Aluminide coating formation on nickel-base superalloys by pack cementation process

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A detailed study was carried out to investigate the effects of pack powder compositions, coating temperature and time on the aluminide coating formation process on a superalloy CMSX-4 by pack cementation. With the aid of recently developed thermodynamic analytical tools, powder mixtures that are activated by a series of fluoride and chloride salts were analysed and the effectiveness of these activators in transferring and depositing Al was evaluated at a range of coating temperatures. The Al chloride vapours formed at coating temperatures from 900°C to 1100°C were also analysed thermodynamically as a function of Al concentration in the original pack for the powder mixtures activated by 4 wt% $CrCl_3 \cdot 6H_2O$. Based on the thermochemical calculations, a series of coating experiments was carried out. Aluminide coatings were formed at temperatures from 850°C to 1100°C for periods varying from 4 hours to 8 hours using powder mixtures activated by NH_4Cl, $NaCl$ and $CrCl_3 \cdot 6H_2O$ and AlF_3. The effects of changing Al concentration as well as adding small quantities of Cr in the powder mixtures on the coating formation process were also investigated. The aluminide coatings were analysed using a range of techniques including SEM, EDX and XRD. The relationships between the mass gain and coating thickness and structure were investigated. The experimental results were compared with the predictions from thermochemical calculations. Based on the understandings established, an effective approach to control the aluminide coating parameters and structures was identified, which made it possible to optimise powder mixture compositions and coating conditions for different coating requirements. © *2001 Kluwer Academic Publishers*

1. Introduction

Pack cementation is a coating technique frequently used to apply protective coatings on metal surfaces to protect them from high temperature oxidation and corrosion damage. For the nickel-base superalloys, Al is the element most commonly deposited by this method to form nickel aluminide coatings. In some cases, inclusion of Cr or Si in the coating layer may also be desirable to enhance the high temperature corrosion resistance. At high operating temperatures, Al in the coated substrate surface oxidises preferentially to form a thin and dense alumina scale that acts as a diffusion barrier and hence substantially reduces the oxidation rates of substrates.

The pack cementation process is essentially an *in situ* chemical vapour deposition coating process. The substrates to be coated are placed in a sealed or semi-sealed container together with a powder mixture that consists of metal elements to be deposited (or their pre-alloyed master alloy), halide activators and an inert filler (usually alumina). The components may be buried in or placed above the powder mixture. The halide activators are usually added in small quantities (2 to 5 wt%) and they may be stable halide or unstable halide salts such as AlF_3, $NaCl$, NH_4Cl and NH_4F. The sealed container is heated under a protective atmosphere of Ar to

a temperature between 700°C to 1150°C and held there for a specified duration. At these coating temperatures, the halide activators react with the metal elements in the powder mixture and form a series of metal halide vapour species such as $AlCl$, $AlCl_2$, $AlCl_3$ and Al_2Cl_6 with a characteristic partial pressure distribution that is determined by their thermodynamic stability in a particular powder pack. The coating is formed via reduction reactions of metal halide vapours at the substrate surface and subsequent solid state diffusion between the metal elements and the substrate. For this reason, the coatings produced using this process are also termed *diffusion coatings*.

The partial pressures of metal halide vapours formed inside the container depend on compositions of powder mixtures and on coating temperatures. They play an influential role in determining the coating growth process on substrate surfaces. For a powder mixture of a specified composition, it is possible to calculate the partial pressures of these metal halide vapours using the available thermodynamic data. The earliest attempt at such thermodynamic analysis was that by Walsh [1] who calculated metal halide vapours at several coating temperatures for a number of simple powder systems containing single Al or Cr element and NH_4F or NH_4Cl

as an activator. Based on thermodynamic analysis, the possibilities of co-deposition of Al with Cr or Si were also discussed.

Levine and Caves [2] were probably the first to attempt to relate the thermochemical calculation results to the nickel aluminide coating formation process in a semi-sealed retort with particular focus on the effects of different activators on the aluminide coating thickness and structure. The activators studied included NaG and NH_4G (G = F, Cl, Br and I). They observed that the fluoride salts were the most, and iodide the least, effective activators for depositing Al. They also found that the changes in the rate of Al deposition as a result of changing activators had an effect on the coating microstructure.

More recently, a few attempts were also made to use thermodynamic analysis methods to predict the coating conditions for co-deposition of Al and Cr on nickel- base superalloy substrates and a certain amount of success was claimed [3–5]. However, coating formation involving co-deposition of multiple elements is a complex process depending not only on the halide vapour pressure distributions within the packs but also on the diffusion kinetics of different elements within the substrates. It becomes increasingly clear that more detailed understanding of the effects of pack compositions and coating conditions on the aluminide coating formation is needed in order to efficiently control the co-deposition process and to produce coatings with controlled microstructure and element concentration profiles. The present study is a detailed investigation into the thermodynamics and kinetics of nickel aluminide coating formation by the pack cementation technique on a nickel-base superalloy CMSX-4. It aims to provide a basis for designing pack compositions and coating conditions for producing aluminide coatings with predictable coating structures and thickness and for co-deposition of Al with Cr or Si or any other elements that could enhance oxidation and corrosion resistance of aluminide coatings.

2. Thermochemical calculations

As described previously, the pack compositions determine the partial pressure of Al halide vapours generated at high temperatures and hence can have profound influence on the aluminide coating formation process. With the aid of the recently developed thermochemical analysing tools, these partial pressures can be readily calculated for any specified pack compositions. In the present study, the ChemSage computer program was used in combination with the SGTE Solution Data Base system to analyse a range of aluminising pack compositions with particular focus on the effects of activators and Al concentration on the level of Al halide vapour pressures generated within the packs. The program carries out calculations using the Gibbs energy minimisation technique and the mass conservation rule [7]. The total pressure within the packs was assumed to be one atmosphere.

2.1. Effects of activators
The effectiveness of different halide salts in transferring and depositing Al from the packs to the sub-

strate surfaces depends essentially on the level of Al halide vapours that they generate within the packs at coating temperatures. In this study, five types of commonly used halide salts were investigated (NH_4Cl, NaCl, $CrCl_3 \cdot 6H_2O$, $AlCl_3$ and AlF_3). The initial pack compositions were comprised of 15 wt% Al and 3 wt% halide salt with the balance being Al_2O_3.

As described before, the halide salts react with Al and a series of Al halide vapour species is formed at high temperatures. Among these vapour species, AlX (X = F, Cl, Br, I) is the one that is mainly responsible for actually transferring and depositing Al onto the substrate surfaces. Therefore, the effectiveness of different activators in transferring and depositing Al may be assessed by comparing only the AlX partial pressures generated within different packs.

Fig. 1 compares the AlCl partial pressures generated in the pack activated by four types of chloride salts in the temperature range of 600°C to 1400°C. It demonstrates that NH_4Cl and $CrCl_3 \cdot 6H_2O$ are the most effective amongst the four activators analysed. Below 1100°C, $AlCl_3$ is more effective than NaCl. But, above 1100°C, the reverse is the case.

Fig. 2 compares the partial pressure of AlCl with that of AlF in the packs activated by $AlCl_3$ and by AlF_3 respectively in the temperature range of 600°C to 1200°C. It can be seen that the partial pressure of AlF is much higher than that of AlCl in the normal coating temperature range of 700°C to 1150°C. Therefore, AlF_3 is a much more effective activator than $AlCl_3$.
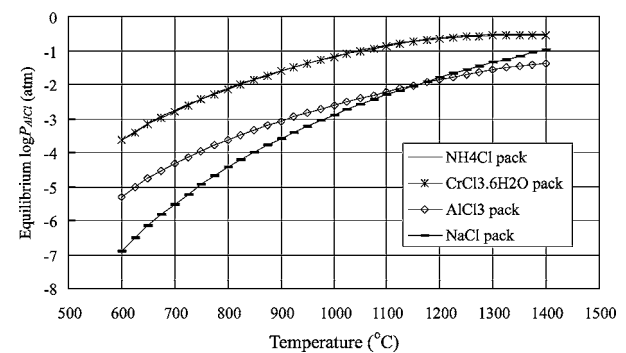

Figure 1 A comparison of equilibrium partial pressure of AlCl in the $AlCl_3$, NaCl, NH_4Cl and $CrCl_3 \cdot 6H_2O$ activated packs.
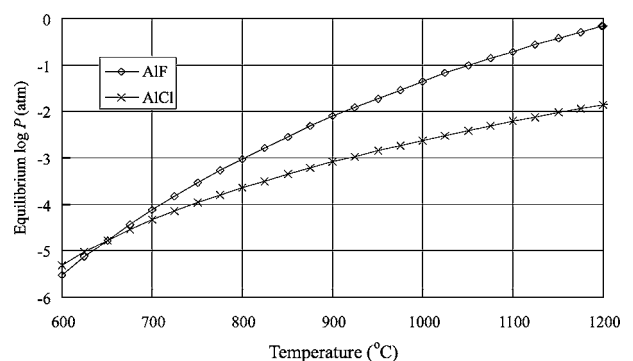

Figure 2 A comparison of vapour pressure of AlF in the AlF_3 activated pack with that of AlCl in the $AlCl_3$ activated pack (Al: 15 wt%, AlF_3 or $AlCl_3$: 3 wt%, Al_2O_3: 82 wt%).
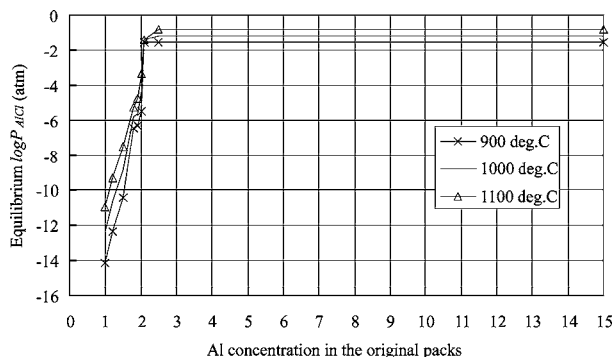
Figure 3 Dependence of AlCl partial pressure on Al concentration in aluminising packs activated by 4 wt% $CrCl_3 \cdot 6H_2O$.

2.2. Effect of Al concentration

The effects of Al concentration on the AlCl partial pressure were investigated for the aluminising packs activated by 4 wt% $CrCl_3 \cdot 6H_2O$. The Al concentration in the original packs was varied from 1 wt% to 15 wt%. The results for coating temperatures of 900°C, 1000°C and 1100°C are presented in Fig. 3. It can be seen that the AlCl partial pressure increased strongly as the Al concentration in the original pack was increased from 1 to 2 wt% and then remained constant with further increase in Al concentration in the original packs. This behaviour can be understood by analysing the Al concentration in the condensed phase at coating temperatures. Fig. 4 is a plot of such concentration against coating temperatures for a pack with an original Al concentration of 15 wt%. It can be seen that the Al concentration in the condensed phase is only slightly over 12.9 wt% at 900°C, indicating that more than 2 wt% of Al is converted to the vapour phase at temperatures higher than 900°C, mostly in the form of aluminium chlorides. Thus, when the Al concentration in the original pack is only 2 wt% or less, Al in the packs will be all present in the vapour phase at temperatures over 900°C and there will not be any Al in the condensed phase, resulting in strong dependence of AlCl partial pressure on Al concentration in the original pack. It can also be deduced from Fig. 4 that when Al concentration in the original packs is above 2.4 wt% there will always be some Al present in the condensed phase to maintain equilibrium with those in the vapour phase at temperatures at or below 1100°C. Therefore, the AlCl partial pressure may only depend on temperature but not on Al concentration in the original pack. The coating experimental results
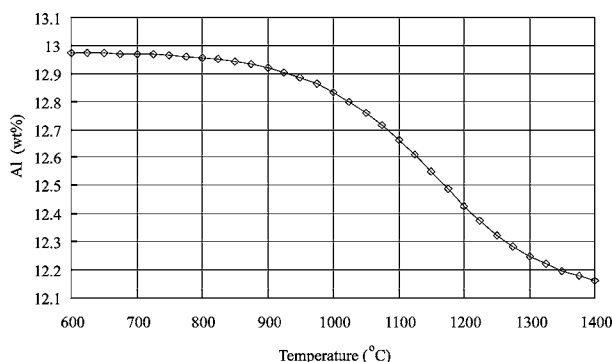

Figure 4 Al concentration in the condensed phase for a pack with an original composition of 15Al-4CrCl$_3$·6H$_2$O-81Al$_2$O$_3$ (wt%).

T A B L E I Nominal composition of the CMSX-4 substrate (wt%)

Cr	Co	Mo	W	Ta	Re	Al	Ti	Hf	Ni
6.5	9	0.6	6	6.5	3	5.6	1	0.1	61.7

to be presented in the following sections demonstrate that Al concentration in the original packs can strongly influence the kinetics of the coating formation process and the characteristics of the coatings formed.

3. Experimental procedures

The substrate used for this study is a commercial alloy, CMSX-4. The nominal composition of this alloy is given in Table I. The alloy rod of about 16 mm in diameter was sliced into buttons with a thickness between 2 mm to 3 mm. The surfaces of the buttons were ground and polished to a 1200 grit finish. The samples were then degreased and weighed before placing them in pack powders.

Pack powder mixtures were prepared by weighing out and mixing appropriate amounts of powders of Al_2O_3, Al and halide salts. The halide salts studied included NH_4Cl, $NaCl$, $CrCl_3 \cdot 6H_2O$ and AlF_3. They were ground using a mortar and pestle before they were weighed and added into the pack powders. The average particle sizes of Al_2O_3 and Al powders were 50 μm and 75 μm respectively.

The packs were prepared by filling the pack powders around the substrates in a cylindrical alumina retort of 30 mm diameter and 40 mm length. The retort was then sealed with an alumina lid and cement. The cement seal was cured for at least one hour at room temperature and then further cured at an oven temperature of about 80°C for at least two hours before the pack was loaded into an alumina tube furnace with gas circulation fittings. Once loaded, the furnace was circulated with argon and the temperature of the furnace was raised to 150°C and held there for 2 hours to facilitate further cure of the cement and to remove any moisture from the pack. After that, the temperature of the furnace was raised to coating temperatures between 850°C to 1150°C at a heating rate of 10°C per minute and was held there for the required duration. The furnace was then cooled to room temperature. The coating times reported were the holding times at coating temperatures.

The weight gain (in mg/mm^2) of specimens was derived by measuring the specimen weight before and after coating and the surface area of specimens.

The cross-section of the coated samples was examined using optical microscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) and back scattered electron imaging facilities. The coating thickness was derived from the EDS data.

4. Results and discussion
4.1. Effects of activator, temperature and time

Initial coating experiments were carried out using packs containing 15 wt% of Al. The effects of coating temperature, time and the type of activators on coating

TABLE II Coating results for the aluminide cementation packs

Sample	Coating temperature (°C)	Coating time (hours)	Weight gain (mg/mm^2)	Thickness (μm)	Major phase
Activator: NH$_4$Cl					
AC1/850/4	850	4	–	110	Ni$_2$Al$_3$
AC1/850/8	850	8	–	120	Ni$_2$Al$_3$
AC1/1000/4	1000	4	0.4780	250	Ni$_2$Al$_3$
AC1/1000/8	1000	8	0.6017	312	Ni$_2$Al$_3$
Activator: NaCl					
AC3/850/4	850	4	–	20	Ni$_2$Al$_3$
AC3/850/8	850	8	–	32	Ni$_2$Al$_3$
AC3/1000/4	1000	4	0.1602	93	Ni$_2$Al$_3$
AC3/1000/8	1000	8	0.3850	216	Ni$_2$Al$_3$
Activator: CrCl$_3$·6H$_2$O					
AC4/900/8	900	8	0.2516	135	Ni$_2$Al$_3$
AC4/1000/2	1000	2	0.2911	156	Ni$_2$Al$_3$
AC4/1000/4	1000	4	0.3936	220	Ni$_2$Al$_3$

thickness, structure and element concentration profiles in the surface layer were investigated. Three types of chloride salts (NH$_4$Cl, NaCl and CrCl$_3$·6H$_2$O) were assessed as activators. For the packs activated by NH$_4$Cl and NaCl, the amount of activators added to the powder packs was 3 wt%. But, for the packs activated by CrCl$_3$·6H$_2$O, the amount of activator added was 4 wt%.

The balance in each case was Al$_2$O$_3$. The substrates were coated at temperatures from 850°C to 1000°C for 2 hours to 8 hours.

Table II summarises the coating parameters obtained. The major phase in the surface layer was determined using XRD measurement on the as-coated surfaces and was found to be Ni$_2$Al$_3$ for all the coatings. Fig. 5
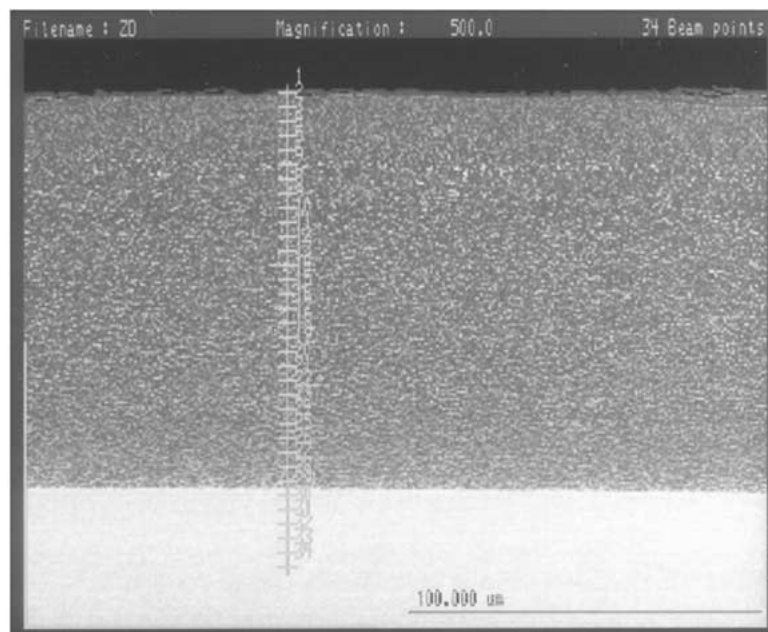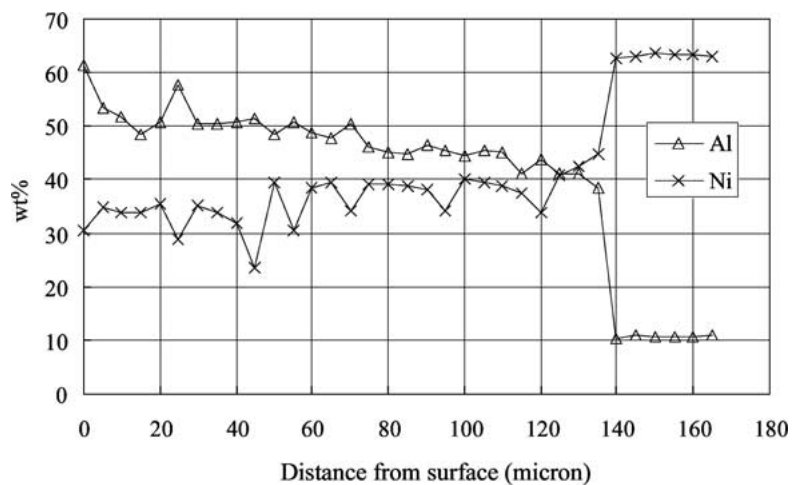

Figure 5 Concentration profiles of Ni and Al and cross-sectional SEM image for the AC4/900/8 sample.

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shows an example of Al and Ni concentration profiles obtained by EDX measurement and a cross-sectional SEM image for a sample coated at 900°C for 8 hours using $CrCl_3 \cdot 6H_2O$ as an activator (AC4/900/8). The SEM images for all other samples had the same features as those shown in Fig. 5. It can be seen that a uniform aluminide coating layer was formed on the surface in which other substrate elements were precipitated, demonstrating that the coating was formed predominantly by inward Al diffusion. The EDX measurements revealed that the bright and speckled looking phase within the aluminide layer contained high concentrations of Cr and W.

Since the microstructures of all the coatings were the same, the relationship between the weight gain and coating thickness should be linear and this linear relationship should not be affected by the type of activators or by the processing conditions used. Fig. 6 plots the coating thickness against the weight gain for all such data from Table II. It demonstrates that the relationship is indeed linear. The solid line in Fig. 6 is the least squares fit to the data points and gives the following relationship

$$h = 13 + 503.6W \qquad (1)$$

where h is coating thickness in μm and W is weight gain in mg/mm^2. Such a simple relationship between the coating thickness and weight gain implies that, for the packs containing 15 wt% Al, activators and coating temperatures may only affect the coating growth rate, but not the coating formation process and the coating structure produced.

Because the coatings were formed by the inward diffusion of Al, the rate of coating formation would mainly depend on the level of AlCl partial pressure generated in the packs. It is expected that a higher AlCl partial pressure would induce a higher coating growth rate. Thus, according to the thermochemical calculations presented in Fig. 1, the coating growth rates for the NH_4Cl and $CrCl_3 \cdot 6H_2O$ activated packs would be comparable, but, both would be much higher than that for the NaCl activated packs. This is in excellent agreement with the thickness data presented in Table II, which showed that under the same coating conditions the coating thicknesses produced by the NH_4Cl activated packs were comparable to those by the $CrCl_3 \cdot 6H_2O$ activated packs, but much thicker than those produced by the NaCl activated packs.
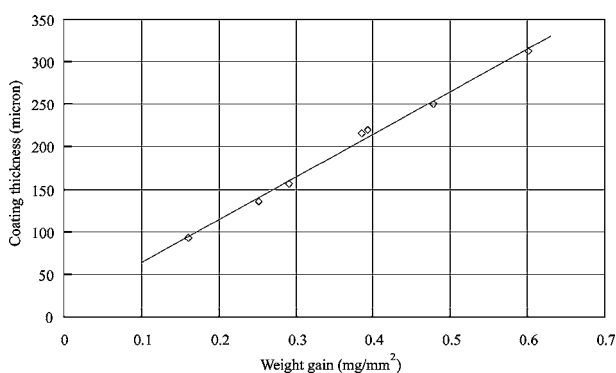
4.2. Effects of Al content

The coating thickness data presented in Table II are for the packs containing 15 wt% of Al. The coating thickness produced by the NH_4Cl or $CrCl_3 \cdot 6H_2O$ activated packs with such a high Al content was higher than 100 μm even when the coating was produced at a temperature as low as 850°C and for only 4 hours. In industrial practice, the aluminide coating thickness is usually in the range of 40 μm to 70 μm for nickel-base superalloys and it is not normal practice to use NaCl as an activator. Therefore, it is clearly necessary to reduce the coating thickness for the NH_4Cl or $CrCl_3 \cdot 6H_2O$ activated packs by adjusting the pack compositions. The most effective way to achieve this is by reducing the Al activity or concentration in the original packs.

In order to investigate the effects of Al content on the coating thickness and structures, four more powder packs with much reduced Al concentration of 1 to 2.5 wt% were studied using $CrCl_3 \cdot 6H2O$ or AlF_3 as an activator. Table III lists the pack powder compositions. The CUK/UNN powder mixture was a commercial powder mix and was supplied by CUK Limited. Using these powder mixtures, the substrates were coated at temperatures from 900°C to 1100°C for 8 or 16 hours. The coating parameters obtained are summarised in Table IV. It can be seen that apart from the AC5/1100/8 sample the coating thicknesses of all other samples were within the more desirable range.

The coating thickness was also calculated from the weight gain data using Equation 1. They were also included and compared with the thicknesses measured by SEM in Table IV.

For the coatings produced with AC5 and CUK/UNN packs, the major phase in the coating layer was Ni_2Al_3. Despite diverse coating conditions and activators used, most of the coatings produced with these packs, apart from AC5/900/8, showed a close agreement between the measured and calculated thickness, the largest difference being only 7% in the case of AC5/1100/8 sample. However, for the AC5/900/8 sample, the calculated coating thickness was 18% higher than the measured one.

In order for Equation 1 to be applicable, the coating must be of an inward diffusion character with Ni_2Al_3 as a major phase and have a uniform structure. Fig. 7 presents a SEM micrograph and concentration profiles of Al and Ni and other major elements in the coating layer for the AC5/900/8 sample. It can be seen that although the coating was indeed formed predominantly by inward diffusion of Al, it consisted of two layers. The outer layer was fully phase separated and had a thickness about 16 μm. EDX and XRD analysis confirmed that this was a Ni_2Al_3 phase layer rich in Al. Underneath

Figure 6 Relationship between coating thickness and gain weight for the aluminide coatings.

TABLE III Pack powder compositions for aluminide coatings

	Composition (wt%)			
Powder mix	Al	$CrCl_3 \cdot 6H_2O$	AlF_3	Al_2O_3
AC5	2.5	4	0	93.5
AC6	1	4	0	95
AC7	1.2	4	0	94.8
CUK/UNN	1–2	0	1–2	Balance

TABLE IV Further results for aluminide coating formation

Sample	Coating temperature (°C)	Coating time (hours)	Weight gain (mg/mm^2)	Thickness (µm)		Major phase
				h_m	h_c	
AC5						
AC5/900/8	900	8	0.0609	36	44	Ni$_2$Al$_3$
AC5/900/16	900	16	0.1157	67	71	Ni$_2$Al$_3$
AC5/950/8	950	8	0.1030	65	65	Ni$_2$Al$_3$
AC5/1100/8	1100	8	0.2331	140	130	Ni$_2$Al$_3$
AC6						
AC6/1100/8	1100	8	0.0327	48	29	NiAl
AC7						
AC7/1000/8	1000	8	0.0461	39	36	NiAl
AC7/1100/8	1100	8	0.1078	77	67	NiAl
CUK/UNN						
CUK/UNN/950/16	950	16	0.1010	65	64	Ni$_2$Al$_3$

h_m: measured thickness; h_c: calculated thickness.

the top layer was a 20 µm thick inner layer in which full scale phase separation was about to occur. The EDX analysis showed that the Al concentration in this layer was on average about 40 wt%, indicating that the major phase in this layer was also Ni$_2$Al$_3$. Therefore, this coating structure did not fully satisfy the conditions for which Equation 1 may be applicable.

Compared with the coatings formed with the 15 wt% Al pack, the occurrence of the two layer structure in the coatings produced by the 2.5 wt% Al pack may be
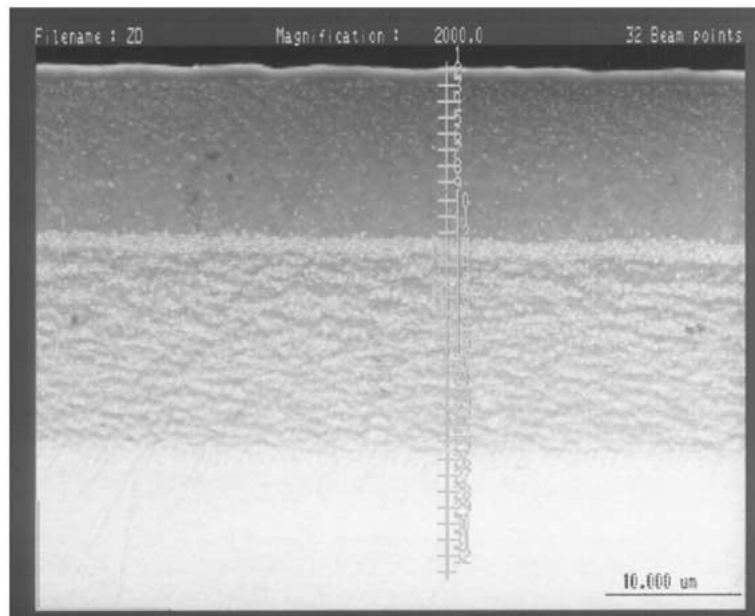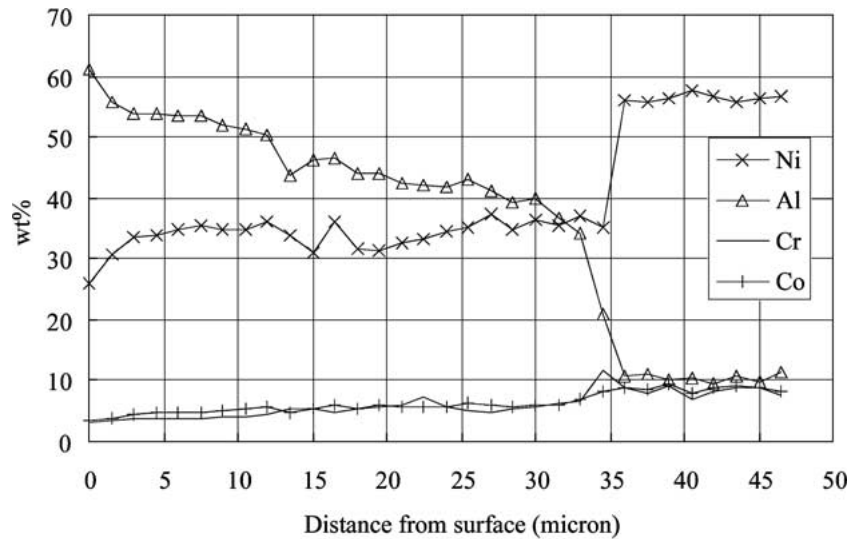

Figure 7 Element concentration profiles and cross-sectional SEM image for the AC5/900/8 sample.
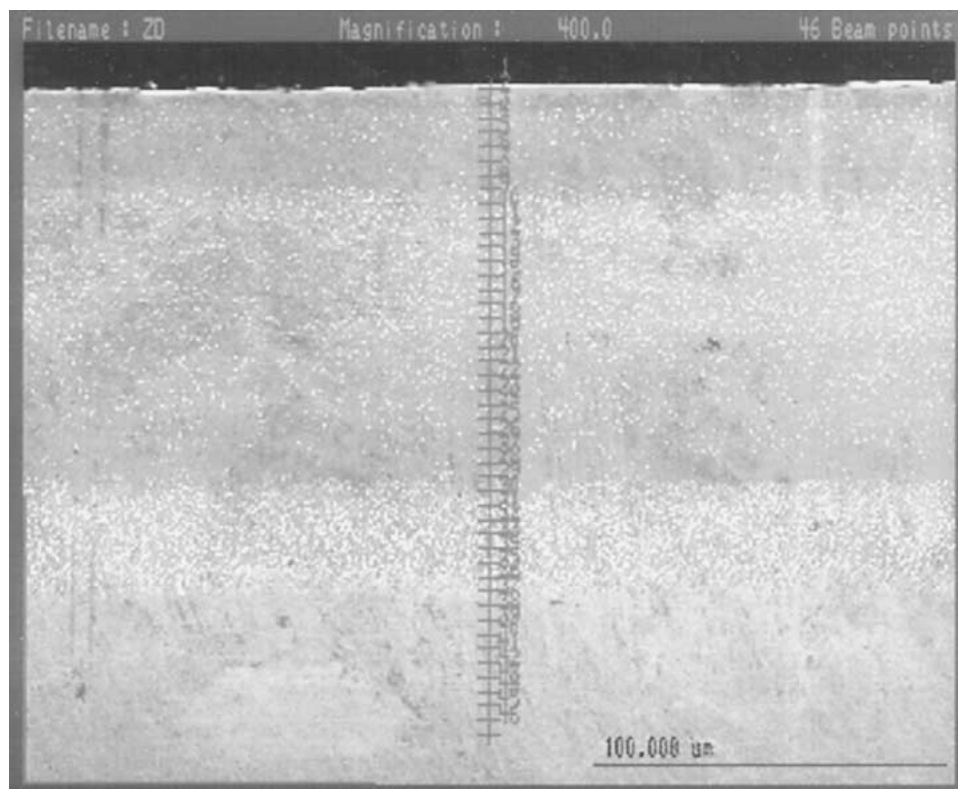
Figure 8 Cross-sectional SEM image for the AC5/1100/8 sample.

attributed to the formation of a much larger Al deple-
tion zone in the latter pack adjacent to the substrate
surface. The formation of Al depletion zone had pre-
viously been observed and discussed by a number of
investigators [2, 6]. The size of it is known to increase
with coating time at any specified coating temperature,
causing progressive reduction in the rate of transferring
Al by the halide vapours. However, it was expected that
such a two-layered structure would not occur at a suffi-
ciently high coating temperature at which the diffusion
of the AlCl vapour through the depletion zone becomes
sufficiently fast. Fig. 8 shows a SEM micrograph for the
AC5/1100/8 sample, which was coated at $1100°C$ for
8 hours using the same pack as for the AC5/900/8
sample. It can be seen that the two-layered structure
indeed did not occur in this coating. However, limited
outward diffusion of Ni became evident in this sample,
although the coating was primarily formed by inward
Al diffusion.

The powder packs of AC6 and AC7 contained only
1 wt% and 1.2 wt% Al respectively. The data in Table IV
revealed that there was usually a large discrepancy be-
tween the measured and calculated coating thickness,
the former was usually larger than the latter. This is
not surprising because it was found that the coatings
produced by these packs had a structure that is fun-
damentally different from those produced by the AC5
packs and packs containing 15 wt% Al.

Fig. 9 shows a SEM micrograph and Al and Ni con-
centration profiles for the AC7/1000/8 sample. All other
coatings produced by AC6 and AC7 packs were of the
same features. It can be seen that the microstructure of
the coating, which was consisted of a well defined top
layer with NiAl as its major phase and a large diffusion

zone underneath, showed some typical characters of the
so called "low activity and high temperature" outward
diffusion coatings [7, 8]. This suggests that the coat-
ing was formed predominantly by outward diffusion
of Ni.

The observed change in the coating formation pro-
cess from inward Al diffusion to outward Ni diffu-
sion was undoubtedly caused by the consequent re-
duction in the AlCl partial pressure in the packs as
the Al concentration in the original packs was reduced
from 2.5 wt% or over to a level well below 2 wt%.
This is consistent with the thermodynamic calculation
results, which showed that the AlCl partial pressure
in packs drops sharply when Al concentration in the
original packs is below 2 wt% (Fig. 3). Thus, it may
be suggested that for the packs activated by 4 wt%
$CrCl_3·6H_2O$ the Al concentration threshold for the
transition of the aluminide coating formation process
from inward Al diffusion to outward Ni diffusion is
about 2 wt%. When the Al concentration in the origi-
nal pack is above 2 wt%, the coating forms mainly by
inward Al diffusion process. When the Al concentra-
tion in the original pack is below 2 wt%, the coating
forms mainly by outward Ni diffusion process. How-
ever, it should be realised that this transition in coat-
ing formation process may only occur at sufficiently
high temperatures at which the Ni diffusion rate be-
comes sufficiently fast. The temperature threshold for
this transition is probably around $950°C$ for the sub-
strate studied here. Only at temperatures higher than
that, may coating formation through outward Ni dif-
fusion be possible when the AlCl partial pressures in
packs are reduced to sufficiently low levels. At temper-
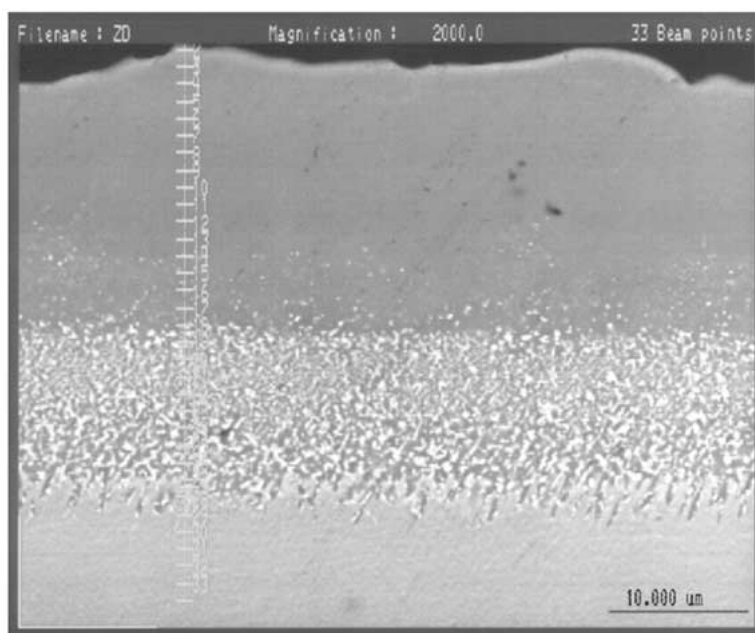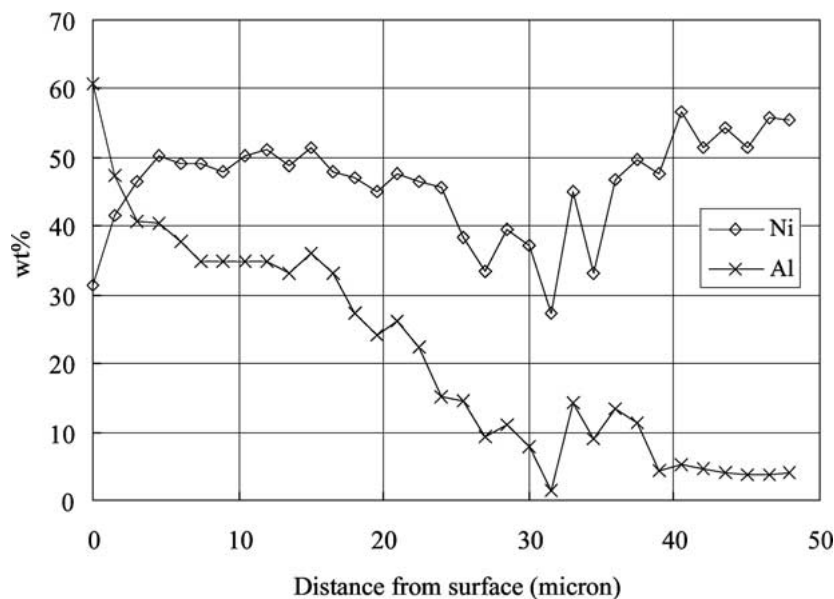atures below $950°C$, coatings may only form through

Figure 9 Al and Ni concentration profiles and a cross-sectional SEM image for the AC7/1000/8 sample.

the inward Al diffusion mechanism even when the Al concentration or AlCl partial pressure in the packs becomes very low.

4.3. Effects of adding Cr

Cr is usually added into the aluminising packs either to regulate the Al activity for effective control of the aluminide coating formation process or to co-deposit Cr with Al onto substrate surfaces. The latter however is a complex process and requires careful control of pack compositions as well as coating conditions.

In order to investigate the effects of adding Cr into the packs on the aluminide coating formation process, 5 wt% of alumina powder in the AC5 pack was replaced by pure Cr powder. Therefore, the resulting pack composition was 2.5Al-5Cr-4CrCl$_3$·6H$_2$O-88.5Al$_2$O$_3$ (wt%) and was designated as ACC10. The substrate was coated using this pack at 1100°C for 8 hours, the same

coating conditions as those used for the AC5/1100/8 sample, and the coating formed was designated as ACC10/1100/8. Fig. 10 shows a SEM photograph and concentration profiles of major elements present in the coating layer for this sample. It can be seen that the coating structure was similar to the AC7/1000/8 sample shown in Fig. 9, consisting of a single-phase top layer and a diffusion zone underneath. The major phase in the coating layer was NiAl as determined by XRD. The thickness of the top layer was almost equal to that of the diffusion zone, both being ∼34 μm. Thus, the ACC10/1100/8 coating was also formed primarily by outward Ni diffusion.

The coating structure for the ACC10/1100/8 sample was in sharp contrast to that for the AC5/1100/8 sample, which was coated using the same coating conditions, but with a corresponding pack that contained no Cr (see Fig. 8). As discussed previously, the former coating developed primarily by outward Ni diffusion and the
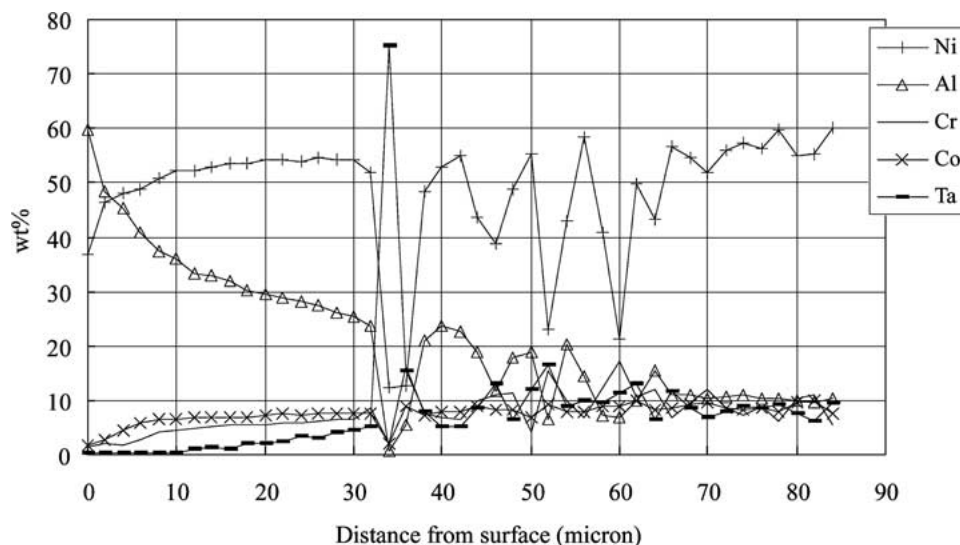
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Figure 10 Cross-sectional SEM image and element concentration profiles for the ACC10/1100/8 sample.

latter by inward Al diffusion. Such a profound change in coating formation process, caused by adding a small quantity of Cr into the aluminising packs, strongly suggests that Cr can induce a substantial reduction in the Al activity and hence the AlCl partial pressure in the pack powders at coating temperatures. However, thermochemical calculations carried out using data for pure Al and Cr elements did not show much difference between the AlCl partial pressure in the ACC10 pack and that in the AC5 pack, both being about 0.15 atm at 1100°C. Therefore, it is likely that Al reacted with Cr and formed an Al-Cr alloy at the coating temperature, which could in turn cause a substantial reduction in the Al activity and hence the AlCl partial pressure in the pack powders. Further studies are clearly needed to confirm this hypothesis.

5. Conclusions

1. Thermochemical calculations were carried out for the aluminising packs activated by halide salts. These showed that the effectiveness of the packs in transfer-ring and depositing Al could be considerably affected by the type of halide salts used. Among the chloride salts studied, the calculated results demonstrated that NH_4Cl and $CrCl_3 \cdot 6H_2O$ are the most effective and NaCl the least effective activators. This was in excellent agreement with the coating experimental results. It was also found that AlF_3 is a more effective activator than $AlCl_3$.

2. For the packs activated with 4 wt% $CrCl_3 \cdot 6H_2O$, the AlCl partial pressure generated at any specified coating temperature at or above 900°C was found to increase strongly with initial increase in Al concentration in the original packs from 1 wt% to slightly over 2 wt% and then remained constant with further increase in Al concentration. This is because when Al content in the original packs is higher than 2 wt%, it can also exist in the condensed phase, establishing an equilibrium with that in the vapour phase at coating temperatures.

3. The effect of the pack Al activity or concentration on the coating kinetics and structure was studied at several coating temperatures in the range of 900°C

to 1100°C for powder packs activated with 4 wt% CrCl$_3$·6H$_2$O. It was found that when Al concentration in the packs was 2.5 wt% or higher, the aluminide coating may only form *via* inward Al diffusion and the coatings formed comprised Ni$_2$Al$_3$. Changing coating temperatures may affect the coating growth rate, but not the coating formation process. However, when Al concentration in the packs was reduced to 1.2 wt% or below. Aluminide coating may only form primarily *via* outward Ni diffusion at coating temperatures higher than 1000°C and coatings so formed consisted of a NiAl layer with a diffusion zone underneath.

4. Adding Cr into the aluminising packs can profoundly influence the aluminide coating formation process and hence the coating structure obtained. It was demonstrated that coating formation process could be changed from an inward Al diffusion to an outward Ni diffusion process by introducing Cr into the packs at 1100°C. This was probably due to the formation of Al-Cr alloys at the coating temperature, which in turn caused a substantial reduction in Al activity and hence in the AlCl partial pressure generated in the pack at the coating temperature.

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