Effects of temperature and Al-concentration on formation mechanism of an aluminide coating applied on superalloy IN738LC through a single step low activity gas diffusion process

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ABSTRACT

Effects of temperature and Al-concentration on formation mechanism of aluminide coating applied on a nickel base superalloy IN738LC via low activity gas phase aluminizing process was studied in this research. In addition, coating microstructures were investigated using optical and scanning electron microscopes; EDS and X-ray diffraction (XRD) techniques. The results showed by increasing the temperature from 850 °C to 1050 °C, formation mechanism of the coating changed. At 850 °C coating formed by inward diffusion of Al, and at 1050 °C it was initially formed by inward diffusion of Al, followed by outward diffusion of Ni. The coating layer in the sample coated at 1050 °C using low activity powder consisted of 4 wt% Al and 2 wt% activator, grown outward, while the coating obtained under other conditions grown inward. By increasing the amount of the Al from 2 wt% to 4 wt% and the activator from 1 wt% to 2 wt% in low activity powder mixture, the concentration of diffused Al in the top NiAl layer decreased sufficiently; so that the top layers gradually became rich in Ni from its interface with interdiffusion zone (IDZ). This process finally can lead to annihilation of NiAl phase rich in Al and form a layer of NiAl rich in Ni on the surface layer of the sample.

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1. Introduction

It is nearly impossible for a bulk monolithic material to possess all surfaces and bulk properties at the same time; therefore much attention has been paid to achieve desirable bulk and surface properties via coating this type of materials [1]. Aluminizing is one of the best methods available for improving oxidation and corrosion resistance of nickel base alloys. This is an application requirement for high temperature components such as turbine blades [2]. At high temperatures, Al in the surface of a coated substrate can be oxidized preferentially and forms a thin and dense alumina layer. This layer acts as a diffusion barrier and substantially reduces the oxidation rate of the substrate [2–4].

Nickel aluminide phases have been recognized as potential high temperature coating materials because of their attractive properties such as high melting point, low density, good high temperature mechanical properties, and excellent corrosion and oxidation resistance [1]. One of the most favorite phases known for stability and oxidation resistance, is the β-NiAl phase in Ni-base superalloys. Other phases such as Ni$_3$Al due to its undesirable oxidation resis-

tance, and Ni$_2$Al$_3$ for its brittle behavior, are not usually useful in these situations [5,6].

Since 1970 pack cementation method was used for coating most of the blades and vanes [7]. However, pack cementation is not a good technique for coating the long and narrow internal air channels of vanes and blades since powder is in touch with the substrate in this method; thus it may not only sinter to the surface of the substrate but also the pack powders may enter in the top coating layer and act as inclusions [8,9]. Formation of an inhomogeneous multilayer structure and coarse grains during pack cementation, are the other disadvantages of this process [9]. To overcome these problems, gas phase diffusion method can be used for coating. In this way powder mixture is physically separated from the specimens [10]. However, other conditions are very similar to pack cementation process [7].

At any specific coating temperature, the activator reacts with aluminum in the powder mixture and produces a series of aluminum halides such as AlCl, AlCl$_2$ and AlCl$_3$. These halides transfer by a carrier gas to the surface of the substrate, where they can form a coating layer via reduction reaction [3]. It has been reported [11,12] that the halide of AlCl$_3$ cannot be decomposed at the surface and therefore it cannot release its aluminum ions; so the aluminide coating which forms on the surface is produced from the subhalides of aluminum.

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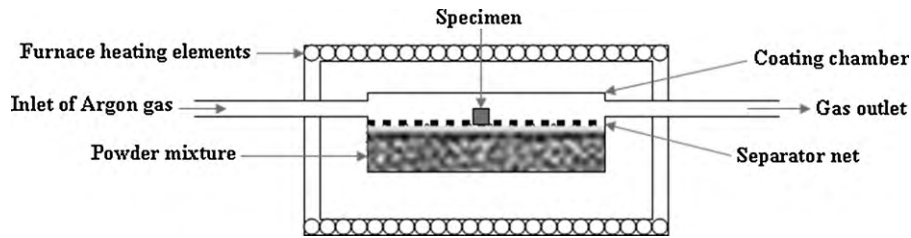 *E-mail address:* H_rafiee@metaleng.iust.ac.ir (H. Rafiee).

Fig. 1. Schematic showing the coating equipment used for the gas phase aluminizing process.

Table 1
Mean chemical compositions of the substrate alloy IN738LC (wt%).

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

Diffusion coating formation mechanism is related to aluminum activity. There are two kinds of diffusion aluminizing, high activity and low activity aluminizing. Aluminum activity is related to the Al-concentration in the Al-source powder used in the powder mixture. When the amount of Al in the Al-source used in the powder mixture is greater than 60 at% the corresponding pack is usually called a high activity pack. Otherwise, the pack is referred to as a low activity one [13,14].

Eslami et al. [15] reported that in gas phase aluminizing, the activity of Al in the gas phase has a direct relationship with its partial pressure. Due to reduction of Al activity in the gas phase, microstructures of the coatings obtained by HTHA gas phase aluminizing were similar to those of the coatings formed by the HTLA pack cementation method.

Formation mechanism of aluminide coatings formed by the low activity pack cementation aluminizing has been widely discussed [13]; however there are a few reports about formation mechanism of coatings when low activity gas phase aluminizing method is used [2,8,15]. In this research formation mechanism of nickel aluminide coatings formed via a single step low activity gas phase aluminizing at two different temperatures has been studied. In addition, the effects of pack compositions and temperature on coating microstructures have been discussed.

2. Material and methods

The coating apparatus used for gas phase aluminizing process is shown schematically in Fig. 1. The powder mixture was placed at the bottom of the coating chamber and the specimens at its top; separated by a separator net. Then the chamber was placed inside an electrical tube furnace and connected to an argon gas supplier.

Small specimens with dimensions 10 mm × 10 mm × 3 mm were prepared from an as-received IN738LC turbine blade having mean compositions shown in Table 1. These samples were ground with silicon carbide emery papers from grade 80 to 1200; ultrasonically cleaned in acetone bath, then dried in air prior to the coating process.

Two different packs, each having specific chemical compositions were used in order to evaluate the effects of the compositions on coating microstructure. These packs were labeled as, "H" for high aluminum content and "L" for low aluminum content. Weight of each pack was 200 g of the powder mixtures shown in Table 2.

In fact the calculated weight percent of pure Al in these packs was 2 wt% for low concentration and 4 wt% for high concentration of the total weight of powder. Each specimen was labeled with a symbol L or H followed by a number indicating the coating temperature.

Table 2
Chemical composition of powder mixtures used in the single step low activity gas phase aluminizing process.

Pack	Composition (wt%)			Equivalent wt% of pure Al
	NiAl	NH₄Cl	Al₂O₃	
L	6.4	1	Bal.	2
H	12.8	2	Bal.	4

After the specimens were placed in the chamber, low activity gas phase aluminizing at 850 °C and 1050 °C for a period of 4 h was carried out. The samples were then cooled in the furnace to room temperature. It is worth mentioning that argon gas was circulated in the chamber, from the start up to 300 °C to keep an inert atmosphere for the coating process. Also after applying coating process for 4 h, argon gas was again circulated in the chamber to reduce the vapor components within the chamber. Then the coated samples were removed from the furnace, and their cross-sections were examined using optical microscopy (OM), scanning electron microscopy coupled with an energy dispersive spectrometry (SEM/EDS) and X-ray diffraction (XRD) techniques. Etchant consisting of 61% lactic acid, 36.5% nitric acid and 2.5% hydrofluoric acid (all in volume percent), was used to reveal the microstructure details.

3. Results and discussion

3.1. Low temperature low activity (LTLA) gas phase aluminizing

Typical cross-sections of the coatings formed by packs L and H via the single step gas phase aluminizing process are shown in Figs. 2 and 3 respectively. These cross-sections indicate that the coatings are uniform and consist of two main layers (inner and outer layers). XRD results shown in Fig. 4 indicate that the coatings of these specimens consist of a Ni rich β-NiAl as a dominant phase. A small amount of γ′-Ni₃Al phase in the outer layer of the coating can also be seen in the XRD result when the coating process via LTLA at 850 °C using H pack was carried out.
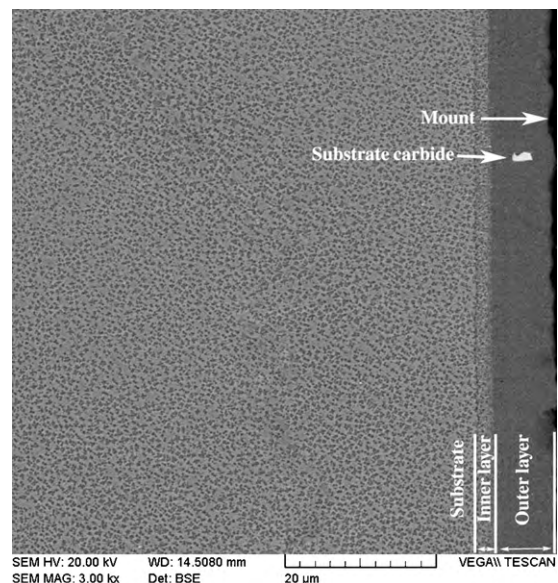

Fig. 2. SEM micrograph of the coating formed by pack L at 850 °C, showing the substrate carbides within the outer coating layer.
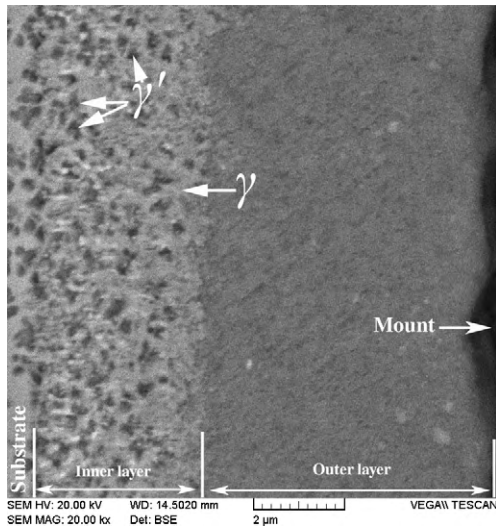
Fig. 3. SEM micrograph of the coating formed by pack H at 850 °C, showing two layers of coating formed at the surface of the sample.

Fig. 4. XRD patterns of the coatings for various conditions.

The substrate carbide within the outer layer of the coating shown in Fig. 2, indicates that the mechanism of coating formation was an inwardly diffusion of Al. This means the coating layer formed under the substrate's initial surface and so the substrate carbide is remained into the coating layer. If the coating layer grew outwardly, so any substrate carbide could not be found in this layer. This kind of observation has also been reported in Ref. [13]. In addition the result of coating process via LTLA in this research conforms the results of the research reported by Xiang et al. [3] who stated
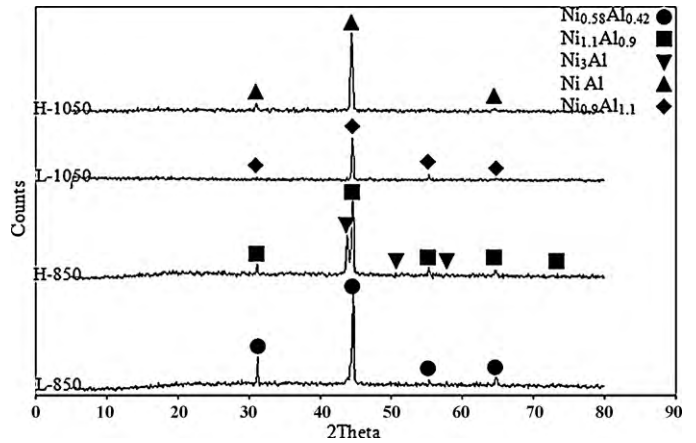
that Ni cannot diffuse at a temperature lower than 950 °C in nickel base superalloys.

As shown in Figs. 2 and 3 the microstructure of the inner layer of the coatings are similar to the substrate's microstructure. This layer formed due to partial reaction of the substrate with incoming aluminum. When the rate of Al received by the substrate is low, one may not expect a full phase transformation due to low concentration of Al occurs within the substrate. However by increasing the amount of the incoming Al, a full phase transformation can occur, so that this layer can be considered as a part of the coating layer.

Typical X-ray maps taken from the profile of the coating of H-850 sample, showing distributions of Al, Ti, W, Ni and Cr presented in Fig. 5. This figure shows concentration of Al on the surface
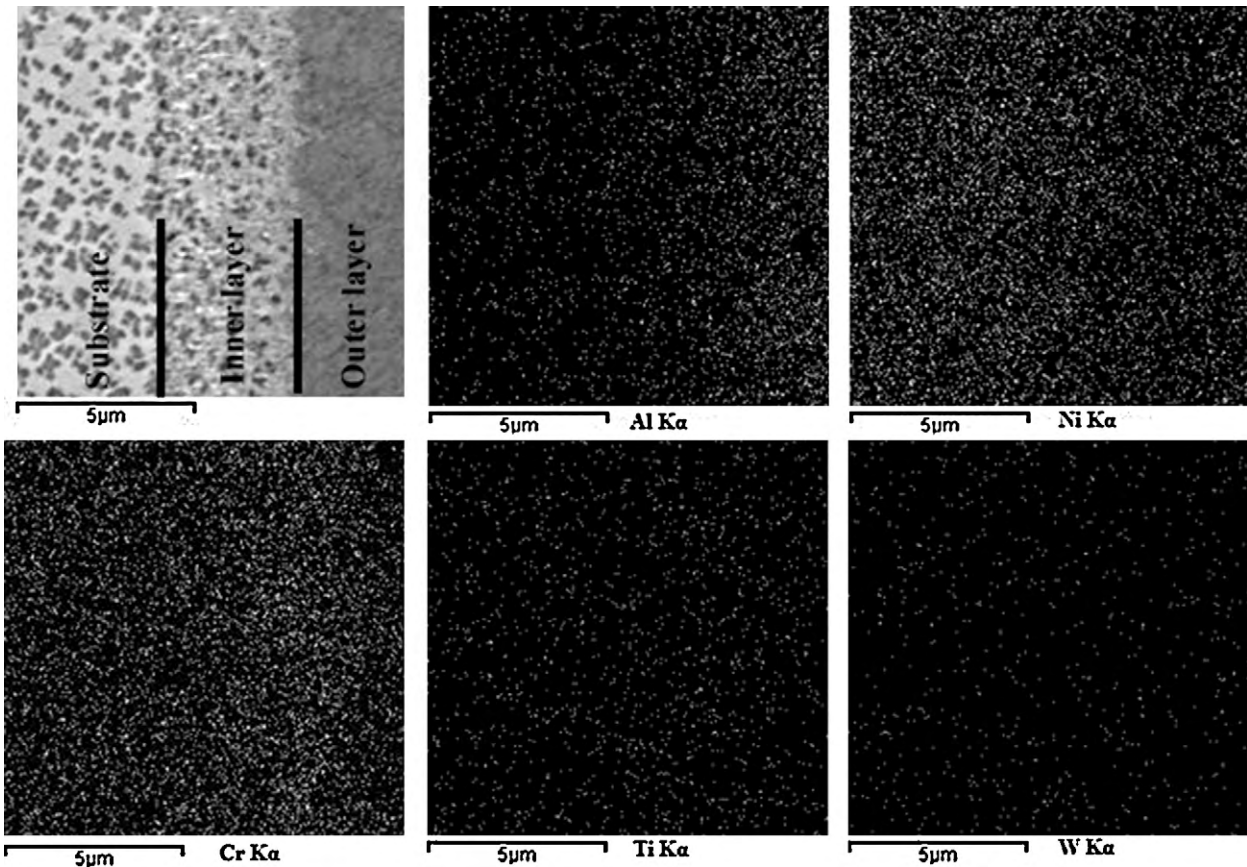

Fig. 5. X-ray map of H-850 sample, showing the distribution of various elements on the coating profile.
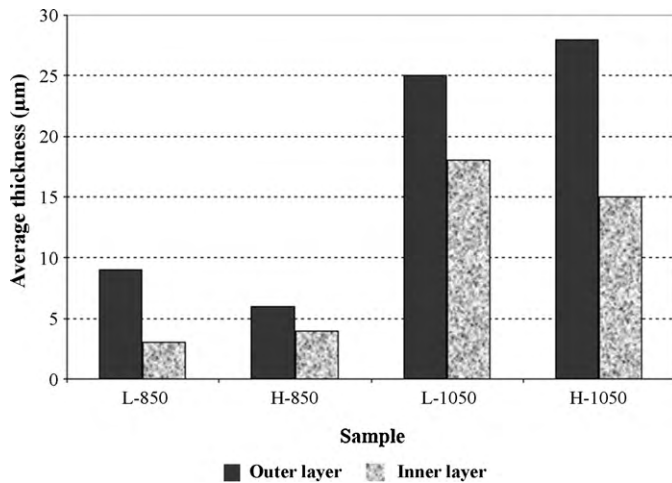
Fig. 6. Comparison of the coating thicknesses for the samples coated under different conditions.

increased; while the concentrations of other elements remained almost constant through out the top coating layer. This is an indication that the formation mechanism of the coating was inward diffusion of Al. Because of additional aluminum from the chamber atmosphere, the Al-concentration in the surface increases, whereas the concentration of other elements is equal to that of the substrate. Thus it is conformed that the formation mechanism of coating in this sample is similar to the L-850 sample, as described before.

The results of measurements of the average thicknesses of the outer and the inner layers of the coatings are shown in Fig. 6. The outer layer thickness of L-850 is larger than that of H-850. It is also richer in Al than the coating formed by H pack, as shown in Fig. 4. It seems by increasing the amounts of Al and activator, feeding of Al ions at the surface decreased. So it seems the effect of increasing the amount of activator in the pack is more than that of increasing the amount of Al.

When the effect of activator in the powder mixture exceeded the effect of Al within the pack, the partial pressure of $AlCl_3$ halide increased more than those of $AlCl_2$ and $AlCl$ halides. Consequently under this condition as mentioned earlier, the rate of release of Al ions on the surface of the substrate is very low, so that the coating cannot be formed to a desired level. Since the rate of coating for-

mation is related to rate of Al-feeding to substrate, decreasing the rate of coating growth is result of decreasing the rate of Al-feeding.

It is worth mentioning that $AlCl_2$ and $AlCl$ halides are relatively more effective than $AlCl_3$ on pack cementation coating process due to their higher partial pressure and higher Al content than $AlCl_3$ [11,12]. Also, release of Al ions from $AlCl_3$ halides on the surface of nickel substrate is very difficult [2,11]. Therefore the presence of $AlCl_2$ and $AlCl$ halides in the pack cementation is said to be more desirable than $AlCl_3$ for obtaining better coating [11,12].

The thicknesses of coatings on both specimens H-850 and L-850 were nearly the same, but the Al-concentration in their layers was different. This was due to release of different amounts of Al at the surfaces of these specimens.

3.2. High temperature low activity (HTLA) gas phase aluminizing

Fig. 7 shows a typical image of the samples coated at 1050 °C for 4 h via HTLA gas phase technique. These coating cross-sections indicate that the coatings are uniform and consist of two main layers; an inner layer knows as interdiffusion zone (IDZ) and an outer layer. In both specimens, the outer layer consists of two sublayers or zones (shown as I and II in Fig. 7). XRD obtained from L-1050 and H-1050 samples are presented in Fig. 4. The outer zone (zone I) of the top layer of sample L-1050 is an Al rich NiAl phase, while zone I in sample H-1050 is NiAl.

IDZ in both specimens shows that outward diffusion of Ni started from this zone, so that the concentration of some substrate elements like Cr, W and Mo at this zone increased and caused a higher contrast at some points to appear within this zone. Worth mentioning the areas rich in heavier elements appear in white color in back scatter images, see Figs. 7(a) and 8(a).

The substrate carbides all over the outer layer of L-1050 coating, shown in Fig. 8, as described for samples coated at 850 °C, indicate that the coating of this specimen grew inward into the substrate. This observation has also been reported by Das et al. [13], who worked on a similar process on another Ni-base superalloy.

The dark particles at the interface of zones I and II of H-1050 samples shown in Fig. 9 are alumina. These particles were on the original surface of the sample prior to aluminizing. The particles became later embedded in the coating, due to the outward growth of the coating during the final stage of the coating process. If this part of coating grew into the substrate, foreign particles would not be seen in the coating layer. These particles can act as markers indi-
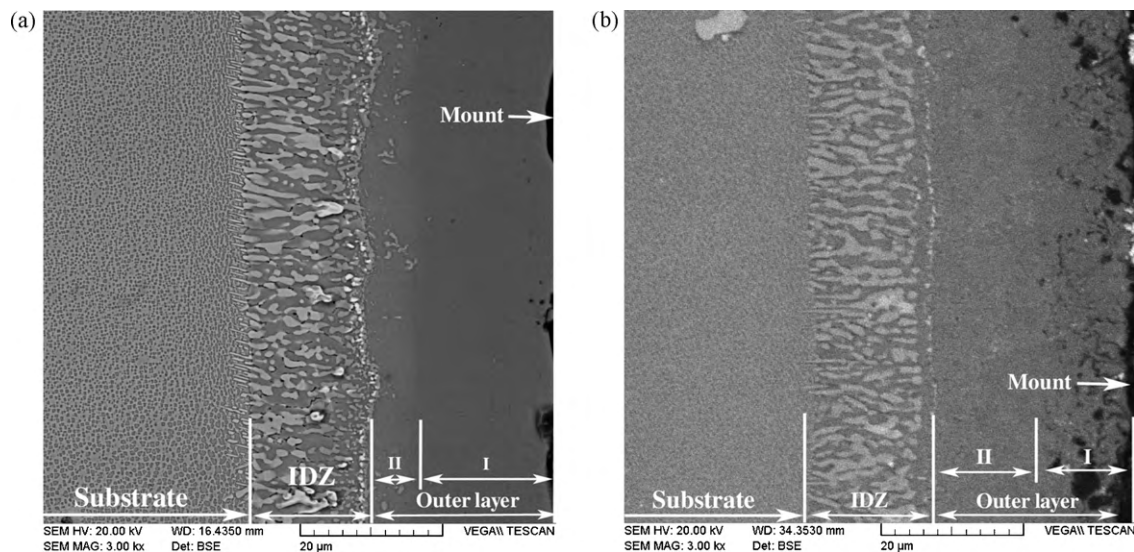

Fig. 7. SEM micrographs of the coatings formed by: (a) pack L and (b) pack H at 1050 °C, showing the coatings formed by both packs have two major layers.
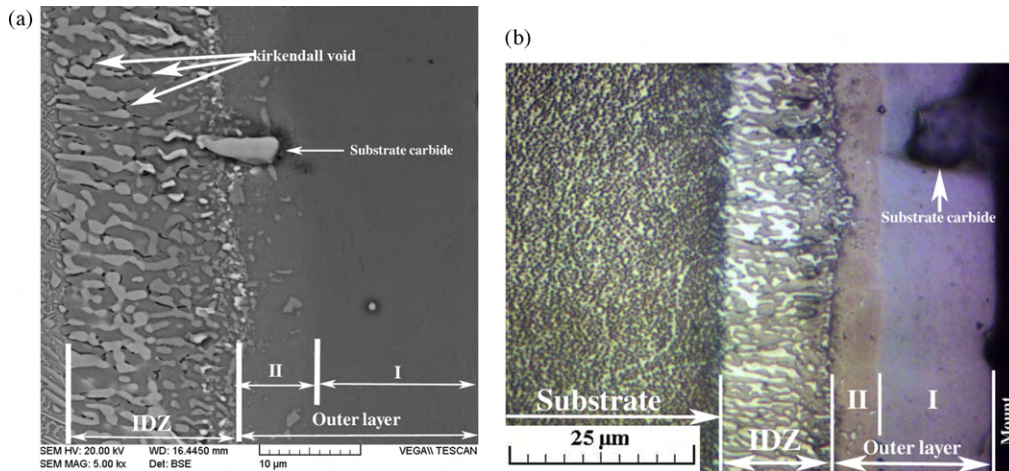
Fig. 8. (a) SEM micrograph and (b) optical image of the coating of L-1050 sample. These micrographs show the microstructure details of the coating.

cating the original surface of the sample when an outward growth of coating occurs [13,16]. The presence of some substrate carbides in zone II of the outer layer indicates that this zone formed by inward diffusion of Al.

A few numbers of porosities can be seen in the zone I of the coating outer layer as shown in Figs. 7(b) and 9, and this zone is not a dense layer as inner zone that is part of the substrate transformed to the coating phase. These might be an indication that zone I grew outwardly.

Kirkendall voids were formed within the IDZ of L-1050 samples and within the IDZ and at the boundary of the inner zone (zone II) and IDZ of H-1050 sample as shown in Figs. 8(a) and 9. This happened probably because the outward diffusion flux of Ni, Co, Mo and other substrate elements could not be fully compensated by the inward flux of Al, according to Xiang and Datta [17].

NiAl phase (type c CsCl structure) with a large non-stoichiometric domain contains between 45 at% and 60 at% Ni. Aluminum atoms are located at the cube edges and nickel atoms at its center in an equiatomic composition. However, for a nickel-rich NiAl phase there is a partial substitution of aluminum atoms by nickel and in aluminum-rich NiAl phase, vacancies are present at

Ni sites [18]. Therefore one expect that by increasing Ni concentration in NiAl phase, the atomic sites occupied with Ni atoms increase and cause a decrease in solubility of refractory elements in those parts of material which received more Ni atoms. This may result to precipitation of refractory elements as independent phases. The EDS analysis of the two zones of the outer layer of L-1050 sample shown in Fig. 10 conform that the outer zone (zone I) is rich in Al while zone II is rich in Ni. In addition, the presence of many precipitates of the refractory elements in the inner zone (zone II) of the coating outer layer conforms the above argument that precipitation of refractories basically occurred in this zone which unlike zone I is rich in Ni, see Figs. 7(a) and 8.

Figs. 11 and 12 illustrate the formation mechanisms of coating for L-1050 and H-1050 samples schematically. Fig. 11 shows the coating was initially formed by inward diffusion of Al that was available on the surface of the sample. This outer layer is a NiAl phase rich in Al, Fig. 11(b). The coating process in this sample fol-
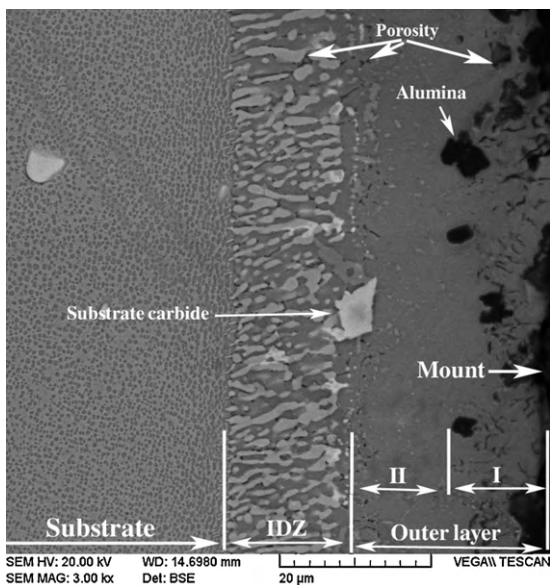

Fig. 9. SEM micrograph of the coating formed by pack H at 1050 °C, shows aluminum oxide in zone I of the outer layer.
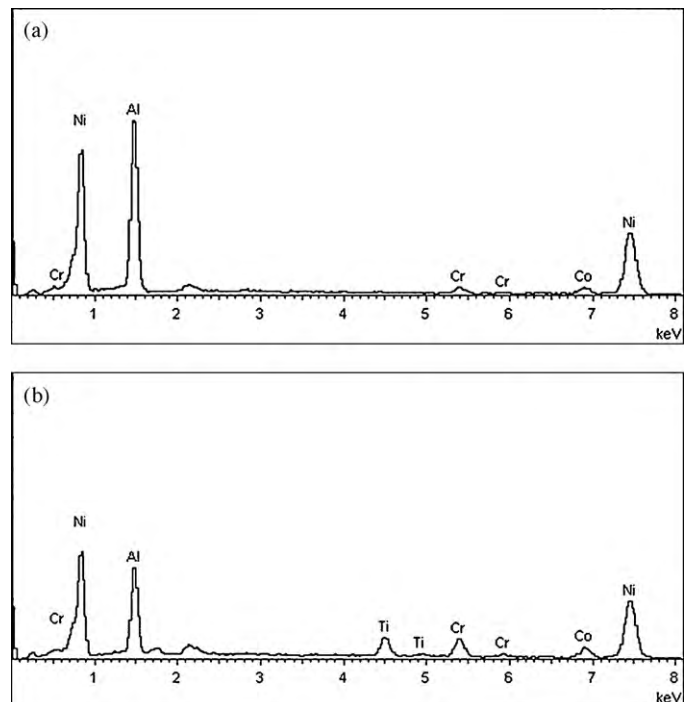

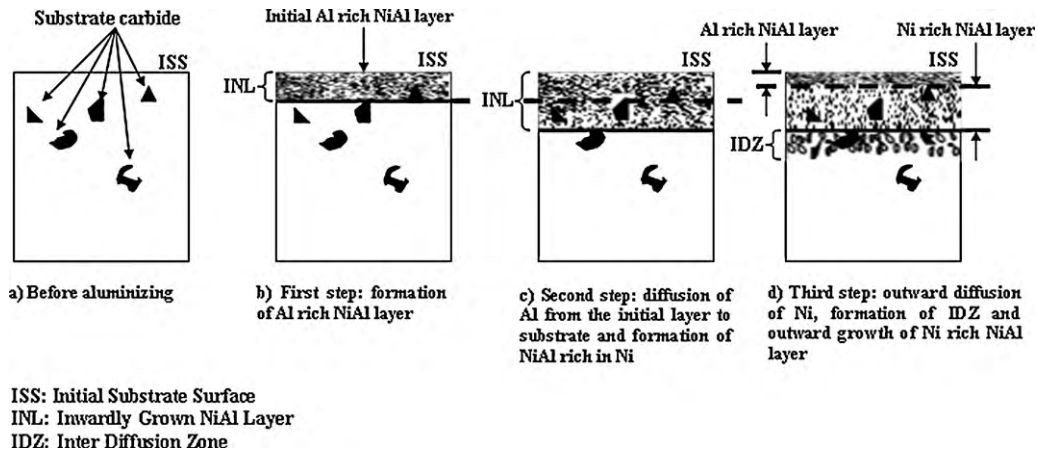**Fig. 10.** EDS analysis of outer coating layer in L-1050 sample (a) zone I and (b) zone II.

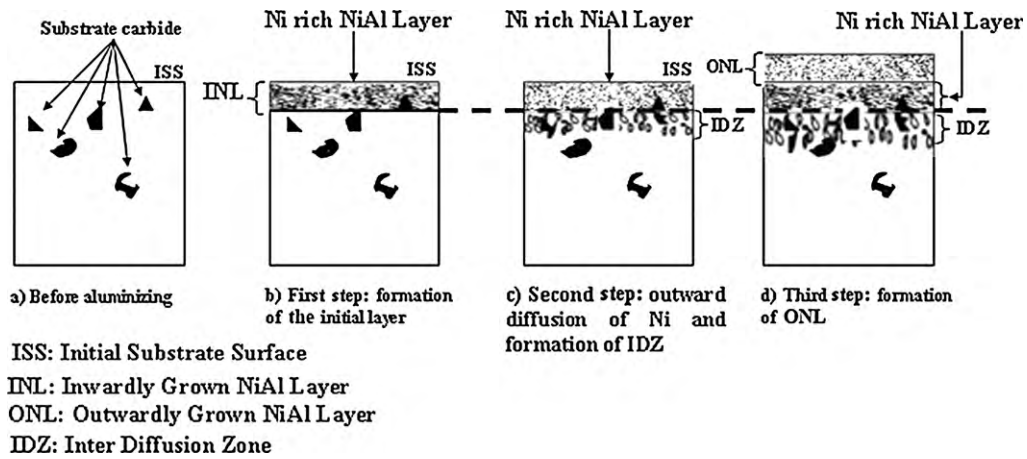**Fig. 11.** Schematic showing the formation mechanism of coating at L-1050 sample.

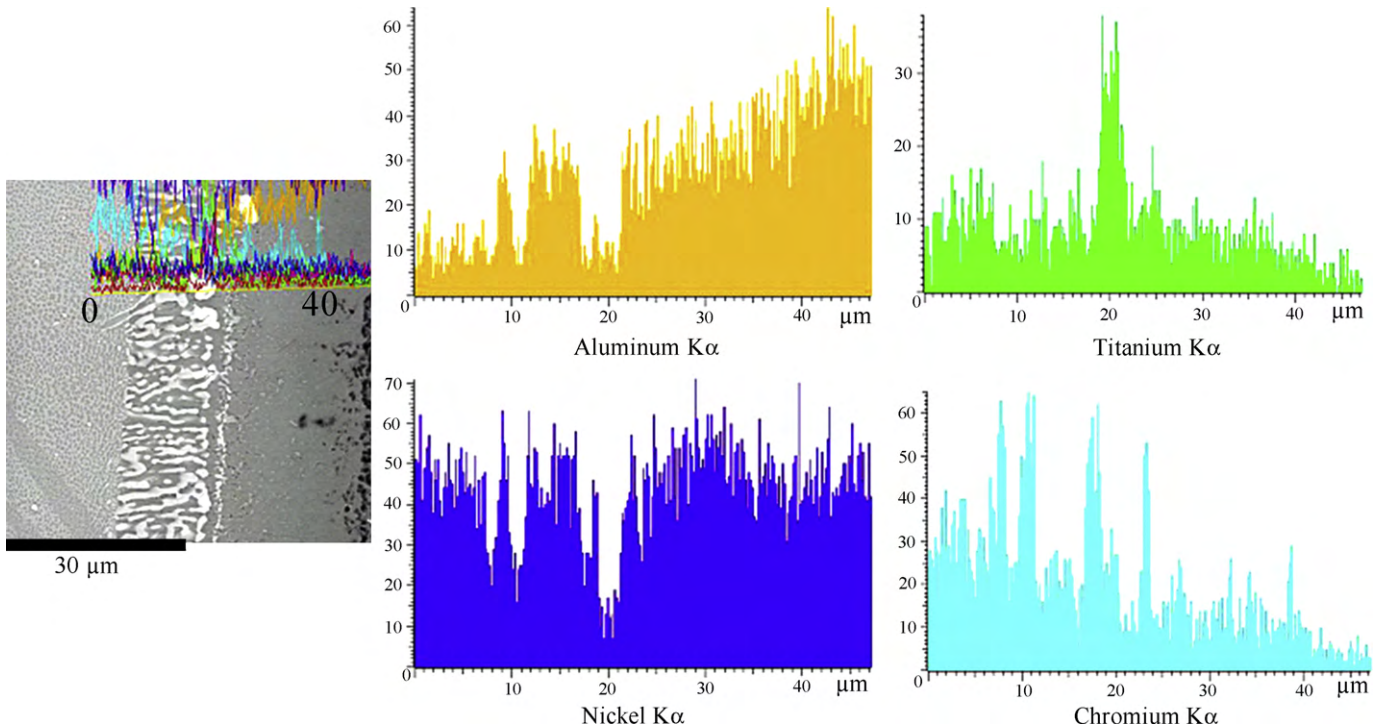**Fig. 12.** Schematic showing the mechanism of coating formation at H-1050 sample.

Fig. 13. Elemental line scan analysis of coating at H-1050 sample, showing the variation in concentrations of Al, Ti, Ni and Cr along the coating profile, shown in the left side of the picture.

lowed by further inward diffusion of Al from the Al rich layer deep into the substrate, and hereby a Ni rich NiAl sublayer was formed under the initial layer, Fig. 11(c). Afterwards Ni could diffuse outwardly; because diffusion of Ni in Ni rich NiAl is faster than that of Ni in Al rich NiAl [7,19]. Finally as the rate of incoming Al from the surface reduced and the diffusion of Ni from the substrate continued, zone II of the outer layer became gradually rich in Ni from its interface side with zone I, Fig. 11(d). In other words, zone II grows outward and zone I of the outer layer should be disappeared gradually. However, due to insufficient time of coating used in this research, although zone I became thinner but it did not completely vanished.

By increasing the Al and activator contents as mentioned earlier, feeding of Al atoms at the surface will be decreased. So the initial NiAl coating layer formed by inward diffusion of Al at the surface of H-1050 sample became rich in Ni. Therefore the outward diffusion of Ni in this sample presumably occurred sooner than that happened in L-1050 specimen. By continuation of the outward diffusion of Ni from the substrate, the initial layer of coating grew outward due to reaction of Ni and Al atoms at the surface of specimen. This has been illustrated schematically in Fig. 12.

Elemental line scan analysis of the coating of H-1050 sample presented in Fig. 13, shows that the concentration of Al, when measured from the substrate towards the surface of the coating, increased; while the concentration of other elements such as Cr and Ti slightly decreased from the interface of the coating outer layer and IDZ towards the surface of the coating. This observation confirms the above suggested formation mechanism of coating for H-1050 sample. Because the outer zone of coating formed after coating process by outwardly diffusion of substrate elements, so the concentration of these elements in this zone is less than the inner zone of coating which is a part of substrate transformed to coating. However, the concentration of Al at the outer zone is more than inner zone, because Al atoms come from surface and diffuse to the inner zone.

4. Conclusions

1- Coating formed at 850 °C was due to inward diffusion of Al. Outward diffusion of Ni did not occur at this temperature. The formation mechanism of coating at 1050 °C was initially due to inward diffusion of Al followed by an outward diffusion of Ni for low activity pack.

2- By increasing the amounts of Al and activator in low activity pack, the amount of incoming Al on the specimen surface decreased. This is a new finding. This occurred due to increasing activator content on the pack which seemed to have more effect on providing less Al subhalides on the surface than that of increasing Al in the pack.

3- Lots of kirkendall voids were created at the IDZ and the interface of outer layer and IDZ of H-1050 sample when using 4 wt% Al in LAHT process.

4- Decreasing the rate of release of Al by increasing Al and activator contents in powder mixture, the outer coating layer formed on the initial surface of the sample was due to outward diffusion of Ni. This has happened at H-1050 sample when using 4 wt% low activity Al.

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