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ARTICLE

Influences of Nb on Impurity C Distribution in Surface and Oxide Film of Zirconium Alloys

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Abstract: Zr-0.75Sn-0.35Fe-0.15Cr-xNb alloys were investigated, and static autoclave tests were conducted in deionized water at 360 °C and 18.6 MPa for 580 d. Secondary ion mass spectrometry was employed to characterize the concentration gradient distribution of carbon from the oxide film surface to the oxide/matrix interface, and X-ray photoelectron spectroscopy was used to analyze the valence states of carbon on the substrate surface. The experimental results show that the C concentration in the oxide film on the rolling surface (S_N) of the Zr-0.75Sn-0.35Fe-0.15Cr alloy was significantly higher than that on the surface perpendicular to the transversal direction (S_T). Adding 0.15wt% Nb can considerably decrease the C concentration in the oxide film and reduce the difference in carbon concentration distribution among oxide films on different surfaces. The C/Zr ratio on the S_N surface of the Nb-free alloy increases more obviously with the rise of temperature, suggesting a potential competitive relationship between Nb and Zr in C binding. In conjunction with experimental observations of corrosion anisotropy of the Zr-0.75Sn-0.35Fe-0.15Cr alloy, this study explored the relationship between C and anisotropic corrosion from the perspective of the effects of Nb on impurity C distribution.

Key words: zirconium alloy; niobium; impurity C; corrosion anisotropy

1 Introduction

Zirconium alloys are widely used as fuel cladding materials in pressurized water reactors due to their low thermal neutron-absorption cross-section and desired mechanical/aqueous corrosion properties. The waterside corrosion of zirconium alloys is a key factor restricting their life in reactors for higher burnup, better reliability in safety, and higher efficiency in economy. High-purity zirconium has desirable corrosion resistance, while industrial pure zirconium exhibits worse or unstable properties because of the impurities such as N, C, and Ti and other impurities in zirconium sponge. Alloying is a crucial method to compensate for the harmful effects of impurities. The main alloying elements of zirconium include Sn, Nb, Fe, Cr, and Cu. Trace elements have a significant influence on the corrosion resistance. For example, when the content of Fe+Cr increases from 0.28wt% to 0.37wt%, the corrosion mass gain of Zircaloy-4 (Zr-1.5Sn-0.2Fe-0.1Cr,

denoted as Zr-4) alloy decreases by about 30% after corrosion in steam at 420 °C for 126 d^[1]. 0.35wt% Bi can significantly improve the corrosion resistance of Zr-1Nb alloy, but 0.85wt% Bi can degrade the corrosion resistance^[2]. Adding Sn to zirconium is to counteract the adverse effect of impurity N in zirconium sponge. However, with the progress of metallurgical processes, the content of impurities in zirconium decreases. Accordingly, the Sn content in zirconium alloys is reduced to improve the corrosion resistance^[3-7].

Carbon is well known as a key element in steel materials, which has a great impact on the structure and performance of steel. Carbon is also considered as an impurity element in zirconium and is detrimental to corrosion resistance. Therefore, the carbon content is controlled to less than 0.027wt% according to ASTM^[8]. Chu et al^[9] reported that carbon affects the corrosion resistance by influencing the precipitation of the second phase particles. Carbon combines with zirconium to form face-centered cubic (fcc)-structured

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ZrC. Second phase particles of ZrC are observed with size larger than 0.4 μm , which could serve as nucleation sites for the basketweave α phase and promote the formation of basketweave Widmanstätten structures^[10]. The size of second phase particles exceeding 200 nm was reported to be a reason for nodular corrosion^[11]. Chen et al^[12] reported that precipitation of $\text{Zr}(\text{Fe},\text{Cr})_2$ second phase particles along α -Zr grain boundaries occurs with the decrease in cooling rate after β phase heating, and the nodular corrosion resistance is also degraded for the Zr-4 specimens after cold rolling and recrystallization annealing. Li et al^[13] found that nodular corrosion spots decrease on polished Zr-4 alloy, whose original surface has isolated polished streaks and contains elements C and Si.

Niobium is a β -phase-stabilizing element and can compensate for the adverse effect of C on the corrosion resistance. During corrosion in superheated steam at 500 $^{\circ}\text{C}$, adding only 0.05wt% Nb to Zr-4 alloy can significantly improve the nodular corrosion resistance of zirconium alloy^[14]. Gao et al^[15] computed that Nb promotes the adsorption of oxygen on Zr (0001) crystal face, and the surface recovers quickly after oxidation, which prevents the entry of oxygen atoms and inhibits the occurrence of nodular corrosion. Sun et al^[16] observed that an anisotropic growth of oxide films existed on Zr-4 alloy corroded in lithiated water, i. e., the oxide film growth rate on the rolling surface (S_N) is faster than that on the surface perpendicular to the transversal direction (S_T) and on the surface perpendicular to the rolling direction (S_R). While N18 (Zr-1.25Sn-0.3Nb-0.38Fe-0.078Cr) and ZIRLO (Zr-1.0Sn-1.0Nb-0.15Fe) alloys with certain Nb content show no obvious corrosion anisotropy, indicating that Nb suppresses the corrosion anisotropy. Besides, the interaction of Nb with C is related with the corrosion resistance of Nb-containing zirconium alloys. However, the influence of Nb on impurity C rarely attracts attention. The influence of Nb on the distribution of impurity C in the oxide film and the matrix of zirconium alloys was studied in this research.

2 Experiment

Alloys adopted in the present work were Zr-0.75Sn-0.35Fe-0.15Cr-xNb with $x=0, 0.15$, and 1.0 (wt%), which are denoted as 0Nb, 0.15Nb, and 1.0Nb, respectively. Sheet specimens with thickness of 2.8 mm (provided by Western Energy Material Technologies Co., Ltd) were fabricated from ingots weighing 24 kg by vacuum non-consumable arc-melting. The sequence of preparation steps was hot forging at 980 $^{\circ}\text{C}$, β phase quenching at 1030 $^{\circ}\text{C}$ for 40 min, hot rolling at 650 $^{\circ}\text{C}$, and cold rolling. The received sheets were cut into specimens with size of 20 mm $\times$ 15 mm and annealed at 580 $^{\circ}\text{C}$ for 5 h. The composition of the alloys was analyzed by inductively

coupled plasma atomic emission spectrometry (ICPAES), and the results are shown in Table 1.

The corrosion test was conducted in deionized water at 360 $^{\circ}\text{C}$ and 18.6 MPa thorough static autoclave test. The thickness of the oxide film was measured through fracture images taken from a JEOL-6700 scanning electron microscope (SEM). The hydrogen content in the corroded specimen was determined by hot vacuum extraction method with a LECO Model LECO-ONH836 equipment, and it was obtained from the mean value of three specimens cut from one sample.

The secondary ion mass spectroscopy (SIMS) measurements were conducted on a D-SIMS PHI ADEPT-1010 device with an ultra-high vacuum (UHV) chamber of a base pressure of approximately 9×10^{-8} Pa and a primary ion beam of 5 keV Cs^+ scanned over the oxide film of 200 $\mu\text{m}\times 200 \mu\text{m}$. The measured C concentrations represent the area-averaged values, and local variations at grain boundaries may exist because the beam spot is significantly larger than the grain size of nano-zirconia. To reduce the test tolerance, oxide films on the S_N and S_T surfaces of the same sample were embedded into the cold test area of 8 mm $\times$ 8 mm at the same time. The secondary ion mass spectrometry (SIMS) raw data represent atomic volume concentration curves of ZrO_2 as the standard sample, and they were plotted against oxide film thickness. In this study, with the ZrO_2 density of 5.89 g/ cm^3 and the metallic Zr density of 6.50 g/ cm^3 , the atomic volume concentrations were converted into mass concentrations, facilitating comparisons with hydrogen concentrations in samples and reported data. Oxygen concentration serves as a relative reference in SIMS analysis based on standard ZrO_2 samples, though its magnitude lacks comparative significance across different samples. During data processing, the oxygen concentration curve was exclusively used to delineate oxide film boundaries: the layer with the highest and the most stable relative content of oxygen was defined as the ZrO_2 layer, the layer with lower and less stable relative content of oxygen was defined as the metallic layer, and the intermediate layer between ZrO_2 and metallic layers was defined as the transition layer.

The samples were placed together to ensure the uniform electric field and avoid edge effect (Fig. 1). The mosaic samples were washed with acetone ultrasonically for 1 min for each time, and they were cleaned for 3 times.

X-ray photoelectron spectroscopy (XPS, Escalab 250 xi) technique was employed with a monochromatic Al $K\alpha$ source under a pressure of 7×10^{-7} Pa to measure the concentrations of alloying elements on the surfaces. The surfaces were treated at 25 $^{\circ}\text{C}$ and 2000 eV Ar^+ for 100 s to remove the contaminates on the surface. Then, the samples were heated to 500 or 600 $^{\circ}\text{C}$, kept for 15 min, and re-cooled to room temperature.

Table 1 Composition of Zr-0.75Sn-0.35Fe-0.15Cr-xNb alloys (wt%)

Alloy	Sn	Fe	Cr	Nb	O	N	H	C	Zr
0Nb	0.72	0.32	0.14	-	0.110	0.006	0.0004	<0.005	Bal.
0.15Nb	0.72	0.32	0.14	0.12	0.110	0.005	0.0005	<0.005	Bal.
1.0Nb	0.72	0.32	0.14	0.97	0.094	0.003	0.0002	<0.005	Bal.

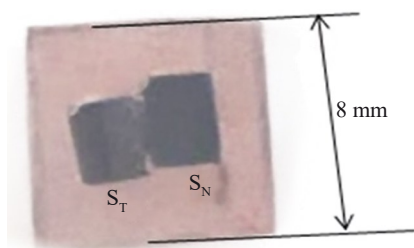


Fig.1 Appearance of sample for SIMS analysis

The spectra of C 1s were acquired at each temperature. The spot size of the X-ray beam was 200 μm to ensure that all spectra can be acquired from the surface. The XPS spectra were processed and analyzed by Avantage software (version 5.934). Charge correction was performed with C 1s of 284.8 eV as the standard. The element binding energy references database was obtained from the website <http://srdata.nist.gov/xps/selEnergyType.aspx>.

3 Results

Fig.2 shows the distribution analysis of C on the S_N and S_T surfaces of 0Nb and 0.15Nb alloys through XPS. The alloys at different states were analyzed separately: etched at 25 $^{\circ}\text{C}$ for 50 s (25 $^{\circ}\text{C}$ /etched for 50 s); heating to 500 $^{\circ}\text{C}$ after aforementioned etching process (500 $^{\circ}\text{C}$); heating to 600 $^{\circ}\text{C}$ after aforementioned etching process (600 $^{\circ}\text{C}$); cooling to 25 $^{\circ}\text{C}$ after aforementioned heating process (cooling to 25 $^{\circ}\text{C}$). It can be seen that after etching at room temperature (25 $^{\circ}\text{C}$) and treatment by Ar ions for 50 s, on the S_N surface of 0Nb alloy (black curve in Fig. 2a), the binding energy peak of about 284.8 eV disappears, and a peak of Zr-C bond at 281.6 eV can be detected. On the S_N and S_T surfaces of the 0.15Nb alloy, C-C bond with binding energy of 284.8 eV and Zr-C

bond with binding energy of 282.1 eV still exist. The binding energy of ZrC is shifted to the right side by 0.5 eV after adding 0.15wt% Nb to the 0Nb alloy. This result indicates that Nb addition makes the formation of ZrC more difficult. After the S_N and S_T surfaces are heated to 500 $^{\circ}\text{C}$, the Zr-C bond (281.6 eV) on the two surfaces becomes significantly stronger. It indicates that the C in the metal diffuses to the surface at an ultra-high vacuum atmosphere. After the S_N and S_T surfaces are heated to 600 $^{\circ}\text{C}$, the Zr-C peaks of both surfaces become weaker than that at 500 $^{\circ}\text{C}$, which may be due to a faster adsorption rate than the segregation rate of C (Fig.2a and 2b).

After the S_N and S_T surfaces are cooled to 25 $^{\circ}\text{C}$, the Zr-C peaks are stronger than that at room temperature before heating, which also indicates the segregation of C on the S_N and S_T surfaces of 0Nb alloy. At the same time, the C-C peaks on the two surfaces reappear after cooling to 25 $^{\circ}\text{C}$, which may be due to the fact that part of the C separated from the Zr surface re-adsorb on the metal surface in the cooling process. Compared with the Zr-C peak on the S_T surface, the segregation of C on the S_N surface is more obvious, which indicates that the diffusion rate of C on the S_N surface is faster.

Surface segregation of C is also detected on the S_N and S_T surfaces of the 0.15Nb alloy. After the S_N and S_T surfaces are heated to 500 and 600 $^{\circ}\text{C}$, the Zr-C bond (282.6 eV) on the two surfaces becomes significantly stronger than that at room temperature. Similarly, when the surfaces on the 0.15Nb alloy are cooled to 25 $^{\circ}\text{C}$, the Zr-C peaks are stronger than that at room temperature before heating.

The atomic ratio of C/Zr (C_C/C_{Zr}) on the S_N and S_T surfaces of 0Nb alloy and 0.15Nb alloy detected by XPS is given in Fig.3. Only C bonded with Zr is counted in the C/Zr ratio. The atomic ratio of C/Zr is approximately 0.24 and 0.10 on S_N and S_T surfaces of the 0Nb alloy, and it is about 0.07 and 0.11 on S_N and S_T surfaces of the 0.15Nb alloy, respectively. After the

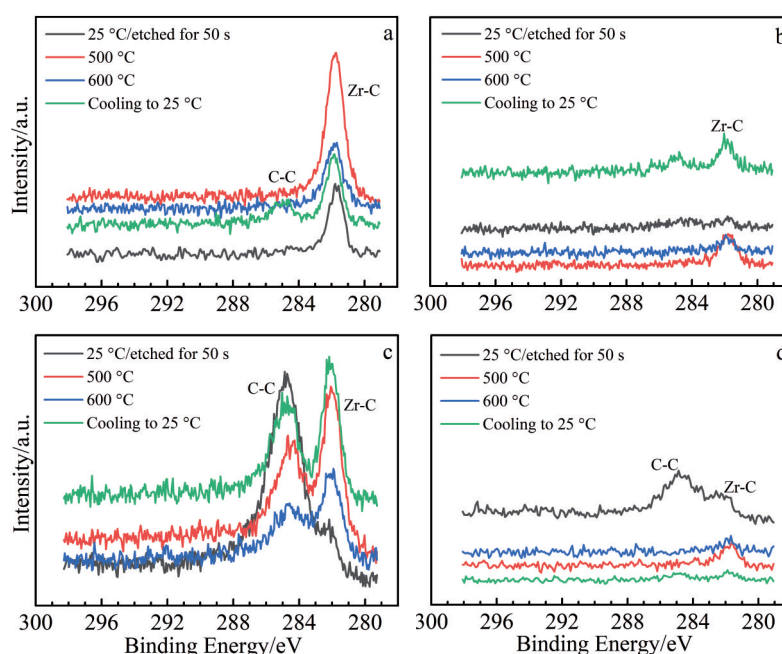


Fig.2 XPS spectra of C 1s acquired on S_N surface (a, c) and S_T surface (b, d) of 0Nb alloy (a–b) and 0.15Nb alloy (c–d) at different states

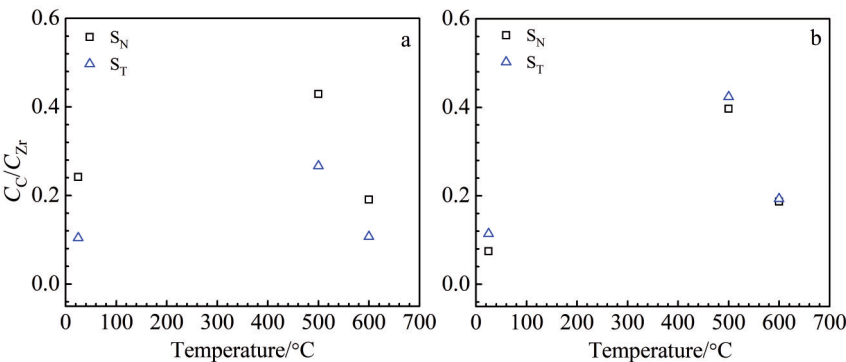


Fig.3 Atomic ratio of C/Zr on S_N and S_T surfaces of 0Nb alloy (a) and 0.15Nb alloy (b) detected by XPS

two alloys are heated to 500 °C , the atomic ratio of C/Zr increases to 0.43 and 0.27 on the S_N and S_T surfaces of the 0Nb alloy, and it is up to 0.40 and 0.42 on the S_N and S_T surfaces of the 0.15Nb alloy, respectively. The C/Zr ratio increases significantly after heating, and the increase is more pronounced on the S_N surface of the Nb-free alloy.

The C concentration analyzed by SIMS in oxide films with various Nb contents is shown in Fig.4. The PL in Fig.4 presents porous layer in oxide film, the CL presents compact layer in oxide film, the TL presents transition layer between oxide film and the matrix, and the M presents the metal matrix. The boundaries of each layer are shown in dotted lines according to O^{2-} concentration analyzed by SIMS at the same time and SEM images of oxide fracture morphology. The thickness of oxide films on 0Nb, 0.15Nb, and 1.0Nb alloys is 3–4 μm. The oxide film is divided into three layers, which are denoted as PL, CL, and TL. It can be seen that the concentration profile

of C in the oxide film on the S_N and S_T surfaces of the three alloys is wavy, but the fluctuation degree of the S_N and S_T surfaces on the 0Nb alloy is greater. The C concentration in the oxide film on 0Nb alloy is significantly higher than that in the metal matrix (about 10 μg/g). The C concentration in the oxide film on S_N surface is about 390 μg/g at the peak, which is higher than that on S_T surface (about 120 μg/g at the peak). While the C concentration in oxide film on 0.15Nb and 1.0Nb alloys decreases to below 60 μg/g at the peak, and the concentration gap between oxide films on the S_N surface and S_T surface becomes smaller. The C concentration in the matrix of different Nb-containing alloys is all about 10 μg/g, showing no obvious difference. There are also no diffusion sources existing in the medium environment. The high concentration of C in the oxide film therefore likely originates from the matrix itself. Therefore, the distribution of C in Zr-0.75Sn-0.35Fe-0.15Cr alloy is heterogeneous. Some ZrC precipitates

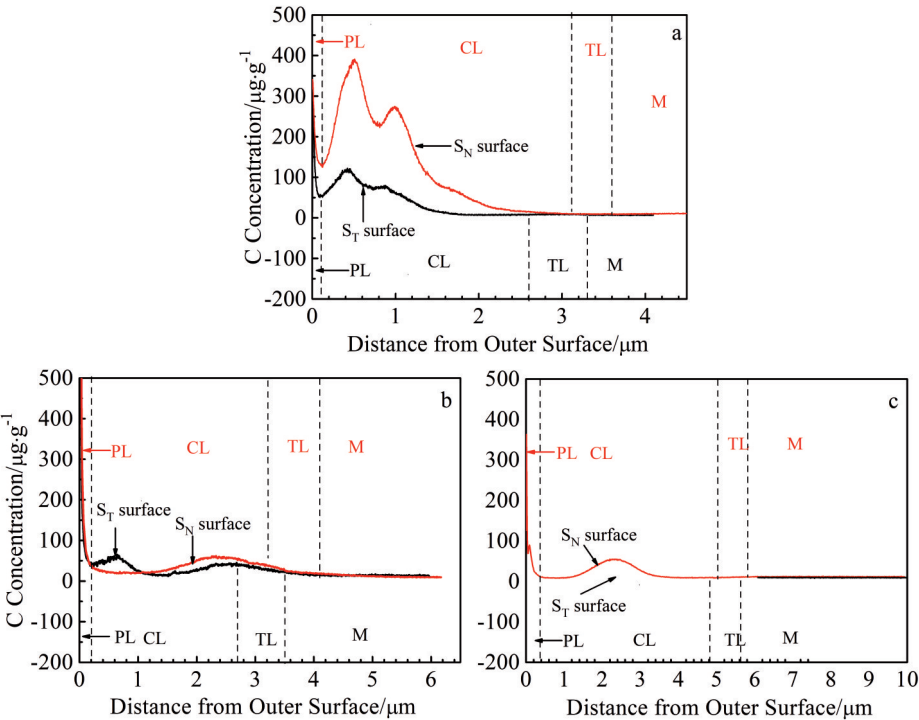


Fig.4 C concentration in oxide films grown on S_N and S_T surfaces of 0Nb (a), 0.15Nb (b), and 1.0Nb (c) alloys after corrosion in deionized water at 360 °C and 18.6 MPa for 280 d

near the surface of zirconium alloy.

4 Discussion

Fig.5 shows the oxide film thickness curves of Zr-0.75Sn-0.35Fe-0.15Cr- x Nb alloys in deionized water at 360 °C and 18.6 MPa. Thickness of oxide films on S_N , S_R , and S_T surfaces of 0Nb alloy is approximately 3.1, 3.2, and 2.8 μm after exposure for 280 d, while the oxide film thickness on S_N , S_R and S_T surfaces is about 21.8, 9.3, and 9.3 μm after exposure for 580 d, respectively. The oxide film on the S_N surface is thicker than that on S_R and S_T surfaces, and the thickness gap among S_N , S_R , and S_T surfaces increases with exposure time. The corrosion of the 0.15Nb alloy shows obvious anisotropic characteristics. Thickness of oxide films on S_N , S_R , and S_T surfaces of 0.15Nb alloy is approximately 2.6, 2.6, and 2.5 μm after exposure for 280 d, while the oxide film thickness on S_N , S_R , and S_T surfaces is 7.6, 6.0, and 6.4 μm after exposure for 580 d, respectively. Thickness of the oxide films on the three surfaces of 1.0Nb alloy also shows similar results with those of 0.15Nb alloy. The thickness gap among S_N , S_R , and S_T

surfaces of 0.15Nb alloy and 1.0Nb alloy becomes smaller than that of 0Nb alloy, which indicates that Nb addition can significantly inhibit the corrosion anisotropy of the Zr-0.75Sn-0.35Fe-0.15Cr alloy.

Fig.6 presents TEM images of the second phase in the Zr-0.75Sn-0.35Fe-0.15Cr- x Nb alloys. The second phase is finely dispersed throughout the matrix, with most particles measuring less than 100 nm in size, though a small number of larger particles (200–300 nm) are also observed. No significant difference in phase size or distribution is noted between the 0Nb and 0.15Nb alloys. When Nb content is increased to 0.5wt%–1.0wt%, the number of the second phase particles rises markedly, accompanied by a slight increase in average size. As reported in Ref. [17], the 0Nb and 0.15Nb alloys primarily contain fcc-structured $\text{Zr}(\text{Fe}, \text{Cr})_2$, with the 0.15Nb alloy additionally exhibiting minor fcc-structured $\text{Zr}(\text{Fe}, \text{Cr}, \text{Nb})_2$ precipitates.

If the material is regarded as a homogeneous mixture, there should be no differences in grain size and distribution of the second phases on the S_N , S_R , and S_T surfaces of the zirconium

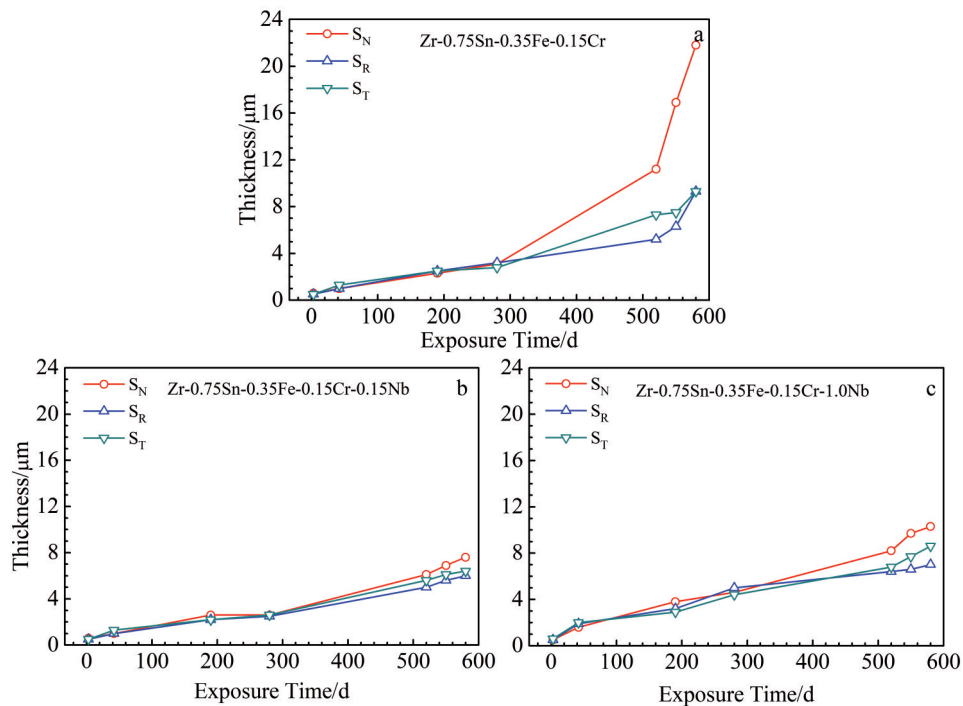


Fig.5 Relationship between oxide film thickness of Zr-0.75Sn-0.35Fe-0.15Cr- x Nb alloys in deionized water at 360 °C and 18.6 MPa and exposure time: (a) 0Nb alloy; (b) 0.15Nb alloy; (c) 1.0Nb alloy

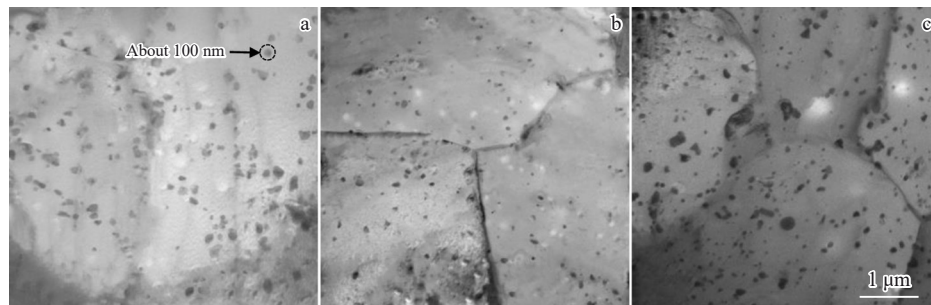


Fig.6 TEM images of microstructures of Zr-0.75Sn-0.35Fe-0.15Cr- x Nb alloys: (a) 0Nb alloy; (b) 0.15Nb alloy; (c) 1.0Nb alloy

alloy. Therefore, neither the grain size of the alloy nor the second phases in the alloy are responsible for the corrosion anisotropy of the Zr-0.75Sn-0.35Fe-0.15Cr alloy. However, as a hexagonal close-packed (hcp) structured metal, zirconium inevitably develops textures during processing. The presence of texture results in a large proportion of grains with the (0001) orientation on the S_N surface, while the grains with the (1120) and (1010) orientations dominate the S_R and S_T surface, respectively (Table 2^[17]). In Table 2, f_N , f_R , and f_T correspond to the texture factors along normal direction, rolling direction, and transverse direction, respectively. Texture is a significant factor contributing to corrosion anisotropy in zirconium alloys. However, the addition of 0.15wt% and 1.0wt% Nb exerts a negligible effect on the texture of the Zr-0.75Sn-0.35Fe-0.15Cr alloy. Nevertheless, even the addition of 0.15wt% Nb remarkably mitigates the corrosion anisotropy of the Zr-0.75Sn-0.35Fe-0.15Cr alloy in deionized water. This result indicates that although texture is a cause of corrosion anisotropy, it cannot explain why Nb inhibits the corrosion anisotropy of the Zr-0.75Sn-0.35Fe-0.15Cr alloy due to the insignificant texture modification induced by Nb addition. Corrosion of zirconium alloys is a process in which O^{2-} or OH^- diffuse through the oxide film to the oxide/metal (O/M) interface. Thus, the properties of the oxide film inevitably play a crucial role in the corrosion of the alloy. Doping effects caused by alloying elements cannot be ignored because the zirconium oxide is a semiconductor.

A thin layer of ZrC was formed with fcc structure in Zr-2.5Nb alloy^[18]. It was reported that this layer of ZrC was formed due to the impurity C diffusing from the bulk to the surface of the samples during the annealing process rather than the carbon present in the atmosphere of the furnace.

Table 2 Texture factors f_N , f_R , and f_T of (0001) lattice plane for Zr-0.75Sn-0.35Fe-0.15Cr-xNb alloys^[17]

Alloy	Texture factor		
	f_N	f_R	f_T
0Nb	0.765	0.059	0.176
0.15Nb	0.658	0.078	0.264
1.0Nb	0.701	0.061	0.238

Adding Nb can promote the diffusion of C to the surface, as shown in Fig. 3. Therefore, more C will exist in the form of C-C, because the binding energy of ZrC becomes higher after Nb addition, as shown in Fig. 2. It can also be seen that the C-C bond cannot be removed after etching the surfaces of 0.15Nb alloy for 50 s. There is a possibility that C on the surface comes from the external environment, and it is not cleaned thoroughly after ultrasonic cleaning. But compared to that on 0Nb alloy, the C-C bond is more likely to come from the impurity C diffusing from the bulk to the surface. The C existing in the form of C-C is more easily removed by preliminary treatment such as ultrasonic cleaning, acid etching, and boiling water cleaning before corrosion test rather than the C in the form of Zr-C. As a result, the whole C content in the bulk is reduced. After corrosion in high-temperature water, the C content in the oxide film reduces correspondingly, as shown in Fig. 4. The high concentration of C in the oxide film of 0Nb alloy analyzed by SIMS is most likely because of the ZrC present in the oxide film. The XPS experiments investigating C segregation were conducted under UHV with in-situ heating. The thermodynamics and kinetics of surface segregation in UHV can be drastically different from those at the solid/liquid interface under high temperature and pressure (360 °C and 18.6 MPa) conditions. However, the diffusion anisotropy of some trace elements may affect the properties of the oxide film.

An interesting phenomenon is that the C distribution patterns in the oxide film of the three alloys agree with the corrosion anisotropy result, as shown in Fig. 5. Regarding the metal itself, although corrosion anisotropy is related to the sample texture, the growth rate of the oxide film is controlled by the diffusion rate of O^{2-} or OH^- ions through the existing oxide layer. Therefore, changing the stress distribution, defects, and evolution of ZrO_2 grains in the oxide film through the precipitation phase all can be the reasons for the Nb-induced inhibition on corrosion anisotropy of Zr alloy. Meanwhile, the distribution of elements in the oxide film after oxidation significantly impacts its semiconductor properties. Compared to the alloying elements like Fe, Cr, and Nb, C diffuses more rapidly. The anisotropic diffusion of C between the metal and oxide film alters the semiconductor

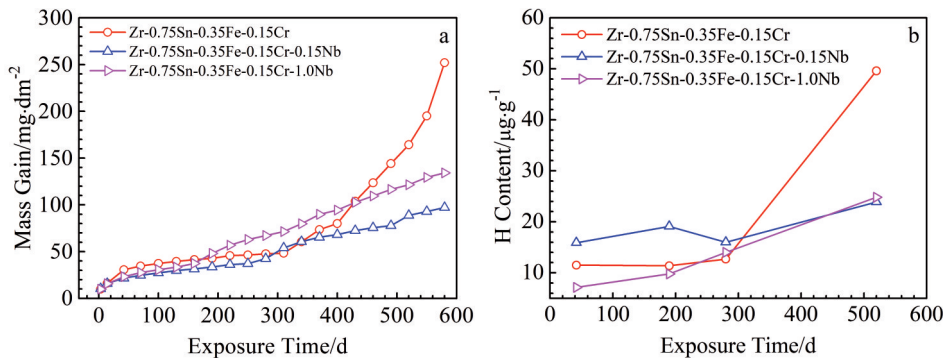


Fig.7 Relationship of mass gains (a) and hydrogen content (b) of Zr-0.75Sn-0.35Fe-0.15Cr-xNb with exposure time in deionized water at 360 °C and 18.6 MPa

characteristics of the oxide layer, which in turn affects the diffusion rates of O^{2-} and OH^- ions within the oxide film, ultimately influencing the corrosion rate. C is thought to be connected with hydrogen. It was reported that ZrC can promote the nucleation and prevent the grain growth of zirconium hydride to make the grains of zirconium hydride finer^[19]. H prefers to stay in the C vacancy, a position where it gains an electron to form a stable $1s^2$ state^[20]. The C vacancy plays a role of hydrogen trap^[21]. The higher the concentration of C in the oxide film, the higher the concentration of H in the oxide film. The high content of C in the oxide film will lead to more hydrogen traps, slowing the hydrogen diffusion in the oxide film. It is also reported that hydrogen solubility at a fixed pressure increased with carbon content in zirconium^[22]. Hydrogen is inevitably produced during corrosion process of Zr with water. Hydrogen produced at the oxide/metal interface has two ways of diffusion, which are diffusing outward to the oxide film and diffusing inward to the matrix. Nb addition can increase the hydrogen pickup of the matrix^[23–24]. Therefore, the problem is to make clear the relationship between hydrogen and the corrosion resistance of zirconium alloy. Chung et al^[25] heated the corroded Zr-4 alloy samples with approximately 170 $\mu\text{g/g}$ hydrogen to 333 °C by in situ TEM analysis and then held for 20 d. They found that zirconium hydride did not dissolve, indicating that zirconium hydride can exist stably at the temperature of at least 333 °C. Corrosion results of hydrogenated Zr-1Nb alloy with hydrogen/zirconium atomic ratio of 1.8 at 300–500 °C superheated steam for 25 h show that the mass gain of the sample is basically unchanged^[26–27]. It also indicates that zirconium hydride can exist stably at 360 °C for a relatively long time. Hydrogen content in all specimens is less than 50 $\mu\text{g/g}$, as shown in Fig. 7, which is lower than the solubility of hydrogen in α -Zr at 360 °C (approximately 160 $\mu\text{g/g}$)^[28]. Besides, the solubility is less than 10 $\mu\text{g/g}$ at room temperature. The autoclave is regularly shut down for sample weighing. Therefore, zirconium hydride precipitates during the cooling process. Hydrogen distribution in the sample is non-uniform. When the sample is reheated to the reaction temperature, in the place where zirconium hydride is concentrated locally, the hydrogen concentration in the sample will be much higher than the average hydrogen concentration in the matrix. This part of zirconium hydride may take a relatively long time to re-dissolve in the α -Zr matrix at corrosion temperature and have an effect on corrosion anisotropy, considering that zirconium hydride has a habit plane. It seems that C has a connection with the corrosion anisotropy of 0Nb alloy. It has to be pointed out that the role of C vacancy complexes as hydrogen traps is a literature-based hypothesis; experimental verification in this system is needed in further study. The distribution of alloying elements on each plane also needs a thorough analysis to fully understand the mechanism of zirconium alloy's corrosion anisotropy.

5 Conclusions

1) Adding Nb can significantly decrease the C concentration in the oxide film and reduce the C concentration

gap in the oxide film on different surfaces of the Zr-0.75Sn-0.35Fe-0.15Cr alloy.

2) Nb can compete with Zr for C, as evidenced by the observed binding energy shift and changes in C diffusion behavior.

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Nb对锆合金表面及氧化膜中杂质元素C分布的影响

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摘 要: 以Zr-0.75Sn-0.35Fe-0.15Cr-xNb合金为研究对象, 在360 °C/18.6 MPa去离子水中进行580 d静态高压釜实验, 借助SIMS检测碳元素由氧化膜表面到氧化膜/基体界面的浓度梯度分布, 通过XPS分析基体表面碳的化合价态。实验结果表明: Zr-0.75Sn-0.35Fe-0.15Cr合金轧制面(S_N)上氧化膜中C浓度明显高于横向垂直面(S_T)氧化膜中的C浓度, 添加0.15wt% Nb可以显著降低 S_N 面氧化膜中的C浓度, 减小不同表面氧化膜的C浓度分布差异。不含Nb合金 S_N 表面的碳/锆比值随温度升高增幅更大, 说明Nb与Zr在与C的结合方面可能存在竞争关系。结合Zr-0.75Sn-0.35Fe-0.15Cr合金在实验条件下表现出的腐蚀各向异性特征, 从Nb对杂质元素C分布影响的角度讨论了C与各向异性腐蚀的关系。

关键词: 锆合金; 铌; 碳杂质; 腐蚀各向异性

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