

# Corrosion Study and Passive Film Characterization of 11% Cr F/M and 15% Cr ODS Steels

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**Abstract:** An ODS (oxide dispersion strengthened) steels are one of the most notable structural materials being developed for future high-temperature energy production technologies, and several studies have been devoted to the development of ODS materials for such applications. However, only little paper focuses on corrosion behavior of F/M (ferritic martensictic) and ODS steels. The corrosion behavior of 11% Cr F/M steel and 15% Cr ODS steel were evaluated using electrochemical methods in borate buffer and 1 kmol m<sup>-3</sup> HNO<sub>3</sub> with or without NaCl and also in boiling 60% nitric acid. The corrosion resistance results clearly indicated the influences of steel alloys composition and chloride ions. The XPS (X-ray photo-electron spectroscopy) results of the pre-passivated surface revealed that the oxide formed were composed predominantly of Fe<sub>2</sub>O<sub>3</sub> along with Cr<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub> layers in ODS steel. The corrosion rate measured in boiling nitric acid for 48 h for both the steels shows high corrosion rate in boiling condition. The SEM (scanning electron microscopy) observation of the pit morphology after corrosion tests appears with shallow pit in both steel surfaces. The corrosion degradation behavior in relation to the composition of the passive oxide film in different electrolytic solutions is discussed in this paper.

Key words: F/M steel, ODS steel, corrosion, passive film, XPS analysis.

# **1. Introduction**

Corrosion phenomena are defined as the deterioration of a material, or its properties by chemical or electrochemical interaction with its environment, and this has become a problem for construction/structural materials worldwide [1, 2]. Corrosion has an enormous economic and environmental impact and causes unpredictable and costly damage to everything from pipelines, bridges and public buildings to oil and gas, chemical processing, petrochemical, automobiles, power and wastewater systems and including home appliances [3, 4]. In addition to causing severe damage, corrosion disrupts operations and requires extensive repair and replacement of failed assets [1, 3, 4]. The annual cost of corrosion worldwide is estimated to 3% to 4% of the gross domestic product of industrialized countries

[3, 4]. This figure is divided evenly between direct costs (materials and structures) and indirect costs (loss of productivity). About 90% of the corrosion is associated with iron-based materials. Although corrosion problems cannot be easily remedied, it is estimated that corrosion related costs can be reduced more than 30% by development and use of better corrosion control technologies [2, 4].

The choices of suitable and appropriate materials are one of the key objectives in Generation IV nuclear reactor development. The F/M steels with 9%-12% chromium and RAFM (reduced activation ferritic/martensitic) steels are one of the most promising materials being considered for higher temperature applications for future advanced fast reactor cladding and structural materials [5-7]. The inherent and desirable properties of these steel alloys include, high void swelling resistance, thermal properties, helium embrittlement, micro-structural stabilities and high recycling potential, which make

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them candidates for application in commercial fission and fusion power plants [5, 6, 8, 9]. Interestingly, the F/M steels do not suffer (or suffer less) from these phenomena than the austenitic steels, and they can be made in reduced activation compositions [6, 8, 9]. The presence of fine and uniform precipitates obtained during the fabrication process in these steel alloys improved most of the above properties [6, 7]. However, one significant limitation of F/M steel is the high temperature strength above 600 °C dissolution and precipitation coarsening leads to abrupt loss of their tensile and creep property [6, 8, 9]. The expected operating temperature of the first wall in future Generation IV fusion reactor is above 700 °C, resulting in improved thermal efficiency up to  $\geq$ 30%-40% [5-7]. The ODS based F/M or ferritic alloys are the most promising materials with a potential to be used at such higher temperatures by microstructure modifications and also based on favourable conventional properties and/or technical maturity [6, 8].

The usefulness and application of any construction and structural materials is based on its mechanical performance. In addition, the corrosion resistance is critical for the materials to be used in any aggressive/corrosive environments. Corrosion control is achieved by recognizing and understanding the different forms of corrosion and its mechanisms. With its many forms, causes and associated prevention methods, corrosion obviously is highly complex and requires extensive expertise and significant resources to control, particularly in a nuclear environment [1, 2, 4]. Depending on specific environmental requirements, two ODS families are presently developed one based on 9% Cr martensitic ODS steels and other on 14%-18% Cr ferritic ODS alloys [5, 6, 8, 9]. Further, one of the in-service degradation phenomena for these steel alloys is uniform corrosion [10]. Hence, the present work was undertaken to explore and investigate the corrosion resistance behavior of 11% Cr F/M steel and 15% Cr ODS ferritic steel in

different electrolytic environments, including in boiling nitric acid solution.

# 2. Material and Experimental Methodology

# 2.1 Materials and Specimen Preparation for Corrosion Test

The chemical composition of 11% Cr F/M steel (Cr 10.52, Ni 0.52, C 0.15, Mn 0.04, W 1.81, Mo 0.40, Fe balance) and 15% Cr ODS steel (Cr 15.15, Ni 0.04, C 0.03, Mn 0.02, W 1.91, Al 3.90, Zr 0.57,  $Y_2O_3$  0.33, Fe balance) all in mass % were used in the present work. The specimens before corrosion experiment were abraded mechanically with SiC paper up to 1000 grit SiC paper on all sides prior to mounting in an epoxy resin, using a brass rod as an electrical connection. The mounted specimens were then abraded again up to 1000 grit SiC paper finish, ultrasonically cleaned in acetone and subsequently used for the experiment.

#### 2.2 Corrosion Rate Measurements

The corrosion tests were conducted by immersion of the 11% Cr F/M and 15% Cr ODS steels specimens into 60% HNO<sub>3</sub> at boiling condition at different time duration up to 48 h. After exposure, the weight changes were measured and the corrosion rate was calculated using an equation:

Corrosion rate (mm/y)  
= 
$$(8.76 \times 10^4 \times W) / D \times A \times T)$$
 (1)

where,

W = weight loss in milligrams;

 $D = \text{metal density in g / cm}^3$ ;

 $A = \text{area of sample in } \text{cm}^2$ ;

T = time of exposure of the metal sample in hours.

# 2.3 Electrochemical Measurements for Corrosion Studies

All the corrosion samples were allowed to stabilize under open circuit conditions for 30 min and subsequently, the OCP (open circuit potential) was measured as a function of time up to 1 h.

potentiodynamic The anodic polarization experiments were carried out in different electrolytic solutions: 0.3 kmol  $m^{-3}$  H<sub>3</sub>BO<sub>3</sub> + 0.075 kmol  $m^{-3}$  $Na_2B_4O_7 \cdot 10H_2O_5$ ; 0.3 kmol m<sup>-3</sup> H<sub>3</sub>BO<sub>3</sub> + 0.075 kmol  $m^{-3}$  Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O + 0.5 kmol  $m^{-3}$  NaCl; 1 kmol  $m^{-3}$ HNO<sub>3</sub>; and 1 kmol  $m^{-3}$  HNO<sub>3</sub> + 0.1 kmol  $m^{-3}$  NaCl solutions at room temperature (about 24 °C) using HABF 5001 potentiostat (Hokuto Denko, Japan). The electrochemical cell consists of three electrodes, reference electrode (Ag/AgCl in saturated KCl), counter electrode (Pt.) and working electrode. The electrode potential was anodically scanned at a scan rate of 0.1667 mV  $s^{-1}$  until the potential at which breakdown occurred. The details of the experimental methods have been already described elsewhere [9, 11].

# 2.4 Surface Analytical and Morphology Characterization

The surface morphologies of the specimens were observed with a SEM (Scanning Electron Microscopy, Joel JSM-6510LA model) equipped with EDX (energy dispersive X-ray) spectroscopy.

The XPS (X-ray photo-electron spectroscopy) measurements were carried out by potential sweep to a passive region. This was followed by holding potentiostatically at the respective passive region for 1 h. The samples were immediately transferred into the XPS analyzer chamber for measurement. XPS measurements were performed using a JOEL JPS-9200 model equipped with dual X-ray source. MgKa (1,253.6 eV) X-ray was used to generate the photo electron. During these experiments, the base pressure was maintained at  $10^{-7}$  Pa. The X-ray gun was operated at 100 W (10 kV, 10 mA) with a takeoff angle  $\theta = 0^{\circ}$  (relative to the sample normal). A survey spectrum was first recorded to identify elements presence and then high-resolution spectra of the following regions were recorded: oxygen (O 1s), carbon (C 1s), chromium (Cr 2p), iron (Fe 2p), chlorine (Cl 2p) and yttrium (Y3d and Y 3p). SpecSurf XPS operating software was employed to collect and process all surveys and high-resolution spectra.

## 3. Results and Discussion

#### 3.1 Corrosion Rate Evaluation in Boiling Nitric Acid

Fig. 1 represents the corrosion rate obtained after the immersion tests in boiling 60% HNO<sub>3</sub> for 48 h. It was observed that all the specimens were covered with a film of interference of pale dark color due to oxidized oxide layers. This study was carried out to evaluate corrosion resistance and its impact in boiling nitric acid solution. Nitric acid is the main process medium used in the reprocessing of the spent fuel by PUREX process, and hence it is essential to understand the performance of materials in such environments [9, 12]. The obtained corrosion rates of both steel alloys are high, and the corrosion rates are in the range of about 2.0-3.5 mm/y for 11% Cr F/M steel and 0.74-1 mm/y for 15% Cr ODS steel. This thereby implies that the corrosion resistance of 15% Cr ODS steel is lower than 11% Cr F/M steel. The surface morphology of the samples after 48 h immersion in nitric acid shown in Figs. 2a and 2b, indicated different morphology of surface attack. The surface appears mostly porous in 11% Cr F/M steel (Fig. 2a), whereas the surface features are mostly compact with a layer of oxide scale structure in 15% Cr ODS steel (Fig. 2b). Thereby, such surface morphology could have also effected on its corrosion resistance.

# 3.2 OCP (Open Circuit Potential) Measurements

The measured OCP of 11% Cr F/M steel in different electrolytic solutions are represented in Fig. 3a. The OCP of 11% Cr F/M steel (Fig. 3a) shows active potential in chloride containing media of borate-buffer + 0.1 kmol m<sup>-3</sup> NaCl (-0.245 V) and 1 kmol m<sup>-3</sup> HNO<sub>3</sub> + 0.1 kmol m<sup>-3</sup> NaCl (-0.215 V). Similarly, the electrolytic solutions without chloride also show active potential in borate-buffer (-0.190 V) and 1 kmol m<sup>-3</sup> HNO<sub>3</sub> (-0.195 V). Moreover, immediately upon immersion all the measured OCP



Still alloys

Fig. 1 The measured corrosion rate of 11% Cr F/M and 15% Cr ODS steels in boiling 60% HNO<sub>3</sub> of 48 h exposure.



Fig. 2 Typical SEM morphology of: (a) 11% Cr F/M steel; (b) 15% Cr ODS steel after corrosion test in boiling 60% HNO<sub>3</sub> (48 h).

shows steady state OCP value thereby indicating stable film formation (Figs. 3a and b). The results of the OCP measured for 15% Cr ODS steel specimen obtained in different electrolytic solutions shown in Fig. 3b is similar to the pattern observed in Fig. 3a. The measured OCP shows active potential in 1 kmolm<sup>-3</sup> HNO<sub>3</sub> + 0.1 kmol m<sup>-3</sup> NaCl (-0.215 V) followed by measurement in 0.3 kmol m<sup>-3</sup> H<sub>3</sub>BO<sub>3</sub> + 0.075 kmol m<sup>-3</sup> Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O + 0.1 kmol m<sup>-3</sup> NaCl (-0.165 V), 0.3 kmol m<sup>-3</sup> H<sub>3</sub>BO<sub>3</sub> + 0.075 kmol m<sup>-3</sup> Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (-0.150 V) and 1 kmol m<sup>-3</sup> HNO<sub>3</sub>

(-0.140 V). The passive film stability of metals/alloys in the corrosive environment depends upon both on the chemical or electrochemical reactions occurring at its surface. Less noble and active potential of both steel alloys in chloride media is attributed to less protective passive film due to Cl<sup>-</sup> [9, 11]. In both the steel alloys, the OCP is the lower in chloride containing solutions and higher in borate buffer solution. According to the mixed potential theory [13], the shift of OCP depends on the change of both anodic reaction rate and cathodic reaction rate. Thus, both decreasing of anodic reaction and or increasing of the cathodic reaction can lead to the shift of OCP.

#### 3.3 Potentiodynamic Polarization Studies

The results of the potentiodynamic polarization

curves of 11% Cr F/M steel obtained in different electrolytic solutions are shown in Fig. 4a. The obtained electrochemical parameters are labeled in the curve shown in Fig. 4a and values derive from the polarization curves are listed in Table 1. In 11% Cr



Fig. 3 The OCP measurement of: (a) 11 % Cr F/M steel; (b) 15 % Cr ODS obtained in different electrolytic solutions.



Fig. 4 The potentiodynamic polarization curves behavior of: (a) 11% Cr F/M steel; (b) 15% Cr ODS steel in different electrolytic solutions.

Electrolytic media	Ecorr (V vs Ag/AgCl)	$i_{\text{pass}}$ (A cm <sup>-2</sup> )	E <sub>BP</sub> (V vs Ag/AgCl)
11% Cr F/M steel			
1 kmol m <sup>-3</sup> HNO <sub>3</sub>	-0.190	$4.41 \times 10^{-6} (0.5 \text{ V})$ $7.06 \times 10^{-6} (0.5 \text{ V})$	1.07 1st 1.62 2nd
1 kmol m <sup>-3</sup> HNO <sub>3</sub> + 0.1 kmol m <sup>3</sup> NaCl	-0.243	$1.25 \times 10^{-3} (-0.1 \text{ V})$	0.043
$0.3 \text{ kmol m}^{-3} \text{ H}_3 \text{BO}_3 + 0.075 \text{ kmol m}^{-3} \text{ Na}_2 \text{B}_4 \text{O}_7 \cdot 10 \text{ H}_2 \text{O}$	-0.665	$1.1 \times 10^{-6} (1.2 \text{ V})$	1.23
$\begin{array}{l} 0.3 \ \text{kmol} \ \text{m}^{\text{-3}} \ \text{H}_3 \text{BO}_3 + 0.075 \ \text{kmol} \ \text{m}^{\text{-3}} \\ \text{Na}_2 \text{B}_4 \text{O}_7 \cdot 10 \ \text{H}_2 \text{O} + 0.5 \ \text{kmol} \ \text{m}^{\text{-3}} \end{array}$	-0.517	$3.11 \times 10^{\text{7}} \ (0.1 \ V)$	0.122
15% Cr ODS steel			
1 kmol m <sup>-3</sup> HNO <sub>3</sub>	-0.121	$9.07 \times 10^{-7} (0.5 \text{ V})$ $8.96 \times 10^{-5} (1.4 \text{ V})$	0.611 1st 1.64 2nd
1 kmol $m^{-3}$ HNO <sub>3</sub> + 0.1 kmol $m^{3}$ NaCl	-0.23	$6.1 \times 10^{-7} (0.5 \text{ V})$ $1.84 \times 10^{-4} (1.4 \text{ V})$	0.850 1st 1.50 2nd
$\begin{array}{ll} 0.3 \ kmol \ m^{-3} \ H_3 BO_3 + 0.075 & kmol \ m^{-3} \\ Na_2 B_4 O_7 \cdot 10 \ H_2 O \end{array}$	-0.66	$1.5 \times 10^{\text{-7}} \ (0.5 \ V)$	1.22
$\begin{array}{l} 0.3 \; kmol \; m^{^{-3}} \; H_3 BO_3 + 0.075 \; kmol \; m^{^{-3}} \\ Na_2 B_4 O_7 \cdot 10 \; H_2 O + 0.5 \; kmol \; m^{^{-3}} \end{array}$	-0.420	$3.05 \times 10^{-4} \ (0.5 \ V)$	0.338

Table 1 Polarization parameters obtains for 11% Cr F/M steel and 15% Cr ODS steel in different electrolytic solutions.

F/M steel (Fig. 4a), the change in the electrolytic solution markedly changes the polarization behavior and differences in  $i_{\text{pass}}$  and  $E_{\text{BP}}$  are evident. The general shapes of most of the potentiodynamic curves are similar, but differences in the  $E_{\text{corr}}$ ,  $i_{\text{pass}}$  and  $E_{\text{BP}}$ could be observed. In borate buffer and 1 kmol m<sup>-3</sup> HNO<sub>3</sub> media without chloride, the polarization curves are characterized by a wider passive range. However, drastic reduction in the apparent breakdown or pitting potential and the sharp rise in the current density is seen in 1 kmol  $m^{-3}$  HNO<sub>3</sub> + 0.1 kmol  $m^{-3}$  NaCl. In the presence of chloride (Table 1), despite lower  $i_{\text{pass}}$  of  $3.11 \times 10^{-7}$  A cm<sup>-2</sup> (borate + 0.1 kmol m<sup>-3</sup> NaCl), higher  $i_{\text{pass}}$  of  $1.23 \times 10^{-3}$  A cm<sup>-2</sup> (1 kmol m<sup>-3</sup> HNO<sub>3</sub> + 0.1 kmol m<sup>-3</sup> NaCl) and low pitting potential (0.125 and 0.04 V) was observed. The breakdown potential/pitting corrosion ( $E_{\rm BP}$ ) is the potential above which pits nucleated and grow. Hence, localized corrosion such as pitting corrosion initiates above certain critical potential above  $E_{\rm BP}$  and repassivate below  $E_{\rm BP}$ . The higher the  $E_{\rm BP}$ , the more resistant are the metal/alloy to pitting corrosion. In presence results, lower pitting potential observed is attributed to low 11% Cr content, surface inhomogeneity or possible inclusions. Further, the presence of Cl<sup>-</sup> ions destroy the passivating film, and the aggressiveness of chloride is attributed to a number of reasons [14, 15]:

(1) Chloride is an anion of a strong acid, and many metal cations are soluble in chloride solutions [9, 15];

(2) Chloride is a relatively small anion with a high diffusivity and also acts as a contaminant, thereby it interferes with passivation; and (3) the presence of oxidizing agents in a chloride-containing environment is extremely detrimental, and will additionally enhance localized corrosion [14, 15].

In Fig. 4b, the typical potentiodynamic polarization curves of 15% Cr ODS steel obtained in different electrolytic solutions is represented, and the measured polarization curves parameters are given in Table 1. Higher  $E_{\rm BP}$  and lower  $i_{\rm pass}$  were observed in 1 kmol m<sup>-3</sup> HNO<sub>3</sub> with or without chloride. However, compared to 11% Cr F/M steel (Fig. 4a), the  $E_{\rm BP}$  in the presence of chloride was not significant in 1 kmol  $m^{-3}$  HNO<sub>3</sub> + 0.1 kmol  $m^{-3}$  NaCl. Moreover, both the steel alloys exhibited lower pitting corrosion resistance in the presence of chloride media. Lower pitting corrosion resistance of ODS alloy may also be attributed to the presence of {Zr, Ti}C that has been detected by EDS and XPS analysis. The presence of such carbides can act as inclusion sites in ODS steels [6, 16]. Once the pit initiates from such inclusion sites, dissolution takes place accompanied by a local drop of pH, and once a critical concentration in chloride is attained, pitting corrosion is initiated [14, 15].

The typical SEM micrographs of 11% Cr F/M steel and 15% Cr ODS steel specimens after corrosion tests are represented in Fig. 5. In 11% F/M steel, the pit morphology shows a deep shallow pit (Fig. 5a) and along with uniform dissolution in nitric acid chloride media (Fig. 5b). Similarly, in 15% Cr ODS, the SEM morphology shown in Fig. 5c reveals that severe pitting has occurred in chloride containing media with lace-like structure. The features of such structure are dependent on dissolution rate of pit solution chemistry [14].

#### 3.4 XPS Analysis of Passive Films in Alloy Steels

The changes in the properties of the passive film

affected the localized corrosion resistance leading to pitting corrosion, crevice corrosion, intergranular corrosion and SCC (stress corrosion cracking) [14, 17]. In the present work, the elemental compositions of the surface film were determined by XPS. The wide survey XPS spectra (not shown) of the passive layer formed in different electrolytic solutions of 11% Cr F/M steel reveals the presence of mostly Fe, Cr, O, C and Cl depending on electrolyte used. Similarly, in the wide survey spectra of 15% Cr ODS steel the presence of Fe, Cr, O, Y, W, C and Cl core level peaks are identifiable. In both steel alloys, it is evident that the passive oxide film is consisted mainly of chromium and iron and presence of W and Y was detected in





Fig. 5 The SEM of surface and pit morphology after corrosion test: (a) 11% Cr F/M steel in 0.3 kmol  $m^{-3} H_3BO_3 + 0.075$  kmol  $m^{-3} Na_2B_4O_7 \cdot 10H_2O + 0.5$  kmol  $m^{-3} NaCl$ ; (b) 11% Cr F/M steel in 1 kmol  $m^{-3} HNO_3 + 0.1$  kmol  $m^{-3} NaCl$ ; and (c) 15% Cr ODS steel in 0.3 kmol  $m^{-3} H_3BO_3 + 0.075$  kmol  $m^{-3} Na_2B_4O_7 \cdot 10H_2O + 0.5$  kmol  $m^{-3} NaCl$ ; solutions.

15% Cr ODS steel.

In Fig. 6a, the appearance of broad metallic peak of Fe<sub>met</sub> (706 eV) in a borate buffer (Fig. 6a(3)) and borate + 0.1 kmol  $m^{-3}$  NaCl (Fig. 6a(4)) shows that the oxide film layer formed is thin. This is followed by a broad shoulder on the side of the higher binding energies of Fe<sub>2</sub>O<sub>3</sub> (710 eV) and Fe(OH)<sub>3</sub> (712 eV). Peak signal appearing in binding energy of 709 eV may also be assigned to Fe<sub>3</sub>O<sub>4</sub>. However, it is not possible to differentiate between Fe<sub>2</sub>O<sub>3</sub> (or their hydrates) or Fe<sub>3</sub>O<sub>4</sub> on the basis of XPS [18]. In 11% Cr F/M steel, the measured Fe atomic % concentration was in the range 8%-18%. In the high-resolution spectra of Fe 2p obtained for 15% Cr ODS steel shown in Fig. 6b, the Fe 2p ionization reveals the presence of metallic Fe<sub>met</sub> (706 eV), Fe (III) oxides (710eV) and hydroxides (712 eV). The Fe metal peak intensity (706 eV) was predominant is most of the electrolytic solutions. However, relative concentration of Fe in atomic % concentration varied in the range of 9-18 at % depending on the electrolytes used. Hence, there appears to increase or decrease in the amount of Fe, probably depending on whether the metal is in the oxidized or reduced state. In Fig. 7a the Cr 2p spectra of 11% Cr F/M steel can be fitted into two to three components. The Cr 2p ionization consists of binding energy at 574 eV that correspond to metallic Cr<sub>met</sub>, the peak at 576 eV is attributed to Cr(III) oxides and hydroxides (577 eV), respectively. The components of the Cr 2p photoelectron peak located at 576 eV (Cr 2p<sub>3/2</sub>) and at 585 eV (Cr 2p<sub>1/2</sub>) are characteristics of Cr<sup>III</sup>-O bonds in a Cr<sub>2</sub>O<sub>3</sub> compound. The Cr 2p peak located at 577 eV (Cr  $2p_{3/2}$ ) and at 587eV (Cr  $2p_{1/2}$ ) are characteristics of Cr-O bonds in a  $Cr_xO_y$ compound (>  $Cr^3$ ) [18]. The detected chromium elements of oxide films are in the range of 8%-12% and hence the Cr content in the oxide layer is low. This thereby indicated that chromium is not significantly enriched in the passive film. In Fig. 7b, the spectra of Cr 2p 15% Cr ODS steel shows a broad peak that appeared at 576 eV related to Cr<sub>2</sub>O<sub>3</sub>,

followed by a small shoulder related to  $Cr_{met}$  (574 eV) toward lower binding energy(Fig. 7b). In most media, the Cr 2p can be fitted to three peaks corresponding to the following components: the one at the lowest binding energy (574 eV) corresponds to metallic Cr, 576 eV are attributed to the presence of Cr(III) oxides (576 eV) and hydroxides (577 eV). The reported corresponding binding energies are in good agreement with the reported values [9, 11, 18].

In Fig. 8a, the overall O 1s spectra formed on 11% Cr F/M steel can be resolved into three components: oxide (530 eV), hydroxide (531 eV) and adsorbed H<sub>2</sub>O (533 eV). Two prominent peaks observed in most electrolytic media at 530 eV and 531 eV can be attributable to  $O^{2-}$  and  $OH^{-}$  attached to metal ions. However, binding energy appearing at 531 eV and at 530 eV may also be attributed to M-OH bonds and M-O bonds [18]. In 15% Cr ODS steel shown in Fig. 8b, the pattern is almost the same. Where, the O 1s exhibited three components, oxide (530 eV), hydroxide (531 eV) and adsorbed H<sub>2</sub>O (533 eV), respectively.

In Figs. 9a and 9b, the spectrum of Cl 2p show doublet peaks signals at 199 eV and 200 eV indicating that Cl ions are incorporated into the passive films in alloys. The measured ions both steel Cl concentrations are in the range of 8%-9% and the presence of such chloride ions are known to have pronounced effects on the protective properties of the passive film [14, 15]. Their presence enhances hydrolysis and reduces the local pH, causing dissolution of passive film. Hence, it is conceivable that poor pitting corrosion observed in both the steel alloys is attributable to the deleterious role of Cl ions in the passive oxide layer. The schematic representations of passive film breakdown and pit/corrosion initiation in these steel alloys are represented schematically in Fig. 10. The event leading to passive film breakdown has a very distinct property of non-uniformity or occurs at а limited number of sites in the whole surface. The most



Fig. 6 The XPS spectra of Fe 2p detected for passive film layer on (a) 11% Cr F/M steel and (b) 15% Cr ODS steel in different electrolytic solutions.



Fig. 7 The XPS spectra of Cr 2p detected for passive film layer on (a) 11% Cr F/M steel and (b) 15% Cr ODS steel in different electrolytic solutions.





Fig. 8 XPS spectra of O 1s detected for passive film layer on (a) 11% Cr F/M steel and (b) 15% Cr ODS steel in different electrolytic solutions.



Fig. 9 The XPS spectra of Cl 1s detected for passive film layer on (a) 11% Cr F/M and (b) 15 % Cr ODS steel in chloride containing electrolytic solutions.



(d) Corrosion/pit initiation

Fig. 10 Schematic representation of passive film breakdown and pitting corrosion initiation in 11% Cr F/M and 15% Cr ODS steels.

decisive factor to control initiation for the breakdown are the imperfections sites on grain boundary, non-metallic inclusions, or micropores in the film that are responsible for the breakdown of the film. Theories for passive film breakdown and pit initiation have been categorized into three main mechanisms [14, 15, 17] that focus on passive film penetration, film breaking, or adsorption. Details of such descriptions are beyond the scope of this work and are discussed in detail elsewhere [14, 17].

The high resolution XPS spectra of Y 3p and Y 3d of 15% Cr ODS steel are shown in Figs. 11a and 11 b. In 1 kmol  $m^{-3}$  HNO<sub>3</sub> and 1 kmol  $m^{-3}$  HNO<sub>3</sub> + 0.1 kmol  $m^{-3}$  NaClY 3d peak can be differentiated into two



Fig. 11 The XPS spectra of (a) Y 3d and (b) Y 3p detected for passive film layer forms on 15% Cr ODS steel in different electrolytic solutions.

sub-peaks for  $Y_2O_3$  phase that appear at 158 eV (3d<sub>5/2</sub>) and 160 eV (3d<sub>3/2</sub>). Whereas, in borate buffer solution peaks of two different Y 3d and Y 3p are observed at 160 and 301 eV, respectively. The Y 3d doublets binding energies of 158 eV and 160 eV show the presence of  $Y_2O_3$ . The metallic Y 3d peak at 156 eV are not observed. Similarly, the additional Y 3p observed at 301 eV (Fig. 11b) not only show the presence of  $Y_2O_3$  but may indicate its existent in more than one chemical state [9, 11].

# 4. Conclusions

The corrosion resistance and passive film characterization of 11% Cr F/M steel and 15% Cr ODS steel in different electrolytic solutions has been investigated. The results of the OCP plots of both steel alloys are strongly dependent on the electrolytic solutions. The OCP is less noble in chloride containing solutions and more noble in borate buffer solution in both the steel alloys. Active potential of both alloys in chloride media is attributed to less protective passive film due to Cl<sup>-</sup>.

potentiodynamic The polarization results demonstrated that 15% Cr ODS steel offers higher corrosion resistance than 11% Cr F/M steel in the absence of chloride. In chloride containing solutions, both steel alloys exhibited low pitting corrosion resistance. However, pitting potential of 15% Cr ODS steel is higher than 11% Cr F/M steel. The XPS analysis of the oxide layers contains mostly Cr<sub>2</sub>O<sub>3</sub> Fe<sub>2</sub>O<sub>3</sub> along with Y<sub>2</sub>O<sub>3</sub> in 15% Cr ODS steel. The SEM micrograph of pit morphology mainly shows shallow pit attack. The measured corrosion rate in boiling nitric acid up to 48 h for both the steel alloys shows high corrosion rate. In summary, the present study provides detail insight into the effects of different electrolytic media on the corrosion resistance corrosion behavior of 11% Cr F/M and 15% Cr ODS steels. In the presence of chloride, low pitting corrosion was observed in both the steel alloys.

# Acknowledgments

One author Dr. S. Ningshen gratefully acknowledged Japan Society for the Promotion of Science, Tokyo, Japan for the postdoctoral fellowship and financial support.

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