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RESEARCH ARTICLE

EFFECT OF HOT CORROSION AND OXIDATION ON COBALT –BASE SUPERALLOYS COATED BY ALUMINUM WITH PRESENCE OF THERMAL BARRIER ZRO₂ AND MIXTURE OF (NaCl) AND (Na₂SO₄) STEAMSALTSAT HIGH TEMPERATURES

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Abstract

The aim of the study was to investigate the Mechanisms properties of thermal barrier coatings (TBCs) to enhance of performance evaluation characteristics and develop TBCs. Cobalt –base superalloy has been used as a substrate and zirconium stabilized Aluminum as ceramic topcoat , in addition the study include degradation behavior of system during thermal cycling (3hr per cycle in furnace) the failure of the aluminized was due to thermally grown oxide (TGO) interface. The fractures propagatethrough the interface and produce a deformation of the bond coating . the effect of cycle will result a spallation failure of the TBCsand this is also corresponding to a slightdegradation .The steam of salt (Nacl)and(Na₂So₄) mixture will affecton the coating lifetimes .The high temperature have a strong effect thermally grown oxide (TGO) which consistent with a first order growth of scale failer variation.

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Introduction:-

Oxidation and hot corrosion is a problem in power generation equipment, turbines engine for airplane ,rocket and ships and in other energy such as chemical processes system . oxidation and hot corrosion another poses asevere problem as the use of low –grade fuels and due to depletion of high –grade fuels as well as high cost in removing the impurities . coating are frequently applied on gas turbine components in order to restrict surface degradation such as oxidation , hot corrosion of the structural material and to thermally insulate against the hot environment there by increasing the turbine efficiency. surface degradation takes place during hot corrosion, oxidation and solid particle erosion [1][14-17]. Oxidation and hot corrosion may pitting the surface, for example act as crack fatigue leading to failure of the component . in combination with other sub-surface damage processes ,which decrease the strength and ductility this lead to faster failure . oxidation and hot corrosion wasshowed in figure(1),where uncoated gas turbine blades removed and replaced after 2500hr sea flight.

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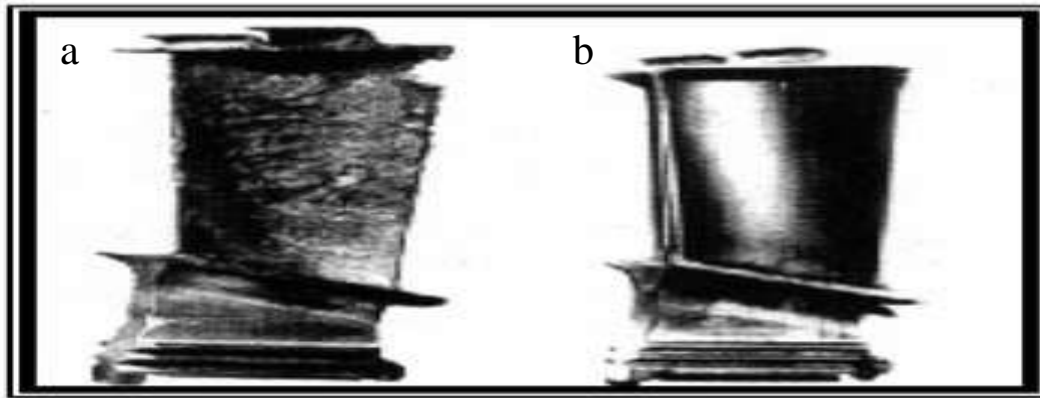


Figure (1):- show (a)oxidation and hot corrosion effect of uncoated and a coated blades (b) gas turbine bland after 2500hr sea fligh from reference [11][18-20]

thermal barrier coatings (TBCs) has resulte an improvement in the efficiency of airplane gas turbines [2 , 9][21-24]. These types of coatings have been used for more years on combustion ,but with advanced thermal barrier coating (TBCs) vanes ,and edges of blades can be coated ,the use differentials the coating of as much as 200°C . Typical systems consist of nickel-base and cobalt-base super alloy substrate coated with a MCrALY(where M =Ni or Co) or diffusion aluminized band coats , on to which is deposited a yttria–stabilized zirconia (YSZ) (TBCs). the band coats are usually deposited diffusion aluminizing processes on alloy powder spray processes .

the resistance of the coating is the most important factor in controlling the life of thermal barrier coating(TBCs) to spallation under the influence of stresses during thermal exposure [3][25-27] .

During samples preparation the oxide grown (thermally grown oxide grown TGO) between the bond coating and the (YSZ) because ofexposure to high temperature .

both thermally grown oxide (TGO) and (YSZ) increase the elastic energy storedof the system after cooling to room temperature.Exposureproduce micro structure and chemical changes, which result a decrease in the fracture toughness and fracture initiates , both propagates through the YSZ and the TGO, the interface between the TGO and band coat can influence the fatigue and the crack Path and the time to failure.

The study is focusing on one single crystal Superalloy substrate (Rene N5) one EBPVD TBC and the influence of band Coats on TBCs, The 8wt% yttrium stabilized zirconia (YSZ) since this TBC is state the bond coast which are considered state are platinum modified diffusion aluminizes and MCrALYcoating.The different Modifications of MCrALY coating and platinum aluminize bond Coats have been studied, As results we obtained the failures of these TBCs modifications were made to obtain new improved system.

In previous studies different result have been obtained by different study of nominally identical coatings these differences arise from variations in the exposure conditions [4][28-31] , an additional objective of this study was to evaluate the exposure conditions on the degradation behavior of the various bond Coats . the efficiency of engines can be enhanced to reduce the temperature of the Super alloy by thermal barrier coatings (TBC) of high pressure turbine blades.

TBC system are composed on external yttrium partially stabilized zirconia ceramic layer applied on a β -NiAlPt layer known as bondcoating . This bond Coat was sure a good adhesion of the ceramic layer on the substance and the oxidation and hot corrosion protection of the substrate[32-36]

Three main bond-coatings in use are: the pt-modified β -NiAl,thept-rich γ -Ni+ γ -Ni3Al ,and the MCrALY (where M=Nior Co) coatings with their composition which consist of high concentration of Cr and Al ,MCrALY coating have a good resistance against high temperature oxidation and hot corrosion [37-39] ,they usually out-perform pt-modified β -NiAlaluminized against type-I and type-II oxidation and hot corrosion [40][41], oxidation and hot corrosion due to salt contaminants such as Na₂SO₄,NaCl,V₂O₅[13], Moreover they contain yttrium , rare elements beneficial for TGO adherence .However,MCrALY coatings do not behave as well as pt-modified aluminize coatings

under oxidation and hot corrosion conditions as they can form chromium and spinel oxides in addition to the continuous protective scale Al_2O_3 . Pt was added to improve oxidation and hot corrosion resistance [42-44]. Pt addition to MCrAlY coatings was also improved TBC system life time [45].

First, attention was focused on the influence of Pt addition on the microstructure of Ni-Co-Cr-Al-Y-Ta bond coatings [46] and on the oxidation behavior of Tribomet® Ni-Co-Cr-Al-Y-Ta bond coatings [47][48].

The effect of Pt on the degradation mechanism of TBC system containing a Ni-Co-Cr-Al-Y-Ta bond coating under cyclic oxidation and hot corrosion conditions was studied. The study also includes the influence of the deposition process and the surface preparation of the Ni-Co-Al-Y-Ta coating, and finally parameters that affect the TBC system lifetime [49-51].

Experimental procedures

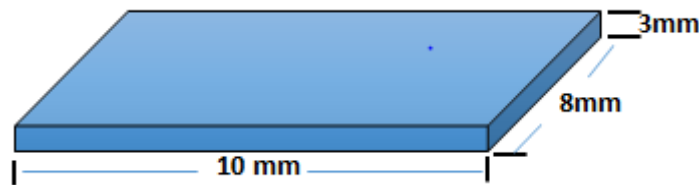
Cobalt base Superalloys (FSX-414) have been studied, its chemical compositions are given in table 1 [13]

Table (1):- Composition of FSX-414 cobalt base Superalloys.

Element	Co	Cr	Ni	Mo	Mn	W	Fe	Si	C
Wt%	Bal.	29.5	10	-	5	7.5	<2	0.9	0.35

All specimens used in this experiment were prepared as a sheet with 3mm thick, 8mm wide and approximately 10mm lengths as shown in figure(2).

Sample sheets were polished using 180, 220, 240, 320, 400, 600, 800, 1000, 1200, 1500 and 2000 grits Sic paper up to $1\mu m$ to eliminate the sharp edges to providing an initially smooth surface for coating, the samples cleaned in alcohol, dried and weighted.



Figure(2):- Show the specimen dimensions.

Coating processes

Pack cementation

Aluminization was carried out by using the pack cementation method to produce aluminized compounds. This process involved the pack mixture in a horizontal furnace having a constant temperature zone about 150mm length figure(3)

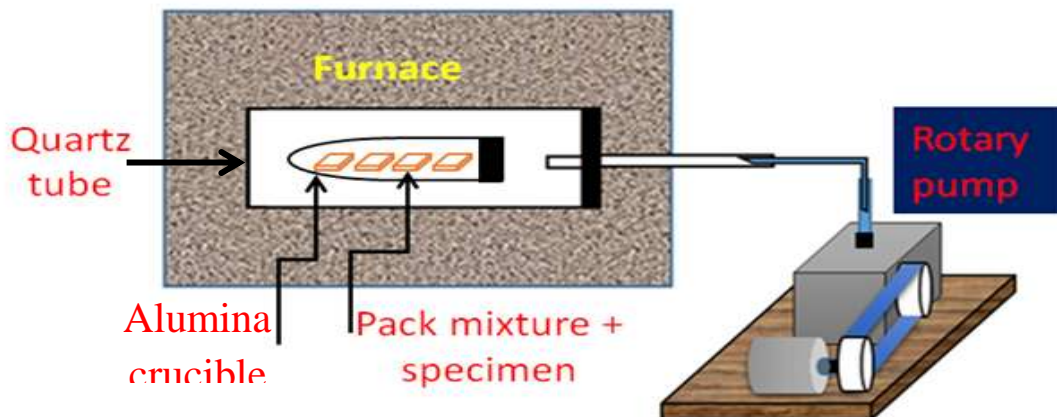


Figure (3):- Coating furnace diagram.

The pack mixture is composed of 25 wt% (AL) pure powder (coating elements) ,5 wt% halide activator such as NH_4Cl or NH_4Br and 70 wt% Al_2O_3 powder alumina as an inert filler. The samples were embedded in the pack cementation mixture held in a horizontal under vacuum by rotary pump or in argon gas (Ar) to avoid the oxidation and hot corrosion process, the pack cementation was maintained at a constant temperature zone. Aluminizations were carried out at 1050°C for 2,4,6,8 hours. In this process the coating may be homogenous and symmetric in thickness and structure [7][8].

Thermal barrier coating (TBC)

The role of thermal barrier coating (TBC) is as their name is to provide thermal insulation of the blade. Coating of about $1\text{-}200\mu\text{m}$ can reduce temperature by up to 200°C . TBC was used either to reduce the need for blade cooling by about (35%) and then maintaining identical creep life of the substrate or increasing the creep life of the blade and then maintaining level of blade cooling (and there for allowing the blade to operate at lower temperature for an identical gas turbine temperature)

Thermal barrier coating (TBC) can be obtained by different process like air plasma spray (APS) electron beam physical vapour deposition (EBPVD). The life time in Jet engine operating conditions, (TBC) coatings obtained by EBPVD has been that equivalent system where the (TBC) was deposited air plasma spray (APS) tends to give the best performances [10].

In this work, we used new technique zirconium oxide (ZrO_2) stabilized base by preparing a lutetium of this rare earth metal which is covered the samples with (ZrO_2), then the samples were aluminized at 1050°C for 2,4,6,8 hours.

Results And Discussion:-

Single Aluminized coating

Aluminizing of cobalt base (Co) Superalloys figure(4) show the coating structure of a 1050°C (a:4hr, b:8hr). we recognize three layers with in the aluminized sample outer layer , inner layer and inter diffusion Zone respectively .

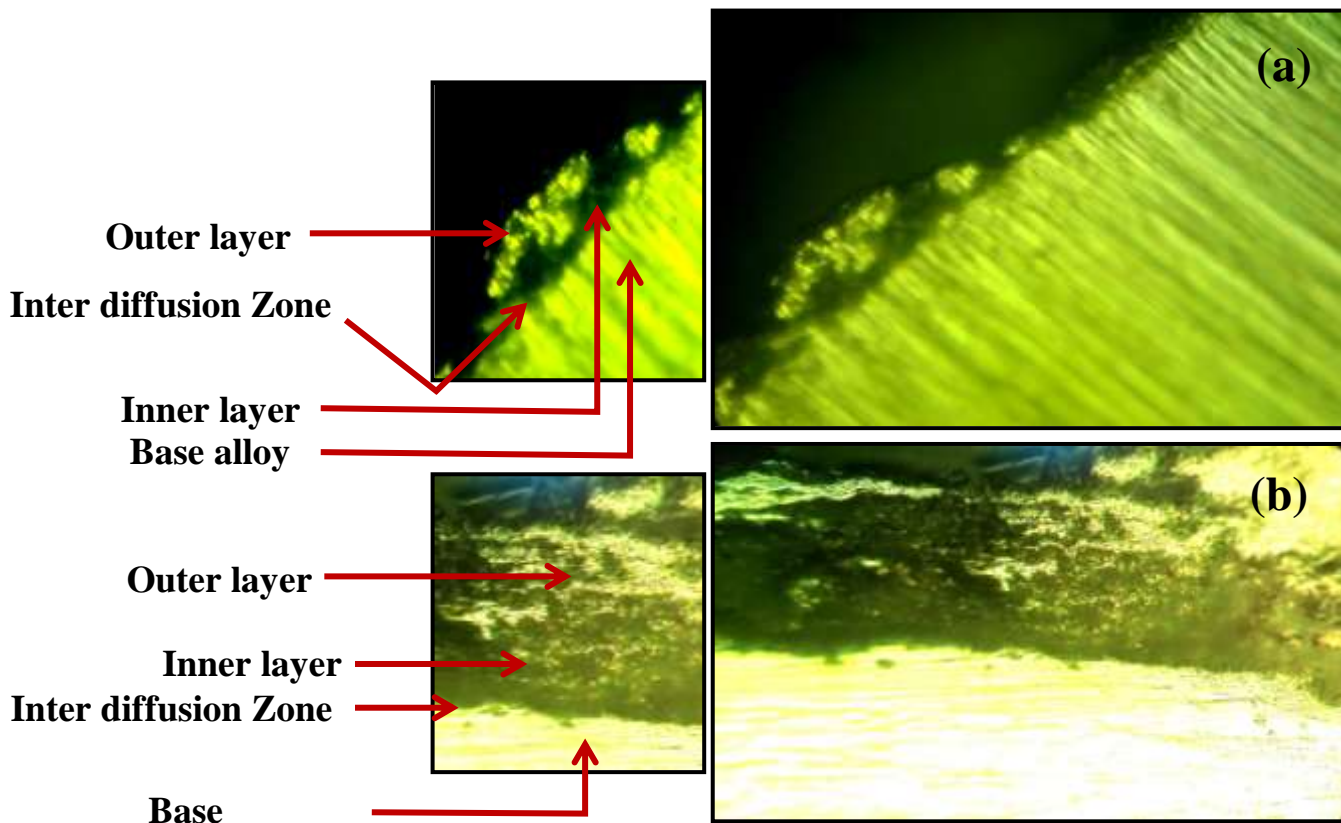


Figure (4):- Surface scale morphology of single aluminized cobalt-base super alloy (FSX-414) at 1050°C (a:4hr, b:8hr).

Figure (5):- X-ray diffraction pattern of single aluminized of cobalt base super alloy (FSX-414) for (8hr)

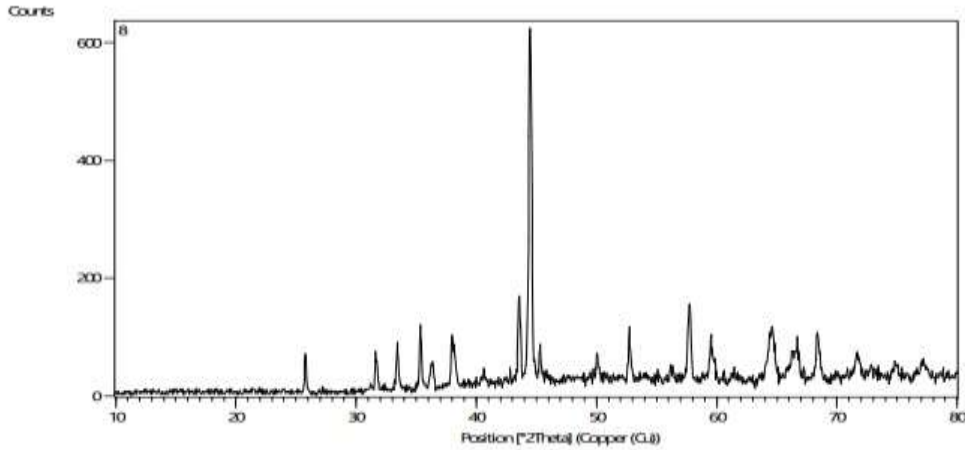
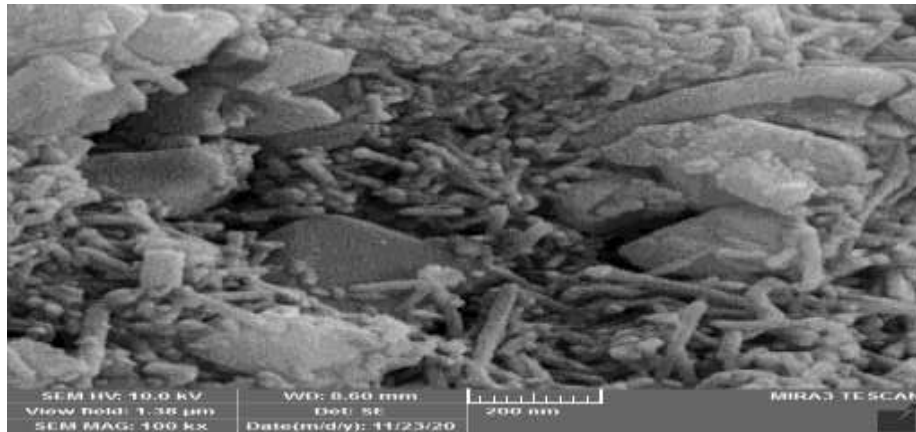
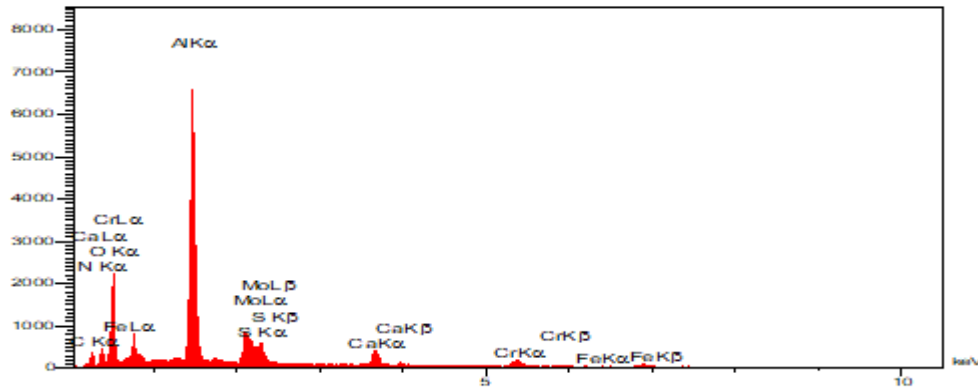


Figure (5):- Show x-ray spectrum , the spectrum reflect the presence of several phases , the strongest peak appeared approximately at 44.5° which belong to β -CoAl and this is consistent with.



Figure(6):- Scanning electron microscope (SEM) image of single aluminized of cobalt base super alloy (FSX-414) for (8hr).

SEM images show the homogenous distribution of aluminum within the super alloy as shown in figure (6) . the most important point was the nano roads structure of aluminum with in 20-40nm diameter ,which enhance the mechanical properties , EDS spectrum show the high presence of aluminum compared with the other elements and this consistent with the X-ray spectrum.



Figure(7):- Energy dispersive spectroscopy EDS of single aluminized of cobalt base super alloy (FSX-414) for (8hr)

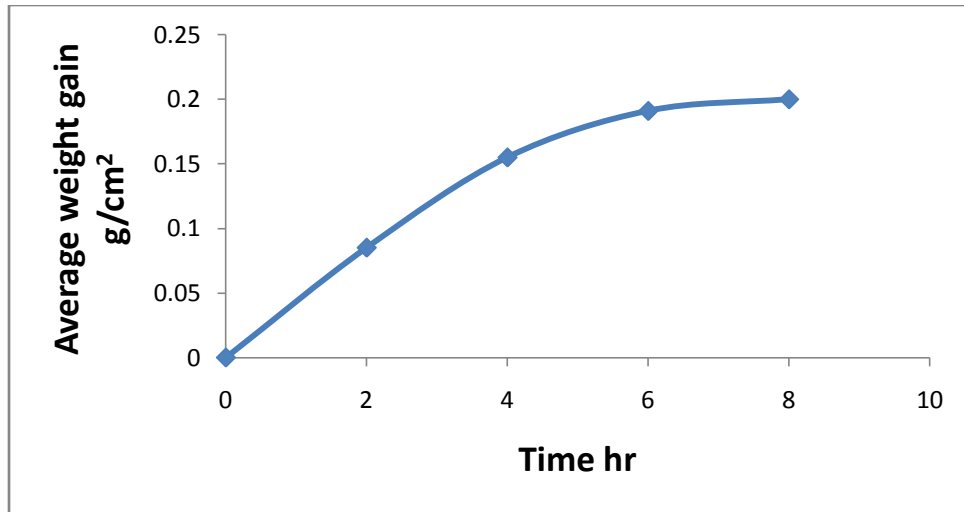


Figure (8):- weight gain of single aluminized of cobalt base super alloy FSX-414 at (105°C) as a function of time

The average weight gain and coating thickness increase with time depend on diffusion process according to parabolic relation as shown in figure (8) and figure (9), the average weight gain increase rapidly in the first 8hr and then extremely saturated while the coating thickness increases sharply in the first 2hr and then remain extremely constant.

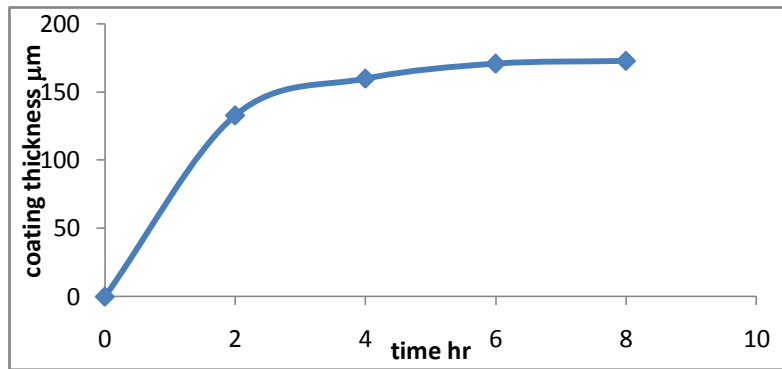


Figure (9):- coating thickness for single aluminized of cobalt base super alloy FSX-414 at (105°C) as a function of time.

The layers thickness within the aluminized sample increases with coating time and this results in an increase in the average weight gain as shown in table (3).

The base of layer coating contains two phases and inter diffusion zone which is about (58, 72, 43) µm, the same two layers are observed for a 1050°C / 8hr concerning the thickness of the cemented zone.

Table (2):- Coating thickness, weight gain and diffusion coefficient of single aluminized for cobalt base super alloy FSX-414 at 1050°C

Temperature °C	Coating Temp.(hr)	Average thickness of coating (µm)				Average weight gain (gm/cm ²)	Diffusion coefficient m ² /sec
		Outer layer	Inter diffusion zone	Inner layer	Total		
1050	2	54	29	50	133	0.0851	1.4x 10 ⁻¹³
	4	62	33	65	160	0.155	
	6	70	36	65	171	0.191	
	8	58	43	72	173	0.200	

Analysis of the coating surface using (XRD) the formations of inter metallic compound (Co₂Al₃) other phases of chromium aluminized because of the rate of the chromium (cr) element in the base alloy (29.5%) see figure(4) the

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 malty phases to be present ($CrAl_5$, $CrAl_2$, NiAl) because of the high activity of pack cementation used this coating layer was formed by in ward diffusion of aluminum powder (Al) in to the substrate and the limited solubility of the (cr) 5% the chromium (cr) can be precipitated as chromium of aluminide see table (2) the phase of (Cr_3Al_2) appear clearly in 8hr coating because of large qarin size.

Table(3):- Testing result of XRD for single aluminize FSX-414 alloys.

Phase	2 θ	intensity
β -CoAl	44,39	Very strong (v.s)
Co_2Al_5	42	Strong (s)
$CrAl_5$	39	Weak (w)
Cr_3Al_2	42,34	Weak (w)
NiAl	60:44	Strong (s)
Zr_4Al_3	40	Weak (w)
$ZrAl_3$	43	Weak (w)

We calculate aluminum up take during aluminize processes and coating thickness increase against time ,See figure(8),figure(9) and table (2).

Aluminizing in presence of thermal barrier coating (TBC)

this coat in used thermal barrier from oxide of some element such as zirconium oxide (ZrO_2) by cover methods before aluminizing.

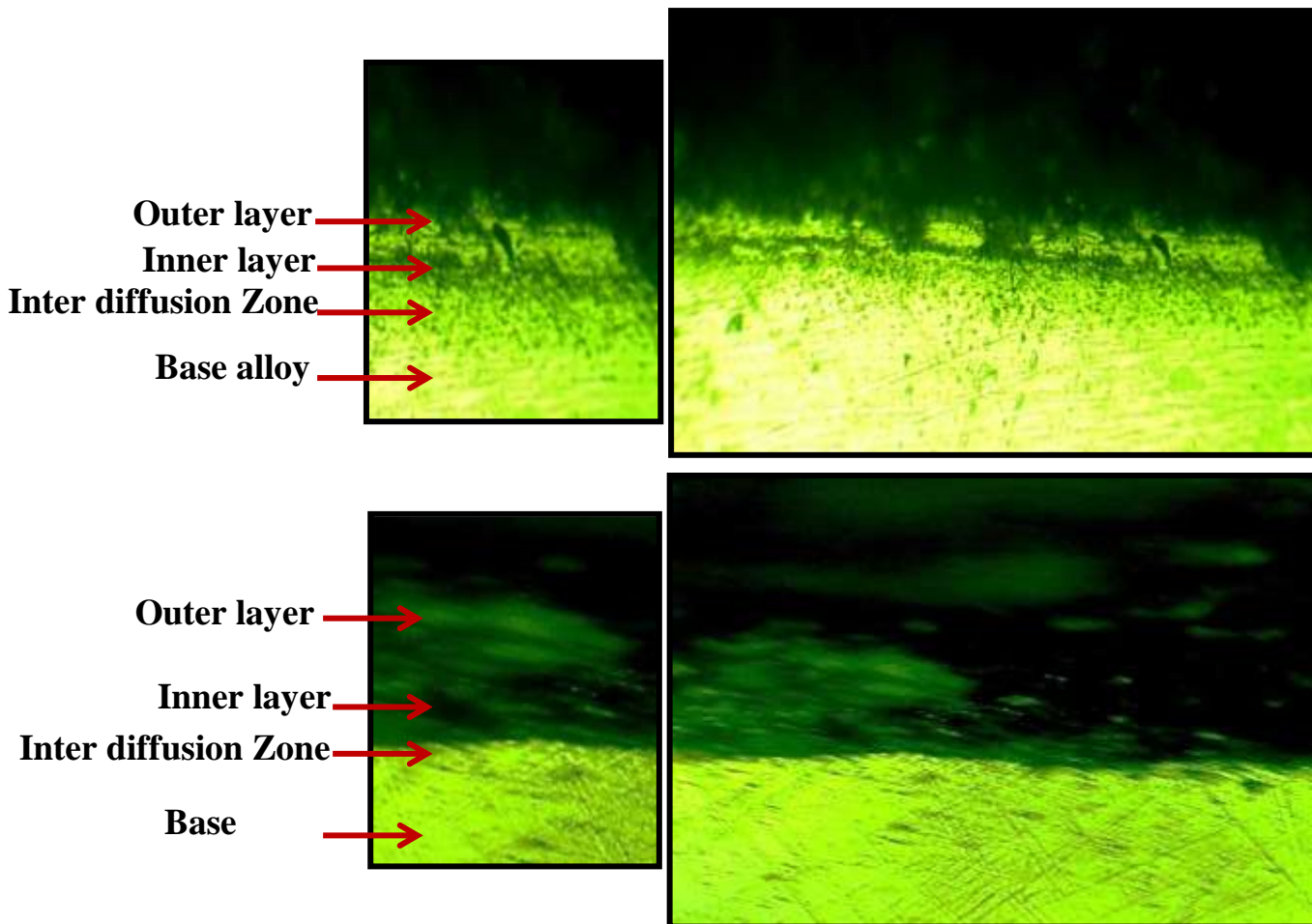


Figure (10):- Cross–section micro structure of aluminized cobalt base super alloy (FSX-414) (a:4hr,b:8hr) in presence of thermal barrier (ZrO_2) at (1050°C).

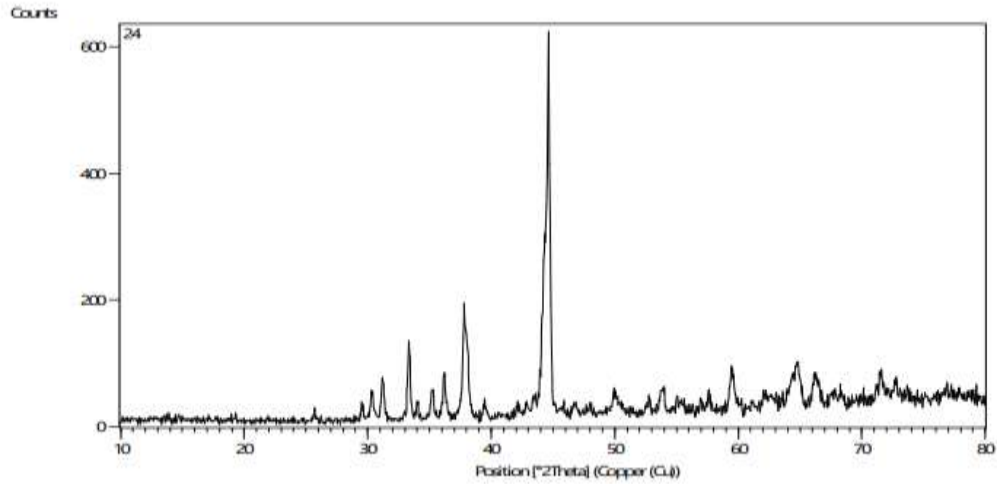
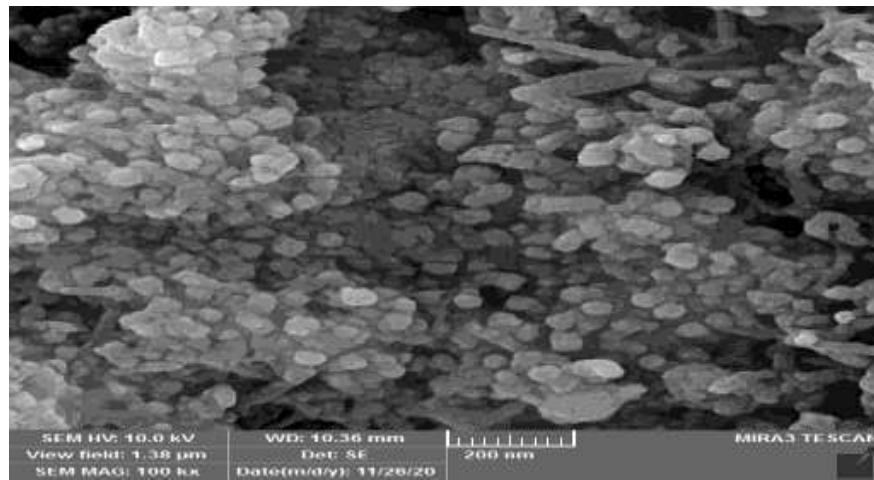
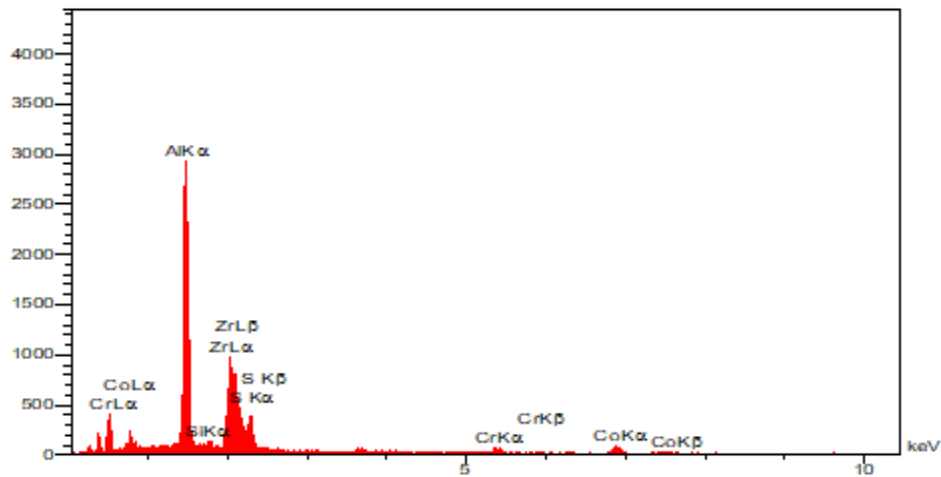


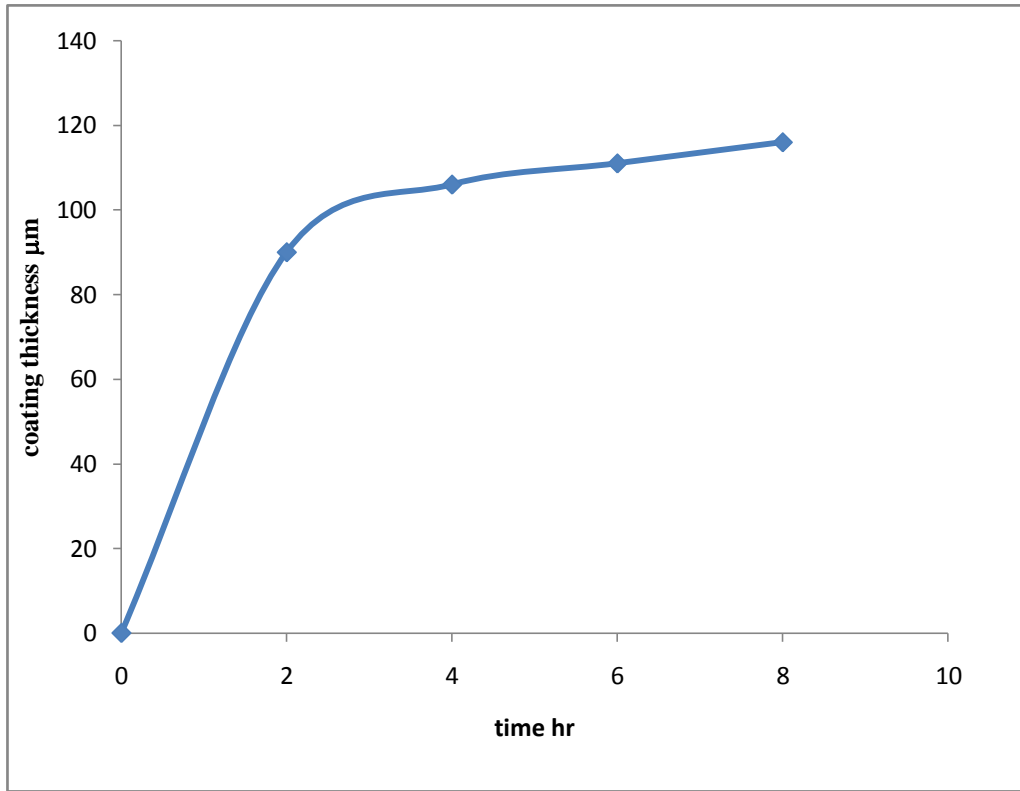
Figure (11):- X-ray diffraction spectrum of aluminized cobalt base super alloy (FSX-414) (8hr) in presence of thermal barrier (ZrO_2) at ($1050^{\circ}C$).



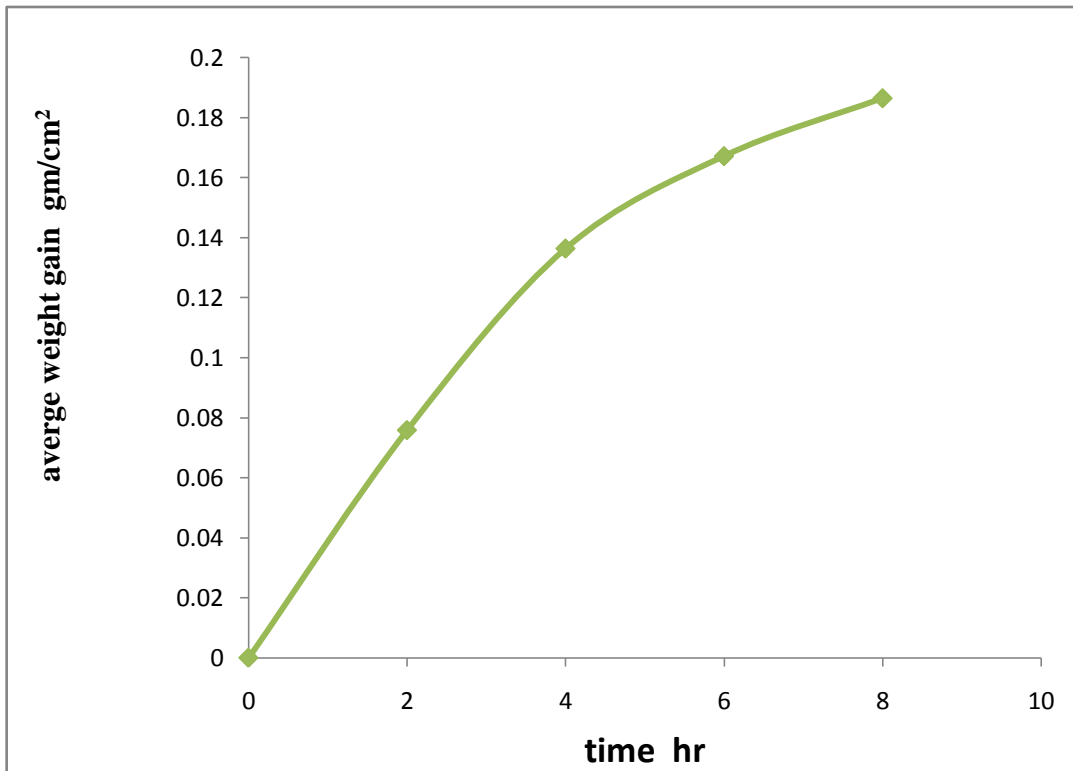
Figure(12):- Scanning electron microscope (SEM) of aluminized cobalt base super alloy (FSX-414) (8hr) in presence of thermal barrier (ZrO_2) at ($1050^{\circ}C$).



Figure(13):- Energy dispersive spectroscopy EDS of aluminized cobalt base super alloy (FSX-414) (8hr) in presence of thermal barrier (ZrO_2) at ($1050^{\circ}C$).



Figure(14):- Coating thickness for aluminized of Cobalt base super alloy FSX-414 in presence of thermal barrier (ZrO₂) at 1050°C as a function of time .



Figure(15):- average weight gain for aluminized of Cobalt base super alloy FSX-414 in presence of thermal barrier Zirconium oxide (ZrO₂) at 1050°C as a function of time .

Table(4):- coating thickness and weight gain of aluminum and diffusion coefficient in presence of thermal barrier Zirconium oxide ZrO_2 for Cobalt base Super alloy FSX-414 at (1050c°).

Temperature ^o C	Coating Temp.(hr)	Average thickness of coating (μm)				Average weight gain (gm/cm ²)	Diffusion coefficient m ² /sec
		Outer layer	Interdiffusion zone	Inner layer	Total		
1050	2	35	22	33	90	0.07586	5.9559x10 ⁻¹⁴
	4	39	32	35	106	0.1364	
	6	39	35	37	111	0.1672	
	8	42	33	41	116	0.1865	

aluminizing (FSX-414) In presence of thermal barrier (ZrO_2) the layer coating show in figure(6) from three layer , outer layer,inner layer and inter diffusion zone coating thickness,

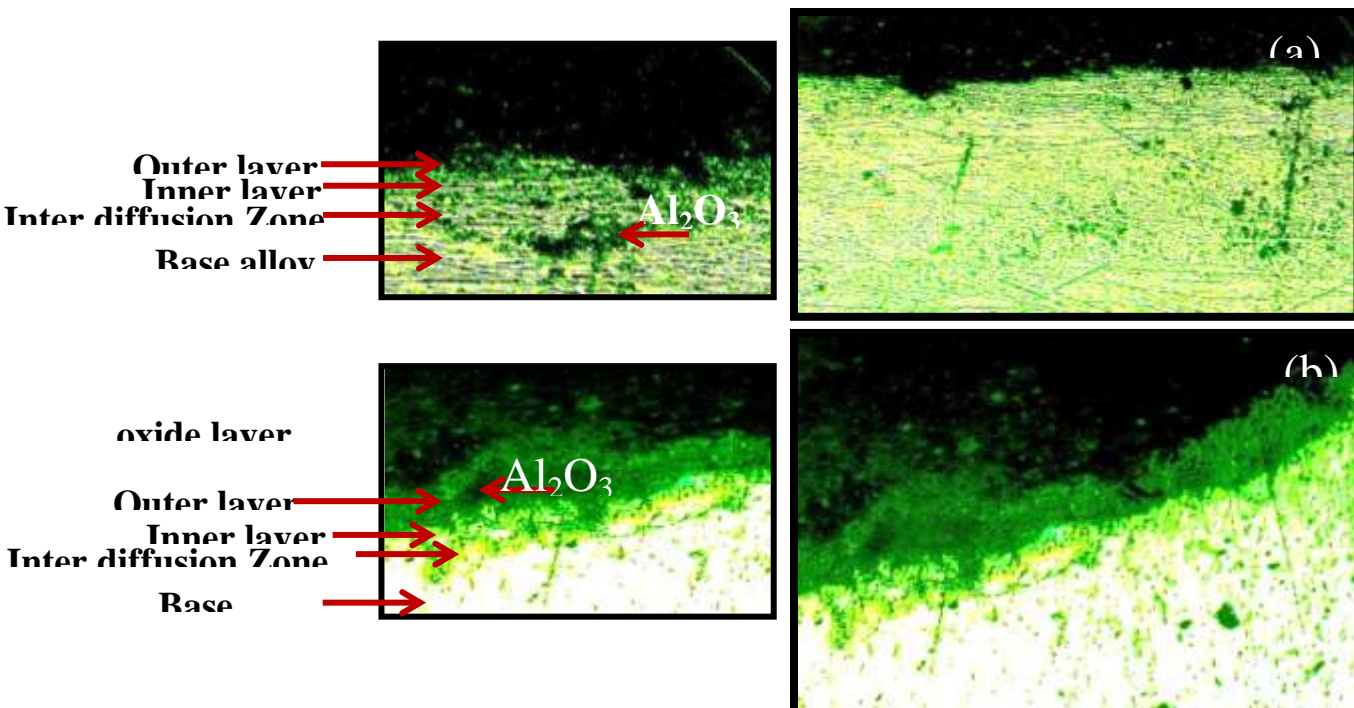
The outer layer including high density of soft grain size precipitation and the others secondary phases while the inter diffusion zone layer is narrow zone with out precipitation and same structure in 4hr and 8hr except the thickness which increase with time .

Spectrum analysis of X-ray diffraction (XRD) shows stability in base phases (NiAl) ,(CoAl) ,while (FeAl) phase can not be found (FeAl) because Iron element (<2 wt%) compared with Cr (29.5wt%) and because of the same crystal structure of two phases solubility in intermetallic compound (NiAl) which give many compound of (Ni-Cr) and many phases with different color as shown in table(3)and figure (10).

Through aluminum up take and thickness calculation during aluminizing processes be increasing against time Obey parabola relationships in figure(8) and figure (9) and aluminum present with thermal barrier coating TBC zirconium Oxide ZrO_2 up take and thickness calculation during aluminized process increase against time obey parabola relationship as in figure (14) and figure(15). Table 4 express Aluminum uptake average thickness. We see all parameters increases with presence of thermal barrier due to zirconium ions diffuses to word lattice of (NiAl) compounds without any change in crystal structure of bases phase

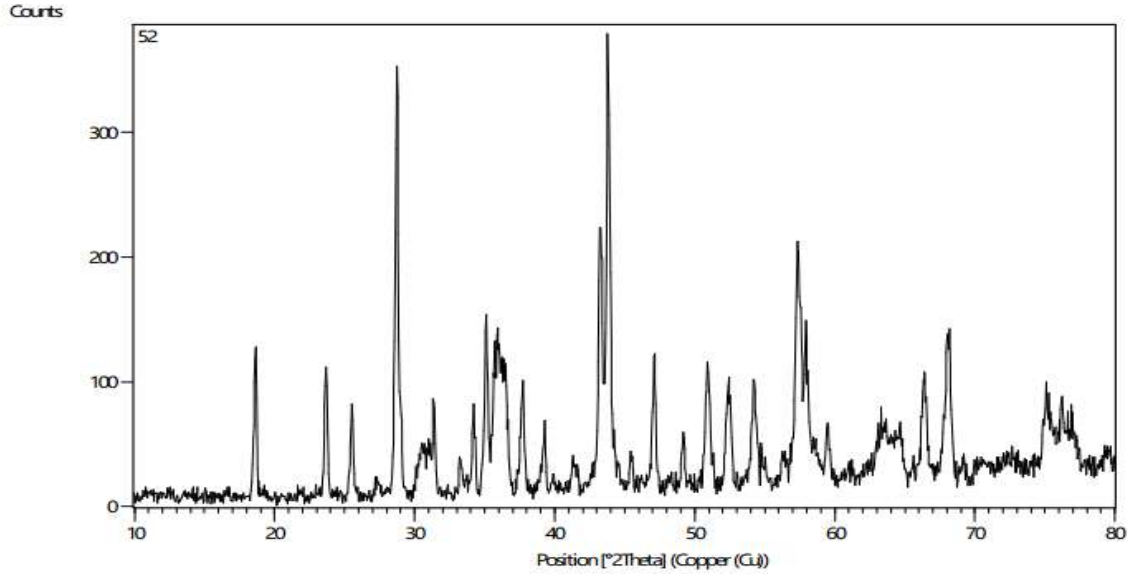
Oxidation and Hot Corrosion

Oxidation and hot corrosion of cobalt base super alloy (FSX-414) which aluminized 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 figure 9 (a and b).

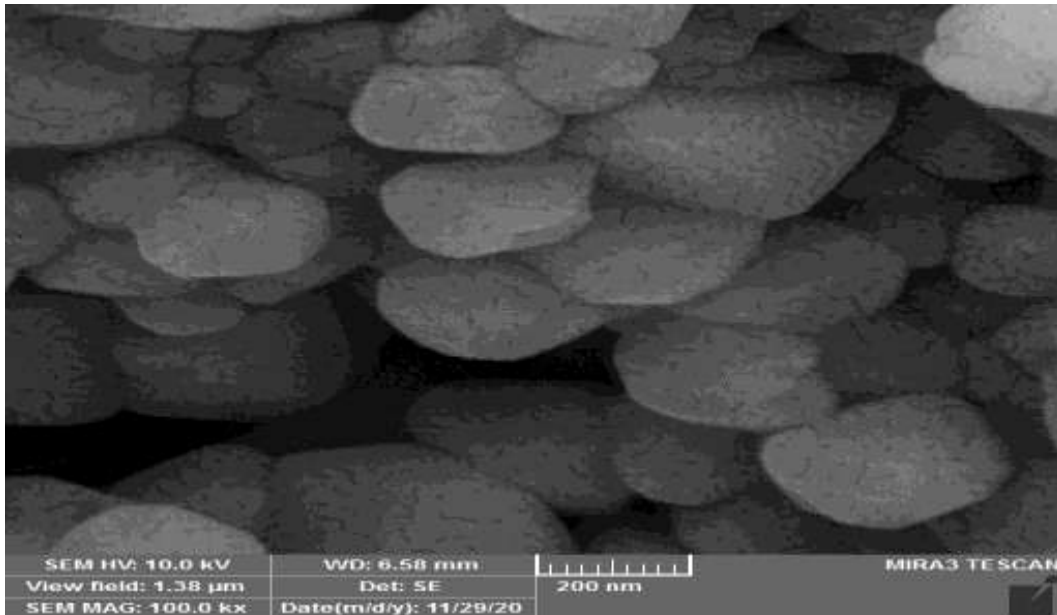




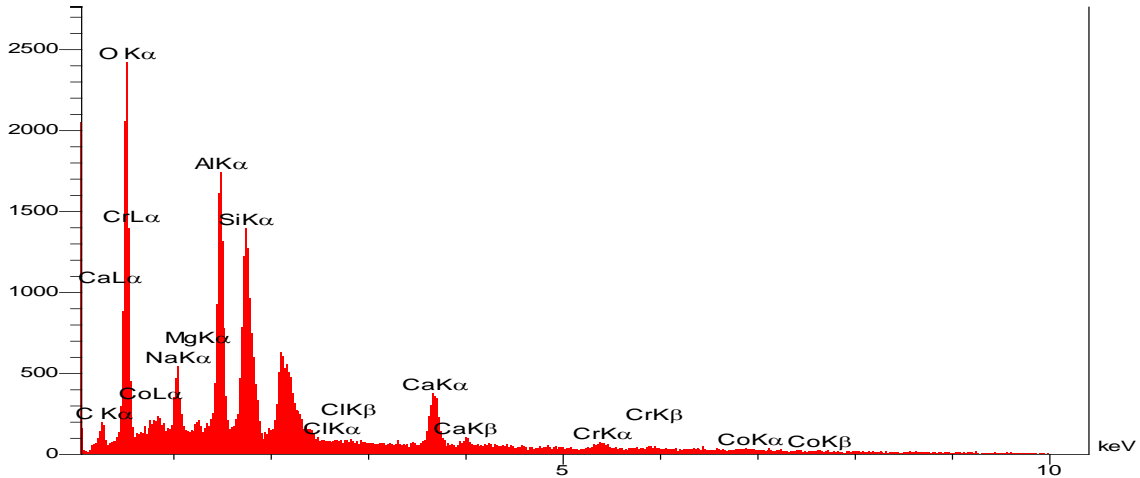
Figure(16) cross-section micro structure of single aluminized cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂SO₄)at 1080°C for 324hr.



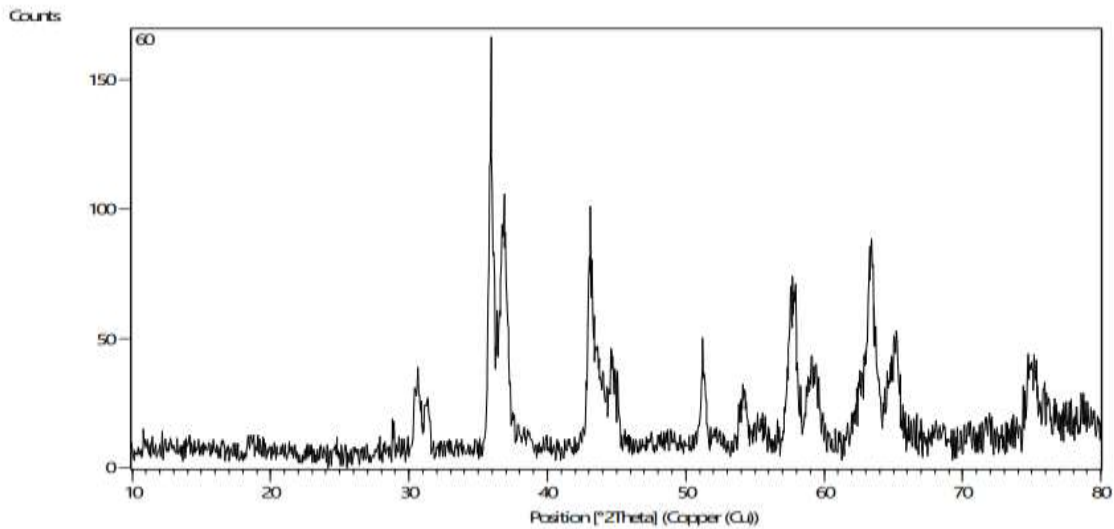
Figure(17):- X-ray diffraction spectrum of single aluminized cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂SO₄)at 1080°C for 324hr.



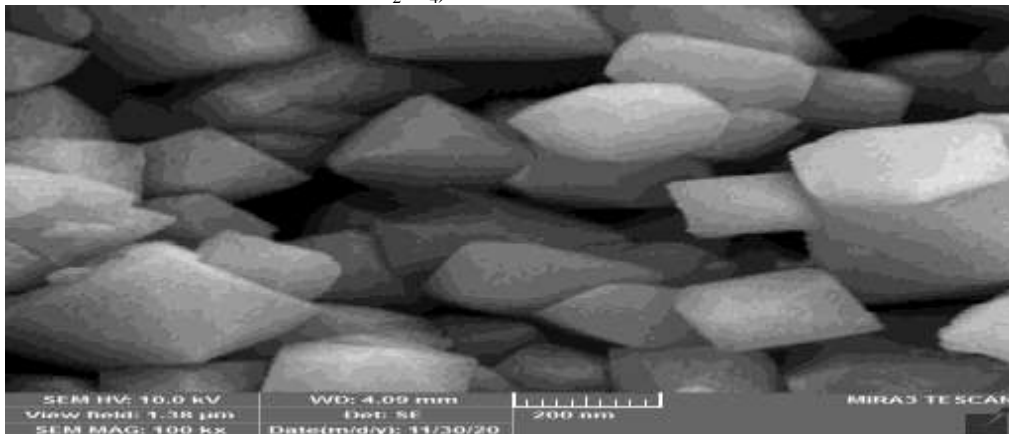
Figure(18):- Scanning electron microscope SEM of single aluminized cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂SO₄)at 1080°C for 324hr.



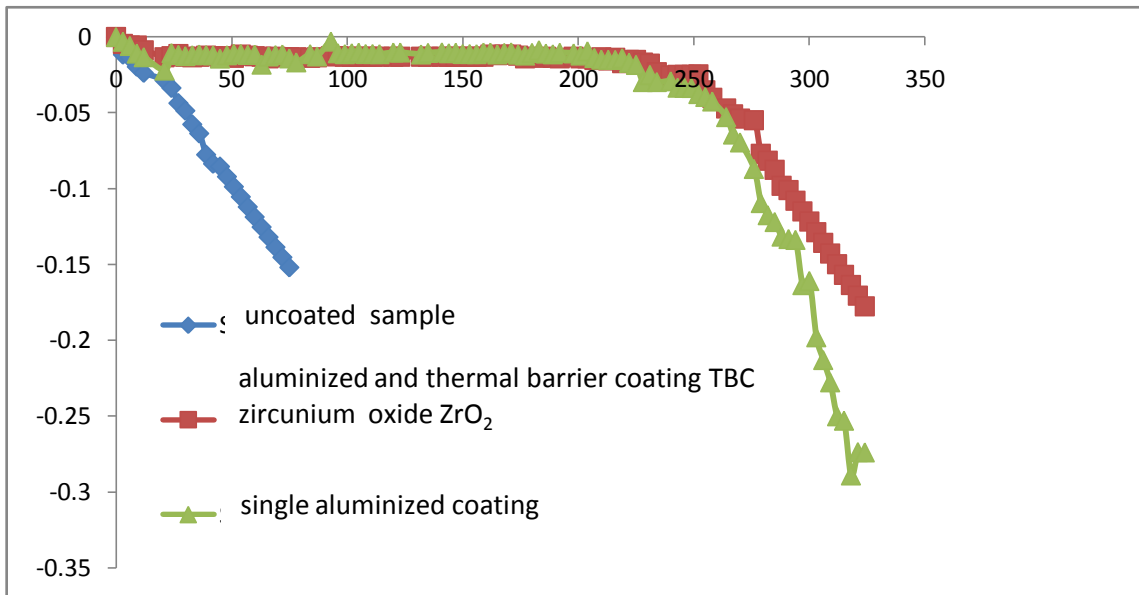
Figure(19):- Energy dispersive spectrum EDS of single aluminized cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂SO₄)at 1080°C for 324hr.



Figure(20):- X-ray diffraction spectrum of aluminized and presence of thermal barrier coating TBC of cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂SO₄)at 1080°C for 324hr.



Figure(21):- Scanning electron microscope SEM of aluminized and presence of thermal barrier coating TBC of cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂SO₄)at 1080°C for 324hr.



Figure(22):- Energy dispersive spectrum EDS of aluminized and presence of thermal barrier coating TBC of cobalt base super alloy (FSX-414) (8hr) in at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂So₄)at 1080°C for 324hr.

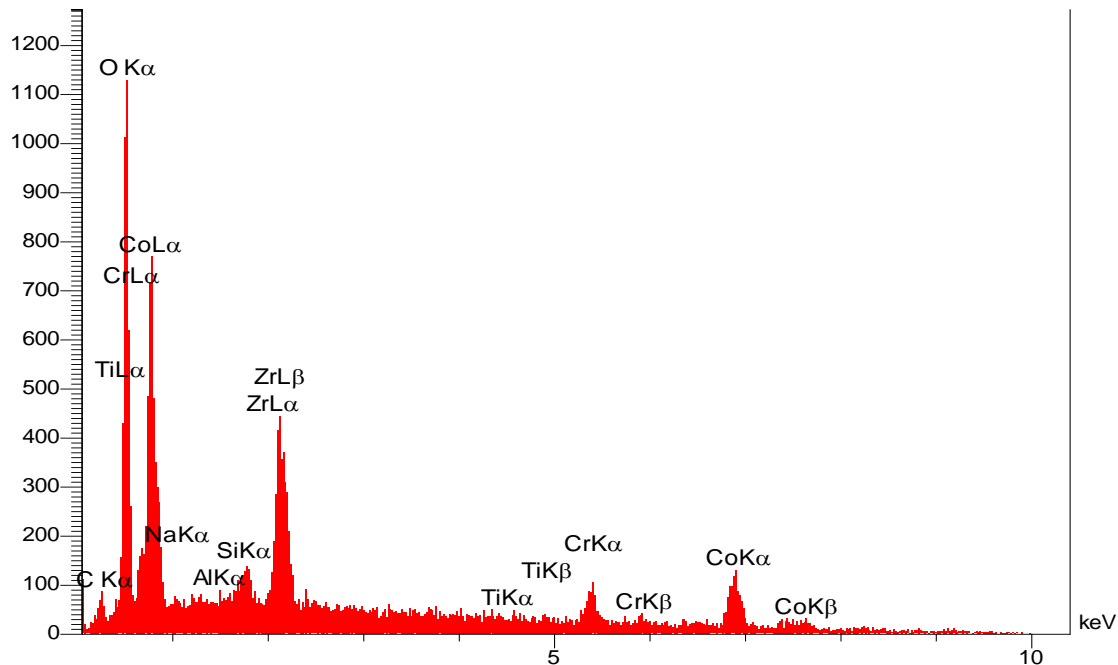


Figure (23):- single aluminized coating and aluminized presence of thermal barrier coating TBC of cobalt base super alloy (FSX-414) (8hr) at (1050°C) and oxidation and hot corrosion in steam salt mixture (NaCl and Na₂So₄)at 1080°C for 324hr.

The specimens that aluminized and thermal barrier coated (TBC) by ZrO₂ show an increase in mass while the uncoated specimen suffer from a decrease in mass due to the unstable oxide scales .

Un coated alloy were tested to compare with coated alloys which seem to be oxide at first testing and pointed for high rate of oxidation and hot corrosion form many scales of (Cr₂O₃, NiO) and Iron oxide but this scalefastly degradation lead to degraded alloys because it does not able to protective layer (Cr₂O₃) and formed oxidation and hot corrosion of many elements ,the diffuse Of cobalt forward coating and aluminum toward 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 several many phases transformation see figure(16) a, b) the inter diffusion zone upper needle structure and this zone 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 X-ray diffraction (XRD) testing show (Ni₃Al) phase in order (Ni Al) more stability.

Conclusion:-

The curve of kinetic hot corrosion and oxidation shows that very good adhesion of protective scale which give good stability with time which agree with many research [5][6][12]

On the other hand we found that the effective of ZrO₂ in adhesion protective scale of alloys have a good protective layers. We see cobalt- base Superalloys coatings like aluminizing and thermal barrier coating ZrO₂ have found to exhibit excellent oxidation and hot corrosion resistance. The formation of oxides and spinals of nickel aluminum, cobalt and chromium contributed to the development of hot corrosion resistance of these coatings which lead to degard the sample fastly

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