Measurement of the Stress Developed in ZrO_2 Thin Film

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1. Introduction

It is well-known that tetragonal ZrO_2 forms in the metal-oxide interface in the early stage of a zirconium oxidation that is protective against a further oxidation. However, as the oxide grows, the stress built up during the oxidation process is relieved. Then the tetragonal phase turns into the monoclinic phase which is non-protective and stable at low stress. Therefore, it is believed that the zirconium oxidation kinetics depends on the phase transformation that take place at 3.1 GPa according to earlier works. In other words, if the transformation is related to holding the oxide stress above the threshold stress, the kinetics would be slow. Nevertheless, so far no one has succeeded in measuring the stress of a thin film oxide above 3.1 GPa. In this study, a stress has been successfully measured using a steam beam apparatus and muffle furnace system above a threshold stress level.

2. Methods and Results

2.1 Experimental

The single side oxidation of the specimen is carried out in two ways. One is a steam beam oxidation in a vacuum system. Another is a air oxidation in an atmospheric system.

Steam beam bend test apparatus using a steam beam is shown Figure 1. Here in the apparatus, Oxidation reaction occurs only at the surface exposed to the steam beam. In order to avoid the oxidation of the other side of a specimen, whole chamber is evacuated down to a high vacuum (down to 10^{-4} Torr).

Putting the specially modified specimen holder into the muffle furnace, the single side air oxidized sample was obtained successfully. The specially modified specimen holder in the figure 2 is designed to prevent the back side of the specimen from being oxidized by filling the space between the specimen and the bottom of the holder with a inert gas, Ar.

The oxide thickness is measured with a weight gain measurement and the curvature of the single side oxidized specimen is measured with a spherometer. Specimen is a thin zirconium foil whose thickness is 40 ㎛ and diameter is 20mm. Only a single surface of the specimen exposed to the steam beam and air is oxidized at 400℃.

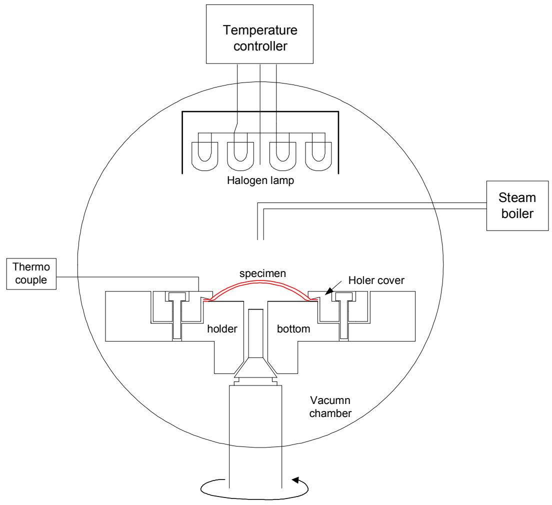

Figure1. Steam beam bend test apparatus using steam beam in high vacuum.

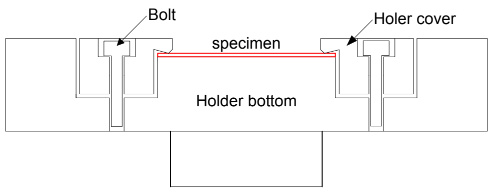

Figure2. The specially modified specimen holder

2.2 Stress measurement

Basically the measurement technique used in this study is based on a curvature build-up during a single side oxidation process. The stress build-up can be directly evaluated according to the Stoney's formula.

$$\sigma_f = \frac{E}{1-\nu}\frac{t_s^2}{6t_f R} \quad (1)$$

Where ,
E : Young' Modulus of metal v : Possion ratio
R : radius of curvature t_f : oxide thickness
t_s : metal thickness

Measured stress from the curvature estimation are plotted as a function of the thin oxide film thickness in Figure 3.

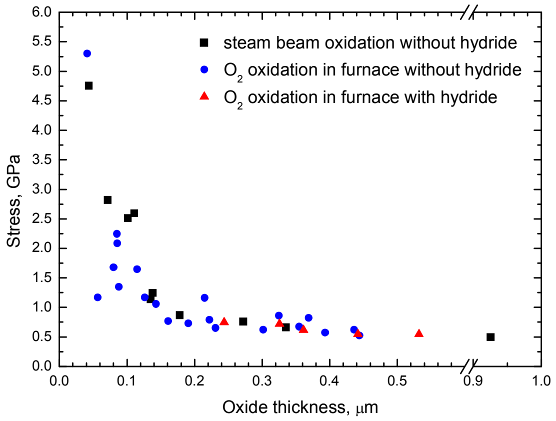

Figure 3. Measured stress from the curvature estimation with thin oxide film thickness.

As shown in the figure, the stress in the oxide increases as the thickness decreases and the highest stress measured in this study is 5.2 GPa which is higher than any other previous work. In fact, the measured correlation between the stress and the oxide thickness is in good agreement with the theoretical prediction. Taking into consideration that the measured stress is the average stress of a whole oxide, not in the interface. Therefore, these results reveal that stress built up in the interface can exceed the threshold value, which supports the phase transformation theory.

3. Conclusion

In this study, stress of a thin film oxide grown on a zirconium metal has been measured using a steam beam in a high vacuum system and using an atmospheric air oxidation system. The highest stress measured in these tests is 5.2 GPa with about a 41nm oxide thickness, which can support the phase transformation theory for the zirconium oxidation kinetics. In the following study, the effect of a hydride precipitation on its transformation will be carried out.

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