# Local Stress And Its Effects On Metastable Tetragonal Phase In Zro$_2$ Film On Zr Alloys

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## ABSTRACT

An in-depth understanding of the phase stability in $ZrO_2$ film is very important for improving the corrosion resistance of zirconium alloys. $ZrO_2$ film formed on the zirconium alloys was characterized by grazing incidence X-ray diffraction. It is shown that there exist the regions of stress concentration in $ZrO_2$ film. In addition to the macroscopic compressive stress and the grain size, the local stress also plays important role in the transformation from the tetragonal to the monoclinic phase. The correlation of the macroscopic compressive stress, the grain size and the local stress was analyzed qualitatively from a thermodynamic viewpoint.

## 1. INTRODUCTION

Zirconium alloys, used in nuclear power industry, have been attracting considerable attentions in last decades because of their high corrosion resistance during exposure to hot water or steam. The highly protective oxide film adhering to the surface of zirconium alloys can serve as a diffusion barrier, stopping hydrogen permeation. Experiments show that the oxide film consists of two layers: the porous external layer and the dense internal one [1]. A full understanding of the corrosion properties of zirconium alloy requires an in-depth analysis of the relations between the corrosion and the microstructure features of the oxide film, like tetragonal phase stability, crack formation, stresses and textures. The question as to why the metastable tetragonal phase is observed in the oxide film always attracts much attention. The tetragonal phase $ZrO_2$ is stable at the temperatures above 1423K, but it can be stabilized at lower temperature in the oxide film because of the presence of high compressive stress. The tetragonal phase stability and the tetragonal→monoclinic transformation are closely related to the formation of full dense oxide film and the generation of cracks. At present, the commonly accepted viewpoint suggests that the presence of metastable tetragonal phase may be attributed to the compressive stress and the grain-size effects. Especially, a very high compressive stress near the metal/oxide interface is regarded to be the main origin of the high proportion of tetragonal $ZrO_2$ near the interface [2-5]. However, some studies on the effects of the compressive stress on the tetragonal phase also yield rather controversial results [6,7]. Very recent studies show that there seems to be no obvious correlation between the compressive stress and the tetragonal phase content [6,7]. Despite numerous works undertaken on the tetragonal phase stability, this problem still remain open. In this paper, we will try to explore the factors affecting the tetragonal phase stability in $ZrO_2$ films on the zirconium alloys.

## 2. EXPERIMENTS

Zr–2.5Nb samples of dimension 30×30×3 mm were machined from a pressure tube. The tube was extruded at 1093–1123 K, cold worked by 20–30% and then stress relieved in steam for 24 h at 673 K. The specimens were cut so that the direction normal to their surface coincides with the radial direction of the tube. After grounded by using SiC paper down to 1200 and polished with vibration polishing equipment, the specimen was oxidized with air flowing condition at 773 K for 16h. Grazing incidence X-ray diffraction was performed using a Rigaku DMax-500 X-ray diffractometer with Cu $K_\alpha$ radiation in order to obtain information about the oxide film. In order to determine exactly the peak position, the peak fitting of the diffraction patterns was performed manually using the PeakFit 4.06 program. The peak shapes were taken to be Pearson type Ⅶ and the background was removed using a simple linear model.

## 3. EXPERIMENTAL RESULTS AND DISCUSSIONS

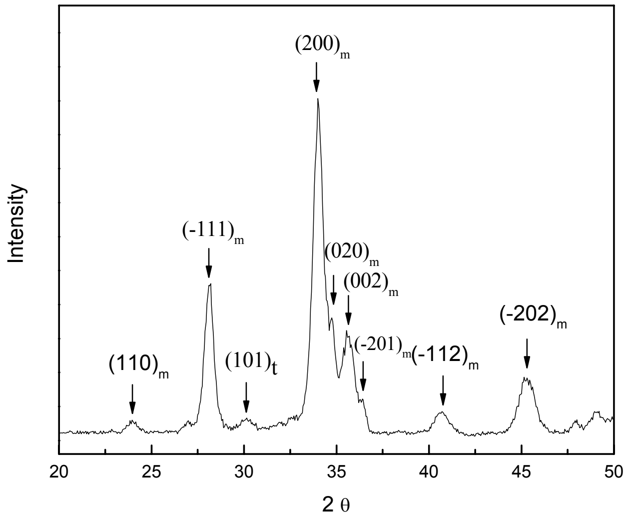

Fig. 1. X-ray grazing incidence diffraction pattern of the oxide film grown on Zr-2.5Nb alloy (incident angle: 7°).

In figure 1, the relative intensities of diffraction peaks have significant change, compared to standard JCPDF, showing the presence of texture in oxide film, as observed previously by other authors [8-10]. The $(110)_m$, $(-111)_m$, $(101)_t$, $(-112)_m$, and $(-202)_m$ peaks are used for analyses in present work because these peaks are clearly separated diffraction peaks visible. The peak positions were determined exactly by using the PeakFit 4.06 program, as described above. One example of such a fit is shown in figure 2.

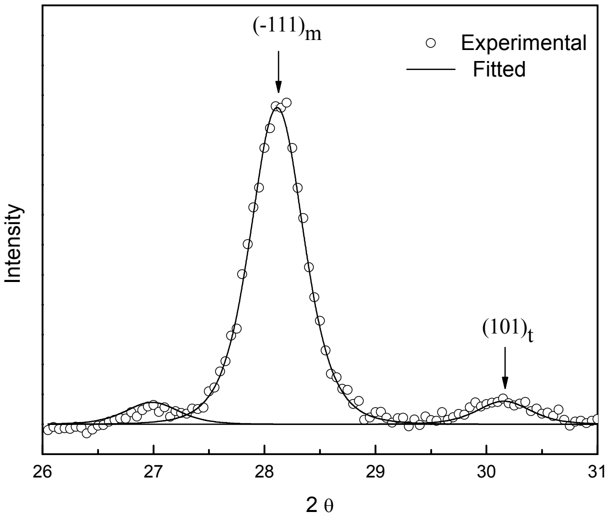

Fig. 2. Peak fit of diffraction pattern taken from oxide film (incident angle: 7°)

The diffraction peaks are identified in Table 1, showing that for different grazing incident angles, the deviations of the diffraction peaks of the tetragonal phase from JCPDF value toward the high angle are always much larger than those of the monoclinic phase. The similar experimental results are found in the works reported by Yilmazbayhan et. al [11], in which the experiments were performed by using Micro-beam X-ray diffraction technology and radiation source of 1.305 Å wavelength (see Table 2).

Table 1 Local strain measured by changing X-ray grazing incident angles ($\theta_{inc}$) (Wavelength: 1.540598 Å)

| **Peak indexing** | **JCPDF** | **$\theta_{inc}$=3°** | **$\varepsilon_{\theta inc=3°}$ (%)** | **$\theta_{inc}$=7°** | **$\varepsilon_{\theta inc=7°}$ (%)** | **$\theta_{inc}$=9°** | **$\varepsilon_{\theta inc=9°}$ (%)** |
|---|---|---|---|---|---|---|---|
| | | 2θ | | 2θ | | 2θ | |
| $(101)_t$ | 29.806 | 30.034 | -0.7419 | 30.157 | -1.1374 | 30.186 | -1.230 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $(110)_m$ | 24.048 | 23.954 | 0.3867 | 23.954 | 0.3867 | 23.997 | 0.2094 |
| $(-111)_m$ | 28.175 | 28.092 | 0.2895 | 28.113 | 0.2161 | 28.190 | -0.0521 |
| $(-112)_m$ | 40.725 | 40.637 | 0.2074 | 40.721 | 0.0094 | 40.723 | 0.0047 |
| $(-202)_m$ | 45.522 | 45.442 | 0.1667 | 45.311 | 0.4410 | 45.364 | 0.3298 |

Table 2 Experimental results in the literature (Wavelength: 1.305 Å) [11]

| **Peak indexing** | **2θ** | **JCPDF** | **ε (%)** |
|---|---|---|---|
| $(101)_t$ | 25.56 | 25.17 | -1.5010 |
| $(110)_m$ | 20.35 | 20.33 | -0.0972 |
| $(011)_m$ | 20.70 | 20.66 | -0.1911 |
| $(-111)_m$ | 23.83 | 23.80 | -0.1241 |
| $(111)_m$ | 26.54 | 26.56 | 0.0740 |
| (200) | 28.74 | 28.81 | 0.2384 |
| $(020)_m$ | 29.04 | 29.00 | -0.1348 |
| $(002)_m$ | 29.71 | 29.77 | 0.1974 |
| $(120)_m$ | 32.48 | 32.47 | -0.0300 |
| $(012)_m$ | 33.12 | 33.19 | 0.2054 |

The local strain, $\varepsilon$, may be defined as

$$\varepsilon = \Delta d / d_0 \tag{1}$$

where $\Delta d$ represents the deviation of $d$ values from the ideal value of perfect crystals $d_0$. Considering Bragg's equation, the equation (1) may be rewritten as

$$\varepsilon = \frac{\sin\theta_0}{\sin\theta} - 1 \tag{2}$$

where $\theta_0$ is the stress free peak positions. The estimated results of strains are given in Tables 1 and 2, showing that in comparison to the monoclinic phase crystallites, the crystallites with tetragonal phase undergo larger compressive strain. This reflects that there are some regions of local stress concentration in $ZrO_2$ film. These local stress concentrations would play an important role in the transformation from the tetragonal to the monoclinic phase.

The tetragonal phase stability in $ZrO_2$ film is analyzed from a thermodynamic viewpoint. The change of the total free energy accompanying the tetragonal→monoclinic transformation, $\Delta G^{t\to m}$, can be expressed by

$$\Delta G^{t\to m} = G^m - G^t = \Delta G^{t\to m}_{chemical} + \Delta G^{t\to m}_{strain} + \left(A^m \delta^m - A^t \delta^t\right) \tag{3}$$

where the superscripts $t$ and $m$ represent the tetragonal and the monoclinic phase, respectively. $\Delta G^{t\to m}_{chemical}$ has negative sign and represents the change in chemical bulk free energy from the tetragonal to the monoclinic phase. $\Delta G_{strain}^{t\rightarrow m}$ has positive sign and represents the strain energy caused by the transformational strain exerted by the transformed $ZrO_2$ crystallites on the adjacent matrix. $A$ and $\delta$ are the specific surface area (per molar) and the surface free energy, respectively.

The specific surface area (per molar), $A$, can be expressed in terms of the number of atoms in each crystallite $n$ as

$$A = \eta N_A \upsilon^{2/3} / n^{1/3} \tag{4}$$

where $\eta$ is the shape factor of $ZrO_2$ crystallites, $N_A$ is Avogadro's number and $\upsilon$ is the atomic volume. With respect to each crystallite, the number of atoms in the crystallites, before and after transformation, is the same though the monoclinic phase has a larger molar volume than the tetragonal phase. Combining Eq. (3) and Eq. (4), we have

$$\Delta G^{t\rightarrow m} = G^m - G^t = \Delta G_{chemical}^{t\rightarrow m} + \Delta G_{strain}^{t\rightarrow m} + \frac{N_A}{n^{1/3}}\left[\eta^m\left(\upsilon^m\right)^{2/3}\delta^m - \eta^t\left(\upsilon^t\right)^{2/3}\delta^t\right] \tag{5}$$

where $\upsilon^t$ and $\upsilon^m$ are atomic volumes of the tetragonal phase crystallites and the monoclinic phase crystallites, respectively. Previous works of Garvie [12] showed that the surface free energy of $ZrO_2$ crystallites of tetragonal phase is smaller than that of monoclinic phase ($\delta^m > \delta^t$). In addition, the transformation from the tetragonal to the monoclinic phase is accompanied by volume dilatation ($\upsilon^m > \upsilon^t$). If assuming that the shape of crystallites, before and after transformation, keeps unchangeable ($\eta = \eta^m = \eta^t$), the third term on the right of equation (5) will be positive. Since $\Delta G_{strain}^{t\rightarrow m}$ also is positive, the latter two terms on the right of equation (5) will act as a role stabilizing the tetragonal phase.

The volume of single crystallite with tetragonal phase, $V^t$, may be expressed as

$$V^t = n\upsilon^t \tag{6}$$

Combing Eqs. (5) and (6), Letting $\Delta G^{t\rightarrow m} = 0$, we have

$$\left(V_c^t\right)^{1/3} = \frac{N_A \eta \left(\upsilon^t\right)^{1/3}\left[\left(\upsilon^m\right)^{2/3}\delta^m - \left(\upsilon^t\right)^{2/3}\delta^t\right]}{-\Delta G_{chemical}^{t\rightarrow m} - \Delta G_{strain}^{t\rightarrow m}} \tag{7}$$

where $V_c^t$ is a critical volume of single crystallite with tetragonal phase. The value of the $V$ depends on the grain size $d$, i.e., $V \propto d^3$, and therefore the Eq. (7) may be rewritten as

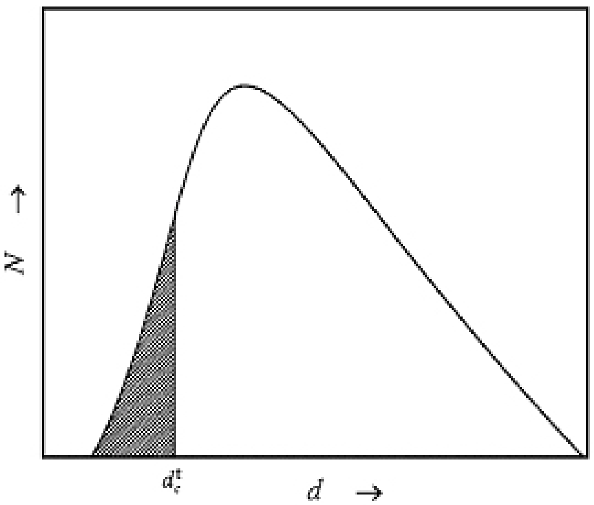

Fig. 3. Schematic distribution of the number of crystallites *N* with grain size *d*

$$d_c^t \propto \frac{N_A \eta \left(\upsilon^t\right)^{1/3} \left[\left(\upsilon^m\right)^{2/3} \delta^m - \left(\upsilon^t\right)^{2/3} \delta^t\right]}{-\Delta G_{chemical}^{t \to m} - \Delta G_{strain}^{t \to m}} \qquad (8)$$

where $d_c^t$ is a critical grain size of tetragonal phase. When the grain size is smaller than $d_c^t$, $\Delta G^{t \to m}$ will be larger than zero, i.e., $G^m > G^t$. This means that the tetragonal phase may be more stable than the monoclinic phase and the transformation from the tetragonal to the monoclinic phase cannot take place.

It is unlikely that all of the $ZrO_2$ crystallites in oxide film have the same grain size. In most of the cases, the grain size distribution may be depicted schematically as in figure 3, with the crystallites lying in the hatched region unable to undergo the tetragonal→monoclinic transformation.

In the process of the oxidation of zirconium alloys, the high Pilling-Bedworth ratio for $Zr/ZrO_2$ leads to the buildup of compressive stresses in the oxide film [5]. The larger compressive stress in the $ZrO_2$ film will produce the larger strain energy that the tetragonal→monoclinic transformation needs to surmount. That is to say, the $\Delta G_{strain}^{t \to m}$ in the equation (8) will increase with increasing compressive stress. Experiments confirmed that there is a stress gradient near the metal/oxide interface of $ZrO_2$ film formed on the zirconium alloys [5]. In general, the stress values near the metal/oxide interface are very high, but just extend over a short distance. This indicates that the crystallites, more adjacent to metal/oxide interface, need to surmount the larger $\Delta G_{strain}^{t \to m}$. According to equation (8), the denominator decreases and the $d_c^t$ value in the figure 3 will become larger, indicating that more tetragonal phase may be stabilized in the region near the interface. This is in an agreement with the many reported results.

It is well known that the stress may be classified into two kinds: the macroscopic stress and the local stress (or the internal stress). It is worth noting that the stress in the literature regarding the $ZrO_2$ film generally refers to the macroscopic compressive stress coming from the metal substrate restriction on the $ZrO_2$ film, not local stress in the some special regions of $ZrO_2$ film. If only considering the effects of the macroscopic compressive stresses on the phase stability, experimental results cannot be completely explained. Pétigny et. al. [6] confirmed that the higher macroscopic compressive stress does not certainly result in the higher component of the tetragonal phase. TME studies also found presence of the tetragonal phase even for the $ZrO_2$ film in which metal substrate has been removed [5]. From the above thermodynamic analyses, it may be concluded that in addition to the macroscopic stress, the effect of the grain size on tetragonal phase stability is also very important. For constrained/unconstrained $ZrO_2$ particles, the works of Garvie [12,13] confirmed that there is a critical grain size below which the tetragonal phase will become more stable than the monoclinic phase. The similar phenomena have also been reported in iron-based nanometer particles [14]. However, even when the effects of the macroscopic compressive stress and the grain size are simultaneously considered, the experimental observations cannot also be explained completely. When the macroscopic stress gradually decreases with the increase of the distance to the $ZrO_2$/metal interface, according to equation (8), the corresponding critical grain size will decrease since $\Delta G_{strain}^{t\to m}$ decreases, indicating that the larger $ZrO_2$ crystallites with the tetragonal phase will transform first to the monoclinic phase with the macroscopic stress decreasing. That is to say, the grain size of tetragonal phase near the interface should be larger than that near surface of $ZrO_2$ film. However, current available experimental results show that the grain size of tetragonal phase has no significant difference from the interface to the surface [15]. This indicates that in addition to the macroscopic stress and the grain size, there also exists other factor affecting the tetragonal phase stability in the $ZrO_2$ film.

Present experimental results show that the compressive strain of the tetragonal phase crystallites is much larger than the monoclinic phase crystallites, which indicates that there are some stress concentration regions in $ZrO_2$ film, in which the tetragonal phase may be partly stabilized by the local compressive stresses. That is to say, in addition to the macroscopic compressive stress and the grain size, the effect of local stress on the phase stability in $ZrO_2$ film is also important. In equation (8), the stress contribution to the $\Delta G_{strain}^{t\to m}$, in fact, comes from two aspects: the strain energy caused by the macroscopic stress and the strain energy caused by the local stress. These stress concentrations could result from two sources. One is different extent of matching between the $ZrO_2$ and Zr-based crystallites. When $ZrO_2$ crystallites grow on the surface of metal substrate, the orientation of $ZrO_2$ crystallites must match with the lattice of metal substrate as much as possible. However, it is impossible that all crystallite orientations are the same in the metal substrate. The high stress concentrations would be produced in some regions, in which the $ZrO_2$ crystallites do not match well with the metal substrate. Therefore, the $\Delta G_{strain}^{t\to m}$ will increase in these regions and the more tetragonal phase may be stabilized by the local stress. Another source of stress concentration is the transformation from the tetragonal to the monoclinic phase. When the macroscopic compressive stresses gradually decrease from the interface to the surface, a part of tetragonal phase will transform to monoclinic phase. Since this transformation is accompanied by volume dilatation, the regions near the transformed crystallites will certainly produce some local stress concentrations. The effect of local compressive stress on phase stability would become very important in the region near the surface because the macroscopic compressive stresses coming from the metal substrate would be there completely relieved. In other words, the decrease of the macroscopic compressive stress may result in some $ZrO_2$ crystallites transforming from the tetragonal phase to the monoclinic phase, simultaneously the local stress, produced by transformation process, will increase, and some large $ZrO_2$ crystallites with tetragonal phase may be stabilized by the local stress. This may explain why the grain size of tetragonal phase does not change significantly when the distance to the metal/oxide interface increases.

## 4. CONCLUSIONS

There are three main factors affecting phase stability in $ZrO_2$ film formed on zirconium alloys. In addition to the macroscopic compressive stresses near the metal/oxide interface and the grain size of $ZrO_2$, the local compressive stress also has an important effect on the stability of the tetragonal phase. The metastable tetragonal phase may be partly stabilized by the local stress. These local stresses would come from two sources: different extents of matching between the $ZrO_2$ crystallites and the metal substrate, and the local tetragonal→monoclinic transformation. These local stresses would also play an important role in cracking formation of $ZrO_2$ film. This aspect will be studied in the further work.

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