STRESS CORROSION CRACKING OF 316 SS AND ALLOY 625 IN SUPERCRITICAL WATER

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Abstract

The supercritical water reactor (SCWR) offers many advantages compared to current light and heavy water cooled reactor. However, one of the key challenges is the selection of materials that can withstand the corrosive conditions that will exist in the core and in downstream components. The materials used in this work were Alloy 625 and 316 SS in tube shape. Water was lost during exposure of capsule specimens at 500^0C and the amount of lost water increases with exposure time. No cracks were observed on Alloy 625 after 3 weeks of exposure at 500^0C, while cracks at the inner wall of the tube were observed on 316 SS only after 4 hour heating at 500^0C. The oxide layer on 316 SS is much thicker than that formed on Alloy 625.

1. Introduction

One concept for GEN IV reactors is the supercritical water cooled reactor (SCWR). Due to high thermal efficiency of supercritical water (SCW) and simple reactor design, the SCWR offers many advantages compared to light and heavy water cooled reactors. Water in the supercritical phase exhibits properties such as the ion product, heat capacity and dielectric constant that are significantly different from water below the critical point [1,2]. However, one of the key challenges is the selection of materials that can withstand the corrosive conditions that exist in SCWR and in downstream components.

A large amount of work is being done world-wide on the corrosion of materials in SCW under various Gen IV program [3-5], including studies of ferritic and austenitic stainless steels, ferritic-martensitic materials, Ni-based alloys, Zr alloys and oxide dispersion strengthened steels.[6-10]. No single alloy currently has been identified that can meet the operational requirements of some key SCWR component. An early study of stress corrosion cracking (SCC) of 316 SS in degassed SCW was reported by Boyd and Pray [11]. Their specimens were loaded with 90% of the stress required to cause rupture in 1000 hours (103 MPa) and exposed to SCW at 732°C and 34.5 MPa. It was found that the specimen failed after one week of exposure. The fracture surface revealed the presence of transgranular cracking. Fournier et al. [12] tested Alloys 690 and 718 in SCW at 400 °C, 25 MPa using constant extension rate tensile (CERT). Alloy 718 failed by intergranular SCC (IGSCC) and exhibited no necking. The cracking was initiated from the oxidation of niobium precipitates in the alloy. Alloy 690 failed by completely ductile rupture and showed a significant amount of necking. Fujisawa et al. [13] studied SCC of 316SS, C-276, 625 and MC alloy in 400 °C SCW containing 8 ppm dissolved oxygen. No IGSCC was observed in pure water, but the addition of small amounts (0.001 mol/l) HCl resulted in IGSCC in both Alloy 316 SS and Alloy C-276.

The majority of previous work has been done in supercritical water (SCW) with lower pressure. Some data suggest that corrosion in high-temperature and supercritical water strongly correlates with density

[14]. Analysis based on data obtained at low pressure usually underestimates the real corrosion rate of a material under SCW condition.

The objectives of the present phase of this work are to

- develop reliable evaluation techniques
- identify SCC resistant materials for construction of pressure tube SCWR.

2. Experimental

The materials used in this phase of the project were Alloy 625 and 316 SS in tube shape. The alloy 625 tube had an outer diameter of 3/8 inch and a wall thickness of 0.065 inch. The outer diameter of the 316 SS tube was ¼ inch and the wall thickness was 0.035 inch. The inner wall of the alloy 625 tubes was polished to 1200# using SiC paper. The 316 SS was used as received. All specimens were cleaned with acetone in an ultrasonic bath. The tubes were filled with a specified amount of deionised water and the two ends then were sealed with caps. As shown in Fig. 1, the specimen was put into a protective tube before placing into a furnace.

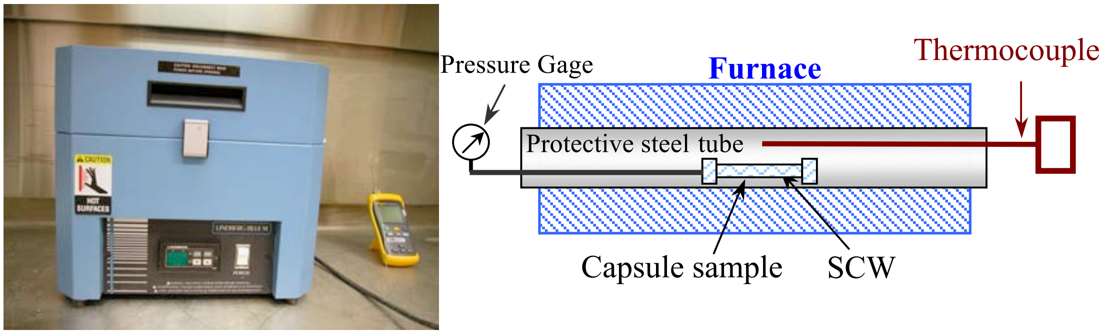

Figure 1 Experimental setup for SCW testing

The pressure of the water depended on its density and temperature, as shown in Fig. 2 [15]. When a tube was fully filled with water, the density was 1 g.mL^{-1} and the pressure at 500^{o}C was about 995 MPa. When a tube was half filled with water, the density was about 0.5 g.mL^{-1} and the pressure at 500^{o}C was about 90 MPa, which is higher compared to real SCWR. In future work, we will reduce the work pressure.

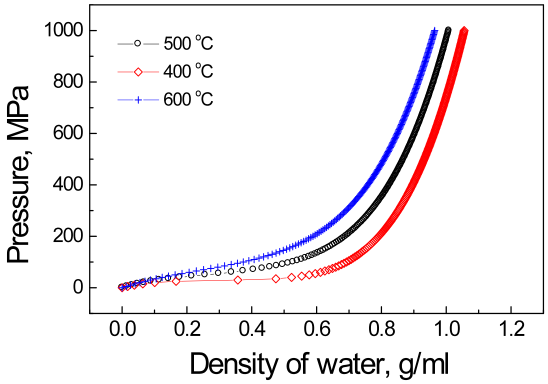

Figure 2 Pressure vs. density of water as a function of temperature [15].

Separate specimens were heated at 500^{0}C for different times. After the tests, the water inside of the tube was taken out and the volume was measured. The amount of water lost during the test was determined.

3. Results and Discussion

3.1 Inconel 625

Alloy 625 tubes were fully filled with deionised water and then heated at 500°C for different durations. The amounts of water lost during the tests, composition of the water, surface morphologies of the inner walls and compositions of the oxides were determined after each test.

No cracks were observed for the specimens tested for three weeks. Due to the oxidation/corrosion and possible water diffusion through grain boundaries (to be confirmed in future work) and the possibility of a bad seal between the caps and the tube, the amount of water after the tests decreased, and the results are shown in Fig. 3.

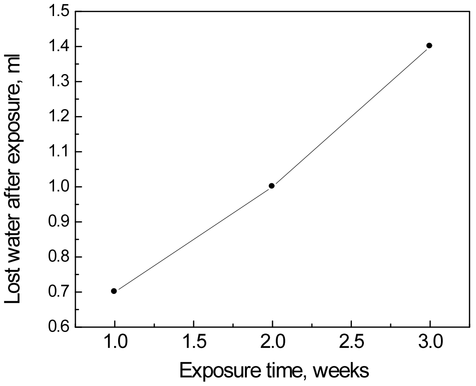

Figure 3 The amount of water lost during test vs. exposure time.

Due to creep at high temperature and high pressure, the inner diameter of the tubes increased and hence the volume of the tube increased with the test duration. Because of water loss and creep of the materials during testing, the density of the water decreased with test duration. After 3 weeks testing, only 76% volume of the tube was occupied by water. The pressure of the SCW inside the tubes decreased from about 995 MPa to 210 MPa, based on data in Fig. 2.

Table 1 The composition of the water after exposure (units in ppm)

Test duration	Ni	Cr	Mo	Fe	Nb	Ta
Detection limit, ppm	0.00006	0.00005	0.00002	0.0037	0.00004	0.00002
1 week	0.642	0.00781	10.3	0.0771	0.00065	0.00105
2 weeks	1.10	0.00231	12.4	0.267	0.00034	0.00056
3 weeks	0.732	0.00193	16.3	0.0854	0.00027	0.00044

The cations in the water after each test were determined using inductively coupled plasma mass spectrometry (ICPMS) analysis, and the results are listed in Table 1. The concentrations of Mo were much higher than those of other cations because molybdenum oxides are very soluble in SCW [14]. The results indicate that molybdenum oxide was formed from Alloy 625 during the test in SCW at 500°C.

Fig. 4 shows the surface morphology of the inner wall of Alloy 625 tube after testing at 500°C for 3 weeks. Cracks were observed in the oxide layer. The same specimen was cut cross-sectionally and the composition at the surface and two points at different depths were determined using energy-dispersive X-ray spectroscopy (EDS). The results are shown in Table 2. More Cr, Nb and O and less Ni and Mo were observed at the surface (Surface 1 and Surface 2) than those in the bulk (Points 3 and 4). Depletion of Mo in oxide layer consisted with the data in table 1.

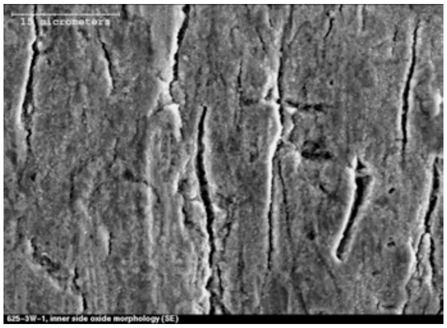

Figure 4 The surface morphology of the inner wall of the alloy 625 tube after testing at 500°C for 3 weeks.

Table 2 EDS results at different points in Alloy 625 tube after tested at 500 °C for 3 weeks (wt%)

	Point 1	Point 2	Point 3	Point 4
Locations	Surface 1	Surface 2	2 µm from the surface	10 µm from the surface
O	3.51	1.67		
Cr	34.72	33.05	18.31	19.67
Ni	50.59	53.51	69.53	69.05
Mo	3.84	3.48	5.72	6.06
Nb	1.54	1.57	1.06	0.70
Fe	4.85	4.63	4.62	4.14

3.2 316 SS

Two 316 SS tubes were fully filled with deionised water and two were half filled with deionised water. Each specimen was tested at 500 ^{0}C. For the tube fully filled with water, the initial pressure was 995 MPa. After 4 h exposure, one specimen ruptured (Fig. 5) and one did not.

Fig. 6 shows the cross section of the 316 SS tube fully filled with water after testing for 4 h at 500°C, which was not ruptured. The right side of the image is the inner wall of the tube. Cracks were detected that initiated at the inner wall of the tube. The crack lengths were in the range 15 to 50 µm.

Fig. 7 shows the morphologies of the oxide formed on the inner wall of the 316 SS tube after testing at 500°C for 4 h. Cracks were also observed on the oxide layer.

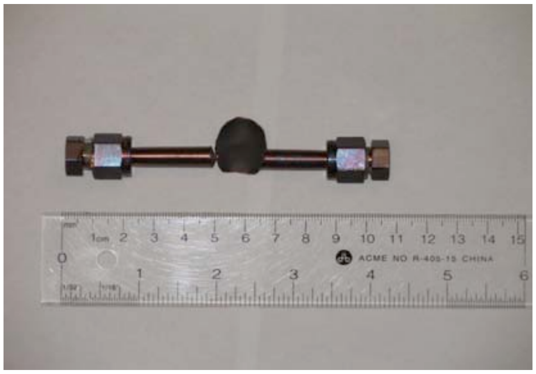

Figure 5 The 316 SS tube fully filled with water after tested at 500°C for 4 hours.

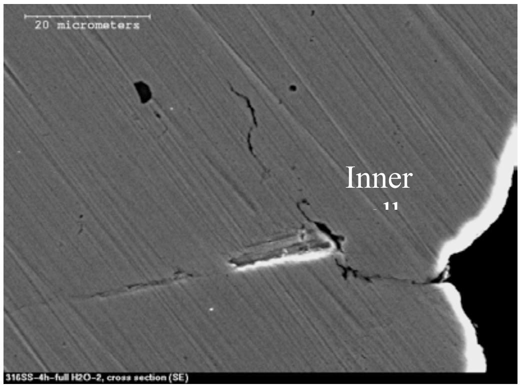

Figure 6 The cross section of the 316 SS tube that did not rupture after testing at 500°C for 4 h. The tube was fully filled with water before exposure.

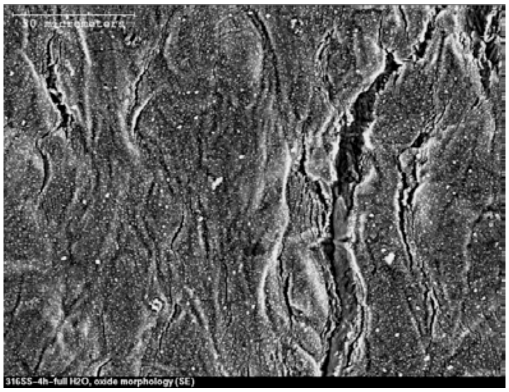

Figure 7 The morphologies of the oxide formed on the inner wall of the 316 SS tube after testing at 500°C 4 h.

Fig. 8 shows the morphology of the cross section of 316 SS tube half filled with water and tested at 500°C for 1 week. The specimen did not rupture after the test. A Ni-P layer was deposited on top of the oxide layer before SEM and EDS analysis. The oxide layer was around 1 μm thick. EDS was used to analyze the elements at the three points shown in Fig. 8, and the results are listed in Table 3. The oxide layer has higher concentrations of Cr, Mo and Ni. Ni and P are due to the deposition of Ni and P on top of the oxide layer. The amounts of Fe and Mn in the oxide layer were less than those in substrate.

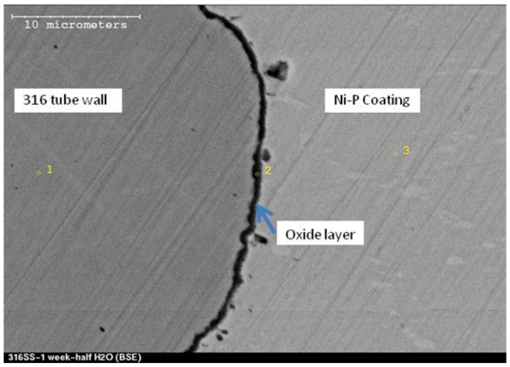

Figure 8 The SEM image of the cross section of 316 SS tube half filled with water and tested at 500°C for 1 week.

Table 3 EDS results on points in Fig. 8 (wt%)

Element	Point 1	Point 2	Point 3
O		1.82	
Cr	15.85	19.85	
Ni	13.41	39.80	95.27
Fe	67.11	33.15	
Mn	2.39	1.89	
Mo	1.24	1.75	
Si		0.33	
P		1.41	4.73

4. Summary

No cracks were observed on Alloy 625 after 3 weeks of exposure at 500^{0}C, while cracks were observed on 316 SS only after 4 h heating at 500^{0}C. These cracks had initiated at the inner wall of the tube.

The oxide layer on 316 SS is much thicker than that formed on Alloy 625. The oxide layers on both alloys are Cr-enriched.

5. References

[1] D. Broll, C. Kaul, A. Kramer, P. Krammer, T. Richter, M. Jung, H. Vogel and P Zehner, Chemistry in Supercritical Water, Angew. Chem. Int, Ed., Vol. 38, Iss. 20, 1999, pp. 2998-3014.

[2] D. Squarer, T. Schulenberg, D. Struwe, Y. Oka, D. Bittermann, N. Aksan, C. Maraczy, R. Kyrki-Rajamaki, A. Souyri, P. Dumaz, High Performance Light Water Reactor, Nucl. Eng. Des., Vol. 221, Iss. 1-3, 2003, pp. 167-180.

[3] S. Teysseyre, J. McKinley, G.S. Was, D.B. Mitton, H. Kim, J-K Kim and R.M. Latanison, Corrosion and Stress Corrosion Cracking of Austenitic Alloys in Supercritical Water, Proc. 11th Int'l Conf. Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, American Nuclear Society, La Grange Park, IL, 2003 pp. 63-72.

[4] J. McKinley, S. Teysseyre, G.S. Was, D.B. Mitton, H. Kim, J-K Kim and R.M. Latanison Corrosion and Stress Corrosion Cracking of Austenitic Alloys in Supercritical Water, Proc. Int. Conf. Global Environment and Advanced Nuclear Power Plants, GENES4/ANP2003, Atomic Energy Society of Japan, Tokyo, 2003, paper #1027.

[5] G.S. Was, Stress Corrosion Cracking of Austenitic Alloys in Supercritical Water, Workshop on Radiation Effects on Water Chemistry of Supercritical Water-Cooled Reactor, SCR-2003, University of Tokyo, Japan, 2003.

[6] L. Tan, M. T. Machut, K. Sridharan and T. R. Allen, Corrosion Behavior of a Ferritic/Martensitic Steel HCM12A Exposed to Harsh Environments, J. Nucl. Mater., Vol. 371, Iss. 1-3, 2007, pp. 161-170.

[7] H. S. Cho and A. Kimura, Corrosion Resistance of High-Cr Oxide Dispersion Strengthened Ferritic Steels in Supercritical Pressurized Water, J. Nucl. Mater., 367-370(Pt. B), 2007, pp. 1180-1184.

[8] Q. Peng, E. Gartner, J. T. Busby, A. T. Motta and G.S. Was, Corrosion Behavior of Model Zirconium Alloys in Deaerated Supercritical Water at 500^{o}C, Corros., Vol. 63, Iss. 6, 2007, pp. 577-590.

[9] H. Hirose, K. Shiba, M. Enoeda and M. Akiba, Corrosion and Stress Corrosion Cracking of Ferritic/Martensitic Steel in Supercritical Pressurized Water, J. Nucl. Mater., Vol. 367-370, 2007, pp. 1185-1189.

[10] S. S. Hwang, B. H. Lee, J. G. Kim and J. S. Jang, SCC and Corrosion Evaluations of the F/M Steels for a Supercritical Water Reactor, J. Nucl. Mater., Vol. 372, Iss. 2-3, 2008, pp. 177-181.

[11] W.K. Boyd and H.A Pray, Corrosion of Stainless Steels in Supercritical Water, Corrosion, Vol. 13, 1957, pp. 375-384.

[12] L. Fournier, D. Delafosse, C. Bosch, T. Magnin, Stress Corrosion Cracking of Nickel Base Superalloys in Aerated Supercritical Water, Corrosion 2001, NACE International, Houston, TX, Paper # 01361, March 2001.

[13] R. Fujisawa, K. Nishimura, T. Kishida, M. Sakaihara, Y. Kurata, Y. Watanabe, Cracking Susceptibility of Ni Base Alloys and 316 Stainless Steel in Less Oxidizing or Reducing SCW, Corrosion 2005, NACE International, Houston, TX, Paper 05395, 2005.

[14] P. Kritzer, Corrosion in High-temperature and Supercritical Water and Aqueous Solutions: A Review, J. Supercritical Fluids, Vol. 29, Iss. 1-2, 2004, pp. 1-29.

[15] http://webbook.nist.gov/chemistry/fluid/