Growth Stress in Alumina Films at High Temperatures

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Introduction

Many metals can be used at high temperatures in oxidizing environments because of the growth of a protective oxide film. A critical factor in the lifetime of such metals is the buildup of stress in these films, leading to cracking, spalling, and delamination. One cause of stress is well understood: When the material is cooled, the metal substrate typically contracts more than does the oxide film, leaving the metal under tension and the oxide under compression. The mechanisms and character of growth stress (stress that develops isothermally during growth at high temperatures), however, are much less well known [1]. This research addresses the most basic questions: How large is the growth stress, and how does it develop with time? Experimental data that help answer these questions are critical to developing appropriate mechanistic models for growth stress in oxide films formed at high temperatures. Previous studies involving high-temperature x-ray diffraction (XRD) measurements of stress in oxide films typically yielded the first data points after several hours of growth.

The high brilliance of the APS allows us to measure stress from thin oxide films at high sensitivity and time resolution. Under the appropriate conditions, a complete stress determination can be made in just 5 min. During this reporting period, we completed a survey of growth stress in alumina formed in air on several alloys in a temperature range of 1000 to 1200°C. It clearly and consistently demonstrated the ability of synchrotron radiation to measure rapid changes in stress states of alumina films that could not be detected by using conventional x-ray sources.

Methods and Materials

Alloy compositions are given in Table 1. Kanthal AF was a commercial rolled ribbon; other compositions were cast and machined to size. Samples were annealed and mechanically polished to a 1-μm diamond-paste surface finish. Strips (approximately 1 × 5 × 100 mm) were clamped between water-cooled Cu electrodes and resistively heated. Temperature was measured by using a Pt/Pt10%Rh (type S) thermocouple spot-welded to the sample a few millimeters from the impingement point of the x-ray beam. The temperature was ramped to the growth temperature in 120 s. Background radiation was reduced by using an x-ray energy of 9 keV, which is above the absorption edges of Fe and Ni, thereby minimizing x-ray penetration into the metal substrates and thus scattering from the substrate. A graphite diffracted-beam monochromator filtered x-ray fluorescence from the sample. Monochromatic undulator radiation was provided by the X-33-ID-D beamline at APS. The diffracted beam was collimated by soller slits; this parallel-beam geometry minimizes the effect of sample displacement on strain measurements.

Table 1. Alloys included in growth stress study.

Alloy	Composition (at. %)
NiAl	Ni-43Al
NiAl(Hf)	Ni-43Al-0.05Hf
Haynes 214	Ni-16Cr-10Al-3Fe-0.5Mn-0.2Si-0.1Zr-0.05C-0.01Y
Kanthal AF	Fe-21Cr-11Al-0.5Si-0.1Ni-0.1Mn-0.08Zr
XFCA95	Fe-20Cr-10Al-0.035Y-0.0065C
XFCA96	Fe-16Cr-9Al-0.8Mo-0.03Hf-0.0075C

Strain was measured by monitoring the Bragg angle of the α-Al_2O_3 $(11\bar{2}6)$ or $(21\bar{3}4)$ reflection at five sample tilts (the $\sin^2\psi$ method [2]). The incident beam was kept at a fixed glancing angle of 5° to maximize the ratio of the film scattering to the substrate-induced background. Stress was calculated by using the temperature-dependent elastic constants of Al_2O_3 [3]. Alumina is sufficiently isotropic so that there is no significant difference between elastic constants calculated by using the Voight and Reuss methods.

Results

In situ stress measurements have been made for alumina films grown on the alloy substrates shown in Table 1. With few exceptions, duplicate runs have been made under every experimental condition, and excellent reproducibility has been demonstrated. Examples of evolution in growth stress are shown in Figs. 1 and 2. Where significant growth stress occurs, early-stage tensile stresses (up to ~1 GPa) are most common. The timescale for stress development and relaxation varies dramatically, depending on the temperature and substrate material (Figs. 1 and 2). In the case of XFCA95, for instance, the stress still increases after 12 h at 1000°C, while, at 1200°C, stress is already rapidly decreasing just 5 min after the start of film growth. In the casse of NiAl, the presence of a small Hf addition (which changes the growth rate as well as, ultimately, the film adhesion [4]) has a significant effect on stress development. Three alloy systems — Kanthal AF, XFCA96, and NiAl — showed growth stresses of <200 MPa over a range of 1100-1200°C.

Interrupted thermal cycling was used to determine the response of the Al_2O_3 films to combined growth and thermal stresses and to explore relaxation processes in more detail. As shown in Fig. 3, the thermal stress (compressive) in XFCA95 relaxes in ~0.5 h at 800°C and is completely relaxed in <5 min at the 1000–1200°C temperature range at which growth stress is studied.

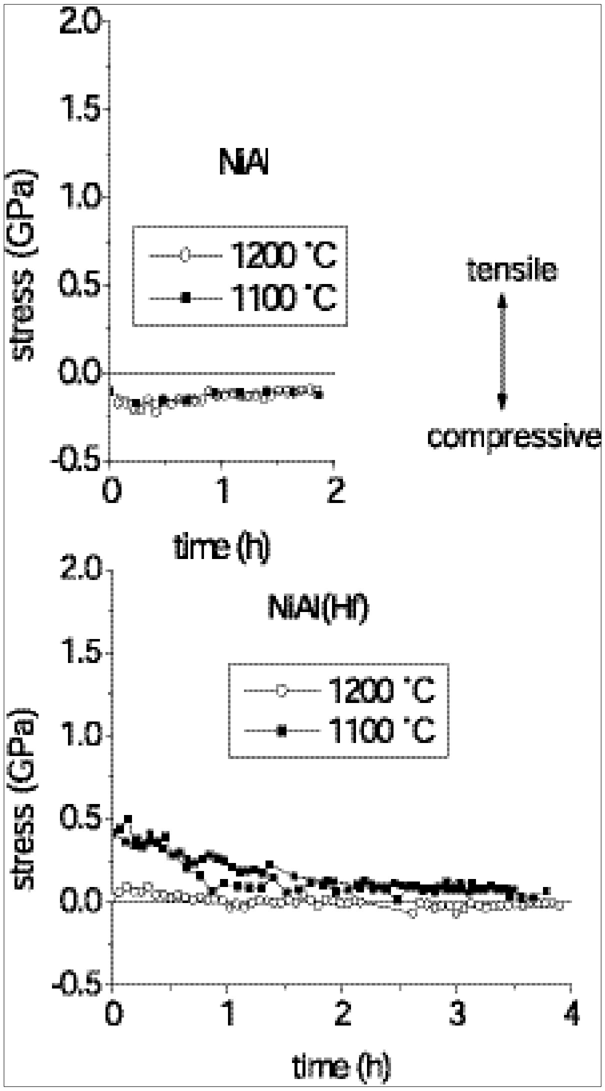

FIG. 1. In-plane stress in Al_2O_3/NiAl.

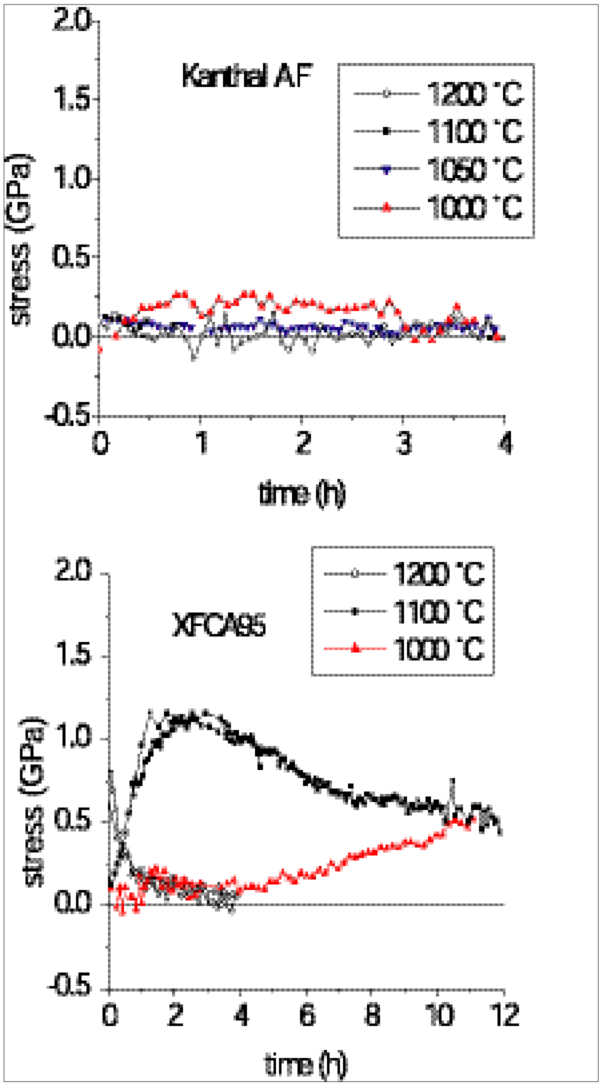

FIG. 2. In-plane stress in Al_2O_3/FeCrAl type alloys.

Discussion

Our results, which show 0.5 GPa of tensile growth stress for α-Al_2O_3 on NiAl at 1100°C relaxing over 2 h, are consistent with those of Shumann et al. [5], who were able to measure growth stress only after 4 h and found it to be near zero. Our results differ from those of Sarioglu et al. [6], who found a 1-GPa compressive stress in Y-doped FeCrAl grown at 1000 and 1100°C for 6.25 h. We found a 1 GPa *tensile* stress at 1100°C in XFCA95 and near-zero stress at 1000°C.

We found that growth stress persists for more than 12 h in XFCA95 at temperatures at which thermal stresses relax in <5 min. These data and data from some of our other runs suggest that the growth stress is a dynamic equilibrium between generation and relaxation.

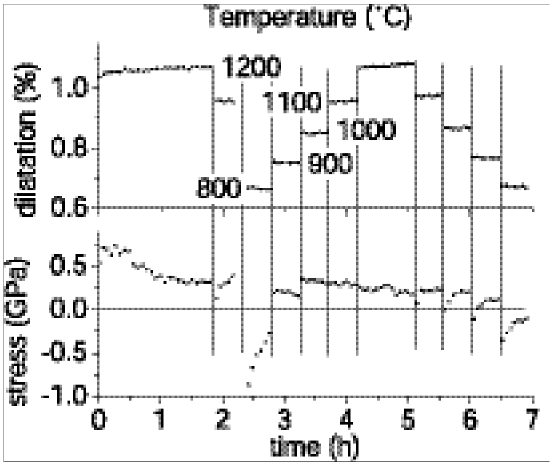

FIG. 3. Stress measurements during interrupted thermal cycling of XFCA95. The dilatation of the lattice indicates the temperature of the film.

Many models of oxide growth at high temperatures predict a compressive growth stress caused by development of Al_2O_3 at either internal alumina grain boundaries or the interface between the film and the metal substrate. In either case, the growing material is geometrically constrained in a confined space [1, 7]. While our initial data were not sufficient to develop a mechanistic description of growth stress development, the present observations of tensile stresses clearly cannot be explained in this way. Other high-temperature models [1], as well as models put forth to explain tensile stresses during film deposition at relatively low temperatures [8], are being examined for their relevance, and other synchrotron experiments are being devised. For example, if the observed tensile stresses are caused by the transformation of a transitional aluminum oxide (e.g., cubic γ-Al_2O_3) to α-Al_2O_3 (because of a net decrease in oxide volume), monitoring both diffraction peaks as a function of time at the temperature should provide the data necessary to demonstrate (or refute) this mechanism. Such experiments are possible only by using the high brilliance of a synchrotron source.

We have shown that growth stress can be measured in the earliest stages of oxide film growth (first few minutes) and that rapid changes in stress can occur on this timescale. Tensile growth stresses as large as 1 GPa can occur over the first few hours of growth. The unexpected observation of tensile stress poses a challenge for modeling of the growth of oxide films on high-temperature alloys.

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