Co-deposition of aluminide and silicide coatings on γ-TiAl by pack cementation process

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Thermochemical analyses were carried out for a series of pack powder mixtures for deposition of aluminide and for co-deposition of aluminide and silicide coatings on γ-TiAl by the pack cementation process. Based on the results obtained, experimental studies were undertaken to identify optimum pack powder mixtures for depositing adherent and coherent aluminide and silicide coatings. Pack powder mixtures activated by 2 wt% $AlCl_3$ was used to aluminise γ-TiAl at 1000°C. With proper control of pack compositions and coating conditions, an aluminide coating of $TiAl_3$ with a coherent structure free from microcracking was deposited on the substrate surface via inward diffusion of aluminium. The results of thermochemical calculations indicated that co-deposition of Al and Si is possible with $CrCl_3 \cdot 6H_2O$ and $AlCl_3$ activated pack powders containing elemental Al and Si as depositing sources. Experimental results obtained at 1100°C revealed that $CrCl_3 \cdot 6H_2O$ is not suitable for use as an activator for co-depositing aluminide and silicide coatings on γ-TiAl. It caused a significant degree of degradation instead of coating deposition to the substrate. However, adherent coatings with excellent structural integrity consisting of an outer $TiSi_4$ layer and an inner $TiAl_3$ layer were successfully co-deposited at 1100°C and 1000°C using pack powder mixtures activated by $AlCl_3$. It is suggested that such coatings were formed via a sequential deposition mechanism through inward diffusion of aluminium and silicon. Discussion is presented on the issues that need to be considered to ensure the deposition of aluminide and silicide coatings with coherent structure free from microcracking on γ-TiAl by the pack cementation process.
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1. Introduction

The intermetallic alloy γ-TiAl has low density and excellent strength retention properties at operating temperatures up to 850°C [1]. It thus offers particularly good potential in critical strength application areas for aerospace and power industries where high specific strength is required in order to enhance performance and operating efficiency, which are vital for fulfilling ever increasing technical, economical as well as environmental requirements. Indeed, it is estimated that, with the use of γ-TiAl, potential component weight savings of over 50% can be achieved over conventional superalloys. However, in order to fully utilise its potentials, efficient and effective technologies must be developed that will ensure its long-term mechanical and structural integrity in oxidative and corrosive environments at high temperatures.

Additions of ternary alloying elements such as Cr, Si, Nb and W can improve its room temperature ductility and also moderately increase its high temperature oxidation and corrosion resistance [2]. But, further alloying usually leads to deterioration of its mechanical properties. It is now generally recognised that deposition of coatings that can form dense, adherent and slow growing oxide scales offers the most promising approach to provide solutions for its long term environmental stability of at high temperatures.

A number of studies were reported on attempts to develop coatings and coating techniques for protecting γ-TiAl. In a recent review, the strategies to develop high temperature degradation resistant coatings for TiAl based intermetallics were discussed [3]. In particular, the coatings of the alloy type MCrAlY (M = Ni, Co) or TiCrAl have demonstrated promising application potentials [4, 5]. These coatings are usually deposited using various thermal or plasma spray techniques and more recently using EB-PVD. These facilities not only require fairly high capital investment but also impose great constraints on operation flexibility and on productivity. More importantly, coatings produced often contain high level of porosity in the case of thermal spray process, which degrades coating's long term performance. Therefore, there is a genuine industrial demand to develop a more efficient process for depositing protective coatings for γ-TiAl.

Pack cementation process is a versatile and economical process normally used to deposit aluminide diffusion coatings on nickel-base superalloys [6–9].

However, it is expected that this generic technology can be further developed to enable deposition of multiple element coatings on titanium base alloys including γ-TiAl. In comparison with other techniques for deposition of coatings on metal alloy substrates, pack cementation process has following distinctive advantages:

a) high volume and economical deposition of diffusion coatings with easily controllable thickness up to 200 μm;
b) simultaneous deposition of multiple elements;
c) superior adhesion between the coating and the substrate;
d) applicable for a wide range of shapes and sizes and not subjected to line-of-sight restrictions;
e) low environmental impact.

The pack cementation is essentially an *in situ* chemical vapour deposition process activated by halide salts such as NH_4Cl, NH_4F or $NaCl$ etc. The substrates to be coated are embedded into (in-pack process) or suspended above (out-pack process) a well-mixed powder mixture consisting of pure or alloyed depositing elements, a halide salt as an activator and an inert filler (normally Al_2O_3). The whole pack is then heated to a high temperature at which the activator reacts with the depositing elements to form a series of halide vapours. The halide vapours would pass through the porous pack to reach the substrate surface. The coating is formed *via* decomposition of these halide vapours on the substrate surface and subsequent solid state diffusion between the deposited elements and the substrate.

The partial pressure distribution of the halide vapours formed within the pack at high temperatures is determined by the composition of pack powder mixture and by coating temperature. They can have a critical influence on the deposition process and hence on the type of coatings formed on the substrate surface. With the assistance of the improved computer software and database systems for thermochemical analysis, the partial pressures of various halide vapours generated at the coating temperatures can be readily calculated. The results may then be used to identify suitable pack powder compositions and coating conditions for deposition and co-deposition of multiple element diffusion coatings on γ-TiAl.

Some research efforts have been made in the past decade to apply the pack cementation process to deposit aluminide coatings on γ-TiAl to enhance its oxidation resistance [10–13]. But, it has been found that the coatings so deposited usually contain large numbers of microcracks, which severely restricts the application potential of these coatings. Further more, no detailed studies have been reported on using the pack cementation method to co-deposit multiple elements such as Al, Cr and Si to form diffusion coatings on γ-TiAl. Incorporation of Cr or Si into the coating layer is known to be beneficial for increasing not only oxidation but also hot corrosion resistance of the coatings [3–5]. This study is an attempt to apply the latest understandings of the pack cementation technique to develop an easily controllable process capable of simultaneously depositing multiple elements on γ-TiAl to form diffusion coatings with de-fined thermochemical and mechanical properties. This paper reports the results of our initial efforts to identify pack compositions and coating conditions suitable firstly for producing adherent and coherent aluminide coating and secondly for depositing aluminide and silicide coatings on γ-TiAl *via* a single step co-deposition procedure.

2. Experimental procedures

The γ-TiAl substrate used in this study was supplied by the ABB Company with a nominal composition of Ti-31Al-8.6W wt%. The alloy rod of about 20 mm in diameter was sliced into buttons with a thickness about 2 mm. Surfaces of the buttons were ground and polished to a 1200 grit finish. 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, Si and a halide salt. The particle sizes of Al_2O_3, aluminium and silicon powders were less than 50 μm, 75 μm and 20 μm respectively. The halide salts used as activator were $CrCl_3 \cdot 6H_2O$ and $AlCl_3$ (anhydrous). These chemicals were ground by hand using an agate mortar and pestle, but not sieved, before being weighed and added into the pack powders.

The packs were prepared by burying the substrates in the pack powders 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. The pack was then loaded into an alumina tube furnace fitted with gas circulation fittings. The furnace was circulated with argon and the temperature was raised to and held at 150°C for 2 hours to facilitate further cure of the cement and to remove any moisture from the pack. The furnace temperature was then raised to a final coating temperature, normally at 1000°C or 1100°C, at a heating rate of 10°C per minute and was held there for a required duration. The furnace was then cooled to room temperature at its natural rate by switching off its power supply while maintaining the argon gas flow. The coating times reported were the holding times at the coating temperatures.

The coated samples were characterised using X-ray diffraction (XRD) and optical microscopy techniques. The cross-section of the coatings were analysed using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and back scattered electron imaging facilities. The coating thickness was estimated from the EDS data.

3. Thermochemical calculations

As discussed previously, the partial pressures of halide vapour species generated at high temperatures have a crucial influence on the coatings and coating structures formed on the substrates. In this study, the Chem-Sage computer program is used in combination with the SGTE database system to calculate these partial pressures for a range of pack powder compositions. The results obtained were used to identify best possible coating conditions and pack powder mixtures for

depositing aluminide and for co-depositing silicide and aluminide coatings on γ-TiAl with a coherent structure free of microcracks. The program performs the calculations based on the Gibbs energy minimisation technique and the mass conservation rule [14]. For all the calculations undertaken in this study, the total pressure within the packs was assumed to be one atmosphere.

4. Results and discussions
4.1. Deposition of aluminide coatings
Deposition of aluminium by pack cementation to form coherent aluminide coatings on the substrate surface of γ-TiAl, or aluminising, is not as straightforward as it seems even to those who familiar with the pack cementation technique. It requires optimum control in pack chemistry and coating conditions. Indeed, only "after numerous trials", Munro and Gleeson [10] identified a pack containing 5 wt% Al, 0.5 wt% NH_4F and 94.5 wt% Al_2O_3 that was capable of producing a smooth and aluminised surface. However, closer examinations under the optical microscope revealed occurrence of extensive microcracking running across the coating thickness in all coatings. Other investigators [11] used similar packs activated by 3 wt% NH_4Cl to study the effects of alloy element additions such as Cr and Nb on the kinetics of aluminide coating growth on γ-TiAl and the properties of the coatings formed. But, extensive microcracking running across the coating thickness also occurred. Further more, it must be pointed out that the halide salts such as NH_4F and NH_4Cl are very unstable and decompose very rapidly at high temperatures, generating considerably high pressure within the crucible or retort. This imposes a real safety risk especially when large batches are used. Therefore, it is clearly necessary to replace NH_4F and NH_4Cl with stable activators in order to establish an industrially viable process in which aluminium deposition and subsequent inter-diffusion processes could be precisely controlled to enable the formation of aluminide coatings free from microcracking.

In this study, halide salts of AlF_3 and $AlCl_3$ were considered as potential replacements for NH_4F and NH_4Cl.

Both salts are relatively stable. For aluminising packs activated by the fluoride and chloride salts, the effectiveness of different activators in transporting and depositing aluminium can be assessed by the partial pressure of the AlF or AlCl vapour species generated at the coating temperatures [6]. Thermochemical calculations were thus carried out for the pack powder composition 15Al-3AlF$_3$ or AlCl$_3$-82 Al$_2$O$_3$ wt%. Fig. 1 compares the partial pressure of AlF in the pack activated by AlF_3 with that of AlCl in the pack activated by $AlCl_3$ in the temperature range of 600°C to 1200°C. It can be seen that the vapour pressure of AlF is much higher than that of AlCl in the temperature range of 900°C to 1100°C. This suggests that, in this temperature range, which is important for aluminising γ-TiAl, AlF_3 is a much more effective activator than $AlCl_3$. However, since the chloride salts are considered more environmentally friendly than the fluoride salts, $AlCl_3$ was chosen in this study as an activator for aluminising γ-TiAl.

A series of specimens were aluminised at 1000°C for 6 hours using packs of varying compositions. After a few trials, it was found that a pack containing 4 wt% Al, 2 wt% AlCl$_3$ and 94 wt% Al$_2O_3$ is sufficient to produce a smooth and aluminised surface layer under the coating conditions used.

Fig. 2 shows a XRD spectra measured from the as-coated surface. It can be seen that the major phase in the surface layer is $TiAl_3$, which is consistent with the results obtained by other investigators [10–12].

Fig. 3 presents a cross sectional SEM image of the as-aluminised specimen and concentration profiles of Al, Ti and W in the coating layer measured by EDS. It can be seen that the coating is very uniform and free of microcracks. The measured concentration profiles revealed a two-layer phase structure across the thickness of the coating layer. The outer layer with a thickness about 18 μm contained about 70 to 66 wt% Al, indicating that this is a uniform $TiAl_3$ phase rich in Al, which is consistent with the XRD result. The inner layer also had a thickness of about 18 μm. The Al concentration in this layer remained reasonably constant, being about 58 wt%, which essentially suggests a phase $TiAl_2$.
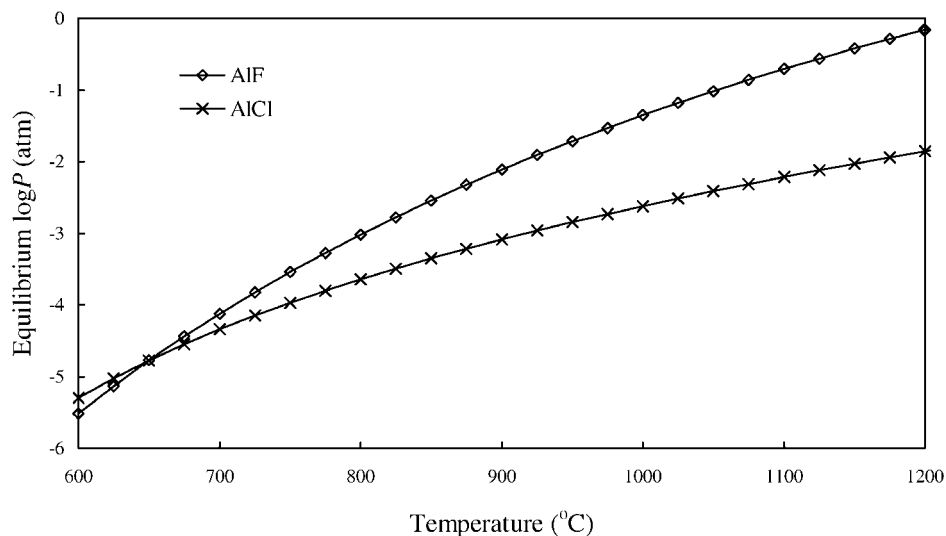

Figure 1 A comparison of vapour pressure of AlF in the AlF$_3$ activated pack with that of AlCl in the AlCl$_3$ activated pack (Composition: 15Al-3AlF$_3$ or AlCl$_3$-82Al$_2$O$_3$ wt%).
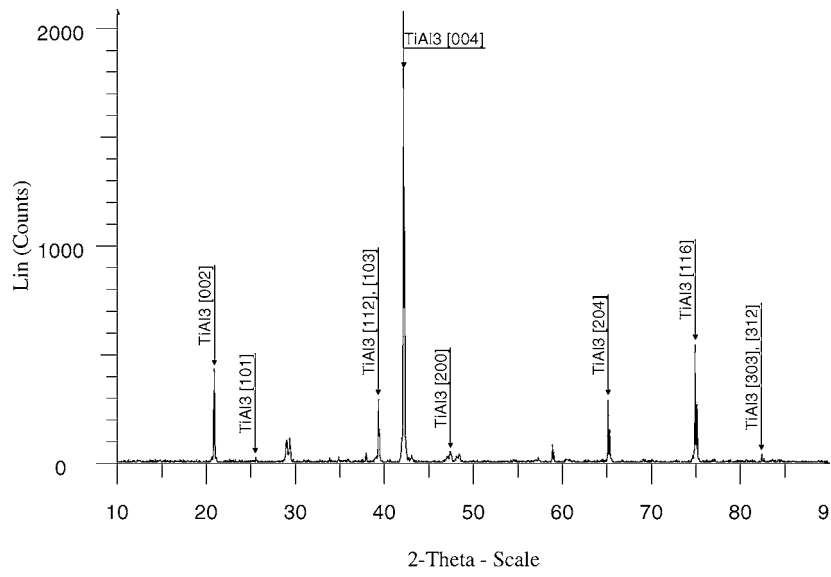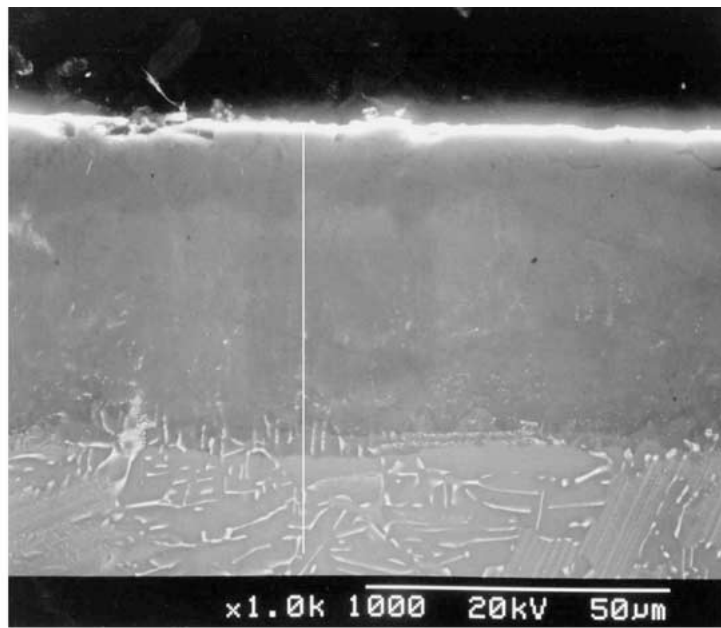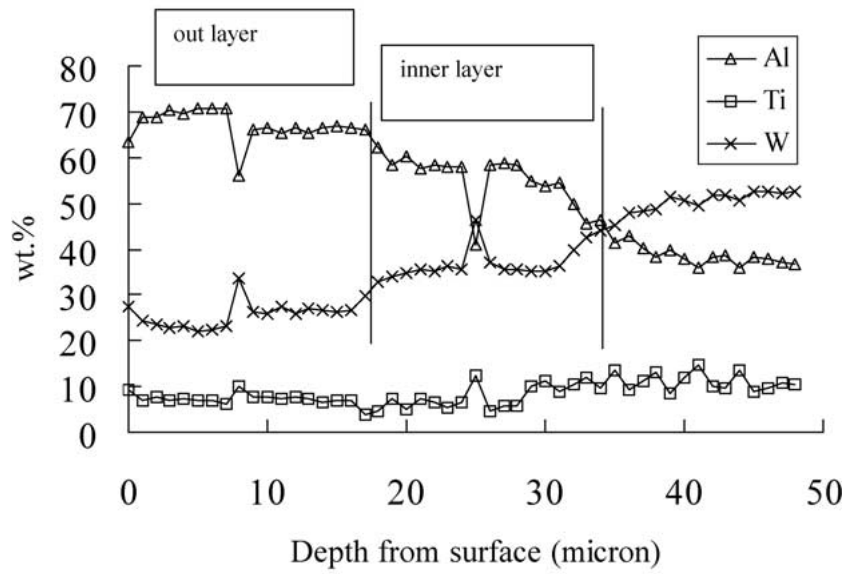
Figure 2 XRD spectrum of the as aluminised γ-TiAl specimen.

(a)

(b)

Figure 3 Cross-sectional SEM image and concentration profiles of Al, Ti and W in the coating layer measured by EDS for a specimen aluminised at 1000°C for 6 hours.

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The observed double layer aluminide structure with an outer TiAl$_3$ and inner TiAl$_2$ layer is in qualitative agreement with the results reported by Munro and Gleeson [10]. However, it should be noted that the ratio of the outer to inner layer thickness obtained in this study is close to 1 whereas the previous investigators reported a ratio varying between 12.5 to 5.6 depending on the coating time. Thus, coatings produced by the previous investigators had an outer TiAl$_3$ layer that was exceedingly thicker than the inner TiAl$_2$ layer, which was undoubtedly one of the major contributing factors for the occurrence of microcracking in their coatings.

It can also be seen in Fig. 3 that the concentration profiles of Al and Ti in the coating layer varied across the coating thickness in a gradual and continuous manner. This is in stark contrast to results of other investigators [10–12], which showed a sudden step change in element concentrations at the boundaries of different layers. The gradual change in the alloy composition across the thickness of the coating obtained in this study provided a smooth transition of thermal expansion coefficient at the boundaries of different layers and, as a consequence, ensured the integrity of the coating during cooling from the deposition temperature of 1000°C.

The difference between the coating structure obtained in this study and those by other investigators can be mainly attributed to the different activators and pack compositions used by different investigators. It should be emphasised that the activator plays a critical role in determining the partial pressure of the depositing vapour species such as AlCl or AlF generated within the packs, which in turn determines the rate of element deposition and hence the rate of coating growth. In this study, AlCl$_3$ was used as an activator. Under the same conditions, the partial pressure of the depositing vapour species generated by this activator (AlCl) would be much lower than those generated by activators such as NH$_4$F, NH$_4$Cl and AlF$_3$ [6]. Therefore, the rates of element deposition and coating growth in the AlCl$_3$ activated packs would be much slower than in the packs activated by NH$_4$F or NH$_4$Cl or AlF$_3$. This can be confirmed by comparing the total coating thickness of only about 37 μm obtained in this study to 72 μm reported under the same coating conditions by Monro and Glesson [10] who used NH$_4$F as an activator. It is thus evident that the slower rate of element deposition and coating growth induced by AlCl$_3$ provided a crucial condition for forming an adherent aluminide coating on γ-TiAl with a coherent structure free from microcracking. This also further demonstrated that with optimum design of pack powder compositions and careful selection of activators, the kinetics of element deposition and subsequent diffusion can be effectively controlled to ensure a deposition process capable of producing aluminide coatings on γ-TiAl with controlled quality and structure.

4.2. Co-deposition of Al and Si on γ-TiAl

The purpose for introducing Si into the surface layer of γ-TiAl is to provide enhanced protection against hot corrosion in addition to against oxidation. Munro and Gleeson [10] were probably the first ones who attempted to deposit Si to form silicide coatings on γ-TiAl by the pack cementation process. A pack powder mixture activated by MgF$_2$ with a composition of 10Si-2MgF$_2$-88Al$_2$O$_3$ (wt%) was used to deposit Si at 1000°C. But, only a porous coating was obtained with large-scale spallation, which rendered the coatings unsuitable for protecting the substrate.

A more attractive approach, both technically and economically, would be to form silicide and aluminide coatings through co-deposition of Si and Al in a single pack cementation step. In a previous study involving co-deposition of Cr and Al on a nickel base superalloy [15], the present authors observed that co-deposition of more than one element under suitable conditions often occurred *via* a sequential deposition mechanism. Therefore, it is anticipated that, with the thermochemical analysis techniques available, suitable pack powder compositions and coatings conditions can be identified and subsequently optimised through experimental studies for co-depositing Al and Si on γ-TiAl using mixtures of Al and Si powders as depositing sources. Using powder mixtures of elements as depositing source instead of using their alloys as conventionally recommended is not only more economical but also provides an easy way of adjusting pack powder compositions and hence their depositing characteristics.

It is known that thermochemical analysis on the vapour species generated in the pack can provide a useful insight into the element depositing properties of a pack powder mixture with a specified composition under a set of defined coating conditions [15]. In order for the intended co-deposition to take place, the vapour pressures of aluminium halides should be controlled in a comparable range to those of silicon halides under the specified coating temperatures. Such thermodynamic conditions may be achieved by adjusting aluminium and silicon contents in pack and by carefully selecting a suitable halide salt as an activator, which determines the partial pressure distribution of halide vapours generated at coating temperatures. In the present study, CrCl$_3 \cdot$6H$_2$O and AlCl$_3$ are evaluated as the activators for co-depositing Al and Si.

Fig. 4 presents a plot of vapour pressures of those aluminium and silicon halides mainly responsible for
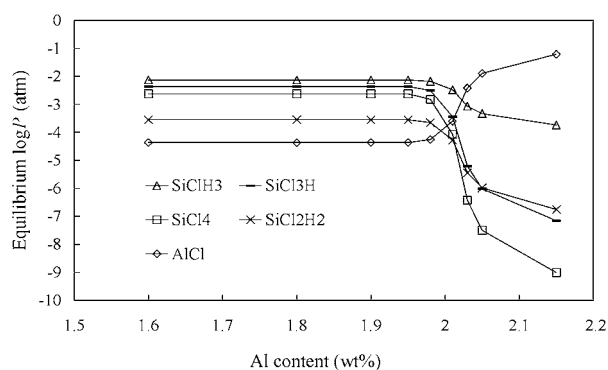

Figure 4 Dependence of vapour pressures of Al and Si chloride species at 1000°C on Al content for the pack series of 3Si-xAl-4CrCl$_3 \cdot$6H$_2$O-(93-x)Al$_2$O$_3$ wt%.
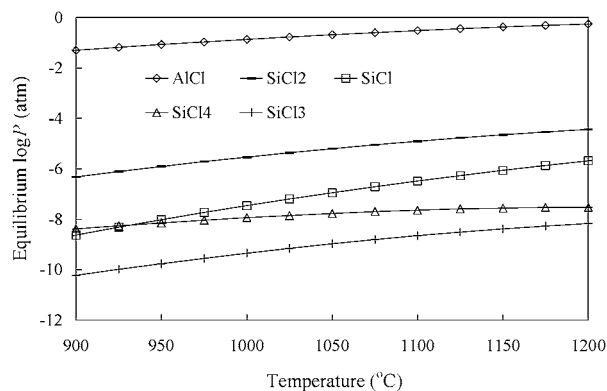
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Figure 5 Dependence of chloride vapour pressures on temperature in a pack 25Si-2Al-4AlCl$_3$-69Al$_2$O$_3$ wt%.

transporting and depositing Al and Si at 1000°C as a function of aluminium content for a pack series of 3Si-xAl-4CrCl$_3$ · 6H$_2$O-(93-x)Al$_2$O$_3$ (wt%). It can be seen that in order for this series to co-deposit Al and Si the aluminium content in the pack should not be much higher than 2 wt%. Ideally, the aluminium content should be controlled in the vicinity of 2 wt% where the vapour pressure curve of aluminium mono-chloride intersects those of silicon chlorides.

Fig. 5 shows a plot of vapour pressures of AlCl and silicon chlorides as a function of temperature for a pack 25Si-2Al-4AlCl$_3$-69Al$_2$O$_3$ wt%. It can be seen that the vapour pressure of AlCl is much higher than those of silicon chlorides in the temperature range studied. Thus, in order to achieve conditions for co-depositing Al and Si, it is likely that the aluminium content in the pack will have to be much lower than 2 wt%.

Based on the results of thermochemical calculations, a series of pack mixtures containing Al, Si, CrCl$_3$ · 6H$_2$O or AlCl$_3$ and Al$_2$O$_3$ powders was formulated and prepared. Coating experiments were then carried out to verify the suitability of these compositions for co-depositing Al and Si.

4.2.1. Packs activated by CrCl$_3$ · 6H$_2$O

The first attempt to co-deposit Al and Si was made using CrCl$_3$ · 6H$_2$O as an activator. A pack mixture with a composition 2Al-4Si-4CrCl$_3$ · 6H$_2$O-90Al$_2$O$_3$ wt% was prepared and the specimens were coated at 1100°C for 8 hours. However, after the coating process, the specimens showed a significant weight loss (more than 0.3 wt%), suggesting occurrence of degradations of the specimens instead of diffusion coating formation. The specimen surfaces turned black and looked very rough, showing evidences of degradation. This indicates that CrCl$_3$ · 6H$_2$O cannot be used as an activator for co-depositing Al and Si in γ-TiAl. Further studies are clearly needed to investigate the exact reasons for the occurrence of such degradation. But, it is highly likely that it was due to the deteriorating effect of large volume of water vapour released from the activator at the coating temperature. In the presence of chlorine, water vapour would react with Cl$_2$ to form HCl with a partial pressure high enough to suppress the element deposition process and cause degradation to the substrate. However, it should be noted that CrCl$_3$ · 6H$_2$O was suc-

cessfully used as an activator to co-deposit Al and Cr to form diffusion coatings on nickel base superalloys with excellent surface finishes [15]. The fact that it caused degradation to γ-TiAl substrate during the coating deposition process provides further evidence that γ-TiAl is very susceptible to attacks by oxidative and corrosive atmospheres at high temperatures.

4.2.2. Packs activated by AlCl$_3$

After observing the corrosive nature of CrCl$_3$ · 6H$_2$O towards the γ-TiAl substrate, major experimental efforts were subsequently shifted to achieve co-deposition with pack powder mixtures activated by AlCl$_3$, which contained no intrinsic water apart from moisture absorbed from the atmosphere. A series of pack powder compositions were formulated and prepared with Al content varying from 1 to 4 wt%, Si 1 to 6 wt%, AlCl$_3$ 1 to 5 wt% with the balance being Al$_2$O$_3$. Samples were coated for 8 hours either at 1100°C or at 1000°C. With careful adjustment of pack compositions, it was found that co-deposition of Al and Si on γ-TiAl could indeed be achieved under these coating conditions.

Fig. 6 shows a cross sectional SEM image and concentration profiles of Si, Al, Ti and W in the coating layer as measured by EDS for a specimen coated at 1100°C. It can be seen from the SEM image that the coating consisted of two uniform layers. The outer layer with a thickness about 8 μm contained mostly Si and Ti with very little Al, suggesting that this is a titanium silicide layer. The inner layer had a thickness about 23 μm and the Al and Ti concentrations across the thickness of this layer remained almost constant, being about 59 wt% and 32 wt% respectively, which corresponds to a phase TiAl$_3$.

Underneath the inner layer there actually existed another layer with a thickness of about 8 μm. This layer could not be visually recognized in the SEM photograph but could be identified from the Al and Ti concentration curves. This is a transition layer in which concentrations of both Al and Ti vary gradually across the depth of this layer into the substrate, providing an essential composition gradient at the boundary between the coating and the substrate, which ensured the integrity of the coating during cooling from the deposition temperature of 1100°C.

The surface of the coating appeared quite smooth and grey in colour with a yellowish tint. Fig. 7 presents a XRD spectrum measured from the sample surface. It shows that the major phase in the outer surface layer is Ti$_5$Si$_4$, although small quantity of TiSi$_2$, TiSi and Si was also detected.

In the inner and transition layers the silicon concentration measured by EDS showed a fairly constant reading of about 3 to 4 wt%. It cannot be certain at this stage whether this is the true concentration level of silicon deposited from the vapour phase or this is due to the system error of the analysing technique. However, it is known that the EDS results become unreliable when element concentration to be analysed is below 3 wt%. This is particularly true when other elements are also present with overlapping energy levels. Further research is required to use other measurement techniques
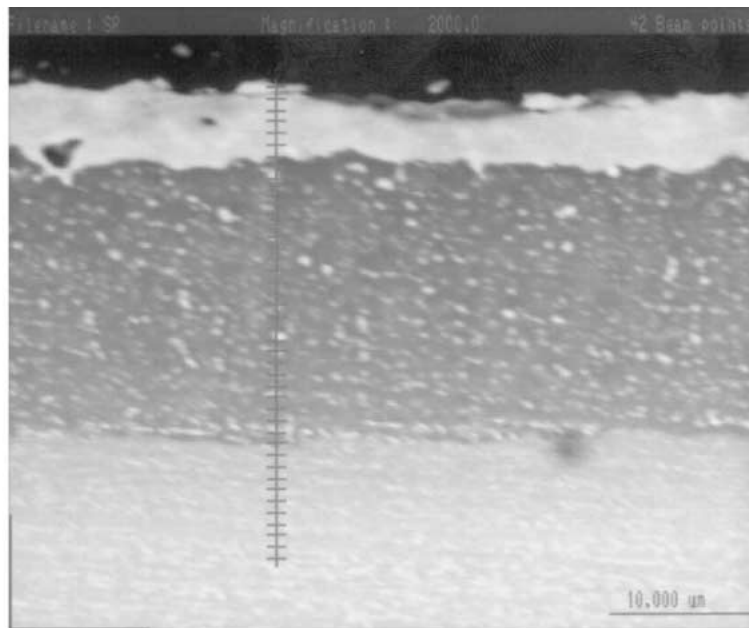
(a)
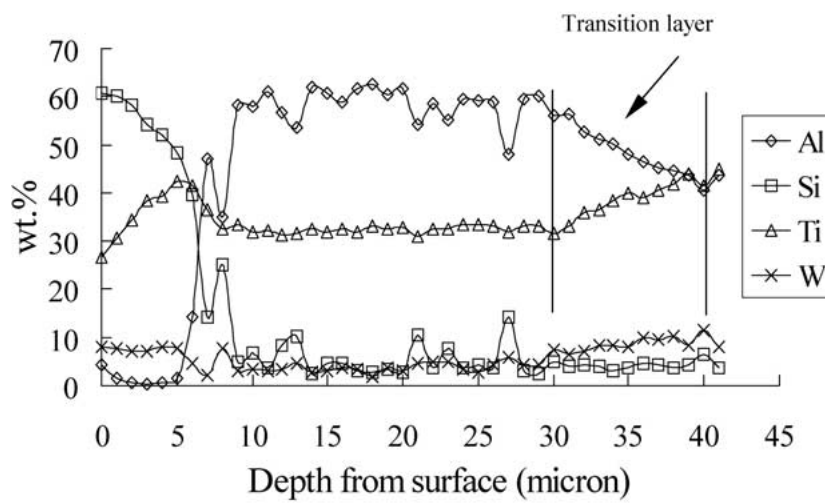
(b)

Figure 6 Cross-sectional SEM image and concentration profiles of Si, Al, Ti and W for a specimen coated by co-deposited at 1100°C for 8 hours.
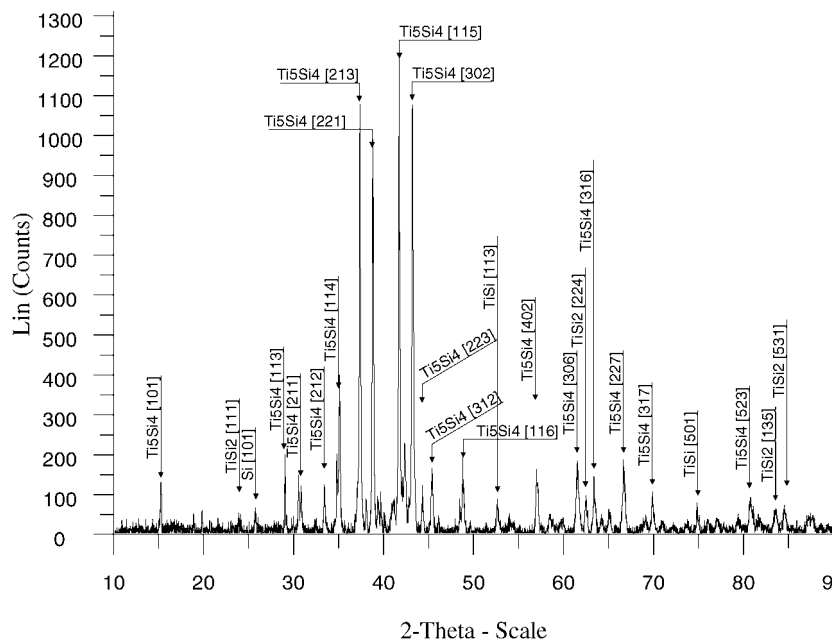

Figure 7 XRD spectrum for a specimen coated by co-deposition at 1100°C for 8 hours.

such as WDS (Wavelength Dispersive Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy) or SIMS (Secondary Ion Mass Spectroscopy), which have better resolutions than EDS, to clarify whether silicon was deposited from the vapour phase in the inner and transition layers.

The observed double layer coating structure strongly suggests that co-deposition of Al and Si occurred in a sequential manner. At the initial stage of deposition process, the element deposited was primarily Al with very little Si, if at all. The aluminide coating was thus formed at this stage *via* inward diffusion of Al. As the deposition process progressed, the Al activity in the pack, particularly in the vicinity of the substrate, became substantially reduced and that of Si increased, creating a condition favourable for depositing Si. Thus, Si was the main element deposited at this later stage and a titanium silicide layer was formed through inward diffusion of silicon. Such a sequential deposition mechanism is very similar to that observed previously in pack powder system designed to co-deposit Al and Cr on nickel-base superalloys [15].

Lowering processing temperature can bring obvious technical and economical benefits. Therefore, attempts were made to co-deposit Al and Si at a lower coating temperature of $1000°C$ while keeping the coating time constant at 8 hours. The coated surface looked very smooth and appeared grey in colour. Fig. 8 shows a cross sectional SEM image and concentration profiles of Si, Al and Ti in the coating layer measured along the two lines defined in the SEM photograph (Fig. 8a). It can be seen that the coating was essentially a $TiAl_3$ deposit with a thin silicide layer covering some of the surface area, confirming that both Al and Si were deposited during the co-deposition process. It is clear that, in some regions of the surface area, Si reacted with Ti and formed the silicide phase, but in other regions, it existed in the solid solution of $TiAl_3$. This is more clearly revealed by the concentration profiles of Si, Al and Ti measured along the two lines starting from these two different surface regions. The Line one starts from a surface region not covered by the silicide phase and it can be seen that the silicon concentration in the surface layer, which is a phase $TiAl_3$, is about 7 wt.%. This is probably the maximum amount of Si that can exist in the solid solution of $TiAl_3$. The silicon concentration profile measured along the Line two, which starts from a surface region of the silicide phase, also showed that silicon concentrations in the $TiAl_3$ phase, which is below the thin silicide phase layer, were all lower than 7 wt.%. The total thickness of the coating was about 38 μm.

Fig. 9 is a XRD spectrum measured from the as-coated sample surface. It can be seen that the major phases in the surface layer are $TiAl_3$ and Ti_5Si_3, confirming again that both Al and Si were deposited.

It has thus been demonstrated that Al and Si can be co-deposited in a temperature range of $1000°C$ to $1100°C$ to form diffusion coatings containing aluminide and silicide phases using pack powder mixtures activated by $AlCl_3$. As a stable activator $AlCl_3$ has clear advantages over unstable activators such as NH_4F and
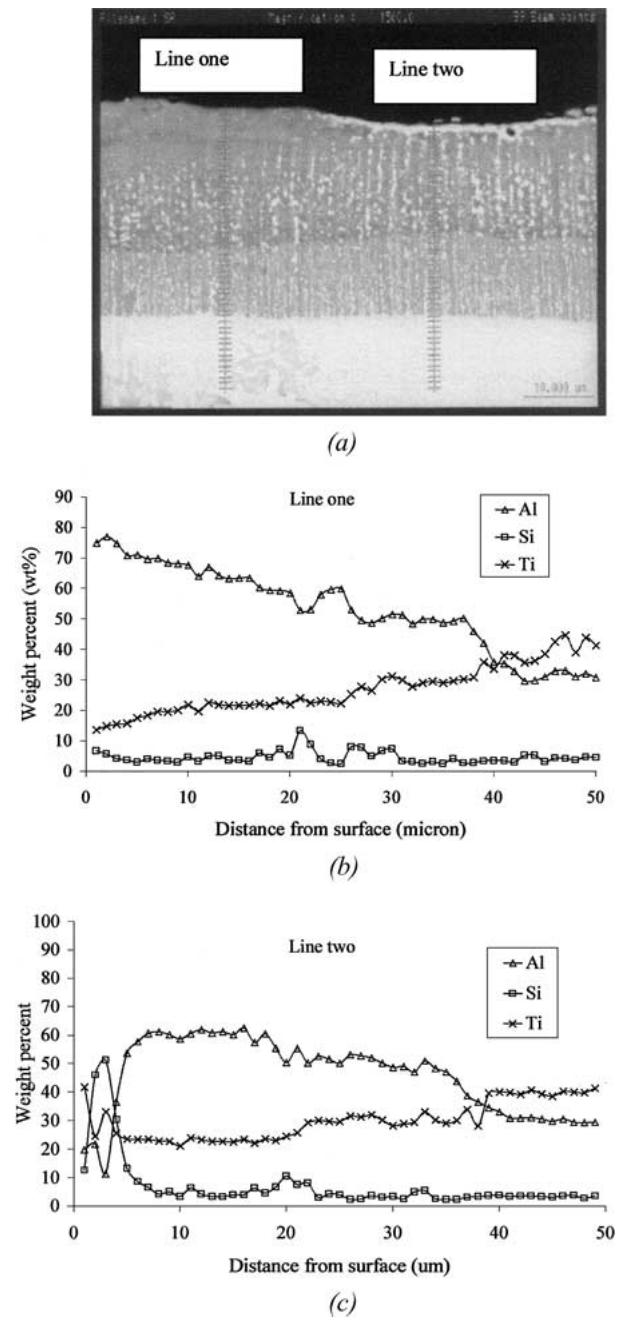
(a)

(b)

(c)

Figure 8 Cross sectional SEM image and concentration profiles of Si, Al and Ti in the coating layer measured by EDS for a specimen coated by co-deposition at $1000°C$ for 8 hours.

NH_4Cl. However, it must be pointed out that although $AlCl_3$ is "stable" at high temperatures it is unstable at room temperature. It can react violently with water and has a strong tendency to absorb large quantity of moisture from the atmosphere. This can greatly alter its activating properties and hence the deposition chemistry of the packs. Activators that are stable both at room temperature and at high temperatures clearly need to be identified for an easily controllable industrial process. In this respect, mixed activators such as AlF_3/NH_4Cl or $NaCl/NH_4Cl$, the ratio of which can be easy adjusted to modify the pack chemistry, could offer some promising opportunities in developing an efficient process for depositing multiple element coatings for γ-TiAl.

The initial results of an oxidation study showed that the co-deposited aluminide and silicide coatings
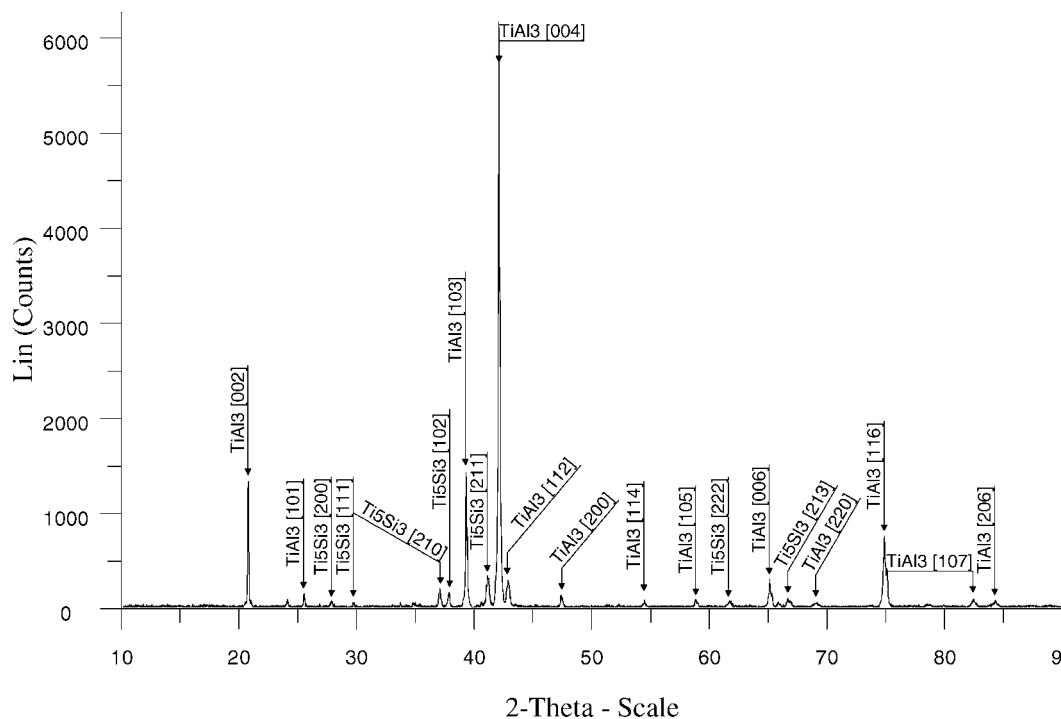
Figure 9 XRD spectrum for a specimen coated by co-deposition at 1000°C for 8 hours.

produced in this study has excellent oxidation resistance and thermal stability at temperatures up to 850°C, the upper temperature limit of γ-TiAl for long-term structural operations. The detailed results and analyses of this study will be presented in another paper.

5. Conclusions

Thermochemical analysis was carried out for a series of pack powder mixtures for depositing aluminide and for co-depositing aluminide and silicide coatings on γ-TiAl by the pack cementation process using a computer program *ChemSage* in combination with the database systems *SGTE*. Based on the results obtained, experimental studies were undertaken to identify optimum pack powder mixtures for depositing adherent and coherent aluminide and silicide coatings. These studies demonstrated that thermochemical calculations of the partial pressures of halide vapours generated at a series of specified coating temperatures can provide a valuable insight into the deposition chemistry of a pack powder mixture with a specified composition. This is particularly significant in designing pack compositions and in selecting suitable halide salts as activators to enable precise control of the deposition process and hence of the microstructure of the coatings produced.

Pack powder mixtures activated by 2 wt% $AlCl_3$ were used to aluminise γ-TiAl. The results showed that, with proper control of pack compositions and coating conditions, an aluminide coating of $TiAl_3$ with a coherent structure free from microcracking could be formed *via* inward diffusion of aluminium. To ensure the integrity of the coatings formed, it is essential that pack compositions and coating conditions be optimised to enable a deposition and diffusion kinetics that results in a continuous and gradual alloy composition transition across the thickness of the coating layer particularly at the boundary between the coating and substrate.

The results of thermochemical calculations indicated that co-deposition of Al and Si is possible with the $CrCl_3 \cdot 6H_2O$ activated packs using elemental Al and Si powders as depositing sources. Experimental efforts were made to use these packs to co-deposit aluminide and silicide coatings on γ-TiAl. However, after the coating deposition process, the specimens showed a significant weight loss, indicating occurrence of degradations. Therefore, $CrCl_3.6H_2O$ is not a suitable activator for co-depositing aluminide and silicide coatings on γ-TiAl.

Thermochemical calculations were also performed for the $AlCl_3$ activated pack powders containing Al and Si. The results suggested that, in order to achieve co-deposition of Al and Si, aluminium content in the packs should not be higher than 2 wt%. The experimental results demonstrated that co-deposition could be achieved at temperatures of 1000°C to 1100°C using pack powder mixtures containing 1 to 4 wt% Al, 1 to 6 wt% Si and 1 to 5 wt% $AlCl_3$, with the balance being Al_2O_3. With careful control of pack compositions and coating conditions, adherent and coherent coatings with a structure consisting of an outer Ti_5Si_4 layer and an inner $TiAl_3$ layer were produced. It was suggested that such coatings were formed *via* a sequential deposition mechanism through inward diffusion of Al and Si.

References
1. M. P. BRADY, *et al*. *JOM* November (1996) 46.
2. W. KAYSSER, *Surface Engineering* **17**(4) (2001) 305.
3. P. K. Datta *et al*., in "Intermetallic Compounds: Principles and Practice, Vol. 3: Process," edited by J. H. Westbrook and R. L. Fleischer, (John Wiley, New York, 2001) [ISBN 0741-4915].
4. D. W. McKEE, *Mat. Res. Soc. Proc.* **288** (1993) 953.
5. M. P. BRADY, *et al*., *JOM* January (2000) 16.
6. Z. D. XIANG, J. S. BURNELL-GRAY and P. K. DATTA, *J. Mater. Sci.* **36** (2001) 5673.
7. J. KIPKEMOI and D. TSIPAS, *ibid.* **31** (1996) 6247.

8. W. D. COSTA, B. GLEESON and D. J. YOUNG, *J. Electrochem. Soc.* **141**(10) (1994) 2690.

9. R. BIANCO and R. A. RAPP, *ibid.* **140**(4) (1993) 1181.

10. T. C. MUNRO and B. GLEESON, *Metallurgical and Materials Transactions* A **27A** (1996) 3761.

11. C. ZHOU, H. BIN and K. Y. KIM, *ibid.* **31A** (2000) 2391.

12. Z. TANG, L. NIEWOLAK, V. SHEMET, L. SINGHEISER, W. L. QUADAKKERS, F. WAND, W. WU and A. GIL, *Mater. Sci. and Eng.* **A 328** (2002) 297.

13. M. YAMAGUCHI, *Mater. Sci. Technol.* **8**(4) (1992) 299.

14. G. ERIKSSON and K. HACK, *Metallurgical Transactions* B **21B** (1989) 1013.

15. Z. D. XIANG, J. S. BURNELL-GRAY and P. K. DATTA, *Surface Engineering* **17** (2001) 287.