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Letter to the Editors

Influence of sulfur content on the thermal creep of zirconium alloy tubes at 400°C

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Abstract

Tests performed at 400°C on various zirconium alloy grades indicate that, among known trace elements, sulfur is probably the one which has the greatest influence on the creep behavior. Thus, in certain cases, the addition of only about 10 ppm sulfur can decrease the creep rate by a factor of three. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The creep strength of zirconium alloys is one of the major reasons for their use for core components in boiling water and pressurized water nuclear reactors. Although the property of concern in practice is the creep behavior under irradiation, it is important to understand first of all the factors which affect the performance in the absence of irradiation. A number of metallurgical characteristics and processing-related parameters are known to influence the resistance of zirconium alloys to thermal creep. For example, in the most common alloys, tin [1–3], oxygen [1,2], carbon [4,5] and niobium [6] in solid solution are known to affect creep. The effect of grain size is complex and appears to depend on the testing conditions [7]. An increase in precipitate size at constant volume fraction, i.e., a decrease in their number, lowers the creep strength of Zircaloy 2 at 400°C [8], while an increase in dislocation density improves the resistance to uniaxial creep. Texture is another metallurgical factor which has a significant influence on creep behavior. Thus, when the [0002] poles approach the radial direction, the transverse creep strength is impaired [9].

As regards the processing conditions, the final annealing treatment has a decisive influence [10]. Recrystallization deteriorates uniaxial creep strength but improves the biaxial creep strength of tubes for moderate circumferential stresses (130 MPa). Modeling has shown this improvement to be due to a change in the active slip mode, from prismatic in recrystallized tubes, to basal or pyramidal in the case of stress-relieved tubes [11]. Intermediate anneals during the multi-cycle processing sequence must also be considered, and are generally taken into account in the form of a 'cumulative annealing parameter' $\sum A$. An increase in $\sum A$ lowers the creep strength of recrystallized Zircaloy 4 [12]. This relationship reflects the effects of grain size, precipitate size and texture. The final cold work cycle also represents a useful parameter for modifying the creep strength [9]. However, although numerous factors affecting the creep behavior have been identified, significant unexplained differences are often observed on tubes [13].

Investigations performed on experimental sheets to determine the influence on functional properties of impurities such as phosphorus, silicon, carbon and sulfur indicated that ppm levels of sulfur could have a significant effect on creep strength, without affecting corrosion resistance.

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Tubes with variable sulfur contents were therefore produced in a number of different grades, for characterization with and without irradiation. The present paper describes the principal results concerning the effect of sulfur on the thermal creep behavior of these zirconium alloys.

2. Materials and experimental techniques

The influence of sulfur contents from 0 to 30 ppm has been studied for a number of alloy grades. However, most of the work has been performed on the Zr–1% Nb alloy which shows great promise as a higher performance future replacement for the Zircaloy 4 grade currently used in PWR reactors [14]. The effect of sulfur has also been studied in Zircaloy 4, which contains 1.5% Sn, 0.2% Fe and 0.1% Cr, and in a Zr–0.5% Sn–0.6% Fe–0.4% V alloy. The latter material has also shown improved performance in PWR reactors compared to Zircaloy 4 [14].

Sulfur additions were made in the form of iron sulfide. Ingots (weight: 100 kg) with variable sulfur contents were produced by double consumable electrode vacuum arc remelting. One-ton ingots were also produced, in which the sulfur content was varied from one end to the other, giving several tubes with different sulfur contents. The ingots were converted to 170-mm diameter billets, which were quenched from the beta phase field, then processed according to standard industrial procedures, corresponding to extrusion, cold pilgering in four or five steps with intermediate annealing, to obtain canning tubes with 9.5 mm o.d. and a wall thickness of 0.57 mm. In the case of the Zr–1% Nb alloy, intermediate annealing was performed at a temperature below the eutectic plateau, situated at 610°C, whereas for the other two alloys temperatures of 700–750°C were employed. The use of standard industrial processing routes enabled the experimental results to be compared with those obtained on commercial products.

The structures of the finished tubes were characterized in terms of grain size, nature and dimensions of the precipitate phases and crystallographic texture. The tubes were analyzed using conventional industrial techniques, and also by glow discharge mass spectrometry (GDMS). The various analytical methods employed enabled determination of the majority of the elements in the periodic table, with a detection limit of at least 0.1 ppm. Creep tests were performed on the tubes, either under uniaxial loading conditions, or with biaxial loading, by the application of an internal pressure. The stress levels employed ranged from 90 to 150 MPa, with test durations between 72 and 720 h. After creep testing, transmission electron microscopy (TEM) examinations were carried out on thin foil samples.

3. Results

3.1. Zr–1% Nb alloy

The Zr–1% Nb alloy tubes were characterized and tested after complete recrystallization, obtained by annealing for 2 h at 580°C. Table 1 gives a typical analysis made on the tubes. Table 2 shows that sulfur has no significant influence on the principal metallurgical characteristics of the recrystallized materials. The precipitate particles are

Table 1
The typical analysis of the Zr-1% Nb alloy

GDMS analysis (ppm)	Convention combustion extraction analysis (ppm)	Plasma extraction spectrometric analysis
Si = 11.5	N = 20	Nb = 1.01%
Sn = 6.6	O = 1200	Ta = 15 ppm
Ni = 5.4	C = 60	Al = 60 ppm
Cu = 4.4	H = 11	Fe = 250 ppm
Ti = 3.3		Cr = 40 ppm
Cl = 2		Hf = 45 ppm
Mn = 2		
P = 1		
W = 0.7		
Mo = 0.6		
Zn = 0.7		
Na = 0.3		
B, Ga, Ca, V, Pb, As, K, Re, Co, Mg, Sb, Ge, Se, Li, F, SC, Br, Rb, Sr, Y, Ru, Rh, Pd, Cd, In, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ha, Er, Tm, Yb, Lu, Os, Ir, Pt, Au, Hg, TI, Th, U, Bi < 0.5 each		
S = 0.4 to 29 depending on FeS addition		

Table 2
Metallurgical characteristics of the fully recrystallized Zr–1% Nb alloy

	$S = 0.4$ ppm	$S = 29$ ppm
Grain size (μm)	2.4	2.2
Precipitate size (nm)	51	49
Nature of precipitates	β_{NB}, intermetallic, ZrNbFeCr	β_{NB}, intermetallic, ZrNbFeCr
Texture, Kearns factor		
fr	0.590	0.582
ft	0.350	0.370
fl	0.060	0.048

uniformly distributed, consisting essentially of niobium-rich (~ 80% Nb) beta phase, and a few ZrNbFeCr intermetallics, with a hexagonal crystal structure ($a = 0.54$ nm, $c = 0.86$ nm) and containing 16–21% Fe + Cr and 43–45% Nb.

Fig. 1 shows the variation of diametral creep strain with time for tubes recrystallized at 580°C with two sulfur levels, in biaxial loading tests with a tangential stress of 130 MPa at 400°C. The effect of sulfur can be seen to be quite marked, considered in terms of either the strain after 240 h, corresponding to the standard industrial inspection conditions, or the steady state secondary creep rate. Fig. 2 shows a similar effect of sulfur for a lower tangential stress of 110 MPa. The secondary creep rates observed for different stresses are plotted on logarithmic coordinates in Fig. 3 for the two sulfur levels. The values of the stress exponent n, given by the slopes of the straight lines, are equivalent for the two materials, and are close to 4, which is typical of a climb-controlled dislocation glide mechanism [13].

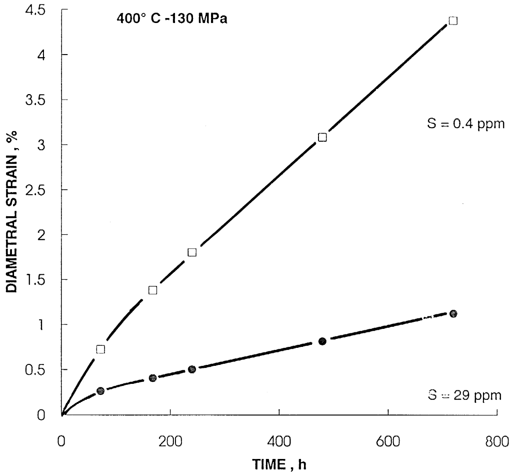

Fig. 1. Variation of diametral creep strain with time in fully recrystallized Zr–1% Nb tube under biaxial stress (circumferential stress = 130 MPa).

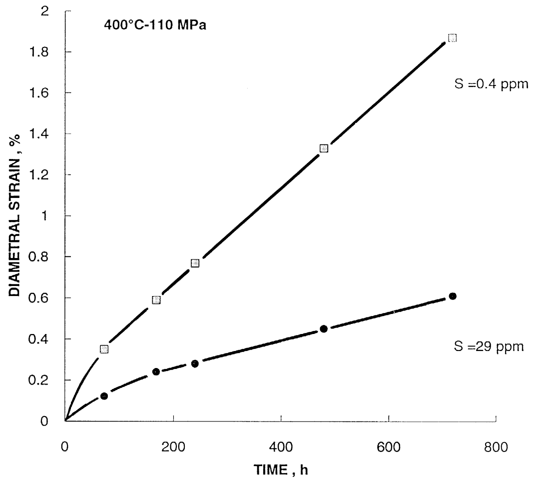

Fig. 2. Variation of diametral creep strain with time in fully recrystallized Zr–1% Nb tube under biaxial stress (circumferential stress = 110 MPa).

TEM examinations of thin foils taken from the tubes after creep testing revealed no significant differences between the 2 and 29 ppm sulfur levels. In all cases, prismatic slip was found to be predominant, with a few rare dislocations pinned by precipitates and a few loops, probably resulting from dislocation climb.

Fig. 4 shows the variation with sulfur content of the creep strain at 240 h, for recrystallized tubes tested under a tangential stress of 130 MPa at 400°C. The effect of sulfur content can be seen to be particularly marked up to about 10 ppm, beyond which no significant further effect is observed.

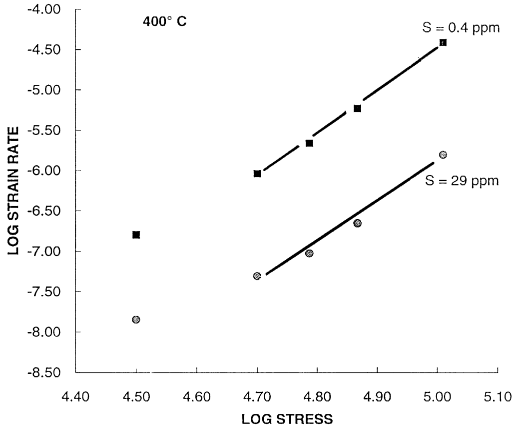

Fig. 3. Stress dependence of diametral creep rate in Zr–1% Nb tube.

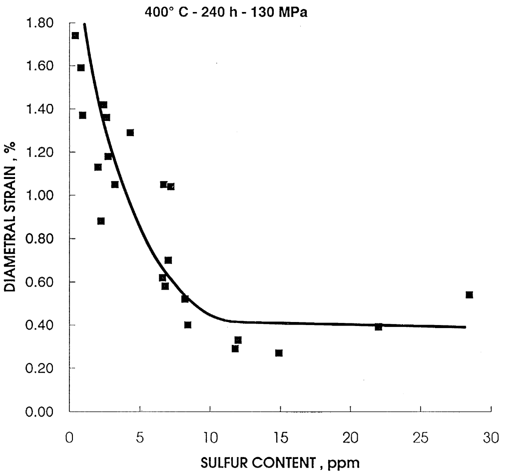

Fig. 4. Influence of sulfur content on the diametral creep strain in Zr–1% Nb tube.

3.2. Zr–0.5% Sn–0.6% Fe–0.4% V alloy

The same investigations as those described above were carried out on Zr–0.5% Sn–0.6% Fe–0.4% V alloy tubes fully recrystallized by annealing for 2 h at 580°C. Fig. 5 summarizes the effect of sulfur content on the diametral creep strain at 240 h, for recrystallized tubes tested in biaxial loading under a tangential stress of 130 MPa at 400°C. For this alloy also, a marked effect of sulfur is observed in the range 0–10 ppm.

3.3. Zircaloy 4

Fig. 6 shows the influence of sulfur on the creep strain at 240 h, for Zircaloy 4 tubes tested at 400°C. Tests were performed on tubes recrystallized by annealing for 1 h at 620°C, both under biaxial loading at a tangential stress of 130 MPa, and under uniaxial loading at a stress of 112.5 MPa. Biaxial loading tests at 130 MPa were also carried out on tubes given a stress-relief anneal of 1 h at 460°C. The beneficial effect of sulfur appears most clearly in the uniaxial loading tests on recrystallized tubes. In the biaxial loading tests on recrystallized tubes, the influence of sulfur is still perceptible, but less marked than for the two previous alloys. In the stress-relieved condition, the effect of sulfur is even less pronounced.

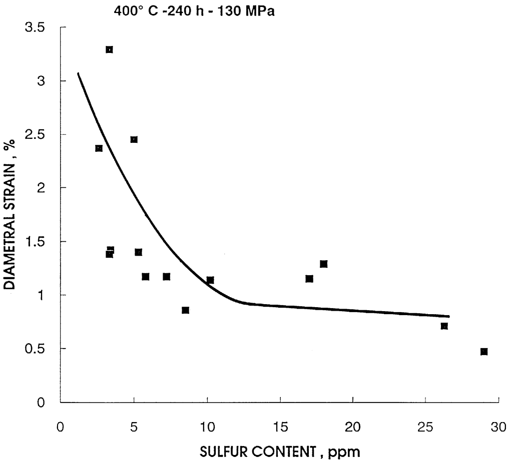

Fig. 5. Influence of sulfur content on the diametral creep strain in Zr–0.5% Sn–0.6% Fe–0.4% V tube.

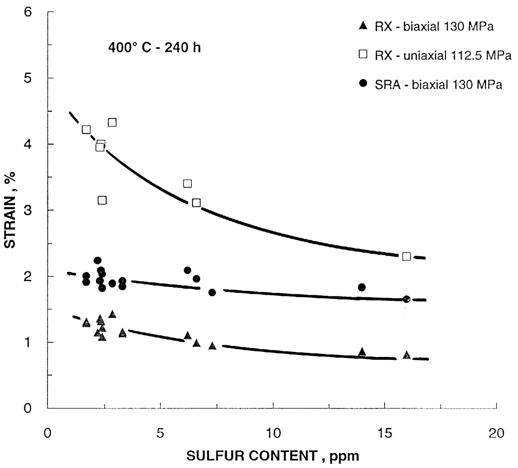

Fig. 6. Influence of sulfur content on the creep strain in Zircaloy 4.

4. Discussion

The extremely beneficial influence of sulfur on creep strength has been revealed in several alloys, in both recrystallized and stress-relieved tubes, and for various test conditions. The effect is particularly important for sulfur concentrations in the range 0–15 ppm. Sulfur does not appear to modify metallurgical characteristics such as grain size, precipitate distribution or crystallographic texture, suggesting that it has an intrinsic action on the zirconium matrix. Similarly, sulfur does not change the creep mechanism, classical climb-controlled dislocation glide remaining predominant whatever the sulfur level.

Our first investigations show that the solubility limit of sulfur in the alpha phase is in the range 10–20 ppm.

So sulfur may thus have a solid solution hardening effect in this range similar to that of oxygen, nitrogen and carbon. By analogy with the mechanisms proposed for oxygen, it would then be necessary to describe the manner in which sulfur atoms can impede the movement of dislocations.

Sulfur is not one of the 30 or so elements specified for routine analysis in zirconium alloys, and GDMS analyses have shown that typical sulfur levels in commercial products lie in the range 0–4 ppm. However, this small range is sufficient to induce significant variations in the creep behavior of recrystallized materials. It would therefore be preferable to increase the sulfur content of standard products to between 10 and 20 ppm.

5. Conclusions

The experimental results show a marked influence of sulfur content on the creep strength of zirconium alloys at 400°C, particularly for concentrations between 0 and 15 ppm. The deliberate addition of sulfur thus offers an attractive means of improving the high temperature mechanical strength of these materials. However, the mechanism by which sulfur affects the creep properties remains to be determined.

References

[1] P. Morize, Franco–Russian Seminar, Saclay, France, February 1976.

[2] D. Charquet, M. Armand, R. Tricot, Report for DGRST Contact no. 74-7-1096.

[3] W.A. McInteer, D.L. Baty, K.O. Stein, ASTM STP 1023 (1989) 621.

[4] D. Charquet, M. Armand, R. Tricot, presentation at ASTM Conference on Zirconium in the Nuclear Industry, Quebec City, Canada, 10–12 Aug. 1976.

[5] D.G. Franklin, ASTM STP 754 (1982) 235.

[6] R.S. Ambartsumyan, A.A. Kiselev, R.V. Grebennikov, V.A. Myshkin, L.J. Tsuprun, A.F. Nikulina, Proc. 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1–13 Sept. 1958.

[7] V. Filderis, Atomic Energy Rev. A 13 (1) (1975) 51.

[8] T. Andersson, G. Vesterlund, ASTM STP 754 (1982) 75.

[9] K. Kallstrom, T. Andersson, A. Hofvenstam, ASTM STP 551 (1974) 160.

[10] J.M. Frenkel, M. Weisz, ASTM STP 551 (1974) 140.

[11] K.L. Murty, Mater. Sci. Eng. 70 (1985) 169.

[12] D. Charquet, E. Steinberg, Y. Millet, ASTM STP 939 (1987) 431.

[13] D.G. Franklin, G.E. Lucas, A.L. Bement, ASTM STP 815 (1983) 31.

[14] J.P. Mardon, D. Charquet, J. Senevat, Proc. Int. Topical Meeting on Light Water Reactor Fuel Performance, West Palm Beach, April 17–21, 1994.