



# The corrosion resistance and passive film compositions of 12% Cr and 15% Cr oxide dispersion strengthened steels in nitric acid media



S. Ningshen<sup>a,b,\*</sup>, M. Sakairi<sup>b</sup>, K. Suzuki<sup>b</sup>, S. Ukai<sup>b</sup>

<sup>a</sup> Corrosion Science and Technology Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

<sup>b</sup> Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060 8628, Japan

## ARTICLE INFO

### Article history:

Received 18 July 2013

Accepted 13 October 2013

Available online 23 October 2013

### Keywords:

- A. Steel
- B. Polarization
- B. XPS
- B. TEM
- C. Passive films
- C. High temperature corrosion

## ABSTRACT

The passive film compositions and corrosion resistance of 12% Cr and 15% Cr oxide dispersion strengthened (ODS) steels in 3 M HNO<sub>3</sub> to 9 M HNO<sub>3</sub> was evaluated. The potentiodynamic polarization plots exhibited a shift in corrosion potential, and higher passive current density with increasing HNO<sub>3</sub> concentrations. In 12% Cr ODS steel, high corrosion rate was observed in all HNO<sub>3</sub> concentrations. However, low corrosion rate observed in 15% Cr ODS steel was attributed to Al<sub>2</sub>O<sub>3</sub> enrichment. The TEM analysis indicated a complex Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> formation in 15% Cr ODS steel, and this may have a role in suppressing intergranular corrosion attack.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

The choices of suitable structural/cladding materials are the key issues that will dictate the design and life of the future fusion reactors [1–5]. This will ensure not only safe, and economical operation of nuclear power systems, but also to achieve higher burn-up and thermal efficiency [1,2,5]. Oxide dispersion strengthened (ODS) steels are high temperature and high performance structural material being developed as cladding materials for fast breeder reactors (FBR) and high-temperature Generation IV reactors [2,3,5]. ODS ferritic/martensitic steels are developed based on advantages properties such as high irradiation resistance [2,5], high temperature mechanical strength and ductility [2,3], low activation, low susceptibility to hydrogen, and/or helium embrittlement [1,3,5], dimension stability under irradiation, corrosion resistance, etc. Further, an increase in operating temperature of the first wall and blanket structures of >700 °C in a fusion reactor may results in improved thermal efficiency of ≥40% [1,3,6,7]. The ODS steels initially developed as cladding material for FBR contain at most 12% Cr. However, depending on application/usage, these steels contain between 9% Cr and 18% Cr. Following hot forming; they are either ferritic or martensitic with a body-centered cubic structure [2,3,5]. The high stable and uniformly distributed fine Y<sub>2</sub>O<sub>3</sub> and/or TiO<sub>2</sub> particles

(2–5 nm) in the metal matrix determine the basic performance in the ODS steels [1,2,5]. The dispersed yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) is used because the free energy of formation is thermodynamically more stable than that of sulfides, nitrides, and carbides phases [1,6]. In addition, it also acts as a strong block for mobile dislocations and serves as a sink for radiation defects at the particle-matrix interfaces; and thereby improving high-temperature strength, and ductility by controlling the grain boundary structure [1,4,5]. Hence, because of many attractive properties, the nano-composite ODS steels are considered as “cross-cutting” materials [8].

The principal aim for reprocessing used fuel is to recover unused uranium and plutonium and thereby close the fuel cycle [9,10]. This enables to provide fresh fuel for existing and future nuclear power plants, an alternative to the waste problem, and avoids the wastage of a valuable resource. The well-proven PUREX (plutonium uranium extraction) process is still the standard method of extraction for the reprocessing of most commercial reprocessing plants. During different stages of the spent fuel dissolution by PUREX process, nitric acid is the main medium used at various concentrations (1 M–14 M) and in boiling condition [9,11,12]. The various stages of PUREX method employ head-end treatment involving chemical or mechanical decladding followed by dissolution of fuel in nitric acid, feed clarification, and chemical conditions of the solution for solvent extraction [9,12]. The operating conditions of high temperatures (boiling condition), and a corrosive environment (highly oxidizing) posed a risk of materials properties degradation or even catastrophic plant failure [11,12]. These efforts have identified different classes of metals and alloys suitable for

\* Corresponding author at: Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060 8628, Japan. Tel.: +81 11 706 7112; fax: +81 11 706 7881.

E-mail addresses: [sningshen@gmail.com](mailto:sningshen@gmail.com), [ning@igcar.gov.in](mailto:ning@igcar.gov.in) (S. Ningshen).

use in various conditions of nitric acid media. These include extra low-carbon and restricted levels of C, Si, P, S, and Mo of AISI type 300 series stainless steel (SS), stabilized austenitic grade or higher Cr, Ni-based nitric acid grade SS [9,11,12], aluminum alloys [13], Ti and Zr based alloys, and recently ODS steels has been also explored for such application [14–18]. As the reprocessing plant is prone to corrosion related failures [9,11,12], it is essential to evaluate and quantify the impact of using ODS steels as a candidate of fuel claddings of advanced nuclear reactors in the reprocessing PUREX environment. Hence, the corrosion behaviors of ODS steels need to be investigated in a large range of dissolution conditions that includes different nitric acid concentrations and boiling temperature. Another specific aspect of ODS steels for nuclear reprocessing application as structural materials is the concern with the uniform/general corrosion resistance [14–18]. It is well known that the corrosion resistance of SS reduces significantly with decreasing Cr concentration below 13%. However, in ODS steels aging embrittlement issue requires not less than 16% Cr [1,3,5,8]. Hence, understanding the corrosion resistance behaviors of acceptable corrosion rate under expected service conditions (nitric acid concentration and temperature) are a key requirement for life-time assessments of components subjected to extreme environments of nuclear reprocessing plants. Further, the feasibility of ODS steels in the fuel dissolution mediums of nitric acid was studied in a limited way, and many corrosion issues are yet to be understood fully. In recent work, Gwinner et al. [17] have shown that in boiling 3 M HNO<sub>3</sub>–9 M HNO<sub>3</sub> medium, the presences of Y<sub>2</sub>O<sub>3</sub> have no influence on the corrosion rate, but significantly dependent on the Cr content. The 18Cr–1 W–Ti ODS steel with higher Cr was found to have lower corrosion rate ( $\leq 0.01$   $\mu\text{m}/\text{d}$ ) than 14Cr–1 W–Ti ferritic ( $\leq 0.1$   $\mu\text{m}/\text{d}$ ) and 9Cr–1 W–Ti ( $\leq 0.01$   $\mu\text{m}/\text{d}$ ) martensitic ODS steels. In 16% Cr ODS steels with or without Al, addition of Al was found to suppress pitting corrosion attack in 1 M HNO<sub>3</sub> [18]. In our recent studies, 9–15% Cr ODS steels show excellent resistance to intergranular corrosion (IGC) attack in different nitric acid concentrations, and this was attributed to the role of dispersed oxide [14,15]. The present study is carried out to develop an understanding of the corrosion resistance and passive film compositions of two experimental ODS steels that are considered a candidate material for fusion reactors and nuclear reprocessing plants. The possible roles of dispersed oxide, correlation of surface morphology, and passive film compositions have been investigated in this work.

## 2. Material and experimental methods

### 2.1. ODS alloy steels and sample preparation

In this study, two experimental ODS steels with the chemical composition of 12% Cr ODS steel (Cr 11.55, Ni 0.34, C 0.16, Mn 0.01, W 1.44, Ti 0.28, Y<sub>2</sub>O<sub>3</sub> 0.37, Fe balance); and 15% Cr (Hf) ODS steel (Cr 15.50, Ni 0.04, C 0.03, Mn 0.01, W 1.80, Al 3.90, Hf 0.59, Y<sub>2</sub>O<sub>3</sub> 0.33, Fe balance); all in wt% were used. The ODS steels are produced by powder metallurgy route. The alloyed powders in a particle size below 150  $\mu\text{m}$  was mechanically alloyed with Y<sub>2</sub>O<sub>3</sub> powders in 20 nm mean diameter for 48 h in argon gas atmosphere using an attrition type ball mill. Mechanical alloyed powders were sealed in cans, and degassed at 400 °C in 0.1 Pa vacuum for 2 h. Then, hot-extrusion was conducted to make bars at 1150 °C. The 12% Cr ODS steel bar was normalized at 1150 °C for 1 h and tempered at 800 °C for 1 h. The 12% Cr ODS steel structure is composed of a ferrite-martensite structure. On the other hand, 15% Cr ODS steel bar was annealed at 1150 °C for 1 h and its microstructure is a full ferrite structure. The detailed method of the ODS steels preparation has been described elsewhere [1,2,14,15,19].

The sample surfaces were abraded up to 1000 grit using SiC papers on all sides before mounting in an epoxy resin, using a brass rod as an electrical connection. The mounted specimens were abraded up to 1000 grit SiC paper finish again. The sample surfaces were ultrasonically cleaned with double distilled water followed by ultrasonic cleaning in acetone to remove the surface contaminants, and air dried and then used immediately for all the electrochemical corrosion experiments.

### 2.2. Boiling and immersion test

The samples for boiling corrosion test were wet ground with SiC paper up to a 1000 grit finish. For conducting the corrosion tests in boiling HNO<sub>3</sub> (120  $\pm$  0.5 °C), 250 ml glass flasks and glass condensers were used. The 12% Cr ODS steel specimens were exposed to different nitric acid concentrations of 3 M HNO<sub>3</sub>, 6 M HNO<sub>3</sub>, and 9 M HNO<sub>3</sub> for 48 h. However, the 15% Cr ODS steel specimens were exposed into different nitric acid concentration of 3 M HNO<sub>3</sub>, 6 M HNO<sub>3</sub>, and 9 M HNO<sub>3</sub> for five 48 h cycles for a total period of 240 h (modified ASTM A 262 standard, practice C Huey test). The solutions were replaced every 48 h, and fresh test solution was used for each period. Subsequently, the specimens were rinsed after the completion of the test in distilled water, cleaned with acetone, dried in a hot air, and the average corrosion rate for five specimens was calculated.

### 2.3. Electrochemical corrosion tests

The open-circuit potential (OCP) was measured prior to the first cathodic scan of the potentiodynamic anodic polarization scans. The OCP was measured in non-stirred condition after immersing the specimen in different nitric acid concentrations of 3 M HNO<sub>3</sub>, 6 M HNO<sub>3</sub> and 9 M HNO<sub>3</sub>. The samples were allowed to stabilize under open circuit conditions for 60 min, and the OCP value was then measured as a function of time up to 60 min.

The potentiodynamic anodic polarization experiments were carried out in different concentrations of 3 M HNO<sub>3</sub>, 6 M HNO<sub>3</sub>, and 9 M HNO<sub>3</sub> at room temperature (24  $\pm$  0.15 °C) using HABF5001 model potentiostat (Hokuto Denko, Japan). The electrochemical corrosion cell consisted of a conventional three electrode system: the working electrode, platinum counter electrode, and reference electrode (Ag/AgCl in saturated KCl). The electrode potential was anodically scanned at a scan rate of 0.167 mV s<sup>-1</sup> until the potential at which breakdown occurred. Two to three sets of electrochemical tests were conducted in each experimental condition, and all the open circuit potential and anodic polarization plots were highly reproducible.

### 2.4. The surface morphology and characterization of passive film compositions

The surface morphology of the specimens after the potentiodynamic anodic polarization and boiling/immersion corrosion test was observed with a scanning electron microscopy (SEM), JEOL JSM-6510LA model, using an acceleration voltage of 10–15 kV.

The specimens for transmission electron microscopy (TEM) were prepared by electro-chemically polishing using a Tenupol-5 and a solution of perchloric acid:acetic acid = 1:19. The distributions of the dispersed oxide particles were analyzed using TEM, JEM-2010 model microscopy with an acceleration voltage of 200 kV.

The X-ray photo-electron spectroscopy (XPS) measurements were carried out on each sample by potential sweep to the passive region. This was followed by holding the samples potentiostatically in the passive region for 60 min: 0.85 V/Ag/AgCl for 12% Cr and 15% Cr ODS steels. Subsequently, samples after the immersion test

Download English Version:

<https://daneshyari.com/en/article/1469048>

Download Persian Version:

<https://daneshyari.com/article/1469048>

[Daneshyari.com](https://daneshyari.com)