Role of Transitional Alumina in Growth Stress in Alumina Scale

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Introduction

Certain metals can be used at elevated temperatures in oxidizing environments because they form a protective scale — an oxide film that limits further oxidation. The useful life of these materials will be limited if the scale cracks and spalls, so it is important to understand and control the stress in the scale that can drive this failure. When the metal is heated or cooled, thermally induced stress arises from the difference in the thermal expansion coefficients between the metal and its oxide. Thermal stress and its effects on oxidation are relatively well understood [1-3]. Stress development when the metal is held at a constant temperature while the oxide grows, however, is not well understood. Even the sign of the resulting growth stress is debated. Still less is known about the magnitude and the effects on failure [4-8].

In our 2001 report, we demonstrated that synchrotron x-ray diffraction can be used for real-time measurement of stress in the early stages of oxidation. We found that a transient tensile stress of ~1 GPa in the Al_2O_3 scale formed on certain NiAl and FeCrAl alloys at 1000-1200°C in air, which relaxed over time scales of minutes to hours, depending on the growth temperature. This result appears to contradict the conventional wisdom that the sign of stress in scale is determined by the Pilling-Bedworth ratio (PBR) of metal volume to oxide volume [8]. Because the metal *expands* to form Al_2O_3, the scale should form under *compression*. In the continuing work we report on here, we have investigated the role of transitional Al_2O_3 in the generation of stress. Al_2O_3 scales grown at 1000-1100°C have been reported to form in metastable, transitional structures, which then transform to the equilibrium α-Al_2O_3 [9]. Al_2O_3 *contracts* during this transition, so a *tensile* stress could result.

Methods and Materials

The alloy compositions were based on the FeCrAl and NiAl systems (Table 1). The Kanthal AF alloy was a commercial rolled ribbon, while the other two FeCrAl-based alloys were made at ORNL by arc melting, casting, hot extrusion, and rolling to sheet. The FeCrAl-based specimens (approximately 1×5 to 7×100 mm) were cut from the ribbon or sheet, annealed, and mechanically polished to a 0.3-µm diamond-paste surface finish. The two NiAl alloys were cast into rectangular plates from which specimens (approximately $1 \times 10 \times 100$ mm) were electrodischarge-machined and then electropolished.

The samples were resistively heated in air. Stress measurements were made by using 9-keV focused, monochromatic undulator radiation in a parallel-beam geometry. The multiple-tilt method was modified to hold the incident beam at a fixed glancing angle of 10° to maximize the ratio of diffraction from the scale to background from the substrate. A graphite diffracted-beam monochromator was used to filter out sample fluorescence. Each stress measurement comprises five tilts and takes ~5 minutes.

Results

The transitional phases are modifications of the cubic spinel structure [10]. Stress measurements were made by using the $Al_2O_3(11\bar{2}3)$ reflection, taking a wide enough scan to include scattering from the (400) reflection of the spinel structure. Measurements were taken at 1000°C and 1100°C, where transitional Al_2O_3 has been reported to form [9]. Only α-Al_2O_3 is observed for FeCrAlY. A peak at the (400) spinel Bragg angle is observed for Kanthal and NiAlHf, but it grows along with α-Al_2O_3 rather than transforming to α-Al_2O_3, so it is more likely to be a stable spinel such as $NiCr_2O_4$, $Fe(Cr,Al)_2O_4$, or $NiAl_2O_4$.

Only for NiAl does the signature of transitional Al_2O_3 appear. A split peak occurs at the (400) Bragg angle, along with the α-Al_2O_3 peaks (Fig. 1), that grows for ~15 minutes, then converts to α-Al_2O_3 (Fig. 2).

TABLE 1. Compositions of Alloys Used in This Study (concentrations are in at. % except for S).

Alloy	Fe	Ni	Cr	Al	Other	S (ppma)
FeCrAlY	70.1		20.1	9.8	0.035 Y	<4
Kanthal AF	67		21	11	0.5 Si, 0.08 Zr	
Ni-43Al		57		43		
Ni-43Al-Hf		57		43	0.06 Hf	

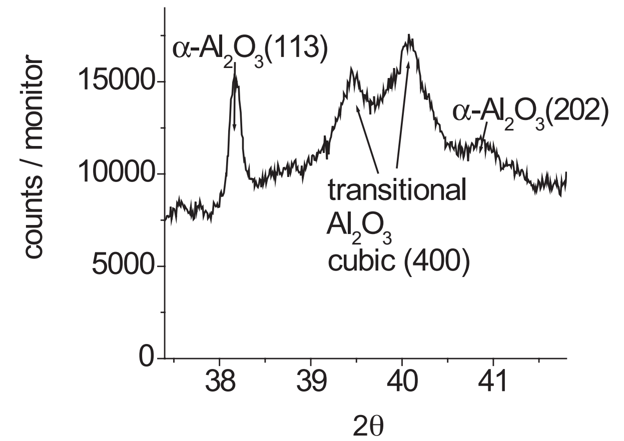

FIG. 1. Diffraction from NiAl, heated in air at 1100°C for 6 minutes.

Tensile stress is observed in α-Al_2O_3 while transitional Al_2O_3 appears. Stress could not be measured for transitional Al_2O_3 because the peaks are broad, weak, and overlapping.

Discussion

A possible cause of tensile stress is the volume change when transitional Al_2O_3 converts to α-Al_2O_3 — volume decreases, giving a PBR of ~0.85. The temporal coincidence of transitional Al_2O_3 and growth stress in NiAl (Fig. 2) supports this mechanism. However, a tensile stress is unexpected when the total reaction of metal to oxide has a PBR of >1. The reaction of metal to transitional Al_2O_3 will occur at the metal-oxide interface, where the metal may accommodate stress by deforming plastically or be less constrained, while the final conversion to α-Al_2O_3 will occur at an oxide-oxide interface, where stress cannot be so readily relaxed. A more serious objection is that while transitional Al_2O_3 can account for tensile stress in NiAl, it is not observed in NiAlHf or FeCrAlY, which have a similar transient tensile stress, so another mechanism would be needed to account for growth stress in this alloy. An explanation that accounted for all results would be more compelling.

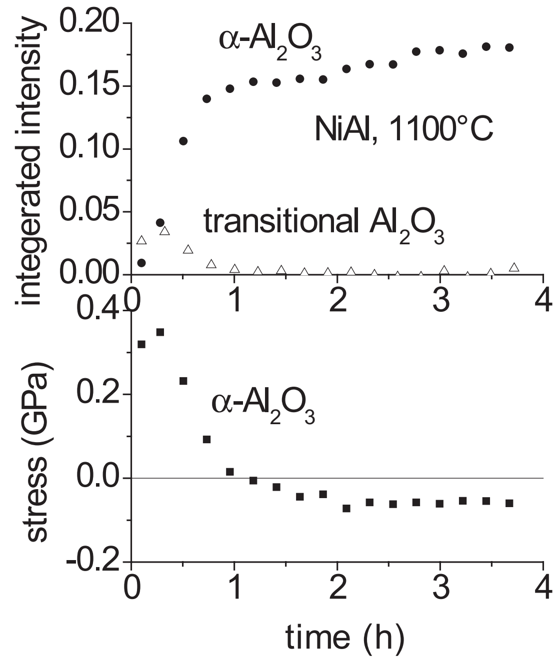

FIG. 2. Integrated area of α-$Al_2O_3(11\bar{2}3)$ and transitional Al2O3(400) Bragg reflections (top); growth stress in a-Al2O3 (bottom).

Acknowledgments

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References

[1] H.E. Evans, Mater. Sci. Eng., A **120**, 139-146 (1989).
[2] M. Schütze, *Protective Oxide Scales and Their Breakdown* (John Wiley and Sons, Chichester, England, 1997).
[3] H.E. Evans, Mater. High Temp. **12**, 219-227 (1994).
[4] A.G. Evans and R.M. Cannon, Mater. Sci. Forum **43**, 243-268 (1989).
[5] F.H. Stott and A. Atkinson, Mater. High Temp. **12**, 195-207 (1994).
[6] R.M. Cannon and P.Y. Hou, in *High-Temperature Corrosion and Materials Chemistry*, edited by P.Y. Hou, M.J. McNallan, and R. Oltra et al. (The Electrochemical Society, Pennington, NJ, 1998).
[7] W.D. Nix and B.M. Clemens, J. Mater. Res. **14**, 3467-3473 (1999).
[8] N.B. Pilling and R.E. Bedworth, J. Inst. Met. **29**, 529-582 (1923).
[9] H. J. Grabke, Intermetallics **7**(10), 1153-1158 (1999).
[10] I. Levin and D. Brandon, J. Am. Ceram. Soc. **81**(8), 1995-2012 (1998).