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Stress release in α-Cr_2O_3 oxide thin films formed on Ni30-Cr and Fe47-Cr alloys

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ABSTRACT

For high temperature materials such as metallic Fe-Cr and Ni-Cr alloys, the oxide film which develops at the sample surface during annealing acts as a protective barrier. However, its mechanical integrity may be affected by strong compressive residual stresses which appear during the thin film growth and cooling processes. This paper reports a detailed study of the physical mechanisms responsible of the subsequent stress relaxation. For that purpose, nondestructive and destructive processes and their combination are carefully analyzed. A noticeable difference is found between the two alloys, grain boundary sliding and delamination mechanisms being dominant physical mechanisms for the Ni-30Cr alloy while a third phenomenon is clearly evidenced for the Fe-47Cr alloy.

1. Introduction

Chromia-forming alloys are regularly used for high temperature applications. The oxide film formed by reaction with air acts as a protective barrier against oxygen and slows down the oxidation kinetics, extending the life time of the material. Durability of the metallic alloys is then closely related to the thermomechanical integrity of the oxide film. However, it is known that during the growth and the cooling step of the oxide scale, compressive residual stresses with magnitude of the order of several GPa are developed in the film as a result of the constraint imposed by the substrate [1–11]. When the stored elastic energy which increases with layer thickness, reaches a critical value, stress relaxation takes place for minimizing elastic energy. Then, two well-known mechanisms may be activated: (i) a destructive process which leads to oxide scale damaging (for instance, delamination, cracking and finally spalling) [12–17] and promote oxidation recovery (ii) a non-destructive process related to visco-plastic phenomena, like creep of the oxide scale or the metal, and more accurately diffusion-creep for temperatures in the range [700–1000 °C], which may also lead to stress release but without film damaging [18]. This later phenomena may also be accompanied by grain boundary sliding already observed in bulk polycrystalline ceramics, their amplitude being quantified by measurements of height differences between neighboring ceramic grains [19–25]. Such delamination [26–28] and diffusion-creep [29,30] phenomena have been recently highlighted in a study concerning thermal oxide scales formed on Ni-30Cr alloys [31]. In this work, a method based on the adaptation of the measurement of height differences between neighboring grains in bulk ceramics has been developed for the polycrystalline oxide ceramic scales formed on metallic substrates. Thanks to this method, quantification of the grain boundary sliding mechanism in such systems has been achieved. Considering literature for this alloy [29,30], it appears that diffusion-creep has already been indirectly evidenced in these types of chromia formers. Indeed, from the modelling of the growth stress evolution, an optimization procedure was used to extract the characteristic thermomechanical parameters of the system at high temperature. In particular, Norton

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exponent for these ceramic films were found to be close to unity which is compatible with either inter or intra granular diffusion-creep. Furthermore, the creep coefficients in the metal are systematically two orders of magnitude lower than the oxide film ones which mean that creep should occur preferentially in the later, the film volume (proportional to the thickness) being at least one hundred times smaller in this system than the one of the metallic substrate. The development of high stresses within the oxide layer or at the oxide/metal interface will be reduced leading then to a beneficial influence on the process of scale failure. Let us notice that no feature related to conventional plasticity has been evidenced in these ceramic films.

The aim of the present work is to investigate the contribution of both destructive and non-destructive processes to stress release phenomena for both Ni-30Cr/Cr_2O_3 and Fe47-Cr/Cr_2O_3 systems. Indeed, to our knowledge, careful comparison between the delamination process on one hand and the diffusion-creep/grain boundary sliding phenomena on the other hand, has not been yet achieved for an identical oxide/metal system. Such a work is necessary to evaluate the interplay between these two main relaxation mechanisms, as well as their evolution with the oxidation time and temperature. Furthermore, quantitative study of the action of these phenomena on other systems than Ni-30Cr/Cr_2O_3 is missing. Experimental investigations will be done for oxidation temperatures in the range [700–1000 °C]. Residual stress magnitude in the oxide scales, delamination ratios and average heights differences between neighboring ceramic grains will be systematically determined after 3 and 18 h upon oxidation and their evolutions with temperature will be analyzed. In addition, the oxide creep activation coefficients J_{ox} will be determined.

2. Materials and experimental procedure

The detailed compositions of the Fe-47Cr and Ni-30Cr alloys are given in Table 1 [32]. A thermal pre-treatment at 1000 °C during 1 h has been achieved to homogenize the metal microstructure.

Samples are plane disks with cylindrical geometries, 12 mm in diameter and 1.5 mm thick. The sample surfaces were all mechanically polished with SiC paper and diamond paste to obtain a 3 μm metallic polishing finish which corresponds to an rms roughness value of about 10 nm [30].

Then, the samples are oxidized in a muffle furnace for 3 and 18 h at 700, 800, 900 and 1000 °C for the Ni30-Cr alloys. The same procedure was used for the Fe47-Cr alloys but at only three different annealing temperatures: 800, 900 and 1000 °C. Actually, the quantification of the stress magnitude and the proper observation of the delamination below 800 °C are difficult to achieve because of the too small thickness of the oxide layer. A maximum temperature of 1000 °C has been chosen to avoid the chromia sublimation [33]. Oxidation times of 3 and 18 h are respectively considered to obtain a microstructural state of the oxide with a maximum magnitude of the growth stresses (after 3 h), and with sufficient stress already relaxed (after 18 h) [34]. The higher cooling rate of 150 °C/min has been selected to minimize the influence of the stress release during cooling [28,30]. Three series of specimens both for NiCr-30 and FeCr-47 alloys have been systematically prepared to check reproducibility. Thermogravimetric analyzes were also carried out to analyze the oxidation kinetics of the two oxide/metal systems.

Stress magnitudes have been determined thanks to Raman spectroscopy for each oxidation condition with the procedure describes in Refs. [28,30]. The calibration determined by Mougin et al. [35] relates the stress magnitude σ to the Raman peak shift Δν for the A_{1g} mode of chromia thanks to the relationship:

$$\sigma = -0.307\Delta\nu \pm 0.005 \tag{1}$$

On each sample, 15 Raman acquisitions at different places of the chromia scale have been performed; the obtained stress uncertainty is about ±50 MPa.

In order to get reliable stress values, measurements have also been done by X-ray diffraction thanks to the $\sin^2\psi$ method [36] on both systems at 900 and 1000 °C for the two oxidation times. Comparison between the two methods of stress determination gives similar stress values at ±75 MPa for each considered system. The corresponding calculation of uncertainties is detailed in Ref. [32] for each method. To conclude, the average value of the stress magnitude obtained by the two methods will be used.

Raman spectroscopy and X-Ray diffraction also allow phase analysis. For all the considered systems, the only observed oxide phase is $\alpha-Cr_2O_3$ as it was expected with such Cr alloy concentration.

Grain boundary sliding corresponds to the relative displacement of a grain with respect to its neighbors, without any rotation along a direction that belongs to the average grain boundary plan. The mean vertical offset between neighboring grains was obtained by atomic force microscopy (AFM) with the same procedure as described in Refs. [22,23,31]. The strain variation Δε due to diffusion creep which occurs between two oxidation periods t and t′ can be calculated thanks to the following relationship:

$$\Delta\varepsilon = 1.4\frac{\nu_T^t - \nu_T^{t'}}{L_T} \tag{2}$$

where ν_T^t (or $\nu_T^{t'}$) and L_T are the mean vertical offset between adjacent grains and the mean grain size respectively for an oxidation time t (or t′) at a given temperature T.

Damages by spalling or buckling which appear at the surface of the oxide scale are visualized by optical microscopy and the delamination ratio is defined by the ratio R between the damaged surface fraction and the total surface of the material S. R is calculated by the following relationship:

$$R = \frac{\sum_0^N S_i^s + \sum_0^{N'} S_j^b}{S} \tag{3}$$

with S_i^s, the surface of spall number i and S_j^b, the surface of buckle number j. N and N′ are respectively the total number of spalls and buckles observed on the oxidized surface. This procedure is the same as described in Refs. [27,30]. Because of the too small thickness of the oxide scale, the mean vertical offset between adjacent grains and the delamination ratio have not been determined on the Ni-30Cr alloy oxidized at 700 °C.

Table 1
NiCr-30 and FeCr-47 alloys composition.

Elements	Ni	Cr	Si	Mn	C	P	S	Fe	N
NiCr-30	69.65	30.22	<0.01	<0.01	230 ppm	30 ppm	40 ppm	–	–
FeCr-47	0.25	47.35	0.1	0.02	200 ppm	–	90 ppm	52.35	0.01