INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

DEVELOPMENT OF NI-BASED SUPERALLOY BY PACK CEMENTATION PROCESS

Mustafa Nash'at Jawhar[*1] **and Israa Abdul-Kadir Aziz**[2]
[*1]M.Sc Research scholar, Production Engineering & Metallurgy Department, university of technology, Baghdad ,Iraq
[2]Ph.D Research scholar, Production Engineering & Metallurgy Department, university of technology, Baghdad ,Iraq

DOI: 10.5281/zenodo.1161734

Keywords: Superalloys, Inconel 600 alloy , Pack cementation process.

Abstract

The aim of this research was to improve the properties of Inconel 600 by diffusion coating process. In this study, Si and Al, and Al, Si and Y_2O_3 were simultaneously deposited by diffusion into Inconel 600 using pack cementation process at 1120ºC for the different time (2,4,6,8)hr. The pack powder mixture consists of 18Al–8Si–$2NH_4Cl$–$72Al_2O_3$(wt.%) for silicon modified aluminde diffusion coating and replaced 1% from Al_2O_3 by Y_2O_3 for yttria doped silicon modified aluminide diffusion coating. The results show that the coatings microstructure had consists of two layers: outer layer and inter-diffusion zone. The coating thickness increase with increase the time of coating process up to 234µm and 153µm at 8hr for two type of coatings. The micro-hardness value decrease from outer layer toward the core of the substrate .The high microhardness value is 823 Kg/mm^2 at 8hr for type I and 902 Kg/mm^2 at 8hr for type II of coatings. The X-ray results shows different inter-metallic compound formed after coatings are Ni_2Al_3, Fe_3Si , Ni_2Si, Ni_3Si_2,$YNi_{10}Si_2$ and $Al_{1.1}Ni_{0.9}$.

Introduction

Fe-Cr-Ni based alloys (Inconel 600 alloy) are Widely used to produce various parts working in high temperature. In these materials high mechanical strength and impact resistance at high temperatures are required. Improving the lifetime of equipment is a critical problem and the age of elements designed for operation at high temperatures depends mainly on the environment, especially the working environment [1]. Diffusion coating are used to protect nickel-based super alloys at high temperatures. These coatings are effective for protecting components from oxidation at high temperatures. Therefore, there is a strong technical incentive to further develop the cementation process by adding various elements such as (Al-Si-Hf-Y-Cr) that can be deposited to form a high-temperature oxidation and corrosion coating resistance [2]. By combining chemical and chemical analysis with experimentation, it was found that co-deposition of Al/Si or Al/Cr can be achieved in fact with sufficient control over the pack combinations and deposition requirements [3]. The process of the cementation activated by halide salts is the process of deposition of chemical vapors in a localized controlled location. The process is low cost and especially suitable for the production of uniform and smooth formation of the coating diffusion of desired thickness on structural alloy components of complex shapes and different sizes. Moreover, according to the reactive element effect (REE), adding in a small amount can improve the adhesion and promote the formation of protective oxide scale simultaneously such as Y, Ce ,La or their oxides[4]. **Jiang et al. [5]** investigated the Al-Si-Y was prepared by arc ion plating and subsequent diffusion treatment, resulting the good protection to the substrate during high temperature oxidation . The objective of this paper is to find favorable conditions for diffusion silicon - aluminum and silicon - aluminum – yttria in nickel base Super alloys by pack cementation process.

Experimental work

The nickel-based high-temperature alloys IN 600 with nominal alloy composition(wt.%) ofNi–15.35Cr–8.32Fe–0.342Mo-0.0254Si–0.175Mn–0.025Cu–0.168Al-0.181Ti-0.074C-0.032V-0.073Co-0.014P was used as a substrate. Rectangular specimens with the dimension of 15.0 × 15.0 × 3.0 mm were grinding by emery paper grade and polishing, then washed by ultrasound washing machine . After that, the specimens were co-deposited with Al- Si and Al-Si-Y_2O_3 by pack cementation process. In a normal pack cementation process, the substrates to be coated are embedded in a sealed or semi-sealed container together with a well-mixed pack powder containing the deposition elements, halide activator and inert filler. The pack powder mixture consists of 18Al–8Si–2NH_4Cl–72Al_2O_3(wt.%) for silicon modified aluminde diffusion coating by replaced 1% Al_2O_3 by Y_2O_3 for yttria doped silicon modified aluminide diffusion coating. The pack process were carried out at 1120°C for different time (2,4,6,8) under argon atmosphere with. The NH_4Cl was dried in an oven at 90°C for 24hr before mixing with other powders. The pack powder was mixed in a ball mill at 300 rpm for 180min. with addition normal-hexane (n-C_6H_{14}) in order to prevent powders oxidation due to frictional heat [6]. The pack was then dried at 75°C for 10 hours. **Fig. (1)** represent the coating system of the study.

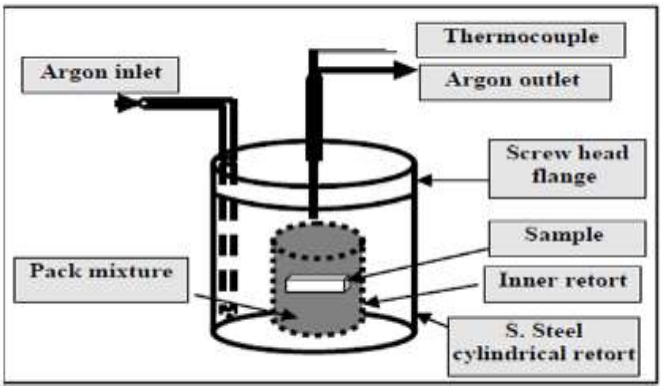


Fig. (1) Coating system design.

Results and discussion

Examination of Microstructure

Fig. (2) and **Fig. (3)** represent of coating layers by SEM of the coated samples at (1120°C) for different times(2,4,6,8)hrs . The results of the cross sections of the resulting sequences indicate that there is an layer characterized by more than phase, the basic phase representing the coatings matrix and the other secondary phases, showing the islands distribution of the coating matrix, as shown by the results of X-ray diffraction.

The cross-section of the coating layers of the specimens after 2,4,6,8 hrs for two types of coating, consist of the outer layer and inter-diffusion zone. The outer layer of each specimen consists of two region, region I called coating layer and region II called middle layer. But the except type two of coatings at 2 and 4hrs the outer layer is one region similar in structure as shown in the **Fig.(3,2hr and 4hr).** The main thickness of the outer layer and inter-diffusion zone for **type 1** of coatings layers are 110, 22, 145, 25 , 198, 27 , 205, 29, and 73,20,114 ,22, 122,22,128 , 25µm for **type 2** of coatings at different times (2,4,6,8)hrs. Middle layer rich in Ni come from substrate by outward diffusion of Ni and free from any precipitates after coating 2 and 8hrs , but after 4 and 6hr contained some amount of precipitates. When nickel diffuses outwardly, its concentration in substrate reduces. This results to the precipitation of the dissolved substrate heavy elements in the form of columns. This microstructure is called inter-diffusion zone (IDZ)[7,8]. Difficult of Y diffuse through the nickel base superalloy because the radius of the yttrium atom is 46% larger than that of the Ni atom, this reason agree with researchers [9] and [10]. **Fig.(4)** represent SEM images of surface coating.

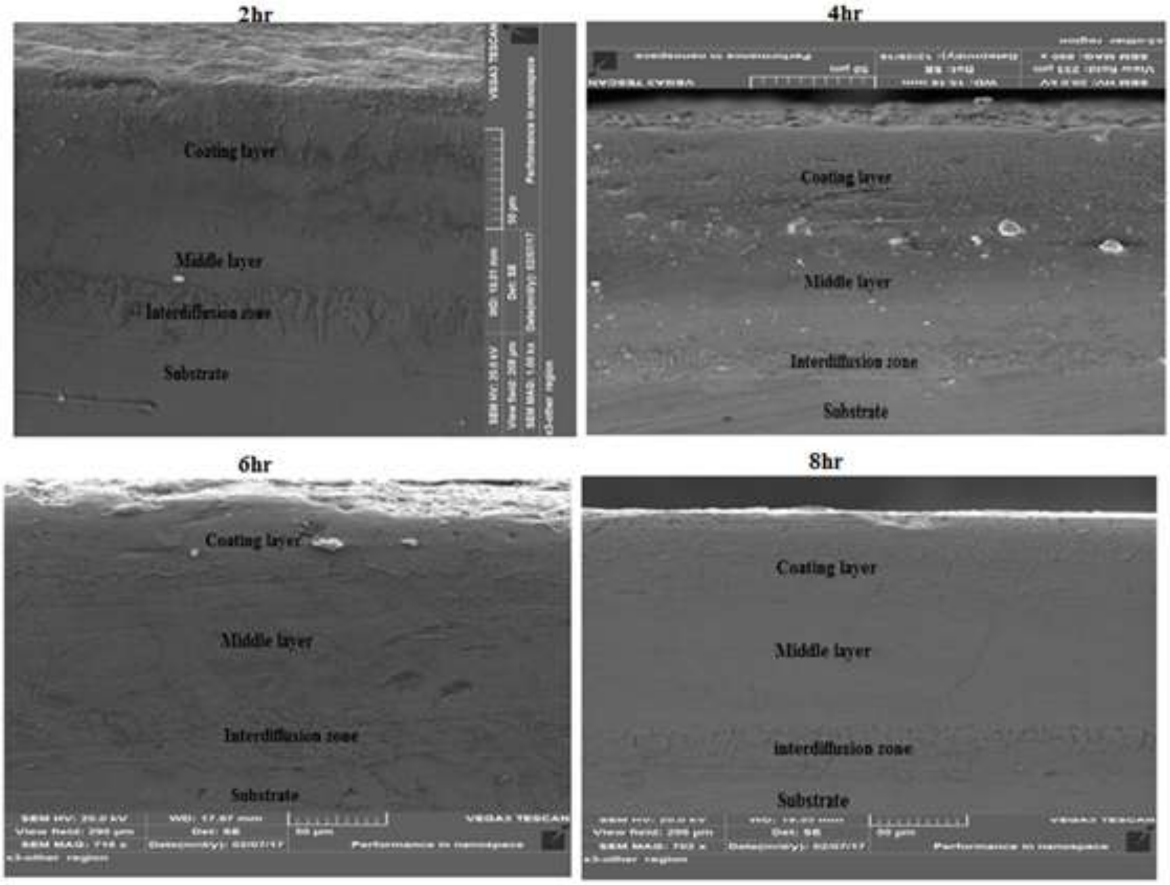
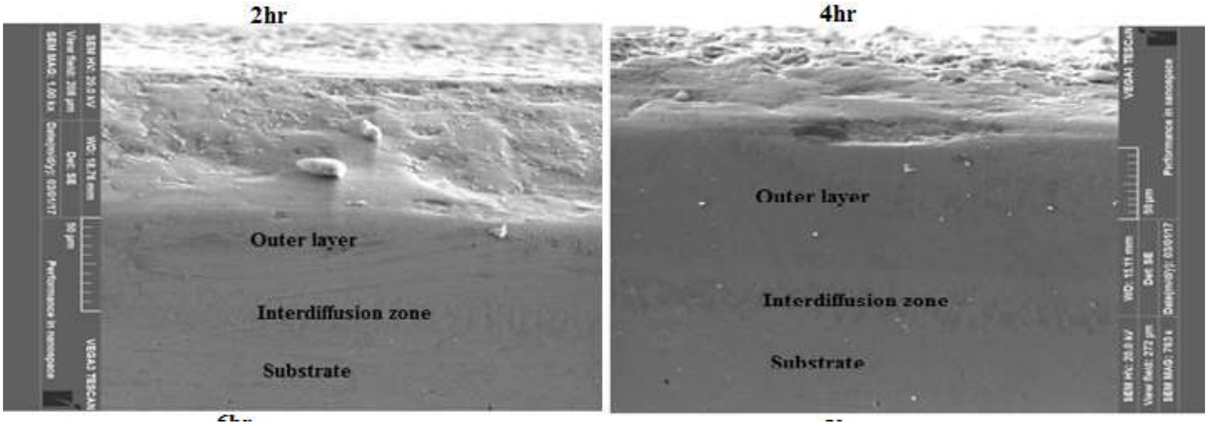


Fig. (2) Microstructure of silicon modified aluminide diffusion coating of Inconel 600 at 1120ºC for (a-2hr, b-4hr, c-6hr, d-8hrs).

As shown in **Fig.(5)** XRD analysis results shows different compound are Ni_2Al_3 , Fe_3Si, Ni_3Si_2, $Al_{1.1}Ni_{0.9}$, Ni_2Si,$YNi_{10}Si_2$ and AlNi. $YNi_{10}Si_2$ is formed in the outer layer of the coating because of the difficulty of the Y from easily diffusion into nickel base superalloy (Inconel 600 alloy).



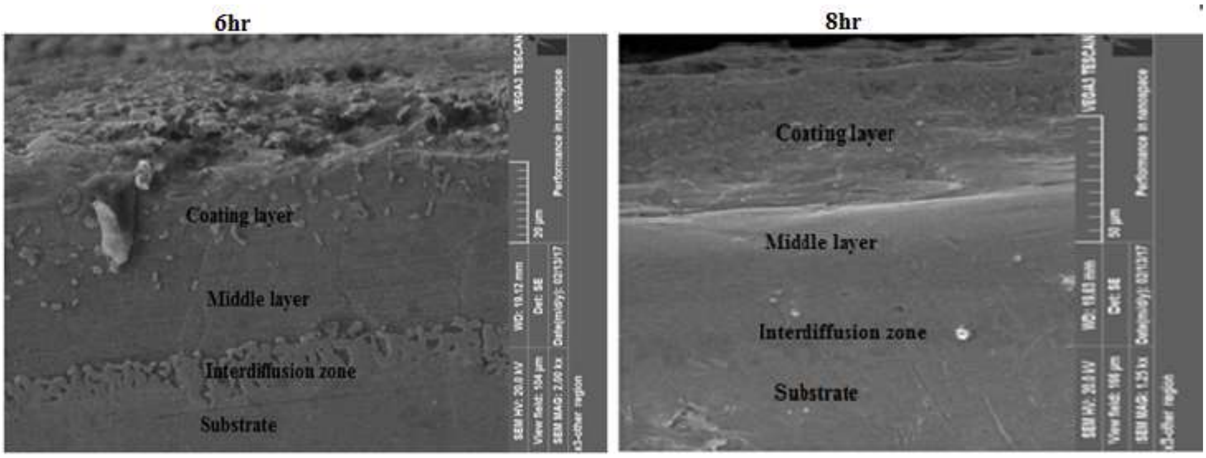


Figure (3) Microstructure of yttria doped silicon modified aluminide diffusion coating of Inconel 600 at 1120°C for (a-2hr, b-4hr, c-6hr, d-8hr).

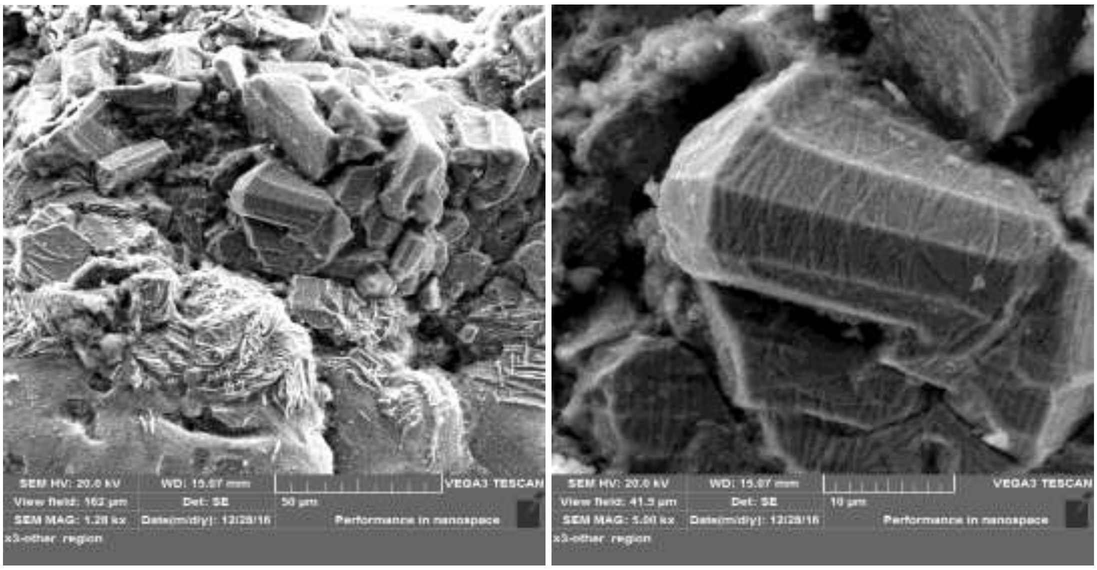
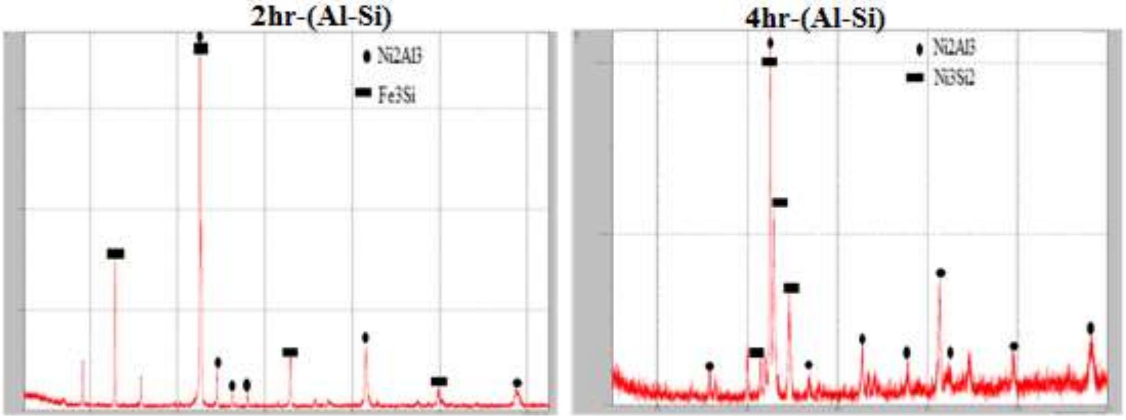


Fig.(4) SEM images of surface after 6hr silicon modified aluminide diffusion coating with several thickness at 1200°C in Ar gas atmosphere.



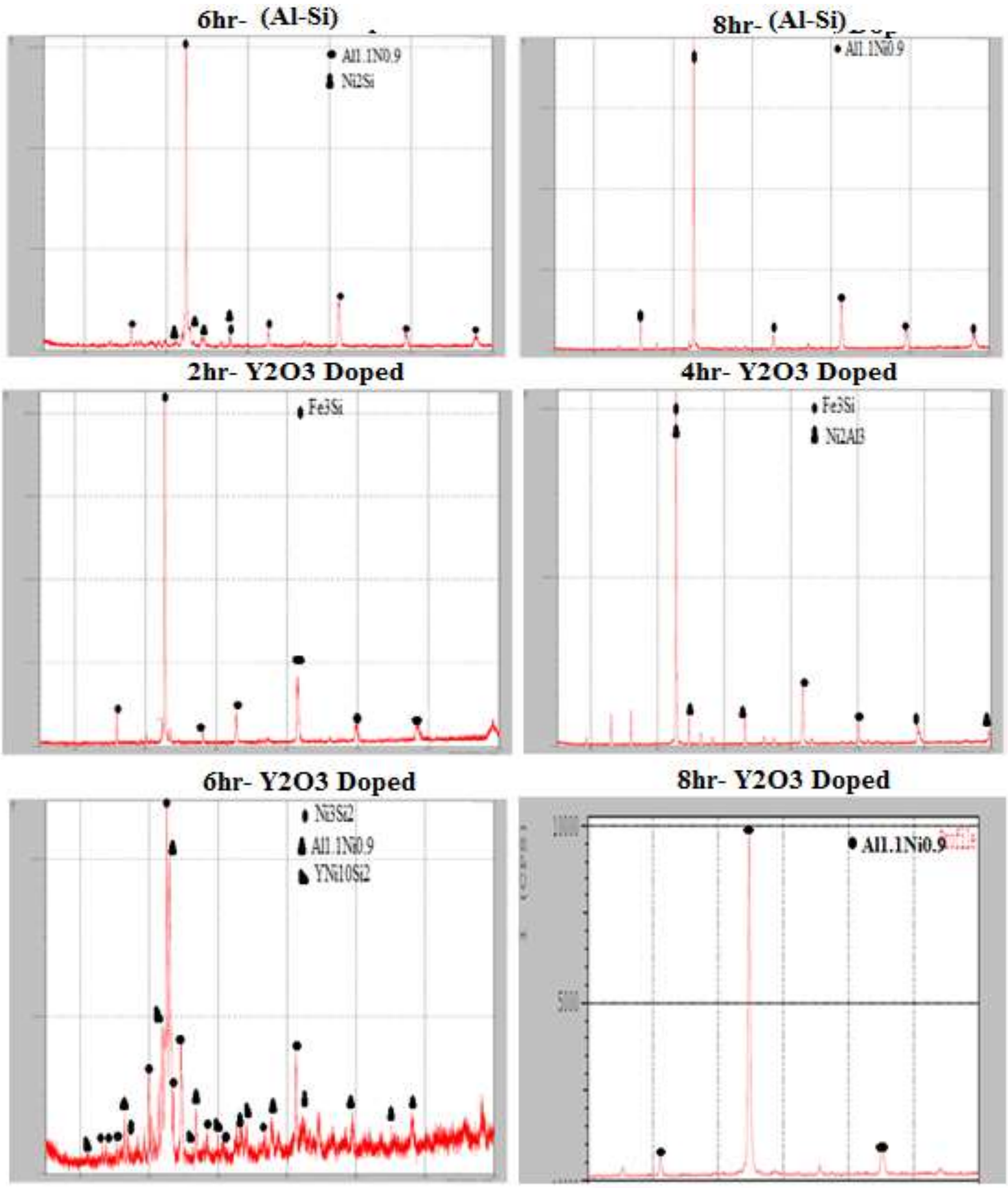


Fig. (5) XRD analysis of two type of coatings of Inconel 600 after (a-2hr, b-4hr ,c-6hr ,d-8hr)at 1120°C.

Coating thickness measurements

The measurements of coating layer thickness formed in two system of coatings , it was indicated that the thickness of the coating layer increase with increase the coating time (2,4,6,8)hr at constant temperature (1120°C) as shown in the **Fig.(6)**. In the **Fig. (6 and7)** observed that increase in coating time leads to increase in coating thickness of the coating layer from 2 to 8 hr for two of coating types . In the type I, the highest value was 234µm and 153µm at 8hr for type II, and this is clearly shown by the gradient of the coating thickness.

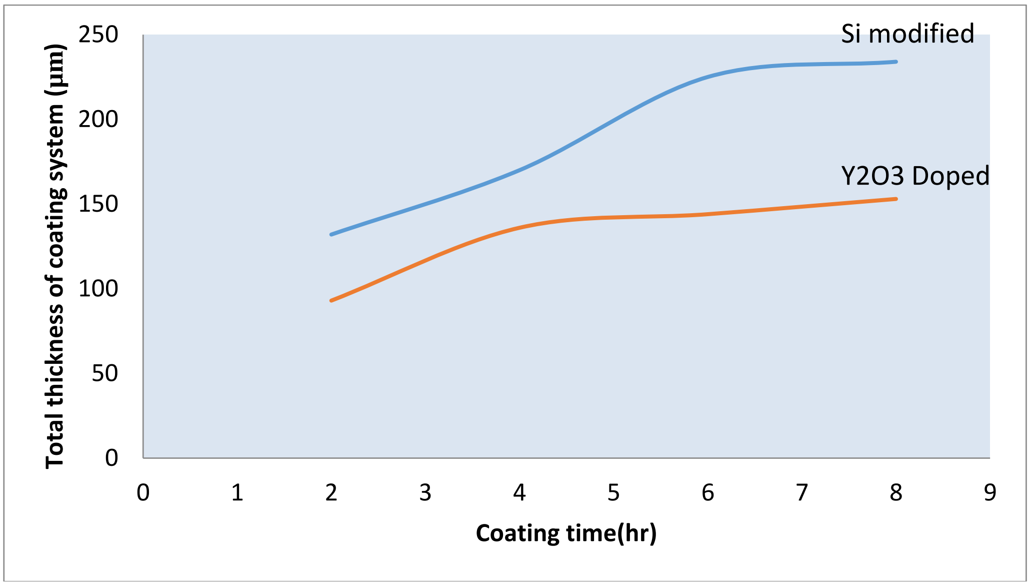
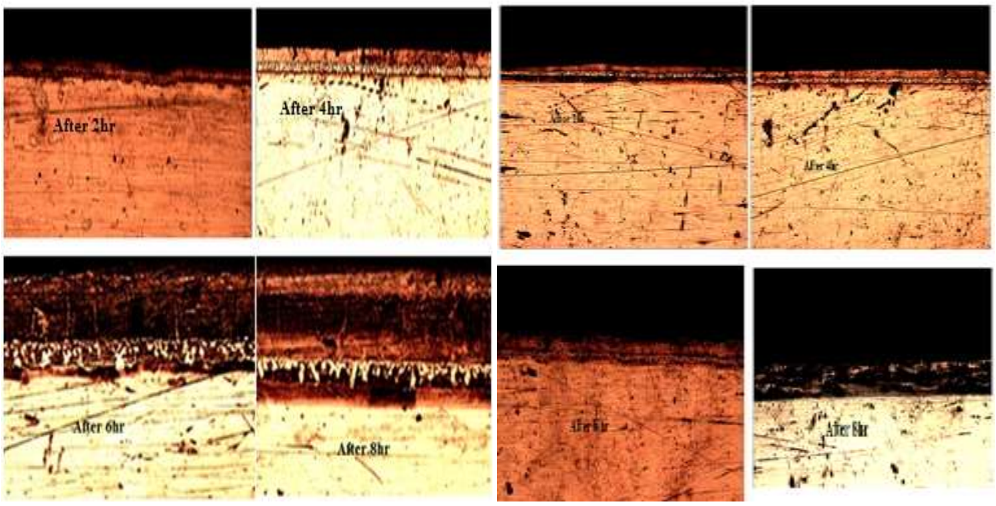


Fig. (6) Average total thickness of the two types of coating.



a-(Al-Si) **b-Y_2O_3 Doped**

Fig.(7) LOM show the increases thickness of coatings layer with deposition time.

Micro-hardness Results

Fig. (8) represent the variation of micro-hardness value in the range from 543 to 802 has been obtained for silicon modified aluminide and from 551to 923 for yttria doped silicon modified aluminide diffusion coating of Inconel 600 alloy. **Fig.(9)** show that the high hardness at the outer layer of coating but decreases gradually until reached to base alloy because the outer layer contain the ($NiAl-Ni_2Al_3-Fe_3Si-Ni_2Si-YNi_{10}Si_2$) as represent by XRD examination. The difference in the hardness resulted, probably, from the difference in microstructure and concentration of element coating. the occurrence of (Ni-Cr-Fe) was the reason for the hardness increase at the surface . Increase the distance from the surface was accompanied by gradual decreasing in the hardness. it was caused by the increase the amount of the Ni-Cr-Fe matrix in the microstructure.

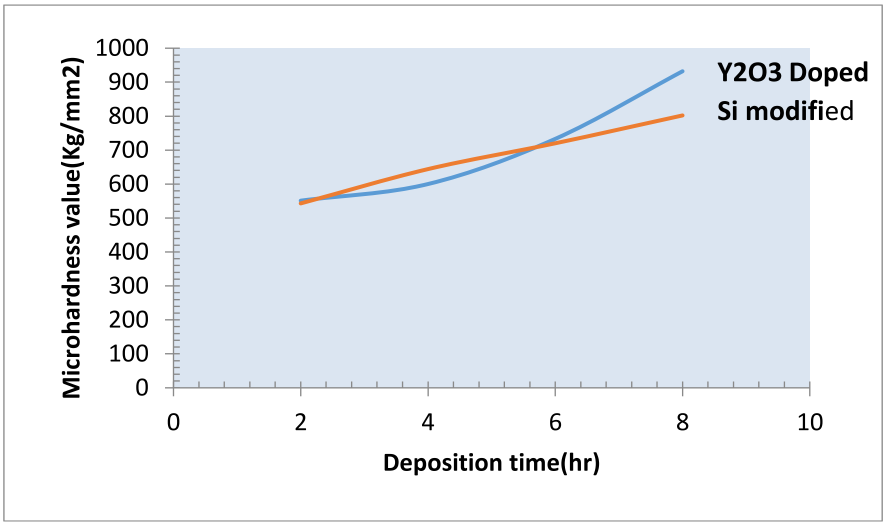


Fig.(8) Vickers micro-hardness vs. deposition times.

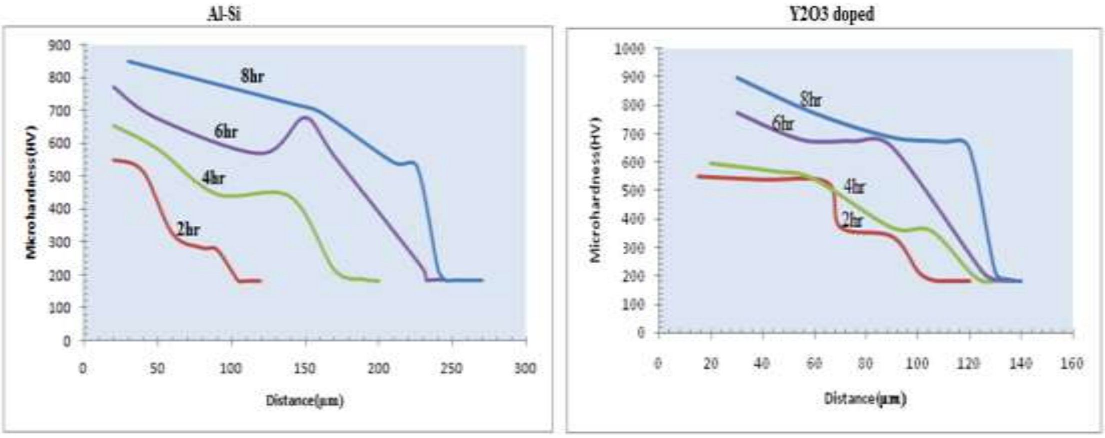
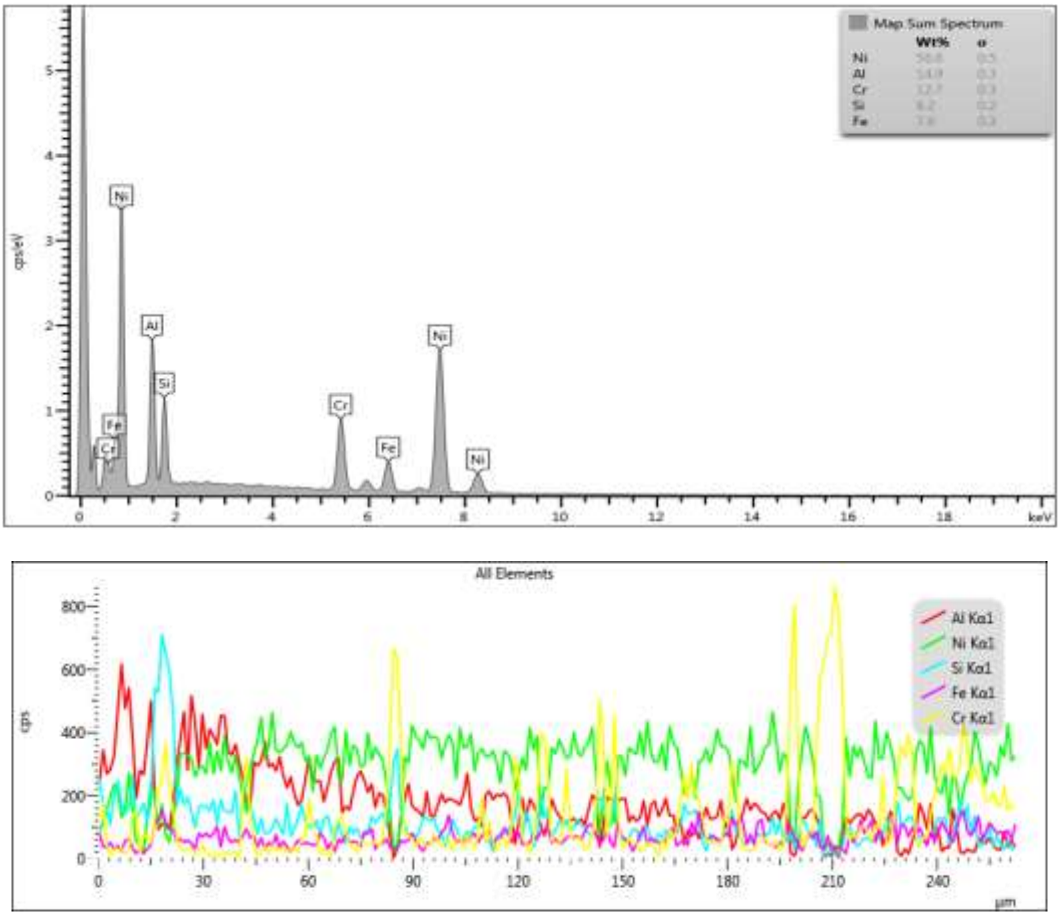


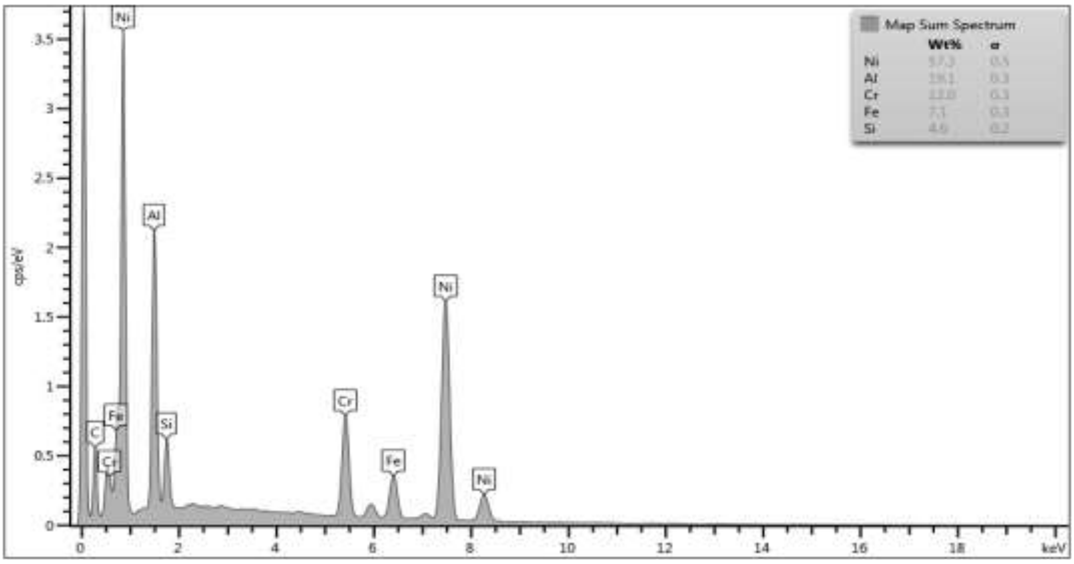
Fig. (9) Vickers micro-hardness vs. depth for different coating times(Al-Si and Al-Si-Y_2O_3).

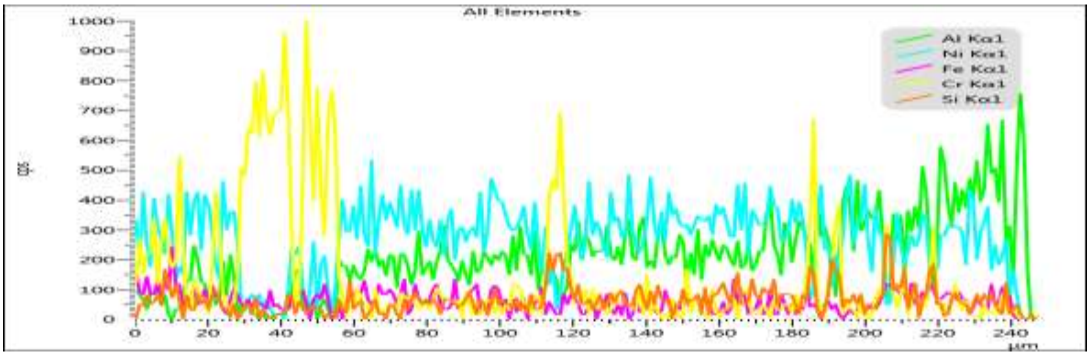
Concentration of element with coating layers formation

The results of EDX from the coating formation by silicon modified aluminide and yttria doped silicon modified aluminide diffusion coating at 1120ºC for (2,4,6,8)hr showed: The Al X-ray line scans, as shown **Fig.(10)** indicates that the Al content in the outer layer higher than that inter-diffusion zone. In the specimens coating with silicon modified aluminide coating outer layer divided into two region, the Al content concentrate in the region I and decrease toward the middle layer , when increase the time of the coating the diffusion of Al in all coating specimens where increased. Although the Si X-ray line scan indicates the Si content increase in the outer layer and decrease toward to the interdiffusion zone , this mean the Si diffuse inwardly to the specimens, this corresponds to the researcher's opinion[3]. The segregation of two main elements of Inconel 600 alloy (Ni and Cr) was clearly visible. it was characteristic of the linear profile of nickel and chromium, that higher nickel content was accompanied by reduced chromium concentration. The Ni , Cr and Fe X-ray lines indicates that these element diffusion outwardly from substrate to the outer layer, Cr is concentrate at the interdiffusion zone ,but Ni is concentrate in the middle sub-layer and decrease the content of Ni towards the coatings sub-layer. As for the presence of yttrium is not found in the coating layers and there is a small proportion on the outside of the sample coatings, shown as **Fig.(11)**.

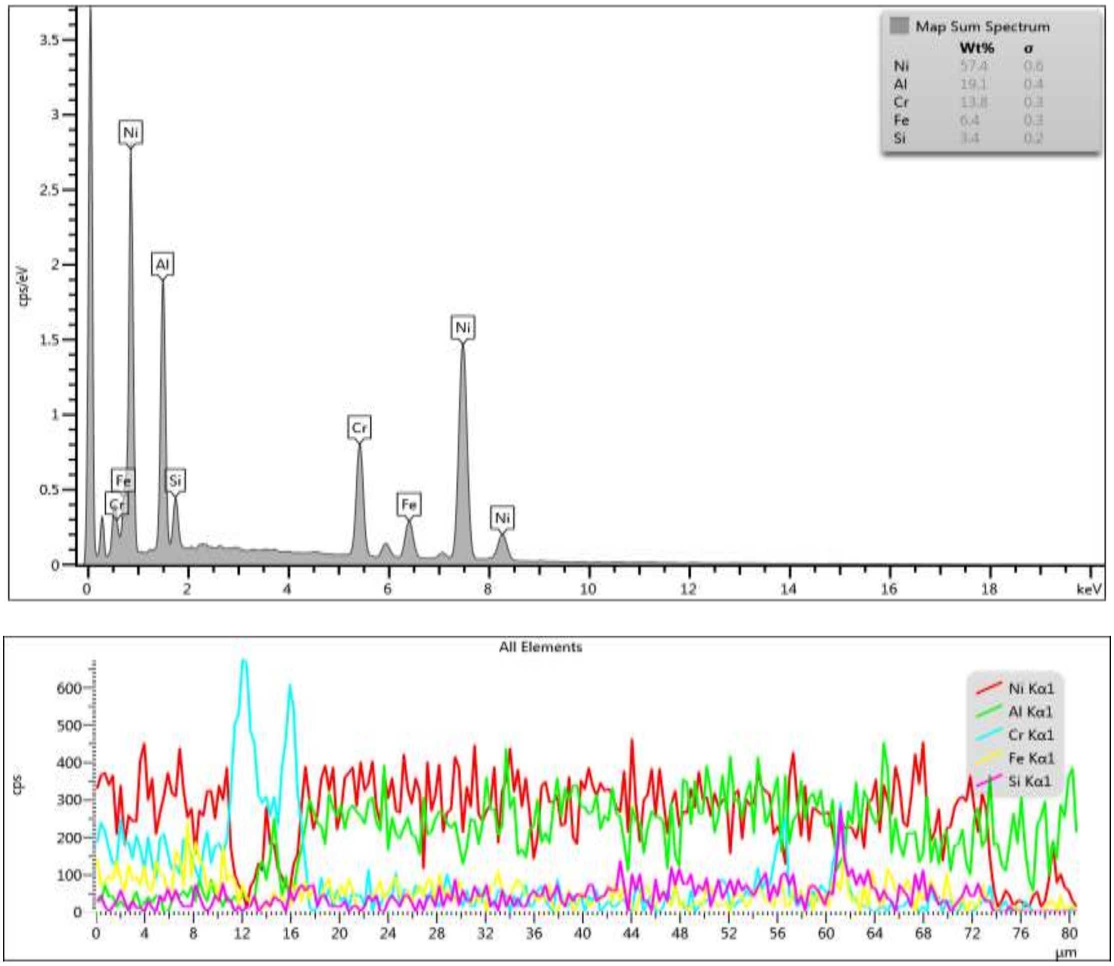

Map Sum Spectrum
Wt% σ
Ni 56.8 0.5
Al 14.9 0.3
Cr 12.7 0.3
Si 8.2 0.2
Fe 7.8 0.3
cps/eV
0
1
2
3
4
5
Ni
Al
Si
Fe
Cr
Cr
Fe
Ni
Ni
0
2
4
6
8
10
12
14
16
18
keV
All Elements
Al Kα1
Ni Kα1
Si Kα1
Fe Kα1
Cr Kα1
cps
0
200
400
600
800
0
30
60
90
120
150
180
210
240
μm

a- 6hr Al-Si

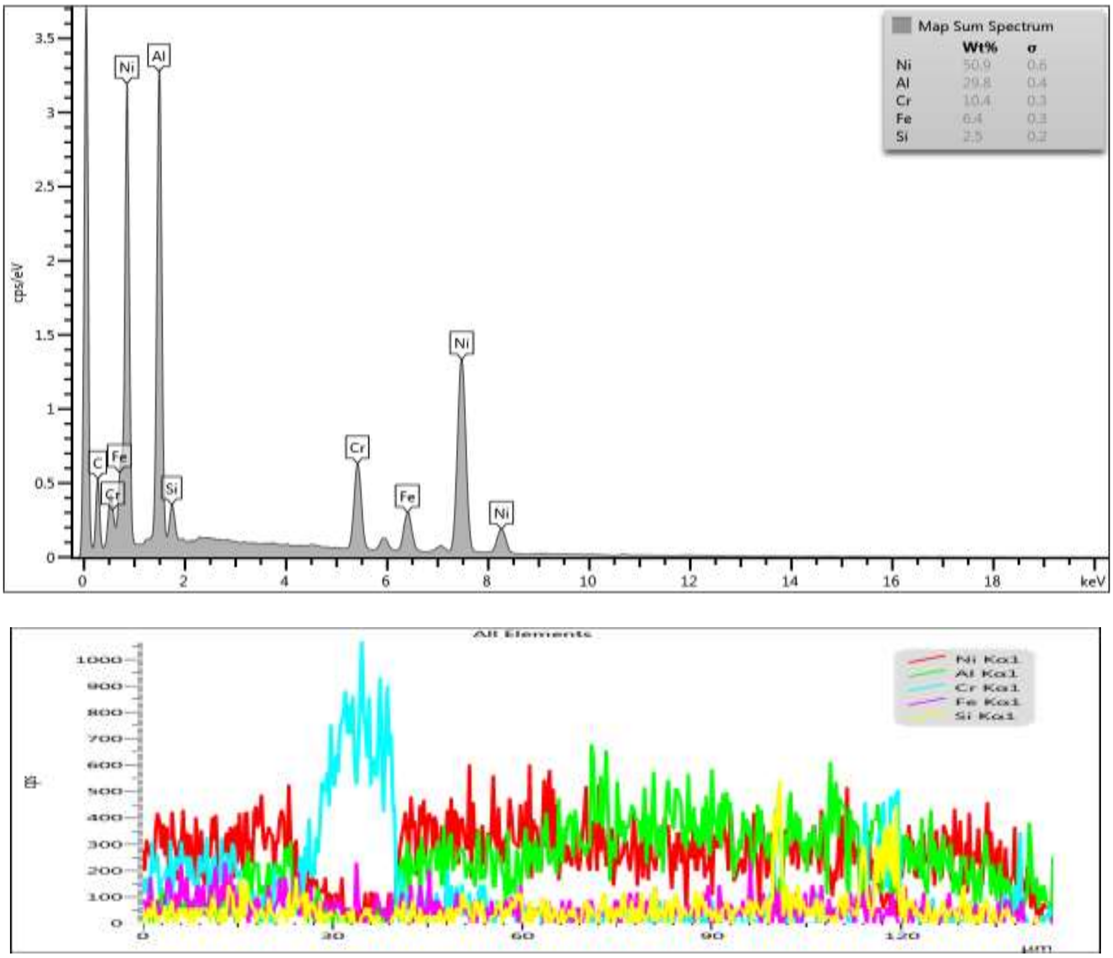

Map Sum Spectrum
Wt% σ
Ni 57.3 0.5
Al 19.1 0.3
Cr 12.0 0.3
Fe 7.1 0.3
Si 4.6 0.2
cps/eV
0
0.5
1
1.5
2
2.5
3
3.5
Ni
Al
C
Fe
Cr
Si
Cr
Fe
Ni
Ni
0
2
4
6
8
10
12
14
16
18
keV



b- 8hr Al-Si



c-6hr Al-Si-Y_2O_3



b- 8hr Al-Si-Y_2O_3

Fig.(10) EDX spectrum and X-ray line.

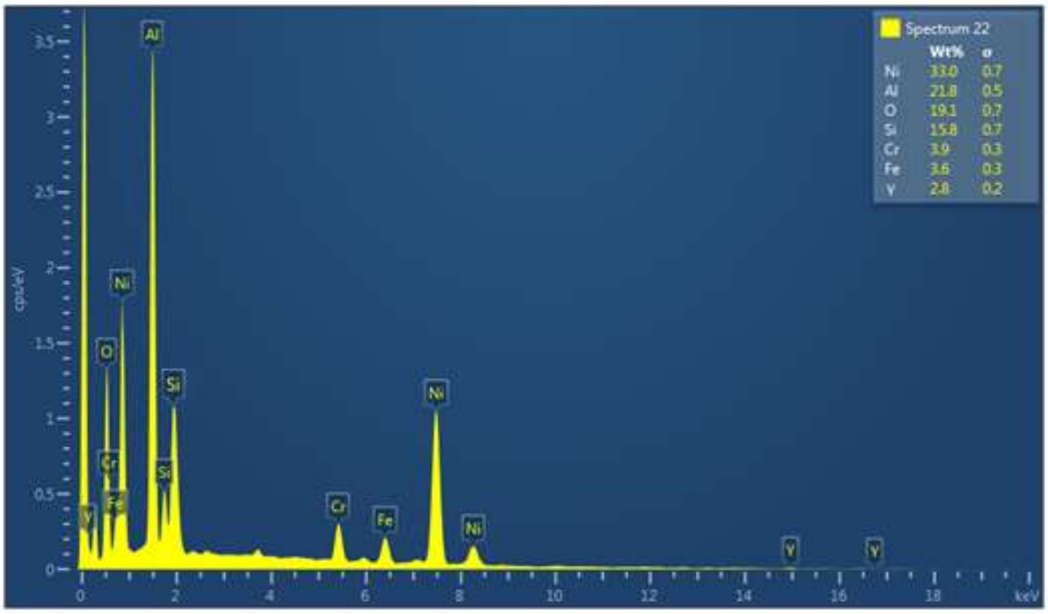


Fig.(11) EDS spectrum to verify the presence of yttrium after 6hr coating with Y_2O_3.

Conclusion

1. The phases formed in the surface layer of as coated specimens for various periods (2,4,6 and 8 hrs) of coating time are (Ni_2Al_3, Ni_3Si_2, Ni_2Si, Fe_3Si, $YNi_{10}Si_2$ and $Al_{1.1}$ $Ni_{0.9}$.
2. The thickness of the coating layer increases with increase deposition time for aluminizing – siliconizing diffusion coating, where the higher thickness obtained at 8 hrs is 234 µm, but 153 µm for Y2O3 doped aluminized-siliconized diffusion coating.
3. The hardness value of Inconel 600 alloy improved with coating by aluminizing-siliconizing, it reached to(802Kg/mm^2), but reached to (923Kg/mm^2) when doped with 1% Y_2O_3.
4. The coating layer contained outer layer, middle layer and interdiffusion zone..

References

[1] M. Qiao and C. zhou ,"Co-deposition of Co and Al on nickel base superalloys by pack cementation process", surface and coatings Technology,Vol.206,2012,pp. 2899-2904.

[2] Agnieszka Kochmańska," Hot Corrosion Resistance Properties of Al – Si Coatings Obtained by Slurry Method", Defect and Diffusion Forum, Vol. 326-328,2012, pp. 273-278.

[3] Z.D. Xiang and P.K. Datta," Conditions for pack Co-deposition of Al and Hf on nickel-base superalloys", Surface and Coatings Technology,Vol.179 ,2004,pp. 95–102.

[4] Z. Liu, X. Zhao and C. Zhou ,"Improved hot corrosion resistance of Y-Ce-Co- modified aluminide coating on nickel base superalloys by pack cementation process", Corrosion Science,2014.

[5] S.M. Jiang ,C.Z. Xu ,H.Q. Li, S.C. Liu , j. Gong and C. Sun," Preparation and oxidation behavior of an Al-Si-Y diffusion coating on a Ni-based single crystal superalloys ", Corrosion Science,Vol.52,2010,pp. 435-440.

[6] R. Mohammed," High Temperature Cyclic Oxidation of Yttrium Modified Aluminide Diffusion Coatings of Stainless Steel", Anbar Journal of Engineering Sciences, 2009, pp. 61-71.

[7] H. Arabi, S. Rastegari, Z. Salehpour & A. Bakhshi," formation mechanisms of silicon modified aluminide coatings on Ni- based superalloys", IUST International Journal of Engineering Science, Vol. 19, No.5, 2009, pp. 39-44

[8] Z. D. Xiang and P. K. Datta ," Deposition of silicon modified aluminide coatings on nickel base superalloys by pack cementation process", Materials Science and Technology, Vol.19, 2003,pp. 935-942.

[9] W. Fuhul , L. Hanyi , B. Linxiang and W. Weitao ," Hot corrosion of Yttrium-modified aluminide coatings", Materials Science and Engineering, A121, 1989, pp. 387-389.
[10] David C. Tu, C. C. Lin, S. J. Liao, and J. C. Chou ," A study of yttrium modified aluminide coatings on IN 738 alloy", Journal of Vacuum Science & Technology A4, 1986,pp.2601-2608