

Ellipsometric Study on Effect of Tetragonal ZrO_2 for Corrosion Resistance in Oxide Film of Zr-Sn-Nb Alloy

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Abstract: Specimens treated in different ways were exposed to 0.01 mol/L LiOH aqueous solution at 350°C, 16.8 MPa in autoclave. Spectroscopy Ellipsometry (SE) was applied to investigate the tetragonal ZrO_2 ($tZrO_2$) in oxide film. It was found that the 580°C / C R / 500°C specimen corroded for 42 days and 190 days have more $tZrO_2$ than other two specimens. It is suggested that the $tZrO_2$ was a main factor to affect the corrosion resistance and the corrosion resistance was improved by the formation of $tZrO_2$.

Key words: zirconium alloy; oxide film; corrosion resistance; spectroscopy ellipsometry

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1 Introduction

Zr-based alloy have been used as fuel cladding materials for its good irradiation stability and corrosion resistance. This paper mainly investigated the corrosion resistance quantitatively for Zr-Sn-Nb alloys affected by the appearance of $tZrO_2$ in different specimen via different heat treatment.

2 Experimental procedures

2.1 Specimens

Zr_{1.0}Nb_{1.0}Sn_{0.3}Fe alloys were treated by 580°C for 3 h and 820°C for 1 h and 1000°C for 0.5 h. The last cold rolling reduction was approximately 50%, and finally annealed at 500°C for 30 h.

2.2 Corrosion test

Corrosion test was conducted in 0.01 mol/L LiOH aqueous solution at 350°C under a pressure of 16.8 MPa after the final heat treatments.

The corrosion resistance of the rectangular specimens was evaluated by measure their weight gain per unit surface area and calculated.

2.3 Ellipsometer test

The ellipsometric measurements were carried out in air at room temperature with SE which adopted variable photon energy between 0.75 ~ 3.5 eV. In our measurements, the refraction index n is determined in the form of I_s and I_c . The model was divide the oxide

film to rough surface layer I_r and oxide layer I_o , the sum of the thickness of the two layers is the thickness of the oxide film. I_s and I_c was measured, then the relation between electron

energy and refractive index was fitted. The fitting model is not suitable for the oxide film when the value of deviation is more than 6, and the feasible value in this step is between 0.2 ~ 3. Proportional change for $tZrO_2$ and $mZrO_2$ in the oxide film was qualitatively investigated by refractive index change.

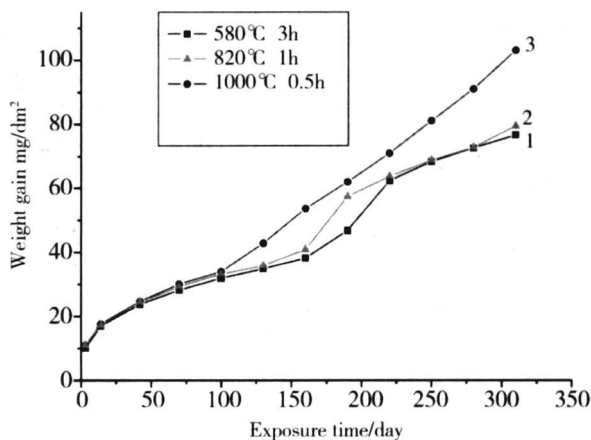


Fig 1 Weight gain against exposed time of Zr-Sn-Nb specimens tested in 0.01 mol/L LiOH solution at 350°C

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3 Results and discussion

SE was performed on the specimens that had been corroded for 42 days and 190 days respectively. It was found that the oxide film had a microstructure consisting of $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$, it was reported the refraction indexes of the tetragonal and the $m\text{-ZrO}_2$ bulks are 2.16 and 2.24 respectively^[3], so the increase in the measured n value at the same photon energy implies the volume fraction of the $m\text{-ZrO}_2$ increased. Proportional change for $t\text{-ZrO}_2$ and $m\text{-ZrO}_2$ in the oxide film was qualitatively investigated by refractive index change.

Compare the different specimen which had corroded for 42 days, the result shows in figure 2 (solid line for specimen 1, dot line for specimen 2, dash line for specimen 3). In figure 1, all the specimens corroded for 42 days, both the weight gain and refractive index change are not distinguished and no impurity contains in the oxide film, it implies the content of $t\text{-ZrO}_2$ in the oxide film for each specimen are approximately the same. When the entrance photon energy reaches 0.75, the refractive indexes (n) are between 2.04 and 2.11, which is close to n of $t\text{-ZrO}_2$. The refractive indexes decreased 0.17 with the increasing of photon energy to 3.5 eV. The specimen 1 has more $t\text{-ZrO}_2$ than other two specimens.

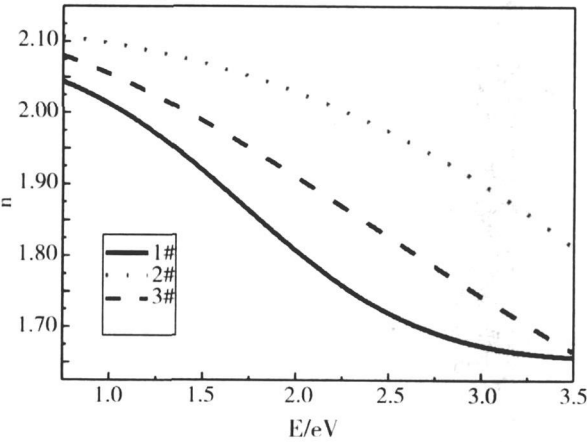


Fig 2 Index of refraction n of oxide film as a function of photon energy for 42 days corrode

Figure 3 is the index of refraction n of oxide film as a function of photon energy for 190 days corrode, the solid, dot, dash line represent to the specimen 1, 2, 3 respectively. The refractive indexes for the three specimens are between 2.1 to 2.3, which are higher than it of the specimens corroded for 42 days. It is considered that transition happened in the specimen corroded for 190 days. The compositions of oxide film are different between the pre-transition and post-transition regions.

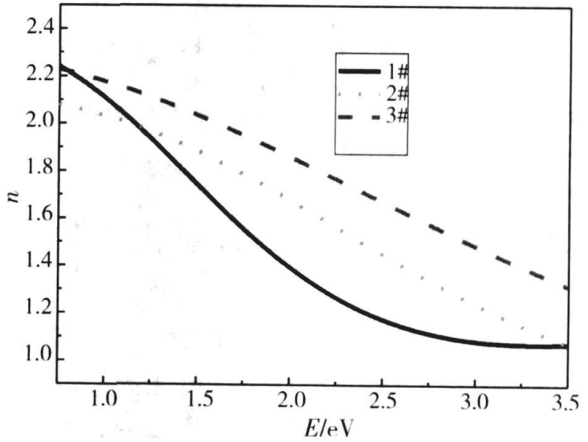


Fig 3 Index of refraction n of oxide film as a function of photon energy for 190 days corrode

In Zhou Bangxin's study^[4], the $t\text{-ZrO}_2$ is an unstable phase and the phase transformation would happen after the corrode transition. The content of $t\text{-ZrO}_2$ decreasing in the post-transition region, and the small content of FeO and NbO precipitated in oxide film make the index of refraction n increased. On the meanwhile, with the same entrance photon energy, specimen 1 has the minimum n and specimen 3 has the maximal n . So the specimen 1 has the highest $t\text{-ZrO}_2$ content, specimen 3 has the lowest content.

The specimen 1 has more $t\text{-ZrO}_2$ than other two specimens in this study, and it has the best corrosion resistance. The value of n increased with the decreasing of $t\text{-ZrO}_2$ content, and the corrosion resistance were improved with the decreasing of the refractive indexes (n). It shows that the $t\text{-ZrO}_2$ in oxide film can improve the corrosion resistance of Zr alloy.

4 Conclusions

- (1) The volume fraction of the $t\text{-ZrO}_2$ in oxide film is increased along with the sequence of 580 °C, 820 °C and 1000 °C when corrosion for 190 days.
- (2) The specimen 1 has more $t\text{-ZrO}_2$ than other two specimens, the corrosion resistance was improved with the formation of $t\text{-ZrO}_2$.
- (3) SE was an effective method for investigating the content of the $t\text{-ZrO}_2$ in the oxide film and the corrosion resistance of Nb36 zirconium alloy.

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椭圆偏振法研究四方氧化锆对 ZrSnNb合金氧化膜耐腐蚀性能的影响

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摘 要: 将经过不同热处理的 ZrSnNb合金样品放在 350℃、16.8mol/L Pa 0.01mol/L LOH溶液的高压釜中进行腐蚀。用椭圆偏振法研究氧化膜中的四方氧化锆, 发现经过 580℃/冷轧/500℃处理的样品在腐蚀 42天和 190天后氧化膜中的四方氧化锆比其它样品的多。四方氧化锆是影响合金耐腐蚀性能的一个主要因素, 四方氧化锆的形成有利于提高合金的耐腐蚀性能。

关键词: 锆合金; 氧化膜; 耐腐蚀性; 椭圆偏振法

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离子束辅助对真空电弧沉积掺氮二氧化钛薄膜特性的影响

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摘 要: 在氮氧混合气体中, 通过离子束辅助, 采用真空电弧沉积了氮掺杂的 TiO₂ 薄膜样品, 研究了离子束流对掺氮二氧化钛薄膜的结构、光学性质和光催化性能的影响。实验结果表明: 离子束辅助沉积的薄膜为非晶态结构, 薄膜经 500℃热处理后向锐钛矿转变, 且锐钛矿的 (101) 面的峰最强。通过 UV分析发现离子束辅助沉积的掺氮二氧化钛薄膜的吸收峰发生红移, 其光催化活性随着离子束流的增大而减小。

关键词: 离子束辅助沉积; 二氧化钛薄膜; 氮掺杂; 光催化

中图分类号: O614