Effect of Coating and Surface Modification on the Corrosion Resistance of Selected Alloys in Supercritical Water

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Abstract

Materials selection is one of the key tasks in Gen-IV reactor development. There is no known material that can meet the expected core outlet conditions of the Canadian SCWR concept (625°C core outlet temperature). High-Cr steels with excellent corrosion resistance are often susceptible to embrittlement due to the precipitation of sigma and other phases in the microstructure. Low-Cr steels such as P91 and oxide dispersion strengthened (ODS) steels exhibit good high-temperature mechanical properties, but the lack of sufficient Cr content makes this group alloy corrode too fast. Improvement in this alloy is needed in order for it to be considered as a piping construction material. In this report, the development of a metallic coating on a P91 substrate is discussed.

Recent effort on selection of in-core cladding alloys has focused on heat-resistant 3xx series stainless steels. These alloys have higher strength at high-temperature ranges, but corrosion and stress-corrosion cracking resistance are a concern. Metallic coating and surface modification are considered as possible solutions to overcome this challenge.

The effects of surface modification on the corrosion rate of austenitic steels were also reported in this paper. As-machined surface showed much better corrosion resistance than polished surface and advanced surface analyses showed distinct differences in the nature and the morphology of the surface layer metal. Possible mechanisms for improved corrosion performance are discussed.

Keywords: corrosion, coating, surface modification

1. Introduction

In the past a few years, research in materials screening and advancement significantly enriched the knowledge base for Gen-IV nuclear reactor development. The Canadian pressure-tube supercritical water (SCW) design involves peak cladding temperature of 825°C and 25 MPa of pressure. High-temperature mechanical properties, corrosion resistance and radiation damage are some of the key challenges. Most of the test results available are below 730^{o}C [1]. There has not been a single commercial material identified that meets all the requirements of the SCWR conditions. Among the requirements for both in core and out of core components, the corrosion resistance has been a main obstacle. Allen [1] summarized corrosion resistance of candidate alloy groups including Ni-based super alloys, stainless and ferritic/matensitic (F/M) steels. Upon SCW exposure, ferritic steels develop a thick but mechanically stable oxide layer, while austenitic alloys develop a thinner oxide layer. Ni-based alloys appear to form very thin surface oxide, however pitting was observed in the vicinity of intermetallic precipitates [2-5], and dissolution of major alloying components could pose significant problems in down stream piping [6]. The corrosion resistant austenitic stainless steels (e.g. 316L) are susceptible to localized corrosion such as pitting, intergranular attack and stress corrosion cracking (SCC) [7].

For feeder pipe applications, low Cr F/M steels provide excellent high-temperature creep resistance. However, steels in this group are generally prone to corrosion by the supercritical water. T/P91 high-temperature alloys have been used as piping in fossil fuel plants at high-temperature locations. Mitton [7] reported the formation of a thick oxide layer on T91 alloy surfaces after a short SCW exposure, where Cr was found to have depleted in the outer oxide layer. In this report, we used atomized high-Cr Fe-Cr alloy as coating material on a commercial P91 alloy. SCW tests in a water loop showed much improved corrosion resistance even with a thin layer of coating.

Limited studies in the literature have showed benefits of surface modification [8-10]. Our preliminary work in this area indicates that surface modification has significant effect on the corrosion of corrosion resistance. A 316L stainless steel was used in this work but it is expected that other 3xx series alloys will be used in this on-going research project.

2. Experimental Details

The coating experiments include the production, atomization and coating of a CANMET made high-Cr steel onto commercial P91 steel coupons. Details of the coating process can be found elsewhere [11]. A few test coupons were coated with the Fe-25%Cr powder using a cold-spray equipment. Both the coated and uncoated P91 coupons were tested in a SCW test loop at 500 °C, 25 MPa for 500 hours. The oxygen content (less than 20 ppb) in the test loop was measured continuously by an online electrochemical oxygen sensor inserted in the low temperature purification circuit in the test loop. Test coupons were taken out for weight change measurements periodically during the test. After the test, the test coupons were examined using a variety of advanced microscopy equipment.

For the effect of surface modification, low-carbon stainless 316L tube specimens in as-machined and polished (polished with 600 grit and 1200 grit) conditions were tested. The SCW corrosion test was carried out in an autoclave at 650 ^{o}C, 25 MPa for 3000 hours. The dissolved oxygen content was 150 ppb. Microscopic investigations using FIB and TEM were performed on the various test samples.

3. Results and Discussion

3.1 Coating Performance

The SCW exposure resulted significant oxidation to the bare P91 alloy. As shown in Figure 1a, the corrosion product is composed of two layers. The outer layer is iron oxide, while the inner is Cr-rich oxide similar to that reported by Tan [8]. The Fe-25% Cr coated P91 sample, as shown in Figure 1b, appears to have very minor surface oxidation. This is supported by the weight change data [11], which show a corrosion rate reduction of at least 70% compared with the un-coated P91 counterpart.

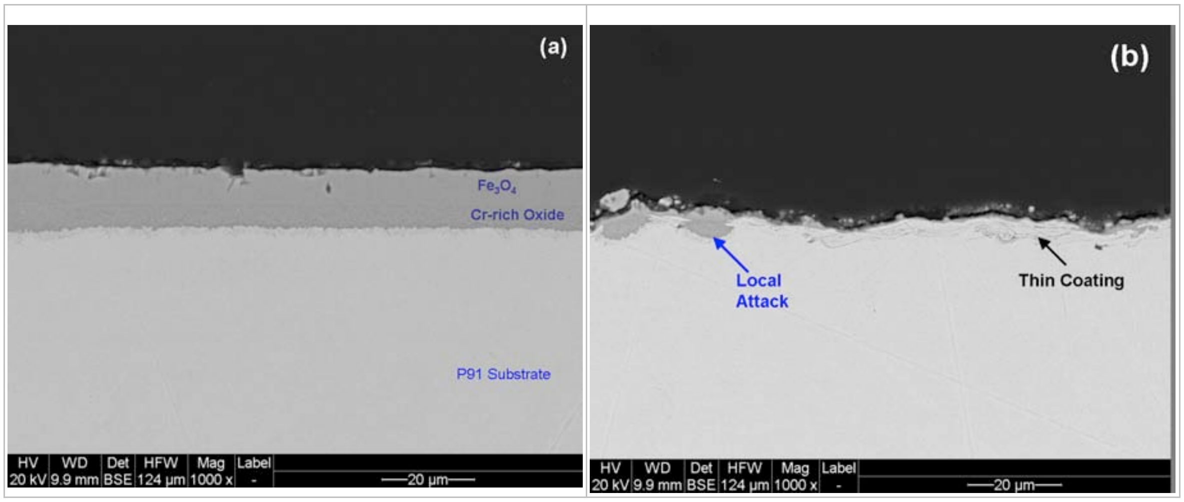

Figure 1 SEM images of test coupons after SCW test (a) bare P91 steel; (b) coated P91 steel

In a typical cold-spray process, high velocity particle impact to the substrate could result in extensive deformation, not only to the incoming particles, but also to the substrate. The microstructure of the particles was investigated using a focused ion beam (FIB) microscope. The FIB microscopes have been used widely in both high-resolution imaging and site-specific TEM specimen preparation [12, 13]. Prior to the cold-spray, the powder particle appear to have fully recrystallized structure as seen in the secondary ion image in Figure 2(a). The FIB cross-sectional view of the coated sample shows severely deformed microstructure in Figure 2(b). The coating appears to have formed extremely fine substructure or it might have dynamically recrystallized into nanometer sized grain. Further TEM work is underway to characterize the coating microstructure in detail. Immediately beneath the thin coating, the substrate develops very fine substructures. The substructure is featured by inhomogeneous grain crystallographic orientation contrast [14]. In addition to the coating protection, the severely deformed microstructure may also have attributed to the much improved corrosion resistance.

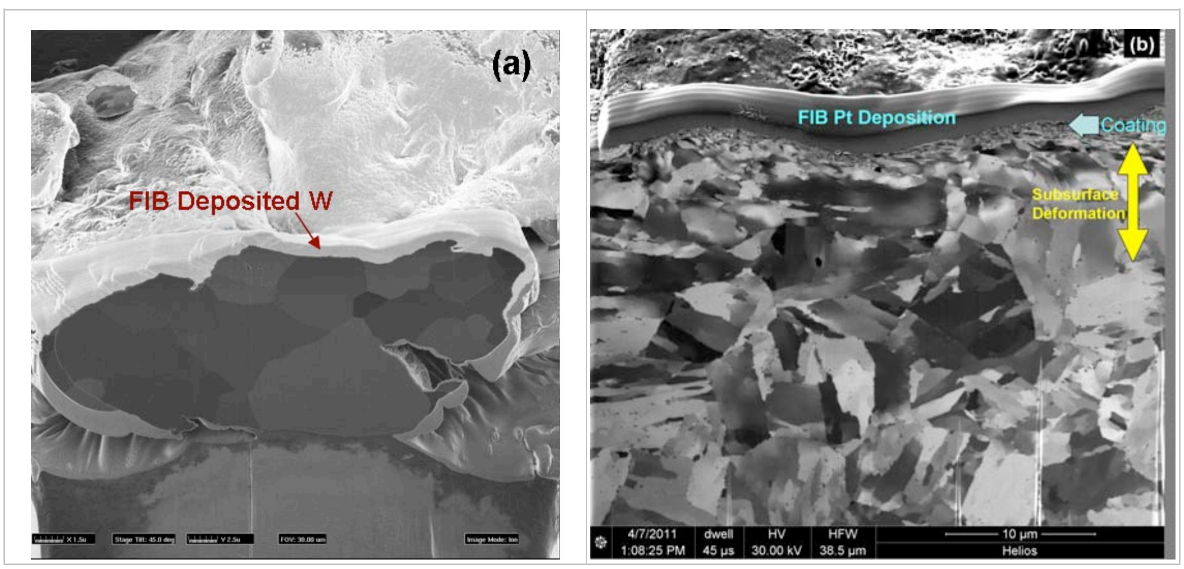

Figure 2. FIB images (a) atomized Fe-25%Cr particle for coating, (b) severely deformed structure in both coating and top surface of the P91 test coupon

3.2 Surface Modification of 316L Stainless Steel

In this work, a series of 316L stainless steel coupons where prepared with different surface conditions. Subsequent SCW exposure resulted in significantly different weight changes [10]. The coupon with "machined" surface was found to have the least weight loss. After SCW exposure for 3000 hours (125 days), the machine surface was seen to be smooth with occasional surface oxide crystals (Figure 3a), while the initially polished surfaces (600- and 1200-grit) appears to have been covered by thick oxide layer (Figure 3b).

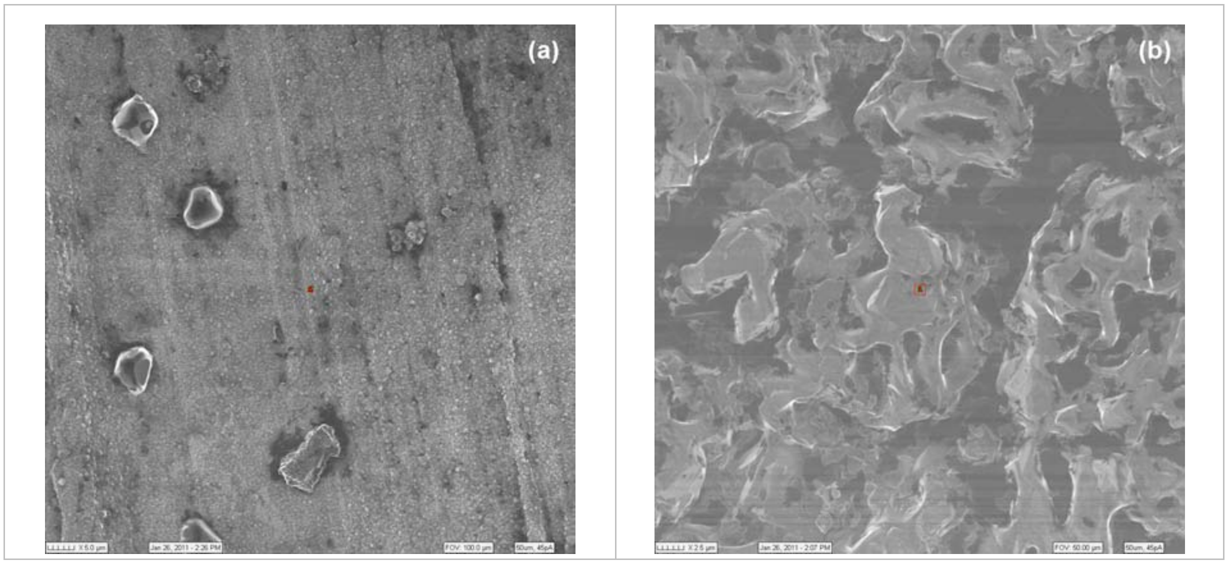

Figure 3 SEM images of surface morphology after SCW exposure (a) machined surface, (b) 600-grit polished.

To obtain subsurface microstructure, a dual-beam FIB microscope was used to perform ion beam cross-sections on two tube specimens (machined and 600-grit polished). Figure 4 shows the substantial difference in the morphology of the two samples.

1) Surface and sub-surface morphology.

The machined surface only formed a very thin surface oxide layer. Immediately beneath this surface oxide is a layer of fully recrystallized microstructure with mostly sub-micrometer sized grains. The tube specimens with initially polished surface formed a thick surface oxide layer, which is iron oxide as confirmed by our TEM analysis. Detailed TEM analysis will be presented elsewhere.

2) Internal oxidation/void formation.

Severe internal oxidation also occurred beneath the oxide layer of the 600 grit polished specimen, and extend deep into the substrate. The internal oxidation also associated with the formation of voids at grain boundaries that will no doubt affect its mechanical properties.

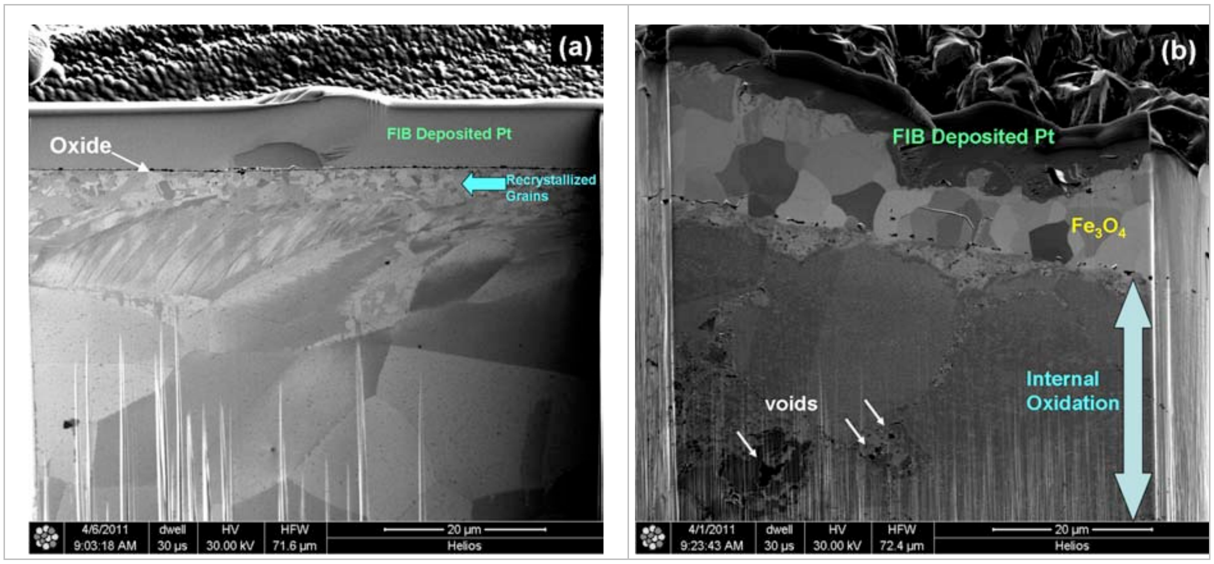

Figure 4 FIB cross section of the SCW tested 316L samples (a) machined surface, (b) 600-grit polished

3) Mechanistic discussions

Detailed mechanism of such significant difference between the machined and polished samples is now under way. However a few possible hypotheses are illustrated as follows.

i) The machined surface exhibit significant residual strain near the surface due to severe deformation during machining. In the subsequent SCW exposure (in this case, at 650 °C), this deformed structure becomes recrystallized, forming the fine-grained microstructure near the surface (Figure 4a). Below this recrystallized layer, the residual strain is not sufficient for recrystallization to occur at this temperature but they appeared to have formed recovered microstructure after the SCW testing. The abundant grain boundaries in the fine grained layer can act as outwards diffusion short circuit for Cr to transport from the bulk. This helps to provide ample Cr near the surface to maintain a continuous Cr_2O_3 passive layer during SCW exposure. The high dislocation density within the deformed layer beneath the fine recrystallized grains also facilitates Cr diffusion.

This effect of machining on the corrosion rate should therefore be similar to the effects of grain-refining in austentitic stainless steels as that reported by Tsuchiya et al. [15] who reported a comparative study of corrosion and SCC properties of normal-size and fine-grain 304L, 316L and 310S stainless steels in SCW of 550 °C containing 8 ppm oxygen. In their 6-week long SCW corrosion tests, the corrosion rate of fine-grain alloys was found to be less than 0.005 mm/per year (with the 310S alloy showing a corrosion rate of only 0.00017 mm/year) while the alloys with normal grain size (>25 microns) showed corrosion rate of generally greater than 0.01 mm/year. Auger Electron Spectroscopy (AES) analysis showed higher level of Cr in the oxide formed on the fine-grain samples than that in the normal material.

ii) Upon SCW exposure, the polished surfaces have the normal coarse grain structures oxidized. The rate of corrosion is affected by both the outward diffusion of Fe to form Fe_3O_4 crystals on the surface, and inward diffusion of oxygen to form interfacial Cr-rich complex oxide. Because the limited densities of grain-boundaries, which are the “short-cut” pathways for Cr diffusion, the fraction of highly protective chromium oxide would be less than in the fine-grained surfaces.

iii) Void formation at or beneath the metal/oxide interface was reported in other studies of nickel based alloys exposed to high-temperature steam. It has been suggested that the oxidation of Mo-rich particles and subsequent evaporation of Mo oxides is the cause of such void in Alloy 625. In austenitic stainless steels tested in SCW, the report of void formation in the interior of the sub-surface microstructure is so far non-existent. Should this be confirmed as a generic degradation problem for 3xx series stainless steel, the implication for SCWR materials selection is significant: the void formed can seriously reduce the creep strength of the alloys at these temperatures and the sites of voids can be initiation sites for surface-breaking or internal cracks.

4. Summary

Cold spray of high-Cr steel coating on P91 steel substrate significantly improved SCW resistance. The cold spray not only produced a protective coating, but also introduced subsurface deformation layer which could be beneficial to corrosion prevention in SCW. Much thinner corrosion film is observed on the cold-sprayed samples than on the un-coated samples.

Appropriate modification of the surface layer microstructure can improve corrosion resistance of stainless steels significantly, as seen in the 316L samples that were tested in as-machined conditions. The machining has introduced significant sub-surface plastic deformation, which led to recrystallization and grain-refining. There is much less oxides formed on the as-machined samples than on the polished samples.

5. Acknowledgement

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