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Letter to the Editors

Phase constitution and steam corrosion resistance of binary Zr–S alloys

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Abstract

The solubility limit of sulfur in alpha zirconium is about 20 ppm. This value is similar to the sulfur content leading to the maximum improvement in creep strength. In amounts up to 850 ppm, sulfur also has an extremely beneficial effect on the steam corrosion resistance at 400 °C. Thus, while sulfur in solid solution markedly enhances creep strength, the presence of sulfide precipitates has an additional favorable influence on the corrosion behavior.

1. Introduction

Sulfur additions up to 20 ppm in weight are known to have a strong beneficial influence on the creep strength of zirconium alloys [1,2], the extent of the effect varying with alloy composition, processing route and final metallurgical condition. Although published data concern sulfur contents no greater than 40 ppm, it is apparent that additions beyond 15–20 ppm have no further influence.

This is confirmed by Fig. 1, which illustrates the marked effect below 20 ppm of sulfur and the absence of any significant improvement between 20 and 600 ppm, on longitudinal creep of sheet specimens.

It has been mentioned that sulfur contents above about 15–20 ppm lead to the presence of sulfur-rich precipitates [2], suggesting that it is essentially the sulfur in solid solution in the matrix that affects the creep strength [3].

The work on binary Zr–S alloys described in the present paper had two principal aims:

- to determine the solubility limit of sulfur in zirconium in order to confirm the assumption concerning the importance of solid solution hardening of the matrix;
- to determine the intrinsic effect of sulfur on the resistance to steam corrosion, which is one of the critical properties required for zirconium alloys used in nuclear engineering applications.

2. Materials and experimental procedure

Binary Zr–S alloys were produced in the form of 50 g buttons by melting in a laboratory arc furnace under a partial pressure of argon. The raw materials employed were Van Arkel crystal bar zirconium and zirconium sulfide (ZrS). The buttons were hot rolled between 750 and 850 °C, down to a thickness of about 2 mm.

After recrystallization at 750 °C for 15 min, the strips were shot-blasted, pickled and polished. Table 1 gives the principal impurity contents analyzed.

Corrosion coupons were cut from the strips and tested in steam at 400 °C and 10.3 MPa pressure in a static autoclave.

Another series of specimens was heat treated in vacuum at temperatures from 700 to 1030 °C, for times from 2 to 10 h, followed by water quenching or forced

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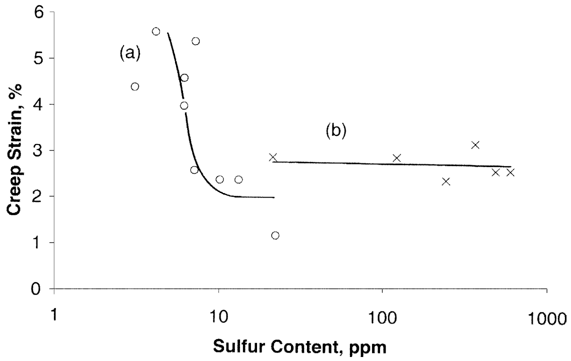

Fig. 1. Influence of sulfur on longitudinal creep of sheet specimens: (a) Recrystallized Zr–1Nb: 400 °C, 240 h, 112.5 MPa. (b) Cold worked Zr–1Nb–0.2Fe: 400 °C, 240 h, 130 MPa.

Table 1
Impurity contents of the experimental alloys

Element	O	Fe	Cr	C	N	Si
Content (ppm by weight)	470	85	<10	70	<10	<10

argon cooling. These treatments were performed either on initially recrystallized samples or on specimens given a prior treatment in the beta phase region. After heat treatment in this way, the specimens were examined metallographically. The precipitate phases were characterized in a scanning electron microscope equipped with an energy dispersive spectroscopy (EDS) system. Thin foils were also studied by electron diffraction and EDS analysis in a transmission electron microscope. Finally, certain precipitates were analyzed in an electron microprobe.

3. Results

In Fig. 2, the results are expressed in the form of a pseudo-binary Zr–S equilibrium diagram for 470 ppm oxygen and 85 ppm iron.

The iron content of the experimental materials is higher than its solubility limit in the alpha phase, leading to the existence of an $\alpha + Zr_xFe$ field, where Zr_xFe includes both Zr_3Fe and Zr_2Fe. At 700 °C, as the sulfur content increases beyond 20 ppm, the principal precipitate phase is Zr_2Fe containing sulfur, indicating that the solubility limit of sulfur in the alpha phase has been exceeded. For between 50 and 100 ppm S at this temperature, the precipitate phase is a mixed zirconium-iron sulfide, whose particular crystal structure was not able to be identified, but whose lattice spacings are large (1.53–1.46–1.39–1.28–1.16–1.02–0.968–0.80–0.72–0.70 nm).

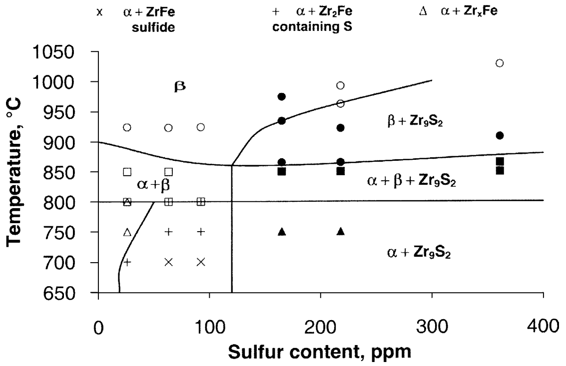

Fig. 2. Pseudo-binary Zr–S diagram for 470 ppm O and 85 ppm Fe.

Beyond about 100 ppm S, the second phase is the tetragonal sulfide Zr_9S_2 (lattice parameters $a = 0.98$ nm, $c = 1.92$ nm).

The solubility of sulfur in beta zirconium is higher than in the alpha phase, but remains relatively small nevertheless.

Fig. 3 shows the results of steam corrosion tests for 1 day at 400 °C. They confirm the very poor resistance of pure zirconium in this environment. The addition of only very small amounts of sulfur markedly improves

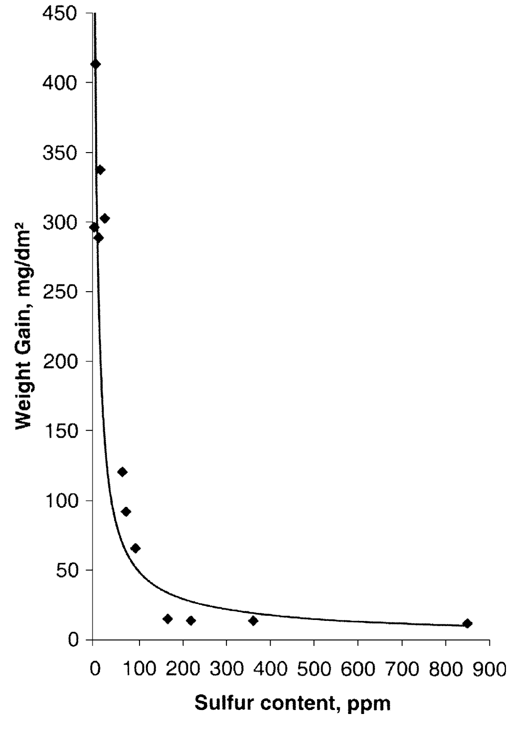

Fig. 3. Influence of sulfur on the corrosion of unalloyed zirconium in 400 °C steam at 10.3 MPa (1 day exposures).

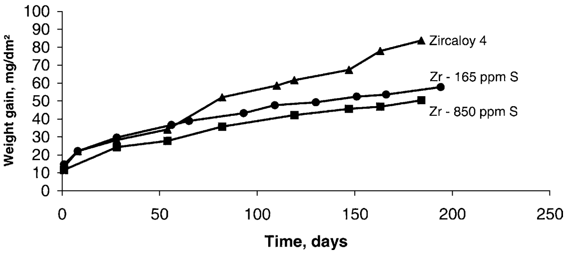

Fig. 4. Kinetics of corrosion in 400 °C steam at 10.3 MPa for binary Zr–S alloys and Zircaloy 4.

the resistance, particularly in the range between 2 and 200 ppm. Thus the beneficial influence of the sulfur content is observed whatever its metallurgical state: in solid solution and mainly as sulfides. When there are sulfides the key factor is probably the volume fraction of precipitates [4]. The plateau of low weight gains starts at about 200 ppm (Fig. 3) that correspond to a volume fraction of Zr_9S_2 close to 0.3% (assuming all S content as Zr_9S_2); it will be noticed that this value is in the range observed in the binary alloys Zr–Fe, Zr–Cr, Zr–Ni [4]. Longer duration tests on higher sulfur alloys confirm the beneficial influence of this element, as can be seen in Fig. 4. Indeed, the addition of sulfur enables a corrosion resistance equivalent to or even better than that of fully recrystallized Zircaloy 4 to be obtained in simple binary alloys.

4. Conclusions

The solubility of sulfur in the alpha zirconium phase is about 20 ppm. This limit corresponds approximately to the level where the influence of sulfur on creep strength reaches a maximum. This confirms that the effect of sulfur on creep strength is essentially due to solid solution hardening.

Sulfur added to unalloyed zirconium has a pronounced beneficial effect on the steam corrosion resistance at 400 °C.

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