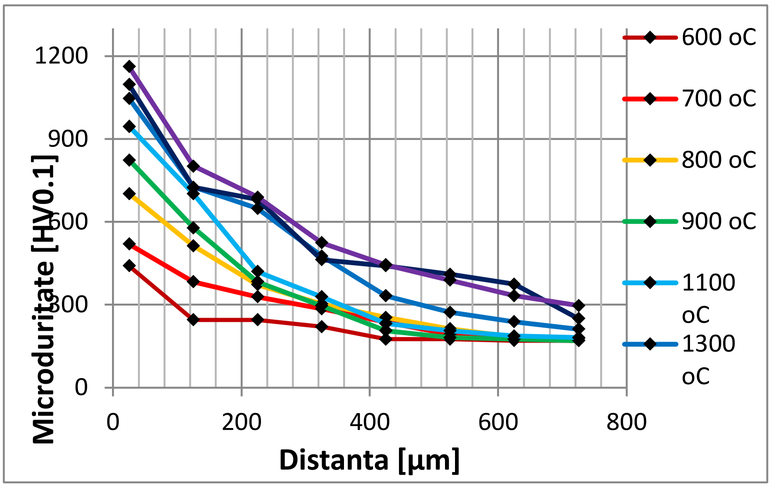


Fig. 11. The influence of the temperature on the micro-hardness
for three cycles of thermal shock of 30s.

The increase of the treatment temperature determines the widening of the high hardness zone on the sample section.

The thermal diffusivity, determined at the temperature of 350°C, the operating temperature of the zircaloy sheath for the fuel element in the CANDU reactors, is shown in fig. 12.

At the same temperature of treatment by thermal shocks, the values show an important decrease of the diffusivity with the number of cycles applied. For the same number of cycles of applied thermal shocks, the diffusivity decreases drastically with the increase of the temperature between 600 and 1600°C. The variation of the diffusivity with temperature is similar to that obtained by isothermal oxidation, but with other values.

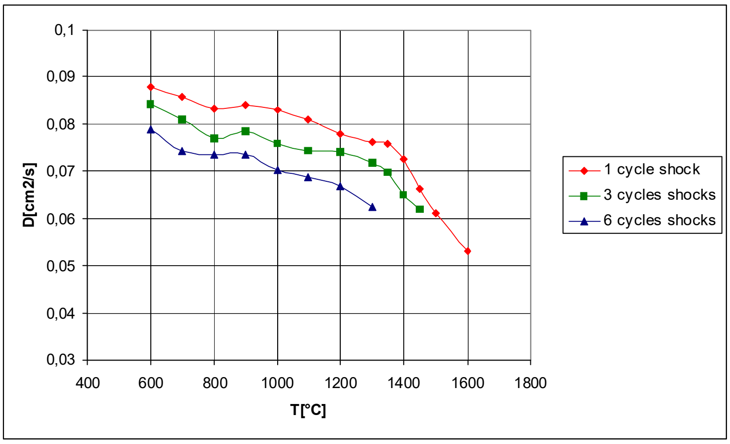


Fig. 12. Influence of the temperature of the thermal shocks with duration of 30s and of the number of shocks applied on the values of the thermal diffusivity determined at 350°C

3. Conclusions

The influence of the oxidation in air under thermal shocks on the microstructure, composition and micro-hardness of the zircaloy-4 samples for treatments with 3 cycles and 6 cycles of thermal shocks and durations of 30 and 60s, applied between 700 and 1500°C had been determined. The formed oxide layers had been analyzed microstructurally, at the surface and in the section, establishing the influence of the temperature of the shocks and of the number of the shocks on their development, on the defects that do appear in the layers and on the compactness.

In the case of samples treated by thermal shocks at temperatures above the allotropic transformation, the formation of a solid alpha solution layer stabilized by dissolving the oxygen had been revealed under the oxide layer.

The layer had a relatively uniform thickness, as opposed to the columnar development of the alpha layers in the treatment of isothermal oxidation; these phenomena can be explained by the duration of the diffusion processes.

The internal stresses that appear during the treatment by thermal shocks determine the occurrence at the oxide-metal interface, of important cracks arranged in directions perpendicular to the interface, cracks that propagate towards the core in needles and platelets of the samples. The cracks formed constitute oxygen diffusion pathways in the metal beneath the oxide layer.

The EDX analyzes revealed the variation of the chemical composition of the samples in the section, as they are correlated with the formation of the oxide layers, of the solid alpha solution stabilized by dissolving the oxygen in the metal under the oxide layer and with the appearance of compactness defects in the layers and the cracks in the metal.

The micro-hardness tests showed the influence of the temperature of treatment by thermal shock on the variation of hardness in the section of samples, correlated with the nature of the formed phases. The increase of the temperature of the thermal shock determine the increase of the zone of high hardness in the section of the sample, explained by the intensification of the diffusion of the oxygen in metal.

The thermal treatment by cyclic shocks determines the decrease of the values of the thermal diffusivity with the increase of the number of shocks applied. For the same number of shocks applied the values of the diffusivity decreases much with the increase of the temperature of the shocks.

The results obtained after the treatment with thermal shock were compared with data from the literature on isothermal and anisothermal treatments and with own results obtained by isothermal oxidation.The research contributes to the development of the database on the Zircaloy-4 alloy and can give directions for the use of this alloy under conditions of thermal shock and thermal fatigue, probably in areas other than nuclear energy.

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