

Oxidation Study of Cobalt- base Super Alloys at High Temperatures in Molten Salt of Na₂SO₄

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ABSTRACT

The major objective of this study was to understand the mechanisms controlling the thermal barrier coatings (TBCs) and use this understanding to develop new TBCs with improved performance characteristics. The system studied consisted of the Cobalt-Base superalloy as a substrate and yttria-stabilized Alumina as a ceramic topcoat. A second objective of the study was to see the degradation behavior of the systems during thermal cycling (three hour cycles in a bottom-loading furnace). The failure mode for the aluminized because of the defects at the coating -thermally grown oxide (TGO) interface and at the TGO bond coat interface. The fractures then propagated along the interface between the bond coat and the TGO. The failure the aluminide was found a coat interface and a deformation mode of the bond coat.

The effect of cycle frequency on the spallation failure of the state TBCs was also found small degradation. The molten salt of (Na₂SO₄) conditions affect the lifetimes of the coatings. Exposure temperature was found to have a strong effect, which is consistent with TGO growth being a first order variable in scale failure.

Keywords: Thermal barrier coating, Diffusion coating, Aluminizing, Hot corrosion, Cobalt base super alloys, protective coating.

دراسة أكسدة السبيكة المحسنة ذات أساس كوبلت في منصهر كبريتات الصوديوم تحت درجات حرارية عالية

الملخص

تتعرض ريش المحركات التوربينية للطائرات ومحطات توليد الطاقة الكهربائية إلى درجات حرارية عالية والتي تتسبب في تآكل هذه الأجزاء وانهارها نتيجة لتفاعلها مع الوسط المحيط وان إحدى الطرائق الفعالة لحماية هذه الأجزاء عن طريق الطلاء الانتشاري وذلك باغناء سطوحها بالألمنيوم وفي هذا البحث تم تحضير نوعين من أنظمة الطلاء الانتشاري:

- بودقة السمينة الاعتيادية (Pack Cementation) وتمت ألمنة النماذج بدرجة حرارة (1000 °C) ولفترات زمنية (9,6,3) ساعة.

- الطلاء بالحاجز الحراري (Thermal Barrier Coating) وقد استخدم اوكسيد لعنصر نادر هو اوكسيد اليتيريوم (Y_2O_3).

لقد تمت دراسة آلية تكون الطلاء على سبيكة محسنة ذات أساس كوبلت (Fsx414) وأظهرت النتائج إن سمك طبقة الطلاء وكمية الألمنيوم المكتسب قد قلت بوجود الحاجز الحراري لان الأوكسيد يعمل على إعاقة انتشار الألمنيوم ولكن تحافظ على التركيب البنوي للطلاء. ومن جهة أخرى تمت دراسة آلية التآكل الحار بطريقة الدورات الحرارية في منصهر كبريتات الصوديوم في درجة حرارة ($1000^{\circ}C$) على النماذج المؤلمة والمؤلمة بوجود الحاجز الحراري وأنموذج قياسي للمقارنة وأظهرت النتائج كفاءة الطلاء بالحاجز والمؤلمة وبنسب متفاوتة وفشل النموذج القياسي بسرعة.

الكلمات الدالة : الطلاء بالحواجز الحرارية، الطلاء الانتشاري، الألمنة التقليدية، التآكل الحار، السبائك المحسنة ذات أساس كوبلت، حماية المعادن.

INTRODUCTION

Hot corrosion is a serious problem in power generation equipment, gas turbines for ships and aircraft, and in other energy conversion and chemical process systems, hot corrosion further poses a severe problem as the use of low-grade fuels is well known and justified due to depletion of high-grade fuels as well as high cost involved in removing the impurities. Coatings are frequently applied on gas turbine components in order to restrict surface degradation such as corrosion and oxidation of the structural material or to thermally insulate the structural material against the hot environment, thereby increasing the efficiency of the turbine. Surface degradation takes place through corrosion, oxidation and solid particle erosion (Miller, 1995). Corrosion pitting of a surface may for example act as a fatigue crack initiation site leading to failure of the component. In combination with other sub-surface damage processes, which reduce the strength and ductility, this leads to an accelerated failure. One example of corrosion is illustrated in Fig. 1, where an uncoated gas turbine blade is compared with an aluminide coated blade. Both blades were removed and inspected after 2500 hr sea flight service at low altitude.

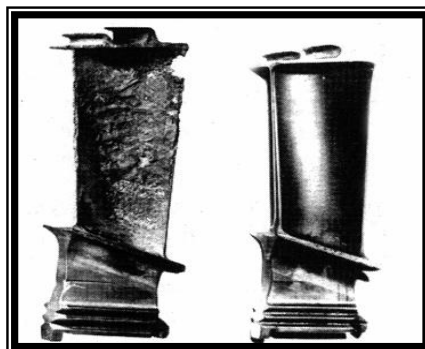


Fig. 1: Illustration of the corrosion effect of an uncoated (left) and a coated (right) turbine blade after 2500 hrs low altitude sea flight service. From ref. (Stiger *et al.*, 1999).

The use of thermal barrier coatings (TBCs) has resulted in a significant improvement in the efficiency of aircraft gas turbines (Bose and DeMasi-Marcin, 1995). These types of coatings have been used for many years on combustion liners, but with advanced thermal barrier coatings, vanes, and even the leading edges of blades can now be coated. The use of TBCs can achieve temperature differentials across the coating of as much as 200° C. Typical systems consist of a nickel-base super alloy substrate coated with a MCrAlY or diffusion aluminized bond coat, onto which is deposited a yttria-stabilized zirconia (YSZ) TBC. The bond coats are usually deposited via diffusion aluminizing processes or alloy, powder spray processes. The major factor controlling the life of thermal barrier coatings (TBCs) is the resistance of the coating to spallation under the influence of stresses generated during thermal exposure (Evans *et al.*, 2001). During fabrication and service a thermally grown oxide (TGO) forms Between the bond coat and the YSZ.

High temperature exposure results in growth of the TGO and sintering of the YSZ, both of which increase the elastic energy stored in the system after cooling to room temperature. Exposure also leads to microstructural and/or chemical changes, which result in regions of decreased fracture toughness. Eventually, fracture initiates and propagates through one or more of the following: the YSZ, the TGO, the interface between the TGO and bond coat or between the TGO and YSZ. A number of studies of TBC degradation have indicated that the fabrication method of the YSZ and bond coat can influence the crack path and the time to failure (Bose and DeMasi-Marcin, 1995). The current study is focusing on one single crystal superalloy substrate (René N5) and one EBPVD TBC and investigating the influences of bond coats on TBCs lives. The TBC is 8 wt.% yttria stabilized zirconia since this TBC is the current state-of-the-art. The bond coats, which are currently considered state-of-the-art, are platinum modified diffusion aluminides and MCrAlY coatings. In this study, different modifications of MCrAlY coatings and platinum aluminide bond coats have been studied. The approach consisted of investigating current state-of-the-art bond coats. As results were obtained on the failures of these TBCs, modifications were made to attempt to obtain new improved systems.

In previous studies, different results have often been obtained by different investigators studying nominally identical coatings. It has been suggested that these differences arise from variations in the exposure conditions (Handoko *et al.*, 2001). Therefore, an additional objective of this study was to evaluate the effects of exposure conditions on the degradation behavior of the various bond coats.

EXPERIMENTAL PROCEDURES

Specimen preparation

The base material used for this study was cobalt-base super alloys (Fsx414). Its chemical composition given in Table 1.

Table 1: composition of Fsx414 cobalt base alloys.

Element Fsx414%	Co	Cr	Ni	Fe	W	C
	Bal	28	10	1	8	0.25

All specimens used in this experiment were prepared as sheets of 5 mm wide, 3 mm thick and were cut to approximately 10 mm lengths.

Samples sheets were polished from 240-grits SiC paper up to 1 μm with diamond paste to eliminate the sharp edges, thereby providing an initially smooth surface for coating, cleaned in alcohol, dried and weighed.

Coating Processes

Pack Cementation

To produce aluminized compounds on these materials, aluminization was carried out by using the pack cementation methods. This process involved the pack mixture in an horizontal furnace having a constant temperature zone of about 150 mm length. Fig. 2 shows a schematic diagram of the pack cementation device used to produce the coating.

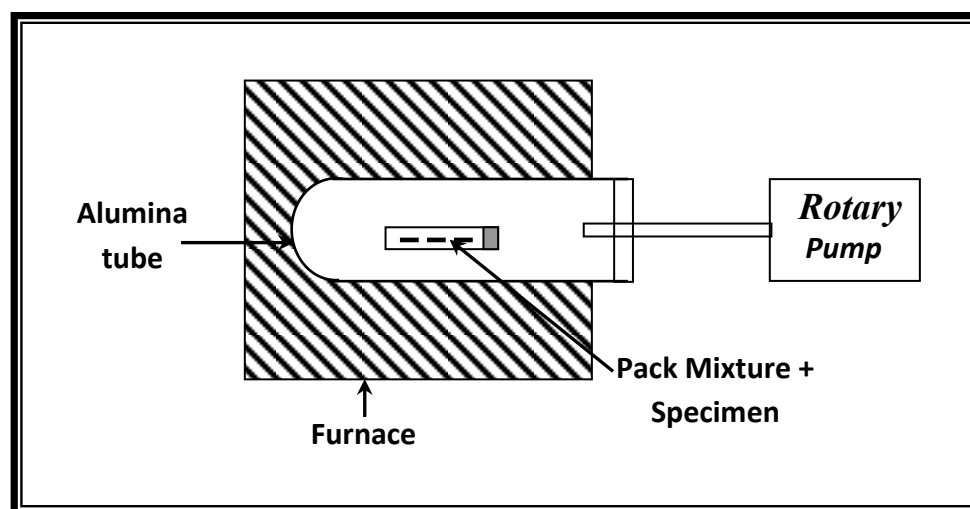


Fig. 2: Schematic diagram of the pack cementation.

The pack mixture is composed of 25 wt.% Al powder (coatings elements), 5.6 wt.% halide activator like NH_4Cl and 69.4 wt.% Al_2O_3 powder as an inert filler. The substrate sample was embedded in the pack mixture positioned in a horizontal under vacuum to avoid the oxidation during the process. The pack was then put into the constant temperature zone. Aluminizations were carried out at 1000 $^{\circ}\text{C}$ for 3,6,9 hours. In this processes the coating may be symmetric and homogenous in thickness and structure (Houngninou, 2003 ; Khana, 2004).

Thermal Barrier Coating (TBC)

The role of thermal barrier coating (TBC) is, as their name suggests, to provide thermal insulation of the blade. A coating of about (1-200) μm can reduce the temperature by up to 200 $^{\circ}\text{C}$.

TBC can be used either :

- to reduce the need for blade cooling (by about 36%), while maintaining identical creep life of the substrate.

- increase considerably the creep life the blade while maintaining level of blade cooling (and therefore allowing the blade to operate at lower temperature for an identical turbine entry temperature).

Thermal barrier coating can be obtained by different processes, such as electron beam physical vapors deposition (EBPVD) or air plasma spray (APS). In jet engine operating conditions, the lifetime of TBC coatings obtained by EBPVD has been reported to be between 8 and 13 times longer than equivalent system where the TBC was deposited by plasma spray in which APS tends to give the best performances (Mumm and Evans, 2000).

Here in this work we used new technique Y_2O_3 _ stabilized base, by preparing a salary of this rare earth metal which is covered the samples with (Y_2O_3), then aluminized the samples at 1000 °C for 3,6,9 hours.

RESULTS AND DISCUSSION

Aluminizing of Co- base Super Alloys, Fig.3 shows the coating structure of cross-section of a1000°C (a:3h, b:9h) aluminized sample seems to be composed of two layers noted out layers represented the base of layer coating contains two phases and inter-diffusion zone which is about (12,18) $\mu m.$, the same two layer is observed for a 1000 °C/3h,9h concerns the thickness of the cemented zone.

A result of XRD appear many peak. Analysis of the coating surface using (XRD) reveals the formations of inter metallic compound (Co_2Al_5), other phases of chromium aluminized because of the rate of Cr in the base (28%) see Fig. 4. The rate solubility of Cr in β -CoAl is less than 5% so that we expect that Cr-Al phases is secondary phase in coating layers and gives layers views malty phases also proved to be present ($CrAl_5$, $CrAl_2$, NiAl). Because of the high activity of the pack used, this coating layer was formed by inward diffusion of (Al) into the substrate. And because of the limited solubility of the Cr (5%), the chromium can be precipitated as chromium aluminide see Table (2). The phase of (Cr_3Al_2) appear clearly in 9 hr coating because of large grain size.

Table 2 :Testing result of XRD for single aluminize Fsx414 alloys.

Phase	$2\theta^\circ$	Intensity
β -CoAl	44,39	Very strong
Co_2Al_5	42	Strong
$CrAl_5$	39	Weak
Cr_3Al_2	42 , 34	Weak
NiAl	60 , 44	Strong

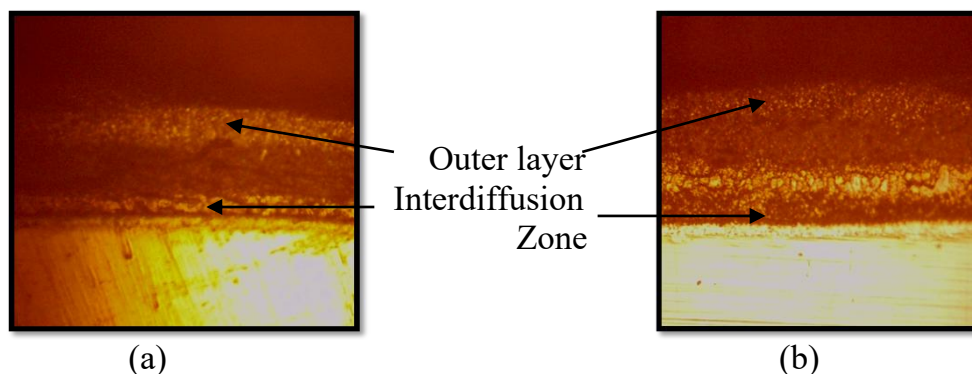


Fig. 3 : Surface scale morphology of single aluminized cobalt – base super alloys at (1000 °C) (a: 3 hr , b:9 hr).

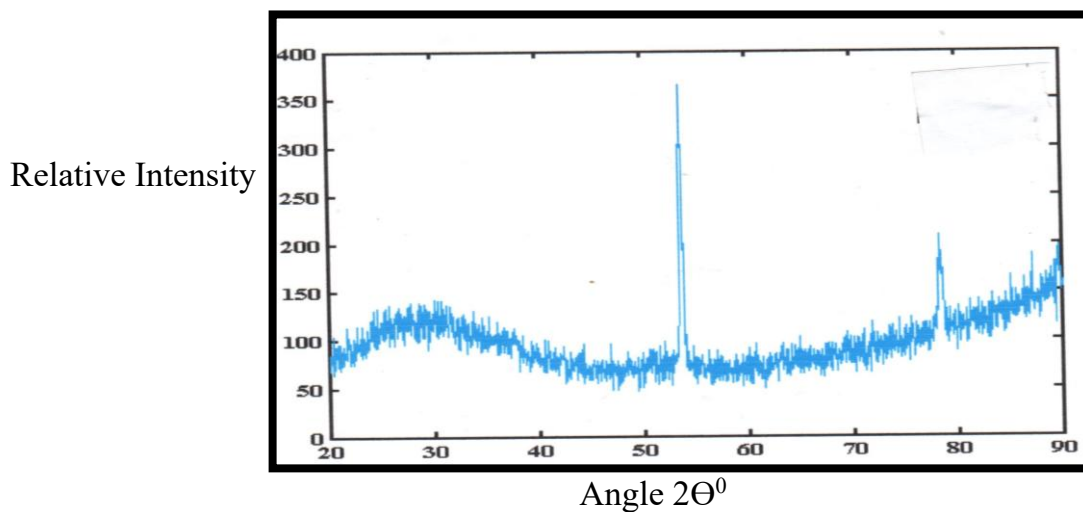


Fig. 4: X-ray diffraction pattern of single aluminized Fsx414 at 1000 °C for (9hr).

We calculate aluminum up take during aluminize processes and coating thickness increases against time see Fig .5 (a,b) and Table.3.

Table 3 : Coating thickness, Weight gain of single aluminized for Fsx414 alloys at (1000°C).

Temp. °C	Coating Time (hr)	Av. Thickness of Coating (μm)				Av. Weight gain (gm/cm ²)
		Outer layer	Interdiffusion zone	Inner layer	Total	
1000	3	83	12	-	95	0.01020
	6	137	14	-	151	0.02443
	9	160	18	-	178	0.030998

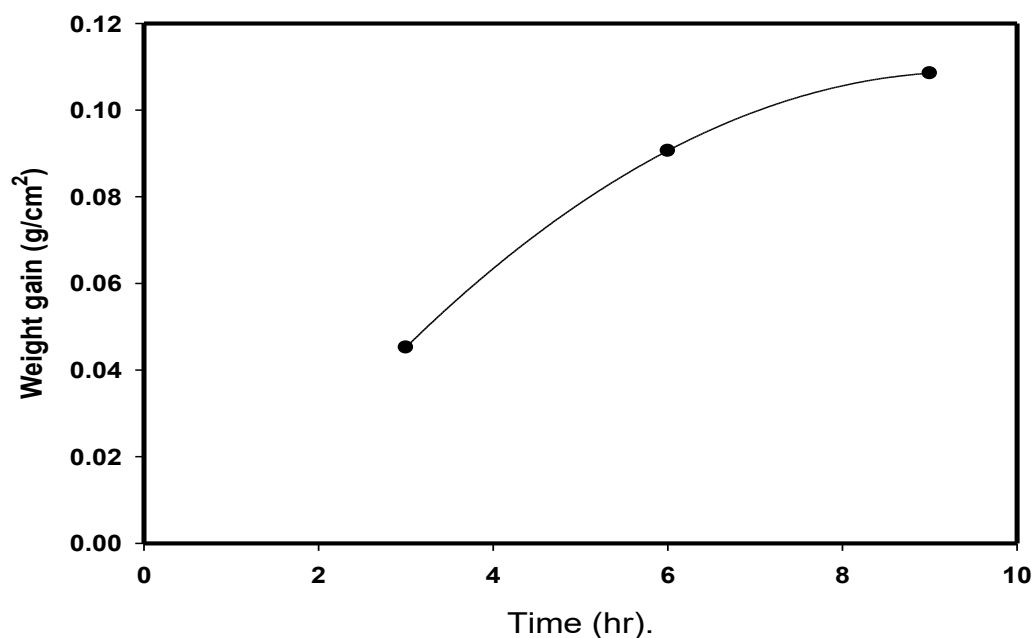


Fig. 5 : (a) Weight gain of aluminum

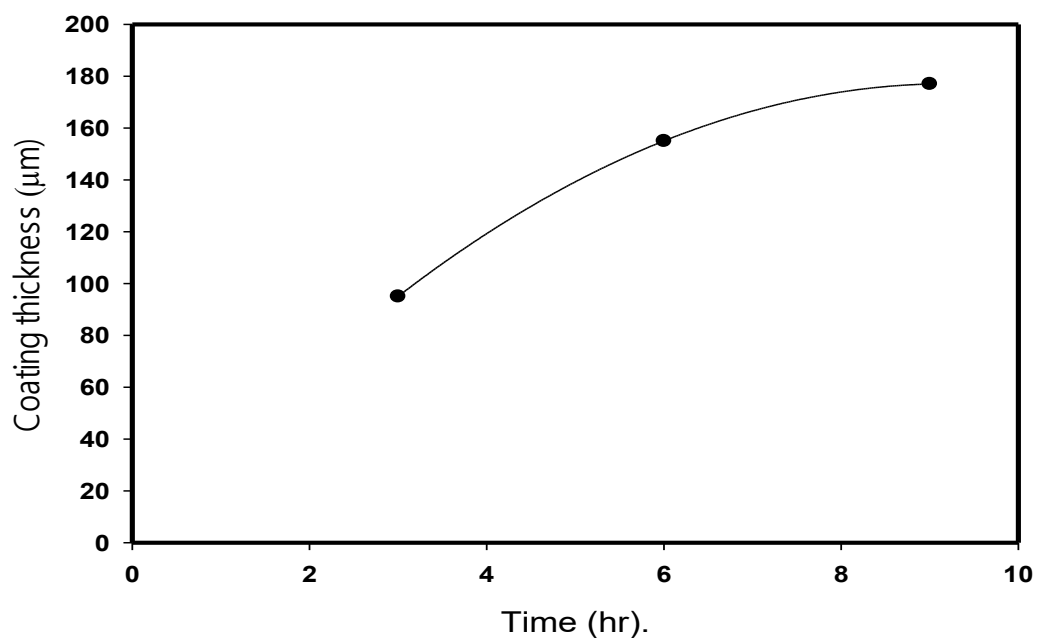


Fig. 5: (b) Coating thickness for single aluminized of Fsx414 super alloys at (1000 °C) as a function of time.

Aluminizing in presence of thermal barrier

This contains uses thermal barrier from oxide of some elements like (Y_2O_3) by cover methods before aluminizing.

Aluminizing (Fsx414) in presence of thermal barrier (Y_2O_3). The layer coating show in Fig. 6 form from one layer containing thick out layer including high density of soft grain size precipitation and others secondary phases.

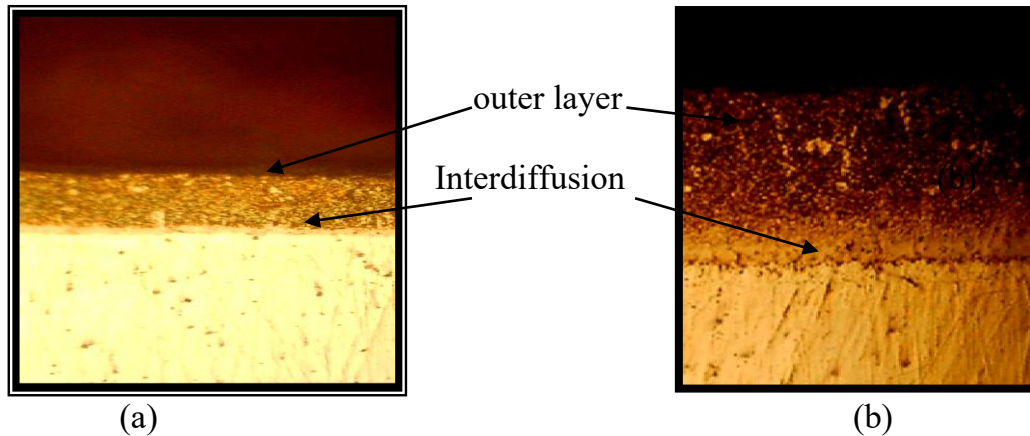


Fig. 6 : Cross-section microstructure of aluminized Fsx414 alloys (a:3hr , b:9hr) in presence of thermal barrier (Y_2O_3) at (1000 °C).

The inner coating layer is narrow zone without precipitation and same structure in 3hr and 9hr but the thickness increase with time.

Spectrum analysis of XRD appears stable base phases (NiAl), (CoAl) but cannot find (FeAl) because of the same crystal structure of two phases. Iron element (1wt %) and presence of Cr (28wt %) with less solubility in intermetallic compound (NiAl) give many compound of (Ni-Cr) and many phases with different cooler see Fig. 6.

Through Aluminum uptake and thickness coating calculation during aluminizing processes be increasing against time obey parabola relation see Fig.7 and Fig. 8.

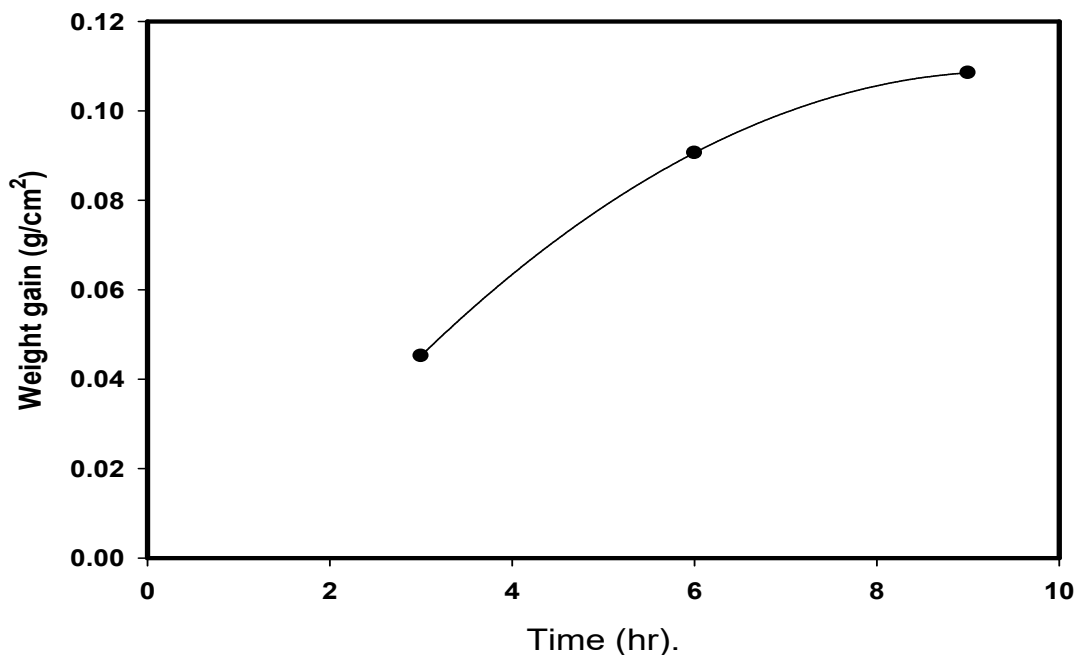


Fig. 7: Weight gain of aluminum.

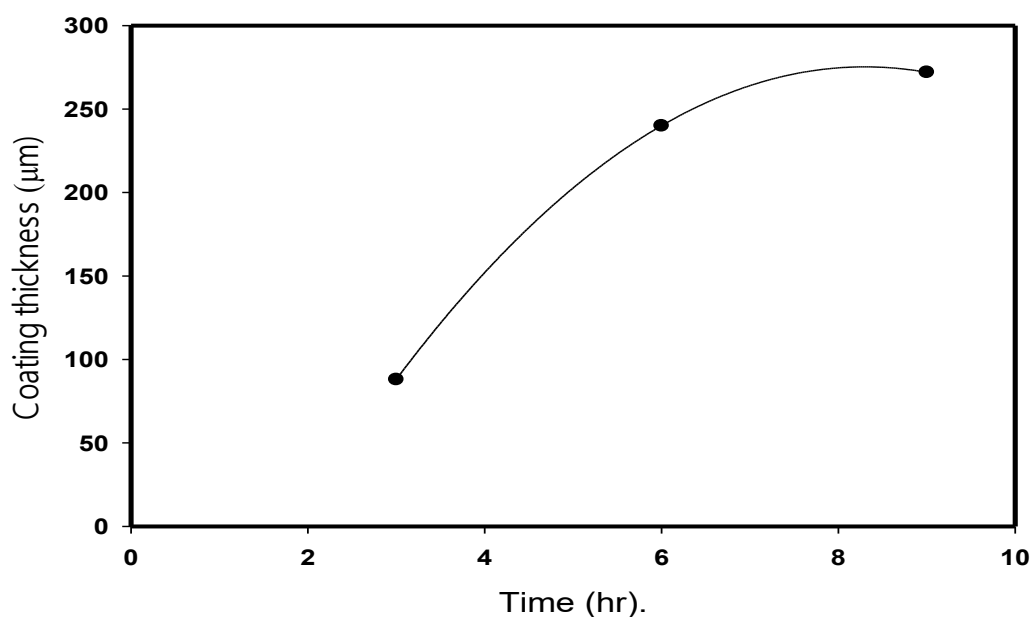


Fig. 8: Coating thickness for aluminized of Fsx414 alloys in presence of thermal barrier (Y_2O_3) at (1000 °C) as a function of time.

Table (4) express Aluminum uptake, average thickness. We see all parameters increases with presence of thermal barrier due to Ytterium ions diffuses to word lattice of NiAl compounds without any change in crystal structure of bases phase.

Table 4 : Coating thickness and weight gain of single aluminized for Fsx 414 alloys at (1000 °C).

Temp. °C	Coating Time (hr)	Av. Thickness of Coating (μm)				Av. Weight gain (gm/cm ²)
		Outer layer	Interdiffusion zone	Inner layer	Total	
1000	3	80	8	-	88	0.04522
	6	205	30	-	235	0.09061
	9	219	32	-	251	0.10851

Hot corrosion of (Fsx414) alloys which aluminized only.

The mechanism of cycles sulphadation of 9hr aluimide specimen pointed to a good stability for mass change against time through testing time which it mean that scales oxide formed be a good adhesion with layer coating and give good protective for alloy see Fig. 9.

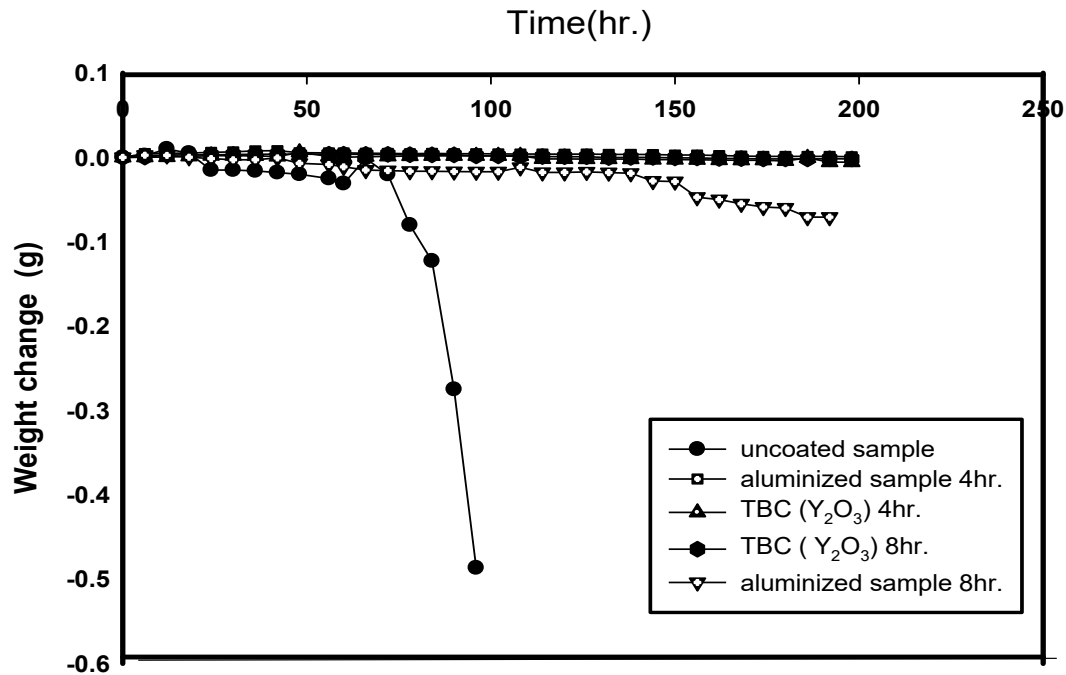
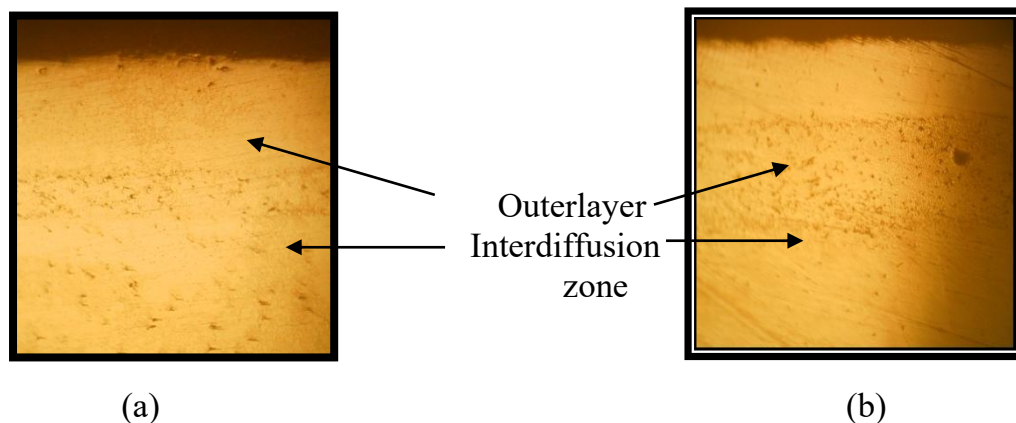


Fig. 9 : Sulphidation mechanism of aluminized Fsx414 at (1000 °C).

Since the 3hr aluminized specimen appear increase in mass and then decrease produce from unstable scales oxide . Uncoated alloys were tested to comparable with coated alloys which seem to be oxide at first testing and pointed for high rate of oxidation and form many scales of (Cr_2O_3 , NiO) and Iron oxide but this scales fastlly degradation lead to degraded alloys because it does not able to reform protective layer (Cr_2O_3) and formed sluphied of many elements. The diffuse of Cobalt for word coating and Aluminum to word base is the main reason of remove protect layer. Microscope testing for specimen proved after the end of testing that the layer coating may be sever many phases transformation see Fig. 10(a,b).

The interdiffusion zone (coating-base) upper needle structure and this zone be wide clearly which pointed to opposite diffuse of Ni toward layer coating which lead to change in base phase coating and this be clear by XRD-testing show (Ni_3Al) phase in order (NiAl).



**Fig. 10: a- Cross-section microstructure of aluminized Fsx414 alloys and ulphidation.
b- Cross-section microstructure of aluminized Fsx414 alloys in presencs of Y_2O_3 and sulphidation.**

CONCLUSION

The curve of kinetic corrosion shows that very good adhesion of protective scales which give good stability through the time of testing agree with many research (Geib, and Rapp, 1993; Zheng and Rapp, 1998; Hannow, 2007). On the other hand we found that the effective of Y in adhesion protective scales of alloys is very good protective layers.

We see Cobalt –base super alloys coatings such as aluminizing and thermal barrier coating Y_2O_3 have been found to exhibit excellent hot corrosion resistance. The formation of oxides and spinels of nickel, aluminum ,cobalt and chromium contributed to the development of hot corrosion resistance of these coatings which lead to degraded the sample fastlly.

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