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Letter to the Editors

Influence of precipitate density on the nodular corrosion resistance of Zr–Sn–Fe–Cr alloys at 500°C

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Abstract

In a Zr–1.3% Sn base alloy, both the addition of increasing amounts of iron and chromium, conserving a constant Fe/Cr ratio, and the reduction of the cumulative annealing parameter ΣA have beneficial effects on the corrosion resistance in 500°C steam. It is shown that these two observations can be rationalized by considering that the important metallurgical factor is the number of precipitates per unit volume rather than their size. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In boiling water reactors, zirconium alloys are sometimes found to undergo a heterogeneous form of surface attack known as nodular corrosion. In the case of Zircaloys 2 and 4, this phenomenon is simulated in the laboratory, in the absence of irradiation, by exposing samples to high temperature steam in an autoclave, for example, for 24 h at 500°C under a pressure of 10.3 MPa. It has been shown that the chemical composition of the alloy and the nature of the 'precipitate phases have a decisive influence on the behaviour in these tests. [1]. Furthermore, for a given alloy chemistry, the other important factors are the size of the precipitates [2,3] or their number density [4,5], the composition of the matrix solid solution [6,7], the degree of cold work or recrystallization [4–8], and the texture [8,9].

For a given zirconium grade, good correlations are found between the corrosion resistance and the precipitate size or number density, but for studies of the corrosion mechanisms, it is useful to know which is the most pertinent physical parameter to be considered. For this reason, an investigation has been carried out in which the size and number density of the precipitates were varied in two completely different ways, by modifying either the alpha phase annealing temperature or the iron and chromium contents in a Zr–1.3% Sn base composition.

2. Experimental procedure

Four zirconium alloys with additions of tin, iron and chromium were prepared in the form of 1 kg ingots by melting in argon, the aim being to obtain a Zr–1.3% Sn base, similar to that of Zircaloy 4, together with a variable sum (Fe + Cr), but with a constant Fe/Cr ratio. The compositions obtained are given in Table 1.

The ingots were forged in the beta phase field to 20 mm thick flat bars and were then processed in standard conditions, corresponding to water quenching from 1030°C, rolling at 750°C to 6.3 mm thickness, cold rolling to 3 mm, intermediate annealing at either 700°C, 730°C or 760°C, further cold rolling to 1.5 mm, and final annealing for 2 h at 700°C. For each alloy, three different values of the cumulative annealing parameter ΣA were therefore available (1.5, 2.2 and 7.3×10^{-17} h), the parameter A for each individual annealing treatment being defined by the relation $A = t\exp(-40\,000/T)$, where t is the time in hours and T the temperature in kelvins.

Specimens of the finished strips were examined by transmission electron microscopy, using both thin foil and replica techniques, in order to determine the nature and composition of the precipitates. Precipitate sizes

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were measured using image analysis associated with scanning electron microscopy [10].

Corrosion tests were performed on samples corresponding to all combinations of composition and ΣA, by exposure in steam for 24 h at 500°C under 10.3 MPa, in a static autoclave.

Table 1
Alloy compositions

Alloy	Sn (%)	Fe (ppm)	Cr (ppm)	Ni (ppm)	Si (ppm)	C (ppm)	N (ppm)	Fe/Cr	Fe + Cr (ppm)
1	1.3	1890	830	<20	15	46	78	2.3	2720
2	1.3	3400	1590	<20	13	44	81	2.1	4990
3	1.3	5200	2400	<20	14	47	72	2.2	7600
4	1.3	7000	3300	<20	12	51	69	2.1	10,300

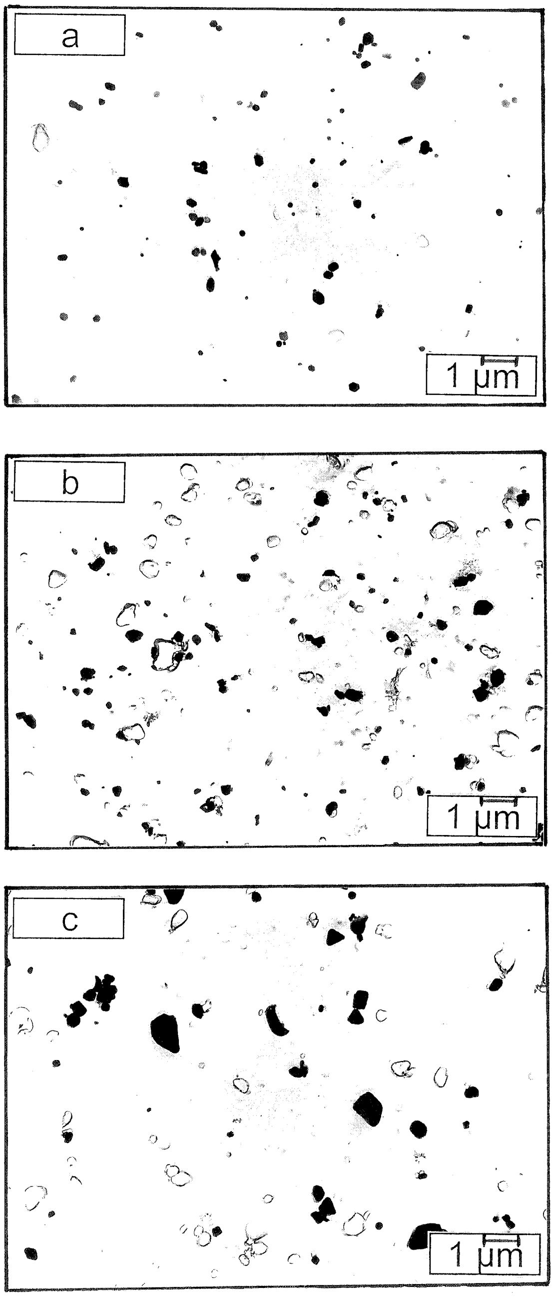

Fig. 1. Extraction replicas of Zr (CrFe)$_2$ particles: (a) Fe + Cr = 2720 ppm; $\Sigma A = 1.5 \times 10^{-17}$ h; (b) Fe + Cr = 10 300 ppm; $\Sigma A = 1.5 \times 10^{-17}$ h; (c) Fe + Cr = 10 300 ppm; $\Sigma A = 7.3 \times 10^{-17}$ h.

3. Results

In all cases, the major secondary phase was shown to be the well-known $Zr(Fe,Cr)_2$ compound (Fig. 1), with an Fe/Cr ratio between 2 and 2.1, i.e., close to the Fe/Cr ratio in the alloys. Table 2 summarizes the mean precipitate diameters and shows that the particle size does not vary significantly with alloy composition, i.e., with the sum (Fe + Cr), for a given value of ΣA, confirming previously published data [10]. It is therefore possible to consider only a single value of the mean particle diameter for the four alloys for each ΣA level (Table 2).

Table 3 gives the relative precipitate number densities, referred to Alloy 1 and the lowest ΣA value. These values were calculated based on the following assumptions. For a given ΣA, the mean diameter and composition of the precipitate particles are identical in all of the alloys. Since precipitation is complete for the treatments employed, and since the residual solubility of iron and chromium in the matrix is negligibly small [10], it can be considered that the precipitate volume fraction is proportional to the sum (Fe + Cr) in the alloy. Furthermore, the precipitate number density was considered to be proportional to $1/\phi^3$, where ϕ is the mean particle size.

Table 4 summarizes the measured weight gains after exposure for 24 h in steam at 500°C and 10.3 MPa. As expected, corrosion decreases with increasing sum (Fe + Cr), corresponding in the present case to an increase in the precipitate number density. It can also be seen that the corrosion resistance is lower the higher ΣA, and this can be interpreted as a detrimental influence of either an increase in precipitate size or a reduction in their number density.

Table 2
Mean diameter of the second phase particles (nm)

ΣA (h $\times 10^{17}$)	Alloy				Mean value for the four alloys
	1	2	3	4	
1.5	176	169	174	183	176
2.2	199	201	204	198	201
7.3	233	237	266	237	243

Table 3
Relative precipitate number density

ΣA (h $\times 10^{17}$)	Alloy			
	1	2	3	4
1.5	1	1.8	2.8	3.8
2.2	0.7	1.2	1.9	2.6
7.3	0.4	0.7	1.1	1.4

Table 4
Nodular corrosion resistance[a]

ΣA (h $\times 10^{17}$)	Alloy			
	1	2	3	4
1.5	860	52	41	41
2.2	990	110	44	41
7.3	2550	250	59	41

[a] Weight gain in mg/dm^2 – 500°C, 24 h, 10.3 MPa.

The results of the corrosion tests are summarized in Figs. 2 and 3. Fig. 2 shows that the corrosion increases with precipitate size, principally when the sum (Fe + Cr) is low, but that the effect of alloy composition is predominant. In Fig. 3, the weight gain is plotted as a function of precipitate number density. It can be seen that, whatever the way in which the number of particles is varied, whether by modifying the alloy composition or the annealing parameter, a good single correlation is obtained between nodular corrosion resistance and precipitate number density. Furthermore, there appears to exist a critical number density beyond which the excellent corrosion resistance is not improved further.

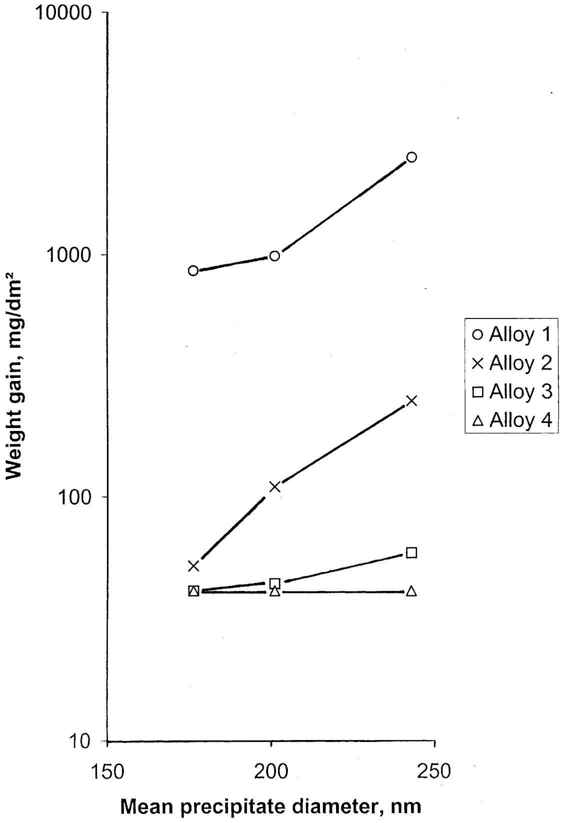

Fig. 2. Variation of corrosion resistance with mean precipitate diameter (24 h, 500°C, 10.3 MPa steam).

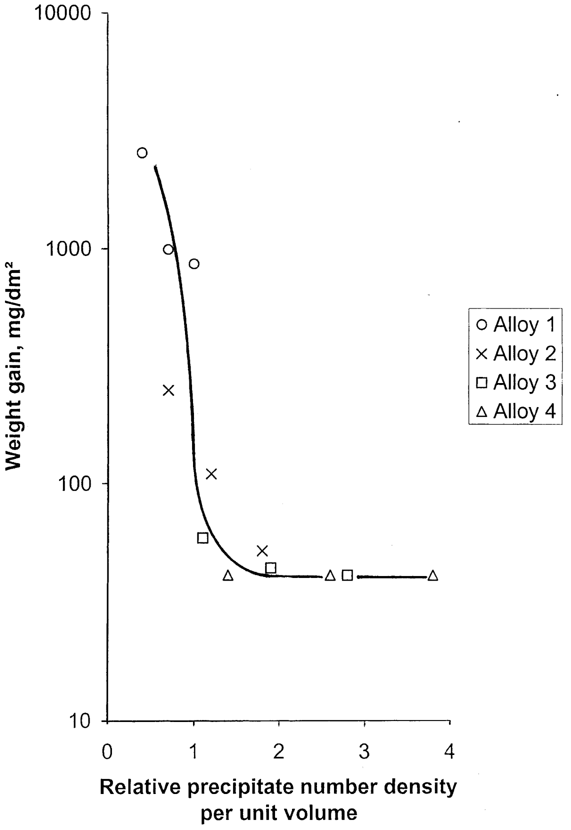

Fig. 3. Variation of corrosion resistance with precipitate number density (24 h, 500°C, 10.3 MPa steam).

4. Conclusions

Classical autoclave tests, involving 24 h exposure in steam under 10.3 MPa pressure at 500°C, have confirmed the known beneficial influences on the nodular corrosion resistance of Zr–1.3% Sn alloys of either increasing the sum (Fe + Cr) or reducing the cumulative annealing parameter ΣA. The combined effects of these two factors can be understood by considering that the predominant factor is the number density of precipitates rather than their size.

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