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Hot corrosion of glass coating on nickel base superalloy

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Abstract

Hot corrosion behaviour of BaO–MgO–SiO_2 based glass coating on nickel base superalloy was studied using 80 wt.% Na_2SO_4 + 20 wt.% NaCl salt mixture, which melts at about 700 °C. In one set of experiments the glass coated superalloy substrates were immersed in the molten salt wherein in the other samples were suspended in the salt vapour at 1000 °C. During the test, mass loss per unit surface area was observed to be higher for specimens suspended in the salt vapour. The phase composition and microstructure of the corroded coating were investigated by X-ray diffraction (XRD), optical microscopy and scanning electron microscopy (SEM) in association with energy dispersive X-ray (EDX) analysis.

Keywords: B. Surfaces; C. Corrosion; D. Glass; E. Engine components

1. Introduction

Corrosion resistant coating has a great demand to withstand hostile environments in different heat engines and heat exchanger used in industries [1]. There they are subjected to combined attack of high temperatures and condensed phases such as Na_2SO_4 and NaCl. Deposition of these salts on the hot zone components leads to severe hot corrosion resulting in accelerated deterioration of the structural materials [2]. Further, to increase the efficiency of these heat engines, efforts are being made to increase the operating temperature and non-availability of ideal material has become a serious limitation. Temperatures associated with hot corrosion degrade the material at a very rapid rate and load carrying ability of the component decreases leading eventually to catastrophic failure [3]. Therefore, an effective surface coating is often applied on these components to protect them from different aggressive environments. Generally, diffusion coating, overlay coating, thermal barrier coating and functionally graded overlayer coating are designed for the surface protection of the substrate material from high temperature hot corrosion [4–7]. Oxide based glass and glass-ceramic coatings with excellent chemical inertness, high temperature stability and superior mechanical properties are also being conceived as a cheap but effective alternative [1]. Because of the excellent combination of properties these coatings can efficiently be utilized to reduce the hot corrosive degradation of high temperature structural materials.

An enamel coating was found to protect TiAl-based alloys from hot corrosion attack [8]. Zheng et al. studied a novel enamel-Al_2O_3 composite coating on a thin NiCoCrAlY bond coated nickel base superalloy for high temperature oxidation and hot corrosion resistance. The composite coating exhibited excellent hot corrosion resistance at 900 °C in molten sulphate salts and oxidation resistance at 900 and 1000 °C [9]. Liu et al. investigated the corrosion behaviour of polycrystalline Ti_3SiC_2 in the mixture of Na_2SO_4–NaCl melts with various mass ratios at 850 °C. They observed that Ti_3SiC_2 suffered from serious hot corrosion attack in the melts when the concentration of Na_2SO_4 was higher than 35 wt.% [2]. Further, Zhang et al. studied hot corrosion behaviour of Ti–Al based intermetallics in 80 wt.% Na_2SO_4 + 20 wt.% NaCl molten salt mixture in three different experimental conditions, which simulate different service conditions. The specimens were either immersed in the molten salt, deposited with the mixed salt or suspended in the salt vapour at 800 °C. They established that the most severe corrosion occurred by the immersion method [10].

The present paper is concerned with the hot corrosion study of BaO–MgO–SiO_2 based glass coating on nickel base superalloy using 80 wt.% Na_2SO_4 and 20 wt.% NaCl molten

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salt mixture at 1000 °C. This coating is designed for the protection of hot zone components of gas turbine engine used in aeronautical applications where service temperature is 1000 °C and the aviation fuel contains significant amount of sulphur as impurity. Therefore to obtain accelerated results, the severity of the condition was enhanced and a corrosive environment containing little more sulphur than in Na_2SO_4:NaCl eutectic composition is selected for the study. The kinetics of material degradation in both the cases were studied and compared.

2. Experimental

The approximate oxide composition of the coating system is shown (in wt.%) in Table 1. Commercially available raw materials were weighed, mixed and sieved to prepare the glass-forming batch. The coating material was prepared by melting the glass-forming batch at 1400 °C for 2 h and quenching the melt to yield the glass frit. The frit was required to be further processed to obtain a uniform coating on the cleaned metallic substrates by conventional spraying. For the purpose, the frit was primarily crushed and subsequently wet milled in a porcelain ball mill for 45 h along with various mill additions such as fume silica: 3.0–5.0 (wt.%); washed Cr_2O_3: 4.0–5.0 (wt.%); cobalt oxide: 0.3–0.5 (wt.%). Wet milling was performed to obtain glass particles of 3–5 μm size. A thick paint like slurry of glass was prepared for application over the cleaned metal surface. The rheological properties of this slurry were standardized to ensure proper application of the coating on the substrate. The nominal composition of the superalloy substrate is given in Table 2. The metallic substrate was thoroughly cleaned by thermal degreasing at 600 °C in an oxidizing atmosphere for 10 min to ensure complete burning of grease/oil/any organic impurities adhering to the surface. Subsequently, the metal substrate was sand blasted to remove all rust and scales from the surface and finally it was cleaned ultrasonically with acetone for 15 min. The coating material was applied on the cleaned metallic substrates by conventional spraying technique. The glass powder coated substrates were dried initially at ambient condition and then at 100 °C for 45 min. The dried samples were heat-treated at 1200 °C for 5 min in an electrically heated muffle furnace to melt the glass powder to obtain continuous impervious coating.

The glass coated substrates were subjected to hot corrosion test by using 80 wt.% Na_2SO_4 + 20 wt.% NaCl molten salt mixture at 1000 °C for 35 h. The melting point of the salt mixture is about 700 °C. Two experimental methods were used. In one case, the weighed specimens were suspended in the salt vapour with hooks in a covered alumina crucible containing molten salts while in the other the specimens were completely immersed in the molten salt mixture kept in an alumina crucible. The specimens were withdrawn at regular intervals, cooled in air, cleaned with a soft brush, washed in boiling water and dried. In this way, salt left on the surface of the specimen was removed and the mass changes were measured by weighing the samples carefully before and after test to establish the corrosion kinetics. For the purpose, an electronic balance with a weighing accuracy of 0.1 mg was employed. The corroded specimens were characterized by X-ray diffraction analysis (P.W. 1710 X-ray diffractometer, Philips Research Laboratory, Eindhoven, The Netherlands), optical microscopy (Vickers Instruments, UK), scanning electron microscopy (SEM, LEO S430i, LEO, UK) and energy dispersive X-ray (EDX, SiLi Detector) analysis.

Table 1
Nominal composition of enamel frit (wt.%)

SiO_2	40–45
BaO	40–45
CaO	2–6
MgO	2–3
ZnO	2–8
MoO_3	2–8

Table 2
Nominal composition of Nimonic superalloy (AE 435) in wt.%

Cr	19–22
Fe	1.0
C	0.12
Si	0.8
Mn	0.7
Ti	0.15–0.35
Al	0.15
Cu	0.07
S	0.01
P	0.015
Ni	Balance

3. Results and discussion

High temperature hot corrosion is basically a form of accelerated corrosion due to the presence of different salt contaminants like alkali sulphates and chlorides in fuel and atmosphere that combine to form molten deposits on the component surface at high working temperature in the range of 850–950 °C. The major corrosive salt in high temperature hot corrosion is Na_2SO_4 because of its high thermodynamic stability. During combustion of fuels in gas turbine engines sodium sulphate can form from sodium or its salts and sulphur,

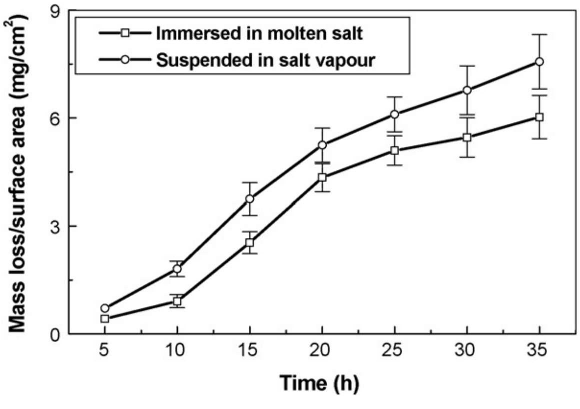

Fig. 1. Hot corrosion kinetics of the glass coating by 80 wt.% Na_2SO_4 + 20 wt.% NaCl melts and salt vapor at 1000 °C.

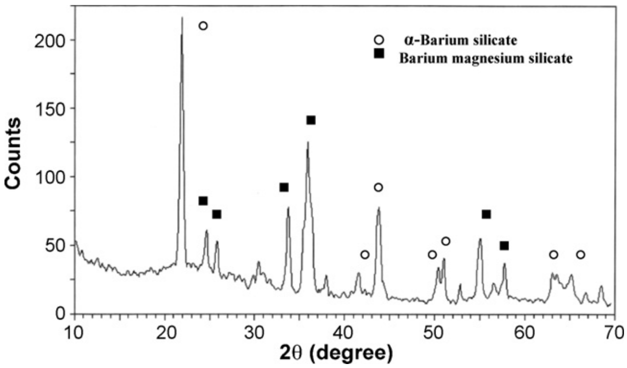

Fig. 2. Typical XRD plot of the corroded glass coating by immersion in the molten salt mixture at 1000 °C for 35 h.

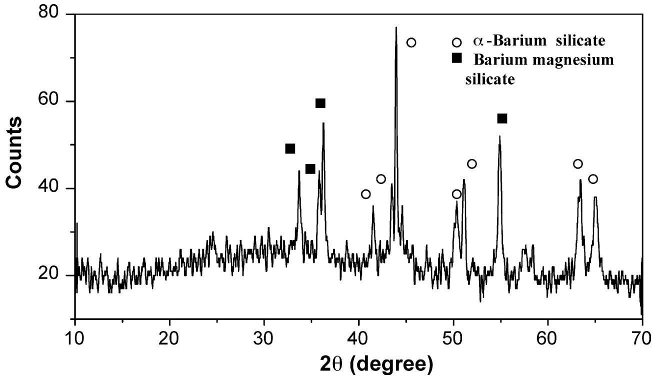

Fig. 3. Typical XRD plot of the corroded glass coating by the salt vapour at 1000 °C for 35 h.

which is again a dominant impurity in different fuels used. A typical such reaction may be expressed as follows [3]:

$$2NaCl + SO_2 + O_2 \rightarrow Na_2SO_4 + Cl_2 \quad (1)$$

Further, NaCl forms a eutectic with Na_2SO_4 and lower down the melting point from 884 to 620 °C, which reduces the incubation period for the hot corrosion [11].

3.1. Corrosion kinetics

Fig. 1 depicts the hot corrosion kinetics of the glass-coated substrates with two different test methods at 1000 °C. The hot corrosion kinetics has been demonstrated in terms of the mass change per unit surface area of specimen with respect to time. When the specimen was corroded by 80 wt.% Na_2SO_4 + 20 wt.% NaCl salt vapour, the mass loss per unit surface area increased monotonically as a function of time. The same trend was noted for the specimen immersed in the molten salt mixture although the reaction is less severe. The final mass loss was about 6 and 7.5 mg/cm^2 after 35 h immersion in the molten salt and suspension in the salt vapour, respectively. This result points out that the glass coating suffered greater hot corrosive attack in the salt vapour than by immersion in the molten salt. This trend in rate of corrosion is expected due to the fact that vapour phase corrosion is normally more severe compared to liquid phase corrosion. This is because during suspension of the glass coated substrate in the salt vapour the corrosive attack takes place at the molecular level involving relatively more thermally energized reacting molecules while in the immersed condition the reacting molecules are in liquid phase and hence less energized. The similar trend of the curves for the two testing methods indicates that the mechanism of hot

Table 3
Corrosion rate of various materials immersed in molten salt mixtures for different test conditions

Material	Composition of salt mixture	Temperature (°C)	Time (h)	Mass loss/surface area (mg/cm^2)
Ti_3SiC_2	75 wt.% Na_2SO_4 + 25 wt.% NaCl	850	10	~75
Ti–48Al	80 wt.% Na_2SO_4 + 20 wt.% NaCl	800	50	~4
Barium magnesium silicate glass coating	80 wt.% Na_2SO_4 + 20 wt.% NaCl	1000	35	~6

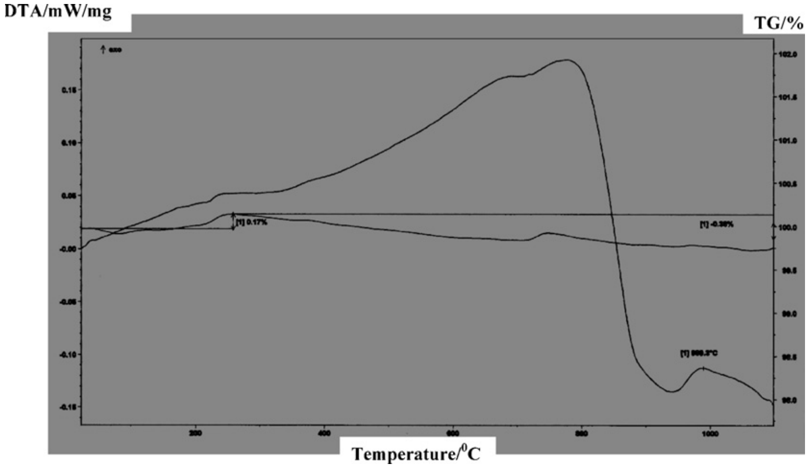

Fig. 4. DTA and TGA curves of the glass.

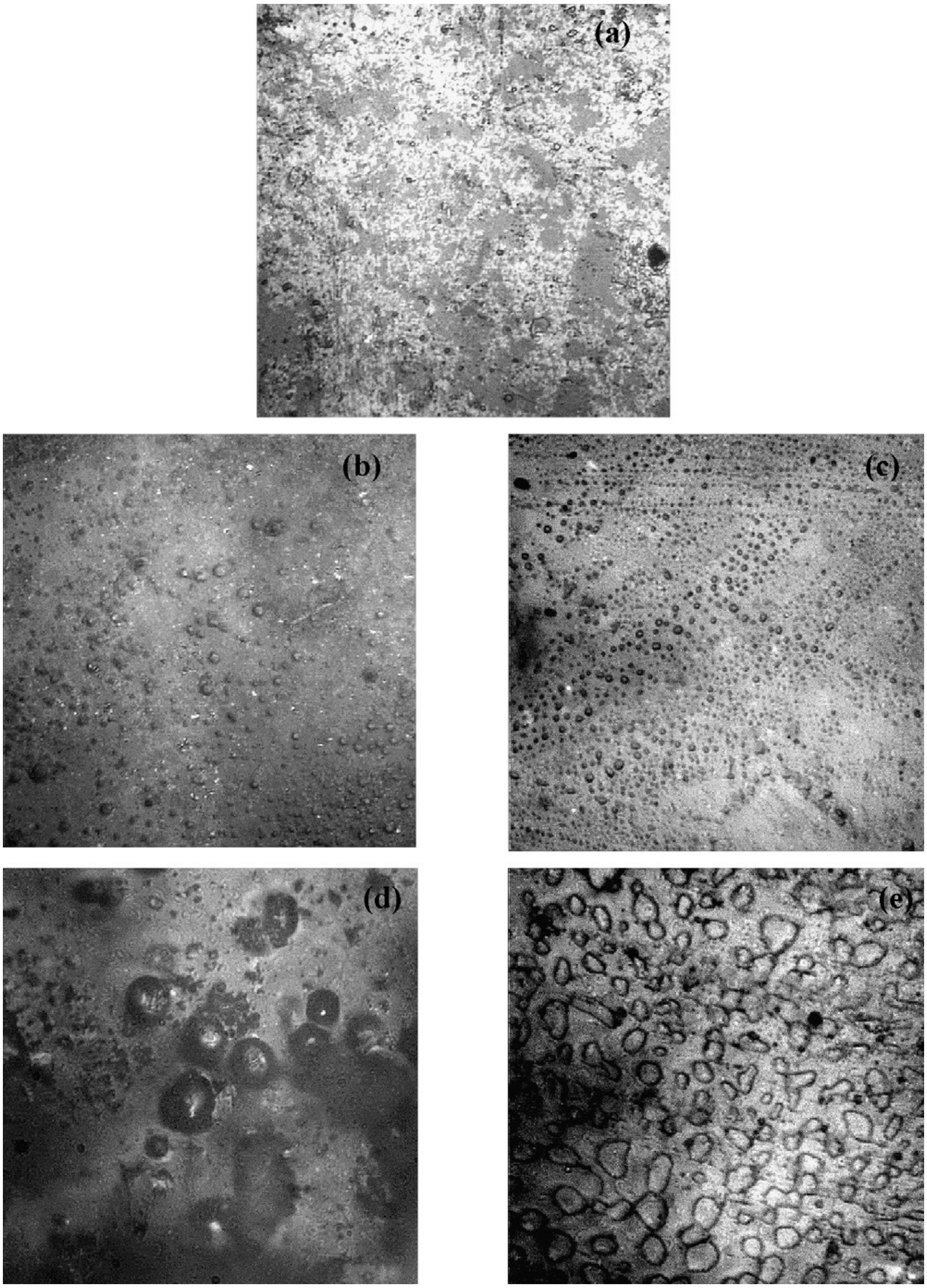

Fig. 5. Optical surface micrograph of the glass coatings (magnification: 400×). (a) Before corrosion; after hot corrosion at 1000 °C for (b) 25 h in the molten salt; (c) 25 h in the salt vapour; (d) 35 h in the molten salt; (e) 35 h in the salt vapour.

corrosion is possibly the same for both experimental conditions while the kinetics is different. Table 3 shows the corrosion rates of different materials in bulk and coating form when they are immersed in Na_2SO_4–NaCl molten salt mixture for different test conditions. This comparison also indicates that the present glass coating has better resistance to hot corrosion than other materials reported elsewhere [2,10].

3.2. Phase composition

X-ray diffraction analysis (XRD) was performed to determine the phase composition of the corroded coating surface. Figs. 2 and 3 show the typical XRD pattern of the corroded specimens after 35 h exposure to 80 wt.% Na_2SO_4 + 20 wt.% NaCl melts and salt vapour at 1000 °C. Major crystalline phases such as barium silicate and barium magnesium silicate were identified to be present on the surface of the immersed and suspended specimens. Therefore, it can be said that the glass coating is crystallized during hot corrosion test at 1000 °C, which is further substantiated by the presence of an exothermic peak in the DTA curve at the same temperature as displayed in Fig. 4. Furthermore, sodium can diffuse rapidly in the glass coating at 1000 °C. The penetration of sodium increases with the increased activity of Na_2O in the corrosive environment. Sodium promotes the devitrification of the glass coating because of its ability to break up the network [12]. The results clearly show that the coating material is dissolved in the corrosive media and no other reaction is taking place, which otherwise would have altered the phase composition of surface region of the corroded coatings.

3.3. Optical microscopy

Surface morphology of the corroded coating was examined by optical microscopy. Fig. 5a–e show the optical micrographs of original glass coating and corroded ones at different hot corrosion test conditions. It is evident from the figures that the original coating (Fig. 5a) is easily distinguishable from the corroded coatings (Fig. 5b–e) from its optical appearance. Fig. 5b and c show that the hot corrosion consumed the coatings and resulted in several corrosion marks of small size on the surface of the coatings, which were exposed to the molten salt and salt vapour at 1000 °C for 25 h. Fig. 5d illustrates the typical spherical type large corrosion marks on the surface of the coating corroded by immersion in molten salt mixture at 1000 °C for 35 h. Severe hot corrosion marks (blister type) were observed on the coating surface after 35 h hot corrosion in the salt vapour at 1000 °C (Fig. 5e). Although no crack was visible on the surface of the corroded coatings, the micrographs indicate the presence of several points where corrosion was initiated (hot spots), the number of which was more in the case of vapour phase corrosion. The size of these hot spots increased with exposure time in both the cases. From the optical microscopy study it can be clearly seen that corrosion of the specimen in both the cases increased with increased time of exposure. The trend of progress of corrosion was similar, which indicates that the mechanism of hot corrosion is the same for both the experimental techniques.

3.4. Scanning electron microscopy

Fig. 6a shows the cross section morphology of the coating on nickel base superalloy, which was corroded by immersion in 80 wt.% Na_2SO_4 + 20 wt.% NaCl molten salt mixture at 1000 °C for 35 h. The SEM observation revealed that the coating appearance was good even after 35 h exposure in the molten salt. The coating–substrate interface region was smooth and crack free as can be seen in the magnified image (Fig. 6b). The cross sectional image of the coating on nickel base superalloy after corrosion in the salt vapour at 1000 °C for 35 h as shown in Fig. 6c shows that the coating condition was quite satisfactory. In addition, no crack or defect was visible at the coating–substrate interface (Fig. 6d). Energy dispersive X-ray analysis of the cross section of the corroded coatings (Fig. 6a and c) was performed at the regions marked as A, B, C, D, E and F. Presence of Si, O, Ba, Mg, Al and Na elements in the coating regions was detected while Si, O, Ni, Cr, Fe and Al elements were detected in the interface regions (Fig. 7a and b and 8a and b). Elements in the substrate regions mainly consisted of Ni, Cr, Fe and Si (Figs. 7c and 8c). Therefore, it can be concluded that

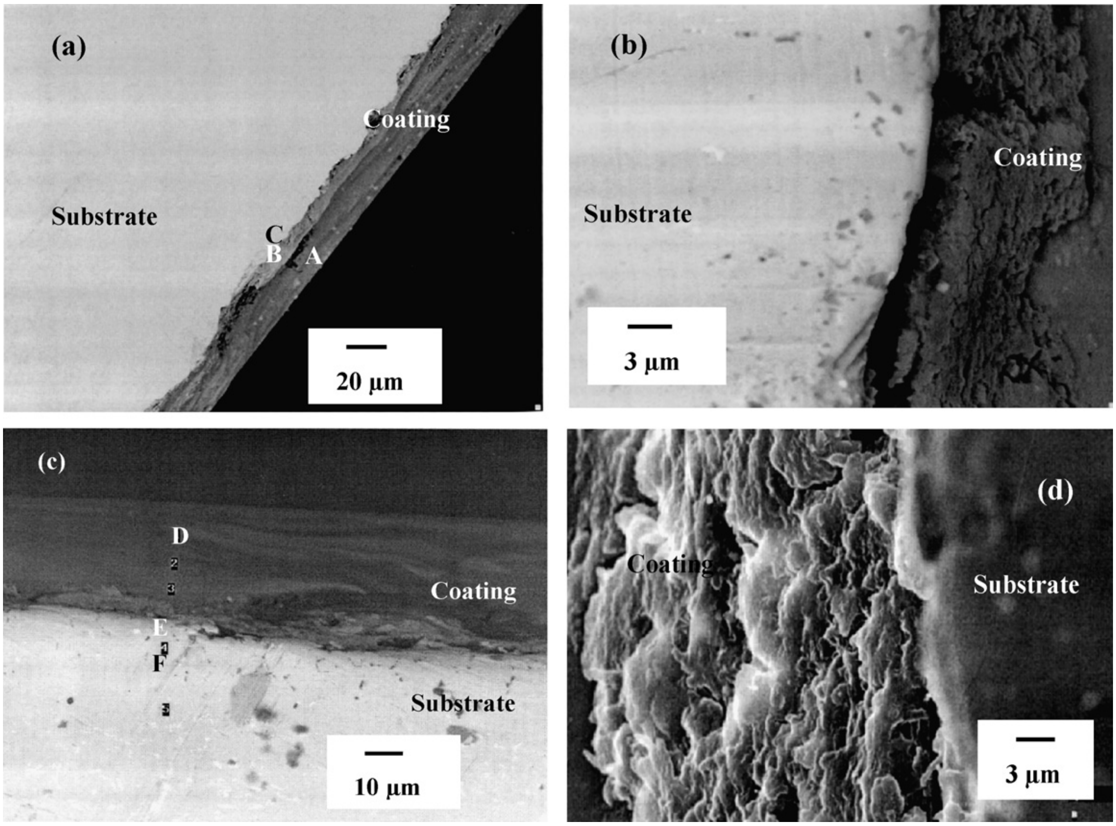

Fig. 6. SEM micrographs showing cross section of the glass coatings after hot corrosion at 1000 °C for 35 h. (a) Immersed in molten salt; (b) magnified interface region in (a); (c) suspended in salt vapour; (d) magnified interface region in (c).

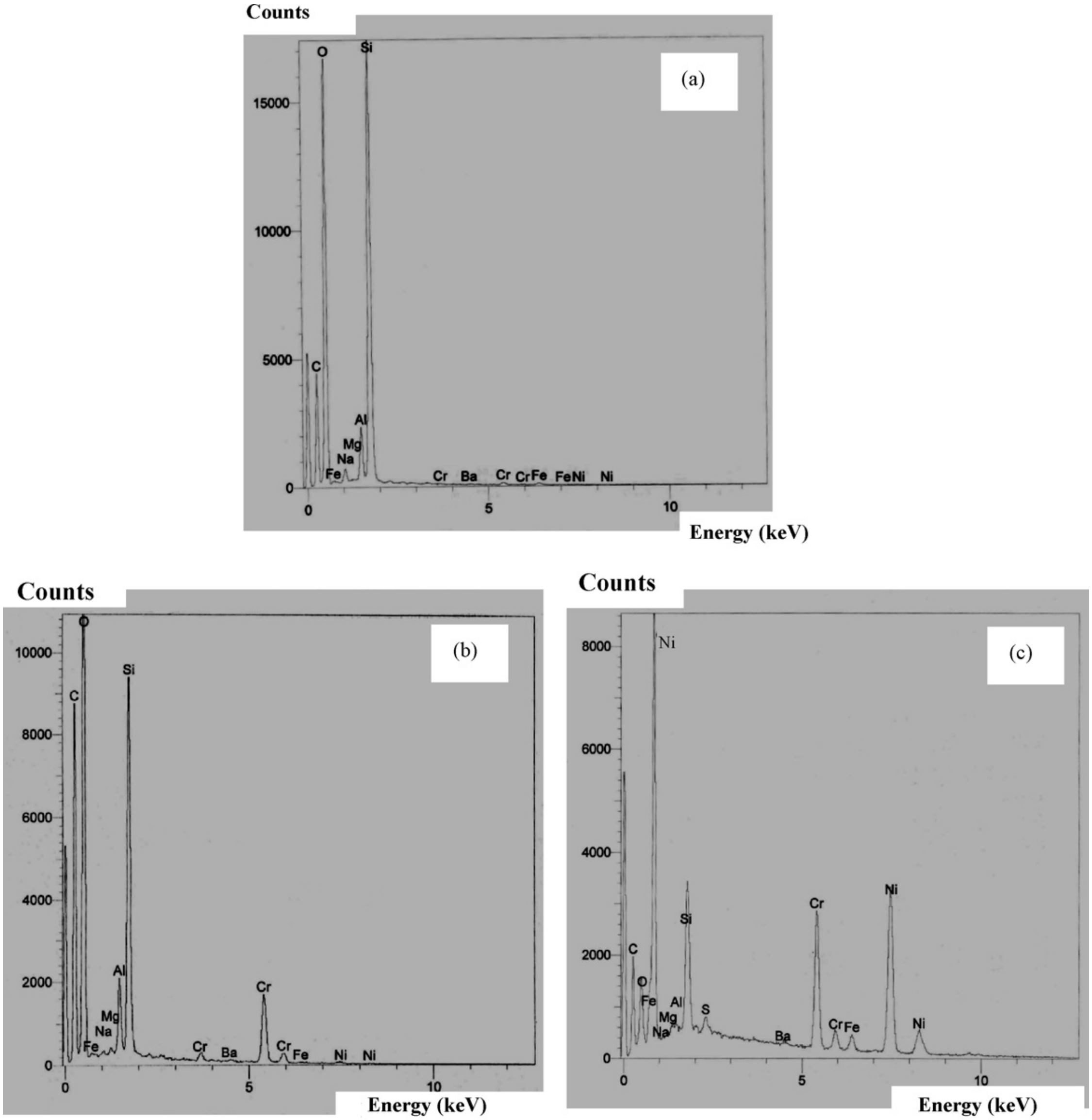

Fig. 7. EDX spectra of (a) region A, (b) region B and (c) region C as shown in Fig. 6(a).

corrosion occurs in the surface of the coating and not in the bulk or coating–substrate interface. This may be attributed to the inadequate diffusion of Na_2O through the glass coating because oxygen diffusion is much slower than sodium diffusion in silicate glasses. The reaction between SiO_2 of the bulk glass coating and the corrosive molten salt/salt vapour is controlled by the diffusion of Na_2O into the coating [13]. Further, no oxide layer formation takes place at the coating–substrate interface region.

3.5. Mechanism of hot corrosion

The exact mechanism for the corrosion of the glass coating by Na_2SO_4–NaCl melts is yet to be understood. The present barium magnesium silicate glass coating contains about 40–45% SiO_2 as a constituent oxide of the coating system. During hot corrosion experiment, the SiO_2 is supposed to react with the basic sulphate melt ($a_{Na_2O} > 1 \times 10^{-11}$ at 900 °C) and form a Na-silicate melt at the Na_2SO_4–SiO_2 interface according to the following reaction [13]:

$$Na_2SO_4(l) + xSiO_2 \Leftrightarrow Na_2O(SiO_2)_x(l) + SO_3(g) \tag{2}$$

Decomposition of the sulphate is the precondition for reaction (2)

$$Na_2SO_4 \Leftrightarrow Na_2O + SO_3(g) \tag{3}$$

The silicate melt is dragged locally away from its point of origin and the transferred silicate melt forms hillocks on the surface of SiO_2 due to their different surface tensions and turbulence effects at their interface. Thus, new bare SiO_2 surfaces are exposed resulting in direct contact between the sulphate melt and the SiO_2, thereby promoting the formation of Na-silicate melt [13]. It is assumed that similar type of reaction occurs when the glass coating is corroded by Na_2SO_4 vapour.

The melting point of NaCl (801 °C) is lower than that of Na_2SO_4 (884 °C). NaCl forms a eutectic with Na_2SO_4 at 620 °C

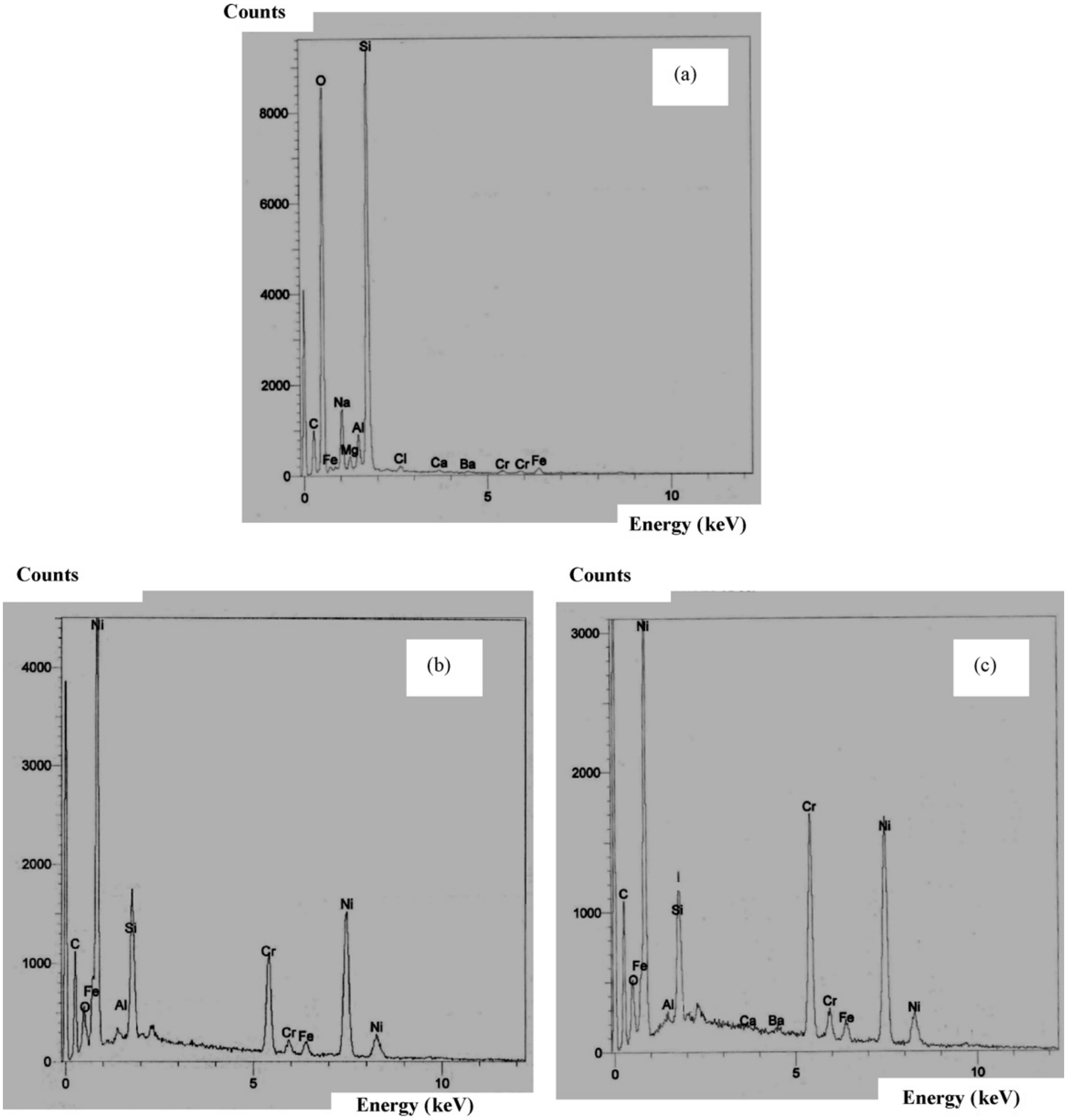

Fig. 8. EDX spectra of (a) region D, (b) region E and (c) region F as shown in Fig. 6(c).

that leads to faster corrosion rate. In addition, NaCl vapour reacts with dissolved oxygen in the melts and SiO_2 according to the following reaction proposed by others [14]:

$$2NaCl(g) + 0.5O_2(g) + 2SiO_2(s) \rightarrow Na_2Si_2O_5(l) + Cl_2(g) \qquad (4)$$

Similar reaction of NaCl vapour with oxygen and SiO_2 of the glass coating also occurs during hot corrosion of the glass coating by the salt vapour. Dissolved oxygen diffuses through the molten salts to the specimen and reacts with the NaCl melt and the SiO_2 of the glass coating. This phenomenon is expected to form Na-silicate melt at the NaCl–SiO_2 interface and as a consequence, the glass coating is corroded by the salt melts [2]. It has been observed that the interaction between SiO_2 and the corrosive salt occurs significantly at the interface. Gradually, silica dissolves in the corrosive molten salt mixture because of the dissolution of the silicate formed via Eqs. (2) and (4) that produces mass loss of the glass coating. In this case, liquid corrosion products are removed by the agitated corrosive liquid exposing fresh surface locally available for the reaction. On the other hand, when the specimen is suspended in the salt vapour, molten salt is vapourized and condensed on the surface of the specimen thus accelerating the corrosion reactions.

4. Conclusions

Glass coating on nickel base superalloy substrate suffered from differential hot corrosive attack at 1000 °C by immersion in the molten salt mixture (80 wt.% Na_2SO_4 + 20 wt.% NaCl) and suspension in the salt vapour of identical composition. Greater mass loss per unit surface area was observed with the specimen suspended in the salt vapour. Even after 35 h exposure in the molten salt and salt vapour the coating appearance as well as the condition of the coating–substrate interface region was found to be only marginally affected and the absolute mass loss was found to be about 6.0 and 7.5 mg/cm^2, respectively. However, the surface of the coatings was significantly affected when they are exposed to the molten salt mixture and salt vapour for 35 h.

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