Effect of Chromium Carbides on PbSCC Behavior of Alloy 690 in Caustic Environments

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1. Introduction

Recently, many cases of secondary side cracking in pressurized water reactors have been associated with the presence of metallic Pb or Pb compounds throughout the world. Pb is present as a contaminant in the secondary side system of PWR nuclear power plants, and is believed to accelerate stress corrosion cracking (SCC) of Alloy 600 and Alloy 690 even at very low concentrations [1]. In the present work, the effect of intergranular carbides on the Pb induced SCC (PbSCC) properties of Alloy 690 in caustic media was studied using C-ring specimens. Carbide precipitation in the alloy was examined for various periods of heat treatment. SCC performance was evaluated in a Pb containing caustic solution. The resistance to PbSCC and cracking mode/morphology of this alloy were analyzed in terms of the role of intergranular carbides through microscopic equipment.

2. Methods and Results

2.1 Experimental Procedures

Alloy 690 tubes were obtained in a 74.2 % cold-pilgered (Alloy 690CP) conditions. The chemical composition of Alloy 690CP is as follows (by weight): 29.2 % Cr, 8.2 % Fe, 0.03 % C, 0.001 % S, 0.16 % Si, 0.02 % Co, 0.16 % Ti, and balance Ni. Each specimen from Alloy 690CP was solution annealed at 1130 ℃ for 10 min., and then water-quenched. Isothermal heat treatment for carbide precipitation was conducted at 720 ℃ for 0.1 – 100 h. Microstructural changes were observed through TEM, optical microscopy and SEM.

SCC tests were performed using a 1 gallon autoclave consisting of a pure Ni wire as a reference, a pure Ni plate as a counter, and a specimen as the working electrode. C-ring specimens for the SCC test were stressed at their outer-diameter, making the two legs touch [2]. A test solution of 40 % NaOH was made using distilled and demineralized high purity water and PbO was added to the solution to make a concentration of 5000 ppm Pb. The test were performed at 315 ℃ for 7 – 21 days. During the SCC test, the potential was raised from the corrosion potential (E_{corr}) to the passive potential regime of 200 mV higher than E_{corr}, at which Alloy 690 has been known to be the most SCC susceptible. After the SCC test, the specimens were subjected to a metallographic examination by optical microscopy and SEM/EDS.

2.2 Carbide Precipitation

Carbides precipitated during heat treatment of Alloy 690 were always identified as chromium-rich $M_{23}C_6$ and had a cube-cube orientation relationship with one grain. In the present study, the precipitation behavior of carbides was focused on the random high angle grain boundary (HAGB), low angle grain boundary (LAGB), and twin boundary (TB), since most grain boundaries are composed of those boundaries in a nickel-base alloy [3]. The intergranular carbide precipitation was retarded (or, delayed) on the LAGB in comparison with that on the HAGB, even though the total volume fractions of carbides after significant growth on the grain boundary seem to be little different in both cases. Incoherent TB carbides after sufficient growth appeared as needlelike precipitates growing parallel to the coherent TB. Carbide precipitation on the coherent TB was not observed under the present annealing conditions. With a long aging time of 100 h, intragranular carbides were found. They were precipitated on the imperfections such as dislocations and stacking faults.

2.3 PbSCC Mode and Crack Morphology

The first noticeable crack initiation was found inside the grain after an immersion of 7 days in a Pb containing solution. However, a crack was initiated after an immersion of 26 days at the grain boundary on the surface in the same caustic environment without Pb addition. These results, therefore, demonstrate that Pb accelerated the crack initiation and changed the cracking mode in this alloy.

All the specimens suffered severe cracking after the duration of 21 days in Pb containing solutions. Figure 1 shows the crack morphology in Alloy 690 thermally treated for 10 h. In the Figure, there were some small regions of intergranular fracture, but the most parts of a crack were transgranular. By thermal treatment, the intergraluar portion increased, however, its incremental effect was marginal. Regardless of the degree of intergranular carbide precipitation, the cracking mode of Alloy 690 was found to be predominantly transgranular in the Pb containing caustic solutions. The cracks in thermally treated Alloy 690 spread many branches and each crack propagated in a disordered and tortuous way, from which it seems that there were some obstacles to crack propagation.

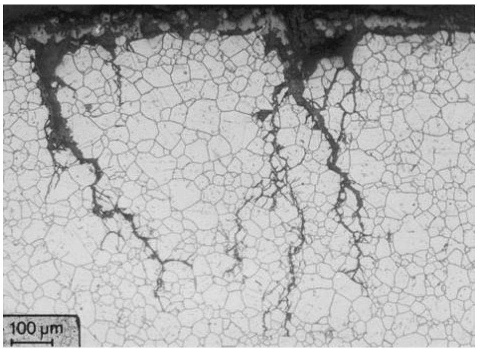

Figure 1. Optical micrograph showing the crack morphology in Alloy 690 after C-ring test in a Pb containing caustic solution.

2.4 Crack Propagation Behavior

The role of intergranular carbides on the SCC resistance of Alloy 690 was studied through metallographic examination of the cracked surface after the C-ring test. Figure 2 shows the cracks and the intergranular carbides after C-ring test under the present experimental conditions.

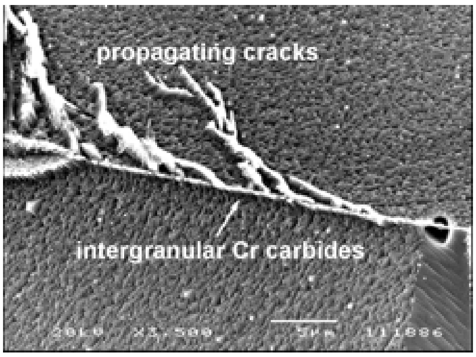

Figure 2. SEM micrograph showing the propagating cracks and the intergranular carbides in Alloy 690 after C-ring test a Pb containing caustic solution.

As shown in the Figure, the propagating cracks were stopped at the grain boundaries, on which carbides were significantly precipitated. This fact indicates that the crack propagating into the grain boundary was interrupted by the intergranular carbides. In some cases, the cracks encountered with a grain boundary, changed their course to advance, and propagated along the grain boundary for a short distance. From the above results, it is expected that the intergranular carbides acted as a physical barrier to crack propagation. Another effect of intergranular carbides on crack propagation can be understood from a different point of view. As reported by Bruemmer et al [4], dislocations in Alloy 690 seemed to be the preferentially emitted from intergranular carbides, and thereby reduced stress concentration around them which attributed to the improvement of the SCC resistance of Alloy 690.

3. Conclusions

PbSCC mode of Alloy 690 in a caustic solution was predominantly transgranular. Pb accelerated the crack initiation, and increased the susceptibility of this alloy to SCC. The propagating cracks were found to be interrupted by intergranular carbides on the grain boundary, therefore, the intergranular carbides seemed to act as a physical barrier to crack propagation during SCC.

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