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Effect of temperature on the stress corrosion cracking of zircaloy-4 in iodine alcoholic solutions

A.V. Gomez Sanchez [a], S.B. Farina [a], G.S. Duffó [a,b,*]

[a] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, Argentina*
[b] *Comisión Nacional de Energía Atómica, Departamento de Materiales, Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, Argentina*

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Abstract

Zircaloy-4 is susceptible to stress corrosion cracking (SCC) in solutions of iodine dissolved in different alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol and 1-octanol). The crack propagation rate is known to decrease as the solvent molecular weight increases, as a consequence of steric hindrance. However, the mechanism that operates during SCC is still unknown. In the present work the effect of temperature on SCC susceptibility was evaluated in 1-butanol and 1-pentanol iodine containing solutions. The dependence of the crack growth rate with temperature follows an Arrhenius law, and the activation energy obtained from experimental data is consistent with a process controlled by volume diffusion of the active species (the iodine–alcohol complex) to the crack tip.

Keywords: A. Zirconium alloy; C. Stress corrosion; C. Intergranular corrosion

1. Introduction

The study of the stress corrosion cracking (SCC) of zirconium alloys is of technological relevance because these alloys are used in nuclear power reactors as fuel rod cladding and also as structural material in the reactor core. The fuel rod cladding is susceptible to SCC

* Corresponding author. Address: Comisión Nacional de Energía Atómica, Departamento de Materiales, Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, Argentina. Tel.: +54 11 6772 7403; fax: +54 11 6772 7388.
E-mail address: duffo@cnea.gov.ar (G.S. Duffó).

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induced by the iodine liberated during the nuclear fission of uranium [1] (a phenomenon called Pellet Cladding Interaction). This phenomenon can be simulated in the laboratory at low temperatures using solutions of iodine in methanol [2,3]. In previous works, the susceptibility to SCC of pure zirconium and Zircaloy-4 alloy was systematically studied in iodine containing solutions at room temperature [4–6]. It was determined that zirconium alloys are susceptible to SCC in iodine solutions of different alcohols (from 1 to 8 carbon atoms) and that the active species for the process is a molecular complex formed between the iodine and the alcohol. The overall crack growth rate decreased as the molecular weight of the alcohol increased, which was attributed to a steric hindrance phenomenon. In all cases it was found that stress corrosion cracks propagated transgranularly and, prior to crack propagation, intergranular attack was observed. This step was identified as intergranular attack assisted by stress and it was assumed that the intergranular attack was a diffusion controlled process [7].

Following the lines of the previous works, in the present work the effect of temperature on the crack propagation rate of Zircaloy-4 in iodine alcoholic solutions was studied, aiming to get a better understanding of the mechanisms involved.

2. Experimental technique

The samples used were 1.2 mm diameter wires of Zircaloy-4 (UNS R60804). The chemical composition (in wt%) is shown in Table 1. The specimens were degreased in boiling ethyl ether and dried with hot air. Then, they were annealed in an argon atmosphere (240 mm Hg) for 2 h at 760 °C. The annealing was made in quartz tubes, with the samples wrapped in tantalum sheets in order to avoid the contamination with silicon. Then the samples were furnace cooled for 24 h. Prior to the tests, the wires were degreased with acetone and dried with hot air.

The experiments were carried out in solutions of resublimed iodine (10 g/L) in 1-butanol (water content less than 0.1%) and 1-pentanol (water content less than 0.1%). The solutions were prepared with analytical grade reagents. Tests were performed at temperatures ranging from 20 °C to 90 °C. Constant elongation rate tests at an initial strain rate of $4.7 \times 10^{-6}\,s^{-1}$ were carried out in a closed conventional glass cell with a thermostating jacket. A Thermomix 1441 Braun thermostat was used to keep a constant temperature (±0.5 °C) throughout the tests. The wires were strained to fracture. After fracture, the specimens were observed in a scanning electron microscope (SEM). The mean crack propagation rate (c.p.r.) was obtained by dividing the length of the brittle zone measured on the fracture surface by the straining time. Tests were performed at least by duplicate.

3. Results

Fig. 1 shows the time to failure as a function of temperature for Zircaloy-4 in solutions of iodine in 1-butanol and 1-pentanol. It can be observed that failure times decrease with increasing temperature in the range from 20 °C to 90 °C.

Table 1
Chemical composition of the material tested

Fe	Sn	Cr	O	H	Zr
0.25 ± 0.01	1.74 ± 0.01	0.13 ± 0.01	0.13	0.0012 ± 0.0008	Balance

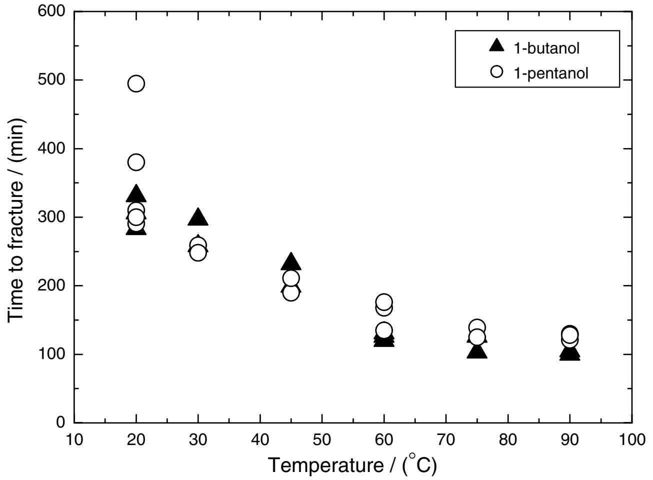

Fig. 1. Time to fracture as a function of temperature for Zircaloy-4 in solutions of iodine in 1-butanol and 1-pentanol.

When observed by SEM, numerous lateral cracks and brittle fracture surfaces confirmed the existence of SCC. In all cases fracture surfaces showed a mixed morphology that is characteristic of the SCC of Zircaloy-4 in iodine alcoholic media [4–6]: an initial zone of intergranular (IG) cracking, followed by a zone of transgranular (TG) propagation and a final ligament that broke in a ductile way by mechanical overload and showed the typical dimples of this type of failure (Fig. 2). The transition from the IG to the TG modes of cracking is clearly observed on the fracture surface (Fig. 3). However, the transition from the TG to the ductile zone is not clearly defined. The TG mode in hexagonal metals is characterized by the presence of striations or flutings [8]. In the present case, due to the small grain size (≈10 μm), flutings are only observed at very high magnification.

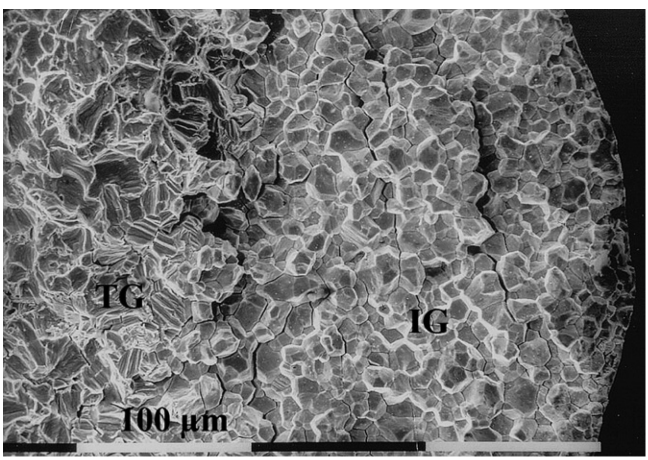

Fig. 2. Fracture surface of Zircaloy-4 strained to rupture in iodine dissolved in 1-butanol at 60 °C. Cracks propagate intergranularly (IG) and then transgranularly (TG).

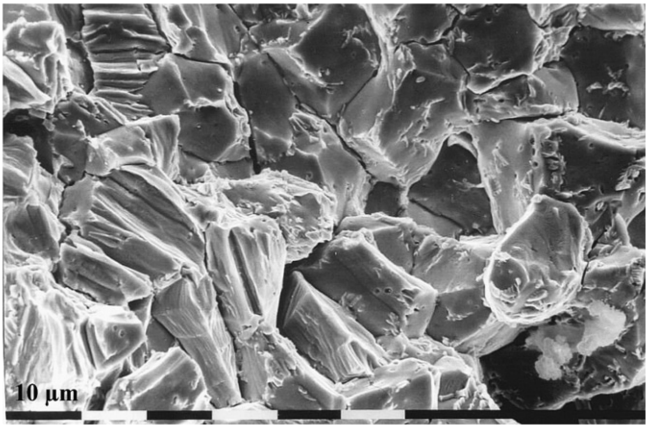

Fig. 3. Fracture surface of Zircaloy-4 strained to rupture in iodine dissolved in 1-pentanol at 20 °C.

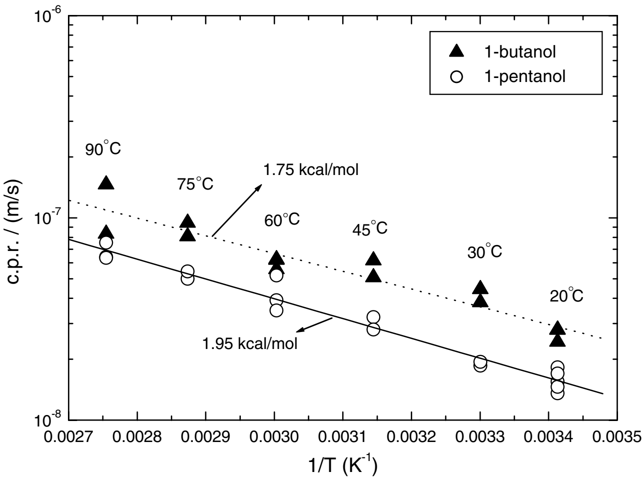

Fig. 4. Crack propagation rate values measured as a function of temperature for Zircaloy-4 in solutions of iodine in 1-butanol and 1-pentanol.

The total length of the brittle area (IG plus TG) measured on the fracture surface divided by the fracture time provided the c.p.r. Fig. 4 shows the measured c.p.r. values as a function of temperature. It was found that c.p.r. values are higher in solutions of 1-butanol than in solutions of 1-pentanol in the whole temperature range studied. The c.p.r. dependence with temperature follows an Arrhenius type law. The activation energy of the process was calculated from the slope of the straight line that better adjusts the experimental results (Fig. 4). The activation energy values obtained for Zircaloy-4 in 1-butanol and 1-pentanol iodine solutions were 1.75 ± 0.17 and 1.95 ± 0.10 kcal/mol, respectively.

4. Discussion

The SCC susceptibility, measured as time to failure and crack propagation rate, increases with increasing temperature (Figs. 1 and 4). Besides, SCC susceptibility of

Zircaloy-4 is higher in solutions of iodine in 1-butanol than in solutions of iodine in 1-pentanol between 20 °C and 90 °C. It was previously reported [6] that, at room temperature, the crack propagation rates decrease when increasing the molecular weight of the alcohol. In the present work this behaviour was found in the whole temperature range studied, from 20 °C to 90 °C. Iodine forms simple charge transfer complexes with alcohols, being this complex the active species that have to arrive to the tip of the crack to promote the attack. Then, the decrease in crack propagation rates when increasing the molecular weight of the alcohols is due to the steric effect of the species involved.

In the present work activation energies for the global process of 1.75 and 1.95 kcal/mol were measured in solutions of iodine in 1-butanol and 1-pentanol, respectively. Scarce data of activation energies of this kind of processes are found in literature. For instance, Elayaperumal et al. [9] determined an activation energy of 3.36 kcal/mol for the temperature dependence of weight loss of Zircaloy-2 stressed specimens in 0.02 g/L iodine in methanol solutions. The authors attributed this value of activation energy to a phenomenon of corrosion assisted by the adsorption of the active species on the metal surface. The difference between the value reported by Elayaperumal and those found in the present work may be due to the fact that Elayaperumal et al. measured weight loss – a parameter not directly related to the SCC kinetics but to a more general process –, while in the present work c.p.r. values were measured – a parameter directly related to the SCC process.

The processes involved in SCC are heterogeneous and consequently involve a series of steps, the rate controlling step (RCS) being the slowest one. The steps involved could be numerous and will be different for different mechanisms. Among others, the steps could be: (a) diffusion of the environment active species; (b) molecular-level crack propagation step; (c) diffusion of the reaction products; etc. This distinction is very important because, when the various authors say that, in the system they are studying, SCC propagates by anodic dissolution, by film induced cleavage, by adsorption of active species, or by surface mobility, implicitly they are assuming that the experiments reported have step (b) as the RCS.

In the system studied in the present work, it was determined that the intergranular attack is a necessary condition for the SCC to occur [6]. On the other hand, the intergranular attack at room temperature was assumed to be controlled by the diffusion of the active species to the tip of the crack [7]. Then, to confirm that the rate controlling step of the global process is the diffusion of the active species, the activation energy of the global process should be comparable to the activation energy for the diffusion of iodine complexes.

Macagno et al. [10] who measured the activation energy for iodine complexes diffusion in acetonitrile reported a value of 1.95 ± 0.05 kcal/mol, being this value similar in most organic solvents [9]. This value is very close to those found in the present work. Then, it can be concluded that, confirming the previous assumptions [6,7], the rate controlling step in the stress corrosion cracking of Zircaloy-4 in iodine alcoholic solutions is the diffusion of the active species (iodine–alcohol complexes) to the tip of the advancing crack.

5. Conclusions

From the present work the following conclusions can be drawn:

- The SCC susceptibility of Zircaloy-4 in iodine alcoholic solutions increases with temperature between 20 °C and 90 °C.

- The crack propagation rates follow an Arrhenius type law and the activation energies found correspond to a diffusional controlled process.
- The rate controlling step in the stress corrosion cracking of Zircaloy-4 in iodine alcoholic solutions is the diffusion of the iodine–alcohol complexes to the tip of the crack.

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