Technical Note

EFFECTS OF TEMPERATURE AND AL-CONCENTRATION ON FORMATION MECHANISM OF AN ALUMINIDE COATING APPLIED ON SUPER ALLOY IN738LC THROUGH A SINGLE-STEP HIGH ACTIVITY GAS DIFFUSION PROCESS

H. Rafiee[*,1], S. Rastegari[1], H. Arabi[2] and M. Mojaddami[1]

* *h_rafiee@metaleng.iust.ac.ir*
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[1] **School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.**
[2] **Center of Excellence for Advanced Materials Processing (CEAMP), School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.**

Abstract: Formation mechanism of an aluminide coating on a nickel base superalloy IN738LC via a single step high activity gas diffusion process has been investigated in this research. Effects of coating temperature and aluminum concentration in powder mixture on formation mechanism were studied using optical and scanning electron microscopes, EDS and X-ray diffraction (XRD) techniques. For this purpose two different packs containing 1 and 2 wt% aluminum powder, were used for coating the samples at two temperatures, 850ºC and 1050ºC. The ratio of Al to activator was kept constant in both packs. By increasing the Al content in high activity powder mixture, the concentration of diffused Al increased in the coating layers, and the thickness of coating increased. At 1050ºC as the rate of diffused Al to the interdiffusion zone increased, this zone gradually transformed to outer coating phases. At 850ºC coating formed by inward diffusion of Al, but at 1050ºC it was initially formed by inward diffusion of Al followed by outward diffusion of Ni.

Keywords: Gas Phase Aluminizing, Formation Mechanism, high Activity, Effect of Temperature, Inward and outward diffusion

1. INTRODUCTION

First stage turbine blades are the most critical components of gas turbines that usually made from nickel-base superalloys. Some of the properties of these alloys can be improved by coating [1]. There are three general coating processes (i.e. diffusion, overlay and thermal barrier coatings) used for coating turbine blades and vanes [1-4]. Aluminizing is one of the most used coating methods for enhancing the life of high temperature components [5, 6]. The diffused aluminum atoms react with the matrix nickel to form very stable nickel-aluminide compounds as a coating layer [6, 7]. At high operating temperatures, Al atoms within the coating layer oxidizes preferentially to form a thin and dense alumina scale that acts as a diffusion barrier, hence substantially reduces oxidation and degradation rates of the components [7].

Gas phase diffusion is an alternative method of pack cementation which unlike pack cementation can be used very efficiently for coating the internal cooling channel surfaces of turbine blades and vanes. In this process, unlike the pack cementation process, powder mixture is physically separated from parts to be coated. Volatile aluminum halides generated in powder chamber are directed toward the specimens located either in another chamber or another part of the same chamber with a carrier gas for releasing aluminum at the surface of the specimens [8].

High aluminum activity coating processes are usually performed via two-steps operation. In the first-step which is performed at a temperature range of 500ºC to 850ºC, Al diffuses inward into the substrate to form a δ-Ni_2Al_3 phase and in the second-step which is done at a higher temperature (above 1000ºC), Ni diffuses outward to form a β-NiAl phases [9, 10]. There are also numerous reports of these types of coatings that have been developed in a single step operation by carrying out the process directly above 1000ºC [5, 8, 10, 11]. Nowadays single step coating is an attractive process, as it leads to the formation of final NiAl coating structure in a single treatment [10].

Table 1. Mean chemical composition of the substrate alloy IN738 LC (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.

The term activity mentioned earlier is related to the concentration of aluminum in the Al source powder used in the pack. If the amount of Al is greater than 60at% in the aluminum source, the process is usually called a high activity aluminizing [10]. This research investigates the microstructure and formation mechanism of aluminide coating applied on IN738LC via a single-step gas phase aluminizing using high activity aluminum source.

2. EXPERIMENTAL PROCEDURE

The IN738LC turbine blade having the mean composition shown in Table 1 was cut to a dimension of approximately $10 \times 10 \times 3$ mm and then ground using SiC abrasive paper up to a 1200-grade finish. The specimens were then cleaned in acetone bath and dried in air. Finally these specimens were subjected to gas phase aluminizing.
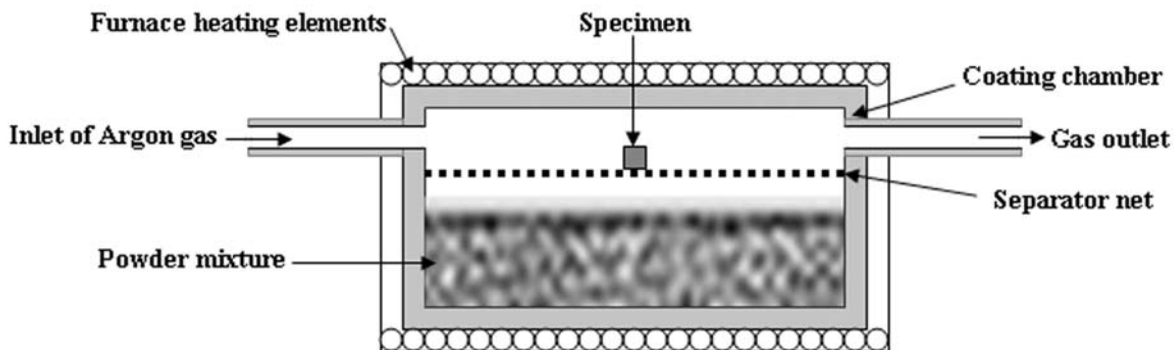
To evaluate the effect of the pack composition on coating microstructure, two different packs containing 200gr powder mixture with

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

| Pack	Composition (wt. %)		
	Al	NH_4Cl	Al_2O_3
L	2	1	Bal.
H	4	2	Bal.

composition shown in Table 2 were prepared. Each specimen was labeled with a symbol L or H followed by a number which indicate the coating temperature.

Gas phase aluminizing carried out at 850ºC and 1050ºC for a period of 4 hours using coating apparatus shown schematically in Fig. 1. As shown 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. The coated samples were kept within the chamber until the temperature drop to room temperature. It is worth mentioning that argon gas was circulated in the chambers, from the start up to 300ºC to keep an inert atmosphere for the coating process. Also after applying coating process for 4 hours, 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. Optical and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), were used to study the coating microstructure and chemical composition of the specimens. X-ray diffraction (XRD) was used to identify phases formed in the surface layer of the coatings. An etchant consisting of 61% lactic acid, 36.5% nitric acid, 2.5 % hydrofluoric acid (all in volume percent), was used to reveal the microstructural details.

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

(a)

(b)
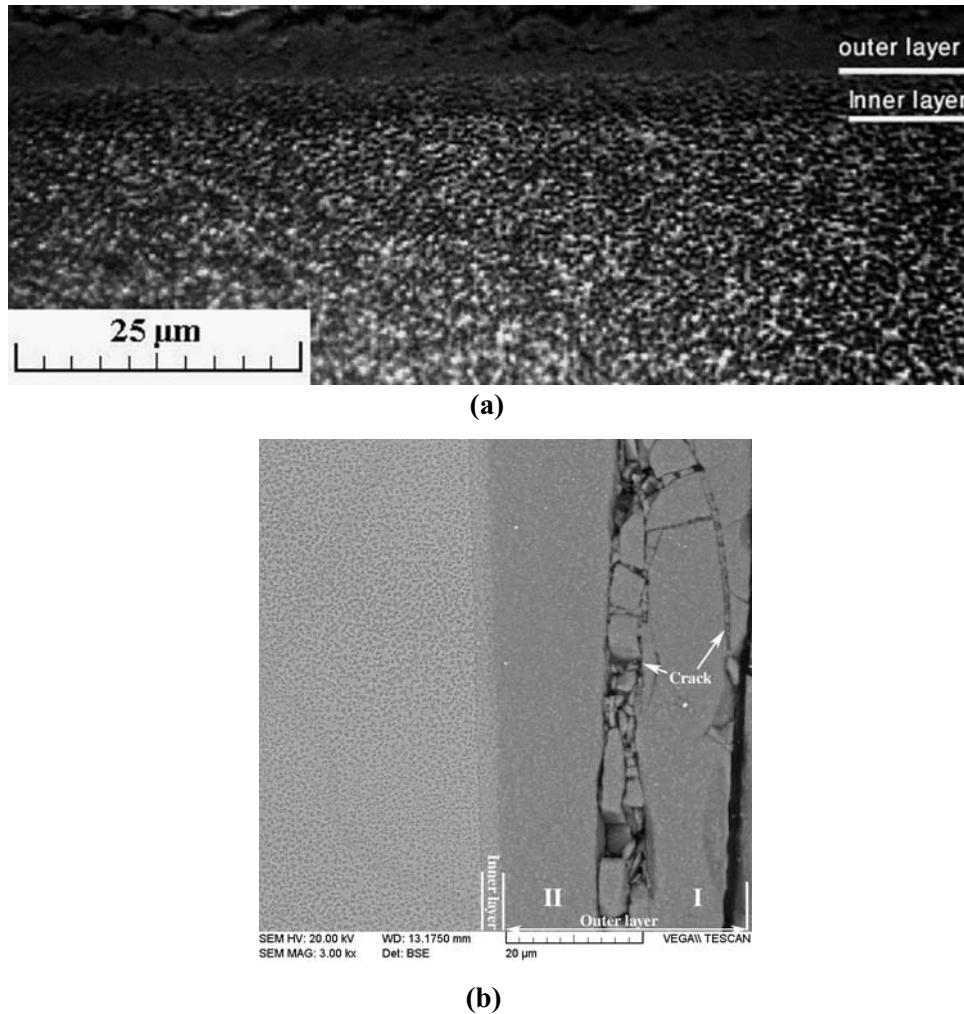
Fig.2. Cross sections of the coating formed by (a) pack L; (b) pack H, at 850ºC, showing the coatings formed by both packs have two major layers.

3. RESULTS AND DISCUSSION

3.1. Low Temperature High Activity (LTHA) Gas Phase Aluminizing

Typical coating cross sections of the samples coated at 850ºC using packs L and H are shown in Fig. 2. The micrographs show that two uniform coating layers were formed on the samples surfaces. The results of XRD pattern for H-850 sample (Fig. 3) indicate that the coating consists of a β-NiAl and δ-Ni$_2$Al$_3$ phases in the outer layer of the coating.

The outer layer of coating formed on the surface of H-850 sample consists of two zones (I and II). Existence of crack in zone I of the outer layer (Fig. 2 (b)) is an indication that this zone of coating is more brittle than the inner zone II. On the base of XRD results obtained from the coating of H-850 sample, zone I is rich in Al which is probably made of δ-Ni$_2$Al$_3$ brittle phase. It has also been reported [12] that δ-Ni$_2$Al$_3$ is a brittle phase, so it seems observation of crack on zone I of the outer layer of the coating can be justified on the base of this report, since by increasing the Al content from 2wt% to 4wt% and activator content from 1wt% to 2wt% in powder mixture, the products of reactions in powder chamber and subsequently the amount of aluminum sub-halides in the chamber will be increased. By increasing the partial pressure of aluminum sub-halides, since the amount of Al ions which can be released on the surface of the substrate has a high rate [7, 13], the concentration

Fig.3. XRD patterns of the coatings at various conditions

Fig.4. Secondary electron SEM image of the inner layer of coating formed by pack H at 850ºC

of Al in the coating layer of H-850 sample is higher than that of L-850 sample (Fig. 3).

The inner layer of the coating formed due to partial reaction of the substrate with incoming aluminum can be seen clearly in Fig. 4. When the rate of Al received by the substrate is low, one may expect to observe such a layer, as phase transformation can not happen completely due to low concentration of Al. Fig. 4 indicates the partial transformation of the substrate γ and γ' phases to Ni_3Al and β-NiAl occurred, subsequently, at the inner layer of H-850 sample.

By increasing the amount of incoming Al in this layer, full transformations can occur so that under such conditions this layer can be considered as a part of the coating.

It is reported [13] that Al diffusion in δ-Ni_2Al_3 phase is much faster (100 times faster) than in β-NiAl,

(a)

(b)

Fig. 5. Optical image of the coating formed by (a) pack L, (b) pack H, at 850ºC, showing the substrate carbides within the outer coating layers

Fig. 6. Schematic showing the mechanism of coating formation in a typical single step LTHA gas phase aluminizing process

Fig. 7. Optical image of the coating formed by pack L at 1050ºC,

so one expect that the outer layer thickness of H-850 sample be more than that of L-850 sample as it can be seen in Fig. 3. Substrate carbides within the coating of samples coated at 850ºC (Fig. 5), demonstrate that the coatings were formed predominantly by inward Al diffusion. Also, it has been reported [7] that Ni can not diffuse at temperatures lower than 950ºC in nickel base super alloys, therefore as stated above the formation mechanism of coating on sample coated at 850ºC using H and L packs must be via inward diffusion of Al. This mechanism has been illustrated schematically in Fig. 6.

**3.2. High Temperature High Activity (HTHA) Gas Phase Aluminizing**

Typical cross section of the coating formed by pack L at 1050ºC is shown in Fig. 7. This cross section indicates that the coating is uniform and consists of two main layers. However the outer layer made of two different zones (I and II). The EDS analyses of the two zones of the outer layer shown in Fig. 8 indicate that zone I is rich in Al while zone II is rich in Ni. It is reported by Benoist et al [14], NiAl phase with CsCl structure (Al atoms at cube edges and Ni atoms at the centers) has a large non-stoichiometric domain, contains between 45 and 60 at.% Ni. Therefore, in an aluminum rich NiAl phase, vacancies can be present at Ni sites. These sites can get occupied with Ni atoms when Ni concentration increases within the coating layer. Under such conditions the solubility of refractory elements can be decreased and thus they may precipitate as independent phases. As illustrated in Fig. 7 unlike the Al rich zone I the Ni rich zone II is containing so many precipitates of these refractory elements.

Existence of substrate carbides in the outer
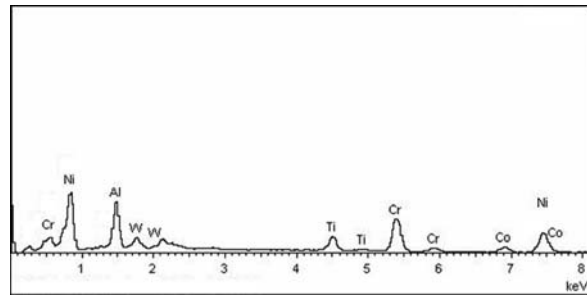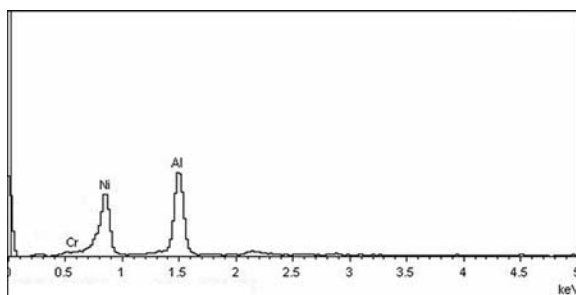
Fig. 8. EDS analysis of the outer coating layer in L-1050 sample: (a) zone I, (b) zone II, indicatethat zone I is rich in Al while zone II is rich in Ni.

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a) Before aluminizing

b) First step: formation of Al rich NiAl layer

c) Second step: diffusion of Al from the initial layer to substrate and formation of NiAl rich in Ni

d) Third step: outward diffusion of Ni, formation of IDZ and outward growth of Ni rich NiAl layer

ISS: Initial Substrate Surface
INL: Inwardly Grown NiAl Layer
IDZ: Inter Diffusion Zone

Fig. 9. Schematic showing the mechanism of coating formation in L-1050 sample

layer coating of L-1050 (Fig. 7) conforms that this coating grew inward into the substrate. Also Fig. 7 shows that there is an interdiffusion layer between the outer layer and substrate of L-1050 sample indicating outward diffusion of Ni occurred in this specimen. On the base of the above observations, a formation mechanism for coating of L-1050 sample has been suggested schematically in Fig. 9. This figure shows the coating was initially formed by inward diffusion of Al, which was available on the surface of the sample, then it followed by further inward diffusion of Al from this Al rich layer deep into the substrate and hereby a Ni rich NiAl sub-layer was formed under the initial layer. Afterwards suitable conditions for outward diffusion of Ni was provided, as diffusion of Ni atoms in Ni rich NiAl is faster than that of Ni in Al rich NiAl [1]. 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. In other words, zone II grew outward and zone I must be gradually disappeared. However, due to insufficient time of coating used in this research although zone I became thinner but it did not completely vanished.

Worth mentioning by increasing the coating temperature from 850ºC to 1050ºC beside the change in formation mechanism of coating, the diffusion rate of Al atoms increased. So the total coating thickness in L-1050 sample became greater than that of L-850 sample as it can be seen in Fig. 5.

Fig. 10 shows a typical SEM image of the cross section for H-1050 sample. This figure shows the coating consist of two main layers (inner and outer layers), and each layer is made of two zones.

As mentioned earlier, by increasing the amounts of Al and activator in the pack, the amount of Al ions at the surface of the sample will be increased. So the initial coating layer formed by inward diffusion of Al (Fig. 11 (b)). As
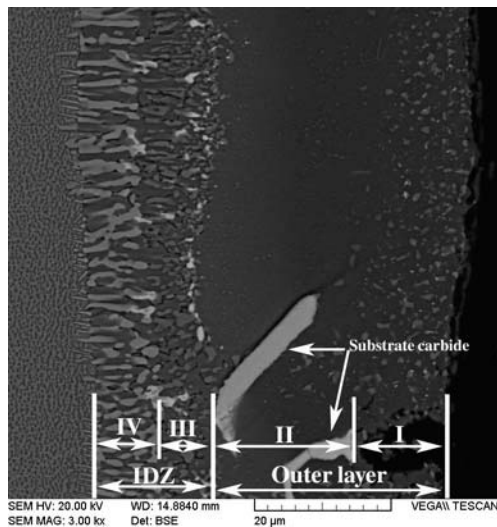

Fig .10. SEM micrograph of the coating formed by pack H at 1050ºC

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ISS: Initial Substrate Surface
INL: Inwardly Grown NiAl Layer
IDZ: Inter Diffusion Zone

Fig. 11. Schematic showing the mechanism of coating formation in H-1050 sample

explained about L-1050 sample, by further inward diffusion of Al from the initial Al rich layer deep into the substrate (Fig.11 (c)), condition for outward diffusion of Ni can be provided as shown in Fig.11 (d). However, as reported by Das et al [10], the outward diffusion of Ni causes the thickness of IDZ to increase which gradually reduces the outward diffusion of Ni. Thus after a while, the inward diffusion of Al overcomes the outward diffusion of Ni and zone II of the coating as shown in Fig. 11 (e), becomes rich in Al. Also, since zone III receives more Al atoms relative to zone IV, it seems that this zone started to transform to NiAl phase sooner than zone IV; this phenomenon is clearly shown in Fig. 10.

It has been reported [14, 15] that δ-Ni$_2$Al$_3$ with hcp structure has a compact structure, therefore the solubility of refractory elements in such a structure decreases and this may cause precipitation of these elements as independent phases, see Fig. 10. Observation of more refractory elements precipitates in zone I in comparison with zone II (NiAl phase with CsCl structure) of coating H-1050 sample conforms the above argument.

4. CONCLUSIONS

1. Direction of coating growth in using a high activity Al source was inward. In other word, the coating formed and grew under the initial surface of the specimen.
2. Coating in LTHA gas phase aluminizing

was formed only by inward diffusion of Al. that is outward diffusion of Ni did not occur at this temperature.
3. Formation mechanism of coating at HTHA process was initially the inward diffusion of Al followed by an outward diffusion of Ni.

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