GAS PHASE ALUMINIZING OF A NICKEL BASE SUPERALLOY BY A SINGLE STEP HTHA ALUMINIZING PROCESS

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Abstract — Ni-based superalloy, GTD-111, was coated using a single step high temperature high activity (HTHA) gas phase aluminizing process. Results indicated that the coatings were uniform and consisted of two main layers. Increasing either Al and/or NH_4Cl in the powder chamber resulted in an increase in the coating thickness. The final microstructure of the coating was similar to that formed in the conventional pack cementation method via the HTLA process. This is a new finding obtained in this research.

Résumé — On a revêtu le superalliage à base de Ni, GTD-111, en utilisant un procédé de calorisation en phase gazeuse à étape unique, à haute température et à activité élevée (HTHA). Les résultats ont indiqué que les revêtements étaient uniformes et consistaient en deux couches principales. L'augmentation soit de l'Al et/ou du NH_4Cl dans la chambre à poudre résultait en une augmentation de l'épaisseur du revêtement. La microstructure finale du revêtement était similaire à celle qui est formée lors de la méthode conventionnelle de cémentation en milieu pulvérulent par le procédé HTLA. Ceci est un fait nouveau obtenu lors de cette recherche.

INTRODUCTION

For many years, blades and vanes made from nickel-based superalloys have been used in hot sections of land-based gas turbines. These parts owe their resistance to high temperature oxidation and hot corrosion due to the aluminide coatings applied on their external surfaces, usually via the well-known pack cementation method. Increasing gas inlet temperatures, a key factor in changing turbine output and efficiency, has recently prompted the complementary application of protective aluminide coatings to the internal surface of cooling channels of turbine blades and vanes. The conventional pack cementation method, however, is not readily applicable to coating of such internal surfaces [1]. Currently, gas phase aluminizing is the pre-eminent alternative process [2-4].

In this process turbine blades and vanes are physically separated from the powder chamber and are placed in the coating chamber. A gaseous transporting agent is generated from the powder chamber and is guided to the coating chamber where diffusion of coating elements can occur. The gaseous transporting agent is produced either by a low or a high activity aluminum source. If the concentration of Al in the aluminum source is more than 60 atomic% it is named as a high activity process; otherwise it is a low activity process [5].

Aluminide coatings formed by the low activity pack are usually developed by one step, i.e. aluminizing at temperatures above 1000 °C for the required duration (typically 3 to 4 hours) [6]. No subsequent heat treatment is essential to obtain the beta-AlNi final phase [6]. Aluminide coatings using high-activity packs are produced at lower temperatures (i.e., 700 to 800 °C) followed by a diffusion treatment above 1000 °C to produce the final beta-AlNi phase [5]. Typical times for high activity aluminizing and the subsequent diffusion treatment are 2 and 4 hours, respectively [5]. Therefore, coatings formed by the low activity packs are produced by a single step process, while coatings formed by the high activity packs are usually developed in a two-step process [5]. Based on the temperature of aluminizing and the activity of the pack, the two aluminizing processes are known as high temperature low activity (HTLA) and low temperature high activity (LTHA) processes. In both processes, the final coating consists of beta-AlNi as its bulk phase. Although high-activity coatings are normally developed in a two-step process, as mentioned earlier, there are also some reports of these types of coatings produced in a single step process by aluminizing directly above 1000 °C [5, 7]. This process is called the high temperature high activity (HTHA) process. It is an attractive process because it eliminates one processing step and leads to formation of the final beta-AlNi coating structure by a single step treatment.

Although the formation mechanism of aluminide coatings formed by the conventional pack cementation technique has been widely discussed [5, 8-10], there is no

report related to the formation mechanism of coatings formed by the gas phase aluminizing technique. In this research, aluminide coatings were formed by the gas phase aluminizing technique and using the single step HTHA aluminizing process. In addition, the effect of pack composition on coating microstructures has been discussed.

EXPERIMENTAL

The coating apparatus used for the gas phase aluminizing process is shown schematically in Figure 1. This coating apparatus consisted of two main parts: the powder and the coating chambers which were placed inside an electrical furnace. Argon gas was circulated in the chambers to keep an inert atmosphere and acted as the carrier gas for the coating process.

Different packs with individual chemical compositions were used in the powder chamber in order to investigate the effect of the pack composition on the coating microstructure. These packs were labelled as Packs A, B, C and D and consisted of 500 g of powder mixtures. The composition of each pack is shown in Table I. Pack A was named as the reference pack. Samples with a dimension of 10×10×5 mm, made from a nickel-based superalloy, GTD-111 with the nominal composition shown in Table II were placed in the coating chamber. The surface of these samples was grounded with 600 grit silicon carbide emery paper and then ultrasonically cleaned in acetone prior to the coating process. Gas phase aluminizing was carried out by using the single step high-temperature high activity gas phase aluminizing process at 1050 °C for a period of 4 hours. The samples were then maintained in the furnace until cooling to room temperature.

After the coated samples were removed from the furnace, they were examined using Optical Microscopy (OM), Scanning Electron Microscopy coupled with Energy
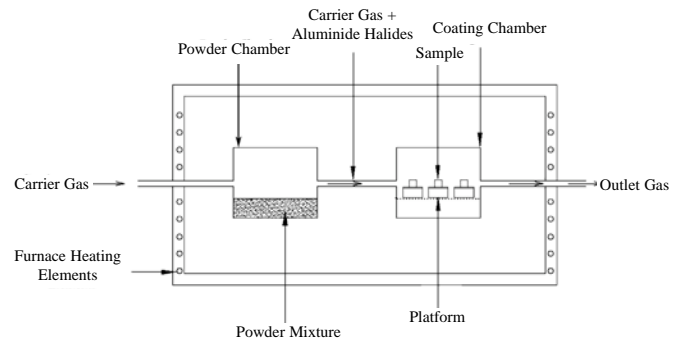

Fig. 1. Schematic showing the coating equipment used for the gas phase aluminizing process.

Dispersive Spectrometry (SEM/EDS) and X-ray Diffraction (XRD) technique.

RESULTS AND DISCUSSIONS

General Description of the Coatings

Typical cross sections of the coatings formed by packs A, B, C and D via the single step high activity gas phase aluminizing process are shown in Figure 2. These cross sections indicate that the coatings are uniform and consist of two main layers; an inner layer (interdiffusion layer) and an outer layer. XRD results shown in Figure 3 indicate that the coatings consist of the bcc beta-AlNi as the dominant phase.

The average coating thickness formed by different packs was measured and is shown in Figure 4. The maximum thickness was 35 μm for pack D and the minimum thickness was 22 μm for pack A. Typical distributions of Al, Ni and Cr elements throughout the coatings are shown in Figure 5. Elemental line scan analysis of the coatings formed by each pack has been shown in Figures 6-9. These figures show that Al concentration decreases when moving from the outer layer of the coating towards the substrate, while the concentration of Ni remains almost constant in the outer layer and decreases within the interdiffusion layer. Also, it can be seen that the concentration of Cr in the interdiffusion layer is much higher than that of Cr in the outer layer of the coatings. This is due to the lower outward diffusivity rate of Cr in the AlNi phases formed during the coating process [5].

Mechanism of Coating Formation

A typical coating formed by a single step HTHA gas phase aluminizing process is shown schematically in Figure 10. It

Table 1 – Chemical composition of powder mixtures used in the single step HTHA gas phase aluminizing process

Pack	Composition (Wt.%)		
	Al	NH$_4$Cl	Al$_2$O$_3$
A	10	5	Bal
B	30	5	Bal.
C	10	15	Bal.
D	30	15	Bal.

Table II – Nominal chemical composition of the substrate alloy GTD-111 (w%)

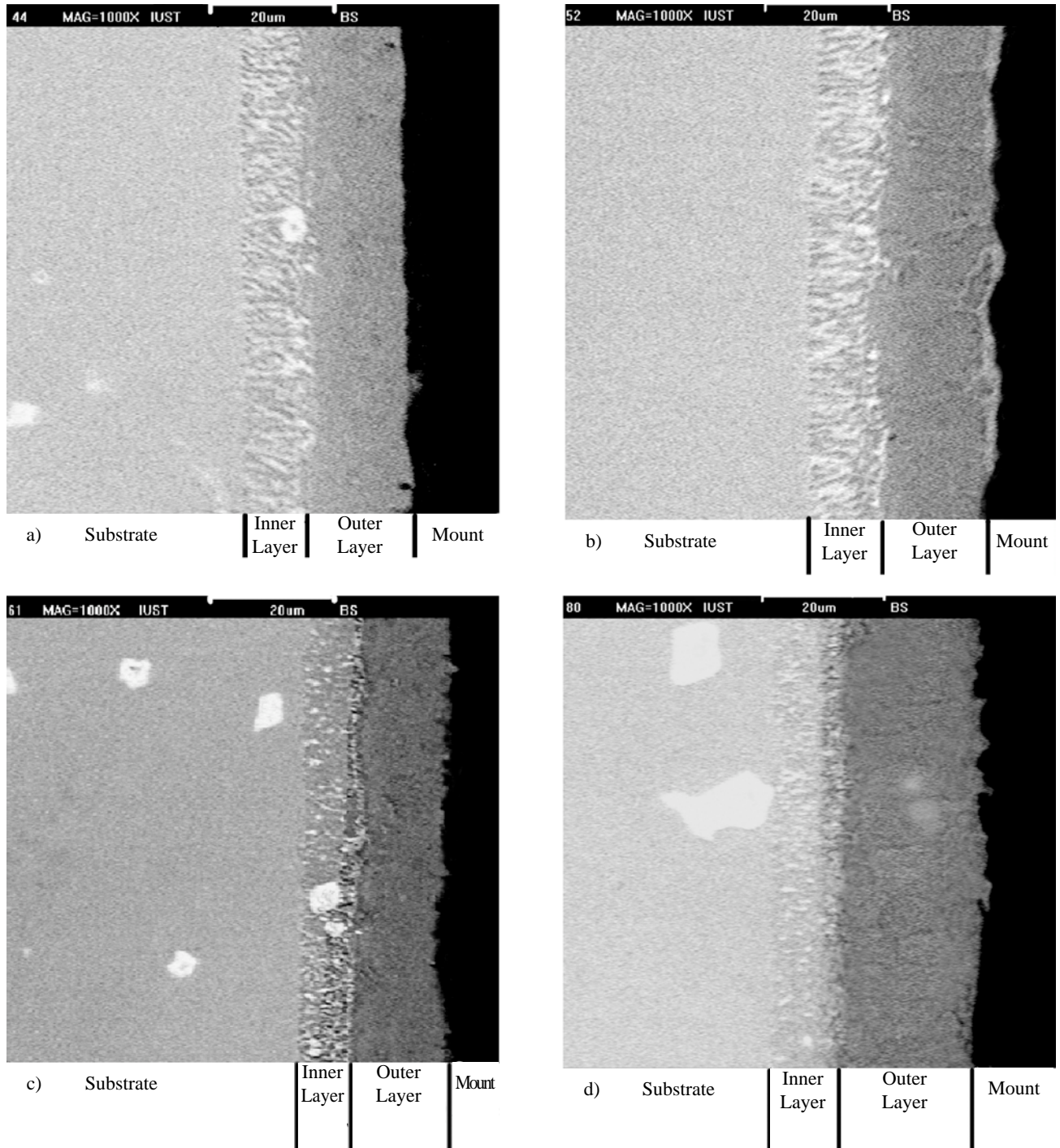| Element	Fe	Hf	Zr	B	C	Ti	Al	Ta	W	Mo	Co	Cr	Ni
wt%	0.2	0.03	0.03	0.01	0.09	4.72	3.21	2.82	3.76	1.41	9.23	13.74	Bal.

Fig. 2.   SEM images of the coatings formed by a) pack A, b) pack B c) pack C and d) pack D.

consists of two layers, an outer AlNi layer (OL) and an interdiffusion layer (IL). No carbides or precipitates were observed in the outer layer.

The formation mechanism of this type of coating can be explained by the primarily outward diffusion of Ni from the substrate. The reaction front (RF) which is located in the outer surface of the coating receives Ni from the substrate and Al halides formed by the pack to form AlNi compounds. The outward growth of the outer layer with respect to the initial surface (IS) is shown in Figure 10. The region below the

Fig. 3. The results of XRD from the coatings surface show various AlNi compounds formed within the coating a) pack A, b) pack B, c) pack C, d) pack D.
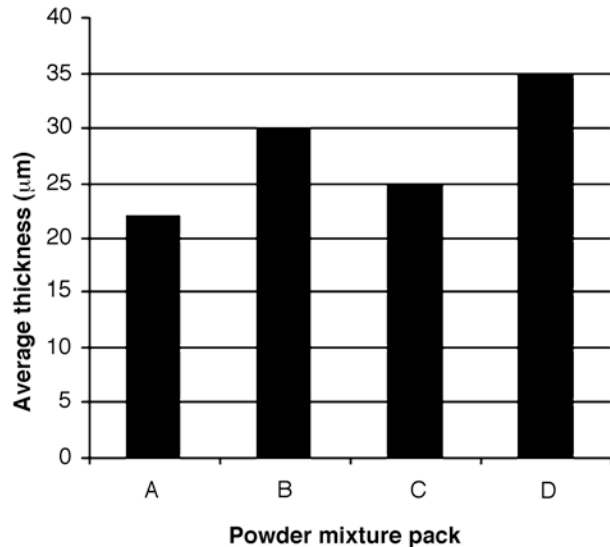

Fig. 4. Coating thickness formed via different packs.

This is totally different from what was expected; a three layer coating formed when using the HTHA pack cementation technique [5]. In detail, the formation mechanism of HTHA gas phase aluminizing coatings seemed similar to HTLA pack cementation coatings [5, 8-10]. Despite using a high activity pack, the final microstructures of the coatings were similar to those formed from low activity packs via the pack cementation technique [5, 8-10]. This is due to the reduction of Al activity in the gas phase within the coating chamber. The activity of Al in the gas phase has a direct relationship with its partial pressure [11]. When $AlCl_3$ halide is mixed with argon inlet carrier gas inside the coating chamber, Al activity will decrease. Therefore, even though the process is a high activity process, the microstructures of the coatings were similar to the microstructures of coatings formed in HTLA pack cementation technique. This is a new finding obtained in this research.

Effect of Pack Composition on Coating Microstructures

To investigate the effect of the concentration of Al and/or activator (NH_4Cl) in the pack on the coating microstructures, powder mixtures having different compositions, as shown in Table I were used.

The concentration of Al in pack B was three times higher than that of pack A and the concentration of NH_4Cl in pack C was three times larger than that of pack A. In pack D concentrations of both Al and NH_4Cl were increased by three times relative to pack A, which was named as the reference pack. Increasing the concentration of Al and/or NH_4Cl caused an increase of coating thickness as shown in Figure 4. Increasing the concentration of Al and NH_4Cl at the same time was more effective in increasing the coating final thickness than increasing either one of them individually. It was also observed that increasing Al concentration in the pack

initial surface has lost Ni due to its outward diffusion, while receiving Al from the outer layer due to its inward diffusion. Therefore, an interdiffusion layer has been developed, shown in Figure 10. Precipitation of different phases in this region was caused by a decrease in Ni concentration in this region.

As previously mentioned, the coating formed by the HTHA gas phase aluminizing consisted of two main layers.
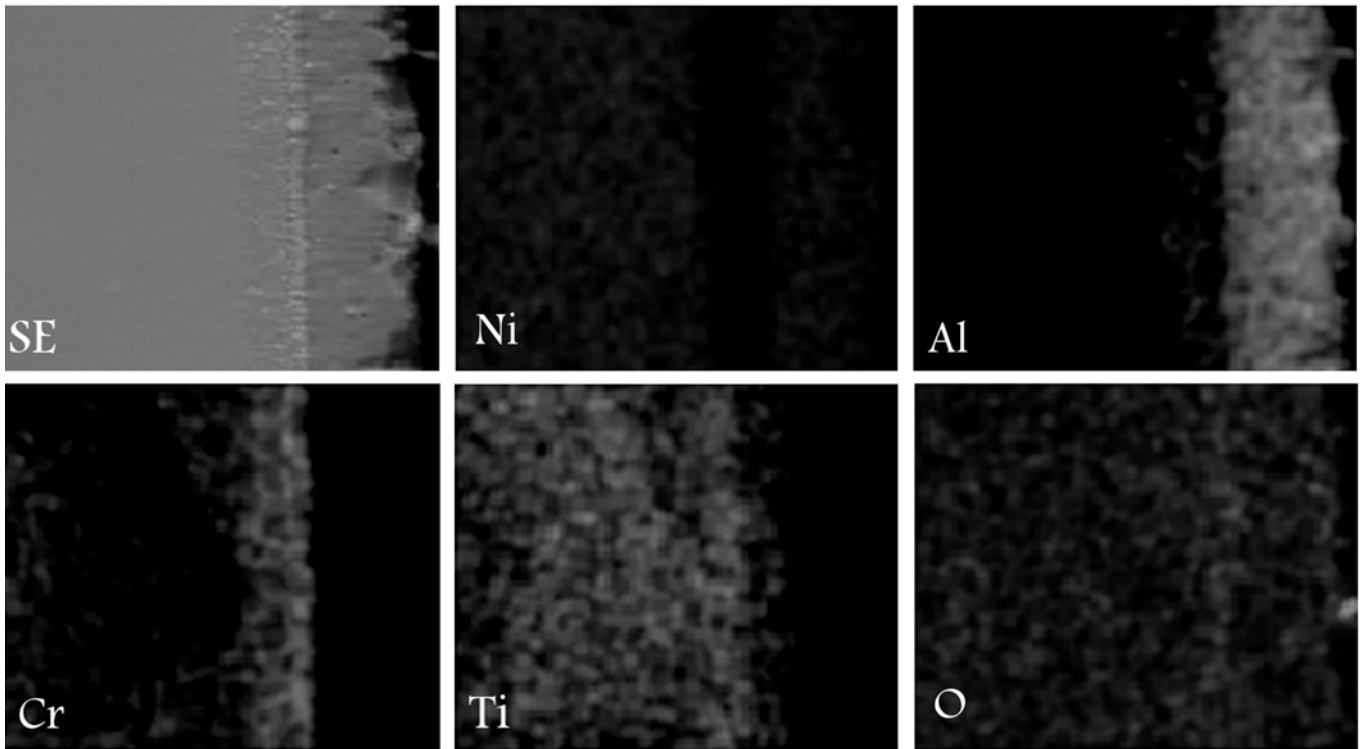
Fig. 5.   Typical X-ray elemental maps of gas phase aluminide coatings formed by single step HTHA gas phase aluminizing process.
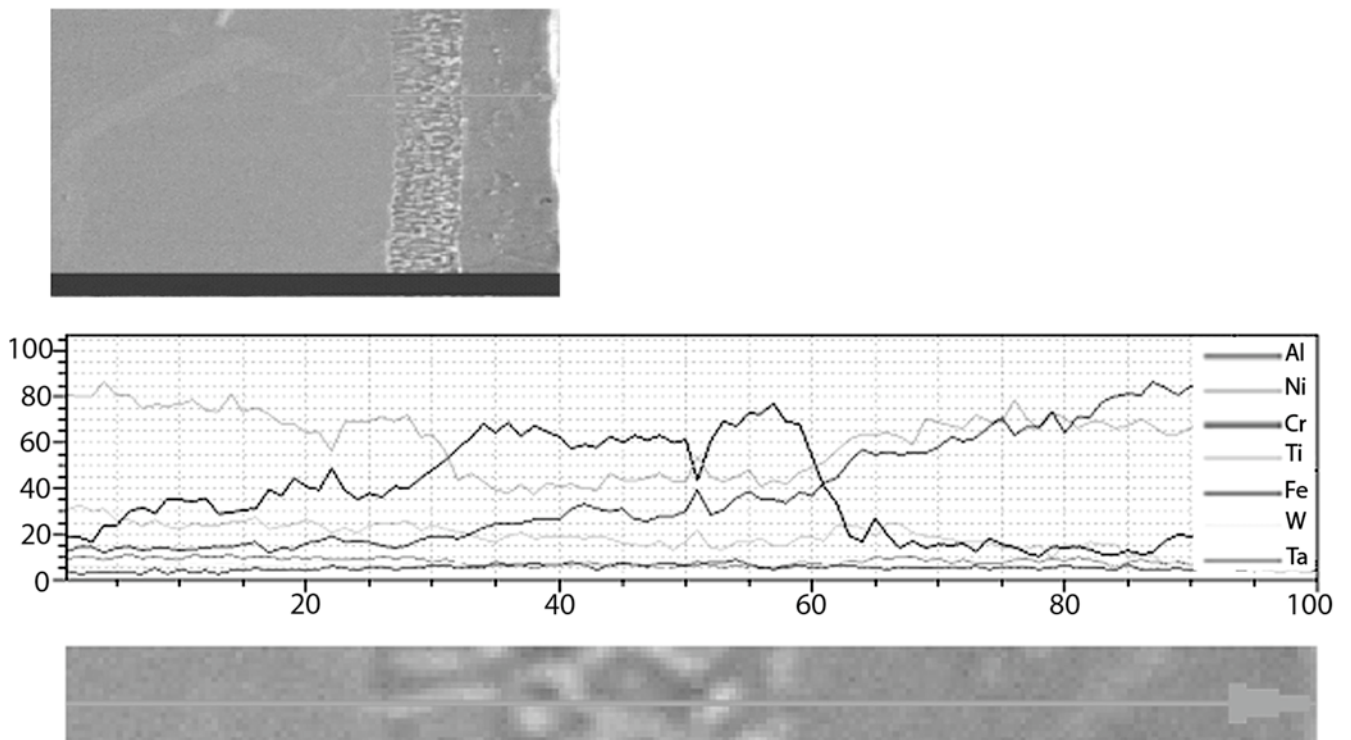

Fig. 6.   Typical elemental line scan analysis of gas phase aluminide coating formed by pack A.
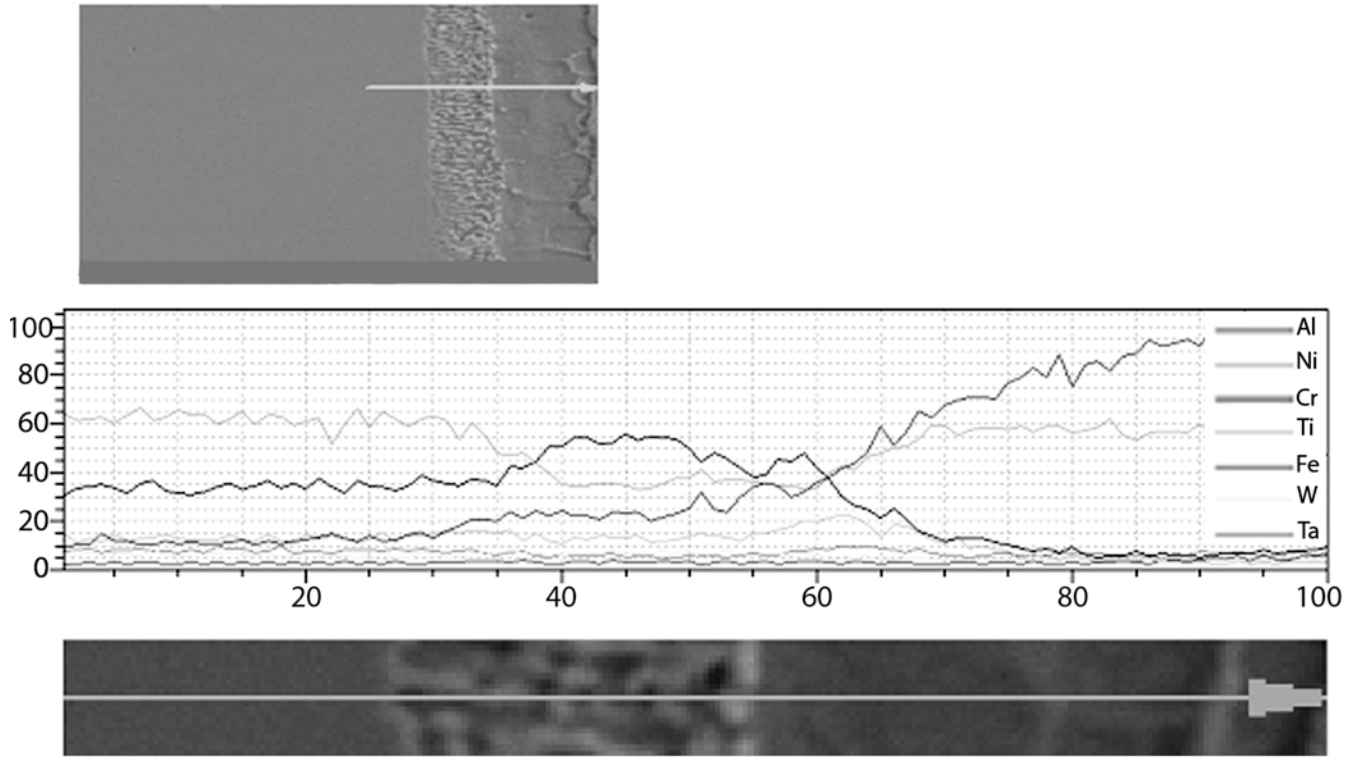
Fig. 7. Typical elemental line scan analysis of gas phase aluminide coating formed by pack B.
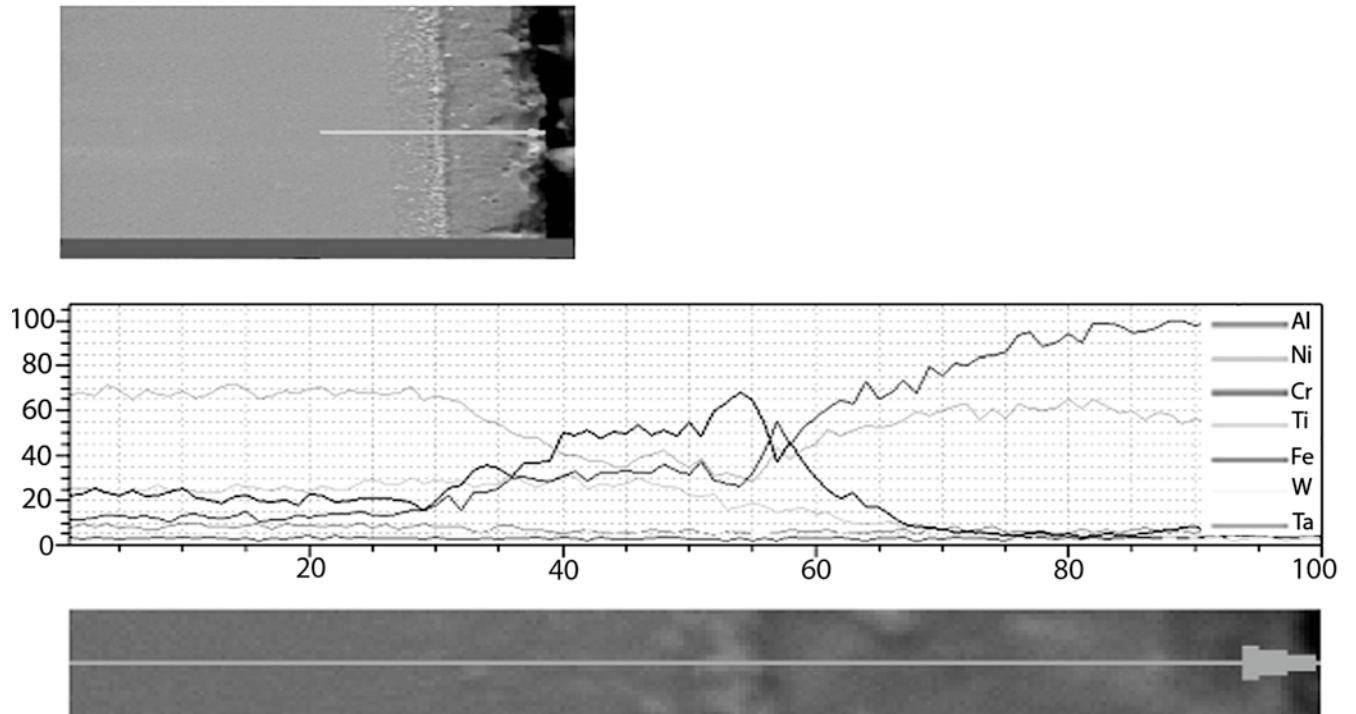

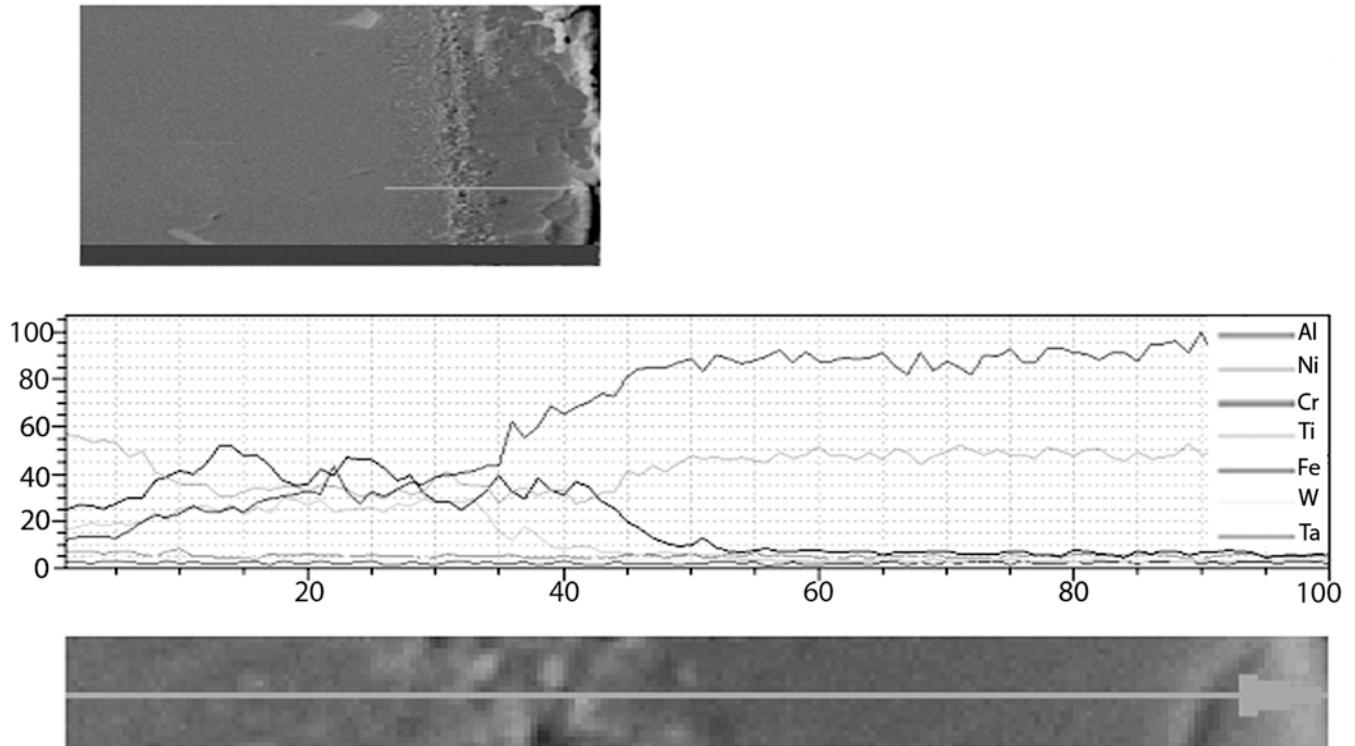Fig. 8. Typical elemental line scan analysis of gas phase aluminide coating formed by pack C.

Fig. 9. Typical elemental line scan analysis of gas phase aluminide coating formed by pack D.

SC : substrate carbides
IS : initial surface
IL : Interdiffusion layer
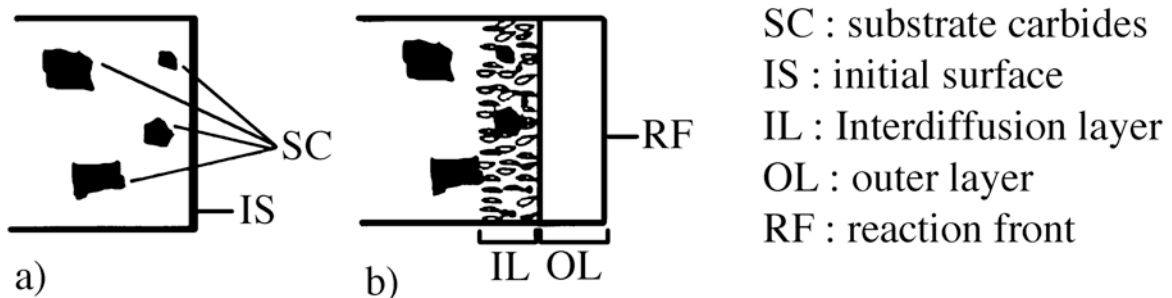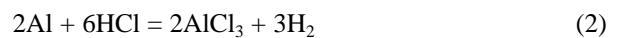OL : outer layer
RF : reaction front

Fig. 10. Schematic showing the mechanism of coating formation in a typical single step HTHA gas phase aluminizing process: a) superalloy substrate showing carbides before aluminizing and (b) coating formed after aluminizing.

was more effective in increasing the coating thickness in comparison to increasing NH_4Cl concentration, see Figure 4. The increase in the coating thickness from increasing Al and/or NH_4Cl can be explained by considering the chemical reactions that occurred in the coating chamber.

According to the following reactions aluminum halides $AlCl_n$ (n<3) are formed at temperatures above 800 °C. Then, the produced aluminum halide $AlCl_n$, will react with the surface of the Ni-based superalloy in the coating chamber to form $AlNi_y$ compounds at temperatures above 800 °C [3]. The index, y, in the intermetallic $AlNi_y$ is between 3 and 1/3 (i.e. $1/3 \leq Y \leq 3$). All these reactions are reversible.

$$NH_4Cl = HCl + NH_3 \qquad (1)$$

$$2Al + 6HCl = 2AlCl_3 + 3H_2 \qquad (2)$$

$$Al + AlCl_3 = AlCl_n \qquad (3)$$

$$AlCl_n + Ni = AlNi_{y +} AlCl_3 \qquad (4)$$

Researchers [3] suggest that $AlCl_n$ is more stable thermodynamically than $AlCl_3$ as the temperature increases. The activator of the reactions, $AlCl_3$, is a product in Equation 4 which is reproduced during the reactions. The reproduced

$AlCl_3$ can then react with aluminum again to form an $AlCl_n$ compound. These reactions explain why increasing the amount of Al and/or NH_4Cl increases the coating thicknesses. Increasing either the amount of Al and/or NH_4Cl favours the formation of $AlCl_3$ during the coating process.

The more $AlCl_3$ is produced in the powder chamber, the more $AlCl_n$ is transferred to the coating chamber and hence a higher amount of $AlNi_y$ will be produced at the surface of the samples during the coating period. The driving force for the formation of $AlNi_y$ intermetallic is provided by the energy release due to the reaction of $AlCl_n$ and Ni.

One of the features of the HTHA process used in this research, is that the final composition of the $AlNi_y$ intermetallic formed as the major coating phase is very close to the beta-AlNi phase (Figure 3).

The proposed mechanism for the coating formation in HTHA gas phase aluminized coatings can well explain the reason behind the differences in the coating thickness and composition. For example, when pack C was used, at the initial stage of the coating process high amounts of $AlCl_3$ were produced in the powder chamber. This led to a concentrated atmosphere of $AlCl_3$ gas, above the sample inside the coating chamber, which then produced an $AlNi_y$ phase rich of Al. According to Goward *et al.* [8, 12] the outward diffusion rate of Ni decreases when $AlNi_y$ phase is rich in Al. This is due to its reaction with Al at the reaction front. Therefore the coating was thickened by gradual outward diffusion of Ni through the initial Al rich $AlNi_y$ phase. On the other hand, when pack B was used, a lower concentrated atmosphere of $AlCl_3$ was introduced into the coating chamber and thus the $AlNi_y$ phase formed in this situation was less rich in Al. This in turn increased the rate of outward diffusivity of Ni resulting in a thicker coating with a slightly lower Al concentration compared to the coating formed by pack C (Figures 4, 7 and 8). Furthermore, the $AlNi_y$ phase formed by pack A was rich in Ni at the initial stage of the coating procedure, but due to the relatively smaller $AlCl_3$ supply in the coating chamber, its thickness did not increase as much as those of pack B and C. On the other hand, the $AlNi_y$ phase formed by pack D was rich in Al at the initial stage of the coating procedure and plenty of Al was continuously supplied by the high levels of $AlCl_3$ available during the coating process as explained by Equations 1 to 4. Therefore a thick aluminide coating rich in Al was obtained as shown in Figures 4 and 9.

CONCLUSIONS

The microstructures of coatings obtained by HTHA gas phase aluminizing were similar to coatings formed by the HTLA pack cementation method. This is a new finding and it appears to be due to the reduction of Al activity in the gas phase. Increasing Al and/or NH_4Cl by three times in the pack powders used in the gas phase aluminizing coating process resulted in an increase in coating thickness. When both Al and NH_4Cl were increased at the same time the increase in coating thickness was greater than when each of these was increased individually. The two main factors affecting the final composition and thickness of the coatings are: 1) concentration of $AlCl_3$ gas inside the coating chamber and 2) duration of $AlCl_3$ supply with a certain concentration inside the coating chamber.

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