Formation mechanism of IDZ during coating of IN738 by single step gas phase aluminising

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The formation mechanism of interdiffusion zone (IDZ) during gas phase aluminising of nickel based superalloy IN738LC and the effects of temperature and Al activity on the microstructure of IDZ were investigated in this research. For this purpose, a single step gas phase aluminising technique was applied for coating the surfaces of IN738LC specimens at two different processing temperatures (i.e. 850 and 1050°C) and various pack compositions. Then the coating microstructures were evaluated using a scanning electron microscope, an energy dispersive spectrometer and an X-ray diffractometer. The results showed that at the low temperature, coating was formed by inward diffusion of Al, whereas at the high temperature, both outward diffusion of Ni and inward diffusion of Al occurred, resulting in the formation of a columnar structure or an IDZ. By increasing the Al activity in the powder mixture, it is shown that the amount of Al within the inner layer of the coating increased.

Au cours de cette recherche, on a étudié le mécanisme de formation de la zone d'interdiffusion (IDZ) lors de la calorisation en phase gazeuse du superalliage à base de nickel, IN738LC ainsi que les effets de la température et de l'activité de l'Al sur la microstructure de l'IDZ. Dans ce dessein, on a appliqué une technique de calorisation en phase gazeuse à étape unique pour revêtir les surfaces des échantillons d'IN738LC à deux températures différentes de traitement (i.e. 850 et 1050°C) et avec diverses compositions de poudre. Ensuite, on a évalué les microstructures du revêtement en utilisant les techniques du microscope électronique à balayage, de l'EDS et de l'XRD. Les résultats ont montré qu'à basse température, le revêtement était formé par diffusion de l'Al vers l'intérieur alors qu'à haute température, tant la diffusion du Ni vers l'extérieur que la diffusion de l'Al vers l'intérieur se produisaient, résultant en la formation d'une structure en colonnes ou IDZ. En augmentant l'activité de l'Al dans le mélange en poudre, on montre que la quantité d'Al à l'intérieur de la couche interne du revêtement augmentait.

Keywords: Gas phase aluminising, Interdiffusion zone, Al activity, Formation mechanism

Introduction

Coating of long and narrow internal air channels of vanes and blades is necessary for enhancing the life of turbine blades and vanes.[1,2] Owing to the small and complex geometry of these channels, and also the difficulties that exist in removing the pack powder mixture from these channels, pack cementation process is not recommended for coating such blades and vanes.[1,3] So aluminising through gas phase diffusion was introduced for this purpose.[2,3] Gas phase aluminising is similar to pack cementation, but unlike the pack cementation in gas phase process, powder mixture is not physically in touch with the specimens.[3–5]

From the viewpoint of aluminium activity, there are two diffusion aluminising processes. If the Al concentration in the Al source used in the initial powder mixture is greater than 60 at-%, the process is known as high activity aluminising, otherwise it is called low activity.[3,6] When high activity aluminising at a low temperature is used, unlike using low activity aluminising at a high temperature, the top layer of the coating becomes rich in aluminium. Phases such as Ni_2Al_3 or

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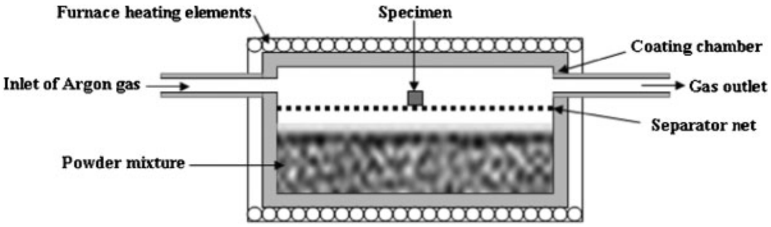


1 Schematic showing coating equipment used for gas phase aluminising process

NiAl rich in Al are not desirable phases to be used for coating and for transforming them to NiAl rich in Ni, therefore, an additional heat treatment is required.[6–8] So many aluminising processes are carried out in a single step process above 1000°C using high activity pack powder.[6,9] This is an attractive technique for eliminating one step in coating process. Also, this process finally leads to the formation of a Ni rich NiAl coating structure in a single treatment, as in the case of a usual low activity coating.[6] Eslami *et al.*[9] reported that the coating obtained by high temperature hydrogen attack gas phase aluminising is similar to that obtained by the high temperature low activity pack cementation process.

It has been reported that aluminide coating usually forms by inward diffusion of Al, produced through Al subhalides in the pack, and outward diffusion of Ni, through the matrix.[10] Because of the outward diffusion of Ni and subsequent enrichment of the substrate by alloying elements, precipitation of these elements occurs within the matrix and an interdiffusion zone (IDZ) with a columnar structure usually forms under the top coating layer.[8]

It is worth mentioning that the temperature for effective diffusion of Ni is ~950°C and only at temperatures higher than this does outward diffusion of Ni have an effective influence on the coating formation mechanism.[3,11]

In this research, the formation mechanism of the IDZ was studied, and the effects of temperature and Al activity on the coating were evaluated.

Materials and methods

Rectangular plates of IN738LC with dimensions of $10\times10\times3$ mm and a mean chemical composition of Ni–8·5Co–16Cr–3·4Al–3·4Ti–2·6W–1·7Ta–1·7Mo–0·9Nb–0·05Zr–0·11C–0·01B (wt-%) were used as the substrate material. These samples were ground with 80–1200 grade SiC emery papers, then cleaned in an acetone bath and dried in air before the coating process.

Two powder mixtures were prepared by weighing the appropriate amounts of filler powder of Al_2O_3, Al source (i.e. pure Al or NiAl powder) for production of Al ions and NH_4Cl as an activator. The Al source used in pack H was pure Al powder and in pack L was NiAl powder, as shown in Table 1. These powder mixtures were labelled either as pack H or pack L depending on the source of Al supply. The amount of aluminium in both packs was 4 wt-% and the weight of each pack was 200 g of the powder mixtures. Eight grams of pure Al powder were used in pack H and 25·6 g NiAl powder in pack L. The amount of activator in both packs was 2 wt-% (4 g).

The specimens were placed inside the chamber of the coating apparatus as shown schematically in Fig. 1. Gas phase aluminising was carried out at 850 and 1050°C for a period of 4 h for both L and H packs. The samples were maintained in the furnace after coating until the temperature dropped to room temperature. It should be mentioned that argon gas was circulated in the chamber from the start of the coating operation until the chamber temperature became 300°C, to keep an inert atmosphere for the coating process, and then the flow of argon gas was cut. After the coating process was ended, argon gas was again circulated in the chamber in order to empty the chamber from the coating halides.

Each specimen was labelled with a code consisting of an initial letter referring to the kind of pack used and a number which indicates the coating temperature.

The coated samples were examined using a scanning electron microscope (SEM; Vega II T-Scan) coupled with an energy dispersive spectrometer and an X-ray diffractometer (Cu K_α: $\lambda=1{\cdot}5418$ Å; JDX-8030; JEOL, Tokyo, Japan). Etchant consisting of 61 vol.-% lactic acid, 36·5 vol.-% nitric acid and 2·5 vol.-% hydrofluoric acid was used to reveal the microstructure details.

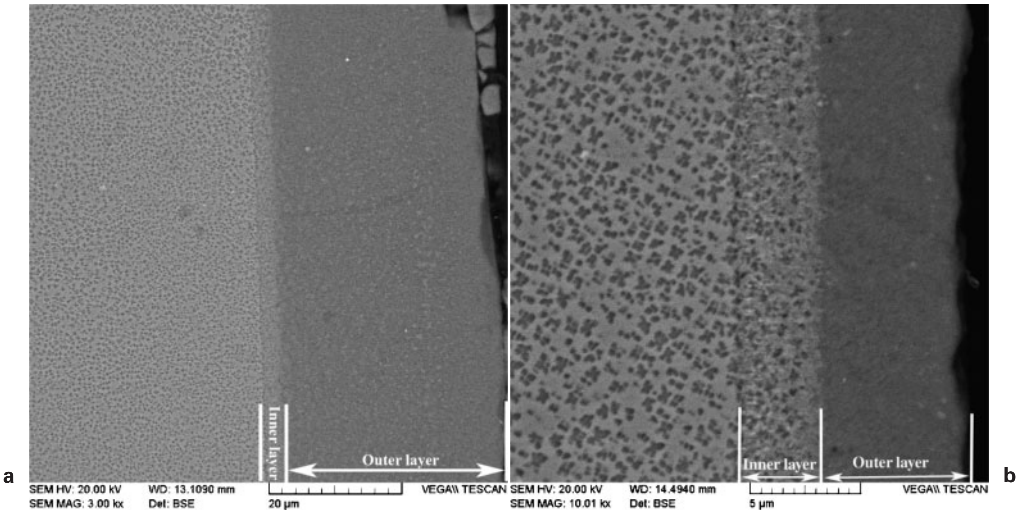
Results and discussion

Low temperature process

Typical cross-sections of the coatings formed by packs L and H via the single step gas phase aluminising process at 850°C are shown in Fig. 2. These cross-sections indicate that the coatings are uniform and consist of two main layers (inner and outer layers). X-ray diffraction results shown in Fig. 3 indicate that Al concentration in the coating formed on H-850 sample is higher than that of L-850 sample. Since the partial pressure of Al in the high activity pack is higher than that in the low activity pack,[9] the kinetics of reactions occurring in the high activity pack is faster than that in the low activity pack. By increasing the partial pressure of Al in the pack, the

Table 1 Chemical composition of powder mixtures used in single step gas phase aluminising process, wt-%

		Composition		
Pack	Al source	Al	NH_4Cl	Al_2O_3
H	Pure Al	4	2	Bal.
L	NiAl	4	2	Bal.



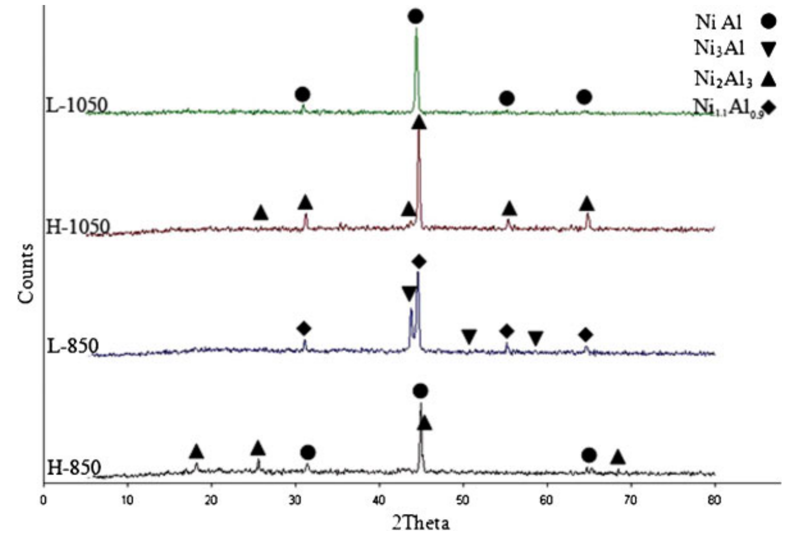
2 Images (SEM) of coatings formed by *a* pack H and *b* pack L at 850°C, showing two layers of coating formed at surface of sample

amount of Al ions released on the surface of the sample can be increased.[12] Thus, the Al concentration in the coating of the high activity pack becomes higher than that of the low activity pack.

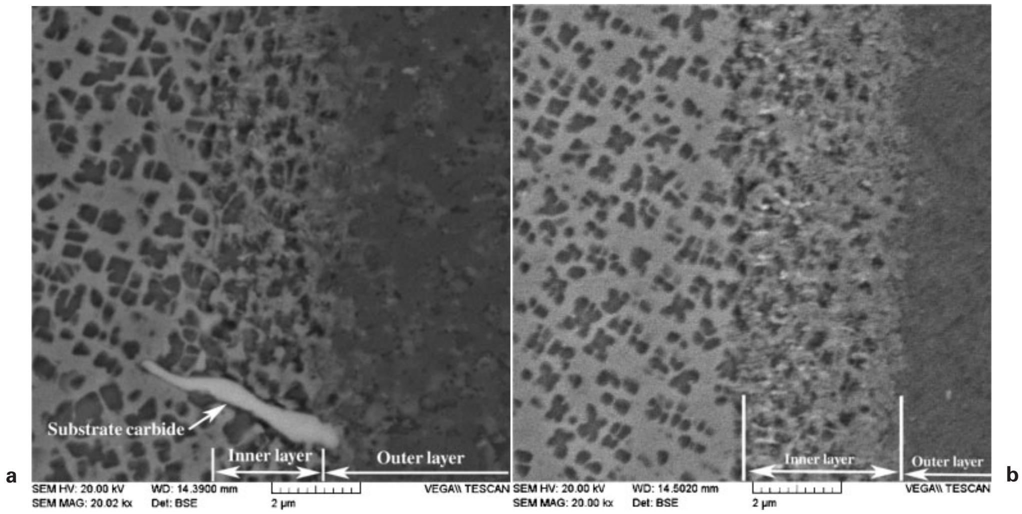
The inner layers of the coatings shown in Fig. 4 indicate that the transformation of substrate structure to coating structure started to occur by receiving the incoming Al from the outer layer of the coating. When the amount of the Al atoms in this layer increases to a sufficient level, transformations occur. Thus, those parts of the substrate that received enough Al atoms gradually become part of the coating. The lack of columnar structure in these specimens confirms that no efficient outward diffusion of Ni from substrate to outer layer of coatings occurred. As mentioned earlier, effective diffusion of Ni in nickel based alloys starts at ~950°C according to Xiang *et al.*[11] Therefore, one may conclude that the results of this research conform with those of Ref. 11.

Figure 2 shows that the amount of substrate transforming to NiAl in the coating layer under the same processing condition is more in the H-850 sample than in L-850, so the thickness of the outer layer of the coating is larger in H-850 sample than in L-850.

However, as shown in Fig. 4, the thickness of the inner layer in L-850 is somewhat larger than that in H-850 but the total thickness of the coating in H-850 is greater than that of L-850. This is due to the variation in the amount of Al atoms entering into the substrate of the two samples. The higher the rate of receiving Al atoms by the substrate, the sooner it transforms to the coating structure, so the thickness of the coating increases more. However, when the rate of incoming Al atoms is low, there will not be enough of these atoms within the substrate to cause transformation completely, so the inner layer becomes thicker, not the outer one.



3 X-ray diffraction results from coating surfaces of samples coated under various conditions

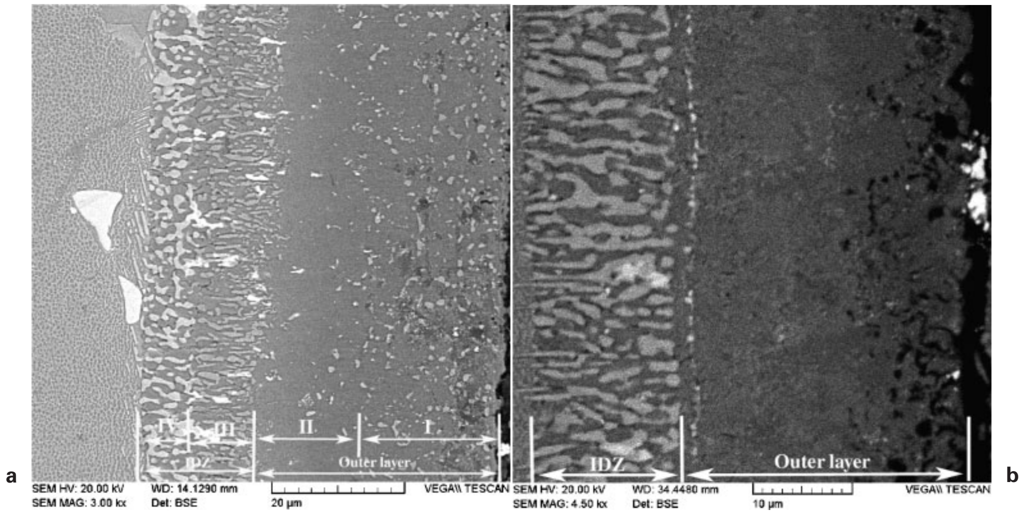


4 Images (SEM) of coatings formed by *a* pack H and *b* pack L at 850°C, showing structures of inner layers in detail

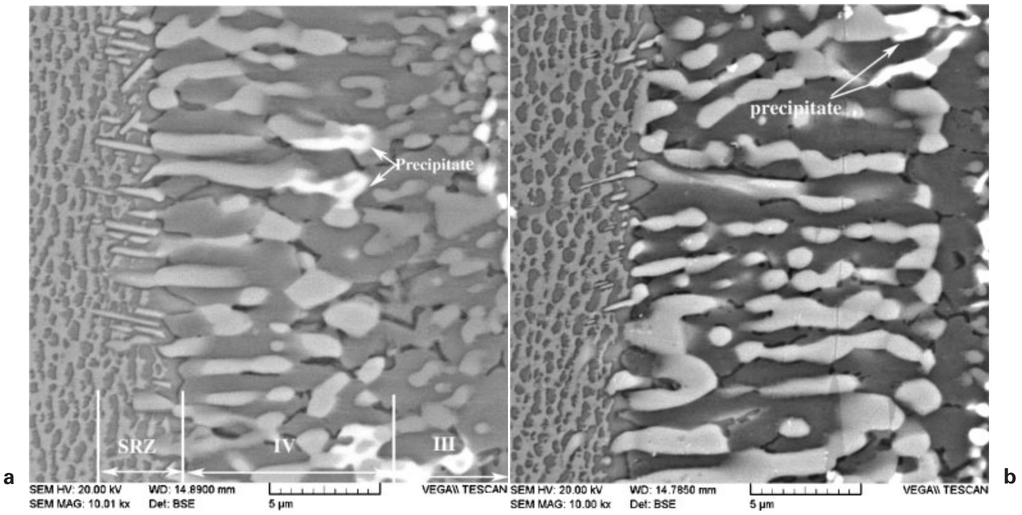
High temperature process

Typical cross-sections of the coatings formed by packs L and H via the single step gas phase aluminising process at 1050°C are shown in Fig. 5. The coatings obtained at 1050°C consist of two major layers. Comparing Fig. 5 with Fig. 2, one can see that the inner layers of these samples are somehow different from those of the samples coated at 850°C. The inner layers (IDZ) of the coated samples at 1050°C have a columnar structure. This is due to the outward diffusion of Ni occurring sufficiently at this temperature. Subsequently, the matrix became rich in alloying elements which accompanied by the precipitation of these elements within the matrix. It is worth mentioning that the area rich in heavier elements appears in brighter colour in backscatter images (*see* Fig. 5). So, by increasing the coating temperature from 850 to 1050°C, outward diffusion of Ni occurred in a large scale in the samples.

Figure 5 also indicates that the IDZ layer of H-1050 sample consists of two zones (i.e. zones III and IV), whereas that of L-1050 sample consists of only one zone. Figure 6 shows higher magnification images of IDZ layer of both specimens. These images show the microstructural details of IDZ of the samples coated at 1050°C. As mentioned earlier, the amount of Al atoms released at the surface of H-1050 sample is more than that of L-1050 sample. X-ray diffraction results shown in Fig. 3 confirm that the aluminium concentration in the surface of the coating of H-1050 sample is more than that of L-1050 sample. Therefore, more Al atoms can enter into the substrate of H-1050 sample than L-1050 and thus they can transform the top layers of the substrate to NiAl phase rich in Al. Subsequently, as the temperature is adequate for Ni diffusion, this element starts diffusing upward towards the surface. However, due to the more Al atoms received in zone III than zone IV, zone III starts transforming to NiAl phase sooner than zone IV. Thus, as shown in Fig. 6, the columns that have already lost some of its Ni atoms, by receiving Al atoms from the top coating layer transform to the coating structure.



5 Images (SEM) of coatings formed by *a* pack H and *b* pack L at 1050°C: coatings formed by both packs have two major layers and there is difference in IDZ layer of them

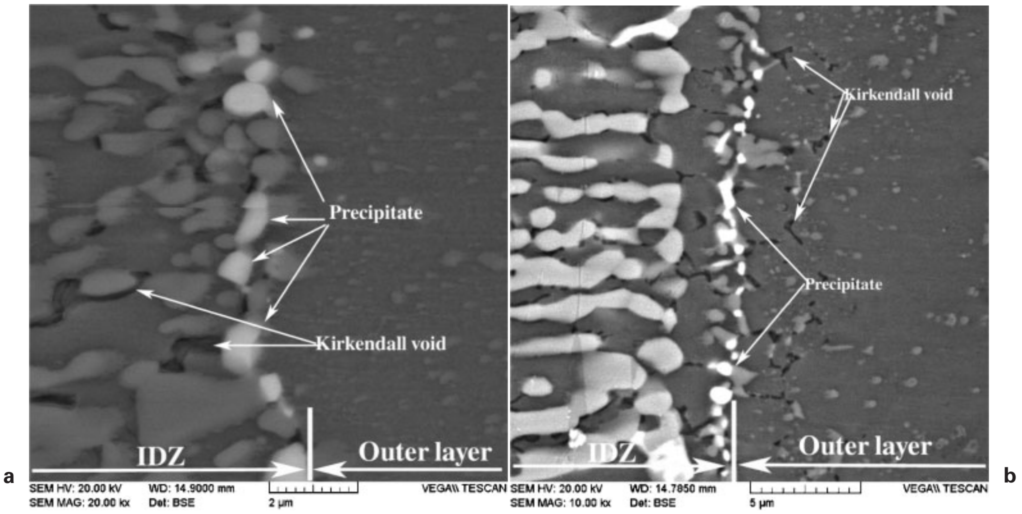


6 Images (SEM) of IDZ layer of coatings formed by *a* pack H and *b* pack L at 1050°C, showing existence of refractory elements precipitates and Kirkendall voids in IDZ

By transforming the substrate to the coating structure, the solubility of alloying elements such as W, Cr and Mo decreases and a suitable condition for precipitation of these elements will be provided. So in IDZ, in the interface of IDZ/outer layer and occasionally in the coating outer layer, precipitation will occur. A similar type of analysis has been reported in Refs. 3, 6 and 13. It has also been reported that because of the low solubility of refractory elements in β-NiAl, they hardly participate in the formation of β-NiAl; instead they precipitate as secondary phases at the interface between the IDZ and the outer layer of the coating.[14] As mentioned earlier, the precipitation of these refractory elements caused a higher contrast at some points to appear within these zones in backscatter images (*see* Figs. 6 and 7). Another phenomenon occurring within the inner layer of the coating is shown in Figs. 6 and 7, and that is the existence of many voids in the vicinities of columnar structures. These voids are probably Kirkendall voids that formed by a large amount of outward diffusion of Ni from this region to the top layers of the specimen, in such a way that could not be compensated with a lesser amount of inwardly diffused aluminium (i.e. Kirkendall effect).[3,15–17]

It has been reported that refractory elements primarily exist in the matrix γ phase of the substrate.[13] Their presence may result in the formation of refractory phases rich in these elements having a topologically close packed (TCP) structure, during high temperature exposure. Figure 6*a* shows the presence of these phases below the IDZ of the coating. A region below the IDZ of the coating that consists of these TCP phases, γ and γ', is called 'secondary reaction zone' SRZ.

These TCP phases are also shown in Fig. 6*b*, which is related to sample L-1050. The amount of these phases in this sample is lesser than that in sample H-1050. This might be because of the lower rate of transformation that occurred in L-1050 sample. In fact, these phases can



7 Images (SEM) of coatings formed by *a* pack H and *b* pack L at 1050°C, showing existence of refractory elements precipitates and Kirkendall voids in coating structure

be formed by depletion of Ni when outward diffusion of this element occurs and subsequently an increase in the concentration of alloying elements happens.[17] It is worth mentioning that, at this stage of coating, aluminium atoms did not penetrate yet into this region.

The TCP phases formed in the SRZ have primarily a needle-like or rod-like morphology.[13] As shown in Fig. 6, TCP phases are grown from IDZ columnar structure. It has been reported that the precipitation of the TCP phases occurs from the supersaturated γ phase of the substrate.[13] It has also been reported that the SRZ growth is comparatively greater within the dendrite cores than in the interdendritic regions.[13] This can result in a wavy appearance of the SRZ growth front as shown in Fig. 6*a*.

The difference of Ni chemical potential between the outer layer and the inner layer of the coating in the H-1050 sample is bigger than that of the L-1050 specimen, so the rate and the amount of outwardly diffused Ni are greater in the H-1050 sample. Thus, the amount of TCP phases and also Kirkendall voids in the H-1050 specimen can be more than those of the L-1050 specimen (*see* Fig. 6).

Conclusions

1. At the low temperature process, the inner layer of the coating was formed by inward diffusion of Al and outward diffusion of Ni did not occur at this temperature, whereas at the high temperature process, inward diffusion of Al occurred initially, followed by an outward diffusion of Ni, resulting in a columnar structure in the inner coating layer of these samples.
2. By increasing the Al activity in the powder mixture, the amount of Al entering into the inner layers increased, so the substrate transformed sooner to the coating structure and more changes occurred in the inner layer of samples coated by high activity powder compared to those coated by low activity powder. Also, the total thickness and Al concentration of the coating in samples coated by high activity powder were higher than those coated by low activity powder.
3. There are so many Kirkendall voids in the vicinities of columnar structures in IDZ and at the interface between the IDZ and the outer layer of the L-1050 sample, indicating that the rates of outward diffusion of Ni from these zones were higher than those of inward diffusion of Al.
4. Owing to the faster outward diffusion of Ni, the amount of Kirkendall voids and TCP phases within the SRZ of the samples coated at 1050°C by high activity powder is more than that of the samples coated by low activity powder under similar processing conditions.

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