Out-of-Pile Performances of Zr-Sn-Nb-Fe Alloys for PWR Fuel Cladding

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Abstract. The safety and reliability of Pressure Water Reactors (PWRs) is closely related to the performances of zirconium (Zr) alloy as fuel rod cladding material. Zr-Sn-Nb-Fe series alloys are one of the important directions for continuous improvement of zirconium alloys for high burn-up fuel element claddings. Two new zirconium alloys, N1(Zr-0.5Sn-0.15Nb-0.5Fe-0.25V) and N2(Zr-0.25Sn-1.3Nb-0.1Fe-0.05V) have been developed to use as advanced PWR fuel rod cladding materials through the studies of the corrosion behavior of Zr-Sn-Nb-Fe Alloys, the composition optimization, the preparation of claddings and the out-of-pile performances and in-pile tests of new zirconium alloys. The results are obtained by out-of-pile performance tests of two Zr alloy claddings. Transmission Electron Microscopy (TEM) results shown that fine and uniform distribution of β-Nb and/or ZrFeV(Nb) particles could lead to excellent out-of-pile corrosion resistance. Autoclave testing in 360 °C/18.6 MPa pure water, 60 °C/18.6 MPa/70 ppm Li\textsuperscript{+} aqueous solution and 360 °C/18.6 MPa/1000 ppm B\textsuperscript{3+}/3.5 ppm Li\textsuperscript{+} aqueous solution indicated that both of N1 and N2 alloys possessed better corrosion resistance than Zr-4 alloy. The hydrogen uptake results of two kinds of alloys from corrosion reactions under various corrosion conditions showed hydrogen uptake increased with the exposure time or oxide thickness, and hydrogen uptake rate of the new alloys after long-term corrosion are lower than Zr-4. Moreover, the new alloys have demonstrated superior or similar out-of-pile tensile, burst and creep properties relative to Zr-4.

1. Introduction

Zirconium alloy is the only ideal fuel element cladding material used in PWR, due to the low neutron absorption cross, good compatibility with UO\textsubscript{2}, appropriate processing performance and irradiation resistance. Higher requirements are raised on the corrosion resistance, hydrogen absorption performance and size stability of zirconium alloy cladding, along with the development of PWR in the direction of higher burn-up, longer cycle, higher thermal efficiency, safety and reliability. To this end, the world’s nuclear developed countries have carried out research and development of new zirconium alloys for advanced PWR fuel assemblies, and have developed engineering applications of E635 [1] and ZIRLO [2], and other prospected zirconium alloys, like N36 [3], M-MDA [4], X5A [5], etc. All the above alloys belong to Zr-Sn-Nb-Fe series, and Sn, Nb and Fe are main alloying elements.
As the important development direction of high performance and advanced PWR fuel element cladding material, the properties of Zr-Sn-Nb-Fe series alloys are closely related to element composition and microstructure [6-11]. A certain amount of Sn could reduce the mobility of additional vacancies generated by impurity replacing O²⁻ in zirconium, and stable t-ZrO₂ phase in oxide film [12-13], which will improve the corrosion resistance in high temperature and pressure water. Besides, Sn has the effect of solid solution to zirconium alloy, which could improve the creep resistance. A certain amount of Nb and Fe is beneficial to the mechanical properties and corrosion resistance, due to their very low solid solubility in α-Zr compared to Sn, thus the Second Phase particles (SPPs) will form and their size, distribution and type have great influence on the corrosion resistance and mechanical properties. Nowadays, Cu, V, Cr and other alloying elements are added into Zr-Sn-Nb-Fe alloys separately, or in combination. Under the interaction of multiple alloying elements, the mechanisms between composition, the SPPs and performance become more complicated and unclear [14-19].

N1 and N2 new zirconium alloys were developed by Nuclear Power Institute of China (NPIC) after composition design and corrosion selection of more than 50 alloys, and then validation and optimization of more than 10 alloys. At present, manufacturing of cladding tubes and research of inside and outside pile properties are conducting on the two candidate cladding materials for CF fuel assemblies in China. In this paper, corrosion resistance and hydrogen absorption performance in 360 °C/18.6 MPa water, 360 °C/18.6 MPa/0.01 mol/L lithium hydroxide aqueous solution and 360 °C/18.6 MPa/1000 ppm B³⁺/3.5 ppm Li⁺ aqueous solution were tested by static autoclave, tensile, creep and internal pressure blasting properties were conducted by mechanical tests, and the relationship between properties and microstructure was analyzed by TEM, which provides theoretical basis and data support for prediction of in-pile performance of new zirconium alloys and design of cladding materials for advanced PWR.

2. Experiments

2.1. Preparation of Cladding Tubes

The experimental cladding tubes of N1 and N2 zirconium alloys were prepared by State Nuclear Bao Ti Zirconium Industry Company (SNZ) of China. Firstly, the 200kg level ingots of N1 and N2 alloys were prepared by vacuum arc melting furnace, and the ingots were remelted for three times to make homogeneity. Then, the alloy ingots were processed into cladding tubes in the same conditions, and the main processing was as follows.

1) The alloy ingots were forged into the billets in the temperature range of 900-1100 °C.
2) Water quenching of the forged billets in the temperature range of 1000-1100 °C.
3) Hot-extrusion of the at tube hollows in the region of 600-650 °C.
4) Cold rolling in four passes with intermediate annealing in temperature range of 550-600 °C.
5) Final annealing at the temperature of 560 °C.

Finally, the finished cladding tubes of N1 and N2 alloy with dimension of φ9.5 mm×0.57 mm were obtained.

2.2. Characterization

The JEM-200CX transmission electron microscope (TEM) were used to visualize the grain morphology of alloy tube samples, crystal structure and composition of the Second Phase Particles (SPPs) in alloy tubes. The size and distribution of the SPPs were observed by FEI NOVA NANO SEM400 field emission scanning electron microscope (SEM), then calibrated by the Mias graphical processing software.

The tube specimens of N1 and N2 alloys were corroded in 360 °C/18.6MPa pure water, 360 °C/18.6 MPa/1000 ppm B³⁺/3.5 ppm Li⁺ aqueous solution and 360 °C/18.6 MPa/0.01 mol/L LiOH aqueous solution by static autoclave, and the hydride uptake of alloy specimens form corrosion reactions under various corrosion environments were analyzed by RH600 hydrostatic tester and Leica DMI5000M Optical Microscope (OM) respectively. In addition, N1 and N2 alloy cladding specimens
were tested for mechanical properties, including the axial tensile test at room temperature and 380 °C with MTS810-100kN hydraulic universal material testing machine, axial tensile creep test at 400 °C/117 MPa/137 MPa/157 MPa with RDL50 electronic creep relaxation tester, and burst test at room temperature and 350 °C with GBM-P-300 internal pressure burst/creep tester. The recrystallized Zr-4(Zr-1.3Sn-0.24Fe-0.12Cr) cladding tubes were used as reference specimens in all the out-of-pile performance tests.

3. Results and Discussion

3.1. Microstructure

Zirconium alloy will undergo α→α+β phase transformation at a certain temperature, although the formed metastable βZr could decompose after deformation and heat treatment, segregation of alloy elements and unequal distribution of second phase precipitates (SPPs) may occur caused by βZr decomposition, which are unfavorable to the properties of the alloy [20-21]. Therefore, designing a reasonable processing and heat treatment process to obtain cladding tubes with excellent structure is necessary. TEM analysis results of hot extrusion tube of N1 alloy showed that the SPPs are FCC-Zr(Nb, Fe, V)₂ with Nb content less than 3wt% (figures 1a, 1b and 1c), and no βZr were found. Since the temperature of α→α+β phase transformation (about 810 °C) is much higher than the designed thermal extrusion temperature (600-650 °C), βZr may not form during the thermal extrusion process, or a small amount of βZr had completely decomposed during the cooling process after extrusion. In fact, βZr can only form when the alloying elements reach certain concentrations which can stabilize the β phase, as well as temperature condition [22]. Compared with the hot extrusion tube (figure 1a), the grains further refined after one-time cold rolling (figure 1d), but the SPPs did not change significantly (figures 1e and 1f).

![Figure 1. TEM images of precipitates in N1 alloy tube billet, corresponding SAD pattern and EDS: (a), (b), (c) extruded billet, (d), (e), (f) 1st-pass cold rolling tube billet.](image)

However, for N2 alloy, due to the low phase transformation temperature (about 650 °C) and the influence of heat generated during the plastic deformation process, the temperature during the thermal
extrusion process exceeds the temperature of the $\alpha \rightarrow \alpha + \beta$ phase transformation. Therefore, after one-time cold rolling of hot extrusion tube of N2 alloy, there existed $\beta Zr$ with a body-centered cubic structure in the alloy tube (figures 2a-2c). Research [20] has shown that the massive $\beta Zr$ usually forms at the grain grain boundary. This is confirmed in this research. In addition, $\beta Nb$ (figures 2d-2f) with a body-centered cubic structure was found in annealed cold rolled tube, which was related to the decomposition of $\beta Zr$ produced during hot extrusion after cold rolling and annealing, and the reaction relationship is: $\beta Zr \rightarrow \alpha Zr + \beta Nb$. A large number of defects, such as vacancies, dislocations, and interfaces, exist in the cold rolled tube matrix and these defects reduce the atomic diffusion activation energy of alloying elements. Therefore, compared with the cold rolled tube (figure 2a), the size distribution of SPPs became more uniform after annealed at a certain temperature (figure 2d).

Figure 2. TEM images of precipitates in N2 alloy, corresponding sad pattern and EDS, : (a), (b), (c) 1st-pass cold rolling tube billet, (d), (e), (f) annealed tube billet after 1st-pass cold rolling.

After several times cold rolling and final annealing at 580 °C of N1 and N2 alloy hot extrusion tubes, the final caldding tubes are mainly equiaxial grain morphology characteristics, and well recrystallized. The SPPs distributed dispersively in the grain and on the grain boundary (figures 3a, 3b, 3d and 3e). The statistical analysis of size distribution of SPPs shows that the density of SPPs in two alloy tubes is similar (figures 3c and 3e). Compared with N1 alloy, the number of SPPs below 100 nm in N2 alloy is relatively larger, and the average diameter of SPPs is relatively smaller.

TEM-EDS analysis results showed that the SPPs in N1 alloy are mainly ZrFeV without Nb and ZrNbFeV (figure 4a) with a small amount of Nb, both with a face-centered cubic structure. While in N2 alloy, there existed a large number of SPPs with a large ratio of Nb/(V+Fe), and the V+Fe content not exceed 0.5 wt% (figure 4b), body-centered cubic $\beta Nb$ SPPs, and face-centered cubic ZrNbFeV SPPs with equivalent amount of Nb and Fe + V.
Figure 3. TEM images of precipitates in alloy cladding tube and corresponding statistical analysis diagram, (a, b, c) N1 alloy cladding tube, (d, e, f) N2 alloy cladding tube.

Figure 4. Relationship between Nb and Fe+V in SPPs of (a) N1 and (b) N2 alloy cladding tubes.

3.2. Corrosion Resistance

Figure 5 showed the corrosion weight gain of N1, N2 and reference Zr-4 alloy tube samples corroded in 360 °C/18.6 MPa pure water, 360 °C/18.6 MPa/1000 ppm B³⁺/3.5 ppm Li⁺ aqueous solution and 360 °C/18.6 MPa/70 ppm Li⁺ aqueous solution. It could be seen that after corroded in pure water for 170 days (figure 5a), B³⁺/Li⁺ aqueous solution for 130 days (figure 5b) and Li⁺ aqueous solution for 100 days (figure 5c), corrosion weight gain got transition and increased obviously. After 500 days of corrosion, the corrosion weight gain of N1 and N2 alloy samples were lower than that of Zr-4 alloy in different corrosion conditions (figure 5d), and the B³⁺ has the effect of inhibiting the corrosion of Zr-4 alloy in Li⁺-containing water, but which does not seem obvious to N1 and N2 alloy.

The corrosion resistance of zirconium alloys is closely related to composition and microstructure. For N1 and N2 alloys, the solid soluble Nb in the zirconium matrix and the small dispersed SPPs containing Nb are the main reasons why their corrosion resistance is better than that of Zr-4 alloy. When Nb atoms solid dissolved in the α-Zr matrix are oxidized, niobium ions will dissolve in ZrO₂ as
 Nb$^+$ and replace Zr$^{4+}$ ions, resulting in a reduction of oxygen ion vacancies, thereby inhibiting the diffusion of oxygen ions and reducing the corrosion rate. On the other hand, during the oxidation of SPPs, ZrNbFe-type SPPs have a greater degree of volume expansion than that of ZrFe-type SPPs, since the P.B. ratio (volume of metal oxide to volume of metal) of Nb is relatively larger than those of Zr and Fe, which is not conducive to the corrosion resistance. Therefore, the weight gain of N1 alloy was lower than that of N2 alloy after long-term corrosion out of the reactor at the same corrosion condition. However, this does not mean that the corrosion resistance of the N1 alloy in the reactor is better than that of N2 alloy, because the SPPs containing Nb have excellent radiation stability under irradiation [23-25].

![Graphs showing corrosion weight gain and corrosion rate over time for N1, N2, and Zr-4 alloys in different corrosive mediums.](image)

**Figure 5.** Corrosion weight gain of N1, N2 and Zr-4 alloy cladding tubes in three corrosive mediums, (a) 360 °C /18.6 MPa pure water, (b) 360 °C /18.6 MPa/1000 ppm B$^{3+}$/3.5 ppm Li$^+$ aqueous solution, (c) 360 °C /18.6 MPa/70 ppm Li$^+$ aqueous solution, (d) Corrosion weight gain contrast.

### 3.3. Hydrogen Uptake

The Hydrogen Uptake Fraction (HUF) was characterized by the ratio of absorbed hydrogen to released hydrogen during alloy corrosion, whose mathematical expression was shown in equation (1).

$$\text{HUF}=8\frac{C_{H(d=0.57)}W_t}{100w_tS}$$

where, the value 8 is the atom mass ratio of oxygen to hydrogen, the $C_{H(d=0.57)}$ is the normalization of measured hydrogen content hydrogen $C_H(d/0.57)$, the $w_t$ is weight (mg), the $w_t$ is weight gain (mg/dm$^2$), and the S was surface area of alloy sample (mm$^2$). Figure 6 showed that the hydrogen uptake fraction of N1 and N2 alloys were both lower than that of Zr-4 alloy after long-term corrosion in three hydrochemical media. Under the same corrosion condition, the hydrogen uptake fraction of N1 was higher than that of N2 alloy, although the corrosion weight gain of N1 alloy was lower than...
that of N2 alloy, which indicated that there is no corresponding relationship between corrosion weight gain and amount of hydrogen uptake. In fact, the main reason why the hydrogen uptake fraction of N1 alloy is lower than that of N2 alloy is that larger amount of V element is added into N1 alloy, leading to more formation of ZrFeV SPPs.

Figure 6. The hydrogen uptake fraction (HUF) of N1, N2 and Zr-4 alloy cladding tubes corroded in three corrosive mediums.

### 3.4. Mechanical Properties

Figure 7 showed the axial tensile strength and elongation of N1, N2, and reference Zr-4 cladding tubes at room temperature and 380 °C. It could be seen that although there are significant differences in composition and SPPs, the axial tensile properties of three recrystallized alloys were similar, with the tensile strength, yield strength and elongation not exceed 5% (figure 7a). At 380 °C, the strength of three alloy tubes were close, and N1 alloy has a slightly higher elongation (figure 7b), showing that the high temperature tensile property of N1 alloy is slightly better than those of N2 and Zr-4 alloys.

Figure 7. The yield strength, tensile strength and elongation of N1, N2 and Zr-4 alloy cladding tubes at (a) room temperature and (b) 380 °C.

The creep process of a material generally contains three stages. The first stage is the deceleration stage where the creep rate is firstly fast and then slow after loaded. The second stage is the steady state stage where the creep rate maintains a dynamic equilibrium. The third stage is the fracture stage where the creep rate accelerates to fracture. Among the three stages, the steady creep rate of the second stage is the key index for evaluating the creep property of a material [26-27]. Figure 8 showed the steady
creep rate of N1, N2, and Zr-4 alloy caldding tubes after axial tensile creep of 200h at 400 °C/117 MPa/137 MPa/157 MPa. It could be seen that the steady creep rate of three alloys increases with increased stress, and N1 alloy has the largest increase. But under the same stress condition, there is no order of magnitude difference on the steady creep rates of three alloys, thus their axial creep properties could be considered to be similar.

![Figure 8](image)

Figure 8. The secondary creep rate of N1, N2 and Zr-4 alloy caldding tubes at (a) 400 °C/117 MPa, (b) 400 °C/137 MPa and (c) 400 °C/157 MPa.

Figure 9 showed the inner pressure blasting strength and circumferential extension of N1, N2, and Zr-4 alloy caldding tubes at room temperature and 350 °C. It could be seen that the blasting strength at room temperature of different alloy tubes is between 680 MPa and 740 MPa, with a difference of no more than 10% (figure 9a). The circumferential extension of N1 alloy after blasting was relatively higher than those of N2 and Zr-4 alloy, though it had the lowest blasting strength. At 350 °C, the blasting strength of three alloy tubes was between 340 MPa and 370 MPa (figure 9b), and the circumferential extension after blasting was 74% to 81%, and the alloy with higher blasting strength had lower circumferential extension, which was consistent with the results obtained at room temperature. The inner pressure blasting properties of three alloy caldding tubes under the above testing conditions are similar.

![Figure 9](image)

Figure 9. The internal pressure burst strength and circumferential elongation of N1, N2 and Zr-4 alloy caldding tubes, at (a) room temperature and (b) 350 °C.

4. Conclusions

(1) Two kinds of new zirconium alloys, N1 and N2 have been developed in NPIC. The results obtained from the out-of-pile corrosion, hydrogen uptake and mechanical tests showed that new zirconium alloys possessed better corrosion resistance than Zr-4 alloy in 360 °C/18.6 MPa pure water, 360 °C/18.6 MPa/70 ppm Li⁺ aqueous solution and 360 °C/18.6 MPa/1000 ppm B³⁺/3.5 ppm Li⁺ aqueous solution.
(2) The hydrogen uptake fraction of the new alloys were lower than Zr-4 after long-term corrosion.
(3) N1 and N2 alloys have demonstrated superior or similar tensile, burst and creep properties relative to Zr-4.
(4) The excellent out-of-pile performances of new zirconium alloys were attributed to the fine and uniform recrystallized grains and the SPPs with uniform distribution of β-Nb and/or ZrFeV(Nb), which will be confirmed by irradiation testing in reactor and recommended for using as the fuel assembly in PWR.

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