A NEW MODEL OF STRESS GENERATION DURING SCALE GROWTH LIMITED BY CATION/VACANCY DIFFUSION

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ABSTRACT

The stress generation during growth of cation-diffusing scales on pure metals is described in terms of intrinsic misfit for a grain boundary in oxides. This model is derived from the experimental observations by means of in situ x-ray strain measurements for the oxides grown on single crystal surfaces of copper. A change in the grain boundary structure which occurs by altering the relative amount of the twin-related oxide orientations present in the oxides on (001) or (111) face of copper leads to a change in the stress generation behavior. Compressive stresses are observed in the oxide with scale thickness of a few micrometers below the brittle-ductile transition temperature of the bulk oxide (300\textdegree{}-400\textdegree{}C). The model which is based on the coincident site lattice model may explain the origin of stresses arising during the growth of cation-diffusing scales at rather moderate temperatures.

INTRODUCTION

Stresses and strains are experimental facts for growing oxide scales. Whether the stress generation during scale growth limited by cation vacancy diffusion is caused by new oxide formation at grain boundaries within the scale [1,2], or whether the origin of stresses is correlated to annihilation of metal vacancies at the metal-scale interface [3], many questions concerning stress generation remain unanswered. In this paper, we present a new evidence which has been obtained from the experimental observations by means of in situ x-ray strain measurements and which leads more rational insight into the oxidation mechanism.

MATERIALS AND METHODS

Materials
Two different types of copper specimens were employed. The
first were single-crystal slices (7x5x0.5mm³) cut from single crystal bars of 99.99wt% purity grown by the Czochralski method. The flat surfaces were approximately (001) and (111) faces. The second were of polycrystalline Cu hot pressed at 900 °C. These specimens were cut by acid sawing and annealed and finally electrochemically polished in a phosphoric acid solution.

Since a purpose of our investigation was to obtain clearer evidence for the correlation between stress generation and the vacancy annihilation in dependence with the surface orientation, it was planned to control the cation-diffusing flux in oxides of the p-type. This was realized by controlling the structure of the oxide film, "the mosaic structure", by changing epitaxial behavior resulted from the difference of surface orientation. A detailed description of the experimental procedures and the surface orientation effect has been reported elsewhere [4, 5].

Strain Measurement
An x-ray diffraction technique has been employed for determining strains in the oxide and the metals, respectively. A hot stage capable of "in situ" measurement of elastic strains at about 1000°C under controlling atmosphere has been used. A schematic detail has been presented previously [6]. The specimen is held in the cylindrical vacuum vessel and mounted at the center of rotation of a goniometer. The x-ray tube and detector are fixed at a diffraction condition. The vessel is equipped with a bar to hold and rotate the specimen in the diffraction geometry and provided with a mylar window for transmission of the incident and diffracted x-ray beams.

The \( \sin^2 \psi \) method was employed for determining elastic strains [7]. This is one of the side-inclination methods, in which diffraction measurement is made with the trace of detector scanning and the primary beam on the same plane and with changing the angle, \( \psi \), between the plane and the specimen surface normal. Since this method is simple to operate and uses a fixed incident angle to the specimen surface, it has an advantage in which error due to mechanical effect is negligible. Moreover, other errors due to mismatch in alignment of the specimen surface with respect to the rotating axis and effects of the slit breadth have been minimized as a parallel beam was used. In this measurement the values of \( \psi \) were taken by two for the single crystals and by several for the polycrystalline specimens. Cr Ka x-rays were used for the present experiment. A peak position of diffraction profile measured with a fixed time counting method was determined by numerical treatments. The least squares method was also used for determining the lattice strain as a function of \( \sin^2 \psi \). The experimental conditions for the diffraction have been shown in Table 1.

A rapid scanning speed (1/2°/min) was employed to minimize the influence of change in strain generation feature during measurement. When the diffraction intensity was weak, as in case of oxide, large time constant (10 sec) and small scanning speed (1/4°/min) were combined to result in a relatively large averaging-of-counts effect to record a proper diffraction profile. The range of the measurable diffraction angle is from 120 to 165 deg in 2θ.