Potential Resistance of Alloy 82 Dissimilar Metal Welds to Primary Water Stress Corrosion Cracking

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Summary

Joints between carbon steel and Alloy 600, containing Alloy 82 weld metal, were exposed to a steam-hydrogen environment considered to simulate exposure to primary water conditions in nuclear power plants. A potentially protective external iron oxide film formed on the inner surface of the component. However, the chromium content throughout the weld is below that which would form an external chromium oxide. The results indicate that low chromium content could allow for internal oxidation below the external iron oxide which could increase susceptibility to primary water stress corrosion cracking (PWSCC) compared with an otherwise similar alloy, such as Alloy 800.

1. Introduction

Alloy 82 dissimilar metal welds are found in several designs of nuclear plants. The Stress Corrosion Cracking (SCC) resistance of these and other nickel-base alloy welds in primary coolant is debatable, and much research has been carried out [1]. Two dissimilar metal welds with parent materials of carbon steel and Alloy 600 were exposed to simulated primary water environments in the present work.

The welds in question have a non-homogenous microstructure. They are composed of dendrites with local recrystallization. Similar nickel alloy welds, such as Alloy 182, have been found to undergo inter-dendritic stress corrosion cracking (IDSCC) in pressurized water reactor (PWR) environments [2].

Internal intergranular oxidation is a well-supported mechanism for PWSCC of nickel alloys. The model was first proposed by Scott and Le Calvar [3] and received support from surface embrittlement studies done in steam and hydrogen at 400 °C [4]. Scenini et al. [5, 6] extended the studies by exposing Alloys 600 and 690 to a steam and hydrogen environment at 480 °C and atmospheric pressure; in all cases they found that chromium was internally oxidized and this caused the expulsion of metallic nickel nodules on the surface [7]. This kind of environment is believed to reproduce selective oxidation phenomena that occur during PWSCC at much lower temperatures. The mechanism involves the ingress of oxygen into the alloy. The oxidation occurs with one or more alloying elements in the material leaving the main solvent material untouched. This is a generalized problem for nickel alloys at low nominal partial pressures of oxygen because alloying elements, such as chromium, can oxidize internally if they are present in insufficient amount, as in Alloy 600.

2. Experimental procedure

Experiments were performed in hydrogenated steam at atmospheric pressure and 480 °C. Higher pressures were not considered in this experiment. Higher pressures with temperatures of 300 °C would result in oxide layers with thicknesses less than 1µm found in this experiment. The experiments were controlled using the hydrogen partial pressure to maintain P_{O2} below the Ni/NiO equilibrium.

2.1 Sample preparation

The welds were cut along the axis parallel to the direction of flow into coupons to reveal their cross-sections. The coupons were abraded down to a 1200 grit finish, and then polished using diamond paste to 0.05 µm. In between each stage, the sample was ultrasonically cleaned in deionized water and dried using air. Figure 1 (a) is a microscopic image of the weld prior to exposure.

The average weld composition in the root, upper filler, and the nominal composition of Alloy 82 are given in Table 1. The weld has elevated iron content due to dilution of the carbon steel into the weld during welding. A carbon steel inclusion remains from the carbon steel. Figure 1 (a) shows this small inclusion at the lower right. The average composition was determined by taking the average of 18 composition measurements across the axial cross-section of the root and filler using energy dispersive x-ray spectroscopy (EDX).

Table 1 – Composition of the Alloy 82 root and filler compared to the nominal composition

Element	Alloy 82 Root	Alloy 82 Filler	Nominal [8]
Ni	52%	64%	67% min.
Cr	13%	16%	18% - 22%
Fe	33%	16%	3% max.
Mn	1%	2%	2.5% - 3.5%
Nb	<1%	1%	2% - 3%
Other (Ti, Si, C, Cu, P, S)	Bal.	Bal.	Bal.

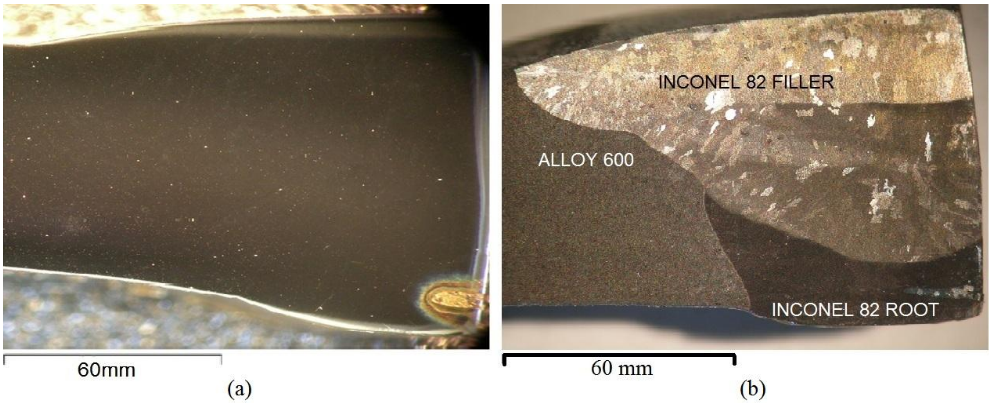
2.2 Atmospheric-pressure reactor testing in steam and hydrogen

Atmospheric pressure exposure of the welds in hydrogen and steam was performed at Surface Science Western. The exposure was done in a tube reactor placed in a furnace at 480 °C and atmospheric pressure. Only hydrogen and steam were present in the tube during exposure. The hydrogen partial pressure and steam flow rate were set to maintain an equilibrium oxygen partial pressure below the Ni/NiO equilibrium within the tube.

2.2.1 Experimental procedure

1. A quartz tube was cleaned using acetone and deionized water. Samples were placed in the centre of the tube and all connections were tightened.
2. The tube reactor was heated to a controlled temperature of 480 °C. An attached stainless steel block was heated to approximately 300 °C. While heating, the air in the tube was purged using argon for 1 hour followed by hydrogen gas for 1 hour.
3. Once the reactor reached 480 °C, steam was fed to the block and from there to the reactor using a peristaltic pump. The steam took approximately 15 minutes to reach the reactor.
4. After exposure for 3 or 5 days the heating and pump were turned off. The reactor was allowed to cool and the samples then removed.

3. Results



(a) (b)

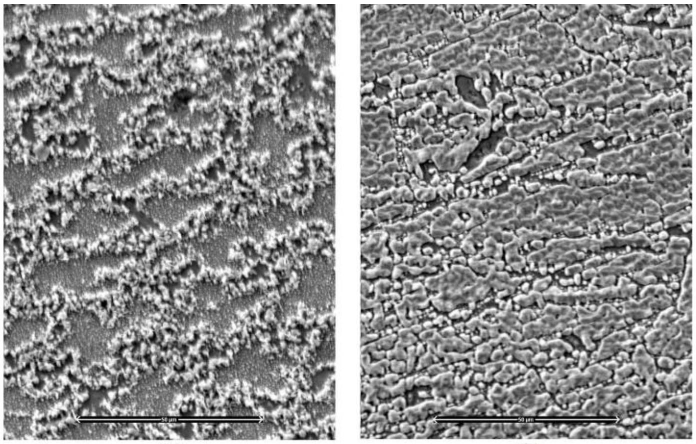
Figure 1 – Microscopic images of a typical mechanically polished Alloy 82 weld prior to exposure (a) and after exposure in the atmospheric reactor (b).

Initial inspection of the samples after exposure showed the formation of an external oxide film on the root of the weld. The filler portion of the weld appeared shiny, which may indicate nickel expelled due to internal oxidation. Figure 1 (a) and (b) show microscopic images of a typical weld sample before and after exposure. The difference in exposure time did not result in a difference in oxidation patterns but thicker oxide layers form over a longer period.

3.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) Analysis

SEM study of weld samples exposed at 480 °C showed different behaviours depending on location within the weld metal. The upper filler material showed a more metallic appearance and nodules on the surface, not dissimilar to those found on Alloy 600. The lower filler had relatively larger nodules which were fused into nearly a continuous layer - shown in Figure 2 (b). The iron-rich root nodules are significantly smaller and contained within an iron-rich oxide, probably a Fe(Cr) spinel - shown in Figure 2 (a). The initial hypothesis was that the nodules on the filler were pure nickel expelled by internal oxidation, while the root was composed of, or associated with, a continuous external oxide film.

Table 1 gives comparisons between the filler, root, and nominal compositions. EDX on the exposed surface was performed on the oxide and nodules shown in Figure 2 (a) and (b). These results indicated that the metallic content of the large nodules in the filler was primarily nickel (> 90 at.%). It was difficult to conclude what the small nodules in Figure 2 (b) were, due to the size of the nodules and error caused by the close proximity of the iron-rich oxide. The large nodules formed are metallic nickel caused by internal oxidation of chromium.



(a) (b)

Figure 2 - Typical SEM images of the Alloy 82 root (a) and lower filler (b) after exposure

3.2 Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS)

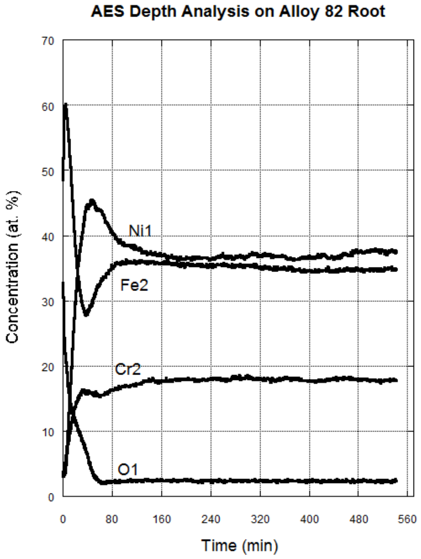


Figure 3 – AES depth profile of the iron oxide film on the Alloy 82 root

AES depth profiling was performed using the PHI 660 Scanning Auger Microprobe at Surface Science Western. A 10 keV electron beam rastered over a small area (typically 100x100 µm) was used. Depth profiling was performed on the darkened film on the root of the weld. The results showed a peak of iron on the surface of the weld, nickel depletion under this region, as well as increased oxygen content. We can conclude that the oxide film on the root of the weld is an iron-rich oxide - Figure 3. In addition, AES indicated that the depth of oxygen penetration was 0.4 µm to 0.7 µm below the surface of the material.

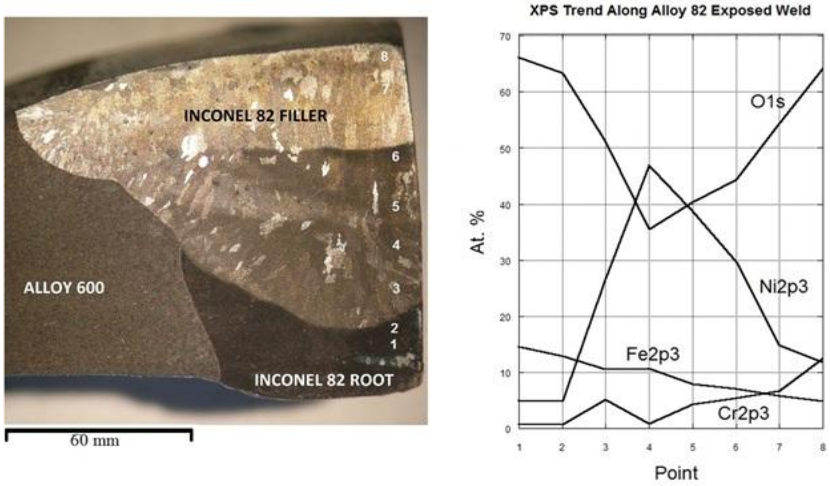


Figure 4 – XPS analysis of the chemical content along the axial cross-section of an exposed weld

XPS surface analysis was done on the Thermo Scientific K-Alpha XPS spectrometer at the University of Toronto. A monochromatic Al-K_α X-ray source was used, with a spot diameter of 400 µm. The chemical state of iron present was identified as primarily Fe_3O_4 and $FeCr_2O_4$. The chemical distribution across the weld is shown in Figure 4. Fe and O are highest in the root of the weld, indicating the presence of the external iron oxides. In the centre of the weld there is a drop in oxygen content and an increase in Ni content where the pure Ni nodular layer is formed. Finally at the edge of the filler the Cr content may be great enough to form Cr_2O_3, which accounts for the increase in Cr and O.

4. Further Discussion and Conclusions

The weld metal composition shows a large elevation in Fe content. The low pressure experiments have shown that the root and filler form surfaces with different appearance and nodule sizes. A potentially protective external oxide, consisting of primarily Fe_3O_4 and $FeCr_2O_4$, formed on the Alloy 82 root. However, the chromium content of the root is below that which would form an external oxide. Internal oxidation of chromium could occur first expelling pure nickel nodules. This would be followed by the formation of the iron oxide layer with doubtful protective properties, which might make the root of the weld susceptible to PWSCC.

The area beneath the external oxide on the Alloy 82 root should be analyzed to determine if there was any internal oxidation of chromium. This can be done using a Focused Ion Beam (FIB) to cut and remove a cross-sectional area including the external oxide and the region beneath. The cross-sectional area can then be analyzed to determine if internal oxidation occurred beneath the external oxide film.

5. References

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