Supercritical Water Corrosion of High Cr Steels and Ni-base Alloys

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1. Introduction

High Cr steels (9 to 12% Cr) have been widely used for high temperature high pressure components in fossil power plants [1,2]. Recently the concept of SCWR (supercritical water-cooled reactor) has aroused a keen interest as one of the next generation (Generation IV) reactors. Consequently Ni-base (or high Ni) alloys as well as high Cr steels that have already many experiences in the field are among the potential candidate alloys for the cladding or reactor internals. Tentative inlet and outlet temperatures of the anticipated SCWR are 280 and 510°C respectively. Among many candidate alloys there are austenitic stainless steels, Ni base alloys, ODS alloys as well as high Cr steels [3].

In this study the corrosion behavior of the high Cr steels and Ni base (or high Ni) alloys in the supercritical water were investigated. The corrosion behavior of the unirradiated base metals could be used in the near future as a guideline for the out-of-pile or in-pile corrosion evaluation tests.

2. Methods and Results

2.1 Experimental Procedures

Commercial grade high Cr steel specimens including two T91, one T92, one T122 steel and three Ni-base (or high Ni) alloy specimens (alloy 625, 690 and 800H) were corrosion tested in the supercritical water. All specimens of 10 by 10 by 2mm were ground with #600 SiC papers and tested in supercritical pure water under 25 MPa for 100, 200, and 500 hr. Test temperatures were from 400 to 600°C. After the corrosion tests the weight change of the specimens was measured and the specimen surface including the cross section was investigated using a grazing incidence (2 °) XRD (X-ray Diffractometer), S.E.M (Scanning Electron Microscope) and T.E.M (Transmission Electron Microscope) with E.D.S (Energy Dispersive Spectroscopy).

2.2 Results; High Cr Steels

Corrosion rate of the specimens in the supercritical water was measured by the weight change after the tests. The test results of high Cr steels are illustrated in figure 1. The effect of the alloying element W (T92) as well as the heat-to-heat variations (T91) on the corrosion behavior was found to be not very significant in the test conditions. In other words the corrosion rates were found to depend mostly on Cr contents of the steel specimens. 12% Cr steel (T122) showed a much lower corrosion rate than that of the 9% Cr steels (T91 and T92). However the corrosion rates as a whole reduced as the test temperature decreased, and also the differences of the corrosion rates among the specimens of different Cr contents reduced significantly as the test temperature decreased.

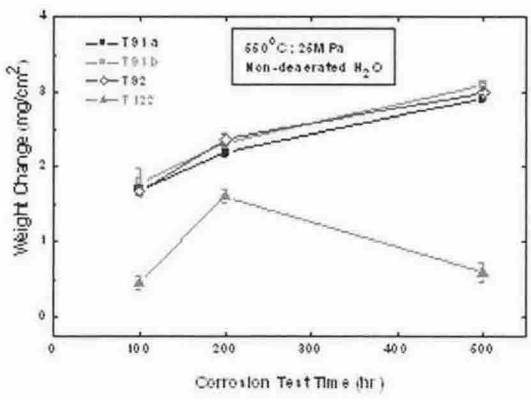

Fig. 1 SCW corrosion test results of high Cr steels at 550 °C

A cross section of the T91 specimen was prepared after a corrosion test at 627 °C for 200 hr. Three distinctive layers were revealed in SEM micrographs. The outermost layer with about a 35 μm thickness shows a coarse columnar structure and revealed, from a grazing incidence XRD analysis, magnetite type Fe_3O_4. A smooth interface between the outermost and the next inner layers seem to be the original surface of the specimen because the next inner layer shows the original microstructural features, like the grain boundaries, lath boundaries, and precipitates.

A cross sectional TEM micrograph shows explicitly the columnar structure of the outermost oxide layer. Also the next inner layer with about a 25 μm thickness was found to be a Cr partitioned $(Fe,Cr)_3O_4$ phase and consists of an agglomerate of very tiny particulates of about 10 nm in diameter. An internal oxidation zone, which seems to penetrate along the grain boundaries and lath boundaries, was also observed next to the matrix. The oxide phase along the boundary contains a much higher Cr content (about 20 to 30 at%) and Si content (1 to 3.5 at%) than the other oxide layers. Consequently Cr depletion in the matrix near the oxide/boundary was apparent. Between the internal oxidation zone and the matrix, a narrow (about 0.5 μm

wide) precipitate-free zone was also detected.

2.3 Results; Ni-base (or high Ni) Alloys

Corrosion test results of three Ni-base (or high Ni) alloys at 600 °C are shown in figure 2. In general Ni-base alloy specimens have shown much lower corrosion rates than those of high Cr steel specimens by about one order of magnitude. Among three Ni-base alloy specimens, alloy 690 showed the best (lowest) corrosion rate.

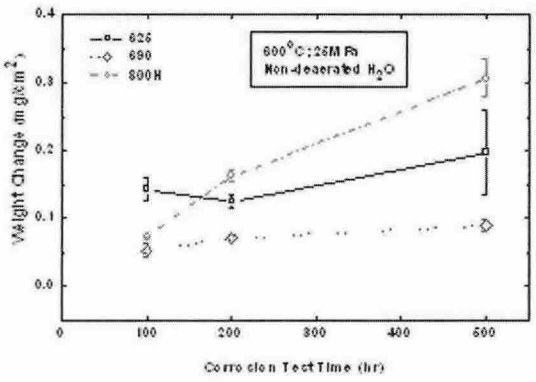

Figure 2 SCW corrosion test results of Ni-base (or high Ni) alloys at 600 °C

3. Conclusion

High Cr steels and Ni-base (or high Ni) alloy specimens were corrosion tested in the supercritical water condition. The corrosion rate of high Cr steels appeared to depend mostly on the Cr content; the higher the Cr content the better the corrosion resistance. The oxide layer of the T91 after 200 hr at 627 °C/25MPa was found to consist of three layers, i.e. Fe_3O_4 at the outermost side, $(Fe,Cr)_3O_4$ at the next inner side, and the internal oxidation zone next to the matrix. A narrow (about 0.5 μm wide) precipitate-free zone was observed between the internal oxidation zone and the matrix. The outermost oxide layer revealed a coarse columnar structure, and the next inner layer appeared to consist of an agglomerate of tiny oxide particles. And Ni-base (or high Ni) alloy specimens showed about one order of magnitude lower corrosion rate than those of high Cr steel specimens in supercritical water. Austenitic stainless steels have been reported that the corrosion rates become greater in the subcritical temperature range than the higher supercritical range [4]. Therefore the corrosion rate change of the high Cr steel and Ni-base (high Ni) alloys would also need to be evaluated across the temperature boundary.

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