Thesis Abstract

Stress Corrosion Cracking of Zirconium and Zircaloy-2 in Methanol-(HCl, Iodine) Solutions

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Zirconium and Zircaloy-2 like stainless steels are passive materials in service, but are, alike, susceptible to localised corrosion phenomena like pitting and stress corrosion cracking This investigation deals with stress corrosion cracking of the above two materials in solutions containing chloride or iodine.

The studies have been carried out using methanol as the carrier solvent. The stress corrosion tests involved constant strain, constant load and constant strain rate techniques. The mechanism of the cracking phenomenon has been analysed using electrochemical polarization techniques and activation energy measurements. The morphology of the cracking has been examined using Optical, Electron and Scanning Electron microscope.

In methanol-HCl solutions, cracking was found to be strongly dependent on the HCl concentration giving maximum susceptibility at 0.4 vol.% HCl. Application of stress increases the anodic dissolution. The susceptibility to stress corrosion is high at low strain rates (6×10^{-6} sec. $^{-1}$) and disappears at high strain rates (1.5×10^{-4} sec. $^{-1}$). Application of anodic potentials decreases the cracking time while application of cathodic potentials increases it. Addition of water induces passivity thereby increasing the stress corrosion resistance. The initial part of the cracking involves intergranular dissolution while the final part is by transgranular mechanical cleavage.

In methanol-iodine solutions cracking occurs even at a very low concentration of 0.002 gpl iodine; the cracking time decreases with iodine concentration (up to 20 gpl), while stress increases the dissolution rate. The cracking in iodine-containing solution is independent of electrochemical imposed potential. However, stress decreases the activation energy for dissolution from 8350 to 3360 cals/mole. This activation energy probably corresponds to the adsorption of the iodine species on the metal surface Here also the cracking involves both intergranular and transgranular stages.

The results in methanol-HCl solution are explained on the basis of electrochemical film breakdown model assisted by the external stress. It basically involves stress-assisted intergranular anodic dissolution at localised places in a protective film followed by mechanical fracture in the final stages. On the other hand, in methanol-iodine solutions, stress assists the dissolution by reducing the activation energy for adsorption of iodine on the surface. This adsorption brings down the surface energy for cracking by a factor of 2.6. thereby making crack propagation easier.

The study has indicated the possibility of cladding failure by the halogens, chloride and iodine. The former may act from the coolant at discontinuities in the protective film while the latter may act from the fuel since it is a major fission product.

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