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## Oxidation behavior of $Zr_9S_2$ precipitates in Zr-0.8Sn-1.0Nb-0.3Fe-0.1Cr-xS alloys

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### ABSTRACT

Effect of trace sulphur (16–540  $\mu\text{g/g}$ , S) on the corrosion resistance of zirconium alloys and oxidation behavior of  $Zr_9S_2$  precipitates were investigated. Results show that S dissolved in  $\alpha$ -Zr is among 63 ~170  $\mu\text{g/g}$ . Layered  $Zr_9S_2$  particles precipitate when S addition reaches 170  $\mu\text{g/g}$ .  $Zr_9S_2$  precipitates oxidize easily and contribute to humps in the oxide films. Oxidation of  $Zr_9S_2$  precipitates causes regular shaped cavities with nanometer size grains at the inner surfaces of oxide films. The presence of cauliflower-shaped humps at the inner surfaces of oxide films is also discussed.

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### 1. Introduction

Zirconium-based alloys have been used for fuel cladding in water-cooled nuclear power plants for almost sixty years due to their low thermal neutron cross-section, fitting corrosion resistance and mechanical properties. The waterside corrosion resistance of fuel cladding is a key factor to restrict service life of high burn-up fuel assemblies.

S was regarded as harmful in zirconium-based alloys till it was reported that S had a strong beneficial influence on the creep strength of zirconium alloys [1–4]. Addition of 20 ~300  $\mu\text{g/g}$  S improved the strength of Zr-Nb alloy without reducing its ductility [1,5]. Regarding corrosion resistance, alloy M5 (Zr-1.0Nb-0.16O, wt%) of the Areva's independent brands was developed from alloy E110 (Zr-1Nb) of the Soviet Union by adding 10–35  $\mu\text{g/g}$  S to the latter [6], and has been widely used in water-cooled nuclear power plants. S content less than 200  $\mu\text{g/g}$  was also reported having a beneficial effect on the corrosion resistance of Zr-1.5Nb-O and pure Zr [4–6]. Considering that previous studies only focus on S effect on the corrosion resistance of Zr-Nb alloy or pure Zr, we have comprehensively studied the effect of S on the corrosion resistance of several kinds of zirconium alloys in Zr-Sn, Zr-Nb and Zr-Sn-Nb series

alloys used in commercial or having application prospect. Results show that 42 ~140  $\mu\text{g/g}$  S can significantly improve Zircaloy-4 (Zr-1.2Sn-0.2Fe-0.1Cr) alloy in lithiated water with 0.01 M LiOH at 360 °C/18.6 MPa [7]. No noticeable improvement effect of trace S on Zr-Sn-Nb alloys was observed according to our studies.

Second phase particles play an important role in the corrosion of zirconium alloys. They have relationships with stress, hydrogen pick-up, crack formation in oxide films [8–10]. Cauliflower-shaped humps were observed on the inner surfaces of oxide films on zirconium alloys corroded in lithiated water [11–13]. These cauliflower-shaped humps showed a non-uniform corrosion locally in zirconium alloys. Pores clusters in oxide films were thought to be related to this morphology by Zhou et al. [11]. But it's hard to explain why cauliflower-shaped humps were seldom observed at the inner surfaces of oxide films in deionized water or steam [14,15]. Although  $\text{Li}^+$  and  $\text{OH}^-$  ions were believed to contribute to the formation of pore clusters, pore clusters still cannot be avoided in oxide films in deionized water or steam during oxidation evolution [12,16]. Tetragonal sulphide  $Zr_9S_2$  precipitates when S contents in  $\alpha$ -Zr beyond about 100  $\mu\text{g/g}$ , as reported by Charquet et al. [3]. Microstructure of Zircaloy-4 + 140  $\mu\text{g/g}$  S alloy and Zr-0.70Sn-0.35Nb-0.30Fe + 190  $\mu\text{g/g}$  S alloy reported also show the precipitation of tetragonal sulphide  $Zr_9S_2$  [7,17]. Nonetheless, the oxidation behavior of this kind of second phase particles was seldom reported. Shape and size of  $Zr_9S_2$  precipitates observed in this study give us some convenience to investigate the role of second phase particles played during the corrosion of zirconium alloy. Oxi-

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**Table 1**  
Measured composition of the experimental alloys.

Alloy	Element(mass fraction,%)					
	Sn	Nb	Fe	Cr	S	Zr
T5-remelted	0.64	0.88	0.31	0.081	–	Bal.
T5 + 16 $\mu\text{g/g}$ S	0.62	0.86	0.31	0.079	0.0016	Bal.
T5 + 26 $\mu\text{g/g}$ S	0.64	0.88	0.31	0.081	0.0026	Bal.
T5 + 63 $\mu\text{g/g}$ S	0.66	0.89	0.33	0.083	0.0063	Bal.
T5 + 170 $\mu\text{g/g}$ S	0.63	0.86	0.35	0.071	0.017	Bal.
T5 + 540 $\mu\text{g/g}$ S	0.63	0.87	0.51	0.082	0.054	Bal.

dation behavior of  $\text{Zr}_9\text{S}_2$  precipitates can give Zhou's idea further explanations. Inner surface of oxide films on Zr-0.8Sn-1.0Nb-0.3Fe-0.1Cr+xS alloys were investigated to understand the oxidation behavior of  $\text{Zr}_9\text{S}_2$  precipitates.

## 2. Experimental

Alloy T5 (Zr-0.8Sn-1.0Nb-0.3Fe-0.1Cr, wt%) from Northwest Institute for Non-ferrous Metal Research and FeS (purchased from Sinopharm Chemical Reagent Co., Ltd; 99 wt%) were used to prepare T5 + xS (x: 0 ~ 540  $\mu\text{g/g}$ ) ingots of 65 g by vacuum non-consumable arc smelting (WK-III mode by Beijing Branch Photoelectric Technology Co., Ltd) in laboratory. The T5 + 0S alloy as reference, was also prepared through the same procedure as other S-containing alloys and was denoted as T5-remelted. Each ingot was turned over and re-melted 6 times for composition homogenization. Then sheet-shaped specimens were formed by the sequence of steps as follows: hot pressing at 700 °C to shape the buttons for hot/cold rolling, beta-phase homogenization at 1030 °C for 40 min, hot rolling from 12 mm to about 1.7 mm in thickness at 700 °C, beta-phase treatment at 1030 °C for 40 min to make alloying elements dissolved in Zr matrix for uniformization, and cold rolling to about 0.7 mm in thickness. Then each sheet after cold rolling was cut into 10 mm  $\times$  15 mm  $\times$  0.7 mm. The final vacuum annealing was performed at 580 °C for 2 h. The specimens were chemically polished for 5 ~ 10 s by a mixed acid solution of 30 Vol.%  $\text{H}_2\text{O}$ , 30 Vol.%  $\text{H}_2\text{SO}_4$ , 30 Vol.%  $\text{HNO}_3$  and 10 Vol.% HF before each annealing process and corrosion tests. S in these alloys was measured by frequency infrared carbon and sulfur analyzer, and the other alloying elements were measured by inductively coupled plasma atomic emission spectrometry. The measured chemical composition of the alloys is given in Table 1. Considering that S is added into the T5 alloy in the form of FeS, Fe is alloyed inevitably. But Fe content changes little in the T5 + xS alloy when minor S added in the T5 alloy less than 170  $\mu\text{g/g}$  measured in Table 1. Therefore, it does not affect the comparison of S influence on corrosion resistance of T5 alloy. Fe content in T5 + 170  $\mu\text{g/g}$  S slightly improved. And T5 + 540  $\mu\text{g/g}$  S was focused on the oxidation of  $\text{Zr}_9\text{S}_2$  precipitates.

The samples were divided into three groups and were respectively corroded in superheated steam at 400 °C/10.3 MPa, in lithiated water with 0.01 M LiOH and deionized water at 360 °C/18.6 MPa in accordance with ASTM G2/G2M-06 (Reapproved 2011). The corrosion resistance of alloys was characterized

**Table 2**  
Typical second phase particles in T5 + xS alloys.

Alloy	Frequency		
	hcp-Zr(Nb,Fe,Cr) <sub>2</sub>	bcc- $\beta$ -Nb	t-Zr <sub>9</sub> S <sub>2</sub>
T5-remelted	Major	Minor	–
T5 + 16 $\mu\text{g/g}$ S	Major	Minor	–
T5 + 26 $\mu\text{g/g}$ S	Major	Minor	–
T5 + 63 $\mu\text{g/g}$ S	Major	Minor	–
T5 + 170 $\mu\text{g/g}$ S	Major	Minor	Minor
T5 + 540 $\mu\text{g/g}$ S	Major	Minor	Minor

by mean weight gain of five samples for each alloy by Mettler Toledo XS105 DualRange ( $d = 0.01$  mg).

The microstructure of the alloys and the inner surface of oxide films was examined by JSM-6700F (JEOL) scanning electron microscope (SEM). SEM images are captured in secondary electron mode: scanning voltage in 10 kV and work distance in 8 mm. The crystal structure and chemical composition of second phase particles were respectively analyzed by selected area electron diffraction (SAED) and energy disperse spectroscopy (EDS) equipped in JEM-2010F (JEOL) high resolution transmission electron microscope (HRTEM). TEM images are captured in TEM mode: accelerating voltage in 200 kV. Then the composition of precipitates was determined using EDX equipped in HRTEM. CARINE crystallography program was used for computing the structure parameters of second phase particles and PDF cards in 2004 edition loaded in Jade 6 program were used for verification.

The SEM observation samples of the alloys were prepared by chemical etching method in the etching solution as the same as pickling specimens for corrosion tests in room temperature. According to reference [18], cut down one piece of oxidized samples with about 3 mm  $\times$  7 mm for inner oxide films observation. Then remove one side of oxide film on SiC abrasive paper of 400#, and dissolve the metal matrix to reveal the metal/oxide interface by the mixed acid solution as mentioned above. The detailed process was illustrated in Fig. 1.

## 3. Results

### 3.1. Second phase particles in the alloys

Fig. 2 shows TEM images of T5 + xS alloys. Alloys were in incomplete recrystallization state and second phase particles were distributed in stringers. S slightly influenced the principal metallurgical characteristics of the T5 alloy, which conformed to results reported by Charquet et al. [4]. Table 2 shows information about the typical second phase particles in T5 + xS alloys. The second phase particles in T5 + xS alloys were hexagonal close packed  $\text{Zr}(\text{Nb,Fe,Cr})_2$  (hcp-Zr(Nb,Fe,Cr)<sub>2</sub>) in majority and body-centered cube  $\beta$ -Nb (bcc- $\beta$ -Nb) in minority when S content added in the T5 alloy was no more than 63  $\mu\text{g/g}$ . Tetragonal  $\text{Zr}_9\text{S}_2$  (t-Zr<sub>9</sub>S<sub>2</sub>) precipitates were present when the content of S was increased to 170  $\mu\text{g/g}$ , as shown in Fig. 2f and Fig. 3. This implies that the maximum S content dissolved in  $\alpha$ -Zr is between 63  $\mu\text{g/g}$  and 170  $\mu\text{g/g}$ . The

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