Corrosion of New Zirconium Claddings in 500 °C/10.3 MPa Steam: Effects of Alloying and Metallography

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Abstract

With the aim of improving corrosion resistance of rod cladding for in-service and accident conditions, six new zirconium alloys (named N1–N6) have been designed. The contents of Sn and Nb were optimized for better behavior at high-temperature pressurized water, and Fe, Cr, V, Cu or Mo elements were added to the alloys to adjust the corrosion behavior. The current work focused on the rapid corrosion behavior in 500 °C/10.3 MPa steam for up to 1960 h, aiming to test the corrosion resistance at high temperature. The structure of matrix and properties of second-phase particles (SPPs) were characterized to find the main differences among these alloys. All the six alloys exhibited better corrosion resistance than N36, and N1 was shown to have the best performance. A careful analysis of the corrosion kinetics curves revealed that Cr was beneficial for severe condition. Elements Fe, Cr, V, Cu or Mo aggregated into SPPs with different concentrations and structures. This was demonstrated to be the main reason for different corrosion resistance. Due to good processing control, all alloys had a uniform structure and a uniform distribution of SPPs. As for N4, N6 and N36, the existing of large-size SPPs (450 nm) might be a contributing factor of the relatively poor corrosion resistance.

Keywords New zirconium cladding · Corrosion behavior · Alloying elements · Metallography · Second-phase particles

1 Introduction

In the primary circuit of pressurized water reactor (PWR), some types of alloys are chosen because of their good properties for the extremely harsh work condition. Zirconium alloy is mostly utilized as the cladding material for a major consideration of low absorption cross section for thermal neutron [1–3]. Currently, the life-limiting factors

of zirconium claddings can be attributed to in-pile corrosion, irradiation growth, creep properties, hydrogen pickup, delayed hydrogen cracking (DHC), etc. Among them, the uniform corrosion property of zirconium alloys in high-temperature high pressurized water constricts the effectiveness of high-burn-up application [4]. The relationship between in-pile and out-of-pile corrosion behavior, though having been widely researched, still remains a problem to be solved [5, 6]. However, in both laboratory and industry, autoclave research is well accepted by scientific studies for its rapid and convenient features [7].

The corrosion behavior out-of-pile has not yet been clearly understood because of the complicated influencing factors such as the alloying elements, basic microstructures and microchemical [8]. All these factors work together to impact on the corrosion. More generally, corrosion is affected by element addition, production processes, heat treatment and water conditions. So far, the production process and heat treatment of zirconium alloys have been well controlled. Through large deformation processing and appropriate annealing condition control, the metallurgical structure of alloys can be largely controlled, leading to better corrosion resistance [9–11]. By applying a process including

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several intermediate processing and intermediate annealing, the size and distribution of second-phase particles (SPPs) remain uniform, and so do the size and microstructures of grains [12]. These factors have played a role in the good corrosion resistance of advanced zirconium alloys.

Besides the production processes, another important development of zirconium alloys is the change in alloy composition. It is confusing that a small amount of alloying additives could dramatically improve the corrosion resistance, turning the oxide structure into a dense protective film [1, 4]. So far, there are numerous experiments carried out on the effects of alloying [13–15]. Besides Sn, Nb, Fe, Cr [16–20], the addition and adjustment of Cu, V, Ge, Mo, Bi, etc. [21–26] have also attracted much attention. But the underlying mechanisms are still not quite clear.

For Sn and Nb, their solubility in Zr matrix is high [17, 18]. Amounts of studies have proved that low tin is beneficial to the corrosion in out-of-pile trials [7, 18]. And that is also a fact that has been proved in reactors [27, 28]. In laboratory studies, Sn is shown to stabilize t-ZrO₂ (tetragonal ZrO₂) phase, causing the presence of large tetragonal grains, which will damage the oxide after t-ZrO₂ transformation [18]. Nb can be dissolved in sponge zirconium up to 0.6 wt% at 600 °C [16]. However, the solubility of Nb is largely restricted by iron, thereby reducing the dissolution of Nb in the matrix [12, 17]. The effect of Nb on corrosion is still confused with solid solution and Nb-containing SPPs. But niobium addition is always necessary for advanced zirconium alloys because hydrogen pickup can be largely constricted by Nb addition, also demonstrated by density function theory (DFT) calculation [29–31].

Many transitory elements were insoluble in zirconium matrix. They are the SPP-forming elements, like Fe, Cr, Cu, V, Mo, Ge and Bi [21–26]. The influence of second-phase particles (SPPs) on corrosion of zirconium alloys was studied on the size, area fraction, composition and distribution in earlier researches [32]. Along with the utilization of state-of-the-art device, it has been able to recognize the microstructure and microchemical properties before and after the oxidizing of SPPs [33–40]. With the phenomenon demonstrated by secondary ion mass spectrometer (SIMS) and three-dimensional atom probe tomography (3D-APT) experiments that hydrogen might prefer to cluster around SPPs [35, 41], and with the fact that SPPs always undergo a delayed oxidizing behavior [39, 40], it is easy to conclude that SPPs might serve as cathode, fast path for electrons or reduction site for H⁺. Therefore, the electrochemical properties and oxidizing properties might be more important for SPPs than the P.B. ratio (Pilling–Bedworth ratio, the volume ratio of oxide to matrix) [42]. The oxidizing states and conduction properties of SPPs may be directly related to hydrogen pickup fraction [34], cubic versus parabolic oxidizing [43] and the transition kinetics. The corrosion behavior of

the SPPs which are embedded in the oxide film has a big relationship with their chemical contents and lattice structure [33]. And these differences in SPPs have been demonstrated to deeply influence the corrosion behavior [13]. Motta et al. [13] had conducted systematic experiments to test the corrosion of zirconium alloys in the supercritical water, and the results showed very obvious influence of SPPs on the corrosion resistance.

Based on decades of practical experience, several new advanced zirconium alloys are being systematically developed with the purpose to possess better uniform corrosion resistance and also better resistance for high-temperature severe condition. In the following sections, the corrosion behavior of the newly designed alloys in 500 °C/10.3 MPa steam and the metallographic characteristics of matrix are discussed. Corrosion resistance of these newly designed alloys for severe conditions is reported, and an attempt has been made to relate the structure and composition to the corrosion resistance.

2 Materials and Methods

2.1 Materials

As mentioned above, six zirconium alloys were chosen for investigation, named N1 to N6. Alloys were designed and manufactured in tubing by the National Key Laboratory for Nuclear Fuel and Materials, Nuclear Power Institute of China (NPIC). The nominal chemical composition of these alloys is shown in Table 1. N36 tube, also designed by NPIC, was used for comparison.

Low-tin principle is a well-proved way to increase the corrosion resistance of zirconium alloys. Therefore, compared to N36 cladding, the content of Sn was reduced from 1 wt% to 0.2–0.5 wt% in N1–N6. The niobium atoms mainly dissolve in the matrix when the content is below 0.2 wt% and this can largely reduce the hydrogen pickup fraction during corrosion. Nb content up to 1.4 wt% was also designed, named N3, to take the advantage of the good corrosion resistance found on some high-Nb alloys. After screening different contents and ratios of the SPP-forming elements, we obtain a ratio of Fe to (Cr, V, Cu or Mo) to be within 1–3. Additionally, the total amount of these SPP-forming elements should be appropriate.

All of these tubes followed the same production process as shown in Fig. 1. In order to get a finer and more uniform structure of zirconium matrix, the triple-melted 200 kg ingots were forged (900–1050 °C), β -annealed, water-quenched and then underwent α -extrusion (600–680 °C) and α annealing. Four times of cold rolling at RT (room temperature) and corresponding intermediate heat treatments (580–650 °C) were conducted. Finally, recrystallization

Table 1 Characteristic chemical composition of the tubes used in this paper

Name	Sn (wt%)	Nb	Fe	Cr	V	Cu	Mo
N1	0.2–0.5	0.1–0.3	0.5	0.2	–	–	–
N2	0.2–0.5	0.1–0.3	0.5	–	0.2	–	–
N3	0.2–0.5	1.1–1.4	0.1	–	0.1	–	–
N4	0.2–0.5	0.4–0.7	0.3	–	–	–	0.1
N5	0.5–0.8	0.1–0.3	0.3	0.1	–	–	0.1
N6	0.5–0.8	0.1–0.3	0.3	–	–	0.1	0.1
N36	1.0	1.0	0.3	–	–	–	–

Fig. 1 Schematic sequence of production processes of the 200 kg-level zirconium alloys

annealing was performed at 580 °C. Each rolling deformation is carefully chosen to get good texture. The final size of tube is 9.5 mm in diameter and 0.57 mm in wall thickness.

2.2 Corrosion Experiment

Tube samples were cut into 50 mm length each. Then the specimens were pickled in the standard metallographic etching solution for zirconium alloys: 10 vol.% hydrofluoric acid, 45 vol.% nitric acid and 45 vol.% distilled water for 1 min. Specimens were then boiled in boiling distilled water for 10 min to eliminate the influence of fluorine. After careful measurement of each tube sample after pickling, we found

that the thickness reduction was only 0.02–0.05 mm, indicating that the chemical treatment had little effect.

The corrosion test was performed in a static autoclave with steam at 500 °C/10.3 MPa. The autoclave was deaerated each time during heat-up at 140–150 °C. As zirconium alloys corroded at 500 °C underwent rapid oxidation, there were only a limited number of testing points lying in the pre-transition period (possible points are 3 h, 24 h and 50 h). We could only acquire quasi-quantitative information on pre-transition. High-temperature steam oxidation at 500 °C/10.3 MPa is widely used to test nodular corrosion behavior and is also a way to evaluate uniform corrosion behavior [13, 44]. The weight gain after transition is usually simplified to a quasi-linear relationship with time. In this study, at least three parallel samples of each alloy were left in the autoclave to ensure an average measuring of weight gain.

The corrosion kinetics curve of this study was divided into two stages, namely the pre-transition and the quasi-linear period. Power law was used to fit the sub-parabolic curves of each alloy at the pre-transition, but it was difficult to distinguish the transition point due to rapid corrosion. We only choose points with a weight gain of less than 45 mg/dm² to fit the pre-transition period, and the remaining points were used for linear fitting [45].

For pre-transition [3, 4, 45]:

$$\Delta W = k_1 \cdot t^n, \quad (1)$$

For quasi-linear period:

$$\Delta W = k_2 \cdot t + C, \quad (2)$$

where ΔW is the weight gain of sample in units of mg/dm², k_1 the rate constant for pre-transition, n the time index for pre-transition, k_2 the rate constant for linear period and C another constant.

2.3 Microscopic Analysis

Electron backscatter diffraction (EBSD) analysis was performed at 18 kV with a scanning step of 0.2 μm and an area of 80 × 80 μm. Tube samples were mounted in axial direction. After vibro-polishing for several hours, samples

were chemically polished for 15 s using the metallographic etching solution at room temperature. The size distribution and average area fraction of SPPs were also determined on scanning electron microscope (SEM). Samples used for determination of SPPs distribution were chemical etched with a solution of 60 vol.% glycerol, 30 vol.% hydrofluoric acid and 10 vol.% nitric acid for about 30 s at 0 °C.

The microstructure of SPPs and matrix were observed on TEM (transmission electron microscope). The composition of SPPs was detected by energy-dispersive spectrometer (EDS) detector. The thickness of the tubes was chemically reduced to 70–100 μm using the metallographic etching solution and then carefully ground to 30–40 μm . The thin foil was finally prepared at $-45\text{ }^{\circ}\text{C}$ (applied voltage and current 15 V/1.0 mA) by the twin-jet polishing with a solution of 10% HClO_4 and 90% $\text{C}_2\text{H}_5\text{OH}$. Basic knowledge of N36 alloy can be obtained from Ref. [46].

Structures and morphologies of the oxide film were characterized for N2 and N36. Tube samples were immersed vertically in the metallographic etching solution for about 8 h before cleaning with distilled water. Oxide films left on the tubes were used for observation of both cross-sectional and internal morphology.

3 Results and Discussion

3.1 Corrosion Behavior

None of the alloys exhibited nodular corrosion behavior in 500 °C steam. They all have good resistance to nodular corrosion. The weight gain profile is shown in Fig. 2. As mentioned above, points with a weight gain of less than

45 mg/dm^2 were chosen to fit the pre-transition period and the remaining points were left for linear fitting. Figure 2b shows the weight gain profiles in the double logarithmic coordinates. In this way, it would be easier to recognize the transition points, because the curves show different gradient in the pre-transition stage and approximate linear stage. The difference in the pre-transition period will lead to a big deviation in the quasi-linear corrosion process as shown in Fig. 2a. N36 has the largest weight gain of 1625 mg/dm^2 , about twice that of N1. N1 shows the best corrosion resistance in 500 °C steam. N5 also oxidized slowly until about 1100 h, after which it gains weight faster. The rest of the alloys have a similar slope in the quasi-linear period.

3.1.1 Corrosion Model

Corrosion is theoretically divided into three stages. First is the pre-transition in which the thickness of the oxide film can reach 1.5–3 μm ; second is transitory stage with a periodic power law profile in which the oxide film could reach a thickness of 15–30 μm , and this stage could also be approximately described as quasi-linear [45]; and third is the true linear period after the second transition (breakaway of oxide). Steam oxidation at 500 °C could largely accelerate the corrosion rate of zirconium, thus making the oxide film thickness excess 30 μm quickly and showing the second transition [7]. N2 shows very good resistance until 530 h, when a sudden second transition occurs and deteriorates the resistance. It is actually obvious that N2, N5, N6 and N36 show the second transition at different weight gains of 200–300 mg/dm^2 . Here we used the power law equation for the pre-transition and used linear equation for both transitory and linear stages.

Fig. 2 Weight gain profiles of the claddings corroded in 500 °C/10.3 MPa steam, **a** total weight gain profiles for the 7 alloys, **b** weight gain profiles within 300 h in the double logarithmic coordinates

Using fitting Eqs. (1) and (2), we get the total numeral fitting results in Table 2. The values of k_1 and n are not in proportion to the weight gain. This indicates the totally different physical meanings of the two parameters. As shown in Table 2, the significant differences also lie in the transition time. Alloys N1, N2, N3 and N5 can achieve a transition time as high as 108 h. This value is about twice that of N4, N6 and N36 claddings. The value of k_2 is credible and can directly reflect the corrosion behavior in the long-term corrosion.

Temperature as high as 500 °C will intensely increase the diffusion process. O^{2-} or OH^- can diffuse toward the O/M (oxide/metal) interface faster. Study on Zry-4, Zirlo and low-tin Zirlo at 360 °C indicated a k_1 value of 4–8 and an n value in range of 0.27–0.38 [7], which were smaller than our results. Factor k_1 represents the diffusion rate of the media from the surface to the interface. It becomes larger with the increase in temperature, which can be seen from the Arrhenius equation [4]. The physical meaning of factor n still leaves a secret for the researchers. It was recently recommended by Couet et al. [43] that the dissolving of divalent or trivalent Nb in the oxide film of Zr–0.4Nb alloy increases the factor n from 0.3 to 0.5. However, their model does not consider the influence of SPPs. When SPPs exist in the matrix, like Zr–2.5Nb alloy, the corrosion factor n will be at about 0.37 [34]. This is the same with our results. The factor n of all the claddings is around 0.4, smaller than 0.5.

The relatively larger n value in 500 °C steam might result from the different stress levels when we compared the results with experiments in 360 °C water or 415 °C steam. According to Ref. [47], we know oxide film shows lower stress for both M5 and pure Zr at higher temperature in steam. If this is true, it would be reasonable that a lower-stress scale in oxide leads to less stress accumulation and less cracking, causing a higher n value in 500 °C steam.

As shown in Table 2, N1, N5 have a smaller k_2 value. This phenomenon can be attributed to the influence of k_1 , n and transition time, t_{tr} . Periodic oxide layers have been confirmed by many experiments [11, 48] and are marked by periodic lateral crack bands. These studies imply that the pre-transition corrosion behavior can deeply influence

the quasi-linear stage. Since transition marks the stage at which oxide film breaks down, the much smaller transition time in some claddings would largely accelerate the time of corrosion degradation. A smaller transition time can intensively increase corrosion rate. Therefore, with larger k_1 , n and a smaller t_{tr} , the corrosion resistance in transitory stage becomes worse, causing a larger k_2 value.

3.1.2 Influence of Alloying Elements

For the six alloys, the low-tin principle contributes a lot to their better corrosion resistance than that of N36. The replacement of Cr with V element, as in the case of N1 and N2, and the replacement of Cr with Cu and Mo, as in the case of N5 and N6, lead to big differences in corrosion behavior. The conclusion is that the composition of the matrix and SPPs is responsible for the differences. Although there are slight differences in the concentration of Sn and Nb, the two cases above show a benefit of Cr addition rather than V, Cu or Mo addition in the out-of-pile 500 °C/10.3 MPa steam.

Interestingly, the two best alloys in this environment are N1 and N5, which happen to be the only two Cr-containing alloys in this study. Following the above two alloys are N2 and N3 alloys, which are exactly the two alloys with V addition. (For N3, high Nb content should be noted.) Therefore, with an optimized composition of Sn, Nb and Fe, alloys with Cr addition would have the best corrosion resistance in out-of-pile 500 °C steam, followed by alloys with V addition. Other additives like Cu or Mo may not work so well. Such behaviors may result from the stability of the elements at high temperature (delayed oxidation).

Motta et al. [13] conducted a series of experiments on the effects of alloying elements for zirconium alloys in 500 °C steam and 500 °C supercritical water. Their results showed that alloy Zr–0.4Fe–0.2Cr and Zr–1Cr–0.2Fe have the best corrosion behavior in all test environments. Comparing our results with theirs, we find that the addition of Nb and Sn is harmful to corrosion at high temperature. Cr and Fe, especially Cr itself, are beneficial to zirconium alloys corroded at 500 °C.

Table 2 Fitting results for both pre-transition and quasi-linear period

Alloys	Pre-transition		Linear profile		Transition time (h)	Maximum ΔW (mg/dm ²)
	k_1	n	k_2	R^2		
N1	7.69	0.402	0.27	0.9988	~108	589.38 ± 25.41
N2	8.35	0.408	0.46	0.9996	~94	904.66 ± 59.73
N3	8.35	0.438	0.45	0.9961	~88	942.65 ± 68.71
N4	9.70	0.374	0.54	0.9954	~57	1016.28 ± 65.63
N5	9.63	0.370	0.35	0.9984	~100	731.24 ± 34.27
N6	11.73	0.337	0.53	0.9986	~43	1106.84 ± 67.52
N36	10.09	0.393	0.83	0.9993	~47	1625.55 ± 53.15

3.2 Relationship to Matrix Structure

The basic metallography of all the alloys taken from EBSD is shown in Fig. 3. EBSD data of N36 tubes have a similar distribution and result.

Information on grain size, distribution and recrystallization fraction is obtained from analysis of the raw data by software. The recrystallization fractions of the as-received tubes are shown in Table 3. Recrystallization annealing of each alloy was performed at 580 °C, and all alloys have a good recrystallization fraction. At least 90% grains are recrystallized (Table 3). Our experience with N36 shows that although there is a large difference between recrystallization annealing and stress released annealing, only a small deviation exists if the recrystallization fraction is high and annealing time is proper. Therefore, the influence of matrix structure can be ignored.

Grain distribution and the average grain size are given in Fig. 4. Average grain size varies from 1.8 to 2.5 μm , and more grains lie in the range of 0.5–1.5 μm . These results demonstrate the uniform structure of the matrix. The corrosion behavior seems to be independent of grain distribution or average grain size. Grain size is not the factor that significantly influences the corrosion resistance especially when the processing is well controlled.

Table 3 Recrystallization fractions of all the claddings after the final annealing at 580 °C

Alloy	<i>R</i> (%)	<i>D</i> (%)	Alloy	<i>R</i> (%)	<i>D</i> (%)
N1	96.1	0.6	N2	90.6	2.6
N3	91.6	1.7	N4	98.6	0.7
N5	98.6	0.6	N6	96.7	1.3
N36	91.0	2.2			

R recrystallization fraction, *D* deformed fraction

For large and uniform samples, the influence of slight difference in anisotropic corrosion behavior of grains with different orientation can be ignored.

3.3 Relationship to Properties of SPPs

The corrosion behavior of zirconium alloys strongly depends on the properties of SPPs [42, 46, 49–51]. The influence of SPPs size still remains one of the confusing issues. Zircaloy alloys would have better corrosion resistance for a larger accumulated annealing parameter in PWR [46, 49], but some zirconium alloys with Nb content show an inverse relationship [50]. Mechanisms vary in alloys.

Fig. 3 Grain orientation images of EBSD analysis in the axial direction

Fig. 4 Frequency distribution of grain size and average grain size

3.3.1 SPP Morphology

The distribution and characteristics of SPPs are illustrated in Fig. 5. The white particles in these figures are second-phase particles demonstrated by EDS results. Statistical results of SPPs of N1–N6 and N36 claddings are shown in Table 4, which indicate that most of the SPPs are in the range of 50–150 nm and the average size is within 68–112 nm. For N1, N2, N3 and N5, size distributions of

SPPs are similar, making the average size less important. Except for changes in the composition of the matrix and SPPs, the average size and area fraction of SPPs did not show a relationship with corrosion. It should be noted that large SPP up to 461 nm is observed in N36, N4 and N6 (as shown in Fig. 5), which may have a large effect on the oxide films. From the corrosion kinetics curves in Fig. 1, it can be seen that N36, N4 and N6 exhibit the worst corrosion resistance in the newly designed alloys, which may

Fig. 5 Size distributions and morphologies of SPPs for N1–N6 and N36 claddings. Except for N4, N6 and N36, in which unordinary large SPPs up to 461 nm exist, the others show similar sizes and distributions

Table 4 Average SPP size, maximum SPP size, the area fraction and counted SPP numbers for N1–N6 and N36 claddings

Alloy	Average (nm)	Maximum (nm)	Area fraction	Numbers studied
N1	71	278.4	0.020	957
N2	92.6	287.3	0.019	1006
N3	89.7	266.2	0.022	1161
N4	91.8	461.5	0.022	979
N5	111.2	294.9	0.017	963
N6	68.7	448.2	0.010	963
N36	104.1	439.2	0.024	1049

be the result of Cu or Mo addition, or may be due to the presence of large SPPs.

The size of SPPs can influence the corrosion through three ways. As delayed oxidation of SPPs will always happen in different zirconium alloys, these SPPs will be embedded in the oxide films [18, 52]. These SPPs will be oxidized when they are a certain distance away from the interface, usually 300–500 nm [39]. The oxidation of them results in volumetric expansion because of the large P.B. ratio [53]. The P.B. ratio of Zr is 1.56, Fe is 1.77, Nb is 2.74, Cr is 2.02 and V is 3.25. Stress distribution around these oxidized SPPs will be changed, and the surrounding oxide grains will be destroyed as suggested by some researchers [53]. Bigger size of SPPs will cause the stress impacts more obvious and destroy the oxide film intensively. Since the unoxidized SPPs in oxide act as the fast transfer paths for both hydrogens and electrons [14], bigger size of SPPs might cause a faster transfer rate of electrons, which will also increase the diffusion rate of O^{2-} ions.

The third way is through formation of tiny cracks at the metal/oxide interface of the embedded SPPs. Those tiny cracks above the delayed oxidized SPPs are frequently observed by both SEM and TEM techniques in the cross section of oxide films [35, 52]. The tiny cracks are also found to be connected to large lateral cracks at the interface [42, 52]. If the size of SPP is large, the adjacent tiny crack will be relatively bigger than the crack forming above a small SPP. Therefore, cracks forming above large SPPs will interconnect with each other and connect with the large lateral cracks more easily [42]. However, it is not sure which of the three influences plays significant role on the bad corrosion resistance of N4, N6 and N36 claddings.

3.3.2 Structure and Composition of SPP

In addition to the size and area fractions, studies also emphasize the importance of SPP structure and chemical composition [35, 36, 54]. The formation of SPPs containing V, Mo and Cr indicates that the solid solubility in the matrix is

very low. Although Cu can be dissolved in the matrix up to 0.2 wt%, the existence of Fe or other SPP-forming elements can decrease the solubility of Cu [44]. These alloying elements are insoluble in the matrix, but they obviously affect the corrosion behavior. SPPs in the matrix have been carefully characterized to evaluate the chemical and structural effects on corrosion. Figure 6 shows the bright-field images of these alloys, the corresponding selected area electron diffraction (SAED) pattern and the EDS result. The structure calibration results of all the alloys are given in Table 5. The composition results show gathering of Nb, Fe, Mo, Cu, Cr and V in SPPs. In most cases, they are FCC structures. But if a high content of Nb exists in the alloy, it would be likely to form SPPs with HCP structure. This means that all the extra elements are gathered into SPPs, and then, the structures are adjusted by changing the crystal structure (FCC vs. HCP or β -Nb) or the crystal constant.

For Nb-containing SPPs (like β -Nb, $Zr(Fe,Nb)_x$), although the structure will vary in Nb concentration [54], the oxidation process always ends with an amorphous oxide product without any change in Nb content [39]. And this phase always disappears on the outer oxide film [40]. But for SPPs like $Zr(Fe, Cr)_x$ or $Zr(Fe, Ni)_x$, results clearly show that Fe or Ni in the SPPs would start to segregate to the bulk of zirconia or the grain boundaries of oxide when the oxidation process reaches a certain degree [36, 55]. Associated with this segregation, the hydrogen pickup and the transmission of O^{2-} or OH^- will be deeply affected [35, 56]. According to those results of SPPs in the oxide films, the chemical properties of SPPs have an important influence during the entire corrosion period.

The corrosion behavior of SPPs will influence the corrosion behavior of zirconium alloys. The corrosion of $Zr(Fe,Cr)_2$ intermetallic phase had been carried out by Zhou et al. [33] to study the corrosion phenomenon of the intermetallic second phase. In their results, the intermetallic alloy corroded slowly. Delayed oxidation of intermetallic SPP was the most important result. Fe was shown to segregate from $Zr(Fe,Cr)_2$ and Zr was oxidized first. Cr kept a metallic state after the zirconium was corroded to some extent. The content of Cr in the intermetallic phase determined the corrosion rate of it. Therefore, with the addition of Cr, delayed oxidation of the $Zr(Fe,Cr)_2$ SPPs which are embedded in the oxide film will become more obvious and they will consume some of the O^{2-} ions to slow down the corrosion rate of matrix. It has also been suggested by Motta et al. [13] that higher Cr content shows the better resistance to corrosion in high-temperature steam. This may be due to the intense delayed oxidation of Cr atoms in SPPs. SPPs containing V atoms have not been studied carefully. However, we suppose that V has the same intense delayed oxidation behavior, which can be figured out from the corrosion result of N1 and N2. Other SPPs containing Cu or Mo would have the same

Fig. 6 TEM data for the all the claddings. The bright-field images, SPP, SAED pattern and EDS results are shown. For different kinds of composition, SAED patterns were analyzed for crystal structure

delayed oxidation behavior as have been observed. However, the corrosion rates and corrosion phenomena of different SPPs are dependent on their chemical contents [39].

Study carried out by Kim et al. [54] suggested that the lattice structure of SPP would influence the corrosion behavior. The results showed that HCP structure of SPPs, which contained higher Nb content, caused harmful damage to oxide film after oxidation of these SPPs. They suggested that this might be attributed to the large P.B. ratio of Nb element [54]. In our results, structure of SPPs varied in different alloys. FCC, HCP and β -Nb

were all observed. However, even the same structure was obtained among different alloys, the chemical composition of these SPPs still kept a big difference. Thus, it would be hard to evaluate the influence of SPPs structure among different alloys. It might be considered that a low Nb content avoids the formation of Nb-containing SPPs, which removes the influence of volumetric expansion of Nb. Nevertheless, the P.B. ratio of V is 3.25, even larger than Nb element. Since we demonstrated a good corrosion resistance in N2 alloy, which contains a high content of V, the influence of volume expansion should be further

Table 5 Structure calibration of all the alloys

Alloy	Stoichiometry	Structure	Crystal parameter
N1	Zr(Fe,Nb,Cr) _x	FCC	$a=0.7271$ nm
N2	Zr(Fe,Nb,V) _x	FCC	$a=0.7441$ nm
N3	β -Nb	BCC	$a=0.3377$ nm
	Zr(Fe,Nb,V) _x	HCP	$a=0.5447$ nm, $c=0.8878$ nm
N4	Zr(Fe,Nb,Mo) _x	FCC	$a=1.2381$ nm
N5	Zr(Fe,Nb,Cr,Mo) _x	FCC	$a=0.7284$ nm
N6	Zr(Fe,Nb,Cu,Mo) _x	FCC	$a=1.2416$ nm
		HCP	$a=0.5423$ nm, $c=0.8773$ nm
N36	Zr(Fe,Nb) _x	HCP	$a=0.5434$ nm, $c=0.8823$ nm

evaluated. Therefore, we suggest that the differences in lattice structure and volume expansion of SPPs do not contribute a lot to the corrosion resistance. Only when the SPPs are large enough, like alloy N4 and N6, the volume expansion might cause obvious effects.

Besides the features found in oxide films, the formation of SPPs also has tremendous influence on the matrix, namely the mechanical properties, the ultimate tensile stress and creep behavior. Whether the corrosion of zirconium alloys has a relationship with mechanical properties is not well studied. However, recently, researches on the mechanism of stress relaxation of oxide film introduced the cooperation of creep in matrix [57]. They emphasized that the creep near interface contributes a lot to the stress relaxation of oxide, which will intensively influence the corrosion behavior by causing tetragonal zirconia transformation. Different properties of SPPs determine the mechanical strength of matrix. After the addition of transition metals like Fe, V, Cr or Cu, it always shows a stronger matrix by formation of SPPs, which can restrict the movement of dislocations. This is one major consideration to add these SPP-forming elements. SPP carries so much alloy information that it is the main source of difference in this study. The Cr-containing SPPs have better corrosion resistance in such environment as discussed above. This conclusion again emphasizes the importance of the intrinsic properties of elements. The mechanism study on the alloying elements will be the next step the authors will follow.

3.4 Microstructure of Oxide Film

Characterization of the oxide film has been performed to demonstrate the difference between N2 and N36. The fracture morphology of oxide film is characterized to show the oxide thickness, the grain structure, the cracks and even pores [36] inside the oxide film [15, 20, 58].

3.4.1 Fracture Morphology

Figure 7 shows the fracture morphologies of alloy N1 and N36 with different corrosion time. The morphologies of N2–N6 claddings corroded for 300 h are also provided in Fig. 7. The oxide film thickness of N36 is about twice that of N1, which is in agreement with the weight gain profiles. The thickness of oxide films of other claddings is also correlated with their weight gain profiles.

The most significant feature of those pictures is the distance between lateral crack bands. As shown in many studies, the transition is a combination of a burst of lateral cracks and the formation of interconnected pores perpendicular to interface [52, 59]. Layers of oxide which are separated by crack bands form the complete oxide film [48]. It has been proved by nano-SIMS combined with the isotope labeling that at pre-transition stage, the $^{18}\text{O}^{2-}$ ions are mostly located at the outer part of the oxide film [41]. When transition happens, $^{18}\text{O}^{2-}$ ions transform into the oxide film. They permeate through the lateral cracks [41]. Therefore, lateral crack band can clearly mark the position where transition happens. The morphologies in Fig. 7 show the proof of the oxide layer structure which can be identified from the bands of lateral cracks. This has proved the existence of pre-transition stage and periodic transitory stage in 500 °C steam. Study of compressive stress in bilayer film shows the periodic spatial stress profile inside the film [57], as is the same case for t-ZrO₂ fraction which shows a periodic profile with an interval of ~ 2 μm [48]. The periodic profile of stress corresponding to tetragonal phase is one of the possible mechanisms for the formation of lateral crack bands.

Difference appears in the number of lateral crack bands in different claddings. We have discussed that these crack bands point out the happening of corrosion transition. Therefore, according to the bands number, we can figure out the transition times of specific cladding when it corrodes for 300 h. There are two crack bands in the cross section of N1 cladding, indicating that two times of transition have already happened at 300 h. The transition time of N2 is nearly three, N3 is three, N4 is five, N5 is about two, N6 is about six and N36 is five. Those numbers correlate well with the transition time we have given in Table 2, which demonstrates that the transition happens periodically and the corrosion mechanism of different transition sequence seems to be the same.

3.4.2 Interface Morphology

The undulated internal surface is another novel topic in the zirconium corrosion field, because the lateral cracks have a good correlation with the undulation of O/M interface [36], especially at the peak of interface undulation [58, 60–62]. The interface morphologies for N1 and N36 at different corrosion stages are shown in Fig. 8. The interface

Fig. 7 Fracture morphologies of alloy N1–N6 and N36. The difference between N1 and N36 corroded for different time is explicit. The differences lie on the oxide thickness and the distance between lateral crack bands

morphologies of N2–N6 claddings corroded for 50 h are also provided in Fig. 8. Initially, very tiny oxide grains form on the interface with obvious lumps. These lumps are found to be the same size as the grains in the matrix. This could be caused by the anisotropy corrosion behavior of the grains with different orientations, as is recommended by Zhou et al. [63]. The anisotropic behavior is obvious at the beginning. From 3 to 50 h, an increase in oxide grain size is observed, and we can see that the lumps of undulation are no longer visible after 50 h. The pictures also show the existence of undulation for all the samples. Therefore, together with the growing of grain size, the undulation of interface also develops in some way. N36 has a larger undulation intensity

(factor of wavelength and amplitude), indicating a rougher and more harmful interface. This result is correlated with the bad resistance of N36. The results from Ref. [52] show that the undulation is independent of grain size and SPPs' average distance, and so is our study. When corroded for the same time, samples of N36 and N6 show larger oxide grain size than other claddings. Other claddings show nearly the same morphologies without distinct difference. The faster growth of oxide grain size for N6 and N36 cladding indicates a rapid oxidation process.

We have found dark spots on the interface of the N36 alloy, which do not appear in the N1 alloy. These dark points are between 50 and 200 nm in size and appear to

Fig. 8 Morphologies of interface undulation of alloy N1–N6 and N36. The differences lie on the oxide grain size and the dark spots

be the place where SPPs are dissolved into solution, as amplified in the last figure of Fig. 8. However, the reason for the absence of tiny dark spots in N1 alloy is not clear, probably because of the different chemical composition.

The possible reason for the increase in wavelength and undulation amplitude in the initial period (pre-transition) is the release of plastic strain energy at the interface [58]. The average compressive stress in the oxide film can be about 3–4 GPa initially and decrease to about 1–2 GPa at the stage of transition [57]. Stress gradient does exist and the highest stress is proved to be at the interface [47]. High compressive stress will cause plastic deformation of the nearby matrix. By using the creep deformation model or elastic–plastic mechanism, finite element analysis gives the distribution of stress and strain at the undulated oxide interface [60–62]. In the work of Ref. [62], authors found that the positive plastic strain is mainly concentrated at the peak of undulation, while the negative plastic strain is concentrated at the valley of interface. Therefore, the stress at the interface will perfectly lead to the increase in wavelength and amplitude. For N36 alloy, a rougher interface than N1 may indicate an easier deformation of matrix near the interface, which finally resulted in a faster transition.

4 Conclusions

This study focused on the corrosion behavior of six advanced zirconium alloys in 500 °C/10.3 MPa steam. The emphasis is on the comprehensive correlation between the corrosion and the overall microstructures and micro-chemical of alloys. All the newly designed alloys show better corrosion resistance than N36 in 500 °C/10.3 MPa steam. The corrosion rates of N1 and N5 are two times slower than that of N36. Alloying elements have a big influence. Cr addition is more beneficial to corrosion in high-temperature steam. Due to the well-controlled processing, the influence of grains and distribution of SPPs are not revealed in our experiment. Some large SPPs are found in N4 and N6. This might be one of the reasons for the relatively poor resistance. The main difference in corrosion is originated from alloying elements. SPPs contain a lot of chemical information. Low-solid-solution elements are gathered in particles, and they influence the corrosion behavior in some ways. The delayed oxidation and volume expansion of SPPs or the modification of mechanical properties of matrix are the possible ways to affect corrosion behavior. The bands of lateral cracks show periodicity

related to transition. The oxide grain size and undulation intensity become larger with time at pre-transition. At transition point, the roughness reaches the largest. Interface of N36 has a rougher interface compared to that of N1 cladding.

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