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Electrochemical characterization of oxide formed on chromium containing mild steel alloys in LiOH medium

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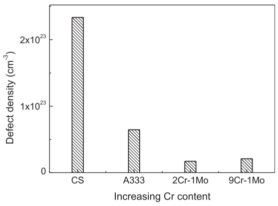
HIGHLIGHTS

- High temperature oxides formed on Cr containing mild steels are less defective.
- Defect densities of oxides decrease with increase in Cr content in the alloy.
- O_2 in solution greatly influences the nature and defect chemistry of oxides.

GRAPHICAL ABSTRACT



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ABSTRACT

Flow accelerated corrosion leads to wall thinning of outlet-feeder pipes in the primary heat transport system of pressurized heavy water reactors and can even necessitate enmasse feeder replacement. Replacement of carbon steel 106-grade-B (CS) with chromium containing carbon steel reduces the risk of this failure. This paper discusses the role of small additions of chromium in modifying the properties of the oxide film. CS and chromium containing mild steels viz., A333, 2.25Cr–1Mo and modified 9Cr–1Mo alloy were exposed to primary heat transport (PHT) system chemistry conditions. The oxide films formed were characterized by electrochemical and surface characterization techniques. Mott–Schottky analysis showed donor type of defects. The densities of defects in the oxides of chromium containing alloys were 3–15 times less than that in CS. In presence of ∼200 ppb of dissolved oxygen, the oxides formed were hematite with two orders of magnitude smaller concentration of defects as compared to that formed under reducing conditions. These results suggest that the presence of chromium lowers the defect density of the oxide film and thus ensures a reduced corrosion rate.

1. Introduction

In pressurized Heavy Water Reactors (PHWR), the corrosion of the reactor primary circuit materials is minimized by maintaining an alkaline pH (at 25 °C) of 10.2–10.6, by the addition of LiOH. Despite maintaining this stringent water chemistry condition, some of the CANDU type of reactors and PHWRs are facing the problem of outlet feeder thinning [1–3]. This phenomenon was attributed to flow accelerated corrosion (FAC). FAC is a process in which carbon steel piping and components corrode in the presence of flowing water or steam–water mixtures with low dissolved oxygen. As water flows over the carbon steel material, stable surface oxide layer (typically Fe_3O_4) dissolves into the flowing stream, thinning the walls of piping over time and resulting in failures due to rupturing [4–6]. The rate of FAC depends upon hydrodynamic factors such as flow velocity, pipe roughness and geometry of the flow path etc., environmental factors like temperature, pH, iron unsaturation, oxygen concentration and metallurgical factors like

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the composition of steel and residual stress. In addition to the general enhancement in corrosion rate due to high velocity prevailing in feeders, limited area of piping face further enhanced wear rate. This is attributable to pipe geometry which causes localized turbulence and eddies [7]. Hence this type of failure is specific only to outlet feeders of certain PHWRs and CANDUs and to certain channels. Periodic in service inspection campaigns are carried out in reactors to assess the residual life of these piping. However, exhaustive measurements in an operating plant are not always feasible and may even be hampered by access restrictions. So predictive models, which account for fluid dynamics and chemistry at each of the locations, are used to make reliable predictions and aid corrosion assessment of inaccessible areas. Many commercial software like CHECKWORKS, BRT CICERO, RAMEK, COMSY etc. are available to predict FAC [8]. The predictions are based on the assumption that the dominating factor is the presence of magnetite on the corroding surface, its solubility under the prevailing chemistry conditions, mass transfer of the dissolved ions to the fluid and subsequent mass transport to the bulk fluid. These models take in to account the fluid dynamics and chemistry at each of the susceptible locations and make reliable extrapolations for inaccessible areas. The input variables for these models are temperature, pipe geometry, fluid velocity, void fraction, chemical composition of the structural material, pH and dissolved oxygen. Research has shown that trace amounts of alloying elements – particularly chromium, greatly reduce the rate of FAC [9,10]. A study by Cheng et al., demonstrated that an increase in Cr content in the steel can reduce the corrosion rate of steel [11].

The passivity of chromium containing steels is attributed to the formation of a Cr_2O_3 film. The development of passivity due to incorporation of Cr in M–O–M network of an iron rich alloy requires that the chromium content should be atleast 10% [12–14]. The amount of chromium that is required to be present in the alloy to reduce the FAC rate has been experimentally found to be $\sim$0.04% [9,10]. Hence, it is of interest to know how such small amounts of chromium would influence the oxide dissolution and subsequent corrosion behavior. In this paper, an attempt is made to understand the role of chromium in modifying the properties of oxides formed on chromium containing mild steel alloys compared to that of Carbon Steel 106 grade B alloy (CS), which is the current feeder material in some of the Indian PHWRs. ASTM A 333 grade 6 alloy contains about 0.33% of chromium and is proposed as a new material to replace the CS feeders. Hence, this study compares the oxide properties of mild steel alloys viz., A333 (Cr $\sim$ 0.33%), 2.25Cr1Mo alloy (Cr $\sim$ 2.25%) and modified 9Cr1Mo (Cr $\sim$ 9%) along with carbon steel 106 grade B (CS).

Oxygen addition to the feedwater is practiced in some pressurized water reactors (PWRs) to protect the carbon steel piping from undergoing FAC, on the secondary side. The added oxygen reacts with the magnetite and converts it to hematite, which has four orders of magnitude lower solubility compared to magnetite. The effectiveness of this modified oxide as a barrier to FAC should also have its origin in the defect density and electronic properties of the oxide film. It is desirable to compare the extent of protection offered by chromium in the alloy and the beneficial effect of added oxygen in the process fluid. This paper also discusses the effect of dissolved oxygen for different chromium containing alloys.

The passive films formed at high temperature are semiconducting in nature and the metal release from these oxide films depends on the number density and diffusivity of the ionic point defects [15–18]. Typical donor defects in oxides are oxygen vacancies and cation interstitials and the acceptor defects are mainly cation vacancies. The influence of chromium in changing the defect structure of the oxide was studied by Mott–Schottky analysis of the measured capacitance as a function of applied electrode potential. The stability of the film in LiOH and the changes occurring at the oxide/solution interface were studied by electrochemical methods such as Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Anodic Polarization (PDAP).

Table 1
Compositions of the alloys studied.

	Carbon steel	A-333	2.25Cr1Mo	Modified 9Cr1Mo
C	0.1	0.24	0.065	0.095
Cr	<0.3	<0.3 (0.5)[a]	2.2	8.1
Si	0.28	0.42	<0.2	0.4
Ni	<0.14	<0.14	0.15	0.13
Mn	0.75	1.07	0.5	0.38
Mo	<0.03	–	1	0.9
Cu	0.16	0.1	0.055	0.07
Co	<0.03	<0.013	<0.009	0.025
Sn	0.015	0.011	<0.008	<0.008
Fe	Bal	Bal	Bal	Bal

[a] Measured by atomic absorption spectrometry.

2. Experimental

All the chemicals used were GR/AR grade. LiOH was prepared by passing Li_2CO_3 through OH^- form of resin. The outlet solution contained 1.5 ppm of Li as analyzed by flame photometry and the pH and conductivity were found to be 10.2 and 45 µS cm^{-1} at 25 °C respectively.

The three different chromium containing alloys and carbon steel (coupons of approximately 1.2 cm × 1.2 cm × 0.4 cm) were exposed to lithiated water (LiOH) at 245 °C in a static autoclave so as to form their respective oxides for 20 days. The surfaces of the specimens were ground up to 800 grit by using silicon carbide papers, cleaned with ultra-pure water and finally with acetone before exposure. The solution was purged with argon gas for 3–4 h before raising the temperature to ensure removal of dissolved oxygen.

One of the parameter that can influence the nature of oxide film is the oxygen content in the solution. Our previous study, wherein the oxide films were formed on these alloys at high temperature by allowing oxygen but only for a short duration, resulted in highly resistive oxides. The composition of the oxides on all the alloys were found to be a mixture of magnetite and hematite in the ratio 3:1 [19]. In the present study, a recirculating autoclave facility was used in order to maintain a steady concentration of oxygen throughout the experiment. In this set of experiments, the specimens were exposed to high temperature simulated PHT conditions, of 245 °C and pH$_{25}$ of 10.2 (by LiOH) in a 2.4 L re-circulating autoclave for 16 days. The flow rate was 10 LPH, thus the water was renewed 4.2 times in an hour. Some of the advantages of switching over to recirculating system from static system were that the solution could always be regenerated and DO could be maintained at 200 ± 10. The chemistry parameters in the source tank, like pH, specific conductivity, dissolved oxygen and redox potential could be measured using an online low temperature chemistry monitoring system. In addition, corrosion potential could be measured online at high temperature and iron-

Table 2
Estimates of oxide thickness on the alloys.

Material	Oxide thickness in µm after 20 d exposure to 245 °C (deaerated condition)	Oxide thickness in µm after 16 d exposure to 245 °C (with DO)
CS	0.77	1.1
A-333	0.81	0.91
2.25Cr-1Mo	1.0	0.66
Mod. 9Cr1Mo	1.09	0.21