New Technique for Measuring Growth Strains in Thermally Grown Oxides

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

Introduction

Here we report on the development of a new technique that uses synchrotron radiation to measure, *in situ*, the development and evolution of strains in polycrystalline films at temperatures up to 1100°C. This effort was motivated by the need to acquire quantitative information about growth strains in thermally grown oxides.

Thermally grown oxides (e.g., chromium and aluminum oxides), provide essential corrosion protection for numerous structural applications that must function at elevated temperatures. Examples include turbine blades for aircraft engines and land-based energy generation systems. However, although protective oxides have long been commercially important and have been extensively studied, growth mechanisms remain poorly understood [1].

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. It has long been recognized that stresses are likely to develop in this growth process. Because of complications resulting from creep in both the oxide and the substrate, it appears to be necessary to measure the strains *in situ*, as oxide growth proceeds at the oxidation temperature. However, it is difficult to measure x-ray diffraction by using conventional in-lab techniques. Consequently, very few measurements have been reported. Uncertainties in reported measurements are large (often comparable to the magnitude of the reported strains), so even the sign of the strain (i.e., whether it is tensile or compressive) is frequently unclear.

In the study discussed here, strain measurements were acquired with high precision (~2×10^{-5} in strain) at frequent (5-minute) intervals during the oxidation process. Results are presented for aluminum oxide thermally grown on β-NiAl. These are compared with recent measurements acquired with a conventional in-lab method. Strains were measured using x-ray diffraction (XRD) at beamline 12-BM at the APS.

Methods and Materials

As shown in Fig. 1(a), x-rays were impinged on a polished alloy sample, at an incidence angle of 2° to 5°. The sample was contained in a horizontal tube furnace. Debye-Sherrer diffraction rings from the sample were recorded by using a Mar 345 image plate detector. The detector has a circular active area with a diameter of about 35 cm. In this arrangement, most of the upper half plane of the diffraction circle was recorded.

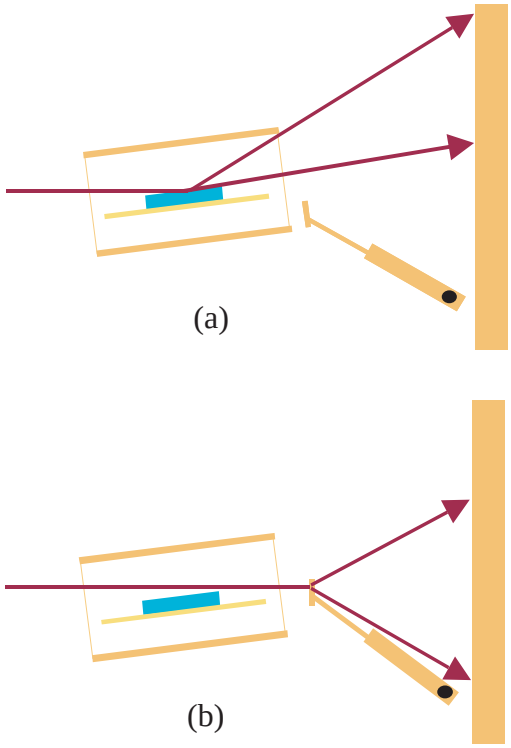

FIG. 1. (a) X-rays strike the sample and generate a Debye-Scherrer diffraction pattern in the upper half plane of the large area detector. (b) To measure the beam position, the sample is lowered and a reference is exposed. The sample is lowered, and a reference sample (porous, sintered alumina) is placed in the x-ray beam. These operations are computer driven so data acquisition is automated

When a film constrained by a massive substrate is experiencing an in-plane (e.g., compressive) stress, an out-of-plane response (expansion) of the free surface occurs, as dictated by the Poisson ratio. Thus, the in-plane and out-of-plane d-spacings of diffracting planes in a stressed 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.

(With conventional methods, measurements are typically acquired at only a few angles in the Debye-Scherrer pattern.)

Figure 2 shows diffraction patterns (a) from an Al_2O_3 film grown on single-crystal β-NiAl and (b) from the reference sample.

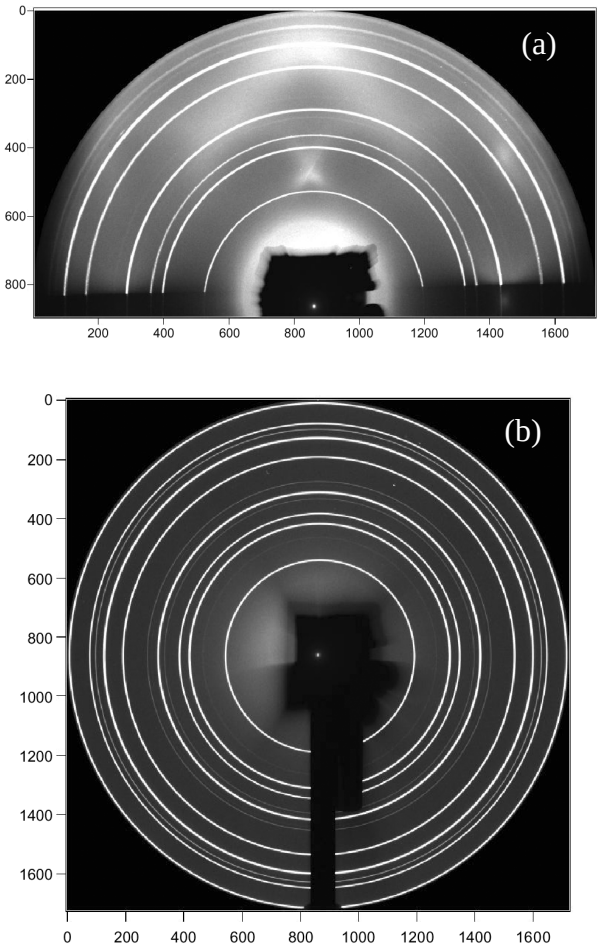

FIG. 2. (a) Debye–Scherrer diffraction pattern from an oxidized sample of β-NiAl. (b) Debye-Scherrer diffraction pattern from a reference sample.

We used the data from all the diffraction angles that contributed to a diffraction ring. We determined the strain in the Ψ direction, where Ψ is the angle between the sample normal and the scattering vector (Fig. 3).

Diffracted intensity from the strained lattice planes must satisfy the condition $\sin\theta = \lambda/(2d_\Psi)$. It can be shown that $d_\Psi = d_0\,(1 + A\sin^2\Psi + B)$, where A and B are functions of elastic compliance parameters. It was assumed that the material is isotropic with no shear. The in-plane strain is then given by $\varepsilon_{in} = [A(1 - \nu)]/[2\nu A + (1 + \nu)(1 + B)]$, where ν is the Poisson ratio. The terms A and B are treated as fitting parameters in the

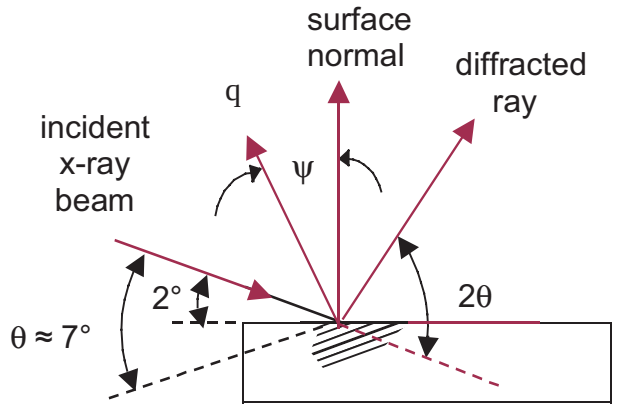

FIG. 3. Schematic of the diffraction arrangement.

θ-dependent diffracted intensity. The intensity is given by $I = I_{bkg} + C\,\exp(2\theta\text{-}2\theta_o)^2/2w^2$, where I_{bkg} is a background term, where $\theta_o = \sin^{-1}[\lambda/(2d_\Psi)]$ is the centroid of an elliptically distorted powder diffraction ring that is generated by the strained crystallites, and where w is the Gaussian width of the diffracted ring. C may be formulated to include the effects of absorption, x-ray beam polarization, and sample texture.

The strain measurement depends on a very precise knowledge of the x-ray scattering center (x_o,y_o), where x-rays travel in the z-direction. Thus, the x-ray beam was tightly focussed and carefully positioned on the sample (i.e., essentially no photons were permitted to overshoot or undershoot the sample, and a diffraction spectrum [half circles] was recorded [Fig. 1a]). Immediately after this, the sample was lowered to permit the beam to pass and strike a thin reference sample that was placed in the x-ray path [Fig. 1(b)]. This transmission experiment yielded full-circle diffraction spectra [Fig. 2(b)], which could be analyzed to accurately obtain x_o and y_o (to ±2 μm) for the beam centroid The reference data also permitted measurement of any detector misorientation (for accurate strain determinations, the normal to the detector plane must be coincident with the x-ray beam, or the misorientation angles must be determined). To perform the fit to a diffraction ring, a given line is selected [e.g., (116) line of Al_2O_3], and a background is subtracted. A function is included to account for the effect of x-ray beam polarization and, if needed, to account for sample texture.

Figure 4 shows in-plane strain measurements for Al_2O_3 thermally grown on β-NiAl. The circles, obtained in this study, were recorded during oxidation at 1100°C. An initial tensile stress (~600 MPa) was observed, which rapidly declined to zero. After 400 minutes of oxidation, the temperature was lowered to 950°C, where it was held for 450 minutes. The reduced

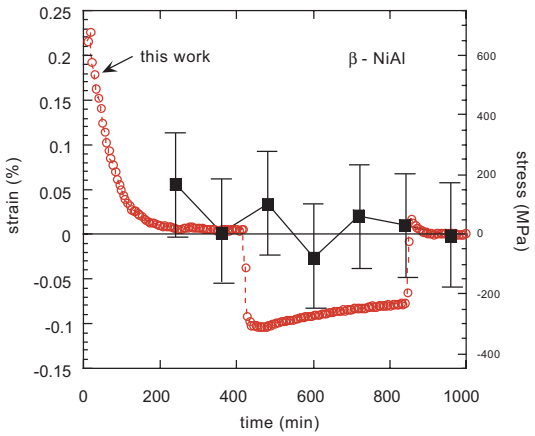

FIG. 4. In-plane strain in Al_2O_3 thermally grown on β-NiAl versus oxidation time at 1100°C. Between 400 and 800 minutes, the temperature was reduced to 950°C, and creep was monitored. The 1100°C data (squares) of Schumann et. al. [2] are also shown.

temperature imposed a compressive stress on the oxide as a result of the thermal expansion difference between the oxide and the substrate. At 950°C, a creep response was observed, which provided strain relief. The temperature was then returned to 1100°C. Also shown in Fig. 4 are recent results from Schumann et. al. [2], all taken in situ at 1100°C. These state-of-the art measurements were taken by using conventional in-lab facilities. It is clear that data with a much higher precision and with a substantially greater point density can be obtained by using synchrotron radiation.

Acknowledgments

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