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High temperature hot corrosion and oxidation of 733E831 based superalloy with TiO_2 thermal barrier coating

Kheder A. Salah, Mahmood A. Hamood, Mazin A. Abed

Department of Physics, College of Science, University of Mosul, Iraq

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The surfaces of turbine blades made of nickel-based alloys were coated with aluminum with thermal barrier titanium oxide (TiO_2) at a temperature of 1050 °C. The coatings protect the surfaces of these alloys from oxidation and hot corrosion in the surrounding atmosphere, as well as from sodium sulfate (Na_2SO_4) dissolved in the fuel. The samples were subjected to periodic oxidation and hot corrosion at a temperature of 1080 °C. The weight gain of samples coated with aluminum as well as the weight loss after oxidation and hot corrosion were calculated. The coating with a thermal barrier (TiO_2) shows good stability.

Keywords: oxidation, hot corrosion, aluminizing, thermal barrier coating.

Високотемпературна гаряча корозія та окислення суперсплаву на основі 733E831 з теплозахисним покриттям TiO_2. *Kheder A. Salah, Mahmood A. Hamood, Mazin A. Abed*

Поверхні турбінних лопаток зі сплавів на основі нікелю покривали алюмінієм з термобар'єрним оксидом титану (TiO_2) при температурі 1050 °C. Покриття захищають поверхні цих сплавів від окислення і гарячої корозії в навколишній атмосфері, а також від сульфату натрію (Na_2SO_4), розчиненого в паливі. Зразки піддавали періодичному окисленню та гарячій корозії при температурі 1080 °C. Розраховано приріст ваги зразків, покритих алюмінієм, а також втрату ваги після окислення та гарячої корозії. Покриття з термобар'єром (TiO_2) показує хорошу стабільність.

1. Introduction

Engineering materials used at high temperatures and in various hard environments are subjected to mechanical and thermal stresses under acceleration conditions; therefore, they must have good resistance to heat, oxidation and hot corrosion at higher temperatures. The low cost superalloy used in gas turbine engine is one of such materials, which includes nickel-based alloys and cobalt-base alloys.

Nickel-based alloys are thermally less efficient, but have higher resistance to oxidation and hot corrosion compared to cobalt-based alloys; the melting point of the $Co\text{-}Co/S_3$ eutectoid is 877°C compared to the $Ni\text{-}Ni/S_3$ eutectoid (645°C), while the spread of sulfur in cobalt superalloys is 100 times less than in nickel superalloys. Cobalt-based alloys are used in the manufacture of burner plates, fans and fuel injectors [1, 2].

Ni-based alloys containing predominantly Ni and other elements are characterized by high values of tensile strength, creep and fatigue strength, ductility, toughness, and oxidation resistance, as well as resistance to hot corrosion; they were developed by Seneca, which designed the 4th generation SC MC-NG alloy in France [3], and the 4th generation LDSX alloy was developed in the UK [4].

The heat treatment of the nickel-based super alloy includes two operations: the first heat treatment is used to homogenize microstructure and reduce the effects of element segregation, while the second heat treatment is carried out to obtain γ-precipitates which enhance the hardening of the alloys [5].

Thermal barrier coatings (TBC_S) have been used to protect gas turbine components exposed to a complex of harsh conditions such as very high temperatures, hot corrosion and oxidation [6, 7]. High temperature stability, thermal conductivity, fracture toughness, and coefficient of thermal expansion are the main characteristics of TBC_S which limit the service life [8, 9].

Thermal barrier coating (TBC_S) typically consists of a metal bond layer and a ceramic coating forming a synergistic system [10]. The thickness of (TBC_S) ranges from a few hundred microns to 1 mm or less, depending on the component and deposition technology. The coating mainly consists of four layers: a metal substrate, a metal bond layer, a thermally grown oxide (TGO) and a ceramic topcoat, as well as aluminum oxide ($3Al_2O_3$) and silica ($2SiO_2$), which are more resistant to oxidation and hot corrosion [11].

In this study, compression under oxidation and hot corrosion conditions was carried out on two samples of Ni-based alloys. The first alloy was coated with aluminum alone using a batch carburization method to protect the alloy by forming Al_2O_3 scale on the surface of the alloy; the second alloy sample was coated by aluminum with a thermal barrier of TiO_2. The samples were then subjected to periodic oxidation and hot corrosion at a temperature of 1080 °C. The weight gain after coating with aluminum and the weight loss after oxidation and hot corrosion were calculated.

2. Experimental Technique

Samples of nickel based super alloy 733E831 were prepared with dimensions suitable for the coating system. The oxide layer on the surface of the samples was removed with silicon carbide sandpaper of grit size (180, 220, 240, 320, 400, 600, 800, 1000, 1200, 1500, 2000); then the samples were washed with a mixture of water and Al_2O_3 powder to remove grease from the surfaces of the samples; finally the samples were cleaned by alcohol and distilled water respectively and left to dried to prepare for the coating process. In our research, the alloy was coated with titanium oxide (TiO_2SB) followed by aluminizing.

2.1 Coating Processes

Pack cementation process

Aluminizing is the first of the diffusion coating methods to provide better resistance to oxidation and hot corrosion [12, 13]. The cementation process was carried out for all samples using cement powder consisting of a mixture of coating materials. The coating material mixture included (25%) aluminum (Al), (5%) ammonium chloride (NH_4Cl) powder as an activator and (70%) alumina (aluminum oxide Al_2O_3), which prevent the mixture from clumping.

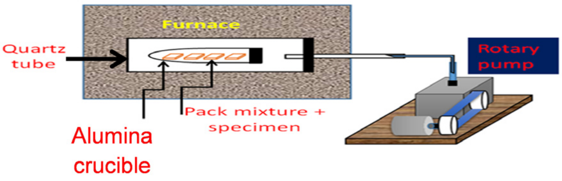

Fig.1.Schematic diagram of the coating system

The samples are completely immersed in the powder mixture contained in the package, the package is hermetically sealed, then placed in a quartz tube that is closed at one end; the other end of the quartz tube is closed with a rubber stopper and tied to a rotary tube to obtain a vacuum atmosphere during the coating process in order to prevent samples from oxidation. The furnace temperature was fixed at 1050°C and the duration of the coating process was varied (2, 4, 6, and 8 hours).

After the coating process, the samples were cooled inside the furnace until a temperature of 25°C was reached. The samples then washed, dried, weighted and kept under the same conditions until tests.

Thermal barrier coating

Rare element oxides as ceramic materials have been used to coat alloys by batch carburization because they have varying resistance to oxidation, hot corrosion and wear, and are better thermal insulators [14]. In our studies, a thermal barrier coating of titanium oxide TiO_2 was applied in two stages: first, the alloy was coated with titanium oxide in a vacuum of about (10^{-3}-10^{-2} Torr), and then annealed at a temperature of 1050°C for various periods (2, 4, 6.8 hours).

2.2 Optical Images of Samples

Obtaining images of samples with optical microscope required several procedures: grinding on silicon carbide paper (180, 220, 240, 320, 400, 600, 800,1000,1200,1500 and 2000), followed by polishing with diamond paste or alumina solution (Al_2O_3); then the samples were washed with distilled water and alcohol respectively and left to dry. Finally, the etching step used Keller's solution, which is a mixture of

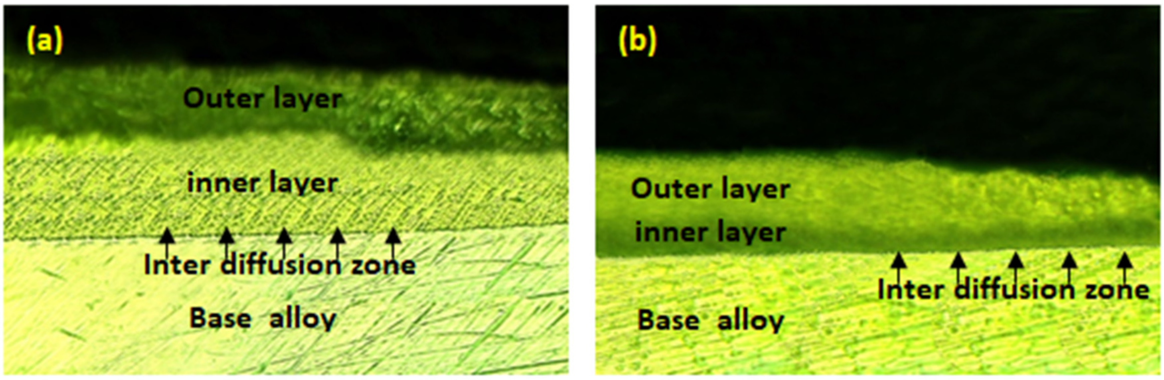

Fig.2. Microscopic composition of a single aluminized coating at 1050 °C: (a) – 4 hours, (b) – 8 hours

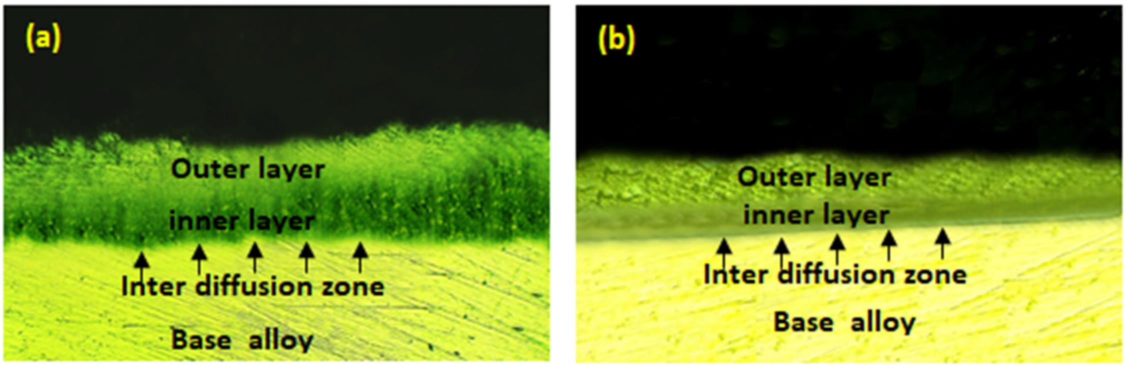

Fig.3.Microscopic composition of TBCS TiO_2 on 733E-831 at 1050 °C: (a) – 4 hours, (b) – 8 hours

hydrofluoric acid (0.5% HF), hydrochloric acid (1.5% HCl), nitric acid (2.5% HNO_3) and the rest distilled water.

3. Results and discussion

3.1 Thermal barrier coating (TBC)

Microscopic images of alloy samples coated by aluminum alone and aluminum with TBC showed the formation of two layers at different time periods of 2, 4, 6 and 8 hours, regardless of the thickness (Fig.2 and Fig.3).

1. The **outer layer** represents the largest part of the coating (it is a thick and dark in color), has secondary phases and is heavily exposed to the etching solution.
2. The inner thin layer below the outer layer (its color is bright and shiny) does not have deposits and is less sensitive to the etching solution.
3. The interdiffusion zone is a narrow area practically devoid of deposits.

The X-ray diffraction patterns show the presence of phases Ni_3Al, Ni_2Al_3, NiAl but the most stable and balanced phase was NiAl which represents the base of the outer coating layer and may be residues of the (Ni_2Al_3) phase. Chromium-aluminum compounds (CrAl, $CrAl_2$, $CrAl_5$) and the ($FeAl_{13}$) phase were deposited as secondary phases; all the phases appear when samples are coated with aluminum in the presence of a thermal barrier at all time intervals (Fig.4).

The inner layer (Ni_3Al) arises due to low internal diffusion of nickel and appears free of sediments. The phases Ti_3Al_5, Al_3Ti, Al_2Ti, Al_3Ti_2 as well as TiO_2 arise from the titanium oxide which is used as a thermal barrier.

The energy dispersive spectroscopy (EDS) shows the presence of all the elements in the alloy samples after aluminizing for 4 and 8 hours. The high aluminum peak results from the presence of primary aluminum among the alloy elements in addition to the aluminum produced by the aluminizing process (Fig. 8).The EDS test after coating with the thermal barrier of titanium oxide show the presence of titanium and oxygen elements. The thermal barrier will prevent the diffusion of the alloy elements; therefore, the alloy elements disappear from the test pattern (Fig. 9).

Figures 10(a) and 10(b) show the uniform distribution of aluminum on the alloy surface after the aluminizing process, as well as aggre-

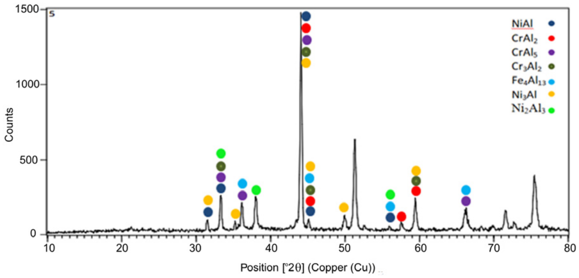

Fig.4. X-ray diffraction pattern showing different phases formed (single aluminized for 4 hr.)

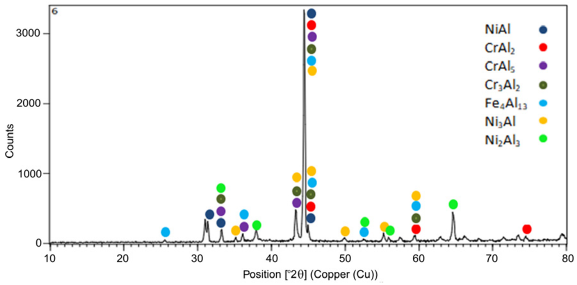

Fig.5. X-ray diffraction pattern showing different phases formed (single aluminized for 8hr.

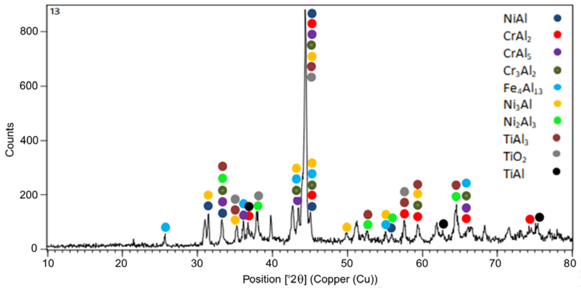

Fig.6. X-ray diffraction pattern showing different phases formed (TBC,TiO_2 , a - 4 hr.)

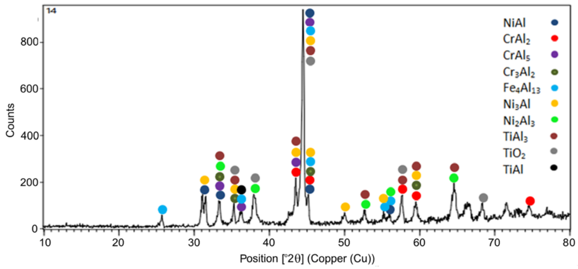

Fig.7. X-ray diffraction pattern showing different phases formed (TBC,TiO_2,b-8hr.)

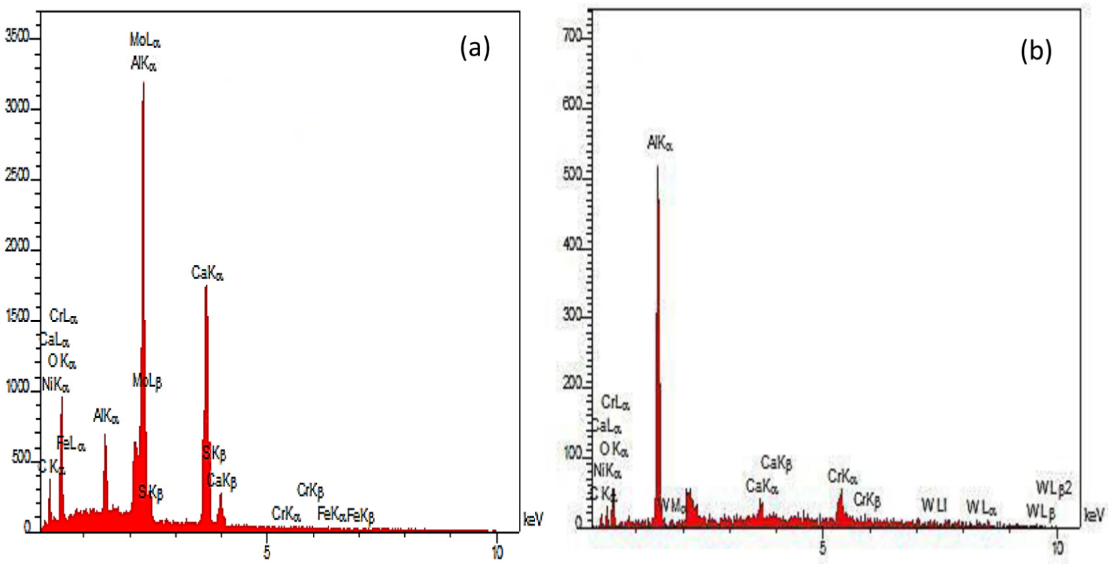

Fig.8. Energy dispersive spectra (EDS) of the single aluminizing on super alloys IN733E-831 at 1050°C: (a) – 4 hours, (b) – 8 hours

gation of the alloy elements with the aluminizing time from 4 to 8 hours.

Due to its porosity, the titanium oxide thermal barrier coating prevents the diffusion of alloy elements to the alloy surface. The structure of the thermal barrier was practically not affected by the high temperatures of the coating process (Figs.10(c) and 10(d)).

The percentage of aluminum decreases with increasing time of application of a single aluminum coating, which is accompanied by an increase in oxygen and carbon content; whereas in the presence of titanium oxide, the percentage of carbon and oxygen decreases with time of coating (Table 1).

This is important for surface modification of advanced alloys in surface engineering processes; this means that the number of casting elements in the original superalloy can be controlled to the required specifications.

Table 1. Quantitative and qualitative ratios of the superalloy

Elt.	Al 4hr (IN733E831)1		Elt.	Al 8hr (IN733E831)2		Elt.	TiO_2+Al 4hr (IN733E831)3		Elt.	TiO_2+Al 8hr (IN733E831)4	
	W(%)	A(%)		W(%)	A(%)		W(%)	A(%)		W(%)	A(%)
C	20.53	34.96	C	36.92	50.87	C	12.53	19.38	C	11.54	16.96
O	25.36	31.40	O	34.22	33.28	N	24.59	31.53	N	35.19	41.82
Mg	0.15	0.11	Mg	0.26	0.18	O	29.82	32.71	O	23.47	25.99
Al	34.34	25.13	Al	21.20	13.16	Al	17.72	12.57	Al	19.26	12.81
S	9.83	5.68	S	3.65	1.32	S	0.00	0.00	S	0.00	0.00
Ca	6.18	1.48	Ca	1.12	0.46	Ca	1.67	0.74	Ca	0.72	0.29
Cr	1.60	0.59	Cr	0.82	0.25	Cr	0.48	0.43	Cr	0.90	0.47
Ni	2.01	0.65	Ni	1.81	0.48	Ni	1.27	0.36	Ni	0.56	0.19
	100.00	100.00		100.00	100.00	TiO_2	11.29	2.28	TiO_2	8.36	1.74
							100	100	100	100	

Elt-element; W-weight percentage and A-atomic percentage

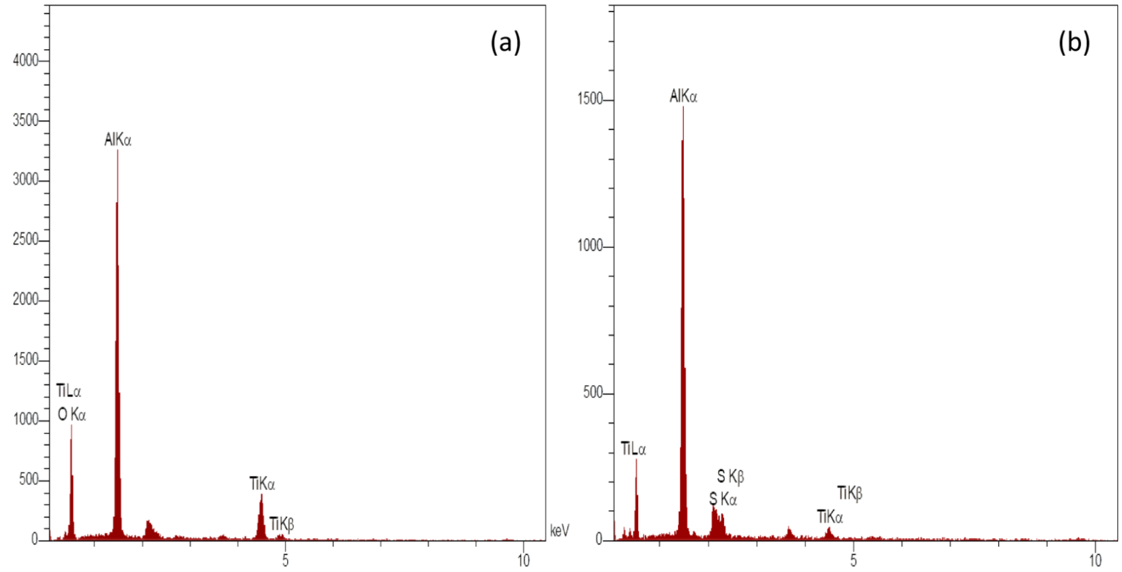

Fig.9. Energy dispersive spectra (EDS) of the thermal barrier coatings (TBC$_S$) TiO_2 on super alloys IN733E-831 at 1050°C: (a) – 4 hours, (b) – 8 hours

The weight gain in aluminizing processes was calculated and it was found that it increases with time according to a parabolic law (Fig. 11), since it is associated with the diffusion process, which, in turn, obeys a parabola.

Coating thickness increases over time for both types of coating (single aluminum coating and aluminum coating with a thermal barrier coating (TBC)).The weight gain of the single aluminum coating is higher than the that of the aluminum coating with the thermal barrier due to the porous nature of the thermal barrier which reduce the diffusion of aluminum to the alloy (Fig. 11).

Fig.12 shows the periodicity of oxidation and the kinetics of hot corrosion when all samples with a single aluminized coating are exposed to a vapor mixture of sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) at 1080 °C for three hours per cycle. Samples coated for 6 and 8 hours showed good weight stability throughout the exposure period, with a slight weight

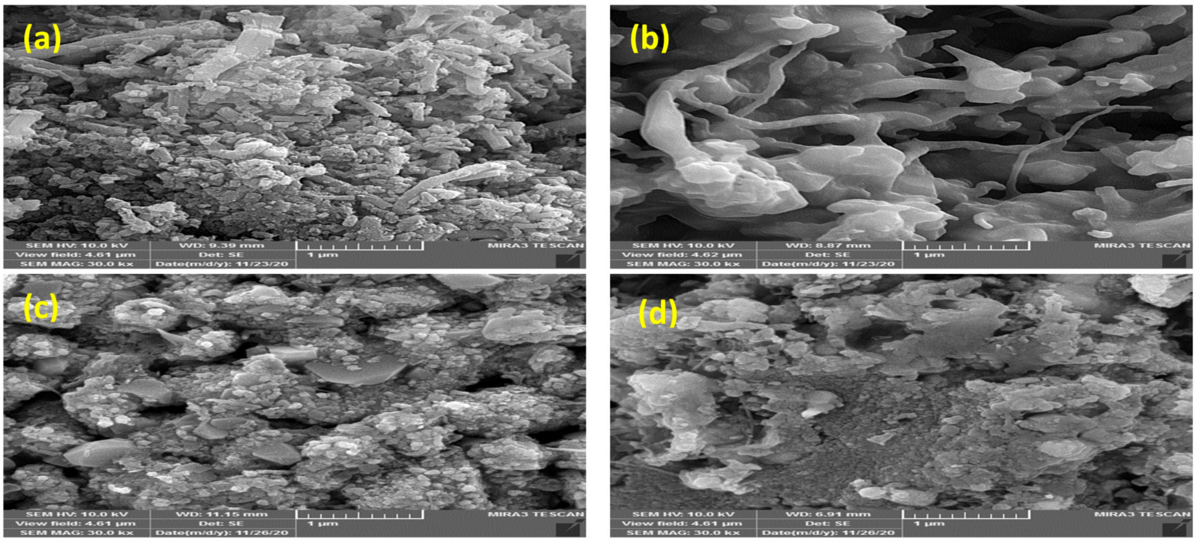

Fig.10. SEM images of a single aluminized coating ((a) – 4 hours, (b) – 8 hours) and a thermal barrier coating (TBCs) ((c) – 4 hours, (d) – 8 hours) on IN733E-831 superalloys at 1050°C.

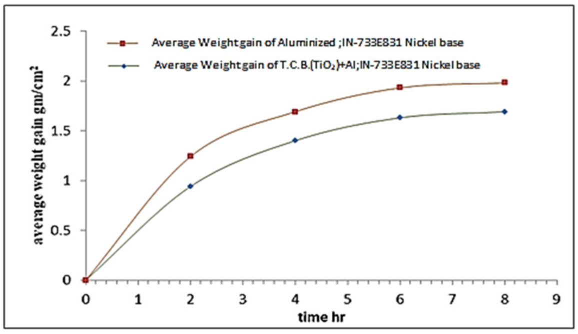

Fig. 11. Average weight gain as a function of the time: (a) single aluminized coating at 1050 °C , (b) aluminized coating with TiO_2 thermal barrier coating (TBC) at 1050 °C .

loss recorded at the end of the exposure period; this is due to the formation of protective oxides that adhere to the surface of the alloy, including Al_2O_3, which protects the alloy from oxidation and hot corrosion. Oxidation and hot corrosion cycles of the coated samples for 2 and 4 hours led to a noticeable reduction in weight due to the high rate of the processes; in this case, the formed protective oxide shell of Cr_2O_3 is converted into volatile CrO_3 compounds at temperatures above 900 °C. In addition, there are a number of oxides such as NiO and FeO, which have low melting points and precipitate below the protective oxides after several thermal cycles. The reason of a slight decrease in the weight during the cycles is due to the formation of unstable oxide (Θ-Al_2O_3), which occurred during the period of transient oxidation and before the formation of a stable protective oxide (α-Al_2O_3).

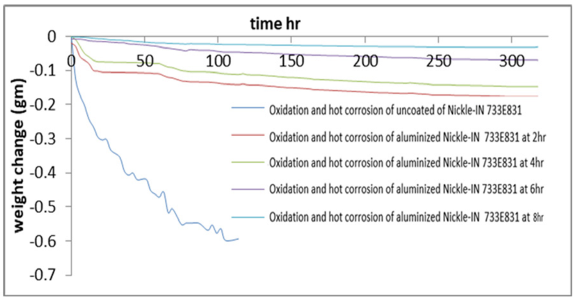

Fig.12. Cycle oxidation and hot corrosion of single aluminized (IN733E-831)in a mixture of steam Na_2SO_4 and NaCl at 1080³C (a) uncoated nickel-IN733E-831 and after different coating periods at 1050³C for (b) 2 hrs. (c) 4 hrs. (d) 6 hrs., and (e) 8 hrs.

The curve of weight change with time shows the kinetics of oxidation and hot corrosion for the samples coated with aluminum with TiO_2 thermal barrier (Fig.13). All the samples exhibited good stability in weight over approximately 300 hours throughout the period of exposure especially for the samples coated for 6 and 8 hours. At the same time, the samples coated for 2 and 4 hours had a slight weight loss after approximately 250 hours of exposure due to the formation of the unstable protective oxide (Θ-Al_2O_3) during the period of transient oxidation and before the formation of the protective stable oxide (α-Al_2O_3). This indicates that the resulting protective oxide crust remains attached to the coating layer, thereby providing the necessary protection. Perhaps, the slight discrepancy in weight recorded at the end of the exposure was caused by falling off of some parts of the protective oxide layer, especially at the 2 and 4 hour application times.

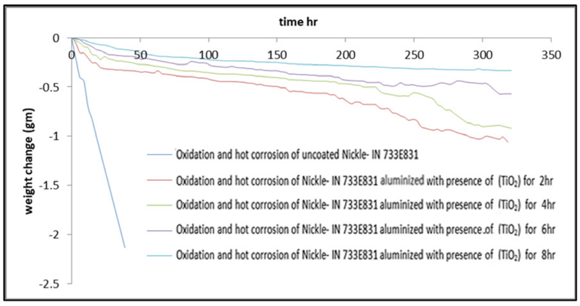

Fig.13.Cycle oxidation and hot corrosion of TBC using TiO_2 of (IN733E-831) in a mixture of steam Na_2SO_4 and NaCl at 1080◦C (a) uncoated nickel-IN733E-831 and after different coating periods at 1050^{3}C with presence of thermal barrier coating TiO_2 for (b) 2 hrs. (c) 4 hrs. (d) 6 hrs., and (e) 8 hrs.

3. Conclusions

Periodic oxidation and hot corrosion of samples coated with aluminum for 2, 4, 6 and 8 hours showed good stability of weight change over time throughout the test period, especially for samples coated for 6 and 8 hours. Although there is a very slight weight change variation for the samples coated for 2 and 4 hours. The reason for the weight loss during the cycles is due to the formation of unstable oxide Θ-Al_2O_3 during the transient oxidation stage and before the formation of the stable protective oxide α-Al_2O_3. This indicates that the resulting oxide crusts remain attached to the coating layer and thus provide protection. The slight decrease in weight recorded at the end of the exposure period may be due to the fall-off of part of the protective oxide crust, especially with coating times of 2 and 4 hours.

The high rates of oxidation and hot corrosion of the uncoated alloy may lead to the formation of Cr_2O_3 and possibly oxides NiO and FeO. These oxides quickly precipitate below the protective oxide Cr_2O_3 during the first thermal cycles, and the protective oxide can turn into volatile oxide CrO_3 at temperatures above 900°C.

Samples coated with aluminum with the presence of the thermal barrier titanium oxide TiO_2 have a good stability throughout the periodic exposure to oxidation and hot corrosion for about 300 hours, especially for samples coated for 6 and 8 hours; whereas samples coated for 2 and 4 hours will lose weight due to peeling of the protective oxide crust after 250 hours of testing. The reason for this may be the formation of an unstable protective oxide Θ-Al_2O_3 during transient oxidation before the formation of stable oxide α-Al_2O_3. The high durability of the coating during exposure is due to the stability of the protective oxide crust associated with two reasons: the first is complete coverage of the surface with the oxide crust; secondly, good continuous adhesion of the protective oxide crust resistant to harsh oxidation and corrosion conditions compared to the uncoated sample.

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