A STUDY ON THE MICROSTRUCTURAL CHANGES OF Cr-MODIFIED ALUMINIDE COATINGS ON A NICKEL-BASED SUPERALLOY DURING HOT CORROSION

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Abstract — Microstructural changes of chromium-modified aluminide coating on IN-738LC superalloy under hot corrosion conditions were studied in this research. Samples were coated using two separate pack cementation processes, i.e. chromizing and aluminizing. Hot corrosion resistance of the coatings was evaluated using the furnace test method. For this purpose the specimens were coated with a thin layer of Na_2SO_4-5 wt% NaCl and then oxidized in air for a period of 1000 hours at 850 °C. The results of the hot corrosion test indicated that lower chromium content in the chromizing pack powder (C10A coating) resulted in the formation of a uniform adhesive surface oxide scale, containing mainly Al_2O_3. However, the C20A coating with higher chromium content exhibited Cr_2O_3 as a major surface oxide. The maximum depth of sulphur penetration in the C10A coating was 60 μm, which was very low in comparison with that of the C20A coating (i.e. 350 μm). In addition, the distribution of elements and precipitates within the coatings and the substrate before and after the hot corrosion tests was analyzed. From this investigation, some suggestions were made for better hot corrosion resistance of the coatings.

Résumé — Dans cette recherche, on a étudié les changements de microstructure d'un revêtement d'aluminide modifié au chrome sur le superalliage IN-738LC sous des conditions de corrosion à chaud. On a revêtu les échantillons en utilisant deux procédés distincts de cémentation solide, soit la chromisation et l'aluminisation. On a évalué la résistance à la corrosion à chaud des revêtements en utilisant la méthode d'essai au four. Dans ce but, on a revêtu les échantillons avec une couche mince de Na_2SO_4 – 5% en poids de NaCl et on les a ensuite oxydés à l'air sur une période de 1000 heures à 850 °C. Les résultats de cet essai de corrosion à chaud ont indiqué que la plus faible teneur en chrome de la poudre de chromisation solide (revêtement C10A) avait pour conséquence la formation d'une écaille de surface adhésive et uniforme contenant principalement du Al_2O_3. Cependant, le revêtement C20A, avec une plus haute teneur en chrome, exhibait du Cr_2O_3 comme principal oxyde de surface. La profondeur maximale de pénétration du soufre dans le revêtement C10A était de 60 μm, ce qui était très faible en comparaison avec celle du revêtement C20A (i.e. 350 μm). De plus, on a analysé la distribution des éléments et des précipités dans les revêtements et dans le substrat avant et après les essais de corrosion à chaud. À partir de cette investigation, on fait quelques suggestions pour une meilleure résistance à la corrosion à chaud des revêtements.

INTRODUCTION

The nickel-based superalloy IN-738LC has been extensively used as a blade material for the hot stage components in industrial gas turbines. Diffusion aluminide coatings are applied to the blades to protect them from environmental degradation at higher temperatures. These coatings provide good oxidation resistance, but limited resistance to hot corrosion. Additions of elements such as Cr or Pt to the diffusion aluminide coatings have been reported to provide increased protectivity under hot corrosion and oxidation environments [1-3]. Chromium-modified aluminide coatings produced by a single or two step pack cementation process provide a high hot corrosion resistance.

The microstructure and corresponding corrosion resistance of Cr-modified aluminide coatings have been extensively studied [3-6]. However, there is little information available on the effect of chromium level

on the microstructure and hot corrosion properties of these types of coatings [4,5].

The structure and hot corrosion behaviour of chromium-modified aluminide coatings is influenced by the coating process as reported in the literature [7]. In the duplex coating process in which chromium is first deposited followed by pack aluminizing, the final distribution of chromium in the coating depends on whether the aluminide coating is formed due to inward diffusion of aluminum or outward diffusion of nickel from the substrate [8,9]. In this case, the mechanism for aluminide growth is dictated by the aluminum activity in the pack which affects the stoichiometry of the aluminide coating. It has been reported [9] that the chromium-aluminide coating formed by inward diffusion has an outer layer containing α-Cr precipitates in a matrix having nearly β-NiAl stoichiometry, while a chromium-aluminide coating formed by outward diffusion has an inner layer enriched in Cr and an outer layer which is Ni-rich hypostoichiometry β-NiAl with approximately 2-5 wt% chromium in solid solution.

Two types of chromium-modified aluminide coatings were applied to a nickel base superalloy IN-738LC using a two-step pack cementation process in this work. The coated samples were subjected to a corrosive environment at high temperature and microstructural changes due to hot corrosion were then investigated.

EXPERIMENTAL PROCEDURE

IN-738LC alloy with the nominal composition as shown in Table I was used as a substrate for this study. The alloy was cut into samples with dimensions of 10×10×3 mm. The samples were mechanically ground up to 600-grit using a silicon carbide (SiC) paper and cleaned in acetone prior to the coating process. The samples were coated using a halide-activated pack cementation process in two separate steps: chromizing and aluminizing.

Chromizing was carried out at 1100 °C for 12 hours using two different powder mixtures given in Table II. The chromized specimens were further aluminized in a low activity pack cementation process at 1050 °C for 4 hours. Details of the coating procedure have been reported elsewhere by Rastegari *et al.* [5]. In this paper, the two chromium-modified aluminide coatings are referred to C10A and C20A on the basis of

Table II – Pack powder composition for the coating processes

Pack	Process	Composition (wt%)				
		Cr	Al	NH_4Cl	NH_4Br	Al_2O_3
1	Chromizing	10	-	2	-	Bal.
2	Chromizing	20	-	4	-	Bal.
3	Aluminizing	-	2	-	0.5	Bal.

chromium content in the chromizing pack powder (see Table II), which is 10 wt% and 20 wt%, respectively.

For the hot corrosion (type I) test, the furnace test method was conducted at 850 °C for up to 1000 hours. The samples were preheated on a hot plate and then coated with a saturated water solution of Na_2SO_4-5 wt% NaCl every 24 hours. The samples were weighed before and after salt spraying to ensure a salt supply of about 2 mg/cm^2 on the surface of each sample.

In order to examine the microstructure of the coatings before and after hot corrosion test, the coated and tested samples were mounted and ground up to 1000 grit with SiC paper and then polished using 1μm diamond paste. The samples were then analyzed using scanning electron microscopy (SEM) with an energy-dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

In order to find a relationship between hot corrosion behaviour and the microstructure of the coatings, the microstructures of as-coated and as-corroded conditions were analyzed. Results are discussed in the following sections.

As-coated Microstructures

Typical microstructure of the C10A coating is shown in Figure 1. The thickness of the coating is about 75 μm within which three sub layers can be observed: an outer layer with a two-phase structure which consists of mainly β-NiAl matrix with small precipitates of chromium-rich α-phase as seen in the X-ray elemental maps shown in Figure 1, a middle layer depleted from Cr and Al elements and an inner layer consisting of

Table I – Nominal chemical composition of substrate alloy (IN-738LC wt%)

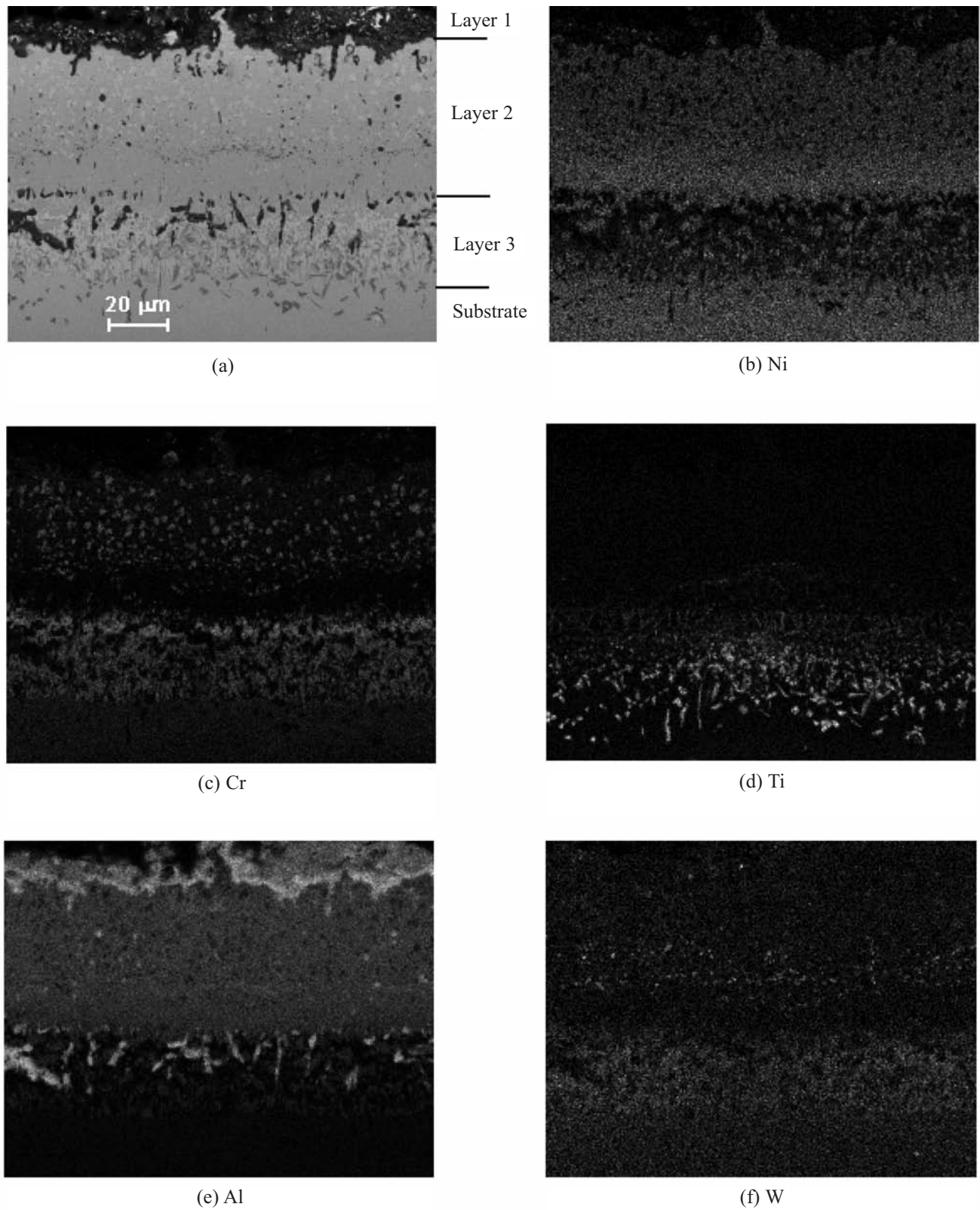| Co	Cr	Ti	Al	W	Ta	Mo	Nb	Zr	C	B	Ni
8.5	16	3.4	3.4	2.6	1.7	1.7	0.9	0.05	0.11	0.01	Bal.

Fig. 1. a) Typical SEM microstructure of the coating formed in the chromizing pack powder C10A and b) to f) EDS maps of shown elements.
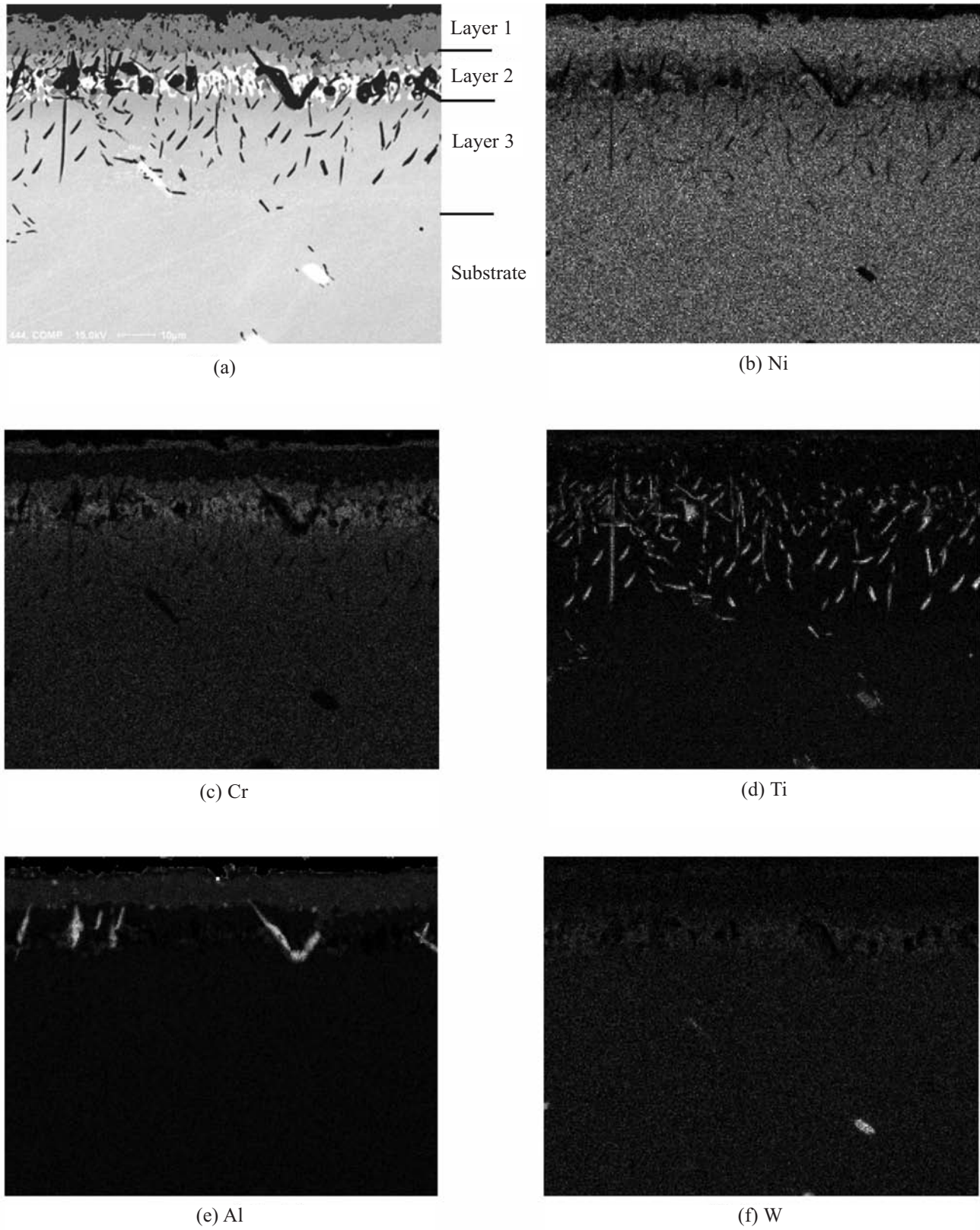
Fig. 2.   a) Typical SEM microstructure of the coating formed in the chromizing pack powder C20A and b) to f) EDS maps of shown elements.

three kinds of precipitates, i.e., chromium enriched α-phase, titanium-enriched and aluminum-enriched precipitates (see Figure 1). Coasta *et al*. [4] in a similar research reported that the titanium-rich particles are possibly Ti(C, N) and the aluminum-rich particles composed of a nonmetallic phase.

Figure 2 shows the microstructure of the C20A coating. This coating is about 60 μm thick and consists of several layers: an outer layer rich in Ni and Al, a middle layer rich in Cr, Al, Ti precipitates and an inner layer rich in Ti precipitates.

Hot Corroded Microstructures

The microstructures and corresponding X-ray elemental maps of chromium-modified C10A and C20A coatings after hot corrosion for 1000 hours at 850 °C are shown in Figures 3 to 6. Figures 4f and 6f show that sulphur diffused deeply throughout the coating and the substrate, while Figures 4e and 6e show the element oxygen is in both the surface of the coating as oxide scale and throughout the coating in the form of internal oxide particles. The thickness of the hot corrosion affected zone in C10A coating was about 80μm as shown in Figures 3 and 5. Figures 4b and 4 show that the dark particles in Figure 3 are enriched in aluminum and oxygen. This observation suggests that the surface oxide scale as well as internal oxides is likely Al_2O_3 which undergo a basic oxide scale fluxing reaction as follow [12]:

$$Al_2O_3+O_2=2AlO_2^-   \qquad (1)$$

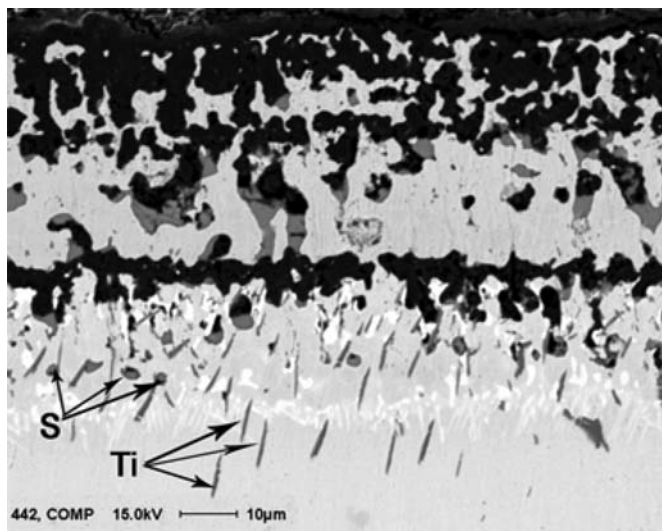The total thickness of the coating layers in the C20A sample was about 380 μm and consisted of a

Fig. 3. Typical microstructure of chromium-modified coating C10A after 1000 hour hot corrosion test at 850 °C.

surface oxide scale and several other layers formed in the chromium depleted matrix. The outermost layer was a thick surface oxide scale which consisted mainly of Cr_2O_3 with small amounts of nickel oxide that was confirmed by X-ray maps shown in Figure 6. This scale is brittle with insufficient adhesion to the underneath material and it dissolves under a basic reaction as follows [12]:

$$Cr_2O_3+O_2=2CrO_2^-   \qquad (2)$$

Underneath the Cr_2O_3 surface scale; there was a layer of NiAl (Figure 6) containing mainly Al_2O_3 particles with some Ti- enriched precipitates. The third layer was a titanium depleted zone containing chromium sulfide precipitates (Figure 6f). The fourth and innermost layer was a chromium depleted matrix in which some fine Cr precipitate can still be seen (Figure 7a). As seen in Figure 7, the layer contains needle-like titanium and aluminum enriched precipitates. These precipitates seem to be formed mainly in closely packed planes of $L1_2$ matrix structure, as it could be recognized from their direction relative to one another. The angle between the needles is about 110 degrees which is an indication that such needle-like particles were formed within an octahedral plane of $L1_2$ structure of the matrix.

Comparing Figures 4 and 6, one can observe that the Ti enriched needle-like precipitates formed in specific directions in sample C20A, did not precipitate in the same manner in C10A. This might be due to additional Cr-content in C20A; however, this requires additional work in order to establish the reason for this behaviour.

Higher chromium content in the C20A sample resulted in the formation of Cr_2O_3 scale, while lower chromium content in C10A sample resulted in Al_2O_3 after being subjected to the hot corrosion test. By comparing the microstructures and depth of the sulphur penetration (Figures 4f and 6f) of the tested samples, it can be speculated that the coating degradation in the coating (C20A) with higher chromium content appeared more severe than that of the C10A. This indicates that alumina is more protective than chromia due to the lower solubility in the molten salt as it also has been reported by Rapp [13] and lower sulphur diffusion rate through the protective scale.

CONCLUSIONS

1. The amount of chromium in the powder used for chromizing is an effective parameter in determining the thickness of the coatings. An increase in the chromium content of the powder pack from 10 to 20% caused a decrease in the coating thickness.
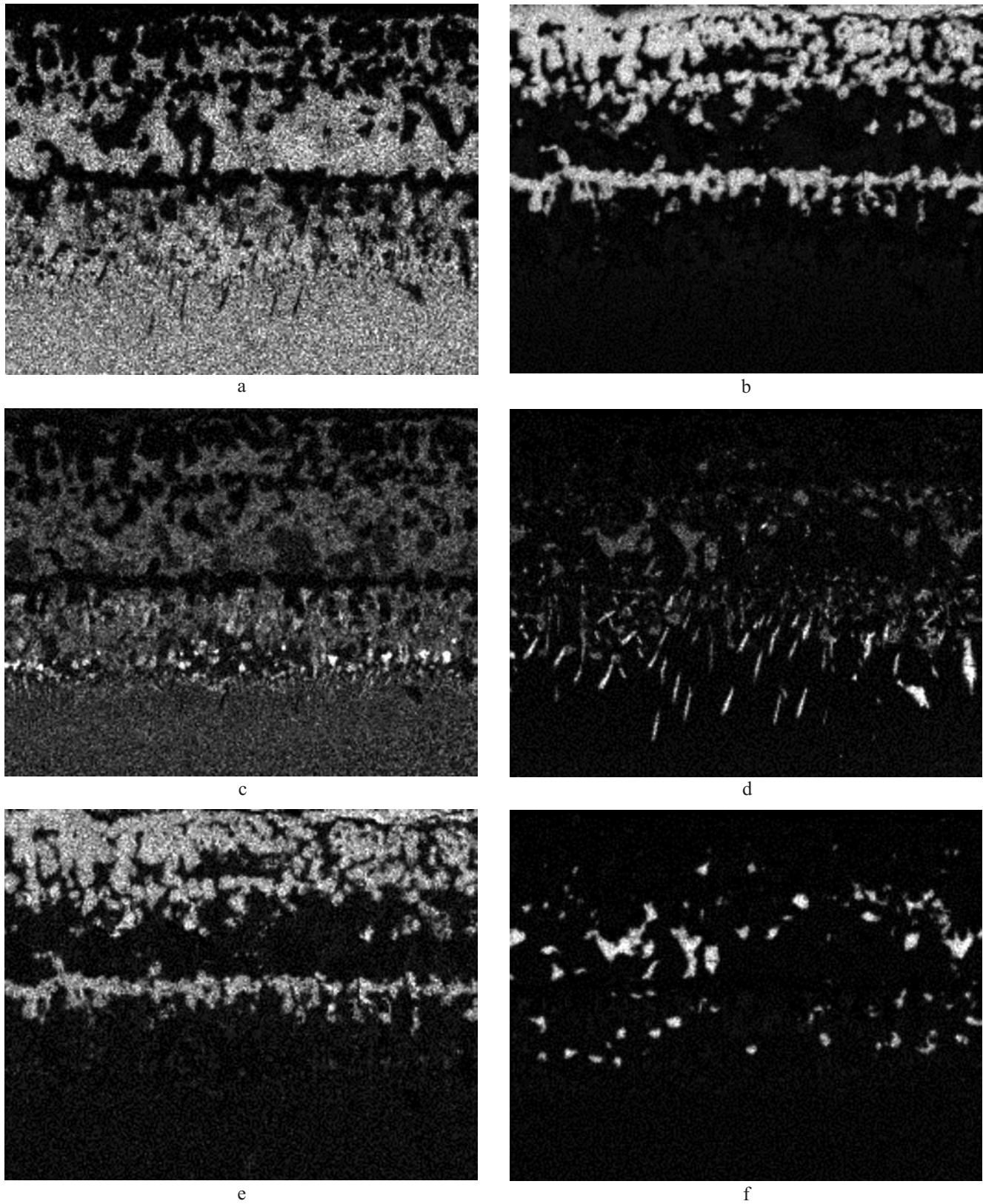
Fig. 4.   X-ray maps of chromium-modified coating C10A after 1000 hour hot corrosion test at 850 °C: a) Ni   b) Al   c) Cr   d) Ti   e) O and f) S.
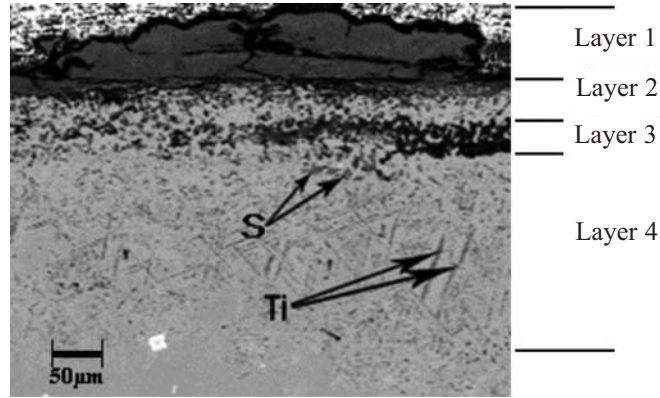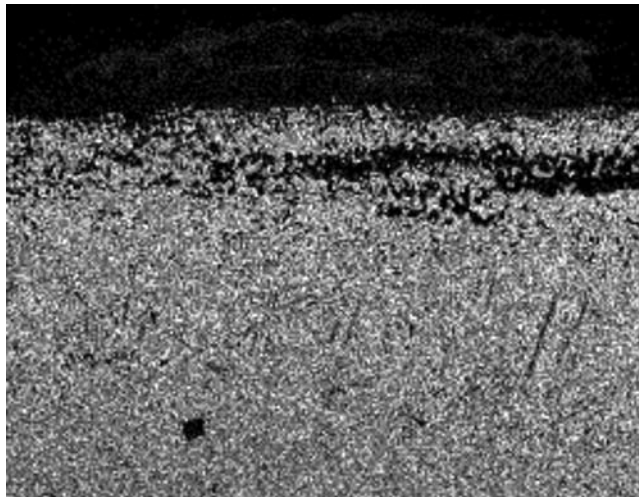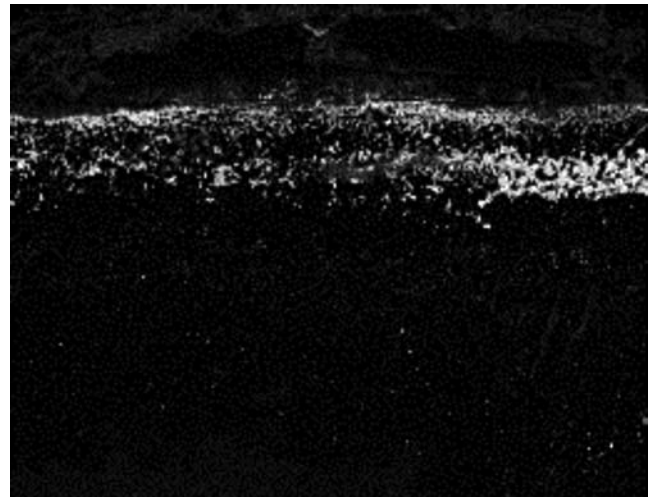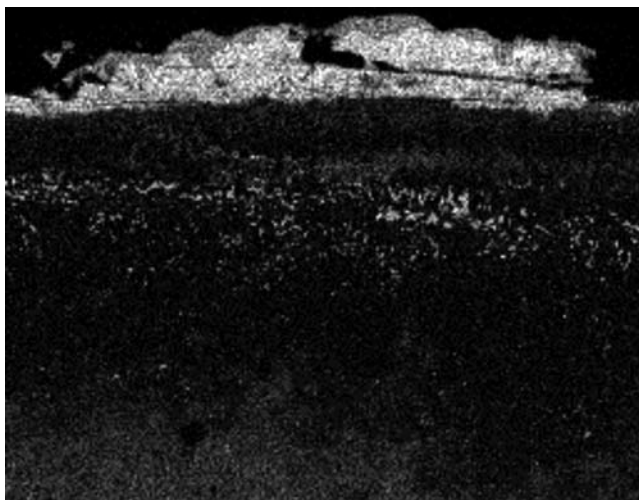
Fig. 5. Typical microstructure of chromium-modified coating C20A after 1000 hour hot corrosion test at 850 °C.
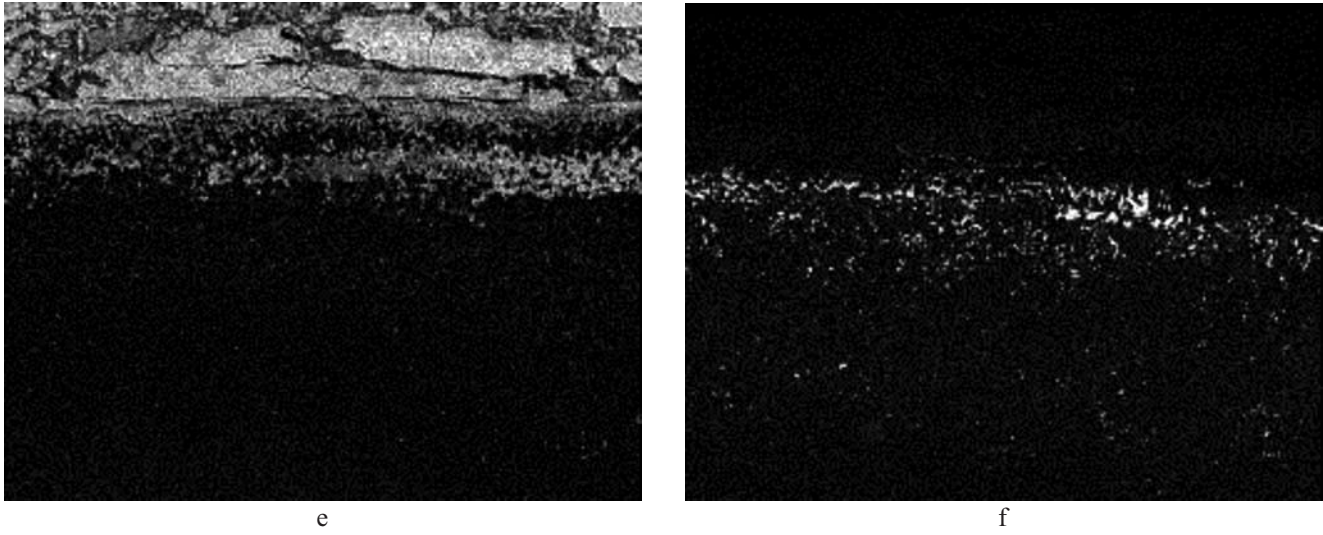
e

f

Fig. 6.   X-ray maps of chromium-modified coating C20A after 1000 hour hot corrosion test at 850 °C a) Ni b) Al c) Cr d) Ti e) O and f) S.
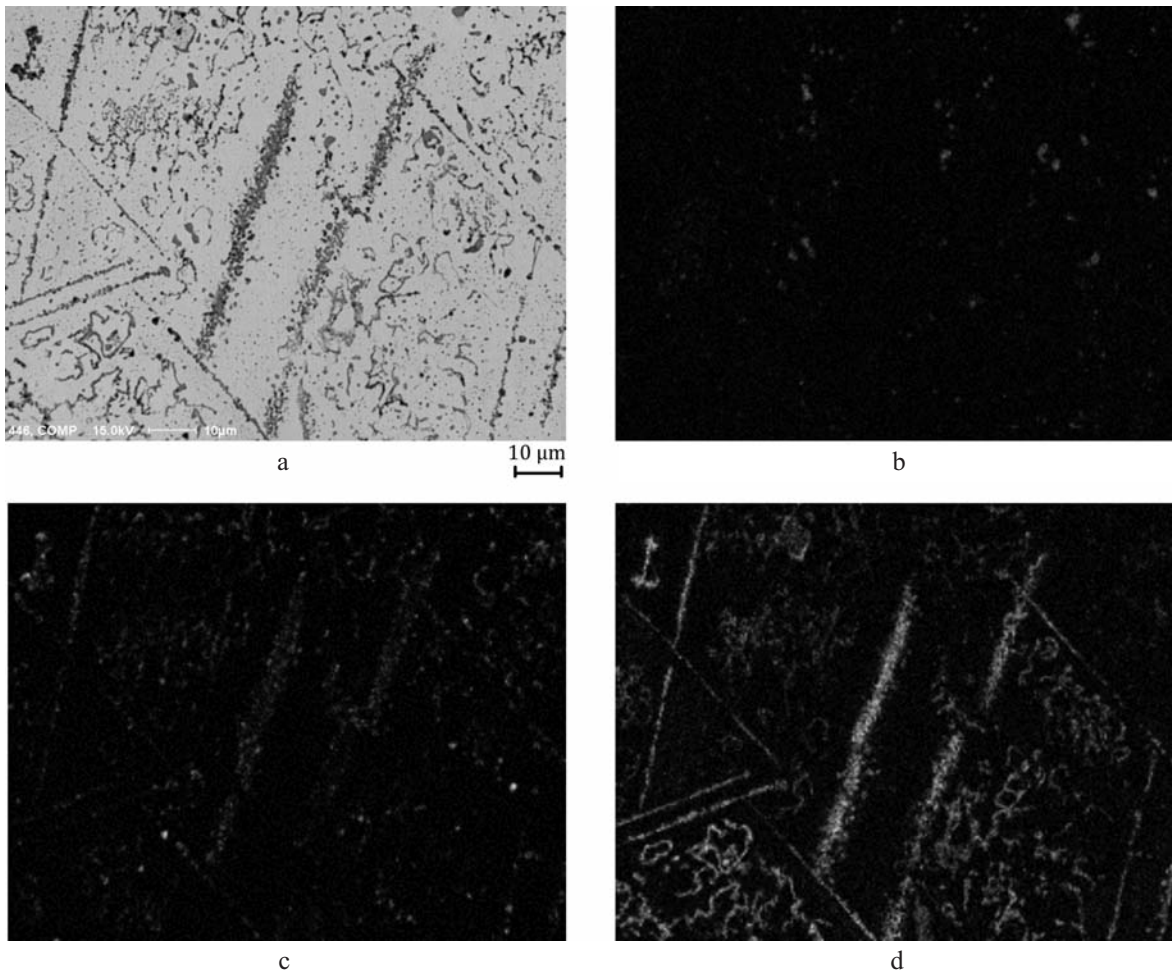

a

10 µm

b

c

d

Fig. 7.   Microstructure and X-ray maps of the forth layer C20A coating after 1000 hour hot corrosion test at 850 °C. a) SEM Micrograph, b) Cr c) Al d) Ti.

2. Chromium-modified aluminide coating is susceptible to sulphur diffusion and sulphidation. In this type of coating, sulphur diffuses through the coating and then interacts to form sulphides

3. The type of the surface oxide scale (i.e., Al_2O_3 or Cr_2O_3) formed on Cr-modified aluminide coating during hot corrosion is influenced by the amount of Cr in the pack powder composition. Aluminum oxide surface that formed on the C10A sample had more resistance against hot corrosion in comparison with the C20A sample which had a chromium oxide scale on its surface

4. The depth of sulphur penetration through the coating with more chromium is more than that with less Cr. This might be an indication that the amount of chromium within the pack should be optimized as the result of this work show that when Cr content increased from 10 to 20 wt%, the depth of sulphur penetration in spite of our expectations increased.

ACKNOWLEDGMENTS

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