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ARTICLE

Correlation Between Microstructure and Corrosion Behavior of Zr-0.8Sn-1Nb-0.3Fe Alloy

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Abstract: Zr-0.8Sn-1Nb-0.3Fe zirconium alloy sheets were prepared by different heat treatment processes. Then OM and TEM were used to analyze the microstructure of the samples, and static autoclave tests were carried out in 360 ºC/18.6 MPa/0.01 mol/L LiOH solution and 400 ºC/10.3 MPa superheated steam to investigate the corrosion behavior. The results show that the second phase particles (SPPs) are mainly C14 type $Zr(Nb, Fe)_2$ with a HCP structure, and the uniformity of SPPs distribution gradually becomes worse when the hot-rolling temperature increases from 600 to 700 ºC. Aging treatment before hot-rolling not only improves the uniformity of SPPs distribution, but also promotes the diffusion of Nb, which increases the amount of *β*Nb SPPs. Extension of final annealing time has little influence on size and distribution of the SPPs, but increases the Nb/Fe ratio in the SPPs. After long time corrosion tests, the corrosion resistance becomes worse when the hot-rolling temperature increases in both corrosion conditions. Aging treatment before hot-rolling can increase the corrosion resistance. Extension of final annealing time can also increase the corrosion resistance in LiOH solution, but decrease the corrosion resistance in superheated steam. The relationship between microstructure and corrosion resistance was discussed, and the size, distribution and the Nb content of SPPs are considered to be the main reason for the difference of the corrosion resistance of Zr-Sn-Nb-Fe zirconium alloys.

Key words: Zr-0.8Sn-1Nb-0.3Fe zirconium alloy; heat treatment; microstructure; corrosion

Zircaloy-4 has been widely used as pressurized water reactor (PWR) fuel element cladding and other reactor internals because of the special nuclear properties. However, as nuclear power reactor technology develops towards the direction of improving the fuel burn-up, reducing the cost of fuel cycle, improving the reactor thermal efficiency and improving the safety and reliability, higher request for corrosion resistance of zirconium alloys, which are the key components of fuel element cladding materials, is put forward. So many countries have developed the Zr-Sn-Nb-Fe series new zirconium alloys by optimizing Zr-Nb and Zr-Sn series alloys, such as ZIRLO, E635, X5A[1], and their corrosion resistance are better than Zircaloy-4.

For the engineering application of zirconium alloy cladding tube and sheet, tube extrusion or sheet hot rolling is one of the key procedures. Usually, the hot working temperature is high so that the plasticity is good, which is good for the material preparation, and the improvement of yield. However, according to the study of M5 and X5A cladding tubes[2,3], using lower temperature processing can obtain small and diffuse distribution of SPPs, which is advantageous to the corrosion resistance. On the other hand, higher hot working temperature can lead to bigger SPPs and even *β*-Zr, which the present indeed decreases the corrosion resistance.

Zr-0.8Sn-1Nb-0.3Fe is a new kind of zirconium alloy developed by China and its $\alpha \rightarrow \alpha+\beta$ transformation temperature is about 680 ºC [4]. In the present paper, different thermal processing were used to prepare the final sheets of Zr-0.8Sn-1Nb-0.3Fe, including α phase (600～650 ºC) hot rolling, $\alpha+\beta$ phase (700 ºC) hot rolling and $\alpha+\beta$ phase hot rolling after low temperature aging (480 ºC /10 h/50 h). The influence of hot rolling temperature, aging and final annealing time on the microstructure and the corrosion resistance in 360 ºC/18.6 MPa/0.01 mol/L LiOH solution

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and 400 ºC /10.3 MPa steam were studied.

1 Experiment

First, button ingots of Zr-0.8Sn-1Nb-0.3Fe were prepared by a vacuum non-consumable arc melted method, and each was about 70 g. After 1050 ºC/0.5 h solid solution treatment and water quenching, the samples were divided into two groups, one group were hot rolled for 600 ºC/1 h, 620 ºC/1 h, 650 ºC/1 h and 700 ºC/1 h. The other group were hot rolled for 700 ºC/1 h after 480 ºC/10 h and 480 ºC/50 h aging, separately. Then the two groups were cold rolled and inter-annealing for the same process and all the samples were finally annealed with 580 ºC/2 h, except for the samples hot rolled at 600 ºC with 580 ºC/2 h and 580 ºC/10 h annealing. Finally, sheets of about 0.6 mm in thickness were obtained.

The sheet samples were cut into 25 mm×15 mm, and then pickled and washed using a standard method. Corrosion tests were conducted in 360 ºC/18.6 MPa/0.01 mol/L LiOH solution and 400 ºC/10.3 MPa superheated steam. Germany Leica MeF3A metallographic microscope (OM) was used to observe the microstructure and JEM-200CX and JEM-2010F transmission electron microscope (TEM) with INCA spectrometer (EDS) were used to analyze the SPPs.

2 Results and Discussion

2.1 Microstructure

Fig.1 shows the grain morphologies along the rolling direction of Zr-0.8Sn-1Nb-0.3Fe specimens at different hot rolling temperatures. Some grains of strip distribution are found in all specimens, but the dynamic recrystallization grains are hardly found when hot rolled at 600 ºC (Fig.1a). When the hot rolling temperature increases, more dynamic recrystallization grains appear (Fig.1b, 1c, and 1d). The microstructure of samples hot rolled at 700 ºC and hot rolled after 480 ºC/50 h aging are almost the same, which indicates that low temperature aging has little influence on the hot rolling stage microstructure.

The hot-rolled Zr-0.8Sn-1Nb-0.3Fe with different heat-treated samples were processed into strips. Fig.2 shows the TEM images s of the final annealing strips samples. All the samples are recrystallized, and the second phase particles (SPPs) are small and distribute evenly and dispersively in *α*-Zr when the hot rolling temperature is 600 and 620 ºC (Fig.2a, 2b). The SPPs are mainly spherical and can be divided into two groups: one with size smaller than 50 nm and the other between 50 and 300 nm. When hot rolled at 650 ºC, the SPPs are locally string shaped distribution (Fig.2c), which may be caused by *β*-Zr. When hot rolled at 700 ºC, the SPPs grow up obviously and distribute more unevenly (Fig.2d). 480 ºC /10 h aging before hot rolling has little influence on the size and distribution of the SPPs, but 480 ºC/50 h aging can make the SPPs distribute more evenly (Fig.2e). Prolonging the final annealing time also has little effect on the size and distribution of the SPPs (Fig.2f).

According to the Ostwald ripening of precipitates[5], the relationship between the SPPs grow-up activation energy Q and coarsening constant k can be described as:

$$\ln(kT^2) = \ln A - Q/RT \tag{1}$$

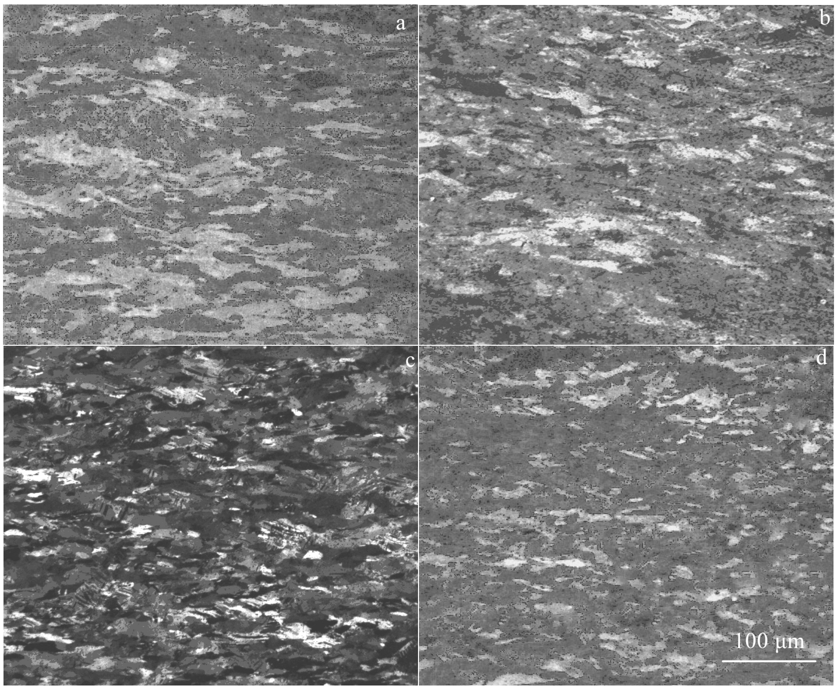

Fig.1 OM microstructures of Zr-0.8Sn-1Nb-0.3Fe specimens along the rolling direction at different hot rolling temperatures: (a) 600 ºC, (b) 650 ºC, (c) 700 ºC, and (d) 700 ºC after aging for 480 ºC/50 h

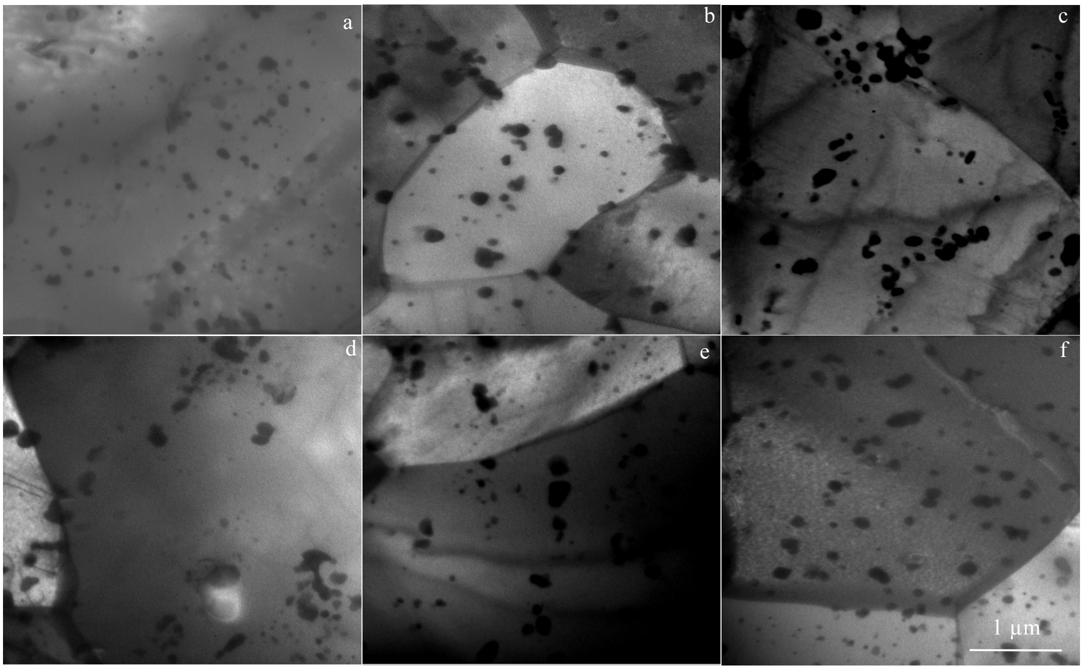

Fig.2 TEM images of Zr-0.8Sn-1Nb-0.3Fe strips: (a) 600 ºC hot-rolling (HR) and 580 ºC/2 h final annealing (FA); (b) 620 ºC HR and 580 ºC/2 h FA; (c) 650 ºC HR and 580 ºC /2 h FA; (d) 700 ºC HR and 580 ºC /2 h FA; (e) 480 ºC/50 h aging and 700 ºC HR and 580 ºC/2 h FA; (f) 600 ºC HR and 580 ºC/10 h FA

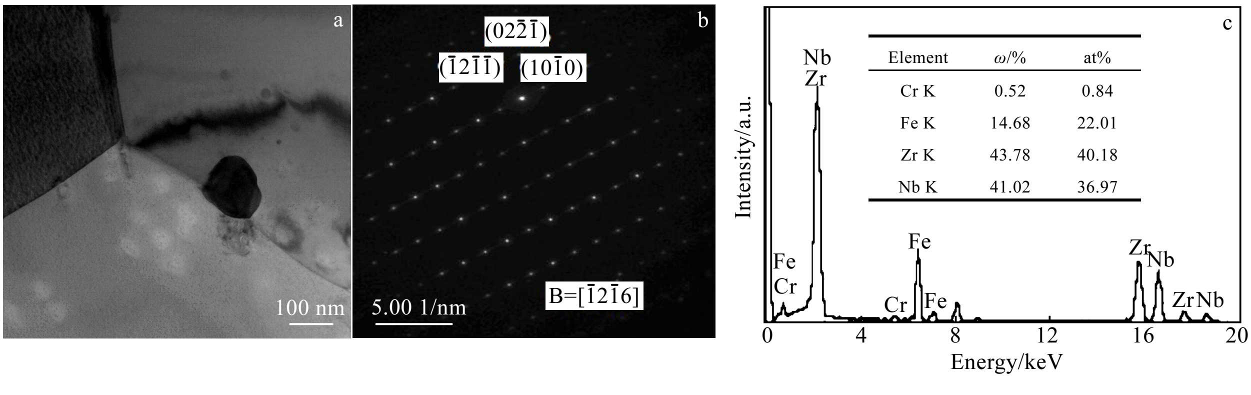

Fig.3 TEM image (a), SAED pattern (b) and EDS results (c) of the SPPs with hot rolled at 700 ºC

Where T is the temperature(K), R is the gas constant (8.314 $L\cdot kPa\cdot mol^{-1}\cdot K^{-1}$) and A is the experiment constant. From the equation, k is decided by Q and k decides the grow-up rate of SPPs. Q is closely related to the defects and elements. When hot rolled at 650 and 700 ºC, the grains are recrystallized, and the number of defects decreases, so that Q value increases, which offsets the increase of k value caused by hot rolling temperature. The uneven distribution of SPPs when hot rolled at 650 and 700 ºC could be related to the processing and heat treatments after hot rolling.

In general, the C14 type Zr(Nb, $Fe)_2$ with a HCP structure SPPs are mainly being in α phase heat-treated Zr-0.8Sn-1Nb-0.3Fe alloy[1,4] and the HCP-Zr(Nb,$Fe)_2$ precipitates are more stable than cubic Zr_2Fe or (Zr, $Nb)_2Fe$[6]. Fig.3 shows TEM image SAED pattern and EDS analysis of Zr-0.8Sn-1Nb-0.3Fe strips hot-rolled at β phase (700 ºC), inter-annealed and final annealed at α phase. The results indicate that the SPPs are similarly Zr(Nb, $Fe)_2$ with a HCP structure, which is considered the β Zr precipitates being from hot-rolling will be completely decomposed though subsequent processing and heat treatment.

Fig.4 shows the Nb/Fe ratio in the SPPs under different processing and heat treatments. After aging for 480 ºC/50 h, the amount of β Nb particles becomes fewer, which indicates that aging promotes the diffusion of Nb (Fig.4a). When final annealed at 580 ºC/10 h, the Nb/Fe ratio becomes higher than 580 ºC/2 h (Fig.4b), which indicates that prolonging annealing time can make more Nb precipitate.

2.2 Corrosion resistance

Fig.5 illustrates the corrosion dynamic curves of Zr-0.8Sn-1Nb-0.3Fe strips samples with different heat treatment. In 400 ºC/10.3 MPa superheated steam (Fig.5a), the samples hot rolled at 600 ºC show the best corrosion resistance. Aging before hot rolling can improve the corrosion resistance to some extent. Samples final annealed at 580 ºC /10 h show worse corrosion resistance than 580 ºC /2 h. In 360 ºC /18.6 MPa/0.01 mol/L LiOH solution, when the hot rolling temperature increases, the corrosion resistance becomes worse (Fig.5b), which may be related to the size and distribution of SPPs. Aging before hot rolling and prolonging final annealing time can obviously improve the corrosion resistance.

The influence of processing and heat treatments on corrosion resistance can be attributed to the microstructures. When hot rolled at 600 and 620 ºC, the SPPs are small and distribute evenly. And the SPPs smaller than 50 nm in the samples hot rolled at 600 ºC are more than that hot rolled at 620 ºC, so that the corrosion resistance is a little better. When hot rolled at 650 or 700 ºC, the SPPs grow up and distribute unevenly, which is harmful to the corrosion resistance. Aging before hot rolling can promote the diffusion of Nb and distribution of SPPs so that the corrosion resistance improves. Prolonging final annealing time shows different influences on the corrosion resistance in 400 ºC/10.3 MPa superheated steam but conducive in 360 ºC/18.6 MPa/0.01 mol/L LiOH solution, which could be caused by the Nb/Fe ratio in the SPPs.

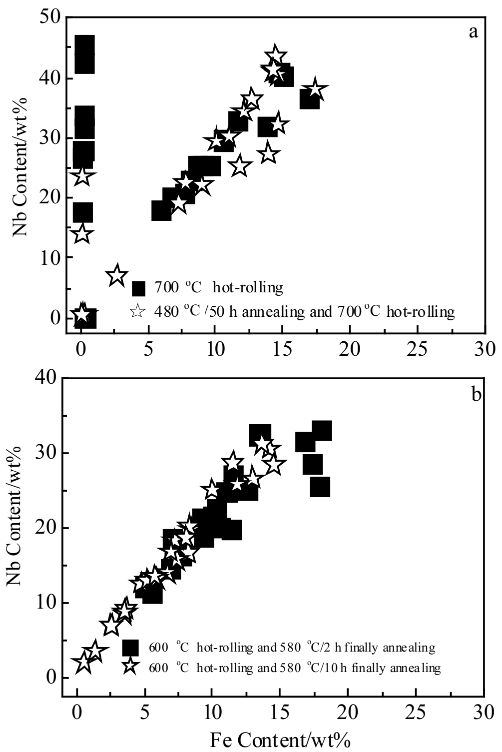

Fig.4 Ratio of Nb/Fe in the SPPs under different processing and heat treatments

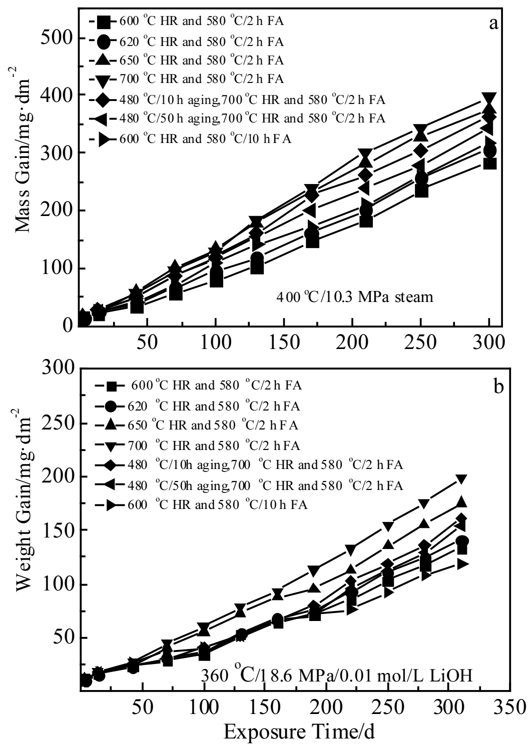

Fig.5 Corrosion dynamic curves of Zr-0.8Sn-1Nb-0.3Fe alloy samples after different processing and heat treatments

3 Conclusions

1) The SPPs of Zr-0.8Sn-1Nb-0.3Fe alloys distribute evenly and dispersively when alloys are hot rolled at 600 ºC and 620 ºC. When alloys are hot rolled at 650 ºC and 700 ºC, the SPPs grow up and gather. Aging before hot rolling can improve the distribution of SPPs, but prolonging the final annealing time has little effect on the size and distribution of SPPs.

2) The SPPs in alloys are mainly C14 type HCP $Zr(Nb,Fe)_2$. Aging before hot rolling and prolonging final annealing time can promote the diffusion of Nb.

3) Alloys hot-rolled at 600 ºC show the best corrosion resistance. When the hot rolling temperature increases, the size of SPPs increases and the corrosion resistance becomes worse.

4) Aging before hot rolling can obviously improve the corrosion resistance. Prolonging final annealing time is not conducive to the corrosion resistance in 400 ºC /10.3 MPa superheated steam but conducive in 360 ºC /18.6 MPa/0.01 mol/L LiOH solution.

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Zr-0.8Sn-1Nb-0.3Fe 锆合金显微组织与耐腐蚀性能关系

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摘　要：采用不同的热处理工艺制备出Zr-0.8Sn-1Nb-0.3Fe合金板材试样，用OM、TEM分析了试样的显微组织，用静态高压釜进行了360 ℃/18.6 MPa/0.01 mol/L LiOH水溶液和400 ℃/10.3 MPa蒸气腐蚀试验。结果表明，随着热轧温度从600 ℃增加至700 ℃时，第二相分布均匀性逐渐变差，第二相主要为C14型HCP-Zr(Nb, Fe)$_2$；热轧前时效改善第二相分布均匀性的同时，促进Nb的扩散，相应增加了βNb的数量，延长最终退火时间对第二相分布影响不大，但增加了第二相中的Nb/Fe比；合金在2种水化学介质中的耐腐蚀性能随热轧温度升高而降低，热轧前时效能改善合金的耐腐蚀性能，延长最终退火时间提高了合金在LiOH溶液中的耐腐蚀性能，但对合金在过热蒸气中腐蚀不利；分析了显微组织与耐腐蚀性能的关系，认为第二相尺寸分布、Nb含量是引起Zr-Sn-Nb-Fe锆合金耐腐蚀性能差别的主要原因。

关键词：Zr-0.8Sn-1Nb-0.3Fe 锆合金；热处理；显微组织；腐蚀

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