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Oxidation Behaviour of IN-738 LC Superalloys in the Presence of Ionic Salts at 1173 K

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Abstract

Oxidation of the alloy having nominal composition Ni-16Cr-8.5Co(wt.%) was studied in the presence of KCl and K_2CO_3 at 1173 K in air. Chemical composition of oxide scales and scale morphologies were determined by means of X-ray diffraction analysis and scanning electron microscopic studies. The oxide scales of KCl- and K_2CO_3- coated alloys showed complex microstructures and compositions. This behaviour was ascribed to the release of volatile metallic chlorides, evolution of CO/CO_2 gas as well as formation of fluxing products. The high temperature oxidation resistance is not only related to the nature of the passive film but is also strongly dependent on the salt environments and the structure of alloy.

Keywords: Oxidation, IN-738 LC Alloy, KCl, K_2CO_3.

Introduction

Nickel-based alloys containing chromium as a major constituent together with cobalt, titanium and aluminium additions are the most widely used materials in turbine blades of jet engines, nuclear power reactors and land-based turbines.

Among a great variety of protective systems to increase the scaling resistance of super-alloys the overlay M-Cr coatings (where M= Ni, Co) offer an advantage of appreciable compositional flexibility. The aluminium addition provides good oxidation resistance where relatively high chromium and cobalt levels ensure hot corrosion resistance. Compositional modification of the overlay coatings, particularly of the Cr:Co ratio, makes them suitable for a variety of service

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conditions. Oxidation and hot corrosion behaviour of M-Cr materials alone or deposited on superalloys substrates have been a subject of many investigations [1-8]. The role of alkali earth metal salts inducing high temperature oxidation studies has been reported [9-12]. The passivity of nickel in Na_2SO_4 / NaCl melts, in air, is destroyed by SO_3, SO_2, and O_2 [13, 14]. Blistering and cracking produced by NaCl exposure have been attributed to the formation of volatile metallic chlorides, like $NiCl_2$, $CrCl_3$ in locally reducing environments [15-17]. Limited attention has been paid to the morphology of attack on nickel-base alloys in the presence of potassium in KCl and K_2CO_3, although chlorides transform to oxides releasing Cl_2 gas under oxidizing atmospheres [18-20]. The purpose of this work was to get information on high temperature corrosion of Ni-16Cr-8.5Co alloy in the presence of KCl and K_2CO_3, oxidized at 1173 K in air, including oxidation kinetics as well as structure and morphologies of oxide scales.

Experimental

The alloy having nominal compositions Ni-16Cr-8.5Co (wt. %) was obtained and homogenized for 4 h in an evacuated (10^{-2} Pa) quartz tube at 1173 K. Chemical compositions of the experimental alloy are given in Table 1. The ingots were spark-machined to get flat discs, diameter of 15 mm and thickness of 1 mm, which were ground on SiC papers up to 800 grit no., then finally degreased in water with detergent and ultrasonically cleaned in acetone.

The polished specimens were uniformly coated with thin films of KCl or K_2CO_3. The specimens were heated to about 573 K and were sprayed with aqueous solutions of the salt till a nearly uniform coating (about 6 µm thick coatings) of the salt was obtained. The salt coated specimens were dried in an oven for about 1 h, cooled to room temperature and weighed. The salt coated specimens were then used for high temperature oxidation studies.

Table 1. Chemical composition of IN-738 LC superalloy (wt.%).

Co	Cr	Al	Si	C	P	Fe	B
8.59	16.08	3.43	0.18	0.11	0.01	0.50	0.05
S	W	Ta	Nb	Ti	Mn	Cu	Ni
0.01	2.67	1.75	0.90	3.38	0.03	0.03	Bal

Kinetic studies on the oxidation of coated IN-738 LC superalloy were carried out at 1173 K in air for periods up to 48 h. The coated specimens were transferred into silica buckets and suspended by helices in a helical thermal balance using a vertical tubular furnace. Variation in mass change was recorded at intervals of every 4 h.

Table 2. Constituent identified in the scales by X-ray diffraction analysis, IN-738 LC superalloy, KCl- and K_2CO_3- coated specimen, oxidized at 1173 K for 48 h in air.

Salt environment	Constituent identified in the scales
KCl	Cr_2O_3, NiO, K_2CrO_4, $CrCl_3$, $NiCl_2$, K_2NiO_2, Al_2O_3, Co_3O_4
K_2CO_3	Cr_2O_3, NiO, K_2CrO_4, Al_2O3, Co_3O_4, K_2NiO_2

Oxide scales of coated IN-738 LC superalloy were examined by taking cross-sections of the specimens, conventionally mounted and polished to a 1 μm diamond finish, in a scanning electron microscope, Jeol JSM-35. After oxidation studies, the representative specimens were examined by X-ray diffraction analysis. The various constituents were identified using a Phillip PW-1730 X-ray diffractometer fitted Fe-, Co, or Cu-Kα targets. Table 2 summarizes the results of the XRD analysis.

Results

The oxidation kinetic data are shown in Fig. 1 for IN-738 LC superalloy with KCl and K_2CO_3, oxidized at 1173 K in air for 48 h. The oxidation rate of KCl-induced specimens result mass gain with increasing time up to 32 h followed by a decrease in mass at longer time. K_2CO_3-coated specimens exhibit invariable mass loss during the first 28 h after which there was mass gain with further increase in time. This could be attributed to the evolution of CO/CO_2 gas which facilitates oxidation attack [21, 22].

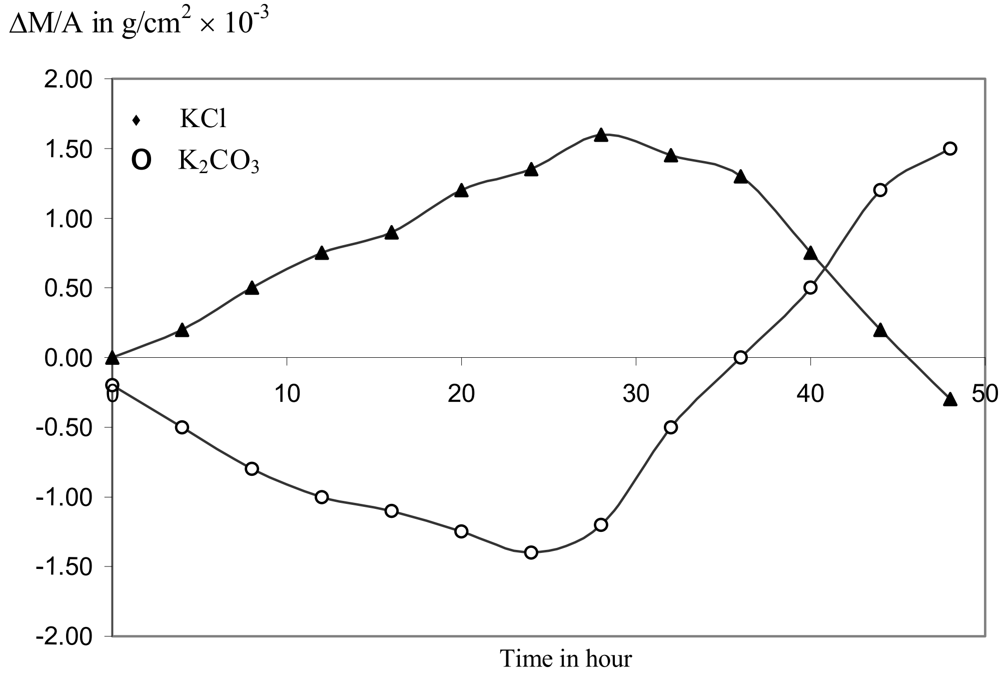

Figure 1. The change in mass with time (oxidation kinetics) for IN-738 LC superalloy coated with KCl and K2CO3, oxidized at 1173 K in air for 48 h.

The scales are separated from substrate at some regions, possibly due to polishing artifacts. The chlorides of chromium and nickel form the outer layers of scales incorporated with Cr_2O_3 and NiO (Fig. 2). Cr_2O_3 has not been found in the inner scales. This might be due to the formation of intermediate volatile species CrO_2Cl_2, some of which evaporates and condenses on the walls of the reaction tube and some of it decomposes and accumulates at the alloy/salt interface in the form of Cr_2O_3 [23]. It appears that during cooling of fluxed mass, stresses are developed resulting in the production of cracks and voids [24].

Figure 2. Scale morphology of IN-738 LC superalloy coated with KCl, oxidized at 1173 K for 48 h in air.

The inner oxide scales of K_2CO_3-coated corroded alloy mainly consist of Cr_2O_3 layers followed by NiO layers (Fig. 3); the middle layers of the scales represent fluxing products such as K_2CrO_4, $NiCrO_4$ and probably K_2NiO_2 [25].

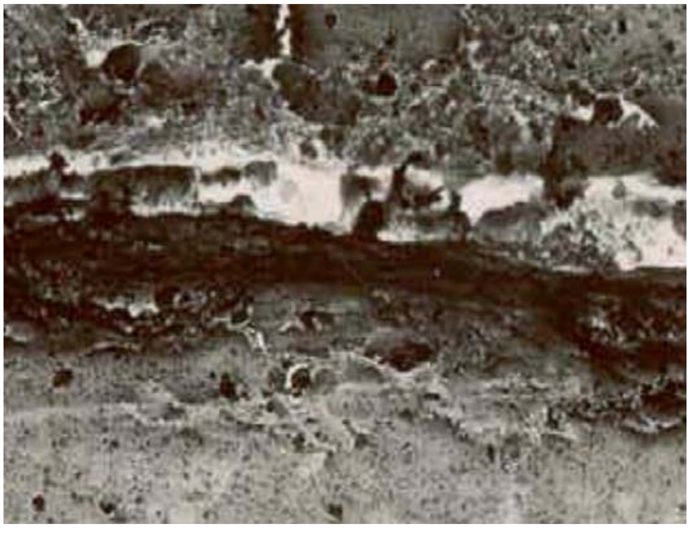

Figure 3. Scale morphology of IN-738 LC superalloy coated with K_2SO_4, oxidized at 1173 K for 48 h in air.

The outer scales represent layered structures comprising of Cr_2O_3 and NiO precipitated from the fluxing product at the salt/air interface. The presence of micro-pores is perhaps the result of evolved CO/CO_2 from K_2CO_3. The crystalline constituents appearing in the middle layers of the scale represent oxides and chromates crystallized out during cooling of the fluxing product after completion of the oxidation run. The formation of a stratified structure of the oxide scales is as that described earlier for Ni-20Cr and Fe-20Cr alloys [26, 27].

Discussion

IN-738 LC corrodes to very large extent in the presence of KCl. The ease of formation of a volatile chloride seems to be the rate determining factor in the high temperature oxidation of the alloy. There is the formation of volatile CrO_2Cl_2 by the interaction of Cr_2O_3 and KCl and its subsequent conversion into volatile K_2CrO_4.

The NiO also reacts with KCl to form volatile $NiCl_2$. In both cases when the chloride comes into contact with air it is converted into oxide [26]. The presence of KCl and K_2CO_3 indicates that the corrosion rates are influenced not only by the nature of the salt but on the amount of the salt deposited on the alloy as well as time.

The aggressive action of KCl can be attributed to several factors, mainly:

1. Reaction of molten KCl with oxide scales forming chlorides and not molten-fluxing products

$$12\ KCl + 5\ Cr_2O_3 + 9/2\ O_2 \rightarrow 6\ K_2CrO_4 + 4\ CrCl_3 \qquad (1)$$

$$2\ KCl + Cr_2O_3 + 3/2\ O_2 \rightarrow CrO_2Cl_2 + K_2CrO_4 \qquad (2)$$

$$2\ KCl + NiO \rightarrow NiCl_2 + K_2O \qquad (3)$$

$$NiO + K_2O \rightarrow K_2NiO_2 \qquad (4)$$

2. After reaction with the oxide scales, the molten KCl further attacks the alloy substrate forming metal halides [15, 25]:

$$4\,KCl + 2\,Ni + O_2 \rightarrow 2\,NiCl_2 + 2\,K_2O \qquad (5)$$

$$2\,K_2O + 2\,Ni + O_2 \rightarrow 2\,K_2NiO_2 \qquad (6)$$

$$12\,KCl + 4\,Cr + 3O_2 \rightarrow 4\,CrCl_3 + 6\,K_2O \qquad (7)$$

$$4\,KCl + 2\,Cr + 3O_2 \rightarrow 2\,CrO_2Cl_2 + 2\,K_2O \qquad (8)$$

$$CrO_2Cl_2 + 2\,K_2O \rightarrow K_2CrO_4 + 2\,KCl \qquad (9)$$

The formation of some volatile products like CrO_2Cl_2, K_2CrO_4 and volatile halides exert sufficient vapour pressure so as to break the protective scale.

3. The chlorides formed by (1), (2) and (3) are released at the air/salt interface and get oxidized to release chlorine gas.

$$4\,CrCl_3 + 3O_2 \rightarrow 2\,Cr_2O_3 + 6\,Cl_2 \qquad (10)$$

$$4\,CrO_2Cl_2 \rightarrow 2\,Cr_2O_3 + O_2 + 4\,Cl_2 \qquad (11)$$

$$2\,NiCl_2 + O_2 \rightarrow 2\,NiO + 2\,Cl_2 \qquad (12)$$

4. The chlorides might be entrapped between inner oxide layers of the alloy and get condensed on cooling and appear distinct and discrete phase(s) in the scale.

The relative ease of formation and volatility of some chlorides can be shown by thermodynamic and thermochemical data reported by [28, 29]. Since the melting point of $NiCl_2$ (1303K) and $CrCl_3$(1423K) at the vapour pressure of chlorides is 10^{-4} Pa.

The high temperature oxidation behaviour of K_2CO_3-coated alloy seems to be aggressive, being an active oxidizing agent providing oxygen during fluxing reaction. However, due to profuse evolution [21, 22] of CO/CO_2, heavy mass losses are observed up to 28 h during corrosion and scales are porous. The consequence of fluxing and evolution of gases are caused the cracking or disruption of the scales with the result that the fused salt would come in contact with fresh metal resulting in high corrosion rates.

K_2CO_3 (m.p. 1164 K) decomposes in the following manner:

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{13}$$

$$4\ K_2CO_3 + 2\ Cr_2O_3 + 3\ O_2 \rightarrow 4\ K_2CrO_4 + 4\ CO_2 \tag{14}$$

$$K_2CO_3 + NiO \rightarrow K_2NiO_2 + CO_2 \tag{15}$$

KCl-induced hot corrosion involves fluxing-oxidation reactions while K_2CO_3-coated specimens seem to behave aggressive due to the evolution of CO_2, having losses incurred as a result of decarburization and ease in the availability of O^{2-} from basic carbonates.

Conclusion

The following conclusions can be drawn on the investigation of oxidation behaviour of IN-738 LC superalloys carried out at 1173 K in air for 48 h.

During the reaction of liquid KCl with oxide scales, chlorides and fluxing products are formed and some volatile products like CrO_2Cl_2, and K_2CrO_4 and metallic chlorides such as $NiCl_2$ and $CrCl_3$, which exert sufficient vapour pressure so as to break the protective scales.

In K_2CO_3–coated corrosion, the appearance of porous and copious scales is attributed to the profuse evolution of CO_2 and fluxing of protective scales.

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