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THE EFFECT OF SUBSTRATE TEXTURE AND MICROSTRUCTURE ON THE OXIDATION KINETICS OF Zr-2.5Nb ALLOY

WPŁYW TEKSTURY I MIKROSTRUKTURY PODKŁADU NA KINETYKĘ UTLENIANIA STOPU Zr-2,5Nb

Measurement of oxidation kinetics of as-received Zr-2.5Nb samples, texture modified Zr-2.5Nb samples, and pure zirconium were carried out by using thermo gravimetric analysis (TGA). A role of substrate texture, substrate microstructure on oxidation kinetics and mechanism of oxidation processes was discussed. The substrate exhibits better corrosion resistance after heat treatment at 560°C, while the corrosion resistance becomes worse after heat treatment at 855°C. The improvement of oxidation resistance of the substrate is due to the decomposition of β-Zr phase, rather than the minor change of texture of α-Zr phase induced by the heat treatment. Among the samples tested, Zr-2.5Nb substrate after heat treatment at 560°C shows the best oxidation resistance, followed by as-received Zr-2.5Nb sample and the Zr-2.5Nb samples with heat treatment at 855°C.

Keywords: Zr-2.5Nb, Texture, Microstructure, Oxidation kinetics

Analiza termograwimetryczna (TGA) była użyta do pomiaru kinetyki utleniania technicznego stopu Zr-2,5Nb wyjściowego, jak również po zmodyfikowaniu jego tekstury i dla czystego cyrkonu. Rozważana jest rola tekstury i mikrostruktury podkładu na kinetykę oraz mechanizm procesu utleniania. Podkład staje się lepiej odporny na korozję po obróbce cieplnej w temperaturze 560°C, a najmniej odporny po obróbce cieplnej w temperaturze 855°C. Polepszenie się odporności na utlenianie podkładu wynika raczej z rozkładu fazy β-Zr niż z nikłej zmiany tekstury fazy α-Zr wynikającej z obróbki cieplnej. Wśród badanych próbek podkład Zr-2,5Nb po obróbce cieplnej w temperaturze 560°C wykazuje najlepszą odporność na utlenianie. Gorsze własności wykazują próbki dostarczonego technicznego stopu Zr-2,5Nb oraz Zr-2,5Nb po obróbce cieplnej w temperaturze 855°C.

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1. Introduction

Zr-2.5Nb alloy is exclusively used as the pressure tube material in CANDU nuclear reactor due to its high corrosion resistance, high strength, and low neutron capture cross section [1]. The high corrosion resistance of zirconium is attributed to the protective zirconium oxide formed on the surface of the pressure tubes. More important, the zirconium oxide layer can also prevent hydrogen permeation into the pressure tubes.

The oxidation of zirconium is known as an inward diffusion oxidation and is affected by microstructure and texture of the oxide layer. Early studies have found that texture of the zirconium oxide grown on the surface of the pressure tube was related to the texture of underlying substrates [2, 3]. The microstructure of Zr-2.5Nb pressure tube is anisotropic because of its manufacturing process, such as extrusion and cold drawing. In the pressure tube, α-Zr phase with HCP crystal structure (major phase in the pressure tube) has texture $(11\bar{2}0)[10\bar{1}0]$, which means that α-Zr grains are oriented in such a way that $(11\bar{2}0)$ prism planes are perpendicular to the radial direction, $<10\bar{1}0>$ direction is parallel to the axial direction of the pressure tube [4].

The corrosion resistance of Zr-2.5Nb alloy can be improved by applying special heat treatment of the substrate to modify the morphology of β-Zr phase [5]. However, the effect of the heat treatment on the texture of the substrates and its consequence on the oxidation behavior of is still unclear. This study illustrates the effect of the heat treatment on the texture, microstructure of the Zr-2.5Nb substrates, and consequently the effect of these change on the oxidation kinetics.

2. Experimental procedures

Zr-2.5Nb samples with dimension of 20 × 15 × 1 mm were cut by diamond saw from the Zr-2.5Nb pressure tube. The specimens were cut so that the direction normal to their surface corresponds to the radial direction of the tube. The way to cut the samples was chosen in order to make sure that the weight gain during the oxidation test is mainly obtained from the surface of interest. Samples before oxidation in air at 500°C, were heat treated in Argon at 560°C and 855°C. The heat treatment applied to the samples is listed in Table 1. The samples were mechanically polished successively

TABLE

Heat treatment procedure for Zr-2.5Nb substrates

Sample	Annealing temperature (C)	Time (hrs)	Cooling method
A	N/A	N/A	N/A
B	855	24	Water Quench
C	560	24	Furnace cooling

down to 600 grit by using SiC paper and followed by chemical polishing with 45 Lactic acid + 45 HNO3 + 5 HF prior to the thermogravimetric tests. X-ray diffraction

was employed for phase identification. Pole figure measurement was conducted on a Siemens D-500 texture goniometer and (100), (002) and (110) pole figures were selected for texture measurement on α-Zr phase.

3. Results and discussions

3.1. Effect of heat treatment on substrate texture and microstructure

Comparing the X-ray diffraction patterns from all investigated samples, it is found that intensity ratio of the diffraction peaks of these samples is different. This indicates that the heat treatment process has an influence on the texture of the substrates. Fig. 1 shows the (002) pole figures of as-received Zr-2.5Nb substrate and the substrates

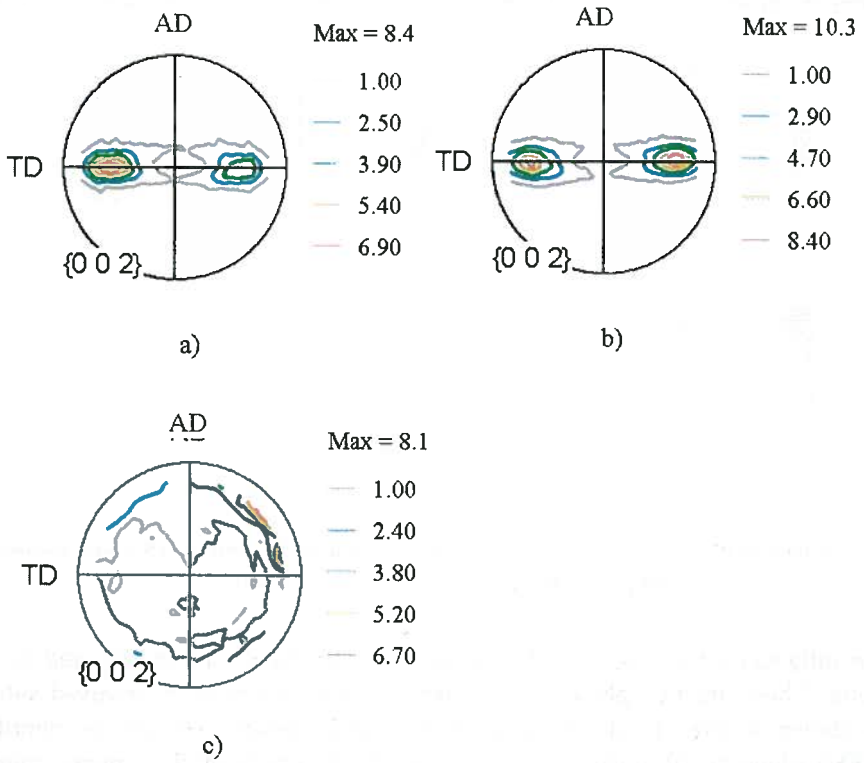

Fig. 1. (002) pole figure of Zr-2.5Nb alloy a) as-received sample, b) substrate after heat treatment at 560°C, c) substrate after heat treatment at 855°C (AD — axial direction of the tube. TD — transverse direction of the tube)

after heat treatment. It is clearly seen that the heat treatment at 560°C for 24 hours has no significant influence on the texture, while heat treatment at 855°C can change substrate texture dramatically. To describe these changes, ODF was calculated from the

measured pole figures using Textools software [5]. The calculated ODFs of different substrates are shown in Fig. 2 for comparison. The texture of the substrate after the heat treatment at 560°C is $(11\bar{2}0)[10\bar{1}0]$, which is the same as for the as- received sample. The difference of ODF of these two samples lies only in the maximum intensity. The ODF intensity for the as-received sample is 18.2, while the ODF intensity for the sample after heat treatment at 560°C is 21.5. Therefore, heat treatment at 560°C for 24 hours makes the texture of α-Zr phase a bit sharper. The reason is that the heat treatment at this temperature is well below the temperature at which zirconium grains can grow. This heat treatment can induce however some minor changes to dislocation density in α-Zr phase [6]. The increase of the intensity of ODF of α-Zr phase might be contributed from the decomposition of β-Zr phase during the heat treatment. When heat treatment temperature reaches β-region at 855°C, texture of the substrate is changed because the grain growth occurs at this temperature. Fig. 2 (c) illustrates the texture with intensity around 3.2, which is similar to the texture of pure zirconium sheet.

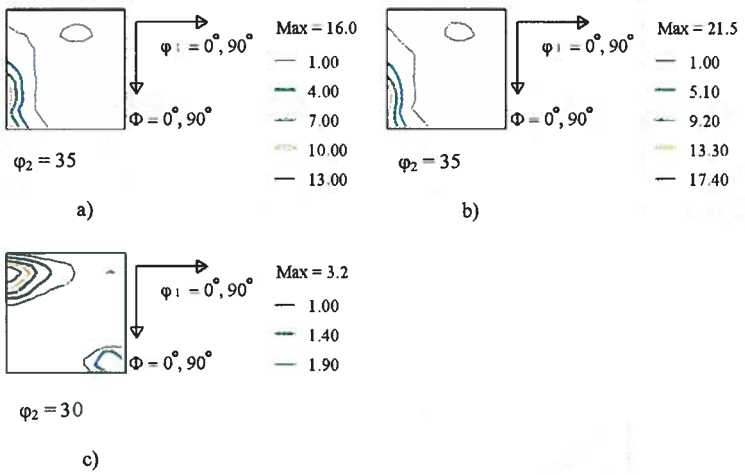

Fig. 2. Calculated ODF of Zr-2.5Nb alloy a) as-received sample, b) substrate after heat treatment at 560°C, c) substrate after heat treatment at 855°C

The influence of the heat treatment on microstructure was investigated by X-ray difftaction. There are two phase α-Zr phase and β-Zr phase in as-received substrate, as it is shown in Fig. 3 (a). The only peak of β-Zr phase that can be identified is from (200) plane at 2θ angle of 51.7 degree. Other peaks of β-Zr phase cannot be observed because of overlapping with the peaks of α-Zr phase or because of weak diffraction intensity. After heat treatment at temperature of 560°C for 24 hours, no diffraction peak from β-Zr phase was observed, see Fig. 3 (b), which indicates that the heat treatment has decomposed β-Zr phase into α-Zr phase and β-Nb phase. Two peaks from β-Nb phase corresponding to (110) at the value of 2θ = 38.2 degree and (200) at the value of 2θ = 55.1 degree were identified. Fig. 3 (c) shows the X-ray diffraction pattern from the sample heat treated at 855°C for 24 hours followed by water quench.

Strong diffraction peak from $(11\bar{2}0)$ plane of ω-phase at the 2θ = 35.7 degree and a (200) diffraction peak from β-Zr phase were observed, while diffraction intensity from α-Zr phase was less. Therefore, there are three phases, α-Zr phase, β-Zr phase, and ω-phase in the sample and the percentage of α-Zr phase is less than that of previous two samples.

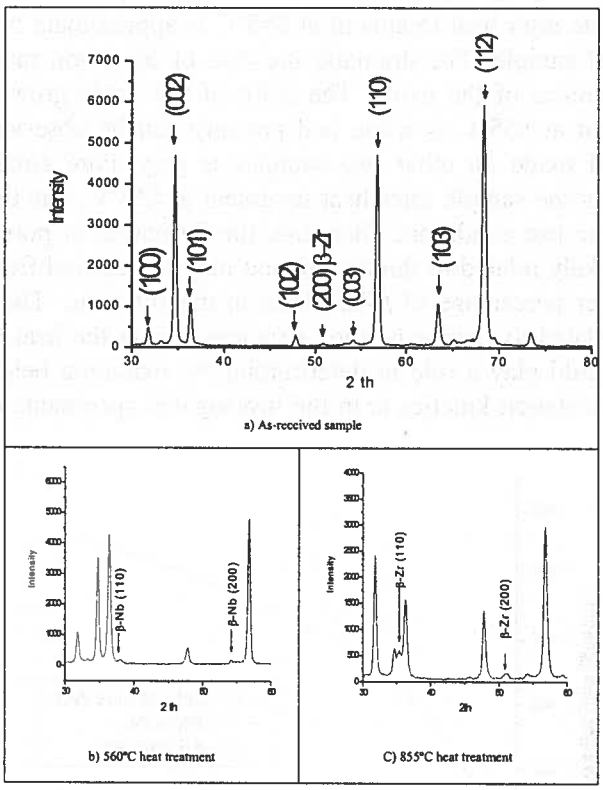

Fig. 3. X-ray diffraction pattern of a) as-received sample, b) substrate after heat treatment at 560°C, c) substrate after heat treatment at 855°C

3.2. Oxide texture and oxidation kinetics

The oxidation kinetics was measured by using thermo gravimetric system versus time at 500°C in air atmosphere environment and the results are shown in Fig. 4 for all investigated samples. Due to the limitation of test time of thermo gravimetric system, the selected oxidation temperature is higher than the working temperature of the pressure tube to obtain a comparable oxide thickness. In addition, the oxidation temperature should be below 560°C to avoid the effect of phase transformation of the substrate during the oxidation process. The oxidation kinetics curves initially follow

parabolic kinetics and gradually become approximately linear. Similar oxidation characteristic has been observed by other authors in water and steam conditions [7, 8]. The acceleration of oxidation due to the loss of protectiveness of the oxide was not observed due to a rather short oxidation time in this study. The sample obtained after heat treatment at 855°C for 24 hours has the highest oxidation rate, followed by as-received sample and the sample heat treated at 560°C for 24 hours. The weight gain of the substrate after heat treatment at 855°C is approximate 5 times higher than that of as-received sample. The dramatic increase of oxidation rate is also reflected through the appearance of the oxide. The color of the oxide grown on the substrate with heat treatment at 855°C is white and porosity can be observed on the surface, while the color of oxide on other two samples is grey. Pure zirconium, which has the same texture as the sample after heat treatment at 855°C, has the lower oxidation rate under the same test condition. Therefore, the formation of pores or cracks in the oxide layer is unlikely related to the texture and may be resulted from the presence of ω-phase and higher percentage of β-Zr phase in the substrate. The oxidation rate of the Zr-2.5Nb is related to change in alloy structure during the heat treatment. Texture of the substrate could play a role in determining the oxidation behavior, however, its influence on the oxidation kinetics is in the investigated specimens less pronounced.

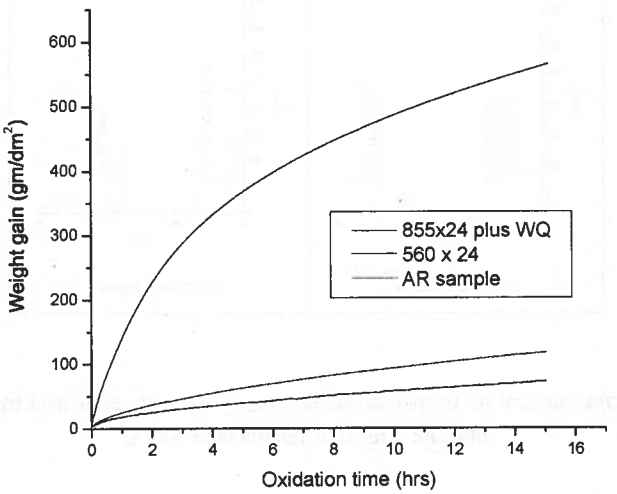

Fig. 4. Oxidation kinetics of as-received sample and substrates after heat treatment. The oxidation was carried out at 500°C in air atomosphere

4. Conclusions

The texture of Zr-2.5Nb substrate shows no significant change after the heat treatment at the temperature that is below Zr-Nb monotectoid temperature. Heat treatment

at 855°C can dramatically modify the texture of Zr-2.5Nb substrate. The oxidation resistance can be improved by heat treatment below monotectoid temperature, but heat treatment at 855°C can increase the weight gain of Zr-2.5Nb by 5 times. The change of oxidation kinetics is related to the elimination of β-Zr phase from the substrate, rather than to the change of texture of α-Zr phase.

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