Microstructural Evaluation of Stressed IN625 and NiCrAlY Coated IN625 Tested in High and Low Density SCW

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Abstract

The goal of this study was to determine the corrosion resistance of NiCrAlY coatings for use in future supercritical water reactors (SCWR). The NiCrAlY coating was applied to IN625 and was tested against bare IN625, under stress, in high density supercritical water (HDSCW) and low density supercritical water (LDSCW). The IN625 samples experienced intergranular corrosion in HDSCW but not in LDSCW as well as oxidation; whereas the NiCrAlY sample experienced oxidation, with no other forms of corrosion observed. Thus, it is likely that NiCrAlY coatings are more corrosion resistant than IN625 in HDSCW.

1. Introduction

Canada is a member of an international consortium committed to the development of next generation (Gen IV) nuclear power reactors. Six reactor technologies have been selected for research and development under the Gen IV program: Gas Cooled Fast Reactors (GFR), Lead-Cooled Fast Reactors (LFR), Molten Salt Reactors (MSR), Sodium-Cooled Fast Reactors (SFR), Supercritical Water Reactors (SCWR), and Very-High-Temperature Reactors (VHTR). Canada has chosen to focus on a pressure tube SCWR design - a natural evolution of existing CANDU technology. It uses a supercritical light water as working fluid. The proposed reactor outlet temperature for the CANDU SCWR may be as high as 650°C [1], at an operating pressure of 25 MPa. The high temperature differential between reactor outlet and inlet enabled by the use of supercritical water allows a high thermodynamic efficiency close to 50%, compared to about 35% for an advanced Light Water Reactor (LWR) [1].

Water is in the supercritical state at a temperature above 374°C and a pressure above 22.05 MPa. The density and ionic dissociation of water drop significantly at or above the point of transition to the supercritical state. At higher pressures, the shift in these physical properties becomes more gradual [2]. Figure 1 shows the drop in ionic product and density at pressures of 24 MPa and 38 MPa. This abrupt shift in physical properties affects the corrosion behavior on materials enormously. Water can vary with temperature and pressure from a high density, high polarity solvent to a low density, low polarity solvent.

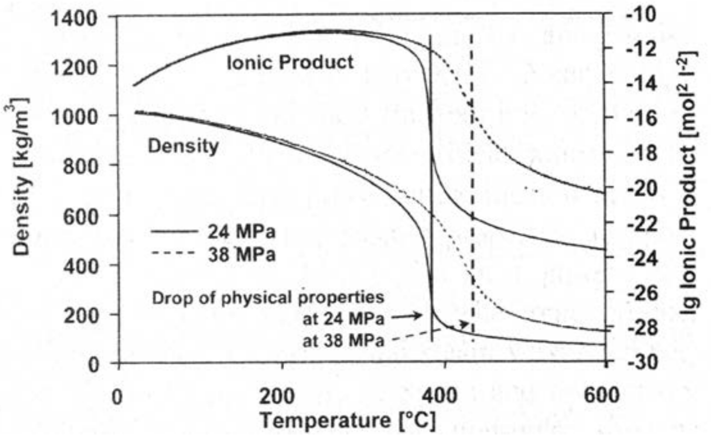


Figure 1: Drop in physical properties of water with temperature [2].

The performance of materials under SCWR conditions has attracted increased research attention in recent years [3]. The critical issues are corrosion, stress corrosion cracking and the effects of irradiation. In the proposed CANDU SCWR, water enters the core below the critical temperature and leaves the core at temperatures of up to 650°C, well above the critical temperature. At the core inlet, the water will be a high density polar solvent in which ionic compounds may have high solubility and in which gases have a much lower solubility. At the core outlet, the coolant will be a weak solvent for ionic compounds but a strong solvent for gases. From a corrosion standpoint, there are several distinct sections of the SCWR circuit, each of which will experience a unique corrosion environment.

Usually, corrosion rates rise with temperature, as reaction rates and diffusion rates increase. However, when the corrosion medium changes state, as water does in going from sub-critical to super-critical, a change in the mechanism of the corrosion phenomena occurs. The reduction in density of water correlates with a drop in ionic solubility. At 25 MPa the dissociation of water peaks at around 300°C with an ionic product concentration that is about 3 orders of magnitude greater than at room temperature. As water transitions to supercritical the reduction in ionic concentrations is about 13 orders of magnitude lower at 500°C than at 300°C. Most metal oxides show increased solubility in either acidic or alkaline solutions, so an increase in the ionic character of water will cause an increase in corrosion. Experiments carried out during the development of supercritical water oxidation processes under acidic, oxidizing conditions at pressures of 24 MPa and 38 MPa [2] showed that the corrosion rate increased at about 320°C regardless of the pressure; and the corrosion rate correlated with the density of the fluid.

This study was undertaken to examine the effects of NiCrAlY coating a Ni based superalloy, IN625, on corrosion performance in high density and low density supercritical water. Furthermore, the effect of stress on corrosion behaviour of IN625 and NiCrAlY coating was also investigated. Based on our previous studies [4, 5], the addition of Al to NiCr alloy system substantially improved the corrosion resistance of alloys in SCW. For this reason, a plasma sprayed NiCrAlY (with 10 wt% Al) was further tested.

2. Materials and Experiment

2.1 Materials

The materials tested in this study were IN625 (1.29 mm thick sheet material) and NiCrAlY coated IN625 (200 µm coating). Coating was applied to IN625 substrate using plasma spraying method. The compositions for IN625 and NiCrAlY are given in Table 1. The process parameters for plasma spraying are summarized in Table 2.

Table 1: Compositions of IN625 and NiCrAlY.

	Ni	**Cr**	**Al**	**Y**	**Mo**	**Fe**	**Ti**	**Nb**
IN625	61.5	21.5	0.2	0	9.0	4.0	0.2	3.6
NiCrAlY	69	20	10	1				

Table 2: Plasma spraying process parameters (Mettech Axial 3 system).

Test	**Powder Designation**	**Nozzle OD (in)**	**Total flow rate (SL/min)**	**%H_2**	**Current (A)**	**Distance (mm)**	**Powder feed rate**	**Carrier gas flow rate (SL/min)**	**Time (s)**	**Rotation (rpm)**	**Pre-heat cycles**
6-2	Ni 343	3/8	230	23	250	150	6	12	80	220	5

2.2 Double Beam Stress Corrosion Test Method

In addition to unstressed IN625 and NiCrAlY coated IN625, stressed samples were also made. These were stressed to the maximum allowable stress for IN625 using a method from ASTM standard [6,7], referred to as the double beam stress corrosion test. The same IN625 sheet material (with thickness *t*) was used as the spacer (thickness *s*), as such dimensions *t* and *s* shown in Figure 2 are equal (*t*=*s*). The ASTM standard also recommended a spacer length (*h*) to be ½ the beam length (*H*). The width of samples was determined based on the inner dimension of the autoclave. The maximum operating stress for IN625 at the autoclaves maximum temperature, 540°C, is 182 MPa [6]. Therefore all stressed samples were built to the geometry which generates this stress.

Note that since the SCW test temperatures are lower than the design temperature, the actual stresses will be slightly higher due to the change in elastic modulus value. The coating thickness was not taken into account, so the calculated stress is at the coating/substrate interface and the coating will experience increased stress on outer the surface.

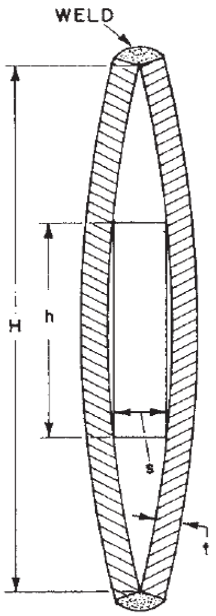


Figure 2: Double beam specimen and various dimensions indicated [7].

To fabricate the stressed samples, a jig was constructed to hold the samples in place during welding (shown in Figure 3). The jig also absorbed most of the heat from welding before it could reach the center of the samples. Hooks were also welded onto the samples to hang them during SCW testing. The welding was carried out using a TIG at 40 amps with a 1/16 sharpened tungsten rod. The unstressed samples were treated in the same way as the stressed samples. For example, even the unstressed samples were welded together without the spacer to account for any effects from the welding process.

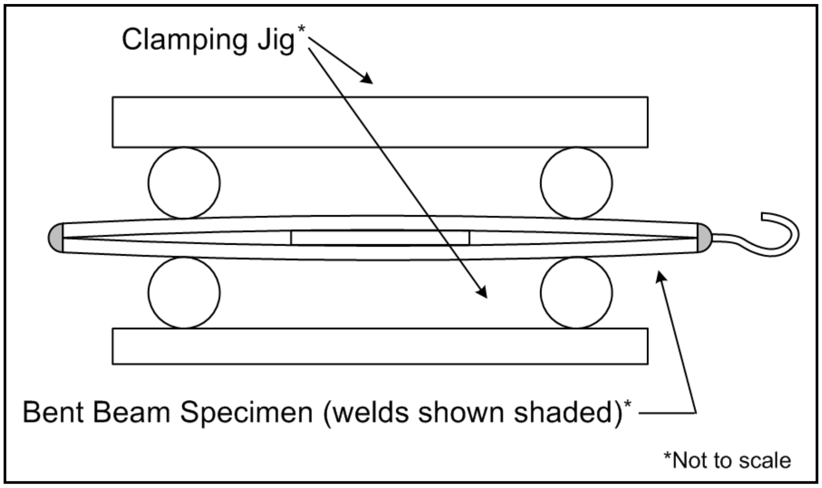


Figure 3: Schematic of welding jig.

2.3 Sample surface preparation

Before the samples were welded and placed in the SCW autoclave, the samples were polished to a mirror finish in order to allow for better observation of the surface condition after testing. The polishing process started with precision grinding followed by manual polishing with polishing wheels. Minor scratches left by the polishing wheel were further removed by polishing with 600 grit SiC sand paper and alumina slurry. The midsections of the samples were then polished to a mirror finish on a buffing wheel with diamond paste. Finally the samples were cleaned in an ultrasonic bath for one hour.

2.4 SCW Test Conditions

Due to the repeated burst ring ruptures, several runs were carried out to achieve the 500 hour test duration in the SCW autoclave. The actual conditions experienced by the samples are as follows:

HDSCW: Burst disc ruptured in the first few hours. Autoclave was recharged and when the desired pressure and temperature of 381°C and 27.5 MPa was reached, the autoclave was held for 500 h.

LDSCW: Initial run at 500°C and 27.6 MPa was terminated after 322h when the burst disc ruptured; the samples were exposed to atmosphere at 500°C for 11 hours before recharging. The 2nd run lasted 178 hours at 470°C and 27.7 MPa, for a total of 500 hours at LDSCW conditions.

The water used for the autoclave was bubbled with N_2 to reduce the dissolved oxygen (DO) range to less than 1 ppm. A summary of samples the tested in this study is given in Table 3 along with sample identifications.

Table 3: Sample matrix showing sample condition and identification

		Untested	**HDSCW**	**LDSCW**
IN625	**Unstressed**	1U1	1U2	1U3
	Stressed	1S1	1S2	1S3
IN625 + NiCrAlY	**Unstressed**	2U1	2U2	2U3
	Stressed	2S1	2S2	2S3

2.5 Sample Preparation and Evaluation after Testing

After the corrosion tests were completed, the samples were sectioned and ultrasonically cleaned. Selected cross sections were mounted in Bakelite, ground and polished using up to 0.3 micron alumina polishing solution. The surface and cross section samples were then examined with a scanning electron microscope (SEM) (Vega II XMU) and with energy dispersive x-ray spectroscopy (EDS) (Oxford system).

3. Results

3.1 Samples in the As-Prepared Condition

The surface microstructure of four as-polished, untested samples (1U1, 1S1, 2U1 and 2S1) are shown in Figure 4. The IN625 samples contain a number of pin holes with 3 - 7 μm in diameter and the NiCrAlY samples show the typical plasma sprayed structure with oxides, unmelted particles and pores. No difference was observed between the stressed (1S1 and 2S1) and unstressed (1U1 and 2U1) samples. Therefore only one EDS reading was taken as representative of each stressed/unstressed pair (1X1 and 2X1). This is done for all following sample sets as well. EDS readings also exclude contamination substances, (for instances silicon, from the autoclave sealant) and light elements like oxygen, since the accuracy is low for lighter elements. EDS analysis of the polished coating showed only slight deviation from the nominal value, see Table 4 and Table 5. An example of the cross section of a coated sample (Figure 5) reveals that the plasma sprayed coating bonds well to the substrate and has minimum porosity and unmelted particles.

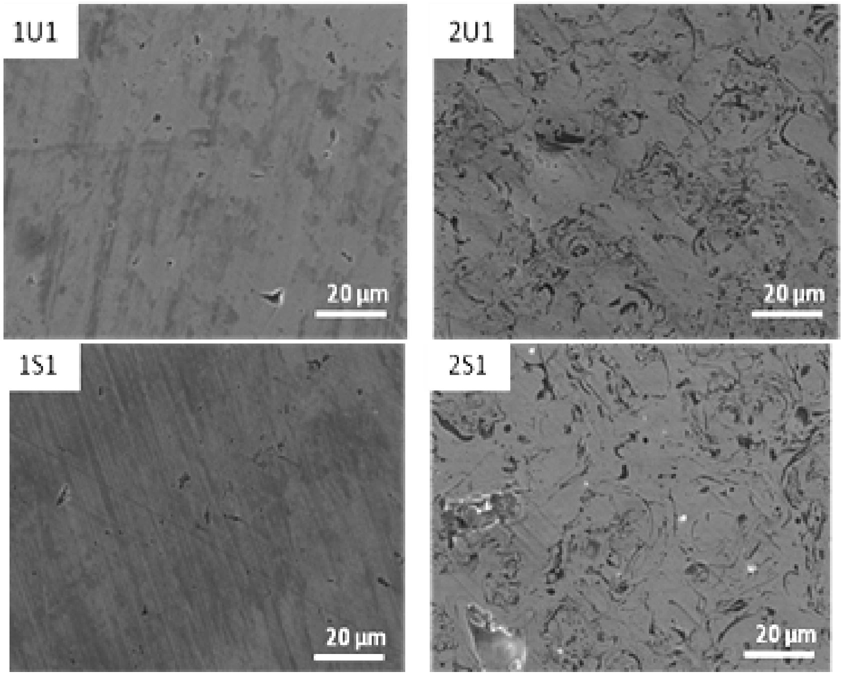


Figure 4: SEM Images of sample surface features in the as-prepared condition.

Table 4: Comparison of nominal IN625 composition to that measured by EDS

IN625	Ni	Cr	Mo	Fe	Nb	Al	Ti
Nominal	61.5	21.5	9	4	3.6	0.2	0.2
1X1 (untested)	63.39	20.60	9.18	3.66	3.18	-	-

Table 5: Comparison of nominal IN625 composition to that measured by EDS

NiCrAlY	Ni	Cr	Al	Y
Nominal	69	20	10	1
2X1 (untested)	66.68	20.93	11.11	1.29

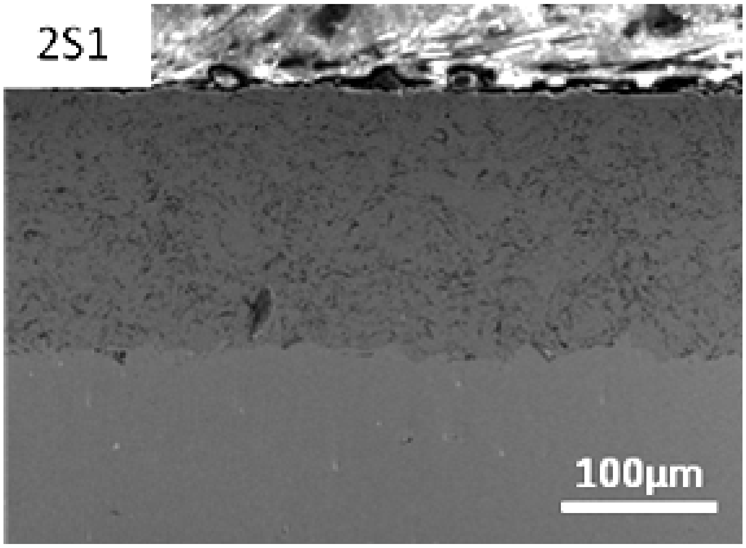
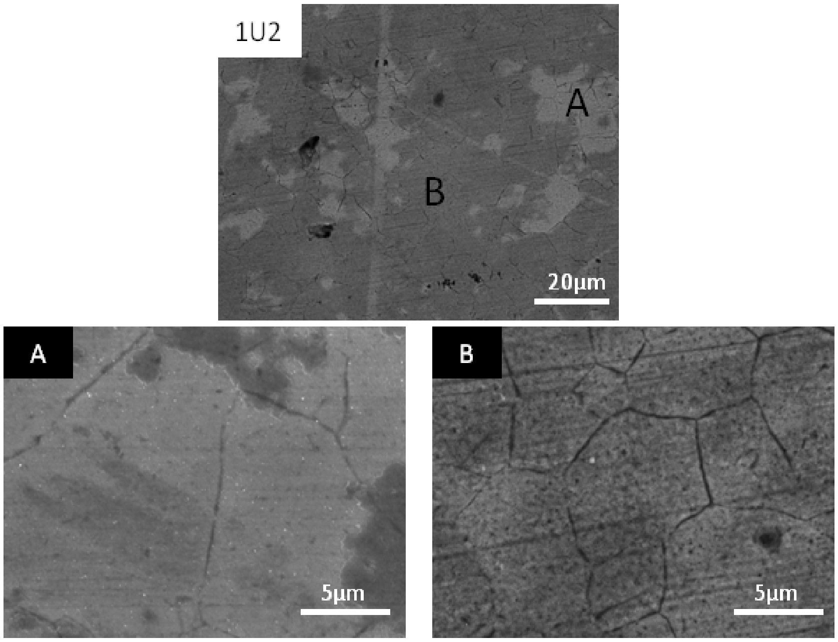


Figure 5: Cross-sectional microstructure of the coated samples in the as-prepared condition.

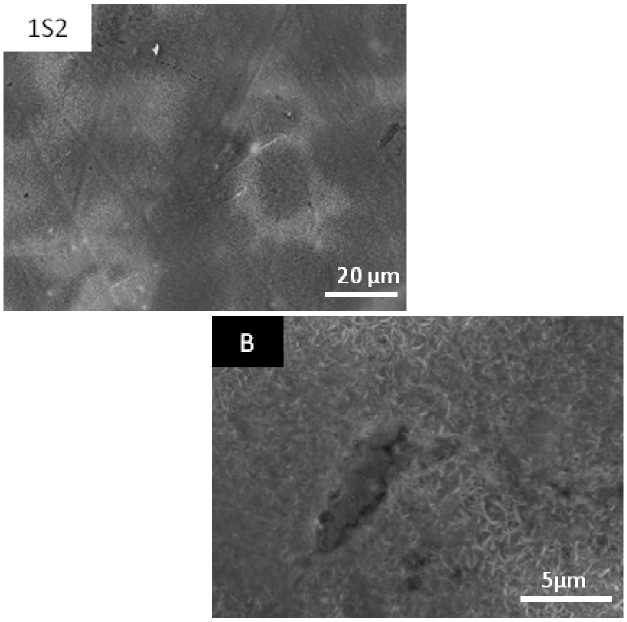
3.2 HDSCW Tested Samples

For the IN625 samples tested under HDSCW for 500 hr, minor intergranular corrosion was observed, as shown in Figure 6. Both unstressed (1U2) and stressed (1S2) samples showed similar features, where grain boundaries were delineated by the corrosion process in HDSCW. Since certain elements will collect at the grain boundaries at these temperatures [3], the composition and stability of the material is compromised there. This lowered stability, combined with the high ionic product of the water (see Figure 1) leads to intergranular corrosion. Lighter and darker regions were also observed, shown in Figure 6. The light regions (marked “A”) in Figure 6 a and b have a slightly different composition (Table 6) to the darker regions (B in Figure 6 a and b) but both are still quite similar to the untested composition. Since a moderate amount of oxygen was detected, these two regions could be two different types of oxide formations.

The coated samples (2U2 and 2S2) did not show any indication of surface or interlamellar corrosion. In fact, the HDSCW tested NiCrAlY samples (Figure 7) have similar features as before HDSCW testing. However, EDS analysis detected high concentrations of oxygen (Table 7), which indicates oxide formation. Again, only slight changes in composition were observed. These changes suggest the types of oxides that are being formed.



(a) 1U2

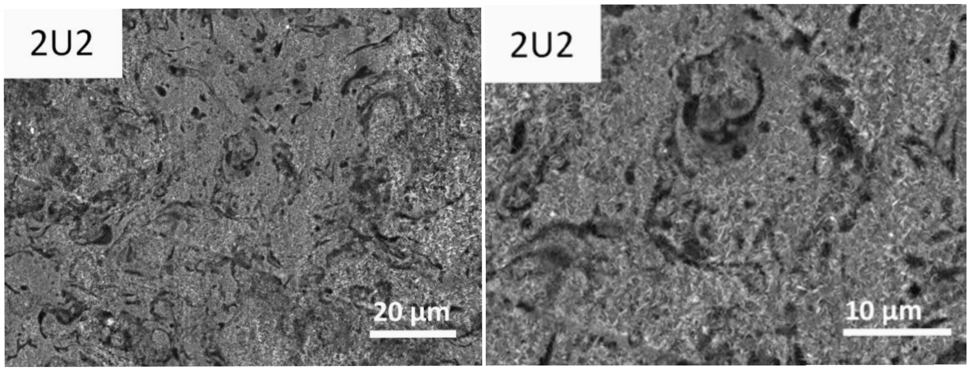


(b) 1S2

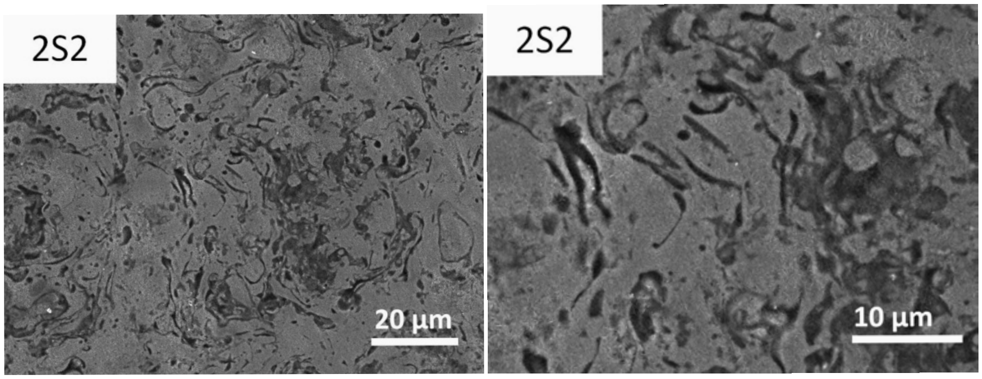
Figure 6: SEM Images of IN625 (stressed and unstressed) after 500 h in HDSCW.

Table 6: EDS composition analysis of IN625 samples after HDSCW testing (wt%).

IN625		**Ni**	**Cr**	**Mo**	**Fe**	**Nb**	**O**
1X2 (HDSCW)	**A (light)**	59.30	20.43	11.56	5.21	3.49	moderate
	B (dark)	59.11	22.97	9.94	4.54	3.44	moderate
1X1 (untested)		63.39	20.60	9.18	3.66	3.18	-



(a) 2U2



(b) 2S2

Figure 7: SEM Images of NiCrAlY coated IN625 (stressed and unstressed) after 500 h in HDSCW.

Table 7: EDS composition analysis of NiCrAlY coated IN625 samples after HDSCW testing (wt%).

NiCrAlY	**Ni**	**Cr**	**Al**	**Y**	**O**
2X2 (HDSCW)	66.29	22.28	10.39	1.05	high
2X1 (untested)	66.68	20.93	11.11	1.29	-

3.3 LDSCW Tested Samples

For the LDSCW tests, again little difference was observed between the stressed and unstressed IN625 samples (1U3 and 1S3 in Figure 8). Similar to that reported in [8], the LDSCW samples had less severe corrosion than the HDSCW ones. Only small pin holes were found. The pin holes in the LDSCW IN625 sample were found to be similar in size to the as-prepared bare IN625 (Figure 4), which suggests that these they were inherited from the original IN625 sheet material. EDS analysis results on the surfaces showed little change from the untested sample and an increase in oxygen content (on spot B in Figure 8 a and b and Table 8). However, the oxygen content was much lower than that found on HDSCW tested IN625 surface. Also, pockets of feathering substances were observed (spot A on both 1U3 and 1S3, Figure 8) on the surfaces of both samples. They were found to be Si-rich contaminants.

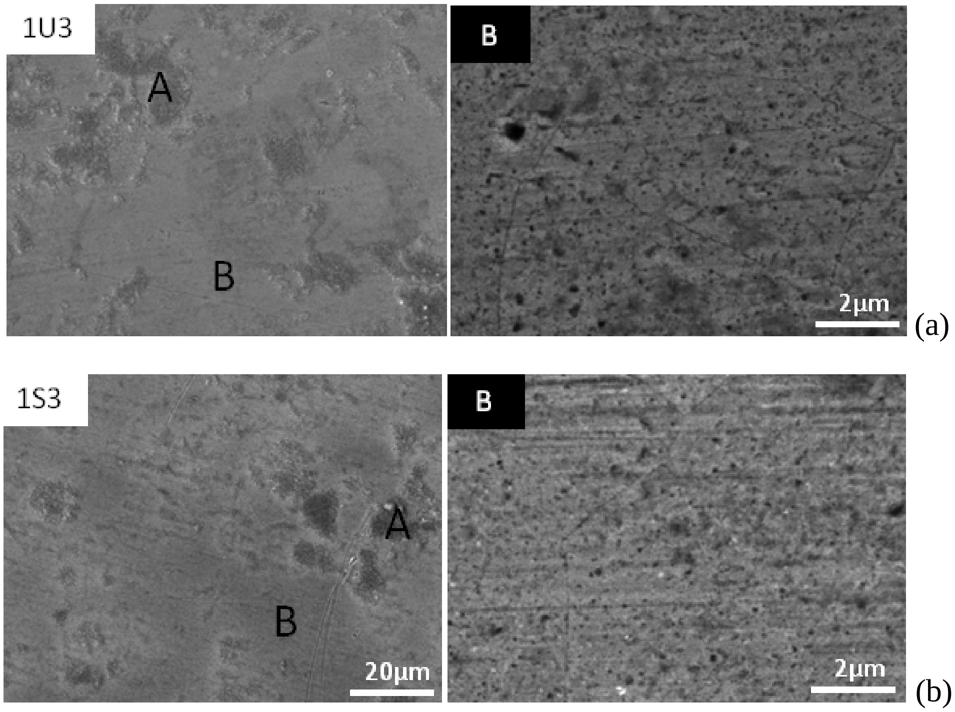
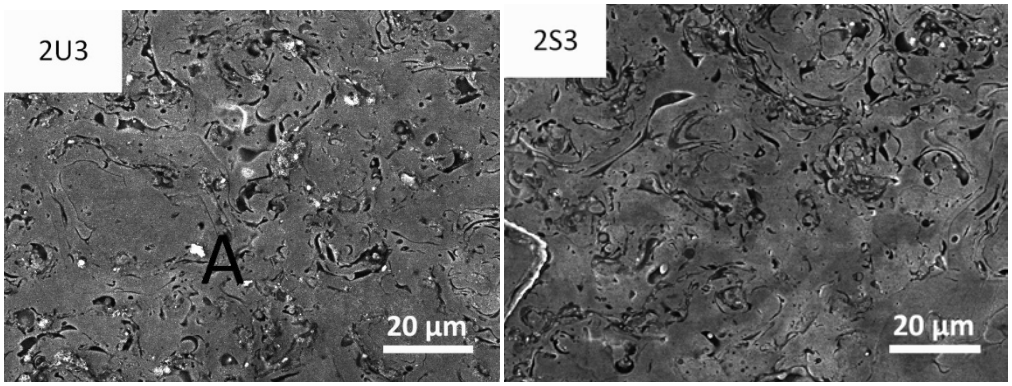


Figure 8: IN625 samples tested in LDSCW for 500 hours.

Table 8: EDS composition analysis of IN625 samples after LDSCW testing (wt%).

IN625	Ni	Cr	Mo	Fe	Nb	O
1X3 (LDSCW)	61.40	21.54	9.80	3.40	3.87	low
1X1 (untested)	63.39	20.60	9.18	3.66	3.18	-

The NiCrAlY coated sample (2U3 and 2S2) after LDSCW testing (Figure 9) appeared very similar to the untested sample (2U1 and 2S1) (Figure 4). Neither general nor selective corrosion was observed on the surface. Both stressed and unstressed samples showed identical features. The occasional Ni-rich phase (NiO) was also identified in the light contrasted region (A in 2U3 of Figure 9). Similar to the HDSCW test, there was very little change in composition compared to the untested sample, and oxidation was apparent, however, the amount of oxidation detected was substantially lower than the HDSCW samples (Table 9).



(a) 2U3 (b) 2S3

Figure 9: SEM images of NiCrAlY coated IN625 tested in LDSCW for 500 hours.

Table 9: EDS composition analysis of NiCrAlY coated IN625 samples after LDSCW testing (wt%). (*peak is very small even when detected, so it is possible Y is there even if it isn't detected)

NiCrAlY	Ni	Cr	Al	Y	O
2X3 (LDSCW)	66.31	22.53	11.16	0.00*	moderate
2X1 (untested)	66.68	20.93	11.11	1.29	-

4. Conclusions

In this study, IN625 and NiCrAlY coated IN625 samples were tested in HDSCW and LDSCW. Both stressed and unstressed samples were included in the test. The results showed that the application of stress (~182 MPa) did not affect the corrosion behaviour of IN625 and the NiCrAlY coating. However, the HDSCW (381°C and 28 MPa for 500 hr) test caused intergranular corrosion on the IN625 samples. This could be due to migration of certain elements to the grain boundaries in IN625, and the higher ionic product of HDSCW than LDSCW. When IN625 samples were tested in LDSCW (500°C and 28 MPa for 500 hr), no intergranular corrosion was observed. On the other hand, the NiCrAlY coating did not show any sign of interlamellar corrosion or surface pitting under HDSCW and LDSCW conditions. Oxidation was observed on all samples, however the NiCrAlY samples were more oxidized than the IN625 samples, and the samples tested in HDSCW had more oxidation than those tested in LDSCW. This is most likely due to the increased reactivity of HDSCW, causing more potential for oxidation. It also suggests that NiCrAlY has a faster forming and/or more stable oxide than IN625. Since the NiCrAlY did not show any signs of corrosion it is likely that its corrosion resistance is greater than IN625. However, as Ni based alloys are susceptible to high neutron capture, swelling and radiation damage [9], its usage within a reactor core may be limited. Therefore use of the NiCrAlY coatings for out-of-core piping components may be beneficial due to its corrosion resistance under HDSCW condition.

It is important to note that IN625 is in general very corrosion resistant. The surface degradation observed over the 500 hour test in HDSCW was minimal. Therefore it would be necessary to have tests of longer duration in order to determine the corrosion rate of both the IN625 and the NiCrAlY coating, and the possible failure mechanisms.

Acknowledgement

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