

FORMATION MECHANISM OF SILICON MODIFIED ALUMINIDE COATING ON A NI-BASE SUPERALLOY

H. Arabi, S. Rastegari, Z. Salehpour & A. Bakhshi

Abstract: Formation mechanism of silicon modified aluminide coating applied on a nickel base super alloy IN-738 LC by pack cementation process was the subject of investigation in this research. Study of the microstructure and compositions of the coating was carried out, using optical and scanning electron microscopes, EDS and X-ray diffraction (XRD) techniques. The results showed that due to low partial pressure of silicon halide in Pack process, the amount of soluble silicon in the coating can not exceed 1 wt % of the total coating composition, although the Si content of the particles present within the outer coating sub-layer could reach as far as 5 wt%. Thus, the small amount of soluble Si within the coating could not provide the necessary conditions for formation of any intermetallic and it seems that the formation and growth behavior of various sub-layers in Si-modified aluminide coating is similar to that of simple aluminide coating. Three sub-layers were detected in the coating structure after being subjected to diffusion heat treatment. They were an outer Ni-rich NiAl sub-layer; a middle Ni-rich NiAl and an inter diffusion sub-layers. The details of formations and growth mechanism of these sub-layers has been discussed in this research.

Keywords: Aluminizing; Si-Modified Coating; NiAl Phase; Formation Mechanism; Pack Cementation; Low Temperature High Activity; Halide

1. Introduction

Diffusion aluminide coatings are routinely used on Ni-base superalloys to protect them from high corrosive environment particularly at high temperature. This type of coating provides good oxidation resistance, but a limited resistance to hot corrosion in comparison to the aluminide coating, modified by elements such as Pt, Cr or Si.

It is said [1] that silicon modified aluminide coatings are being produced either by pack cementation or by slurry techniques, enhances resistance to high temperature oxidation, possibly by aiding the formation and adherence of the alumina scales. In addition, modification of aluminide coating by Si is reported [2] to improve the resistance to type II acidic fluxing, which is said to be due to insolubility of oxide scales in acidic corrodents. Silicon modified

aluminizing process is one of the so-called high activity process. The growth of coating layers in this type of coating is usually controlled by inward aluminium diffusion [3] and [4]. At the initial stage of coating, a single coating layer of Ni_2Al_3 having a small amount of Si forms on the surface of the substrate [5] and [6]. At this stage no intermediate layer between the base material and the coated layer has been reported. It is only after additional heat treatment that a layer of NiAl will form of the boundary of the original coating layer and the base metal. The formation of this layer is mainly due to decomposition of the original coating layer Ni_2Al_3 and inter-diffusion of Ni and Al. Worth mentioning that in pack cementation process, aluminum-silicon alloy powder reacts with halide compounds to produce metallic halide vapor species which diffuse into the component surface [7] and [8]. However, in the modified pack diffusion coating with silicon this process is difficult owing to the large difference between the aluminium and silicon halide vapor pressures [5].

2. Experimental Procedures

The base material used for this research was a Ni-base superalloy IN-738 LC, the nominal composition is given in table 1.

Low temperature high activity (LTHA) process using pack cementation technique was employed for coating. The pack powder contained merchandize powder of

Paper first received April, 15, 2006, and in revised form May. 20, 2008.

H. Arabi: Professor, Department of Materials & Metallurgical Engineering, Iran University of Science & Technology, Tehran-Iran. arabi@iust.ac.ir

S. Rastegari, Assistant Professor, Department of Materials & Metallurgical Engineering, Iran University of Science & Technology., Tehran-Iran, rastegari@iust.ac.ir

Z. Salehpour, Research assistant, Department of Materials & Metallurgical Engineering, Iran University of Science & Technology, Tehran-Iran, salehpourz@iust.ac.ir

A. Bakhshi, MSc. Student, Department of Materials & Metallurgical Engineering, Iran University of Science & Technology, Tehran-Iran, Ali_Bakhshi51@Yahoo.com

Al-12% Si powder, halide activator salt NH_4Cl , and an inert alumina (Al_2O_3) as filler powder. Specimens with dimensions of $15 \times 15 \times 5$ mm from the base material were embedded in pack powder within a heat resistant stainless steel retort. The retort was then placed in Bell furnace, purged with argon, heated to 750°C and held for a period of 3 hours, then cooled in furnace. The retort was then opened and the coated substrates were cleaned. The coated samples were then subjected to diffusional heat treatment cycles at 1030, 1050 and 1080°C for either 4 or 8 hours. Finally, the microstructures and the compositions of each coating were investigated, using SEM, EDS and XRD techniques.

Tab. 1. Chemical composition of Ni-base superalloy IN738LC (wt %)

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

3. Results

Figure 1 shows a typical Image of the samples coated at 750°C for 3 hours by pack cementation technique. Typical X-ray spectrum, figure 2, obtained from the corresponding sample shown in figure 1, indicating that the single layer observed in this figure is Ni_2Al_3 and typical EDS analysis, figure 3, shown that this single layer, Ni_2Al_3 , having small amount of silicon and other elements which were present within the substrate.

Figure 4 shows a typical cross section of the coated samples which subjected to heat treatment at 1030, 1050 and 1080°C for a period of either 4 or 8 hours. This figure shows there are three discrete sub-layers formed within the coating layer after heat treatment. The result of X-ray diffraction, figure 5, shows that the outer sub-layer is basically a NiAl Phase and SEM images (figure 4) show that this layer contains some refractories precipitates. The types of these precipitates, forming mainly during pack cementation process (figure 1) depends on the compositions of the base materials. In a similar research [9] and [10] has been established that the forming elements of these types of precipitates are nearly insolvable in phases such as Ni_2Al_3 and NiAl; thus they appear mainly in the form of particles within the NiAl sub-layer.

Typical results of elemental analysis of the major elements present in the outer NiAl sub-layer of various coated samples subjected to different heat treatment presented in table 2 and figure 6. The results show this area is rich in Ni and Al and while the amount of Ni increased with increasing temperature the amount of Al decreased. In addition, the amount of Si detected in the outer layer for all of the heat-treated samples was always less than 1wt%. The middle sub-layer in figure 4 does not contain any precipitate, and is basically rich in Ni; however, the amount of its Al has slightly increased relative to that of outer NiAl. Observation of

a similar area has been reported [3] in a similar research. They found that this sub-layer is a Ni-rich NiAl phase, gaining more Al atoms in comparison to the outer NiAl which loses Al atoms during heat treatment. This sub-layer forms mainly due to inward diffusion of Al, which becomes available due to decomposition of the original Ni_2Al_3 coating layer in a low temperature high activity (LTHA) process [3].

Figure 4 also shows the interdiffusion sub-layer. This area formed due to outward diffuse of Ni from the base material and inward diffusion of Al [6]. This area consists of columnar phase formed mainly in the direction of diffusion and distributed within the original base material which then became poorer in Ni and richer in Al.

The effect of time and temperature on the thickness of various sub-layers can be seen in figures 7&8. Figure 8 shows by increasing the time of heating from 4 to 8 hours at 1050°C , the thickness of inter-diffusion and the middle sub-layers increase while the thickness of the outer sub-layer remained unchanged. In addition, the sizes of the columnar phase within the inter diffusion layer increased while the thickness of the area A shown in figure 9 slightly decreased with increasing heating time and temperature (see figure 7). However, although the thickness of area A decreased with increasing heating time and temperature but the overall thickness of the interdiffusion and middle sub-layers increased. Thus, the total thickness of the coating layer has increased as a whole.

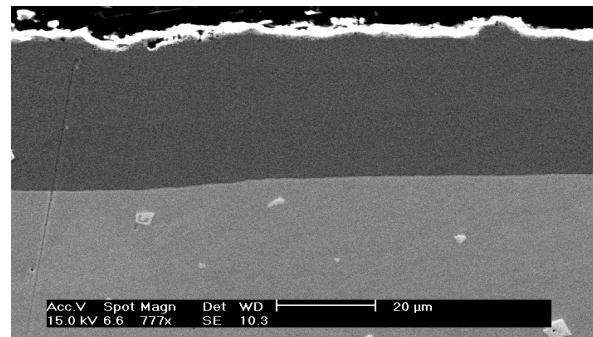


Fig. 1. Typical SEM image of a single coating layer Ni_2Al_3 phase after pack cementation process at 750°C for 3 hours.

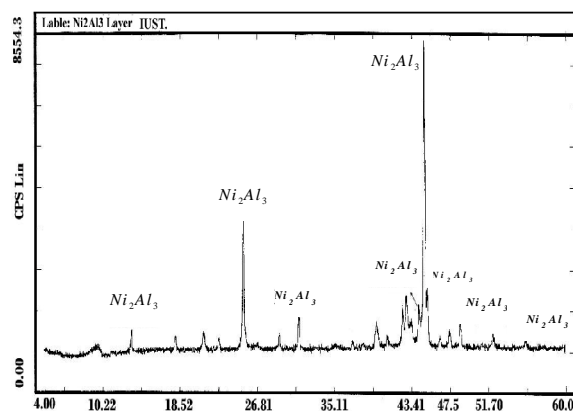


Fig. 2. Typical XRD analysis of outer surface coating layer shown in Fig.1.

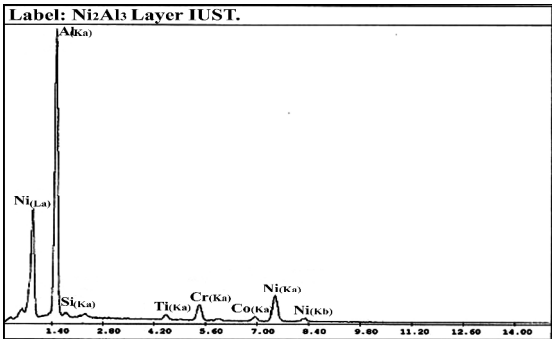


Fig. 3. EDS analysis of the outer coating layer before heat treatment

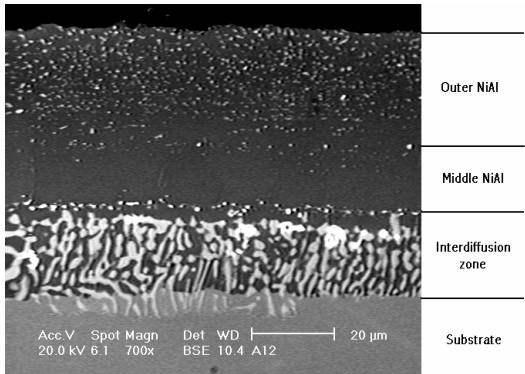


Fig. 4. Typical microstructure of silicon modified-aluminide, coating produced after heat treating the coated samples at 1030, 1050 and 1080°C for a period of either 4 or 8hrs.

Tab. 2. Average weight percent of Ni, Al and Si as function of temperature in the outer coating layer of various samples heat treated for 4 hrs.

Temperature, °C	Wt% of Ni, Al, Si within the outer surface on NiAl layer		
	Ni	Al	Si
1030	51	27	0.7
1050	54	25	0.8
1080	57	23	0.8

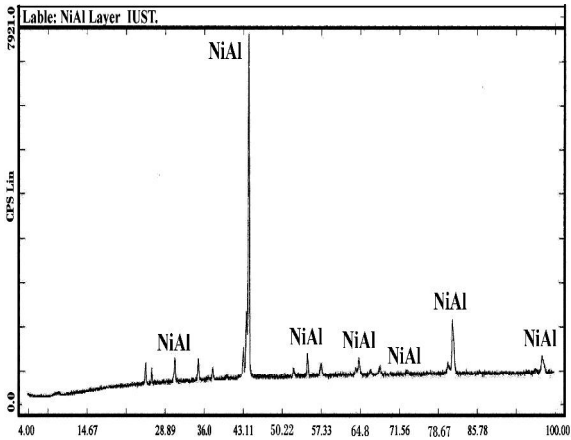


Fig. 5. XRD analysis of coating after heat treatment at 1050°C for 4 hrs

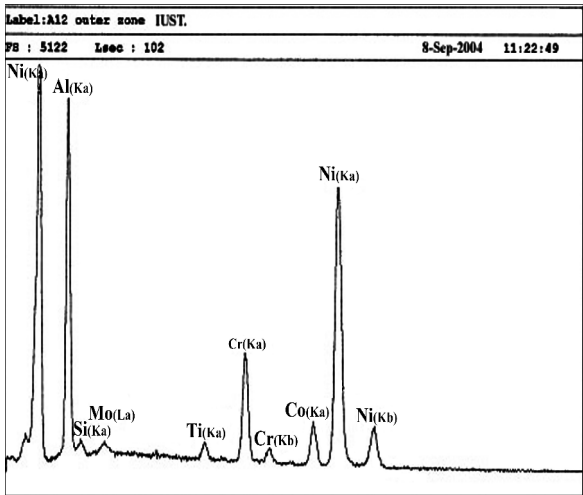


Fig. 6. Typical EDS analysis of outer NiAl layer in the surface of sample heat treated at 1050 °C for 4 hrs

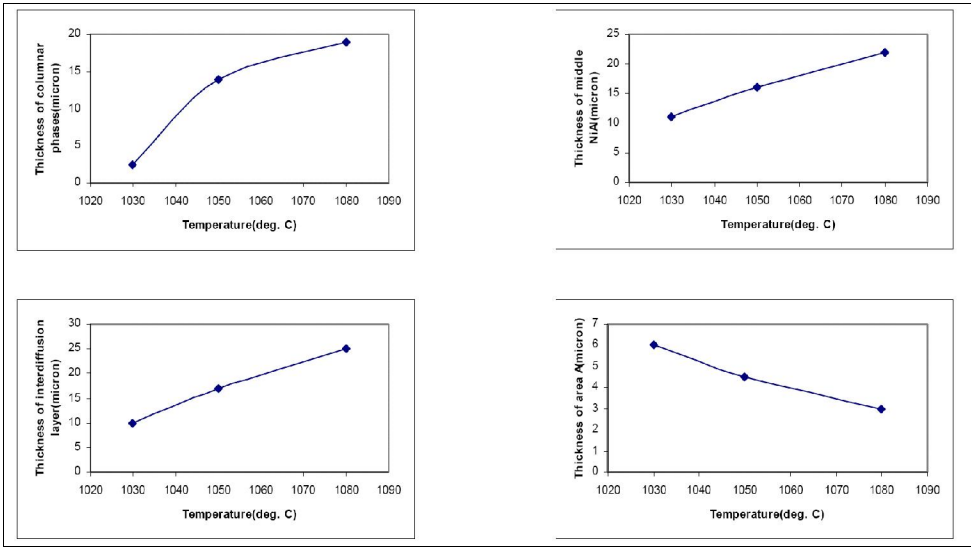


Fig. 7. Variation of the average thicknesses of the coating sub-layers as function of heat treating temperatures

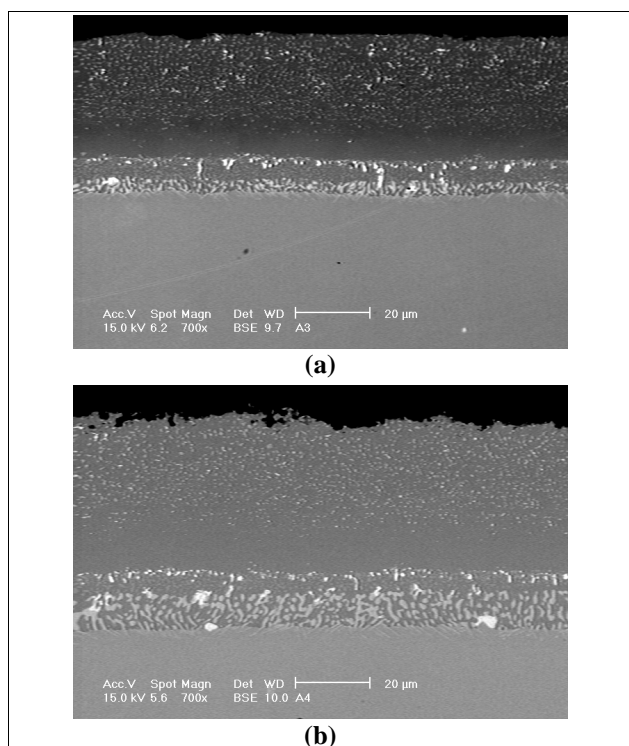


Fig. 8. Profiles of Coating layers formed in the samples heat treated at 1050°C for periods of a) 4hrs b) 8hrs.

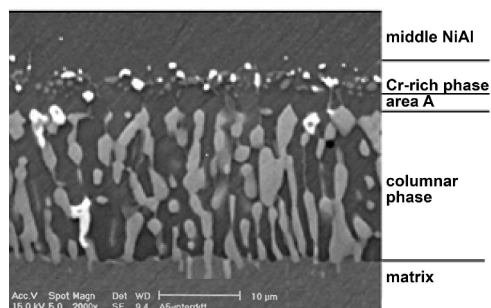


Fig. 9. Typical inter-diffusion sub-layers formed in the sample heat treated for 8 hrs at 1050°C.

4. Discussion

4-1 Thickness of the Coating Sub-Layers

The measured thicknesses of the three sub-layers indicated that the thickness of the interdiffusion and the middle NiAl sub-layers increased substantially during heat treatment of the coated samples, due to strong dependency of their growth mechanism on the interdiffusion of Ni and Al at high temperature [6]. Meanwhile, the thickness of the outer NiAl sub-layer remained constant (i.e. $30 \pm 2 \mu\text{m}$). This indicates that variation of heat treatment time and temperature did not affect noticeably the thickness of this sub-layer. Thus, since other parameters affecting the coating thickness were kept constant, one may conclude that thickness of the external NiAl sub-layer is independent of the time and temperature of heat treatment applied after coating process.

Interdiffusion sub-layer consists of three separate zones (see figure 9). The first zone contains Cr-rich phases.

The formation of this zone is said [11] to be firstly due to outward diffusion of Cr and Ni from the base material during heat treatment and secondly, since the outgoing Cr atoms have a limited solubility in the NiAl phase [12], most of these atoms accumulated at the interface of the middle NiAl and interdiffusion sub-layers and caused the formation of Cr rich phases there. The second zone is free from any precipitate (area A in figure 9), and the third zone contains columnar phases rich in refractories elements. Comparing the scanning electron micrographs presented in figure 8, one may conclude that by increasing the heat treatment time from 4 to 8 hours at 1050° C, the overall thickness of the interdiffusion sub-layer increased; however, the thicknesses of the three zones within this sub-layer responded differently with increasing time. So, while the thickness of columnar zone increased with time the thickness of area A within this sub-layer slightly decreased and the thickness of Cr-rich zone remained constant. Dependency of the interdiffusion zone growth rate on temperature can be seen in figure 7.

4-2. Distributions of Elements Within the Outer Sub-Layer

Results of elemental analysis from the outer layer presented in Table 2 show that by increasing the temperature from 1030°C to 1080°C, the amount of Al in the outer NiAl decreased while, the Ni content of this sub-layer increased, however the amount of Si in this sub-layer remained nearly constant and always less than 1wt%. It is said [5] that the amount of Si (i.e. < 1wt %) in the outer NiAl is a characteristic of Si modified aluminide coating applied by pack cementation technique.

Typical analysis of the particles within the outer NiAl showed in figure 10. This figure shows that these particles have less than 5wt% Si. This observation has also been reported by Zheng et al. [13] who said that Si content of the particles within the coating NiAl sub-layer can be up to 5 wt% of the total compositions of the particles. However, there is an exception for the case of M_6C which may have up to 9 wt % Si.

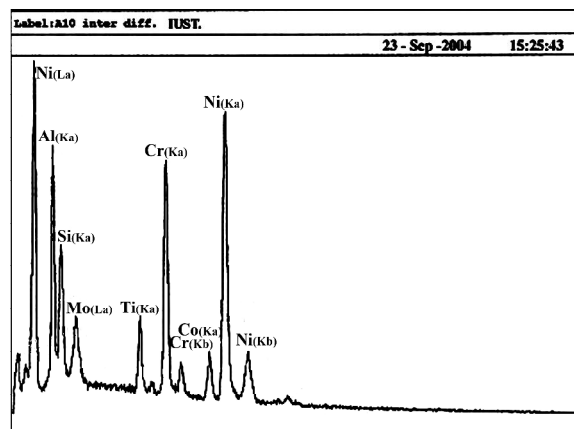


Fig. 10. Typical EDS analysis of carbide particles shown

Within the area identified by Cr rich phases in Fig.9. Zheng et al. [13] also stated that the amount of soluble Si in Fig.9 NiAl is less than 0.4 wt%, therefore the most of Si present within the outer NiAl must be concentrated in the carbide particles within this sub-layer. Thus, one may say that the small amount of soluble Si in the NiAl did not form any intermetallic phase during heat treatment of the samples, as no such phases were observed in this and other researches.

4-3. Formation Mechanism of Sub-Layers

Diffusion of Ni in Ni_2Al_3 original coating layer during heat treatment is negligible according to Janssen and Reich [14]. On the other hand, the possibility of Al diffusion which became available from the decomposition of the original Ni_2Al_3 , towards the γ -matrix has been reported by various researchers [5, 6, and 14]. Therefore, as heat treatment started (i.e. $t = 0$ sec) the inward diffusion of Al, caused the formation of Ni-rich NiAl sub-layer in the original interface of Ni_2Al_3 and the matrix (area between line AA and line CC in figure 11(b)). In addition, the decomposition of Ni_2Al_3 and its transformation to Al rich NiAl above the original interface (i.e. line AA) caused the formation of other interface above the line AA (line BB), as it is shown schematically in figure 11(b).

Lines AA, BB and CC shown in this figure are the new interfaces formed, indicating respectively; the interface of NiAl rich in Ni formed under the original interface and the NiAl rich in Al due to decomposition of Ni_2Al_3 ; the front line of transformation of Ni_2Al_3 to NiAl rich in Al and finally, the line CC which is the interface of the NiAl rich in Ni and the matrix.

The interface BB moved upward during heat treatment of the coated samples and caused the growth of Al rich NiAl outwardly. This line will finally reach the surface of the coating, when the whole of the original Ni_2Al_3 decomposes into Al-rich NiAl. However, at the interface CC, since the rate of upward diffusion of Ni in Ni-rich NiAl (area between the interfaces AA and CC) is more than that of inward diffusion of Al [15], therefore the controlling factor of the interface CC is the downward diffusion of Al. On the other hand the line CC can only move downward, towards the matrix and formed the interdiffusion sub-layer (figure 11(c)). EDS analysis of this sub-layer indicated that the matrix of this area contained approximately 18 wt% Al which is lower than the amount of Al in the outer NiAl sub-layer. This is a good indication of inward movement of the line CC, which causes thickening of the interdiffusion sub-layer.

Siegel and Shankar[15] by measuring the diffusion coefficient of Al and Ni in NiAl showed that the diffusion coefficient of Ni in Ni-rich NiAl is 3.5 times more than that of Al in this phase, while the diffusion coefficient of Al in Al-rich NiAl is about 10 times more than that of Ni in Al-rich NiAl. Therefore the controlling factor of the interface AA (interface between Ni-rich NiAl and Al-rich NiAl zones) is the outward diffusion of Ni. In other words, the line AA

can only move outward, towards the surface of the coated samples.

The outward movement of the line AA affected the growth of the middle Ni-rich NiAl, lowered the Al content of the outer NiAl. Thus, at the same time that the decomposition of Ni_2Al_3 to Al-rich NiAl occurs, the outer NiAl loses a great deal of Al atoms and thus becomes rich in Ni. However, its Al content is higher than that of the middle NiAl sub-layer.

The growth of columnar zone within the interdiffusion sub-layer seems to be occurring in both outward and inward direction (figure 11(c) and (d)).

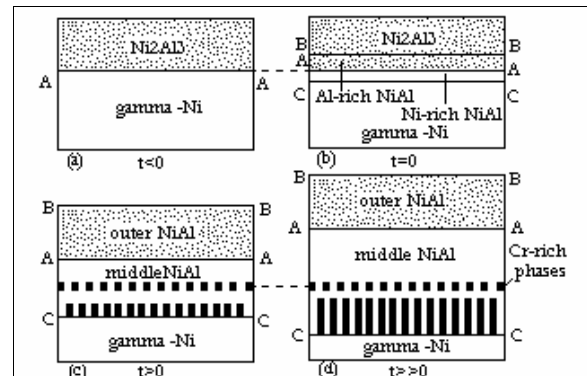


Fig. 11 (a-d). Show formation mechanism of the coating sub-layers with respect to heat treatment time schematically

Reduction of the thickness of area A within this sub-layer is an indication of the outward growth of this zone. However, since the amount of thickness reduction of area A is very small, it can not be the only factor accountable for the large growth of columnar zone observed in figure 9. Therefore, one may conclude that the interface CC moved inward, so that it is mostly responsible for the large growth of columnar zone and consequently the thickness of the interdiffusion sub-layer.

5. Conclusions

1. Formation mechanism of Si modified aluminide coating applied by pack cementation technique seemed to be similar to that of simple aluminide.
2. Most of Si in the outer Ni-rich NiAl was concentrated in the carbides within the outer sub-layer and the Si content of NiAl was always less than 1wt % of the total composition of this phase.
3. The formation of the outer Ni-rich NiAl was due to firstly decomposition of the original Ni_2Al_3 to Al-rich NiAl and secondly due to transformation of Al-rich to Ni-rich NiAl during the heat treatment of coated samples
4. The growth direction of the outer and middle NiAl sub-layer is outward toward the surface of the original coating towards the matrix.
5. The thickness of the outer NiAl was independent of the time and temperature of heat treatment cycle.
6. The growth direction of the interdiffusion sub-layer was inward, while the columnar zone within this

sub-layer moved in both directions but with different rates.

References

- [1] Swadzba, L., Formanek, B., Maciejny, A., "Modified Heat Resistant Protective Coatings for Nickel Base Super Alloys", Int.J.Mater. Prod. Tech., Vol.8, 1993, pp. 155-169.
- [2] Goward, G.W., Canon, L.W., "Pack Cementation Coatings for Super Alloys, a Review of History; Theory and Practice", Gas Turbine Conference and Exhibition, Anaheim, California, May31-Jun4, 1987.
- [3] Hancock, P., Malik, M., "Coating Systems and Technologies for Gas Turbine Applications", Materials for Advance Power Engineering, Part 1, 1994, pp. 685-690.
- [4] Xiang, Z.D., Datta, P.K., "Co-deposition of Al and Si on Nickel Base Super Alloys by Pack Cementation Process", Mat. Sci. Eng., 2003, A356, pp. 136-144.
- [5] Kirche, T.A., McMordie, B.G., McCarter, A., "Performance of a Silicon-Modified Aluminide Coating in High Temperature Hot Corrosion Test Conditions", Surface and Coating Technology 68/69, 1994, pp. 32-37.
- [6] Das, D.K., Singh, V., Joshi, S.V., "Evaluation of Aluminide Coating Microstructure on Nickel-Base Cast Super Alloy CM-247 in a Single-Step High Activity Aluminizing Process", Metallurgical and Metals Tran. A, 1998, pp. 2173-2188.
- [7] Seigle, L.L., Gupta, B.K., "NASA Contract Report 2939 Prepared for Lewis Research Center Contract NGR-33-015-160", NASA Scientific and Technical Information Office, 1978.
- [8] Shahriari, F., Ashrafizadeh, F., "Formation and Micro Structural Characterization of Silicon Modified aluminide Coating on a Nickel Based Super Alloy", Transaction of Mat. and Heat Treatment, Vol.25, No. 5, 2004, pp. 657- 660.
- [9] Nicoll, A.R., "A Survey of Methods Used for the Performance Evaluation of High Temperature Applications, 1983, pp. 269-339.
- [10] Duret, C., Pichoir, R., et al., "Recent Approaches to the Development of Corrosion Resistant Coatings", High Temperature Alloys for Gas Turbines, 1982.
- [11] Streiff, R., Boone, D.H., "The Modified Aluminide Coatings Formation Mechanisms of Cr and Pt Modified Coatings", Reactivity of Solids, Elsevier, Amsterdam, 1985, pp. 195-200.
- [12] Fitzer, E., Maurer, H.J., "Diffusion and Precipitation Phenomena in Aluminide and Cr-Aluminide Coatings on Iron and Nickel Base Alloys", Materials and Coatings to Resist High Temperature Corrosion, Applied Science Publishers, 1980, pp. 265-276.
- [13] Zheng, Y., Cai, Y., Heng Mo, L., Yang, Z., "Formation of Super Alloys", J. Mater. Eng., 1991, pp. 39-46.
- [14] Janssen, M.M.P., Rieck, G.D., "Reaction Diffusion and Kirkendal Effect in the Nickel-Aluminum System", Trans. Metall. Soc. of AIME, 1967, Vol.239, pp. 1372-1385.
- [15] Shankar, S., Seigle, L.L., "Inter Diffusion and Intrinsic Diffusion in the NiAl Phase of the Al-Ni System", Metall.Trans. A, Vol. 9A, 1978, p.1467.