Microstructure and hot corrosion behavior of hot dip siliconized coating on Ni-base superalloy IN738LC

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Abstract
Nickel-based superalloys are widely used at elevated temperature applications because of their high corrosion and oxidation resistance characteristics as well as high stability. To improve the hot corrosion resistance of Nickel-based superalloys, different coatings are applied. In this study, nickel-base superalloy Inconel 738LC was coated via a novel hot-dip diffusion siliconizing process and the corrosion behavior was investigated by XRD, SEM and EDS analyses. A severe degradation and poor hot corrosion resistance was detected by the uncoated sample, while the siliconized coated sample possessed high corrosion resistance. It was figured out that the high hot corrosion resistance of the coated sample was due to the formation of SiO2 protective scale in the surface layer which protects the substrate elements in the hot corrosion environment.

1. Introduction
Nickel and nickel-based superalloys are widely used in space, aviation, chemical and petrochemical industries owing to their relatively high strength at high temperatures [1–3]. But their hot corrosion resistance needs to be improved through various surface treatments [4–7].

IN738LC is a special nickel base superalloy which is extensively used to make hot section components [8–10]. It has been reported that IN738LC has a high temperature strength due to multiphase microstructure conferred by the fine particles of Llγ type ordered γ′[Ni3(Al,Ti)] phase which is precipitated coherently in the FCC structured γ matrix [11]. Since alloying requirements reduce the corrosion resistance, surface coatings are applied for these gamma prime materials. Hence, a high-strength substrate alloy is used to withstand the stress and a surface coating is applied to protect the substrate against the environment corrosion [12].

There are several methods to apply a protective coating onto Ni-based superalloys including ion implantation [13], electro-discharge coating [14, 15], high velocity oxy-fuel (HVOF) [16], laser surface modification [17, 18], plasma spraying (APS, LPPS, VPS, AXPS) [19] and pack cementation. Amongst different surface modification routes, the hot dip coating process is an advantageous way because of its being simple, fast and cost effective [20].

Silicon can form a promising protective barrier to withstand the diffusion of oxygen in high-temperature oxidation conditions, through formation of silicides [21]. Therefore, a protective layer, containing SiO2, could be formed through the hot dip siliconizing of Ni-based superalloys [22, 23]. This inhibits the oxygen diffusion into the surface of base metal [21]. Kochmanska et al [24] applied Al–Si Coatings on cast steel by slurry cementation and reported that the internal layer formed on the surface was enriched in silicon, chromium and iron which enhanced the thermal shock resistance. In other research, Fukumoto et al [25] used pack-cementation method for Si surface alloying into stainless steels and reported the enhancement of the high-temperature corrosion of the siliconized steel.

Within the recent years, no significant report has been published on hot dip siliconizing process for hot corrosion resistance enhancement of Ni-based superalloys through a mixture containing molten Si powder and
KCl/NaCl/NaF/Na$_2$SiF$_6$ salt. Hence, the aim of this study is to deposit siliconized coating on Ni-base superalloy Inconel 738 through a novel hot-dip siliconizing process. The investigation of hot corrosion behavior was performed by XRD, SEM and EDS analyses.

2. Experimental procedures

2.1. Material and specimens
The nickel-base superalloy IN738LC plate was used as the substrate material. The nominal composition of used superalloy is listed in table 1. To produce specimens for corrosion tests, four samples with dimensions of 10 × 10 × 3 mm were cut by water-cooled cutting machine. At the first step, the specimens were degreased in an acetone bath. Then they were cleaned with ethanol through ultrasonic procedure, and dried in air to prepare for hot dipping.

A mixture of silicon powder (10.0%) and various salts (90.0%), presented in table 2, was prepared and homogenized completely through ball mill for 20 min. The mixture was next melted in an alumina crucible at 850 °C. Two specimens were immersed in the molten salt via stainless steel wire. Due to the activity of F$^-$ and Cl$^-$ in the salt mixture, any existing oxide layer is removed from the substrate surface. Upon immersion for 180 min, the specimens were pulled out and cooled at room temperature. A mixed aqueous solution (containing phosphoric acid, nitric acid and water in a volume ratio of 1:1:1) was prepared at 25 °C to clean the hot-dipped specimens.

2.2. Hot corrosion tests
One of the dominant salts deposited on the surface of the superalloys exposed to hot corrosion is Na$_2$SO$_4$. The sulphur and sodium impurities are introduced into the combustion air from fossil fuels, and seawater, respectively [26]. Therefore, a mixture of Na$_2$SO$_4$-25% wt. NaCl salts with a weight ratio of 3:1 was poured in a beaker containing distilled water to obtain a supersaturated aqueous solution. To ensure suitable adhesion of the salt to the specimens, the latter were first heated in an oven (∼200 °C). A layer of the mixed salts was then applied on the warm specimen uniformly, through dipping in the supersaturated solution. To maintain the amount of salt on the surface almost 3 mg cm$^{-2}$, the samples were measured (weight) with and without the salt mixture on the surface. The specimens were next placed and dried in a furnace, followed by heating to about 750 °C and kept for 60 and 100 h. The samples were taken out from the furnace and cooled down to room temperature at interval of 20 h. The specimens were boiled in distilled water to remove remaining salts prior to weighing [27, 28]. The weight of specimens was measured with an electronic balance having 0.1 mg accuracy to investigate the hot corrosion rate. Table 3 demonstrates the coding of the specimens.

2.3. Characterization methods
X-ray diffraction (XRD) carried out to identify the phase structures of the specimen surface via EQUIPOX3000 model (INEL Co. France) with Cu-K$_\alpha$ radiation and $\lambda = 1.540510$ Å. The voltage and electric current of XRD instrument tube were 40 kV and 30 mA, respectively. The cross-sections and surface morphologies of specimens were investigated using scanning electron microscopy (SEM). The thickness of the coating was measured through SEM and energy-dispersive spectrometry (EDS) data by plotting the element concentrations as a function of depth from the surface.
3. Results and discussion

3.1. XRD characterization

Figure 1 illustrates the XRD patterns of the as-received IN738LC for A, A60 and A100 specimens at 720 °C. The x-ray patterns of A60 specimen denote to the presence of Cr2O3, TiO2 and NiCr2O4 phases on the surface. The oxidation reaction of Cr and Ti and formation of Cr2O3 is given below [28]:

$$4\text{Cr} + 3\text{O}_2 = 2\text{Cr}_2\text{O}_3$$  \hspace{1cm} (1)
$$\text{Ti} + \text{O}_2 = \text{TiO}_2$$  \hspace{1cm} (2)
$$\text{Cr}_2\text{O}_3 + \text{NiO} = \text{NiCr}_2\text{O}_4$$  \hspace{1cm} (3)

Kamal et al [29] also reported the formation of NiCr2O4 resulted from the reaction between Cr2O3 and NiO phases in the oxide scales in the hot corrosion of a nickel-based superalloy after 10 cycle of testing. With further exposure, hot corrosion proceeds by crack initiation and propagation. Molten salts diffuse through cracks and Cr2O3 layer is dissolved and re-precipitated along the cracks. The reactions are presented below:

$$8\text{NaCl (l)} + 2\text{Cr}_2\text{O}_3 (s) + 5\text{O}_2 (g) = 4\text{Na}_2\text{CrO}_4(s) + 4\text{Cl}_2 (g)$$  \hspace{1cm} (4)
$$\text{Cr}(s) + 3/2\text{Cl}_2 (g) = \text{CrCl}_3 (g)$$  \hspace{1cm} (5)
$$2\text{CrCl}_3(g) + 3/2\text{O}_2(g) = \text{Cr}_2\text{O}_3(s) + 3\text{Cl}_2(g)$$  \hspace{1cm} (6)

These reactions also occur for Ni and Ti. Park et al [30] also reported the presence of TiO2 after hot corrosion of nickel-based superalloys. The Cr2O3 phase is corrosion resistant, in contrast to TiO2 and NiCr2O4 [31]. It should be noted that, no peaks were found in the XRD spectra representing the Cr2O3 phase in A100 specimen which, in turn, denote to the weak hot corrosion resistance in the as-received IN738LC specimen.

The XRD patterns of the S, S60 and S100 specimens are depicted in figure 2. As it can be seen the peaks existing at 32°, 38°, 47°, 52° and 57°, in the XRD pattern of S sample, are attributed to (101), (210), (121), (310) and (301) planes of NiSi, respectively. The peaks existing at 35°, 46° and 49° also represent the Ni$_2$Si phase. The obtained x-ray patterns are in good conformity with XRD spectrum of NiSi and Ni$_2$Si phase in Chiu et al [32] study, in the course of which they succeeded to synthesize nickel silicide nanowires via chemical vapor deposition method.
As it is shown in figure 2, the x-ray diffraction of S60 sample represents the presence of SiO₂ phase on the surface, which confess a good corrosion resistance. Ni₂SiO₄ phase is also observed which is formed through the following reaction:

\[
2\text{NiO} + \text{SiO}_2 = \text{Ni}_2\text{SiO}_4
\]  

Furthermore, there are some peaks representing the presence of Ni₂SO₄ and Ni₂S that may weaken the hot corrosion behavior.

Following 100 h hot corrosion, the XRD pattern of S100 sample also represents the presence of non-protective oxides like NiCr₂O₄ and TiO₂ phases, which may result in a very mild degradation in the surface.

3.2. Microstructure analysis

The cross-sectional BSE images along with line scan curves of the S sample with thickness of about 37 ± 0.3 μm are presented in figure 3. The diffusion coating is formed between the silicon layer and the substrate.

External and internal zones are visible in the coating. A dense and uniform structure was found in the internal area, whereas the external one shows a porous structure. It can also be seen that the coating structures is dense and continuous with the even distribution of main elements. Based on figure 3, the substrate elements had outward diffusion along the thickness of the coating. The demonstrated spots of 1, 2–8 and 9 are attributed to Si topcoat, diffusion layer, and the IN738LC superalloy substrate, respectively. The relative content and distribution of various elements in the coating are listed in table 4.

The outer layer contains 28% Si and 49% Ni, while there is 14% Si and 43% Ni in the substrate-coating interface. It is demonstrated in the x-ray diffraction of the S specimen that the coating has NiSi and Ni₂Si phases. Hence, the downward diffusion of Si could be demonstrated by XRD and EDS results as well as Ni-Si phase diagram.
A brief mechanism for the formation of NiSi and Ni2Si on the substrate in hot-dip siliconized coating in molten salt is based on the production of M–Si bonds. This results in the production of silicide deposits as shown the reactions below [36]:

\[
2\text{Si}^{2+} + 2\text{Ni}^{3+} = \text{Si}^{4+} + \text{Ni}_2\text{Si}
\]

\[
2\text{Si}^{2+} + \text{Ni}^{3+} = \text{Si}^{4+} + \text{NiSi}
\]

Figure 4 shows the cross-section of the coated sample and EDS analysis of four layers formed across the coating layer. As seen, the Si content is high in B, C, and D layer which confirms the presence of the siliconized

| Distance from surface coating (µm) | Ni content (%) | Si content (%) | Cr content (%) | Co content (%) |
|-----------------------------------|---------------|---------------|---------------|---------------|
| 0                                 | 49            | 28            | 8             | 9             |
| 12.5                              | 49.5          | 28.5          | 7.5           | 11            |
| 25                                | 41            | 29.5          | 3             | 4             |
| 37.5                              | 48            | 25            | 13            | 7             |
| 50                                | 43            | 14            | 25            | 5.5           |

Figure 4. SEM micrograph and EDX analysis of internal and external layers of S sample.
layer on the substrate. The outer layer mainly consists of NiSi. However, there is low amount of Si in the internal A layer. The diffusion of other elements such as Ni, Cr, and Ti along the coating layer are also observed.

3.3. Hot corrosion behavior

Figure 5 represents the cross-section of S60 and S100 specimens. No damage and cracks were found in the substrate and substrate-coating interface in the S100 specimen. This demonstrates that the coating provides good hot corrosion resistance, especially for IN738LC, needless to say that after 100 h hot corrosion, a flat microstructure was formed in the layers and surface of the coating. Furthermore, the obtained EDS results showed that the substrate elements were well protected in hot corrosion environment, owing to the presence of SiO₂ protective layer.

The cross-section of the A60 and A100 samples are depicted in figure 6. It is obvious that the A60 sample surface is corroded and the (production was a little destructed), whereas by increasing the corrosion time, the diffusion of the corrosive elements and corrosion diffusion depth increase. This could be attributed to vertical diffusion of aggressive species into the interface [37].

An eventual mechanism for this phenomenon could be the loose oxide layers being formed by reaction products along the interface as well as reactive chromia evaporation [38]. These phenomena make a laminar
structure, in which the layers easily grow and are detached from the surface. Furthermore, the sample’s EDS results demonstrate that valuable elements in the substrate such as Ni and Cr take part in the corrosion reactions, through a mechanism similar to thermal oxidation. It should be noted that, more intensive damage is created by hot corrosion than thermal oxidation, owing to the presence of molten corrosive salts. In addition, the intensity of corrosion damage in the grain boundaries is higher [37].

The SEM micrographs of the S60 and S100 samples are presented in figures 7(a)–(c) also shows the EDS analysis of S60 sample. It can be seen that after 60 h the SiO₂ layer is formed. This is in good conformity with XRD results. EDS results shows a little amount of Cr and Co in S60 surface and preserving the valuable elements. Due to the trace amount of these elements the peaks in XRD analysis was not detectable. Despite the oxide layer was scaled slightly, no particular change was found in the morphology of S100 sample.

3.4. Corrosion kinetics

Figure 8 represents the hot corrosion kinetic curves of the S and A samples. There are two processes that lead to mass change including mass gain and mass loss, in which the former is due to formation of the scales, whilst the latter arises from scale spallation. Therefore, the mixed effects of these two processes represent the mass change of the sample in molten salt.
As depicted in figure 8, a different corrosion behavior is shown in the molten salt, exemplified in A and S samples. It is obvious that the A sample shows a weak hot corrosion resistance. This corresponds to chloride volatility effect. Since most metal chlorides have high vapor pressure and low melting points, chlorine tends to diffuse outward through oxide scale quickly, followed by its reaction with the alloying elements including Al and Cr at the interface of oxide and metal which leads to volatile chlorides formation [31, 39]. Additionally, the presence of Cr₂O₃ phase may lead to weight loss. This too can be attributed to volatility of chromium oxides and hydroxides, and leads to Cr loss at the surface. Furthermore, there are phases with low-melting-points at the grain boundaries that can play the role of quick diffusion channels [12], through which the molten salt can diffuse and react with the alloy quickly. The siliconized coating obviously improved the hot corrosion behavior of the IN738LC. At the first stage of 40 h immersion in the molten salt mixture, the mass change was increased, in which the maximum mass reached 2.8 mg cm⁻². However, the kinetic curve shows a steady state along with a little mass loss in the second stage. This could be attributed to equalization of oxidation rate of film growth to its ‘peeling off’ rate at this stage.

4. Conclusion

The Ni-based superalloy IN738LC was coated through a novel hot-dip siliconizing process, in which the samples were immersed in a mixture of molten Si powder and KCl/NaCl/NaF/Na₂SiF₆ salts. The molten salt applies a coating which contains high amounts of Si on the surface of IN738LC. The investigations represented that the coating was specifically composed of NiSi and Ni₂Si phases, based on the production of M-Si bonds which results in the production of silicide deposits. The corrosion kinetic investigation revealed that during the first 40 h of immersion of the coated sample in the molten salt mixture, an increase in the sample mass occurred and the maximum mass changed of 2.8 mg cm⁻² was achieved. The mass changed with a steady state trend with a little mass loss in the second stage representing the enhancement of hot corrosion resistance and preserving the valuable elements.

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