Influence of tempering treatment on microstructure and pitting corrosion of 13 wt.% Cr martensitic stainless steel

Sunil Kumar Bonagani[a,c,*], Vishwanadh Bathula[b], Vivekanand Kain[a,c]

[a] *Materials Processing & Corrosion Engineering Division, Bhabha Atomic Research Centre, Mumbai- 400 085, India*
[b] *Materials Science Division, Bhabha Atomic Research Centre, Mumbai- 400 085, India*
[c] *Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094 India*

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ABSTRACT

Tempering of 13 wt.% Cr martensitic stainless steel resulted in nano-sized M_3C carbides at 300 °C, nano-sized Cr-rich $M_{23}C_6$ carbides at 550 °C and sub-micron sized Cr-rich $M_{23}C_6$ carbides at 700 °C. Austenitization resulted in lath martensite with undissolved $M_{23}C_6$ carbides. Pitting resistance for tempered condition was lower than the austenitized condition with least resistance at 550 °C. The observation was attributed to the presence of a Fe-rich surface film and massive carbide precipitation with a Cr depletion zone of 7–9 nm at carbide interface for 550 °C tempered condition as opposed to a Cr-enriched passive film for the austenitized condition.

1. Introduction

Martensitic stainless steels (MSSs) are based on the Fe-Cr-C ternary system and contain 11.5–18.0% Cr and 0.1–1.2% C to obtain a fully austenitized condition at elevated temperatures [1–3]. Depending on the properties required, the carbon (C) and chromium (Cr) concentration levels are selected. A high Cr content will lead to the formation of δ-ferrite − an undesirable phase in MSSs [4–6]. MSSs widely used in many industries like nuclear power plants, steam generators, mixer blades, pressure vessels, turbine blades, oil and gas valves, naval applications and chlorinated plastic injection molds because of their good mechanical properties and reasonable corrosion resistance [2,7–10]. MSSs are typically heated to a temperature, between 980 and 1100 °C, in the austenite phase region in accordance with chemical composition and then cooled at a suitable fast rate to obtain martensite with body centred tetragonal crystal structure in as-quenched condition [2,11]. The hardened MSSs are too brittle for processing therefore tempering is commonly employed to improve ductility and toughness. MSSs are tempered in the temperature range of 200–700 °C to have a better combination of strength and ductility [6,12]. The tempering treatments decrease the dislocation density induced during quenching from austenitization temperature and cause nucleation of new secondary phases such as carbides. The precipitation and coarsening of the secondary phases (mainly carbides) during the tempering treatments play a key role in determining the properties of the MSS in service conditions [13].

Microstructure is one of the important aspects affecting susceptibility to localized corrosion of stainless steels. The characterization of the precipitates formed during the austenitization and tempering heat treatments contributes to a better understanding of the precipitation process and also provides a better interpretation on the material performance in a given environment. Tao et al. characterized the precipitates formed in X12CrMoWVNb10-1-1 steel after different tempering treatments and showed the precipitation sequence of carbide phase with increasing tempering temperature is Fe-rich M_3C → Cr-rich M_7C_3 → Cr-rich $M_{23}C_6$ [13]. In a recent study by Si-Yuna Lu et al. showed the formation of Fe-rich M_3C type of carbides at tempering temperature of 300 °C and formation of $M_{23}C_6$ carbides after tempering at 500 and 650 °C. The precipitation sequence in 13 wt.% Cr MSS is given to be Fe-rich M_3C carbide → Cr-rich $M_{23}C_6$ [14]. Prabhu Gaunkar et al. also reported the formation of M_3C type carbides in the lower tempering temperature range of 150–350 °C, M_3C and M_7C_3 type carbides in the tempering temperature range of 350–500 °C, formation of M_7C_3 and $M_{23}C_6$ type carbides in the temperature range of 550–650 °C and $M_{23}C_6$ and $M_2(C, N)$ (M = Fe and Cr) type carbides in higher tempering temperature of 650–750 °C in 12 wt.% Cr MSS [12]. Therefore, the type of the carbides formed during tempering treatment is dependent on chemical composition of the material, tempering temperature and tempering treatment duration. [12–16]. Since, MSS are always used in a tempered condition, localized corrosion (pitting and intergranular) is a potential degradation issue due to the precipitation of Cr-rich carbides at prior austenitic grain (PAG) boundaries and also at martensitic lath boundaries. The precipitation of the Cr-rich carbides results in Cr depletion at the interface of carbide and matrix. So far, to the best of our knowledge, no technical papers are available on the

* Corresponding author at: Materials Processing & Corrosion Engineering Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India.
E-mail address: bsunil@barc.gov.in (S.K. Bonagani).

extent of Cr-depletion region at the carbide-matrix interface region in tempered 13 wt.% Cr MSS. The authors measured the degree of sensitization in 13 wt.% Cr MSS developed with tempering treatments by a modified double loop electrochemical potentiokinetic reactivation test and showed tempering at 550 °C makes it highly susceptible to interlath corrosion [17]. This drastic reduction in corrosion resistance of tempered 13 wt.% Cr MSS is attributed to the presence of Cr depletion at the carbide-matrix interface regions. Until now, a few studies are available on the pitting corrosion behaviour of MSS with different tempering treatments [9,14,16,18–20]. In general, pit nucleation occurs at the surface active sites/heterogeneities such as inclusions, precipitates and the regions with weak passive films [1,21–23]. The surface oxide film formed over Cr depleted regions (sensitized regions) is known to be weak (and not stable) therefore leads to preferential corrosion attack. Sensitization increases the susceptibility to localized corrosion due to the formation of the Cr-rich carbides and associated Cr-depletion at the carbide-matrix interface. Pitting corrosion of sensitized stainless steels has been shown to be dependent on the carbide interfaces and also the carbide interfaces having Cr depletion regions [23–26]. There are no reported studies on the nature of the passive films formed on tempered 13 wt.% Cr MSS and their influence on localized corrosion. Therefore still the questions remain on how to relate microstructure (carbide precipitation and extent of Cr depletion at carbide matrix interface) and passive film properties with pit initiation in MSS with different tempering treatments.

In the present study, the microstructural changes with tempering treatments, are studied using X-ray diffraction and transmission electron microscopy (TEM) coupled with energy dispersive spectroscopy (EDS). The Cr concentration profiles at carbide-matrix interface were established for tempered MSS. The localized corrosion studies were carried in 0.1 M NaCl solution using electrochemical techniques and passive films formed at open circuit potential were characterized by X-ray photo electron spectroscopy (XPS). The relationship between type of the precipitates formed during tempering and pitting corrosion behaviour of 13 wt.% Cr MSS in NaCl solution is discussed.

2. Experimental procedure

2.1. Materials, heat treatments and microstructural characterization

The chemical composition of the material used in the present study was analyzed using spark-optical emission spectroscopy and is given in Table 1. Specimens of size 60 mm x 12 mm x 12 mm were austenitized at 1020 °C for 0.5 h in a muffle furnace followed by oil quenching to room temperature. Subsequently, the austenitized specimens were tempered at 300, 550 and 700 °C for 2.5 h followed by air cooling.

The presence of phases in the tempered specimens was analyzed by XRD technique (Bruker make, D8 discover) with Cu K$_\alpha$ radiation with step size of 0.02°. The volume fraction of the retained austenite was estimated from the integrated intensities of austenite and martensite peaks [27]. The microstructural changes occurring with different tempering treatments were characterized using TEM (FEI TECHNAI F 200 kV). The TEM samples were prepared in two steps. First, a 0.2 mm thick slice was pre-thinned to 80 μm by grinding on successively finer emery papers of 240–600 grit. From such 80 μm thin sheet, 3 mm discs were punched out. The pre-thinned 3 mm discs of 80 μm thick specimens were then twin-jet polished in a mixture of 10% perchloric acid and 90% methanol at −40 °C and 20 V potential to create a small hole

Table 1
Chemical composition (in wt.%) of the 13 wt.% Cr martensitic stainless steel used in the present study.

C	Cr	Mn	Mo	Ni	V	P	Cu	Si	Fe
0.31	13.3	0.81	0.09	0.27	0.04	0.025	0.48	0.33	Rest

approximately in the centre of the disk. Selected area diffraction (SAD) patterns were acquired from the precipitates and matrix to identify the phases and precipitates. The chemical composition of the matrix and precipitates was analyzed using TEM-EDS (Oxford instruments). The uncertainty in the EDS measurements is less than 0.5 wt.%. It is difficult to precisely analyse the C content in the precipitate by TEM-EDS and so C content is not reported in the present study and only the elements of Fe and Cr are considered in EDS analysis. The width of the lath in all the conditions is measured using image-J software by taking a minimum of 20 laths for each condition.

The precipitates formed in tempered specimens (550 and 700 °C) were extracted by dissolving the martensitic matrix electrochemically in 10 vol.% hydrochloric acid-methanol solution to identify the precipitates by XRD technique. The tempered specimens were ground up to 400 grit emery paper and ultrasonically cleaned in acetone. The dissolution was done by applying a potential difference of 1.5 V between the specimen (anode) and the platinum foil (cathode) for a period of 48 h at room temperature (26 °C). The precipitates were extracted by centrifuging the solution. The extracted precipitates were transferred on glass slide for XRD analysis.

2.2. Electrochemical measurements

All the electrochemical studies were carried out in a conventional three-electrode cell using a Pt foil as the auxiliary (counter) electrode, saturated calomel electrode (SCE) as the reference electrode and the MSS specimen as the working electrode. The MSS specimen was provided an electrical contact from one side of the specimen and was set in a cold setting resin to expose the opposite side of the specimen. The electrical connection wire was insulated to avoid contact with the test solution. All the specimens were ground metallographically using emery papers with grit size up to 1200 and then mirror polished using 1 μm diamond paste before each electrochemical experiment. The specimens were cleaned with a soap solution, degreased in ethanol and dried in warm air. The contact regions between the test specimen and the resin were covered with a lacquer to avoid presence of any crevice when exposed to the test solution. The 0.1 M NaCl solution was prepared using distilled water and reagent grade NaCl. The solution was deaerated for 45 min using Ar gas and then the working electrode was introduced into the cell. The Ar gas bubbling was continued during the experiment. All the specimens were cleaned cathodically at −1 V$_{SCE}$ for 2 min to remove the air formed oxide film after specimen's immersion into the solution. The potentiodynamic polarization tests were performed in 0.1 M NaCl solution at room temperature in deaerated condition. A scan rate of 1 mV/sec was employed. After polarization tests, the tested specimens were examined using optical and field emission − scanning electron microscopy (FE-SEM; Carl Zeiss make). The potentiodynamic polarization tests were repeated twice for each specimen. The average and standard deviation (σ) was calculated from the set of three data points and reported in Table 2.

Potentiostatic polarization tests were also performed in 0.1 M NaCl solution to investigate the metastable pitting corrosion for MSS specimen tempered at different temperatures. The potentiostatic polarization tests were carried out at −100 mV below the E$_{pit}$ expect for the specimen tempered at 550 °C, for which the test was carried out at 20 mV above the E$_{corr}$.

Rectangular coupons of the austenitized and specimens tempered at 550 °C were exposed in deaerated 0.1 M NaCl solution for period of 15 h and the formed surface film was characterized by X-ray photo electron spectroscopy (XPS) (SPECS) technique. After immersion in the test solution, the specimens were cathodically polarized at −1 V$_{SCE}$ for 2 min to remove any air formed oxide film. The XPS analyses were carried out in an electron spectrometer using a monochromatic Al K$_\alpha$ X-rays (hν = 1486.74 eV) as the primary radiation source. The binding energies were calibrated with respect to the Ag 3d$_{5/2}$ peak occurring at 368.26 eV. The energy spectra of the photoelectrons were analyzed by