The Effect of Weld Chemistry on the Likely Primary Water Stress Corrosion Cracking Susceptibility of Alloy 82 Dissimilar Metal Welds

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Summary

Alloy 82 dissimilar weld joints between carbon steel and Alloy 600 were exposed to a simulated primary water environment consisting of hydrogenated steam at 480 °C and 1 bar. Dilution from the carbon steel to the weld was significant, particularly in the root where Fe was enriched to 35 at. % and Cr was depleted to 10 at. %. The heterogeneous composition of the weld from root to crown resulted in differences in internal and external oxidation tendency. An Fe-rich external surface oxide formed on the weld root which may help to prevent embrittlement and SCC by internal intergranular oxidation.

1. Introduction

Alloy 82 is a Ni alloy weld metal commonly used for weld joints in the primary circuit of CANDU plants. These welds are often located between a dissimilar parent material, such as stainless steel or carbon steel, and a nickel alloy, such as Alloy 600. The stress corrosion cracking susceptibility of Alloy 82 dissimilar metal welds is debatable, and has been studied extensively [1, 2].

Dilution due to mixing with dissimilar parent materials can result in a weld with a significantly different composition compared to Alloy 82. In addition, impurities from parent materials have been found to segregate to dendrite and grain boundaries resulting in increased cracking susceptibility [1]. Dilution results in the oxidation behaviour, and possibly the primary water stress corrosion cracking (PWSCC) susceptibility of dissimilar metal welds, being different than expected.

Hydrogen is added to primary water which reduces the potential of Ni alloys into the range of the Ni/NiO equilibrium potential; such reducing conditions suggest the possibility of internal intergranular oxidation, which has been found to embrittle Alloy 600 [3, 4]. Internal oxidation can occur in Ni-Fe-Cr alloys in conditions where the oxygen partial pressure is in the range of the dissociation pressure of the more-noble metal oxide, NiO; the reactive element, Cr, when below a critical concentration can oxidize internally rather than externally. Internal volumetric stress is relieved through the expulsion of the solvent element, Ni, to the surface [3, 4]. The phenomenon was first observed at a scanning electron microscopy (SEM) level of resolution by Rapp et al. in Ag-In alloys [3, 4]. Internal oxidation was first proposed as a mechanism of PWSCC by Scott and Le Calvar [5]. Scenini et al. exposed Alloy 600 to a steam and hydrogen environment at 480 °C and atmospheric pressure; they found chromium was internally oxidized and stress relief was achieved by the expulsion of metallic nickel to the surface [6]. Further work by Persaud et al. revealed that internal oxidation occurred inter- and intragranularly in

Alloy 600 after exposure to 480 °C hydrogenated steam for 120 h [7]. In addition, internal oxidation was, remarkably, found to occur intragranularly in Alloy 690 due to hindered lattice diffusion kinetics at 480 °C [8]. The validity of hydrogenated steam as an accelerated PWSCC environment was investigated by Economy et al. [9]; they found that the crack growth rate of Alloy 600 U-bend samples exposed to 400 °C hydrogenated steam and 360 °C primary water lay on one Arrhenius line [9].

In the present work, Alloy 82 dissimilar metal welds between Alloy 600 and carbon steel were exposed to hydrogenated steam environment at 480 °C and 1 bar. The expected large variation in weld-metal chemistry due to dilution in different regions of the weld will be investigated. The effect of oxidation behaviour from root to crown on the likely PWSCC susceptibility of Alloy 82 dissimilar metal welds will be discussed.

2. Experimental Methods

2.1 Materials

Alloy 82 dissimilar metal welds were extracted from piping joints between Alloy 600 (SB-166 NO0600) and carbon steel (SA-106 Gr. C); the nominal compositions of Alloy 82, Alloy 600 and carbon steel are given in Table 1. The root of the weld is the initial joint on the inside of the pipe and the crown of the weld is the final pass on the outside of the pipe; the root of the weld is of particular importance because it is the point of exposure. It was desirable to extract the cross-section to reveal the area from root to crown because it was anticipated that dilution from carbon steel would result in a heterogeneous composition. Flat samples were fine polished to a 0.05 μ m finish prior to exposure.

Table 1 Nominal compositions of Anoy 62 and parent materials, carbon steer and Anoy 660.										
Element	Ni	Fe	Cr	Mn	Cu	S	Nb	Ti	Si	С
Alloy 82	Bal.	≤3.0	18-22	2.5-3.5	≤0.50	≤0.015	2.0-3.0	≤0.75	≤0.50	≤0.10
Alloy 600	Bal.	6-10	14-17	≤1.0	≤0.50	≤0.015	_		≤0.50	≤0.050
C. Steel	≤0.40	Bal.	≤0.40	0.3-1.0	≤0.40	≤0.035	_	-	≥0.10	≤0.35

Table 1 Nominal compositions of Alloy 82 and parent materials, carbon steel and Alloy 600.

2.2 Experimental Conditions and Procedures

Experiments were carried out in a tube reactor encased in a furnace at Surface Science Western (SSW), similar to the design by Scenini et al. [6]. A hydrogenated steam environment at 480 °C and 1 bar was used to simulate primary water conditions by maintaining an oxygen partial pressure well below the Ni/NiO dissociation pressure; this was done by manipulating the ratio of H_2 to steam. Experiment duration was 120 h. Determining the equilibrium dissociation pressure of oxygen and the necessary H_2 and steam flow rates was done through simple thermodynamic calculations and can be found in [10]. Further description of the atmospheric reactor, with a detailed process flow diagram and experimental procedures can be found in literature [10].

2.3 Analysis Equipment

Initial surface imaging and energy dispersive x-ray spectroscopy (EDX) of the pristine Alloy 82 dissimilar metal weld was done using the Hitachi S-570 scanning electron microscope (SEM) at an

accelerating voltage of 20 keV at the University of Toronto. After exposure, SEM imaging was done at low voltage, 1-2 kV, using the LEO-Zeiss 1540XB FIB-SEM at the Nanofabrication Facility, University of Western Ontario, London, ON, Canada; the attached focused ion beam (FIB) was used to mill trenches and EDX was done with the equipped Oxford Instruments x-ray system.

3. Results and Discussion

EDX was used to perform an elemental composition line scan along the weld from the root to the crown; approximately 35 at. % Fe is present at the point of exposure, the root, which is significantly more than the expected Fe content of Alloy 82. Cr and Ni are depleted in the root to approximately 10 at. % and 55 at. % respectively [10]. The heterogeneous composition of the weld and change in element composition is due to dilution of the weld by carbon steel. Dilution decreases from the root to the crown of the weld reaching approximately 17 at. % Cr at the crown.

Figure 1 shows an Alloy 82 dissimilar metal weld cross-section after exposure to 480 °C hydrogenated steam for 120 h. SEM imaging is provided for the root, Figure 1 (a, b), and the crown, Figure 1 (c, d) [10]. In the root there is evidence of an external oxide which is formed favourably on the surface of grain boundaries that act as short circuits for fast diffusion; the oxide was confirmed to be Fe_3O_4 using EDX [10] and is present due to the significant increase in Fe content from dilution. In the crown, there is visible evidence of internal oxidation occurring inter- and intragranularly resulting in the expulsion of metallic Ni to the surface. The internal oxides in the crown were confirmed to be Fe- and Cr- rich using EDX [10], similar to 600SA [7]. Nodules were also confirmed to be metallic Ni using EDX [10].



Figure 1 Alloy 82 dissimilar metal weld after exposure to 480 °C hydrogenated steam for 120 h (left) and SEM micrographs (right) of the weld root (a, b) and the weld crown (c, d) [10].

Figure 2 shows FIB trenches beneath the external oxide on the root (a) and the metallic Ni layer on the crown [10]. There is visible evidence that inter- and intragranular penetration of oxygen has occurred in the crown of the weld, likely embrittling this portion of the weld should it ever be exposed to primary coolant. There is no evidence of oxygen penetration beneath the root of the weld.



Figure 2 FIB trenches beneath the Alloy 82 dissimilar metal weld. Trenches were milled beneath the oxide on the root (a) and beneath the metallic Ni layer on the crown (b) [10].

EDX maps were generated beneath the root and are shown in Figure 3 [10]. There is limited penetration of oxygen occurring. The external oxidation at grain boundaries assists in increasing the likely PWSCC resistance of Alloy 82 dissimilar metal welds by limiting oxygen diffusion and preventing intergranular embrittlement. However, there is evidence of intergranular minor element segregation, such as sulfur, which may be detrimental. EDX maps which were generated beneath the Ni layer in the Alloy 82 crown, Figure 2 (b), are available in ref. [10]. Oxygen, Fe, and Cr are enriched beneath the surface both inter- and intragranularly beneath the Ni layer indicating that internal oxidation is occurring, similar to what was observed in Alloy 600 [7]. Penetration of oxygen is approximately 2 µm beneath the Ni layer; given the hindered lattice diffusion rates at 480 °C and in 360 °C primary water, diffusion rates must be enhanced by the presence of short circuit dislocation paths, which may be produced through mechanisms discussed in [10].





4. Conclusions

- Alloy 82 dissimilar metal weld joints between carbon steel and Alloy 600 undergo dilution during welding resulting in depletion of Ni and Cr and enrichment of Fe, particularly in the weld root.
- Internal oxidation of Cr occurred in all areas of the weld resulting in metallic Ni expulsion, except the root where an external Fe-rich surface oxide formed.
- FIB sectioning revealed that the Fe-rich oxide on the root of the weld consumes oxygen and likely impedes inward intergranular oxygen diffusion. Away from the root, internal oxidation of Cr occurs both inter- and intragranularly which may result in intergranular embrittlement if exposed to primary water.

• While external oxidation is beneficial, segregation of impurities to the grain boundaries, such as sulfur, may increase the SCC susceptibility of Alloy 82 dissimilar metal welds.

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6. References

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