Effect of Thermal Cycling on Oxidation of Nickel Based Superalloys in Presence of Aggressive Ions

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Superalloys are considered potential candidates to be used in high temperature applications. In the present study, experimental measurements of high temperature oxidation in presence of aggressive ions of Nickel base superalloy (Hastelloy-X) have been carried out at 700°C, 800°C and 900°C for exposure time durations of 1, 3, 5, 10, 20, 50 and 100 hours. The oxidation behavior of superalloy Hastelloy X in the presence of aggressive media, normally, NaCl and Na_2SO_4 is to identify the surface scales that have been formed. After oxidation experiments, the samples were characterized using Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) to find out the formed phases. The results showed that the major corrosion products formed are Nickel Chromites $NiCr_2O_4$ with some Chromium Cobalt Oxide $CoCr_2O_4$ spinels in additions to chromium oxide Cr_2O_3. The obtained results of Hastelloy X were compared with the results achieved previously for Inconel 617. In this study, the activation energy of Hastelloy X was estimated and found to be Ea = 57.84 KJ/mole.

Introduction

Due to its excellent oxidation and corrosion resistance at elevated temperatures, Nickel-based alloys are utilized in many applications such as, gas turbines, aerospace, heat-treating industries, nuclear reactors, electric-resistance heaters and petrochemical industries [1-2]. The resistance of nickel-based superalloys to oxidation and hot corrosion depends on the contents of chromium and other reactive elements including W, V, and Mo [3]. Hastelloy X is a nickel-chromium-iron-molybdenum alloy. It has an exceptional combination of oxidation resistance and high temperature strength; it also has an exceptional resistance to stress corrosion in petroleum, petrochemical industries and power generation plants [4, 5].

In power plants or gas turbines, there are residual fuel oil and combustion gases which may contain sodium sulphate (Na_2SO_4) and sodium chloride (NaCl). The aggressive mixture of Na_2SO_4 and NaCl has a melting temperature of 620^oC [6]. The aggressive mixture and impurities in the fuel at high temperatures cause oxidation depositing on turbine blades. The corrosion rate rapidly increases due to the faster transport phenomena in liquid phase causing catastrophic corrosion phenomena [7-8].

The aim of this work is to study the oxidation behavior of the superalloy Hastelloy X in the presence of aggressive media, normally, NaCl and Na_2SO_4 to identify the surface scales that have been formed at the specified test temperatures (700, 800 and 900^oC).

Experimental Procedure

Material and sample preparation

Hastelloy X is used as a substrate material. The alloy composition is given in Table (1). Disc specimens, of 10 mm diameter and 2 mm thick, were cut from the original superalloy rod by wire electrical discharge machining. The specimen's surfaces were polished using emery papers of 320, 600, 800, 1000 and 1200 grit sizes followed by cloth polishing with alumina suspension (1µ). They were then washed by distilled water and cleaned with alcohol in ultrasonic device. The alumina boats used for oxidation experiments were preheated for 8 hr at 900°C in order to get rid of any moisture. Weight of alumina boats containing samples was conducted using a digital weighting balance (model Mettler Toledo AG245) of 0.01 mg accuracy. The specimens were sprayed with a solution containing 1% NaCl + 1% Na$_2$SO$_4$ for 10 minutes.

Oxidation testing

The superalloy specimens were exposed to oxidation in a silicon carbide furnace (model Carbolite Furnaces RHF12/13). Seven samples were tested at each temperature. The exposure times were 1, 3, 5, 10, 20, 50 and 100 hrs. The oxidation investigations were carried out at 700°C, 800°C and 900°C for the specified time periods mentioned before. The weight gain measurements were carried out each time after the specimens cooled for 20 minutes at room temperature to estimate the oxidation kinetics. After achieving oxidation tests, the samples were examined for their surface morphology with Scanning Electron Microscope (SEM) model no. JEOL JSM 5600 LV and the surface oxidation products were investigated by XRD model no. D8 advance X-ray diffractometer, Bruker AXS.

Results and Discussion

In many high temperature applications, the alloy degraded severely, due to deposition of molten salts specially alkali metal sulfides, alkali metal chlorides or mixture of these salts [9]. The molten salts of these compounds provide a medium for the transport of oxidant inward toward the metal and dissolved metal ions outward. It was stated that the presence of NaCl in the mixtures of NaCl, Na$_2$SO$_4$ initiates attacks in high chromium content alloys [10, 11].

Thermogravimetric analysis

The specific weight change (ΔW/A) versus time in hours for Hastelloy X is presented in Figure (1). The square of the specific weight change for time periods up to 100 hrs at 700°C, 800°C, and 900°C is shown in Figure (2). The parabolic rate content (k$_p$) at each temperature was calculated in mg^2. cm^{-4}. h^{-1} from the plots of (ΔW/A)^2 versus time according to the following equation:

$$\left(\frac{\Delta W}{A}\right)^2 = K_p.t \tag{1}$$

The values of the parabolic rate constant (k$_p$) for Hastelloy X at 700°C, 800°C, and 900°C are 0.2603 , 0.4717 and 0.6487 (mg^2. cm^{-4}. h^{-1}) respectively.

High temperature parabolic oxidation indicates that the thermal diffusion process is the rate determining. The lower k$_p$ value leads to the higher oxidation resistance and vice versa. The K$_p$ values are compared with K$_p$ for Inconel 617 [12, 13] which clearly show that Hastelloy X shows oxidation resistance with lower kp value than that of Inconel 617.

Hastelloy-X oxidation rate was confirmed by determining the activation energy (Ea). From Figure (2), the parabolic rate constant Kp at 700 °C, 800 °C and 900°C are determined. Figure (3) shows the natural logarithm of the calculated parabolic rate constant for Hastelloy-X versus the reciprocal of temperature in degrees Kelvin. From the Arrhenius equation (2) [14], (ln K$_p$ vs.1/T), Figure (3) straight line with a gradient (Ea/R) gives the activation energy (Ea).

$$\ln K_p = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \frac{\Delta S}{R} \tag{2}$$

Table (1): Nominal Composition of Hastelloy X Specimens (wt %)

	Ni	Cr	Mo	Co	W	Mn	Si	Al	Nb	P	Ti	S
Hast-X	48.172	21.127	8.59	1.55	0.59	0,51	0.3	0.12	0.1	0.02	0.01	0.001

The Hastelloy-X activation energy was estimated and it is Ea = 57.84 kJ/mol and the change in the entropy $\Delta S = 0.052$ kJ/mol.K. The chemical reaction rate due to oxidation of the specimens is directly proportional to the temperature. According to the spontaneity of the oxidation process with the temperature, the reaction is endothermic.
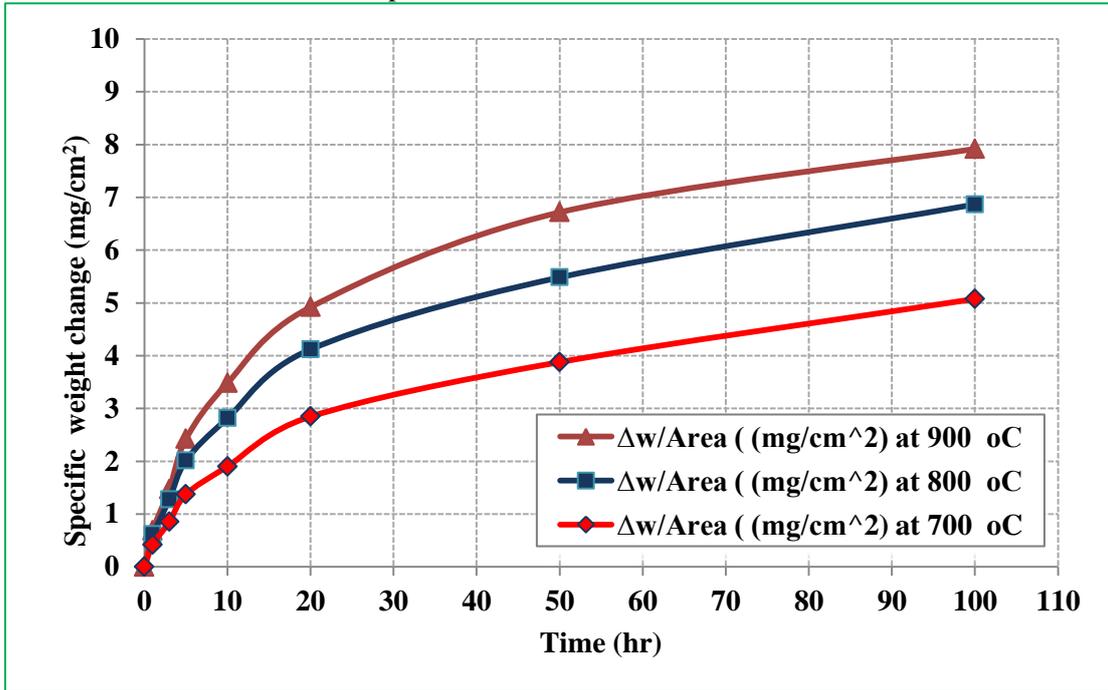
Figure (1): Hastelloy X specific weight change with time up to 100 hrs due to oxidation at 700°C, 800°C, and 900°C
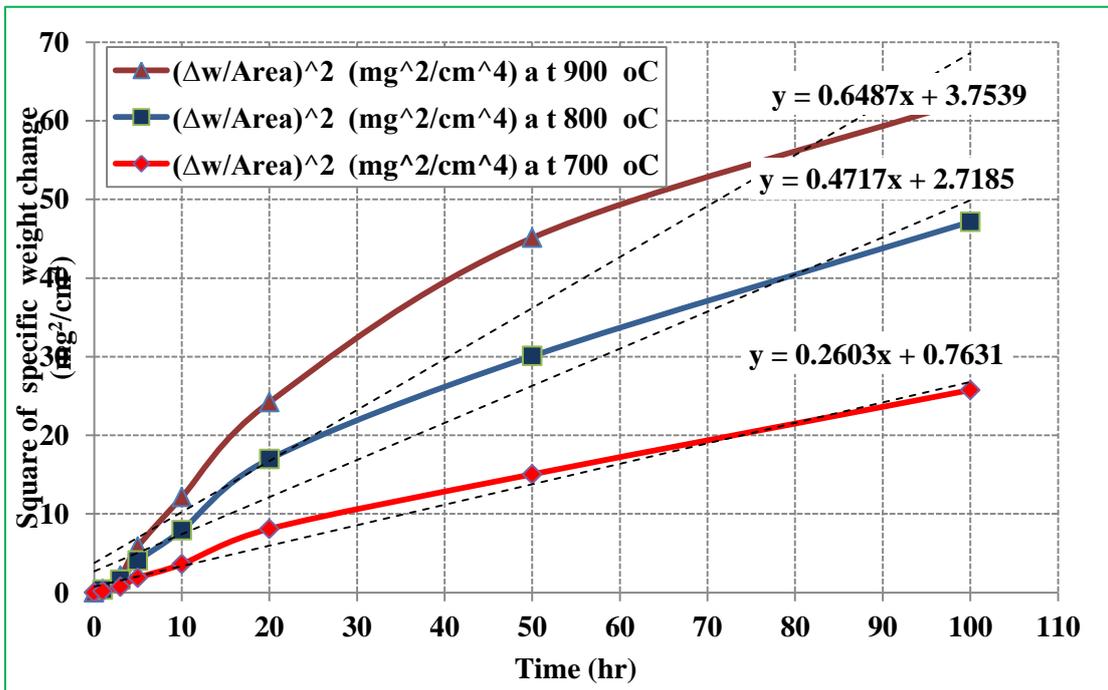
Figure (2): Hastelloy X square of specific weight change (mg^2/cm^4) due to oxidation for time periods up to 100 hrs at 700°C, 800°C, and 900°C
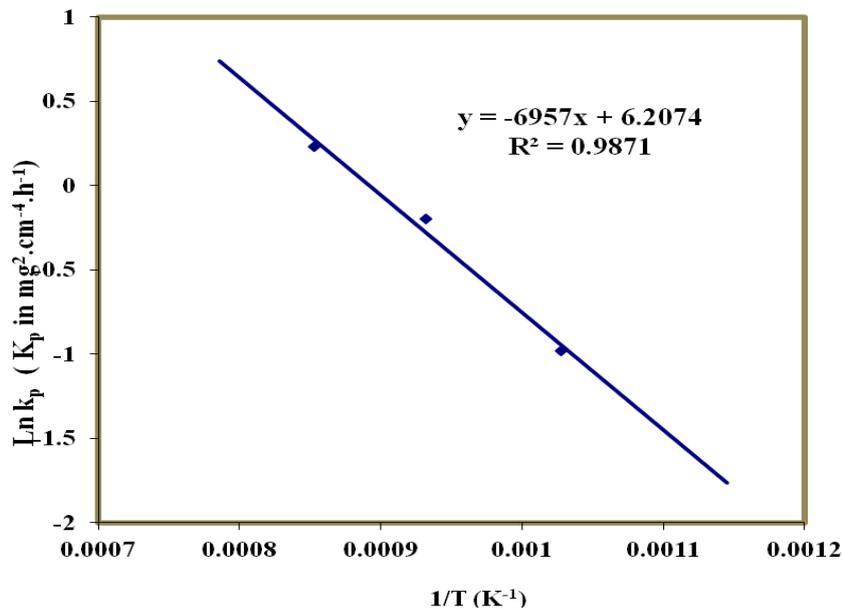
Figure (3): The natural logarithm of the calculated parabolic rate constant for Hastelloy-X versus the reciprocal of temperature in degrees Kelvin

Oxidation mechanism

From the thermogravimetric analysis, it was noticed that the superalloy Hastelloy X shows parabolic behavior at exposure times up to 10 hrs. After 50 hours, it was found that there is a complete rupture of scale. The presence of NaCl accelerates the oxidation rate as it reacts with oxides and thus releases the chlorine which in sequence reacts with oxides to form the volatile chlorides, as per the following reactions [15];

$4NaCl(l) + Cr_2O_3(s) + 5/2\ O_2(g) \rightarrow 2Na_2CrO4(s) + 2Cl_2(g)$
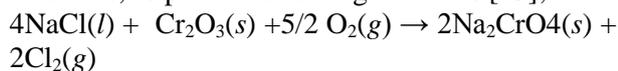
The chloride is able to penetrate through oxide scales rapidly along the cracks and reacts with the substrate elements such as Cr, then volatile chloride is formed:

$Cr(s) + 3/2\ Cl_2(g) \rightarrow CrCl_3(g)$
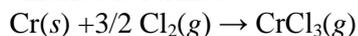
Through the grain boundaries, the chlorides may reoxidize on the surface of scales, Cl_2 is then regenerated and corrosion was repeated:

$2CrCl_3(g) + 3/2O_2(g) \rightarrow Cr_2O_3(s) + 3Cl_2(g)$
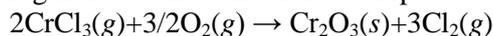
Surface morphology

In Hastelloy X, the greenish oxide layer appears after 5 hrs and the oxide color remains constant until 100 hrs. The long lasting color appeared on the surface after oxidation indicates that the main phases were formed during thermal oxidation of Hastelloy X. The green color indicates that nickel oxides and chromium oxide were formed, while the dark grey represents the combination between chromium and nickel oxides. At a low temperature, the color was dark or dark grey because the oxides were formed from Cr_2O_3, Ni_2O_3 and NiS or Cr_2S_3, while at 800 and 900°C, the color of the surface seems to be greenish due to the formation of the oxides, Cr_2O_4.

Microstructure investigation

Figure (4) shows the SEM images of Hastelloy X subjected to oxidation at three different temperatures, namely 700, 800, and 900°C, for different exposure times. For Hastelloy X tested at 700, 800, and 900°C for 5 hrs, the SEM images show that the thickness of the formed scale increased with increasing the temperature, and the internal oxidation increases at temperatures 800°C and 900°C. After 20 hrs of exposure time, the scale formed on Hastelloy X became thicker with the increase of the temperature to 800°C and 900°C. After 50 hrs of exposure time, the internal oxidation started at 700°C was found to be increasing at 800°C and 900°C. Internal oxidation occurs frequently in the iron, nickel and cobalt

alloys commonly used in high temperature applications upon forming a Cr_2O_3 or Al_2O_3 [16-19].

X-ray diffraction (XRD) analysis

The analysis of scale formed on Hastelloy-X of oxidized specimens after exposure at 700°C, 800°C and 900°C for exposure times of 5 hrs, 20 hrs and 50 hrs, are shown in Figures (5a, b, and c). The major and minor phases detected at the surface of the specimens show a dramatic change in the intensity of the peaks with the change of the experiment temperature and exposure time. The XRD pattern of the base alloy before exposure to high temperature shows a peak for CrNi. At 700 °C, (Figure5a), there are detected peaks for $NiCr_2O_4$, Cr_2O_3, Cr_3O_3 and Cr_2S_2. At 800 °C(Figure 5b), there are peaks for $NiCr_2O_4$, Cr_2O_3 and $CoCr_2O_4$. At 900 °C (Figure 5c), the observed peaks are for $NiCr_2O_4$ and $CoCr_2O_4$.

Hast-X	700°C	800°C	900°C
5 hrs			
20 hrs			
50 hrs			
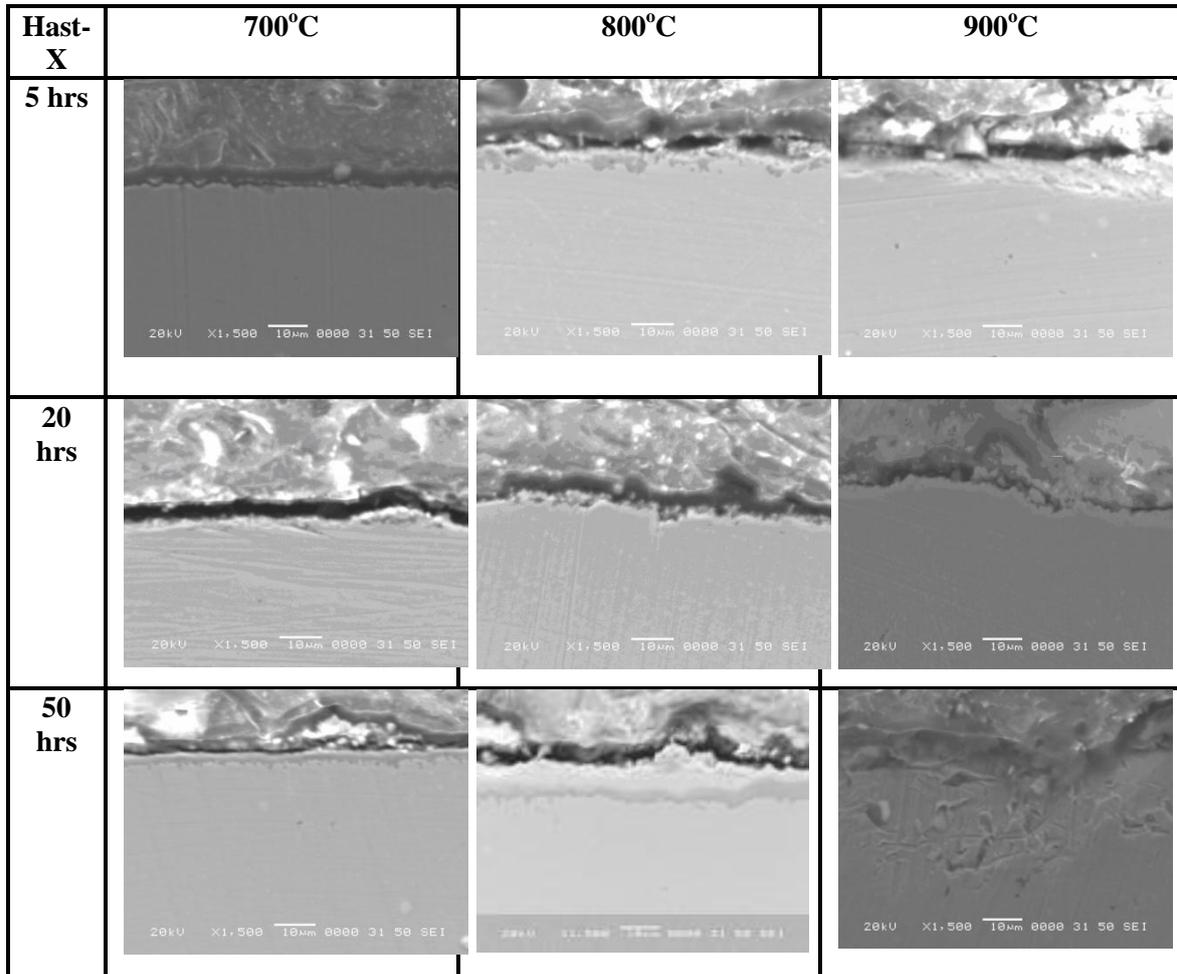
Figure (4): SEM images of Hastelloy X subjected to oxidation at 700, 800, and 900°C for different exposure times

In the case of presence of NaSO$_4$; the formation of chromium sulfate could be more, which can affect the corrosion resistance. It is well known that oxidation resistance can be accredited to the formation of a highly adherent protecting scale. Some of additives to alloys such as Si, Mo, and Ti will enhance the oxidation resistance [20]. The scale thus formed in alloys containing chromium and nickel is a mixture of nickel and chrome oxides. These combine to form nickel chromites (NiCr$_2$O$_4$), which has a spinel-type structure to improve the oxidation resistance. Therefore, the phases that were formed during the oxidation indicate the performance of alloys to resist high temperature corrosion. The oxidation stability of nickel-based alloys has been associated with the existence of Cr$_2$O$_3$ in the oxide layer. Also, the existence of different phases in a thin layer might inflict strict strain on the film, which could result severely in cracking and peeling of scale. Thermal cycles might have also produced cracks in the scale due to different values of thermal expansion coefficient of the substrate and oxides formed

Figure (5): XRD patterns of Hastelloy-X after oxidation at: (A) 700 °C, (B) 800 °C and (C) 900°C

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Conclusions

The thermal oxidation behavior of nickel-based superalloy was examined at different temperatures and exposure times in the presence of aggressive ions. The following conclusions can be extracted:

1) Hastelloy-X shows a good oxidation resistance in the condition of the present experiments as the k_p lower than In617.

2) Parabolic rate constant for Hastelloy-X at 700°C, 800°C and 900°C are 0.2603, 0.4717 and 0.6487 (mg^2. cm^{-4}. h^{-1}) respectively.

3) Major oxides responsible for protection against high temperature oxidation are $NiCr_2O_3$, $NiCr_2O_4$, $CoCr_2O_4$, Cr_2O_3 and Cr_2S_2.

4) The Hastelloy X oxidation rate increased with increasing the temperature and the process is endothermic (activation energy, Ea = 57.84 KJ/mole).

Acknowledgment

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