Growth Strains in Chromium Oxide Grown on Fe-Ni-Cr Alloy: Test of Rhines-Wolf Model of Oxide Growth

B.W. Veal, A.P. Paulikas, J. Linton, G. Jennings
Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Subjected to a high-temperature oxidizing environment, the austentic alloy 55Fe-25Cr-20Ni (wt. %) will develop a Cr_2O_3 oxide layer that is adherent, slow growing, and self-healing and that serves as an effective protective layer against oxidative and corrosive attack. Such thermally grown protective oxides have long been commercially important and consequently have been extensively studied. However, the mechanisms that control oxide growth and adhesion remain poorly understood.

One of the elusive issues has been the role of growth strains. Oxide growth occurs when metal atoms from the substrate encounter oxygen atoms from the atmosphere in a cross-current diffusion process. Rhines and Wolf [1] have argued that counterdiffusing oxygen and metal ions might meet within the existing oxide and combine to produce new oxide growth. They reasoned that new growth internal to existing oxide would lead to the development of large compressive growth strains, since the oxide remains confined during growth by the relatively massive substrate. To date, the validity of the Rhines-Wolf model has not been explicitly demonstrated [2].

We have used synchrotron radiation to develop a new technique for measuring, *in situ*, the development and evolution of strains in polycrystalline films at temperatures up to 1100°C. With this technique, we can monitor the strain response in films subjected to a stress perturbation and examine both creep and growth processes. These high-precision measurements acquired with a high point density enable us to demonstrate, for the Fe-Cr-Ni alloy, that new growth must occur within the oxide to establish a large in-plane compressive stress.

Strain measurements were acquired using x-ray diffraction (XRD) by exploiting x-ray synchrotron radiation at beamline 12-BM at the APS.

Methods and Materials

X-rays were impinged on a polished alloy sample, at an incidence angle of 2° to 5°, contained in a horizontal tube furnace. Debye-Scherrer diffraction rings from the sample were recorded by using a Mar 345 image plate detector that has a circular active area with a diameter of about 35 cm. In this arrangement, most of the upper half plane of the Debye-Scherrer diffraction pattern was recorded.

When a film constrained by a massive substrate is subjected to an in-plane (e.g., compressive) stress, there will be an out-of-plane response (expansion) of the free surface, as dictated by the Poisson ratio. Thus, the in-plane and out-of-plane d-spacings of diffracting planes in a stressed polycrystalline film are different. This results in an elliptical distortion of the Debye-Scherrer diffraction rings. We measured and analyzed this ellipticity, exploiting the entire available diffraction pattern in the upper half plane to determine the strain in the film.

Results and Discussion

As shown in Fig. 1, the sample was rapdily heated in air (at 1000°C/h) from room temperature to 800°C, where it was held for 4 hours. Three abrupt 40°C temperature changes (drops) were subsequently imposed, with each change followed by 4 hours of isothermal oxidation. Finally, the temperature was rapidly returned to 800°C and held for an additional 4 hours. In-plane strain measurements were obtained in approximately 5 minute intervals during this oxidation run. The earliest oxide (Fig. 1) showed a very substantial compressive growth strain. With increased

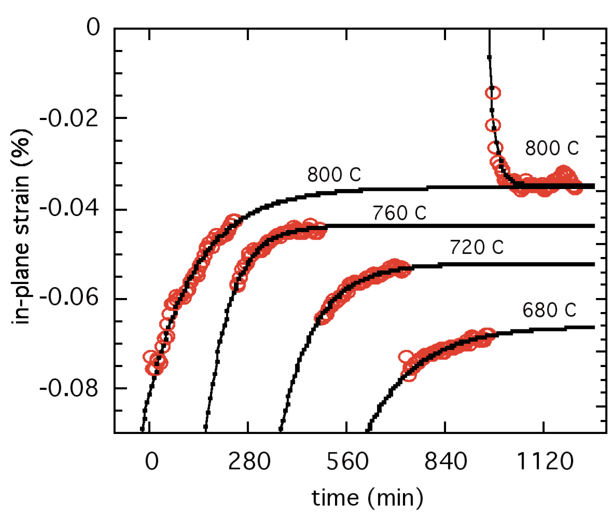

FIG. 1. ***In situ*** *measurements of strain in Cr_2O_3 scale thermally grown on an Fe-25Cr-20Ni alloy plotted versus oxidation time. Temperature excursions change the stress state in the oxide because of the thermal expansion difference between the oxide and substrate.*

oxidation at 800°C, the magnitude of the compressive strain declined dramatically, apparently revealing a strong influence of creep in the early oxide.

After 4 hours of oxidation, when the magnitude of the compressive strain steadily declined, the temperature was abruptly dropped to 760°C. Since the thermal expansion of the metal substrate was much larger than that of the oxide, an additional compressive stress was imposed on the constrained oxide. In the subsequent 4 hours, the strain relief was again observed as new growth occurred and creep continued to manifest itself. Strain relief was also observed after subsequent temperature drops to 720°C and 680°C. However, the time dependence for strain relief was different for each of the isothermal holds.

After 16 hours of oxidation, the sample was rapidly (1000°C/h) returned to 800°C (from 680°C). With this temperature rise, the compressive strain was reduced by approximately the sum of the strain imposed by the three previous temperature drops. Since so much strain relaxation had occurred during the isothermal holds, the magnitude of the compressive strain was now much smaller than the previous value at 800°C (e.g., at 4 hours).

Remarkably, we now observed a dramatic reversal: a rapid increase in the compressive stress as new oxide formed. This buildup in compressive stress ran counter to the influence of creep. This re-establishment of a substantial compressive stress during isothermal oxidation, from a low-stress condition, must have resulted from new growth that occurred internal to the oxide, on those grain boundary planes that were aligned normal to the sample surface (or, more precisely, with a geometrical component that was normal to the sample surface). We believe that these measurements provide direct confirmation of the Rhines-Wolf model, which was initially proposed to account for compressive growth strains in NiO [1].

We have argued that the behavior shown at 800°C in Fig. 1, which demonstrated the restoration of a compressive stress in the oxide, resulted from the deposition of new oxide on grain boundaries (GBs) that were aligned with a component perpendicular to the sample surface. During the recovery process (re-establishment of the compressive stress), about 100 Å of new oxide was added to the existing oxide, which was about 0.8 μm thick. We calculated the fraction of this new growth that was deposited within the oxide to re-establish compressive stress by comparing the observed strain change with the strain change that would result if all new growth appeared (uniformly distributed) on the grain boundaries. This analysis indicates that, for the conditions examined here, about 17% of new growth occurred within the oxide.

We did an analysis, taking into account both creep and growth processes, to extract relaxation times at different temperatures from the data of Fig. 1 (solid lines in Fig. 1). From these results, an activation energy for creep of about 2 eV was obtained.

Acknowledgments

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References

[1] F.N. Rhines and J.S. Wolf, Metall. Trans. **1**, 1701 (1970).
[2] D.E. Clarke, Acta Mater. **51**, 1393-1407 (2003).