

Hot Corrosion Study of Ni-Cr Alloys

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Abstract—The hot corrosion behavior of three nickel base alloys are investigated in fused salts (Na_2SO_4 - 10 wt% NaCl) environment. The oxidation kinetics, scale morphologies, phases and porosity are measured by thermo gravimetric analysis (TGA), Field electron microscopy (FE-SEM), EDS and image analyzer respectively. In addition to FE-SEM analysis, microstructure of the samples are seen by optical microscope. Susceptibility to hot corrosion was found to be correlated to the scale formed during oxidation. Alloys containing Cr as an element, they formed Cr_2O_3 scale on surface which is stable, below 800°C , but above 800°C , Cr form CrO_3 scale which is volatile in nature. In case of alloy with Al as an inhibitor forms stable alumina scale above 800°C , which reacts with fused salt and formed NaAlO_2 (Sodium aluminate) which has high melting point (1650°C), thus, it is stable at high temperature. The relevant hot corrosion mechanisms are discussed.

Keywords: Ni-Cr alloy; FE-SEM; Hot corrosion.

Introduction

Nickel-based alloys are traditionally composed of nickel as a base, chromium and other elements. However, these materials lack the creep strength needed for longevity when they are being used as boiler tubing alloy [1-2]. Nickel-base super alloys are used in numerous high-temperature applications which require both mechanical strength and oxidation resistance. Virtually all such alloys in use today were developed empirically through a judicious selection of strengthening elements and elements required for oxidation resistance. Elements usually added to improve corrosion resistance properties include Al, Cr and other elements through solid solution. In order to develop high strength nickel-base alloys with improved oxidation resistance, it is necessary to determine the influence of these elements upon oxidation properties. However, before it is possible to examine the effect of different elements on the oxidation behavior of nickel- base super alloys, it is necessary to study the oxidation mechanisms for simpler but related alloys such as Ni-Cr, Ni-Cr-Al alloys etc. The resistance of Ni-Cr alloys to attack by both sulfur dioxide and Na_2SO_4 induced

hot corrosion has been shown to increase with increasing Cr concentration, particularly above 30 wt.% [3]. The oxidation behavior of Ni-Cr alloys containing less than 40% Cr has been extensively investigated, however, the oxidation of the single phase and two phase alloys containing more than 40% Cr has received little study. The oxidation rate of Ni-Cr alloys shows maximum with increasing Cr concentration between 10 and 18% depending on temperature in the range 800 to 1200°C [4]. The increased oxidation rate of nickel with additions of up to 10% Cr is explained in terms of an increased number of cations vacancies in the NiO scale due to doping with Cr ions. The scale on these dilute alloys consists of a layer of NiO with a small amount of Cr in solid solution and a porous inner layer of NiO which contains a dispersion of NiCrO_4 particles and is saturated with Cr. According to Giggins and Pettit [4] Ni-Cr alloys containing more than 30% Cr form continuous Cr_2O_3 scales very early during the oxidation process and show oxidation rates comparable to those of pure chromium. External Cr_2O_3 formation on these alloys is accompanied by some internal oxidation of Cr. This can result from a steep Cr concentration profile in the alloy along with a flat oxygen gradient. The authors are not aware of published studies of the oxidation kinetics of alloys containing more than 40% Cr which may contain one or two phases depending on temperature and composition. Most of the researcher reported the synthesise of Ni-Cr alloy by various route [5-10]. Very limited literature is available on synthesise of Ni-Cr alloy by powder metallurgical route. Since powder metallurgical processes are more flexible and economical as compared to melting casting process. Therefore, in the present work Ni-Cr alloys (Ni-50%Cr, Ni-60%Cr, Ni-40%Cr-10%Al) were synthesized by powder metallurgical route and their hot corrosion studies were done in the environment of Na_2SO_4 - 10 wt% NaCl at 1000°C for 50 hrs.

Experimental

In present work, Ni-Cr alloys (Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al) were prepared by using powder metallurgical process. Mole fraction of the constituent element in the alloys was controlled by adjusting the Ni, Cr and Al

weight ratio. The starting materials were used analytical grade of nickel, chromium and aluminum powder of 200 mess size. The above chemicals were used without any further purification. According to the stoichiometry, nickel, chromium and aluminum powder were mixed by high energy ball mills (mechanical alloying). The cylindrical specimens of approximately 12 mm diameter are made from the mechanically allowed of nickel, chromium and aluminum powder and cylindrical compacts are made by laboratory manual press (15 Ton capacity). Finally, compacts are sintered at 940°C in argon atmosphere. The Standard conditions for synthesizing the Ni-Cr alloys and their relevant data are given in **Table 1**. The samples are subjected to FE-SEM/EDS and optical microscope analysis.

FE-SEM/EDS (FEI, Quanta 200F) has been used to characterise the microstructures of the samples at an acceleration voltage of 20 kV. The morphology and phase constituent of corroded products of samples are characterised by FE-SEM/EDS.

Hot corrosion studies under cyclic conditions are performed in molten salt of Na₂SO₄ - 10 wt% NaCl environment up to 50 cycles. The samples are mirror polished down to 1µm alumina on a wheel cloth polishing machine. Each cycle consisted of 1 hr of heating at 1000°C, in silicon carbide tube furnace, followed by 30 minute of cooling at room temperature for up to 50 cycles. The samples are cleaned using acetone and heated in an oven at about 250°C for ten minutes. Thereafter, a layer of Na₂SO₄ - 10 wt% NaCl mixture, prepared by mixing it with distilled water, is applied uniformly on the warmed polished samples with the help of camel hair brush. The amount of salt coating is maintained within the range of 3-5 mg/cm². The salt coated samples are kept in the alumina boats and then inserted into SiC tube furnace for 3-4 hrs at 100°C for drying and proper adhesion of the salt. Subsequently, the dried salt coated samples are again weighed and introduced in to the silicon tube furnace at 1000°C. During hot corrosion runs, the weight of boats and samples is measured together at the end of each cycle with the help of an electronic balance Model CB-120 (Contech, Mumbai, India) with a sensitivity of 1 X 10⁻⁵ g. During each cycle, the weight changes measured for samples are used to calculate the corrosion rate.

Table 1 Standard conditions for synthesis of Ni-Cr alloys

Composition Porosity (%)	Synthesis precursors weight (g)			Alloy density (g/cm ³)
	Nickel	Chromium	Aluminum	
Ni-50%Cr 17.1	4.5	4.5	0.0	7.9548
Ni-60%Cr 16.5	3.5	5.4	0.0	7.7893
Ni-40% Cr-10% Al 13.8	4.5	3.6	0.9	6.7187

The spalled scale is also included at the time of measurements of weight change to determine total corrosion rate. The kinetics of hot corrosion is determined from the weight change measurements.

Results and Discussion

The hot corrosion kinetics is determined from the weight change (mg/cm²) versus time plots for the sample, subjected to hot corrosion in Na₂SO₄ - 10 wt% NaCl environment at 900 °C up to 50 cycles as shown in **Fig. 1(a)**. The Ni-50%Cr alloy showed a higher weight gain as compared to Ni-60% Cr and Ni-40% Cr-10% Al alloy. Ni-40% Cr-10% Al alloy sample showed a least weight gain among them. The hot corrosion behavior of both alloy samples (Ni-60% Cr and Ni-40% Cr-10% Al) followed a parabolic rate law but the Ni-50%Cr alloy sample slightly deviates from parabolic rate as shown in **Fig. 1(b)**. The parabolic rate (**Fig. 1 (b)**) constant K_p is calculated by a linear least-square algorithm to a function in the form of $(W/A)^2 = K_p t$, where W/A is the weight gain per unit surface area (mg cm⁻²) and ‘t’ indicates the number of cycles represents the time of exposure. The calculated K_p for the Ni-60% Cr and Ni-40% Cr-10% Al alloy is found to be $0.272 \times 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, and $0.125 \times 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ respectively. It is very less as compared to the K_p value of $1.101 \times 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ obtained for the Ni-50% Cr alloy sample.

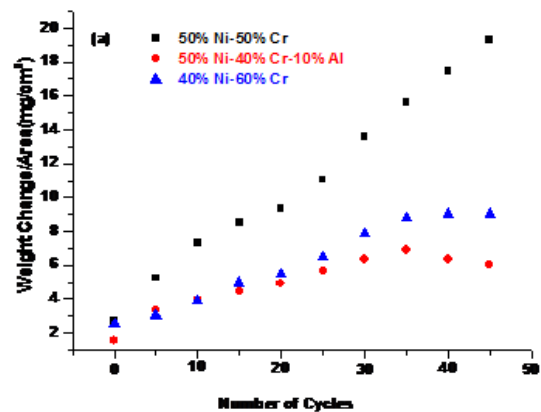
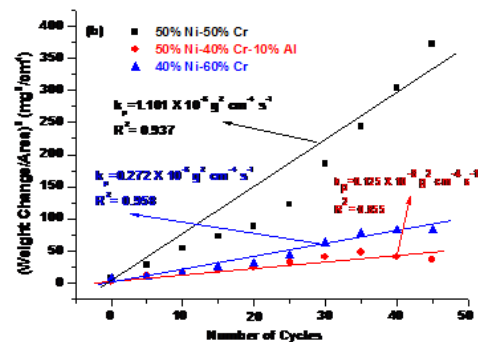
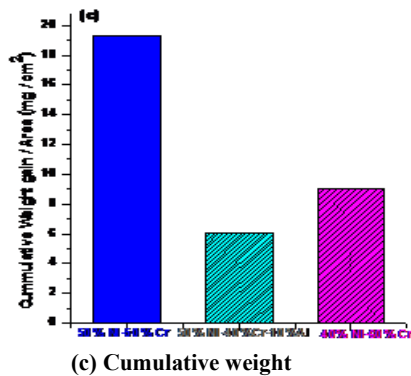


Figure 1 (a) Weight changes/area (mg/cm²) versus number of cycles



(b) Parabolic rate constant, K_p (Weight change/area)², mg²/cm⁴ versus number of cycles, for bare and coated samples oxidized in molten salt environment at 1000°C



Cumulative weight gain per unit area for Ni-50%Cr, Ni-60%Cr, and Ni-40%Cr-10%Al alloy are shown in Fig. 1(c). It is observed that there is 68.6% and 53.2% saving in overall weight gain for Ni-40% Cr-10% Al alloy and Ni-60%Cr alloy with reference to Ni-50%Cr alloy.

FE-SEM/EDS microstructures of Ni-Cr alloy (Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al) are presented in Fig. 2 (a-c). Fig. 2 (a) exhibited the microstructure of the Ni-50% Cr alloy, the grey color represented the Cr-rich phase, whereas silver color indicates the Ni-rich phase. Fig. 2 (b) shows the microstructure of the Ni-60% Cr alloy, the dark grey color is Cr-rich phase, where as light grey color is the Ni-rich phase. Fig. 2 (b) revealed that there is large area of the dark grey color (Cr-rich phase) as compared to the light grey color area (Ni-rich phase) in Ni-60% Cr alloy, it confirmed that the Ni-60% Cr alloy contains more Cr element as compared to Ni element. Similarly Fig. 2 (c) represents the microstructure of the Ni-40% Cr – 10% Al alloy, the white color indicates the Al-rich phase, dark grey and light grey color exhibits the Cr-rich and Ni-rich phase. All phases in Ni-Cr alloy are confirmed by EDS analysis.

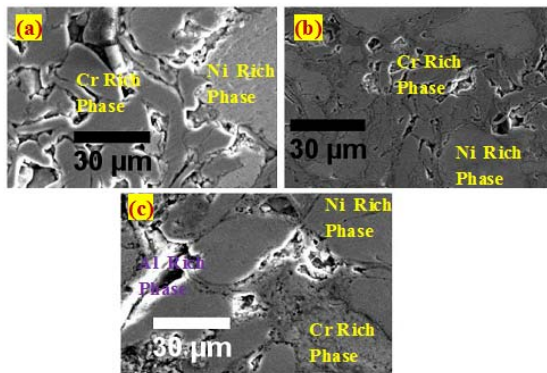


Figure 2 FE-SEM/EDS surface micrographs Before oxidation (a-c) of Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al alloys, alloys (a) Ni-50%Cr, (b) Ni-60%Cr, and (c) Ni-40% Cr-10% Al

Optical microstructures of Ni-Cr alloy (Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al) are furnished in Fig. 3 (a-c). Fig. 3(a) and Fig. 3(b) presented the microstructure of Ni-50%Cr

and Ni-60%Cr alloy, whereas Fig. 3(c) shows the microstructure of Ni-40% Cr-10% Al alloy after etching. It is clearly seen in Fig. 3(a-b) that it have two different morphology whereas in Fig. 3(c) it has three different morphology. FE-SEM/EDS (Fig. 2(a-c)) and Optical microscope analysis (Fig. 3(a-c)) convinced that samples are composed of Ni, Cr, Al elements.

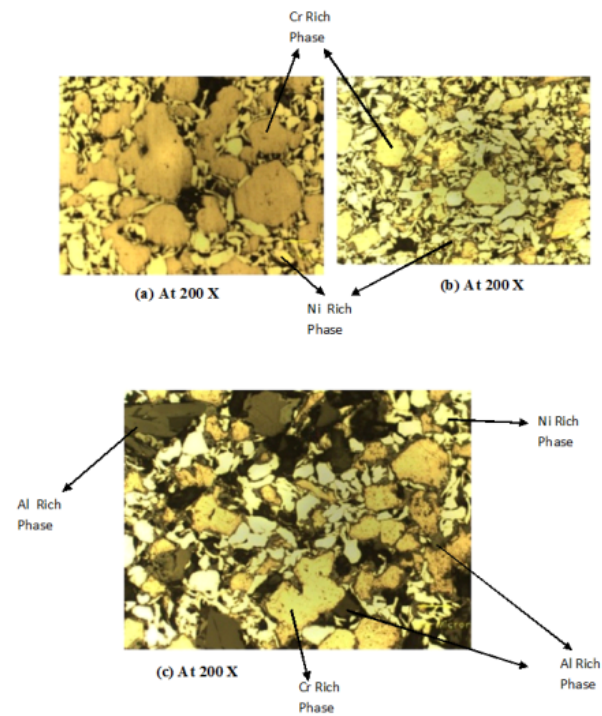


Figure 3 Optical micrographs before oxidation (a-c) of Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al alloys, alloys (a) Ni-50%Cr, (b) Ni-60%Cr, and (c) Ni-40% Cr-10% Al

FE-SEM/EDS microstructures of oxidised Ni-Cr alloy scale (Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al) at 1000°C in molten salt environments for 50 hr are exhibited in Fig. 4 (a-c). Fig. 4 (a) corresponds the microstructure of the scale formed on the surface of Ni-50% Cr alloy after 50 hr oxidation in molten slat environments at 1000°C. Whereas, Fig. 4 (b) corresponds the microstructure of the scale formed on the surface of Ni-60% Cr alloy after 50 hr oxidation in molten slat environments at 1000°C. It is clearly seen in Fig. 4 (a-b) that the morphology of NiO oxide scale which is rod type is increased in size i.e. there is slightly growth in rod type morphology by increasing the Cr contents in binary alloy. Morphology of the Cr₂O₃ oxide scale formed in both Ni-50% Cr and Ni- 60% Cr alloy (Fig. 4 (a-b)) after oxidation in molten salts environment is small spherical shape. In addition to these phases there is spinel phase of NiCr₂O₄ which formed in both alloy (Ni-50%Cr, Ni-60%Cr) after oxidation at 1000°C for 50 hrs in molten salts environment and is shown in Fig. 4 (a-b). Fig. 4 (c) shows the microstructure of the scale formed

on the surface of Ni-40% Cr – 10% Al alloy after oxidation at 1000°C for 50 hrs in molten salts environment. **Fig.4(c)** revealed two important information: (i) The morphology of oxide scales formed on the surface of the alloy after oxidation are changed in Ni-Cr alloy by reducing the Cr contents from 60 % to 40 % and addition of 10% Al, (ii) microstructure of NiO oxide scale formed on the Ni-40% Cr – 10% Al alloy after oxidation at 1000°C for 50 hrs in molten salts environment is thin sheet forms, Cr₂O₃ oxide scale morphology is thin lamellar type, whereas Al₂O₃ oxide scale morphology is thin and short rod form (**Fig. 4 (c)**). The FE-SEM/EDS analysis of the Ni-Cr and Ni-Cr-Al alloy before and after oxidation was carried out using the EDAX genesis 32 software. FE-SEM/EDS analysis confirmed the presence of NiO, Cr₂O₃, NiCr₂O₄, and Al₂O₃ oxide scale in Ni-Cr and Ni-Cr-Al alloys after oxidation.

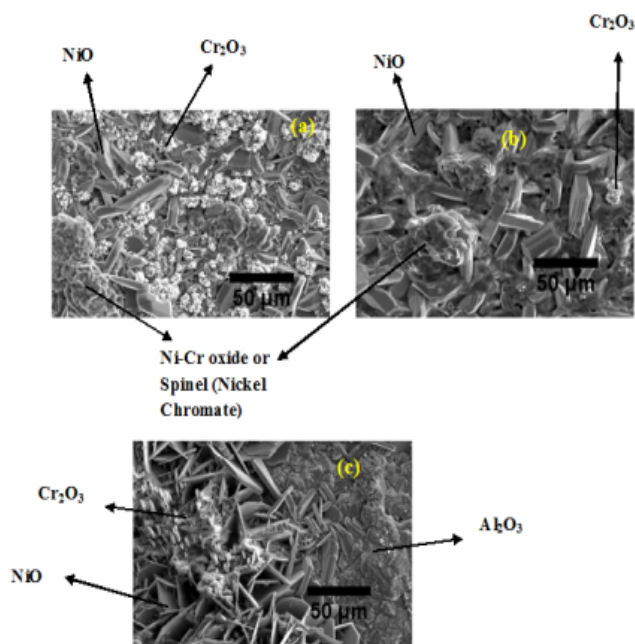


Figure 4 FE-SEM/EDS surface micrographs after oxidation (a-c) of Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al alloys, alloys (a) Ni-50%Cr, (b) Ni-60%Cr, and (c) Ni-40% Cr-10% Al

Hot Corrosion Mechanisms

Weight change data for the Ni-Cr alloys (Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al) subjected to hot corrosion test in molten salt of Na₂SO₄ - 10 wt% NaCl environment at 1000°C are plotted in **Fig. 1 (a)**. Severe hot corrosion suffered by Ni-50%Cr alloy. The reason might be due to high porosity level (17.1%) as compared to Ni-60%Cr alloy (16.5 %) and Ni-40% Cr-10% Al alloy (13.8%). Through this pores easily sulphur diffused and reacts with Ni and Cr at 1000°C and formed volatile sulfide compounds. The Ni-40% Cr-10% Al alloy has oxidised at high temperature (1000 °C) and formed oxides of Al, Cr, Ni and NaAlO₂ spinel phases at the grain boundaries and within open pores. The melting point of

NaAlO₂ spinel phase is around 1650°C, thus NaAlO₂ will stabilize the melt chemistry and consequently prevent the dissolution of the protective oxide scale [11]. During the subsequent cycles, the formation of oxides have blocked the pores and acted as diffusion barriers to the inward diffusion of corrosive species. This would relatively minimize the weight gain and result in the steady state oxidation behavior with the progress of long term high temperature exposure.

The overall weight gain of 19.29, 9.04 and 6.05 mg/cm² is observed for the oxidized Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al alloys at 1000°C (**Fig. 1(c)**), respectively. The Ni-40% Cr-10% Al alloy at 1000°C temperature has been found successful in reducing the weight gain by around 86.6% of that gained Ni-50%Cr alloy, which is also evident from the parabolic rate constant ($K_p = 0.125 \times 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$).

Better performance of Ni-40% Cr-10% Al alloy at 1000°C temperature in molten environment might be due to the fine, dense and protective scale formed on the surface mainly consisting of Al, Ni and Cr, presence of these elements along with oxygen represents the formation of oxides of Al, Ni, Cr and NaAlO₂ spinel phases. Besides, Ni-40% Cr-10% Al alloy has very less porosity (13.8%) and thus it slows down the corrosion attacks and increases the hot corrosion resistance of alloy in molten salt environment, which is confirmed by thermo gravimetric analysis in **Fig1(a-c)**. The lower corrosion rate of Ni-40% Cr-10% Al alloy observed in the present work is in accordance with the results of W. Long et al. [10] and P. Berthod [12].

Conclusions

The hot corrosion kinetics of Ni-Cr alloys (Ni-50%Cr, Ni-60%Cr, and Ni-40% Cr-10% Al) has been compared and found that the parabolic rate constant is very less for the Ni-40% Cr-10% Al alloy, which is due to the less porosity and formation of fine, continuous, nonporous, adherent and protective oxide scale over the surface. The Ni-40% Cr-10% Al alloy has improved their oxidation resistance as well as the scale-metal adherence as observed in the present work.

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