

# Effect of heat treatment on coating microstructure applied by high activity diffusion process on IN738LC

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To study the effect of heat treatment on the microstructure and composition of high activity aluminide diffusion coating, a number of IN738LC specimens were coated at 850 and 1050°C via high activity aluminising process for 4 h and then heat treated at 1120°C for 2 h. Then, the microstructures of the coatings were examined via X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). For the high temperature process, the thickness of the outer layer of the coating increased basically due to the inward diffusion of aluminium, which demonstrated that a chemical potential gradient exists for the inward diffusion of aluminium even after 4 h of inward diffusion at 1050°C. The EDS results provided the evidence that the partition of interdiffusion zone into two separate zones could be due to the outward diffusion of chromium. Surprisingly, the decomposition of the precipitates formed in the first step was observed, indicating that those precipitates were not stable.

**Keywords:** Aluminising, Superalloy, Coating, Interdiffusion

## Introduction

Aluminising is one of the commonly used coating methods for enhancing the life of high temperature components.<sup>1–9</sup> Owing to the small and complex geometry of long and narrow internal air channels of vanes and blades and also the difficulties of removing the pack powder mixture from these channels, pack cementation process is not recommended for coating such internal air channels in blades and vanes.<sup>3,10</sup> Aluminising through gas phase diffusion is much more efficient and useful for such purposes.<sup>10,11</sup> Gas phase aluminising is similar to pack cementation technique; however, unlike pack cementation, powder mixture is not physically in touch with the specimens in this technique.<sup>10–13</sup>

From the view point of aluminium activity, there are two different aluminising processes. If the aluminium concentration in the aluminium source used in the initial powder mixture is >60 at.-%, the process is known as high activity aluminising; otherwise, it is called low activity.<sup>10,14</sup>

High aluminium activity coating processes are usually performed via a two-step operation. In the first step, which is performed at a lower temperature range (i.e. 500–850°C), aluminium diffuses from powder mixture inwardly into the substrate and usually forms  $\delta$ -Ni<sub>2</sub>Al<sub>3</sub> phase. In the second step (i.e. heat treatment step), which is carried out at a higher temperature (i.e. usually >1000°C) in the absence of powder mixture, nickel

diffuses outwardly to form  $\beta$ -NiAl phase.<sup>14,15</sup> There are also some reports on the possibility of a single step coating operation when the coating process is carried out directly above 1000°C.<sup>1,3,14,16</sup>

The published articles on low temperature high activity (LTHA) process referred to some general aspects of heat treatment so far, and to the best of our knowledge, no detailed report on the effect of heat treatment on high temperature high activity (HTHA) coating microstructure has been published. Therefore, it seems that investigating the effects of heat treatment on the coating microstructure can be useful for obtaining desirable coating microstructure and properties. This research attempted to investigate the microstructural details of the heat treated coatings formed via LTHA and HTHA gas phase aluminising and to compare these microstructures with the ones obtained before the application of heat treatment.

## Experimental

A few number of specimens having dimensions of 10 × 10 × 3 mm were cut from IN738LC bars. The mean chemical composition of this alloy is shown in Table 1. The specimens were ground using silicon carbide emery papers from grade 80 to 1200. The composition of the powder mixture used for coating these specimens is shown in Table 2. NH<sub>4</sub>Cl was the activator to react with aluminium in the powder mixture to produce a series of aluminium halides such as AlCl, AlCl<sub>2</sub> and AlCl<sub>3</sub>. In this mixture, Al<sub>2</sub>O<sub>3</sub> had the role of filler.

Some of the samples were coated at 850°C (coded LTHA sample) and others at 1050°C (coded HTHA

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sample) for a period of 4 h. The coating process has been described elsewhere.<sup>10</sup> Briefly, the aluminium halides were produced in the furnace due to the reaction of activator and aluminium source in powder mixture. Through transfer of these halides to the surface of the substrate and reduction reaction, aluminium atoms diffused into the substrate and the coating was formed.

The microstructure of the coated specimens before being subjected to heat treatment was evaluated using scanning electron microscopy (SEM) (VEGA II TESCAN) and X-ray diffraction (XRD) (JEOL, JDX-8030, Cu  $K_{\alpha}$  radiation,  $\lambda=1.5418 \text{ \AA}$ ) techniques. Then, the specimens were placed into a furnace, and the temperature was increased from room temperature to  $1120^{\circ}\text{C}$ . It took 36 min to get to this temperature. The specimens were heated at  $1120^{\circ}\text{C}$  for 2 h, and then they were cooled down in air. Heating and cooling within the furnace were carried out under argon atmosphere in order to protect the specimens against oxidation. Subsequently, XRD tests were conducted for the phase analysis. Then, the specimens were mounted, ground up to 2500 grit silicon carbide emery paper, polished with 1 and  $0.25 \mu\text{m}$  diamond pastes and etched in a solution of 61% lactic acid, 36.5% nitric acid and 2.5% hydrofluoric acid (all in vol.-%) to reveal their microstructural details. Finally, the specimens' cross-sections were examined using SEM equipped with an energy dispersive spectroscope (EDS).

## Results and discussion

### As coated specimens

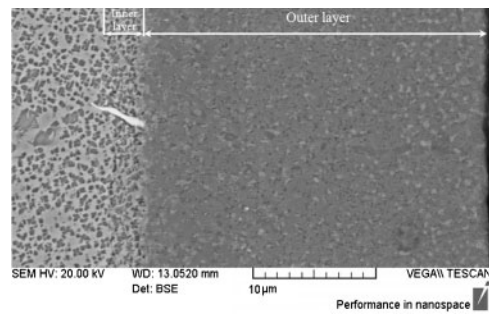
#### LTHA sample

Figure 1 shows the cross-section of the coated LTHA sample. This profile shows that, within the coating, two major layers were formed. The average thicknesses of the inner and outer layers were approximately 3 and  $28 \mu\text{m}$  respectively.

XRD results presented in Fig. 2 show the presence of  $\text{Ni}_2\text{Al}_3$  in the outer layer.  $\text{Ni}_2\text{Al}_3$  was formed by the inward diffusion of aluminium from the surface of the specimen. Owing to the difference in the concentration of aluminium on the surface and in the bulk of the specimen, a chemical potential gradient was formed, which resulted in the inward diffusion of aluminium.<sup>17</sup> Similar observation has been also reported in the literature.<sup>18</sup> The inner layer of the coating is a transient zone. Its structure is similar neither to that of the substrate nor to that of the outer layer, which seemingly is due to extra aluminium atoms arriving from the outer layer to this zone. It appears that the number of aluminium atoms arriving to this zone were not enough to transform this zone to  $\text{NiAl}$  phase. This implies that coating formation is not completed and could have been grown inwardly if a longer time or a higher temperature was used.

#### HTHA sample

The cross-section of the coating applied on the HTHA sample had two layers (Fig. 3). Each layer had two distinct sublayers. Each sublayer is called a region in this



1 Image (SEM) of coating cross-section of LTHA sample before heat treatment

research. The mean thicknesses of the inner and outer layers of this sample were approximately 19 and  $36 \mu\text{m}$  respectively.

XRD results obtained from this coating (Fig. 4) showed that region I consisted of  $\text{NiAl}$  and  $\text{Ni}_2\text{Al}_3$ . High temperature and high rate of aluminium inward diffusion (aluminium had a high activity for this sample) seemed to be responsible for the transformation of a part of the substrate to  $\text{Ni}_2\text{Al}_3$  intermetallic. Furthermore, it has been reported<sup>17</sup> that at high temperature, an outward diffusion of nickel occurs. The outward diffusion of nickel can be specified by the formation of two inner regions (III and IV) having white columnar precipitates similar to those reported in Refs. 19 and 20. 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.<sup>20</sup> This microstructure is called interdiffusion zone (IDZ). The bright contrast seen in these columns demonstrates that they are rich in heavy elements like Cr and W. The absence of this microstructure in Fig. 1 shows that, in LTHA sample, the outward diffusion of nickel either did not happen or is negligible due to low temperature.

In region I of the coating's outer layer, some bright precipitates can be observed. These precipitates were formed due to low solubility of the substrate's heavy elements in  $\text{Ni}_2\text{Al}_3$ , which was the dominant phase of region I. It has been reported that  $\text{Ni}_2\text{Al}_3$  has a compact hcp crystal structure.<sup>21,22</sup> Therefore, these precipitates can be formed by rejection of the heavy elements from this compact structure, within which the bright precipitates can be observed.

### After heat treatment

#### LTHA sample

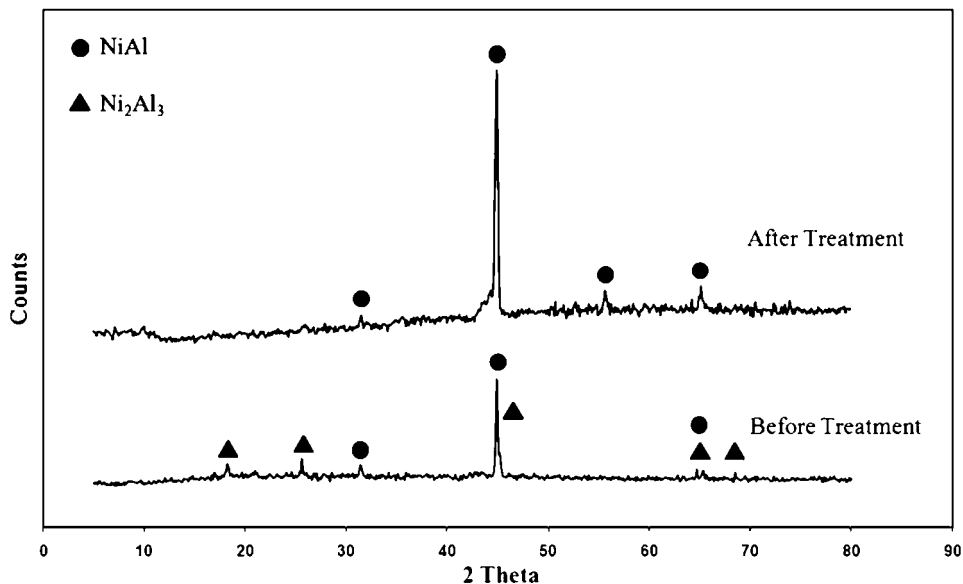
Figure 5 shows the cross-section of the coated LTHA sample after heat treatment. Significant changes can be observed in the coating thickness of this sample after heat treatment when it is compared with Fig. 1. The

Table 2 Chemical composition of powder mixture used in this research

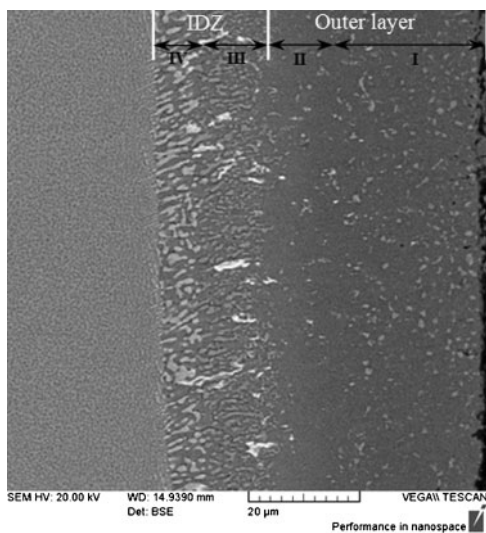
Composition	Commercially pure Al	$\text{NH}_4\text{Cl}$	$\text{Al}_2\text{O}_3$
Content/wt-%	4	2	Bal.

Table 1 Mean chemical composition of IN738LC specimens used in this research

Element	Cr	Co	Al	Ti	W	To	Mo	C	Zr	B	Nb	Ni
Content/wt-%	16	8.5	3.45	3.45	2.6	1.75	1.75	0.17	0.5	0.01	0.09	Bal.



2 XRD pattern of coating of LTHA sample before and after heat treatment

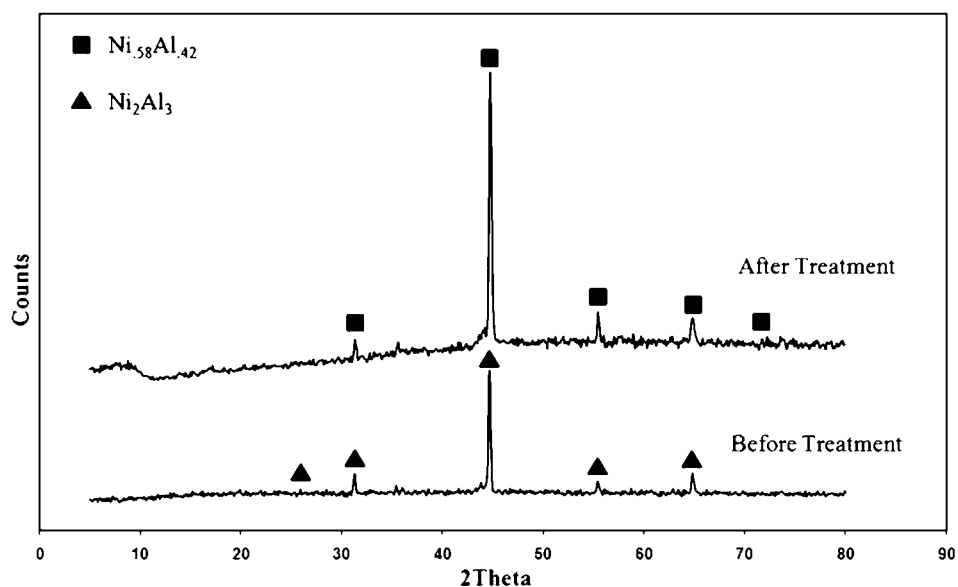


3 Image (SEM) of coating cross-section of HTHA sample before heat treatment

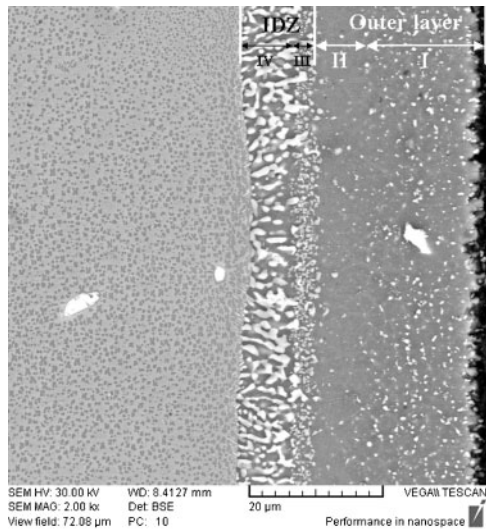
mean thickness of the inner layer increased considerably from 3 to 13  $\mu\text{m}$ , while the mean thickness of the outer layer did not change substantially. This confirmed that the major source of overall increase in the coating thickness was outward diffusion of nickel when the coated sample was heated at 1120°C for a period of 2 h. This was not the case when the coating was carried out at 850°C. Since, in that case, the inward diffusion of aluminium was the dominant mechanism of the coating formation. In the following sections, the mechanism of transforming inner layer to IDZ is presented.

**HTHA sample**

The coating cross-section of the HTHA sample after heat treatment is presented in Fig. 6. This figure shows that the average thicknesses of the outer layer and IDZ increased  $\sim 4$  and 3  $\mu\text{m}$  respectively relative to those before heat treatment. Furthermore, region I of the outer layer became very narrow after heat treatment. This region contained a very low number of precipitates. The XRD results obtained from the outer region of the



4 XRD pattern of coating of HTHA sample before and after heat treatment



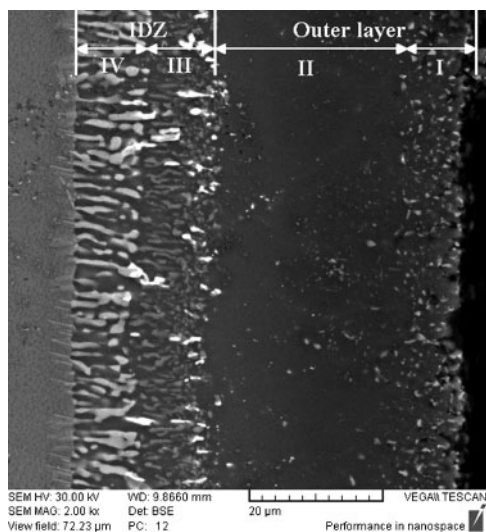
5 Image (SEM) of coating cross-section of LTHA sample after heat treatment

coating show that Ni rich NiAl was the dominant phase of the outer layer after heat treatment.

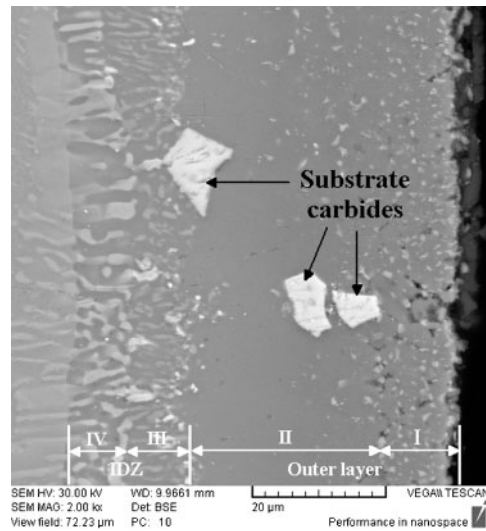
As mentioned in the section on ‘As coated specimens’ on ‘HTHA sample’, formation of hcp-Ni<sub>2</sub>Al<sub>3</sub> during the coating process led to the precipitation of heavy elements in the form of various carbides. Comparing Fig. 3 with Fig. 6 indicates that the distribution, size and amount of precipitates within the outer layer changed substantially after heat treatment. Most of these precipitates were decomposed when the outer layer was transformed from Ni<sub>2</sub>Al<sub>3</sub> to Ni rich NiAl. Therefore, one may conclude that these carbides are not stable carbides.

The presence of these carbides may affect mechanical properties of the coating. If a blade with such coating and without any heat treatment is used in industry, high temperatures in service can lead to the decomposition of these precipitates and can lower the mechanical properties of the coating.

The slight increase in the thickness of the outer layer is an inward increase due to inward diffusion of aluminium. A few carbides were observed within the outer



6 Image (SEM) of coating cross-section of HTHA sample after heat treatment



7 Substrate carbides in coating of HTHA sample indicating outer layer of coating was formed by inward diffusion of aluminium

layer of the coating (Fig. 7). This kind of carbides is originally present in the substrate, and their formation during the coating process is not possible. The presence of these carbides on the outer layer showed that this part of the coating was a transformed substrate (i.e. due to inward diffusion of aluminium within the substrate), not a newly outwardly grown layer on the surface of the substrate. Therefore, these carbides can be considered as natural markers, justifying the direction of the coating growth.<sup>14,19</sup> If the coating layer grew outwardly, no substrate carbide could be present in this layer.

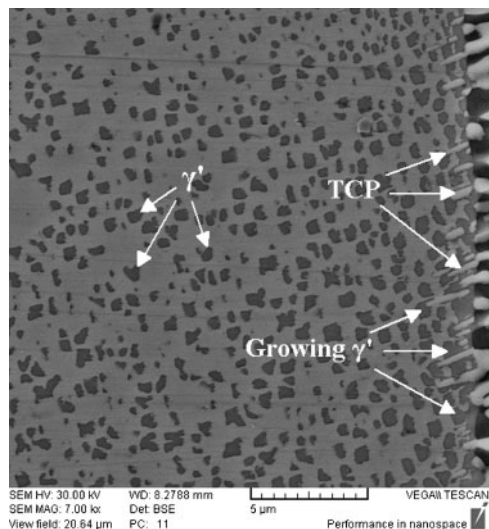
Inward growth of the coating’s outer layer happens at the time of inward diffusion of aluminium. It implies that, even after the sample was held 4 h at 1050°C, there was still a reasonable chemical potential gradient within the coating outer layer, which caused the inward diffusion of aluminium.

**IDZ’s precipitate shapes and its growth mechanism**

As mentioned earlier, in both specimens, IDZ had two regions (III and IV) with different shapes of precipitates. The EDS results obtained from the IDZ cross-sections (Table 3) can support the idea that this difference could be attributed to the differences in the contents of some elements (chromium, nickel and aluminium) in each region. Before the inward diffusion of aluminium, the concentration of substrate heavy element was balanced all over the specimen. The inward diffusion of aluminium decreases the concentration of substrate heavy elements in the outer layer of the coating. The difference between the concentration of these elements in IDZ and outer layer formed a chemical potential gradient for their outward diffusion. However, due to the differences

Table 3 EDS results obtained from IDZ cross-section of both samples after heat treatment (at-%)

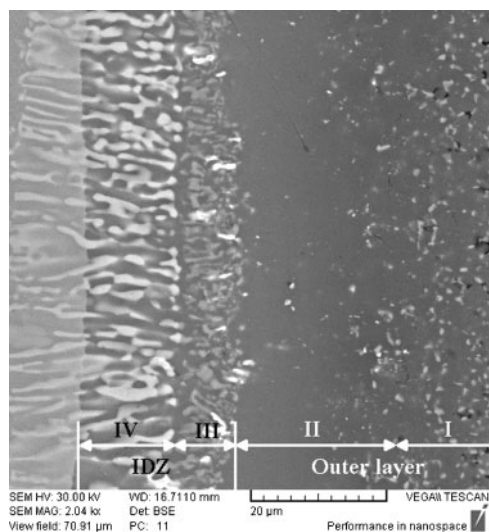
Sample	Region	Al	Ni	Cr	Co	Ti	Mo	W
LTHA	III	14.29	40.68	31.6	6.61	3.79	1.91	1.12
	IV	12.61	40.81	25.19	9.33	6.97	2.72	2.36
HTHA	III	14.68	40.19	31.55	6.57	1.36	3.47	2.17
	IV	13.76	45.23	23.06	9.97	1.02	4.32	2.64



**8 Growing  $\gamma'$  phases in interface of IDZ and substrate of LTHA sample after heat treatment**

in their atomic radius, solubility, content and diffusivity, it would be easier for chromium to diffuse outwardly. By the outward diffusion of chromium from all parts of IDZ, its concentration decreased in region IV, and this phenomenon changed the shape of precipitates in this region. There are some reports<sup>3,16,23</sup> on the presence of more chromium content around the interface of IDZ and outer layer, which could be useful for the readers.

The IDZ growth had several steps, as can be observed in Figs. 8 and 9. The initial stage of the IDZ growth can be seen in Fig. 8. At this stage, the outward diffusion of nickel from the substrate happened. The outward diffusion of nickel can be specified by two signs. The first one is the formation of topologically close packed needles,<sup>24</sup> and the other one is the growth of  $\gamma'$  ( $\text{Ni}_3\text{Al}$ ) phase.<sup>25</sup> Outward diffusion of nickel gradually results to the richness of some parts of substrate in heavy elements such as W, Cr and Mo, which appears as the columnar structure similar to IDZ precipitates. Worth mentioning, the area rich in heavier elements appears in brighter contrast in back scattered images. Figure 9 indicates that these nickel depleted columns are those that



**9 Substrate precipitates connected to IDZ columns of HTHA sample after heat treatment**

eventually appear in the form of IDZ. However, the contrast observed in the vicinity of these white columns, beneath IDZ, was not as dark as the coating's matrix, which can be an indication of the fact that aluminium did not reach this region for changing the matrix phase to the coating phase. As mentioned above, the presence of light elements (i.e. aluminium in this case) in an area is responsible for dissimilarity of its contrast to other regions having heavier elements.

## Conclusion

The overall thicknesses of the coatings during heat treatment were increased by the outward diffusion of nickel and inward diffusion of aluminium. Although the outward diffusion of nickel was the predominant phenomenon in LTHA sample, the opposite was true for the sample subjected to LTHA. Furthermore, the formation of hcp- $\text{Ni}_2\text{Al}_3$  during the coating process led to the precipitation of carbides having heavy elements. During heat treatment and transformation of  $\text{Ni}_2\text{Al}_3$  to Ni rich NiAl, most of the newly formed precipitates decomposed, which implies that they were not stable. This phenomenon can reduce the mechanical properties of the coating. In addition, the precipitates of the outer region of IDZ were smaller than those of the lower region. According to the EDS results, chromium seemed to be responsible for changing the shape of the IDZ outer region's precipitates by means of its outward diffusion.

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