


Volume 51, Issue 9, September 2009 ISSN 0010-938X



CORROSION SCIENCE

The Journal on Environmental Degradation of Materials and its Control
Editor-in-Chief: G. T. BURSTEIN, University of Cambridge, U.K.
An Official Journal of the Institute of Corrosion

CONTENTS

Letter	
A. SEYED, M. LIU, P. SCHMUTZ, G. SONG, A. ATHENS and P. MARCUS	1883
Papers	
K. ARAMAKI and T. SHIMURA	1887
R. NISHIMURA and O. M. ALYOUSIF	1894
C. A. HUANG and Y. C. CHEN	1901
J. KANG, Y. YANG and H. SHAO	1907
T. JOHNSON, B. PUJILAKSONG, S. HALLSTROM, J. AGREN, J.-E. SVENSSON, L.-G. JOHANSSON and M. HALVARISSON	1914
F. CALVO, J. C. VELAQUEZ, A. VALOR and J. M. HALLÉN	1925
A. OSTOJARI, S. M. HOSSEINI, M. PEKARI, S. R. SHAHZADEH and S. J. HASHIMI	1935
N. WENZER, P. XU, S. BENDER, T. GROSS, W. E. S. UNGER and C. E. CROSS	1950
K. F. KHALED and M. A. AMIN	1964
K. V. SUBRAMANIAM and M. BI	1976
I. REZIC, L. ČURKOVIĆ and M. UJEVIĆ	1985

Contents continued on outside back cover
<http://www.elsevier.com/locate/corsci>

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Short Communication

On the relation between damage rate and stress level evolution in α -Cr₂O₃ thin films growing on Ni–33at%CrR. Siab^a, C. Huvier^b, M. Kemdehoundja^b, J.L. Grosseau-Poussard^b, J.F. Dinhut^{b,*}^a Centre Universitaire El-Tarf, BP 73, El-Tarf 36000, Algeria^b LEMMA, Université de La Rochelle, Avenue M. Crépeau, 17042, France

ARTICLE INFO

Article history:

Received 9 April 2009

Accepted 24 May 2009

Available online 2 June 2009

Keywords:

C. Oxidation

C. Effects of strain

Stress relaxation

ABSTRACT

The blistering phenomenon has been studied in chromia films formed between 700 and 900 °C on Ni–33at%Cr. The experimental conditions of the blister occurrence and the damaged surface by blisters and spalls have been determined. From the comparison between the growth stress evolution in the oxide film – which has been related to the oxide microstructure development – and the damage rate the stress relaxation by creep is shown to prevent the formation of blisters and spalls.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Many applications of high temperature alloys in oxidizing atmosphere require thermal barrier coatings (TBC) and/or the formation of thermally grown oxide films (TGO) to protect against subsequent oxidation. Chromia and alumina are suitable TGO because of their high oxidation resistance mainly due to the oxidation characteristics: slow-growing and well adherent formed films. Under oxidation, oxide films endure stresses induced by the scale growth process [1,2] (growth stress) and by the thermal expansion coefficient mismatch (thermal stress) when thermal cycling is needed [3,4]. Since the stress can lead to failure of the protective scale, one of the major questions is to preserve a good adherence of the oxide film despite of the stress level induced during either the oxidation treatment or the subsequent thermal cycles. In stressed chromia at sufficient high temperature, oxide creep is expected to occur, and could lead to a possible decrease of the stress level beneficial to the integrity of the protective oxide.

Although many studies have been devoted to the buckling phenomenon in alumina scales [5–8], similar works in chromia have not often been under much investigations. However, chromia is an important component of the protective oxide in different stainless steels and it is essential to understand the exact reasons leading to the occurrence of buckling and spalling.

We report measurements performed at room temperature of the damage rate in chromia scales formed in air between 700 and 900 °C on Ni–33at%Cr (called NiCr₃₀). The damage rate is re-

lated to the microstructure development in the oxide film, and consequently to the reached growth stress level before cooling rather than to the final residual stress. The stress relaxation, either by creep or by blistering, is analyzed with respect to the stress level and the oxidation temperature.

2. Experimental procedure

In the used alloy with a chromium content of 33at% only chromia forms under oxidation [3,4]. The results given in this paper have been obtained on cylindrical samples (diameter: 12 mm, thickness: 1 mm). The specimen preparation have been described in details previously, with special attention to the surface preparation [9]. In alumina scales, blisters can grow at room temperature first slowly and then rapidly before spalling [8]. So, it has been verified in the chromia films formed on NiCr₃₀ that in the first 48 h, no evolution happens in the oxide cooled at room temperature.

Stress determination has been performed thanks to microprobe Raman spectroscopy equipped with an in situ heater device, assuming no microstructural evolution during each measurement due to the low acquisition time (less than 1 min) [10,11]. From the five peaks of the chromia spectrum, the frequency (ν_1) corresponding to the A_{1g} vibration mode is measured with a precision equal to 0.1 cm⁻¹. The source is a helium–neon laser ($\lambda = 632.817 \mu\text{m}$) and the $\times 50$ and $\times 100$ objectives were used so that the analyzed surface is about 1 μm^2 . Unstressed chromia obtained from scrapped oxide has been chosen as a reference state in the residual stress measurements performed at room temperature. The corresponding wave number determined for the free-of-stress state (551.55 cm⁻¹) is in agreement with previous

* Corresponding author. Tel.: +33 5 46 45 82 19; fax: +33 5 46 45 72 72.
E-mail address: jfdinhut@univ-lr.fr (J.F. Dinhut).

results of Birnie et al. (552 cm^{-1}) [12] and Calvarin et al. (553 cm^{-1}) [13]. The stress determination is based on the wave number shift with respect to the reference by mean of the law established by Birnie et al. [12] and confirmed by Mougin et al. [14]. Determination of the growth stress is performed at the oxidation temperature and need the knowledge of the corresponding free-of-stress state at each temperature [11]. To this end, the scrapped film has been heated under vacuum up to $900\text{ }^\circ\text{C}$ and the reference spectrum has been recorded versus temperature (Fig. 1). In order to deduce the stress (σ) in the constrained chromia at each oxidation temperature, the following expression has been used: $\sigma = 0.307 \times \Delta\nu \pm 0.005$, where $\Delta\nu$ is the wave number shift in cm^{-1} and σ the stress in GPa.

The procedure used for the determination of the damaged surface is justified by the quasi-circular shape of the defects (Fig. 2) which has been verified to be independent on the substrate geometry. When the size of blisters and spalls has a narrow distribution range, a mean diameter is defined for each type of defects (D_b for blisters and D_s for spalls) and the number of blisters (N_b) and spalls (N_s) is measured all over the entire surface. The damage rate is deduced by: $R = (N_b A_b + N_s A_s) / A$, where A_b and A_s are, respectively, the mean area of blisters and spalls, and A is the substrate area. When a larger size distribution is observed, the size range is divided in slices, and for each of them the number of defects is measured; then R is deduced with the same procedure leading to: $R = \sum_i (N_{b_i} A_{b_i} + N_{s_i} A_{s_i}) (1/A)$ assuming i slides.

3. Results and discussion

After oxidation, three cooling rates have been used: a rapid water quenching, an air quenching by removing the NiCr_{30} samples from the furnace, and a slow air cooling by leaving the samples in the switched off furnace.

On the slow cooled NiCr_{30} , blisters or spalls have never been observed whatever the temperature and the oxidation time. On the opposite, at higher cooling rates by quenching in air or in water both types of damage can be counted. This observation is an additional proof of the appearance of blisters during the cooling stage of thermal cycling. Moreover, the cooling conditions, and especially the cooling rate appear as a determinant factor.

Using the above described procedure the damage rate has been determined at different oxidation times in the temperature range $700\text{--}900\text{ }^\circ\text{C}$. The variations in R , shown in Fig. 3, can be schematically described in the following way: starting from zero, a rapid increase in the damage rate during the first (three) hours of oxidation and a saturation (at $700\text{ }^\circ\text{C}$) or a slight decrease in R at longer oxidation times are observed.

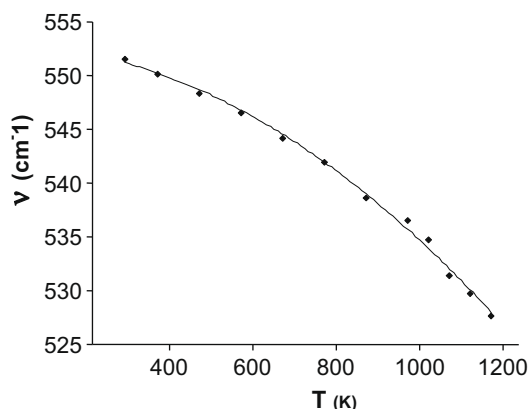


Fig. 1. Variations in the reference wave number for free-of-stress chromia.

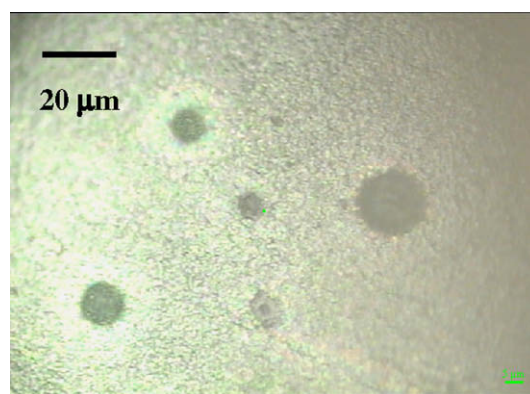


Fig. 2. General view of quasi-circular buckles in air-quenched $\text{Cr}_2\text{O}_3/\text{NiCr}_{30}$.

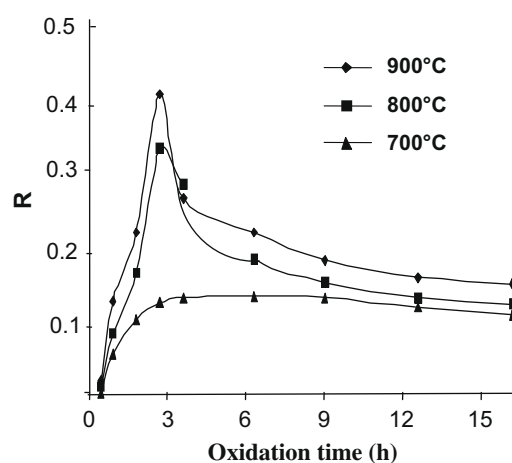


Fig. 3. Damage rate versus oxidation time in chromia grown on NiCr_{30} in the oxidation temperature range $700\text{--}900\text{ }^\circ\text{C}$.

Based on the use of different cooling rates, the damage observed at RT has been shown to take place during the cooling stage from the oxidation temperature. This result can be mainly related to the stress increase due to the thermal stress generally written [15]:

$$\sigma_{th} = \Delta\alpha \cdot \Delta T \cdot \left(\frac{E_{ox}}{1 - \nu_{ox}} \right) \quad (1)$$

where $\Delta\alpha$ is the difference in thermal expansion coefficients of the oxide (α_{ox}) and the metal (α_m), ΔT is the temperature drop, E_{ox} and ν_{ox} are, respectively, the Young's modulus and the Poisson's ratio for the oxide. In this simplified formula an elastic behavior is assumed and the oxide thickness is also assumed low – less than $1\text{ }\mu\text{m}$ in the current work [9] – with respect to the substrate thickness – more than 1 mm in the present case. For a given oxidation temperature, the thermal stress component, only related to ΔT , is the same whatever the used cooling rate, so that, it seems very difficult to explain the variations in R (Fig. 3) from the thermal stress contribution.

The nominal stress in the oxide after cooling (residual stress), has also to take into account the initial growth stress induced by the oxidation process. The relative variations of growth and residual stresses as a function of the oxidation time are shown in Fig. 4.

At short oxidation times ($t < 3\text{ h}$), the increase in growth stress magnitude (up to 2.3 GPa) induces an increasing stored elastic energy in the oxide and then, on cooling, a corresponding increase of the damaged surface via blisters and spalls as observed in Fig. 3.

It has been shown [11] that for longer oxidation times ($t > 3\text{ h}$) a relaxation mechanism by creep, related to the oxide grain size, occurs during the oxidation process inducing a growth stress release (Fig. 4). A corresponding decrease in the stored elastic energy takes

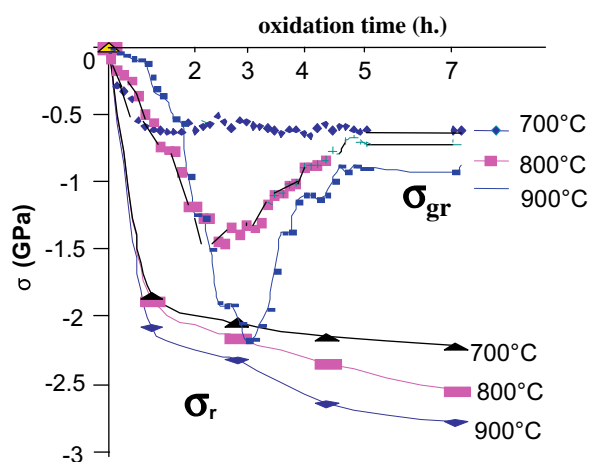


Fig. 4. Growth and residual stresses in chromia for various oxidation times of NiCr₃₀ in the temperature range 700–900 °C.

place in the film during the isothermal oxidation. So, the remaining energy to be relaxed on cooling requires a less important damage rate in the oxide as observed after long oxidation times (Fig. 3).

When increasing the oxidation temperature, the compressive stress (in absolute value) increases when $t < 3$ h. As a consequence, the damage rate R increases due to a larger elastic energy stored in the film. When $t > 3$ h, despite of a more efficient relaxation by creep, the growth stress level increases with the oxidation temperature (Fig. 4), so that, the energy to be relaxed by damage, is most important at higher temperature.

The above explanation is based upon the growth stress evolution rather than the thermal or residual stress values obtained after cooling. Indeed, the oxide grain size kinetics mainly increases with the oxidation temperature, and an efficient creep relaxation will occur [11] when the growth stress level is high enough (Coble creep or Herring-Nabarro creep). Then, the microstructure in the oxide film during the oxidation process is the relevant parameter to explain the creep relaxation in the oxide and, as a consequence, the local damage by blistering and spalling.

This approach could also explain why, when a slow cooling rate is used after oxidation, blisters and spalls are not observed. From the oxidation kinetics, it can be assumed that no appreciable oxidation takes place at temperatures below 600 °C [9]. The temperature decrease from 900 to 600 °C in a slow cooling experiment needs more than 1.5 h [15]. In these experimental conditions, (Fig. 4) the creep phenomenon induces an important decrease in stress and is very likely responsible for the disappearance of relaxation via blisters and spalls. When cooling is performed by air (or water) quenching, the temperature decrease from 900 to 600 °C requires only a few minutes and does not allow a sufficient efficiency of the creep mechanism so that the high stress level reached during

the course of oxidation has to be relaxed otherwise making possible the blistering process.

The above explanations are consistent with previous results and interpretations [9,11] but do not take into account others stress relaxation processes. It has been proposed that the measured relaxation may occur in the underlying substrate. In our experimental conditions the thickness ratio film/substrate is less than 10^{-3} , then, in order to verify the force balance equality at the oxide/substrate interface, the stress in the substrate is less than 3 MPa. Such a stress level seems too low to induce an efficient plastic deformation in the substrate, even at 900 °C. A stress relaxation via micro-cracking could also be effective and then explain the growth stress relaxation [3]. Such a mechanism is conceivable and is also sensitive to the evolution of the mean grain size. However, micro-cracking and subsequent crack healing are expected to decrease the chromium content in the substrate and an additional increase in the mass gain which has not been clearly detected [9].

Complementary experiments are in course to provide additional details about the exact nature of the creep mechanism in the temperature range 700–900 °C.

4. Conclusion

As a conclusion, the stress relaxation process in chromia films developed at 900 °C on NiCr₃₀ can be observed via two complementary mechanisms: a rather uniform stress relaxation, presumably via a creep mechanism or local debonding of the oxide film (by blistering or spalling). A low creep efficiency due to a large oxide grain size or a rapid cooling promote local blistering and spalling phenomena; a large stress relaxation by creep prevents the damage by blisters and spalls.

References

- [1] F.N. Rhines, J.S. Wolf, *Metal. Trans.* 1 (1970) 1701.
- [2] D.R. Clarke, *Acta Mater.* 51 (2003) 1393.
- [3] M. Schütze, *Protective Oxide Scales and Their Breakdown*, Wiley, Chichester, 1997.
- [4] A.M. Huntz, B. Pieraggi, *Oxidation des Matériaux Métalliques*, Hermes Science, Paris, 2003.
- [5] H.E. Evans, M.P. Taylor, *Surface and Coatings Technology* 94–95 (1997) 27.
- [6] V.K. Tolpygo, D.R. Clarke, *Acta Mater.* 46 (1998) 5167.
- [7] J.S. Wang, A.G. Evans, *Acta Mater.* 47 (1999) 699.
- [8] V.K. Tolpygo, D.R. Clarke, *Mater. Sci. Eng. A* 278 (2000) 151.
- [9] M. Kemdehoundja, J.F. Dinhut, J.L. Grosseau-Poussard, M. Jeannin, *Mater. Sci. Eng. A* 435 (2006) 666.
- [10] M. Kemdehoundja, J.L. Grosseau-Poussard, J.F. Dinhut, *Appl. Phys. Lett.* 92 (2008) 241924.
- [11] M. Kemdehoundja, J.L. Grosseau-Poussard, J.F. Dinhut, B. Panicaud, *J. Appl. Phys.* 102 (2007) 1.
- [12] J. Birnie, C. Craigs, D.J. Gardiner, P.R. Graves, *Corros. Sci.* 33 (1992) 1.
- [13] G. Calvarin, A.M. Huntz, A. Hugot Le Goff, S. Joiret, M.C. Bernard, *Scripta Mater.* 38 (1998) 1649.
- [14] J. Mougín, T. Le Bihan, G. Lucazeau, *J. Phys. Chem. Sol.* 62 (2001) 553.
- [15] A.M. Huntz, S. Daghigh, A. Piant, J.L. Lebrun, *Mater. Sci. Eng. A* 248 (1998) 44. see also S. Daghigh, Ph.D. thesis, université de Paris XI Orsay (1996).