

DISCUSSION

*M. A. Maguire*¹ (written discussion)—(1) Did you analyze the phase component of the impedance? Did you have any correlation between the phase diameter and oxide behavior?

(2) Surface impedance is strongly dependent on temperature. Did you perform any high temperature measurements?

T. Kubo and M. Uno (authors' closure)—(1) We analyzed the Cole-Cole plots. Real and imaginary components described a semicircle on the complex plane with its center located slightly under the real axis. The d-c resistivities were determined from the semicircles. The d-c resistivity tends to decrease with a decrease in the nodular corrosion resistance of the samples. These results were described in the report.

(2) We did not perform high temperature measurements. All measurements in the present experiment were performed at room temperature.

*D. G. Franklin*² (written discussion)—Your resistivity ranking of the materials appears to be the opposite of that of Urquhart et al.³ Do you know the source of this difference?

T. Kubo and M. Uno (authors' closure)—Urquhart et al. carried out *in situ* measurements of potential differences across growing oxide films under high pressure steam at 500°C. On the starting material (Zry-4 fabricated through conventional process) the potential difference was initially low but, after several hours, increased rapidly to about 600 to 700 mV (Zr negative), while on the heat-treated materials (beta-quenched Zry-4) the observed potentials never exceeded a few millivolts. Urquhart et al. felt that very fine precipitates on grain boundaries in the beta-quenched materials gave short-circuit paths for the electronic conduction through oxide films, which inhibited the development of large potential difference across the films.

The present impedance measurement for thin oxide films on Zry-2, which was carried out in an electrochemical cell at room temperature after oxidation at 400°C for 12 h, showed that the beta-quenched material had the highest electrical resistivity, indicating that fine precipitates in the beta-quenched material had only slight effects on electronic conduction.

Although we do not exactly know the source of the difference between the two measurements mentioned above, it should be noted that the techniques, test conditions, and oxide thickness, among others, of the two measurements were quite different. For example, Urquhart et al. sputtered very thin (about 150 Å) Pt electrode spots on Zry-4 surface. The presence of electrode influenced the corrosion process (i.e., nodular oxides, which normally formed on the starting material without electrode, were suppressed under the open-circuit electrode, indicating that the electrochemical state on the surface and in the oxide films was significantly different from that without the electrode).

The present TEM observations showed that there was a dissolution of precipitates in the oxide films during the corrosion process. In an additional observation (not described in the present report) relatively large precipitates were occasionally found, but smaller ones were

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not found, in oxide films formed at 500°C for 1 h. This indicates that fine precipitates disappear by dissolution at 500°C within 1 h and it should not be probable for very fine precipitates to provide short-circuit paths for electronic conduction through the oxide films.

*C. Lemaignan*⁴ (*written discussion*)—In the way you prepare the thin foils for TEM, it is difficult to know the exact location of the precipitate with respect to the metal oxide interface. Could you give further information on this point?

T. Kubo and M. Uno (authors' closure)—As you point out, it is difficult to know the exact location of the precipitate with respect to the metal/oxide interface. We believe, however, precipitates were located at about midpoint between the oxide surface and oxide/metal interface, since oxide films were sputtered by Ar ions from both surfaces. Conditions were carefully controlled for both surfaces to be sputtered at an almost equivalent rate—for example, by alternating the sputtering angle between about -15 and $+15$ deg. The sputtering rate at the two surfaces may be different, but we believe it is slight, since the oxide films formed under the present conditions were relatively thin (about 1 or 2 μm) and almost homogeneous.

Oxide thickness before sputtering was about 1 and 2 μm for samples oxidized at 400 and 475°C, respectively. The size of the precipitates analyzed by EDX was about 0.5 to 0.7 μm , which was not so small compared with oxide thickness. Thus we believe that our results give information on precipitates located at a distance between about 0.5 to 1 μm with respect to the oxide/metal interface.

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