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Stress heterogeneity of thermally grown polycrystalline nickel oxide layers

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Abstract

Mechanical properties of NiO films developed at approximately 800 °C in air for 26 h on a 99.9% pure polycrystalline Ni substrates have been investigated by X-ray diffraction, transmission electron microscopy and atomic force microscopy. The oxide layers, 8 μm thick, exhibit a duplex structure with a slight {1 1 1} texture. The average stresses in the oxide films have been deduced by X-ray diffraction to be 330 ± 35 MPa in compression. Detailed analyses of the oxide films performed by atomic force microscopy show surface undulations on the nanometer scale located in some of the grains. These well-defined periodic structures are due to high growth stress heterogeneity from grain to grain in the oxide layer. From a linear analytical model, it is deduced that growth stresses as large as 4 GPa can be developed locally during the high temperature oxidation process as a result of the strong in-plane anisotropy.

Keywords: Oxide; Wrinkles; Residual stresses; XRD; AFM

1. Introduction

In recent years, extensive studies of oxide growth on metallic substrates and their effects on fatigue life and other bulk properties have been carried out [1]. Mechanical properties of these oxide layers are crucial to the understanding of these phenomena. Nickel is generally chosen as a model material for the oxidation studies since it is known to develop only one f.c.c. oxide, NiO. The residual stress that develops during the growth of the oxide layer is essential to the understanding of the mechanical behavior and the ageing of the metal/oxide structures. The internal stresses can lead to fracture and spallation of the oxide layers leaving the underlying metal prone to further oxidation. The internal stress can be simply described as the sum of the stress that develops during the oxide growth at the oxidation temperature, called growth stress and the stress resulting from temperature changes, called thermal stress. Basically, the growth stress depends on lattice mismatch and microstructure, while the thermal stress arises from the difference in thermal expansion coefficients when cooling to room temperature. This thermal stress has been shown to be dominant over the growth stress at room temperature in the case of thermally grown oxide (TGO) on pure Ni substrates [2,3]. The residual stresses can be estimated at room temperature by several methods, such as curvature (Stoney method), X-ray diffraction (XRD) [4–6] or using high temperature XRD [2,3].

It is accepted that a stress gradient probably exists in the nickel oxide film thickness [7–9] ranging from a highly compressive stressed NiO/Ni interface to a relaxed NiO upper surface. The residual stresses determined by XRD experiments are average values over the entire film [4–6] due to the large probe size and are deduced assuming in-plane isotropic and homogeneous conditions. During the oxidation, stresses are generated in the oxide layer while macroscopic dimensional changes are observed in the composite metal/oxide layer. It has been shown that growth on single crystalline surfaces

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can lead to large anisotropic strains in the oxide lattice, potentially influencing growth kinetics or stress modification [10,11].

Fine surface undulations (wrinkles) of wavelength of a few μm, the order of magnitude of the surface scale thickness, have been reported in several oxides studies [12–15] and are suspected to arise from a relaxation mechanism concurrent with stress generation in the course of the oxidation process at high temperature [16]. It has been established that these surface undulations transform the biaxial stress in the planar oxide to triaxial stress with a component normal to the oxide surface [17] and can be related to the growth stresses since these wrinkles appear during isothermal oxidation. Finally, it has been deduced from single crystalline samples that the underlying crystallographic orientation is important at the very beginning of the oxidation process, since the wrinkle morphologies are very different from one orientation to another, but become less sensitive after prolonged oxidation [15].

This paper gives evidence of a high stress heterogeneity from grain to grain during the growth of nickel oxide layers.

2. Experimental

Specimens of pure polycrystalline Ni (99.9%) were cut to parallelepipeds of dimensions 25 mm × 4 mm × 1 mm. Both surfaces were carefully polished using 1 μm diamond paste resulting in a mirror finish. The samples were oxidized in air for 26 h at approximately 800 °C and then cooled in air. The average residual stresses were measured by XRD using the $\sin^2\Psi$ method [18] and the (4 2 2) diffraction peak. Texture measurements were performed on a Seifert MZ VI diffractometer using Cu Kα radiation. The (2 0 0) pole figure was obtained using the reflection technique up to a maximum tilt angle of 70°, in 5° polar and radial intervals. The oxide microstructure was investigated by cross-sectional transmission electron microscopy (XTEM) and surface topology analyses were performed by atomic force microscopy (AFM) in intermittent contact mode, using a highly sharpened cantilever.

3. Results

The microstructure of the entire oxide layer viewed by XTEM is observed in Fig. 1. As expected at such a growth temperature [6,19], it consists of the stacking of two distinct layers developing different morphologies. The inner layer, close to the metal/oxide interface, is composed of small equiaxed grains with diameters in the range 100–400 nm. The thickness of this layer varies from 1 to 3 μm depending on the underlying microstructure, that is Ni grain or grain boundary. The grain boundary acts as a diffusion short circuit, giving rise to an enhanced inward oxidation [6]. The outer layer, 5 μm thick, is built with more columnar grains. The total width of this duplex layer is approximately 6–8 μm, in agreement with

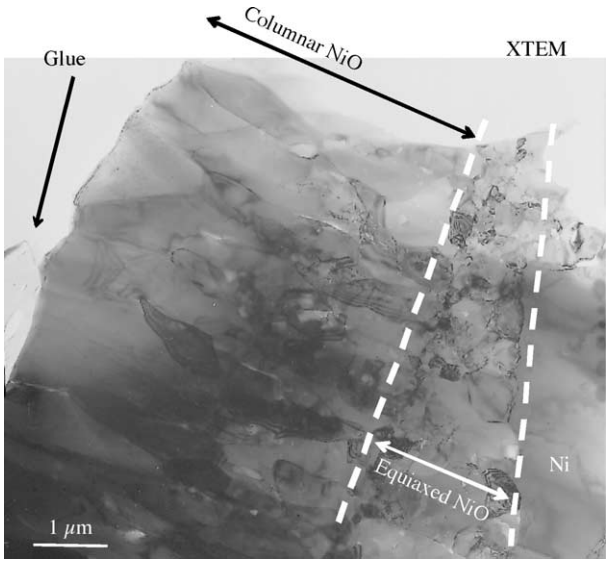

Fig. 1. NiO layer with a duplex morphology viewed by cross-sectional transmission electron microscopy. The inner layer, 1–3 μm thick, and the outer layer, 5 μm thick, consist of small equiaxed and acicular grains, respectively.

previous reports on growth kinetics [20]. The oxide layer appears dense with very few pores observed within the grains. Such pores have been reported by Kim and Hobbs [21] after oxidation at temperatures higher than 1000 °C for several hours for Ni and Ni–1Cr alloys.

The texture of the outer layer as well as the room temperature residual stresses have been investigated by XRD. Fig. 2 shows the (2 0 0) pole figure in iso-intensity level representation. An increase of the reflected intensity is observed located approximately at the 55° tilt angle ring. This angle corresponds to that between the [1 1 1] and [2 0 0] directions in the f.c.c. structure. However, as several spots on the ring dominate the reflected intensity (black and grey dots in Fig. 2), it can be concluded that the NiO does not exhibit a perfect axisymmetrical {1 1 1} fiber texture. These spots exhibit a three-fold symmetry and are likely to result from at least two different sets of (1 1 1) planes; their discrete positions arise

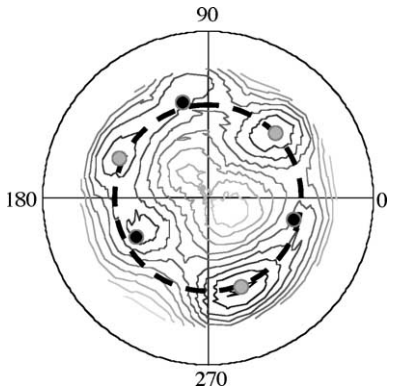

Fig. 2. X-ray pole figure of (2 0 0) Bragg reflection from the NiO film outer layer. The figure is plotted with iso-intensity lines from 1000 to 2200 (arbitrary units).