

**Chapter-2**  
**Material and Methods**

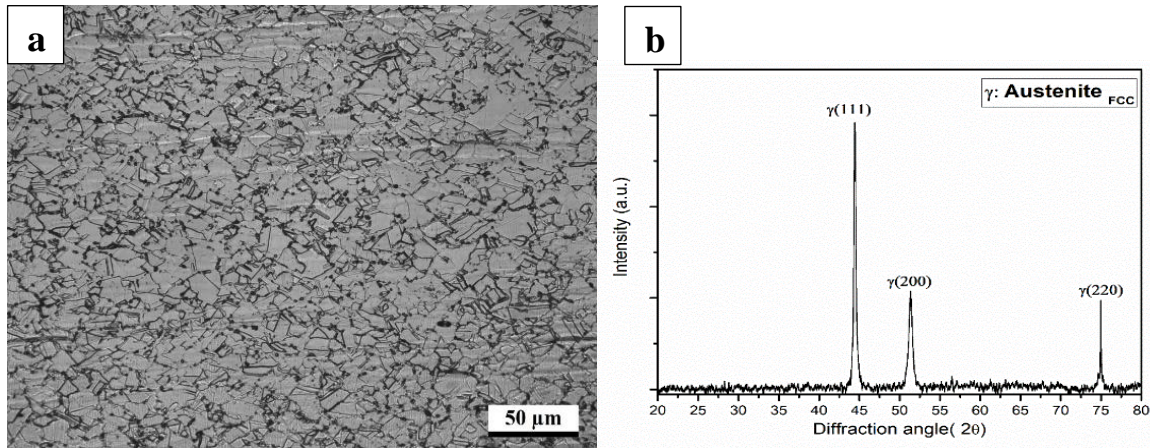


## 2.1 Introduction

This chapter presents outline of the Fe-18Cr-21Mn-0.65N austenitic stainless steel and the method of experimentation used, it is divided into three sections. The first section shows the composition, grain size, and mechanical properties of the material in solution annealed condition. The second section presents experimental methods and parameters used for different studies viz. oxidation, metal dusting, solid particle erosion, and potentiodynamic corrosion. The third section describes the technique used for the characterization such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Electron Probe Micro Analysis (EPMA).

## 2.2 Material

The low nickel Fe-18Cr-21Mn-0.65N austenitic stainless steel was procured in form of hot rolled plate of size 330x330x16mm<sup>3</sup> from M/s Jindal Stainless Steel Ltd. Hisar. Chemical composition was: 0.057C, 18Cr, 21Mn, 0.33Si, 0.65N, 0.2Mo, 0.08Ni, 0.05Cu and 59.63 Fe by wt%. The hot rolled plate was cut into small pieces and solution treated at 1050°C for 1 h, and quenched in water. Disc shaped samples of 8mm diameter and 4mm thickness were prepared for microstructural characterization. These samples were polished up to 2000 grit emery paper followed by cloth polishing with 0.5µm alumina paste and electrolytically etched in 10% oxalic acid solution at 5V for 90 seconds and examined under optical microscope. Optical microstructure of the solution treated material is shown in Figure 2.1 a. Figure 2.1 b shows the X-ray diffraction plot with exclusive peaks of austenite,  $\gamma$  phase.



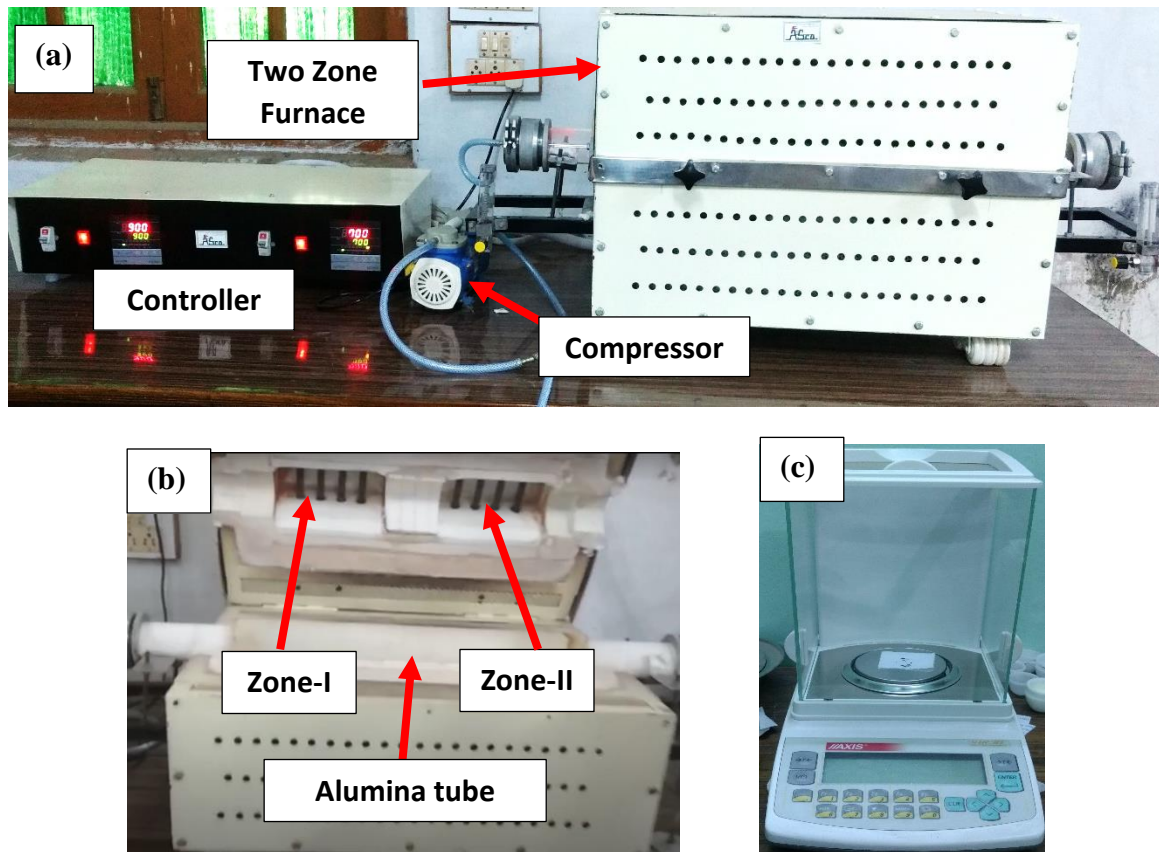
**Figure 2.1** (a) Optical microstructure and (b) X-ray diffraction of Fe-18Cr-21Mn-0.65N austenitic stainless steel in solution annealed condition.

## 2.3 Experimental Methods

### 2.3.1 Oxidation Test

The disc shaped samples of 8mm diameter and 4 mm thickness of the solution treated material were mechanically polished on emery papers up to 2000 grit and ultrasonically cleaned in acetone, for oxidation tests. Cyclic oxidation tests were performed in static air (SA) and dynamic humid air (DA) at two flow rates of 2 lpm and 6 lpm at 400, 500, 600, and 700°C, up to 100 h, at 1 atm pressure.

A two-zone tube furnace with  $\pm 2^\circ\text{C}$  temperature control was used for oxidation study (**Figure 2.2**). The relative humidity of air was maintained at 95% at 25°C. Each specimen was loaded in individual alumina boat and weighed before placing inside the furnace. To ensure reproducibility, five samples were tested at each temperature in each condition. The cyclic oxidation test consisted of first 6 cycles of 5 h soaking and rest 7 cycles of 10 h soaking, followed by air cooling to room temperature. The weight change was measured using Axis electronic balance of  $\pm 0.1\text{mg}$  accuracy.



**Figure 2.2:** (a) Photograph of the oxidation test set up (b) inside view of two zone split tube furnace, and (c) Axis digital balance.

### 2.3.2 Metal Dusting

Coupons of  $17 \times 15 \times 2.5 \text{ mm}^3$  size were prepared from solution treated pieces of the material and a hole of 3 mm diameter was drilled  $\sim 2 \text{ mm}$  below the top edge in the middle to hang the sample in the furnace. The coupon is shown in the experimental setup as item no. 9 in **Figure 2.3**. The coupons were mechanically polished by SiC emery papers, up to 2000 grit, and ultrasonically cleaned in acetone for 5 min before loading in the furnace. The initial weights of the coupons were recorded using Axis electronic balance with an accuracy of  $\pm 0.1 \text{ mg}$ .

Metal dusting tests were carried out at four different temperatures of 400, 500, 600, and  $700^\circ\text{C}$ , for 300 h, in a gas mixture of 75%  $\text{H}_2$  and 25 %  $\text{CO}$ , at 1 atmosphere pressure.

Considering the reactions 1.10 and 1.12 in equilibrium, the activity of carbon ( $a_c$ ), and oxygen partial pressure ( $p_{O_2}$ ) was calculated using reactions 1.11, 1.13, and 1.15 [83, 84].

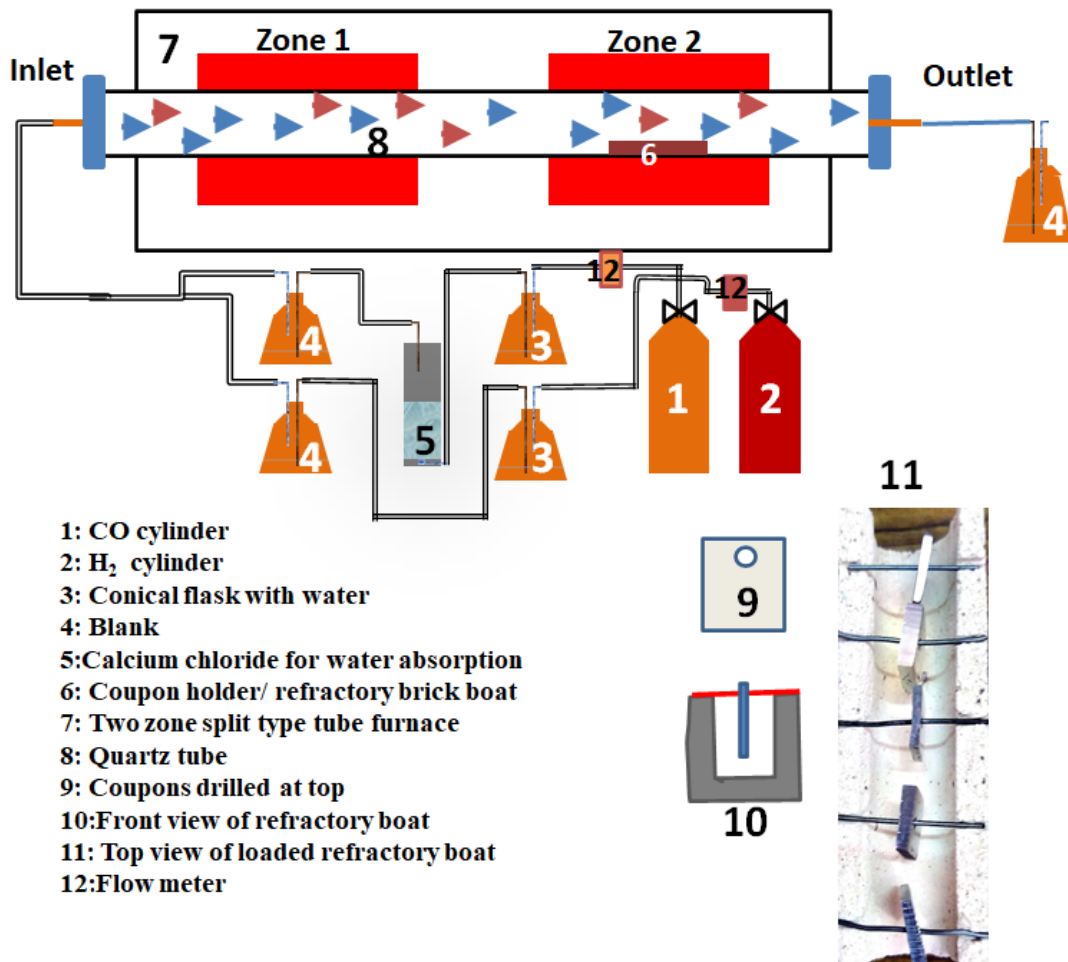
**Table 2.1:** Carbon activity and partial pressure of oxygen at corresponding temperature.

T(°C)	$a_c$	$p_{O_2}$ (atm)
400	4750	$6.422 \times 10^{-28}$
500	205	$1.44 \times 10^{-23}$
600	18	$2.65 \times 10^{-20}$
700	2.7	$1.63 \times 10^{-17}$

The activity of carbon and partial pressure of oxygen were different at different temperatures is given in table 2.1. It has been reported that addition of water in the gas mixture lowers the activity of carbon compared to that in the gas mixture without water content [46, 85]. In the present investigation, a gas mixture was selected without water content to accelerate the process of metal dusting. The experimental setup for metal dusting test is shown in **Figure 2.3**. The temperature inside the furnace was controlled within  $\pm 2^\circ\text{C}$  of the set temperature. Gas cylinders of high purity (99.9%) hydrogen and carbon monoxide were used for the supply of  $\text{H}_2$  and  $\text{CO}$  gas during metal dusting test. The gas flow rate was maintained at 200 ml/min at all the temperatures, with a final gas mixture velocity of 1.18 mm/sec. Reproducibility of the tests was ensured by placing five coupons at each temperature of exposure. Coupons were hanged by nichrome wire above a boat made of corundum brick, as shown in **Figure 2.3** (item no.11) in such a way that the polished surface of coupons was exposed parallel to the gas flow direction.

Nitrogen gas was passed for one hour to flush the air inside the tube furnace and reduce the oxygen partial pressure, before the temperature was raised to the set temperature. Once the set temperature was reached, the ratio and mass flow rate of the gas mixture was regulated. Cyclic thermal exposure was given to all the test coupons at all four temperatures, by removing the coupons at intervals of 10 h, up to 100 h. After 100 h of exposure, coupons

were taken out at regular intervals of 50 h, up to 300 h. The coupons were cooled to room temperature in air and weighed after each cycle. Before removing the test coupons from the furnace, nitrogen was passed for 15 min to flush the gas mixture, at all the test temperatures after each cycle. After weighing, the coupons were kept back in the furnace and nitrogen was flushed for 15 min to remove traces of air/ oxygen, before passing the syngas mixture. At the end of each cycle, coupons were examined for carbon deposition and weighed. Coupons were ultrasonically cleaned in acetone and the carbon left in acetone was carefully collected for further studies. The coupons exposed at 400 and 500°C, with deposited carbon, were directly characterized under SEM.



**Figure 2.3:** Experimental setup for metal dusting test.

### 2.3.3 Solid Particle Erosion Test

Samples of  $25 \times 25 \times 5 \text{ mm}^3$  size were prepared from the solution treated high manganese nitrogen stainless steel and mechanically polished on 2000 grit SIC emery paper, finally with  $0.5 \mu\text{m}$  alumina paste for mirror finish. The polished samples were exposed in air at 400, 500, 600, and  $700^\circ\text{C}$  for 100 h and subjected to erosion test at the respective temperatures of pre oxidation ( $400, 500, 600,$  and  $700^\circ\text{C}$ ), as per ASTM G76-95 standard, in a DUCOM air jet erosion tester as shown in **Figure 2.4**. The unexposed samples, without pre oxidation at elevated temperature, were tested for erosion at room temperature. Alumina particles of average size  $50 \pm 1.7 \mu\text{m}$  were used as erodent. The physical properties of alumina particles and operating conditions for erosion test are shown in Table 2.2 and 2.3, respectively. **Figure 2.5 a & b** shows SEM micrographs and particle size distribution of alumina particles, respectively. Three different impact angles of  $60^\circ, 75^\circ,$  and  $90^\circ$  were employed. To ensure reproducibility, three samples in each condition, were tested. Samples were kept in a specimen holder, placed in furnace and heated at  $5^\circ\text{C}$  per min. Once the test temperature was reached, the erodent particles were bombarded on the sample surface. After each test, samples were ultrasonically cleaned and weighed with an Axis digital balance of  $0.01\text{mg}$  accuracy. The weight loss was recorded after a 5 min interval and the erosion rate (g/g) was calculated after 20 min, using the following equation:

$$\text{Erosion Rate} = \frac{\text{weight loss of target material}}{\text{weight of the erodent particle impinging on the target surface}} \quad (2.1)$$

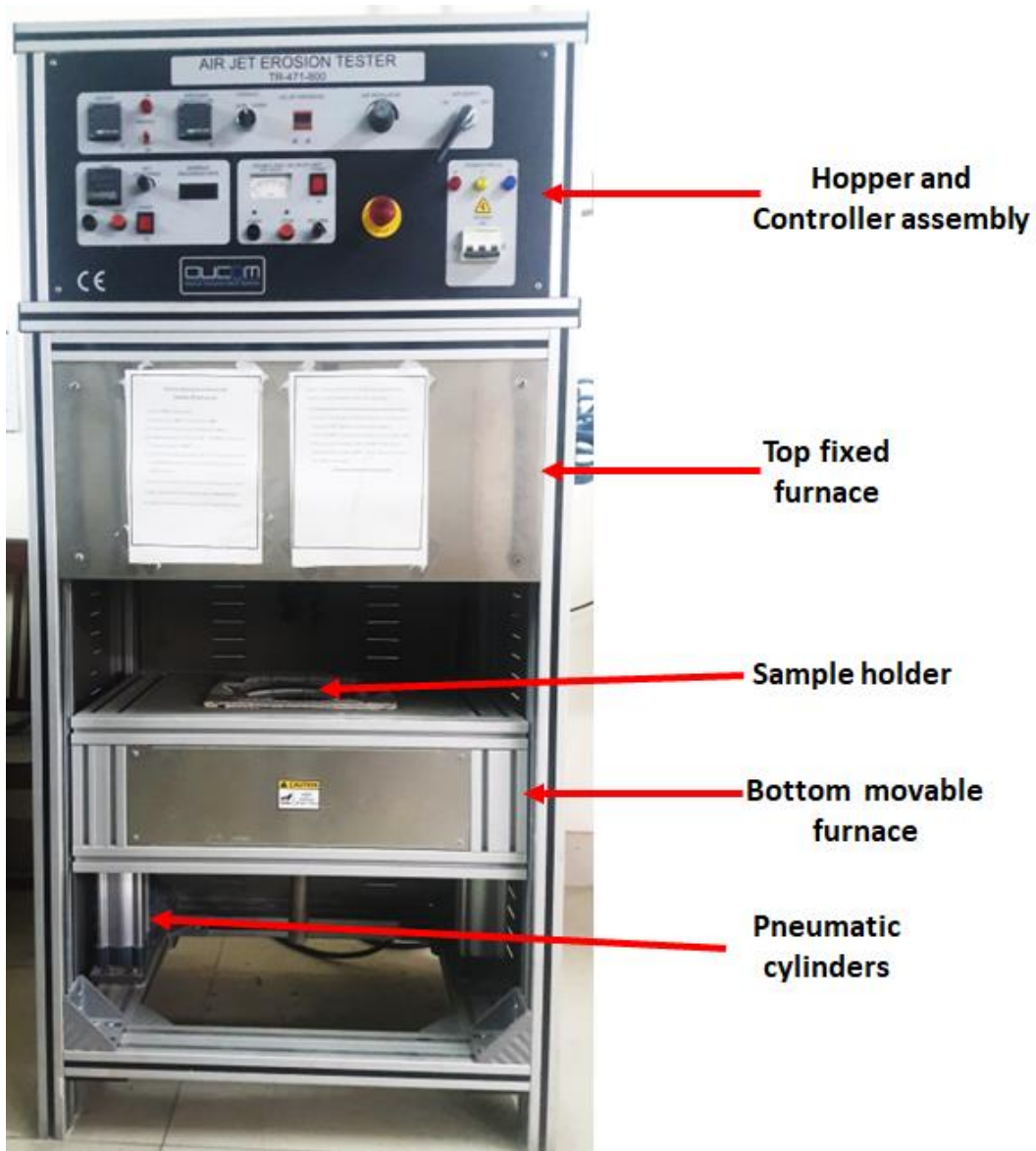
**Table 2.2:** Physical properties of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) erodent.

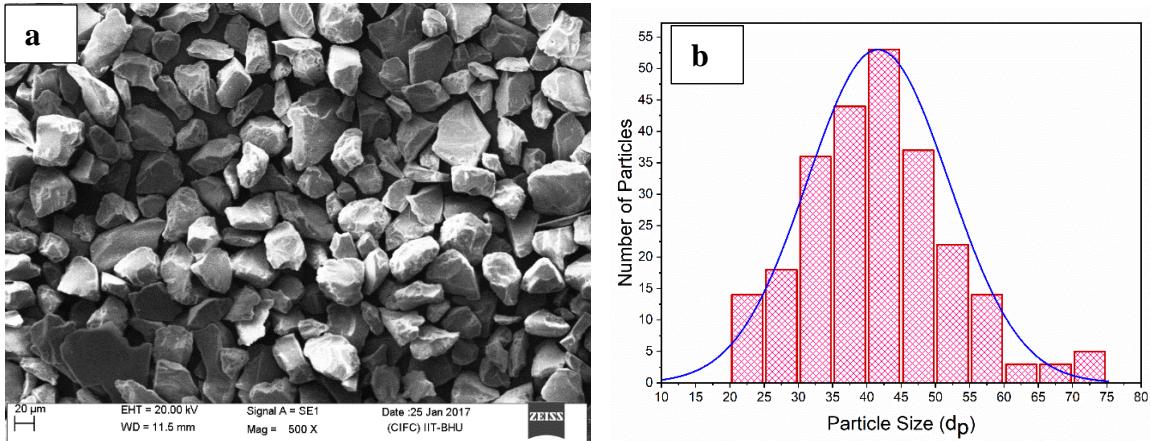
Crystal Phase	Alpha
Specific Gravity	$3.95 \text{ g cm}^{-3}$
Particle Shape	Sharp, angular
Vickers Hardness	1600 Hv
Average particle size	$50 \mu\text{m}$



**Table 2.3:** Operating conditions for solid particle erosion test.

Nozzle diameter	1.5 mm
Standoff Distance	10 mm
Test gas	Dry compressed air
Test duration	1 h (10 min cycle time)
Test temperature	Room temp, 400°C, 500 °C, 600°C and 700°C
Impact angle	60°, 75°, 90°
Abrasive flow rate	4.5±0.5 g min <sup>-1</sup>
Impact velocity	100 m s <sup>-1</sup>

**Figure 2.4:** Photograph of Ducom air jet erosion tester.



**Figure 2.5:** (a) SEM micrograph of alumina particles and (b) Particle size distribution of erodent particles ( $\text{Al}_2\text{O}_3$ ).

### 2.3.4 Corrosion Test

30 coupons of dimension  $25 \times 25 \times 16 \text{ mm}^3$  were prepared from the solution treated pieces and these were exposed at 400, 500, 600, and 700°C for 5, 50, and 100 h, to study the effect of duration of exposure, at the above temperatures, on corrosion behavior. Disc shaped samples of diameter 12mm and thickness 3mm were machined from the coupons exposed at different temperatures, for corrosion test. At each temperature and time of exposure, two samples were tested to check reproducibility of the data. The samples were polished on SiC paper to 2000 grit size and then cloth polished to mirror finish and ultrasonically cleaned for 10 min in acetone to remove dust particles/ alumina particles, if any, from the surface. Two samples were tested also without exposure at elevated temperature, for comparison.



**Figure 2.6:** Photograph of CorrTest electrochemical work station, with flat type corrosion cell.

Potentiodynamic polarization scanning was performed on CorrTest electrochemical workstation (Model no. C52350), shown in **Figure 2.6**. Regular three electrode system was used, in which there was a platinum sheet as counter electrode, Ag / AgCl (KCl saturated) as a reference electrode, and sample surface of 1 cm<sup>2</sup> as working electrode. Corrosion tests were carried out in 0.5 M NaCl solution, dissolving 35 grams of analytical grade NaCl in 1 liter of distilled water. Open circuit potential was measured at frequency of 1 Hz for 1 h for all the samples to ensure the stability of working electrode surface. Electrochemical impedance spectroscopy was carried out after OCP measurement for analysis of the passive layer. EIS was performed in frequency range of 100 kHz to 10 mHz at OCP and 5 mV amplitude. The potentiodynamic polarization test was performed at -400 mV vs OCP to 700 mV vs. OCP at scanning rate of 1mV/s. After corrosion, test samples were cleaned and preserved for further characterization.

#### 2.4 Characterization Techniques

Surface morphology and cross sections of the oxidized, metal dusted, eroded, and corroded specimens were characterized using scanning electron microscope (SEM-Carl Zeiss-sigma and HR-SEM Nova Nano SEM 450 and Zeiss EVI/18) and the composition at the surface was analyzed by energy dispersive spectroscopy (EDS-Oxford instruments-INCAx and Octane Plus and Hikari Pro and Oxford instruments-INCAx) at 10 kV. The phases after oxidation and metal dusting were characterized by X-ray diffraction technique using Rigaku MiniFlex500 diffractometer and PANalytical diffractometer using Cu K $\alpha$  radiation with  $\lambda=1.514 \text{ \AA}$  and Co-K $\alpha$  radiation ( $\lambda=1.79021 \text{ \AA}$ ) respectively. The precipitates formed due to high temperature exposure were examined by transmission electron microscopy (TEM) (Tecnai G2 20 TWIN FEI) operating at 200 kV. TEM foils were prepared from thin slices, partitioned parallel to the oxidized surface, using Buehler saw. The thin sections were reduced to a thickness of  $\approx 40 \text{ \mu m}$  by mechanical polishing on emery papers and discs

of 3 mm diameter were punched out. TEM foils were prepared by electropolishing of 3mm discs using a twin jet polisher (Struers-Tenupol-5) in an electrolyte of 5% perchloric acid (HClO<sub>4</sub>) and 95% methanol; cooled to -25°C, at 20V.

The cross section of metal dusted coupons was subjected to Electron Probe Micro Analyzer (EPMA) for analysis with CAMECA SX Five instrument at a voltage of 15 kV and current of 10 and 20 nA with a LaB<sub>6</sub> source in the electron gun. After potentiodynamic polarization test, samples were subjected to XPS analysis to characterize the corrosion products formed. A Thermo Fisher Scientific Make K-Alpha spectrometer with Al K $\alpha$  X-ray was used for XPS analysis. The position of hydrocarbon carbon C<sub>1s</sub> peak was assumed to be at 284.6 eV and was used as a standard for determining the binding energy of other photoelectron peaks. A Shirley background subtraction was used to fit the XPS data using XPS Peak Fit 4.1 software.

The variation of hardness from the subsurface of erosion scars to bulk was recorded using Vickers hardness tester LV-700AT with 10g applied load, for 10 s dwell time. Tensile tests were, carried out using cylindrical samples of size 15.5 mm gauge length and 4.5 mm gauge diameter, pre-exposed at 400, 500, 600, and 700°C for 100 h, at 400, 500, 600, and 700°C respectively, using Instron UTM.