

## LOCALIZED CORROSION OF ZIRCONIUM AND ZIRCALOY-4 IN IODINE ALCOHOLIC SOLUTIONS

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**Abstract**— The stress corrosion cracking (SCC) susceptibility of zirconium and one of its alloys, Zircaloy-4, was studied in 10 g/L iodine dissolved in various alcohols: methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol. SCC was observed in all the systems studied and the crack propagation rate was found to vary depending on the size of the solvent molecule. When the molecular weight of the solvent molecule increased, the crack propagation rate decreased. Intergranular attack was also found in all the solutions tested, and the rate of intergranular corrosion also varied with the size of the solvent molecule. This behavior is attributed to a steric effect, which hinders the access of the corrosive species to the tip of the crack. The results found agree with the predictions of the surface mobility-SCC mechanism.

**Keywords**— Zircaloy-4, zirconium, stress corrosion cracking, pitting, intergranular attack.

### I. INTRODUCTION

Zirconium alloys are used in power nuclear reactors as fuel element cladding and also as structural material. The fuel element cladding is susceptible to stress corrosion cracking (SCC) induced by the iodine liberated during the fission of uranium (Cox, 1973). On the other hand, the structural components undergo embrittlement mainly due to the precipitation of zirconium hydrides.

Numerous authors have studied the SCC of Zircaloy-4 (Zry-4) in iodine vapor at 300°C simulating the conditions existing in a nuclear reactor and the results were reviewed by Cox (1990). However, some authors have shown that this phenomenon can be simulated in the laboratory at low temperatures using solutions of iodine in methanol (Schuster and Lemaignan, 1989; Cox, 1977). Elayaperumal *et al.* (1972/3) studied the SCC of Zircaloy-2 in boiling methanolic solutions of iodine and they found that the susceptibility to the phenomenon increased with the iodine concentration, but that it was independent of the applied electrochemical potential. Cox (1975), who studied the SCC susceptibility of zirconium alloys in iodine solutions in various organic solvents, found that two groups of solvents could be distinguished: those in which SCC only takes place on precracked specimens, and those in which SCC also takes place on smooth specimens. Cox attributed this difference to the degree of stability of the complex

formed between the iodine and the solvents, no reference being made to the effect of the size of the solvent molecules.

On the other hand, Mori *et al.* (1966) studied the SCC of Zr and Ti in HCl dissolved in three different alcohols, and determined that the higher the molecular weight of the alcohol molecule used, the higher the time to fracture of the specimens. From this work the possibility arises that the SCC susceptibility of zirconium and its alloys in iodine solutions depends on the size of the solvent molecule employed. For this reason in the present work, the SCC susceptibility of Zr and Zry-4 was systematically studied in solutions of iodine in several alcohols, at room temperature. Also the possible existence of other types of localized corrosion was considered.

### II. EXPERIMENTAL METHOD

The samples used were 1 mm diameter wires of Zr and Zry-4. The chemical compositions (in w/o) are shown in Table 1.

The specimens were degreased in boiling ethylic ether and dried with hot air. Then, they were annealed in argon atmosphere (240 mm Hg) for 48 h at 800°C in the case of Zr, and for 2 h at 750°C in the case of Zry-4. In both cases the annealing was made in quartz tubes, with samples wrapped in tantalum sheets to avoid the contamination with silicon. After annealing, the samples were furnace cooled for 24 hours. Prior to the tests, the wires were degreased with acetone and dried with hot air.

The experiments were carried out in solutions of iodine in the following alcohols: methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol. In all cases the concentration of iodine was 10 g/L and the solutions were prepared with analytical grade reagents. All the experiments were performed at room temperature. The constant elongation rate tests were carried out using a conventional glass cell described in a previous paper (Galvele *et al.*, 1974), at the corrosion potential and at an initial strain rate of  $4.7 \times 10^{-6} \text{ s}^{-1}$ . The wires were strained to fracture. After fracture, the specimens were observed under a scanning electron microscope (Philips SEM 500) and then metallographically mounted and sectioned in order to measure the crack depth. The mean crack propagation rate was calculated by using two alternative methods. One was based on the SEM observation, the length of the brittle zone was measured on