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Pack cementation process for the formation of refractory metal modified aluminide coatings on nickel-base superalloys

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The vapour phase compositions of a series of pack powder mixtures containing elemental Al and Hf or W powders as depositing sources and $CrCl_3{\cdot}6H_2O$ or AlF_3 or CrF_3 as activators were analysed in an attempt to further develop the pack cementation process to codeposit Al and Hf or W to form diffusion coatings on nickel base superalloys. The results suggested that Al could be codeposited with Hf, but not with W, from the vapour phase. Compared with both AlF_3 and CrF_3, $CrCl_3{\cdot}6H_2O$ has been shown to be a more suitable activator for codepositing Al with Hf. The optimum coating temperature was identified to be in the range of 1050°C to 1150°C. Based on the thermochemical analysis, a series of coating deposition studies were undertaken, which confirmed that codeposition of Al and Hf could be achieved at a deposition temperature of 1100°C in the $CrCl_3{\cdot}6H_2O$ activated packs containing elemental Al and Hf powders. The coating obtained had a multilayer structure consisting of a $Ni_7Hf_6Al_{16}$ top layer and a NiAl layer underneath, followed by a diffusion zone, which revealed that the coating was formed by the outward Ni diffusion. It is suggested that the compositions suitable for codeposition of Al and Hf could be effectively identified by comparing the vapour pressures of $HfCl_4$ and $HfCl_3$ with that of AlCl in the packs activated by chloride salts. It has also been experimentally demonstrated that, although W could not be deposited from the vapour phase, a high volume of fine W particles can be entrapped into the outer NiAl coating layer formed by the outward Ni diffusion using a modified pack configuration. This leads to the formation of a composite coating layer with W particles evenly distributed in a matrix of NiAl. It is suggested that this modified pack process could be similarly applied to develop nickel aluminide coatings containing other refractory metals that may not be codeposited with Al from the vapour phase. *© 2003 Kluwer Academic Publishers*

1. Introduction

Nickel-base superalloy components are normally designed to operate at temperatures higher than 700°C. In aggressive environments containing sulphur and other impurities, sulphidation, a hot corrosion process causing rapid formation of metal sulphides, is a major mode of degradation. Under the conditions of low oxygen and moderate level of sulphur potentials, the rate of sulphidation is usually several magnitudes higher than that of oxidation [1]. In recent reviews [1, 2], the differences between the alloys or coatings for oxidation resistance and those needed to combat sulphidation have been considered and the criteria for the development of sulphidation resistant alloys or coatings have been discussed in detail. It has been shown that alloys or coatings containing sufficient level of refractory metals such as W, Hf, Mo, Ta and Re can be effective in providing protections against sulphidation particularly in reducing atmosphere due to their low rate of forming stable metal sulphide scale that prevents otherwise rapid sulphur penetration into the substrate at elevated temperatures.

Pack cementation is a diffusion coating formation process traditionally used to deposit Al on nickel base superalloys to form nickel aluminide coatings resistant to oxidation [3, 4]. More recently, some attempts have also been made to use this process to codeposit Al and Cr on nickel-base superalloys and on low alloy and stainless steels to form diffusion coatings resistant to hot corrosion caused by molten salts such as Na_2SiO_4 [5–8]. But, few detailed studies have been reported on the feasibility of applying this technique to codeposit Al with refractory metal elements to form diffusion coatings, despite the fact that chemical vapour deposition (CVD) process has been successfully applied to produce coatings and free-standing components of pure refractory metals such as W and Re and their alloys [9]. This paper reports the results of an

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investigation by means of thermochemical analysis in combination with experimentaion into the feasibility of applying the pack cementation process to codeposit Al with Hf and W on nickel-base superalloys to form diffusion coatings resistant to high temperature sulphidation degradation.

2. Thermochemical considerations

In a normal pack cementation process, the substrates to be coated are placed in a sealed or semi-sealed container together with a well-mixed pack powder mixture containing the depositing elements (or their alloy), a halide salt activator and an inert filler (usually alumina). The substrates may be buried in (in-pack process) or suspended above (out-pack process) the pack powder mixture. The whole pack is then heated to and held for a required duration at a predetermined high temperature in the range of 700°C to 1150°C under a protective atmosphere of an inert gas. At high temperatures, the halide salt would react with the depositing elements. In a pack of specified composition, a series of halide vapour species containing the depositing elements would then be produced. In order to achieve the intended codeposition, the partial pressures of halide vapours of different depositing elements should be ideally controlled in a comparable range at any specified depositing temperatures. This may be accomplished by adjusting the content of the depositing elements in the pack and by carefully selecting a suitable halide salt as an activator.

2.1. Pack powder mixtures for codeposition

Pack powder mixtures for codepositing Al with Hf and W are normally expected to consist of master alloy powders of Al-Hf or Al-W as the depositing source, a halide salt as an activator and Al_2O_3 powders as the inert filler. The purpose of using a master alloy as the depositing source is believed to modify the activity of the depositing elements within the pack so that the halide vapour pressures of the two depositing elements could be adjusted within a comparable range favourable for the intended codeposition process [6, 7]. However, it is often not a simple matter to prepare master alloy powders of the required particle size with an accurate and infinitely adjustable composition. Therefore, there is a strong technical incentive to use a simple mixture of element powders as the depositing source. Thus, in this study, attempts are made to use a mixture of pure Al and Hf or W powders as the source for codepositing Al with Hf and W. Halide salts of AlF_3, CrF_3, $CrCl_3{\cdot}6H_2O$ are investigated as possible activators and Al_2O_3 as the inert filler.

2.2. Method of analysis

Partial pressures of halide vapours for a range of pack powder compositions were analysed with the assistance of the ChemSage computer program in combination with the SGTE database systems. The calculations were based on the Gibbs energy minimisation technique and the mass conservation rule [10]. For all the calculations undertaken in this study, the total pressure within the packs was assumed to be one atmosphere.

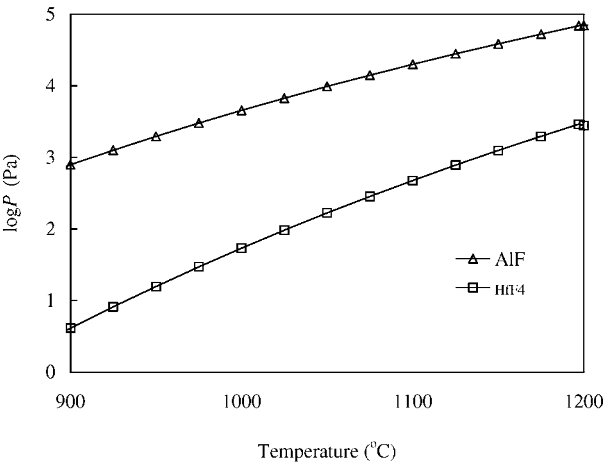

Figure 1 Equilibrium partial pressures of AlF and HfF_4 as a function of temperature in a pack activated by AlF_3.

2.3. AlF_3 and CrF_3 activated Al-Hf packs

Of all the vapour species generated in these packs, those containing Al and Hf are of major importance for codepositing Al and Hf. They include AlF, AlF_2, AlF_3 and HfF_4. Among the vapour species containing Al, the AlF species is predominantly responsible for transporting and depositing Al within the pack [3]. Thus, it is only necessary to compare the partial pressure of AlF with that of HfF_4 in order to identify possible pack compositions and deposition conditions for codepositing Al and Hf. Fig. 1 compares the vapour pressure of AlF with that of HfF_4 in a pack of $1.2Al\text{-}5Hf\text{-}2.5AlF_3$ or $CrF_3\text{-}91.3Al_2O_3$ wt%. Replacing AlF_3 by CrF_3 did not show significant effects on these vapour pressures, indicating that the depositing tendency of the pack would not be affected by replacing AlF_3 with CrF_3. It can be seen that the vapour pressure of AlF is more than an order of magnitude higher than that of HfF_4 in the whole temperature range of 900°C to 1200°C, suggesting that the pack is more likely to deposit Al than to deposit Hf. However, codeposition may occur at the high end of the temperature range where the difference between the vapour pressures of AlF and HfF_4 is less than at the low end of the temperature range.

2.4. $CrCl_3{\cdot}6H_2O$ activated Al-Hf packs

Among the vapour species containing Al, AlCl is responsible for transporting and depositing Al [3, 5]. The Hf-chloride vapour species include $HfCl_x$ ($x = 1$ to 4). There have been so far no convincing experimental evidences that could clarify which one of these species is responsible for depositing Hf in cementation packs. Therefore, all of these species were considered together with AlCl in assessing the tendency of the packs to codeposit Al and Hf.

A key condition to deposit Hf from the vapour phase is that a sufficiently high level of vapour pressure of Hf-chlorides can be generated within the packs. To examine whether this is achievable, a simple pack mixture containing only Hf was analysed, before efforts were

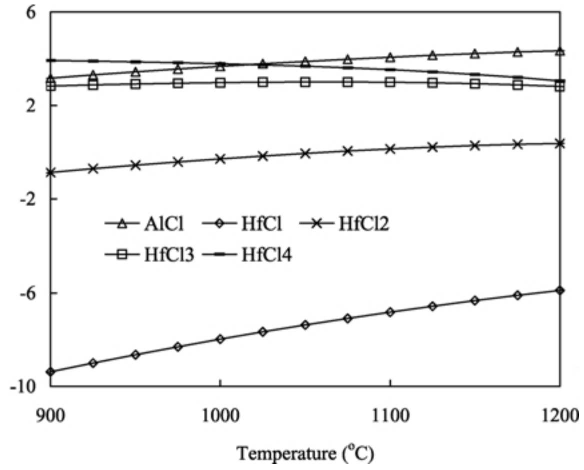

Figure 2 Equilibrium partial pressures of Hf- and Al-chlorides in a pack of 20Hf-4$CrCl_3 \cdot H_2O$-76Al_2O_3 (wt%).

made to analyse more complex packs containing both Al and Hf. Fig. 2 plots the partial pressures of $HfCl_x$ and AlCl as a function of temperature for a pack mixture 20Hf-4$CrCl_3 \cdot H_2O$-76Al_2O_3 (wt%). It can be seen that considerably high levels of vapour pressures of $HfCl_4$ and $HfCl_3$ can indeed be generated in this pack in the temperature range of 900°C to 1200°C, suggesting a strong possibility of depositing Hf from the vapour phase. Compared with the vapour pressures of $HfCl_4$ and $HfCl_3$, those of $HfCl_2$ and HfCl are at least 3 orders of magnitude lower and hence may be considered insignificant in determining the depositing tendencies of the pack.

A striking feature of Fig. 2 is the high vapour pressure of AlCl in the pack. It can be seen that the vapour pressure of AlCl is within the same order of magnitude as those of $HfCl_4$ and $HfCl_3$ in the range of 900°C to 1150°C. Since the pack contains no Al metal, the source of this AlCl vapour must be Al_2O_3, which is used as the inert filler in the pack. The possible mechanism for converting Al_2O_3 to AlCl in the pack probably involve the following reactions:

$$3Hf + 2Al_2O_3 = 3HfO_2 + 4Al$$

$$2Al + CrCl_3 = 2AlCl + CrCl$$

Fig. 2 appears to suggest that codeposition of Al and Hf is achievable in this pack even though it contains no Al metal. It needs to be pointed out that these vapour pressures were calculated for a system assumed to be under equilibrium, a thermodynamic condition rarely truly maintained in a real coating deposition process. It would be of technological significance to experimentally determine whether the rate of converting Al_2O_3 to Al-chlorides in this pack is fast enough at high temperatures to facilitate a viable process of codepositing Al and Hf.

After confirming that a significant level of vapour pressure of Hf-chlorides can be generated in the $CrCl_3 \cdot 6H_2O$ activated packs, a range of pack powder mixtures containing both Hf and Al were analysed in detail. It was found that the composition of these mixtures could be adjusted to bring the partial pressures of AlCl, $HfCl_4$ and $HfCl_3$ within the same order of magnitude. This is demonstrated in Fig. 3, which shows the vapour pressures of AlCl, $HfCl_3$ and $HfCl_4$ as a function of temperature for a pack 1.2Al-5Hf-4$CrCl_3 \cdot 6H_2O$-89.8Al_2O_3 (wt%). It can be seen that, in the range of 900°C to 1200°C, the vapour pressure of AlCl is within the same order of magnitude as that of $HfCl_4$, and at temperatures lower than 1050°C, it is within the same order of magnitude as those of both $HfCl_4$ and $HfCl_3$. Therefore, if either $HfCl_4$ or $HfCl_3$ or both were depositing species responsible for releasing Hf on the substrate, the pack would have a strong tendency to codeposit Al and Hf. The optimum deposition temperature would be in the range of 1050°C to 1150°C in which the vapour pressures of all three species are within a narrow range.

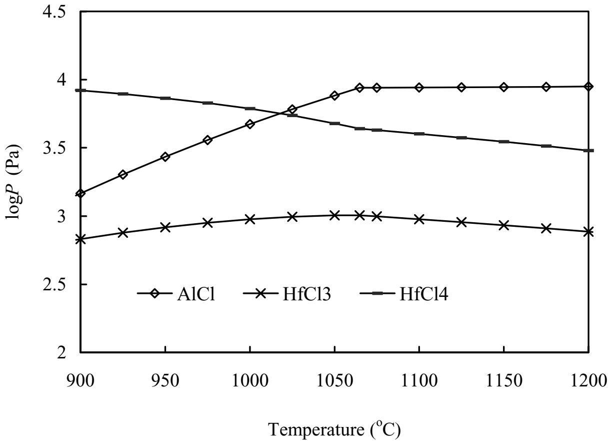

Figure 3 Equilibrium partial pressures of AlCl, $HfCl_3$ and $HfCl_4$ in a pack of 1.2Al-5Hf-4$CrCl_3 \cdot H_2O$-89.8Al_2O_3 (wt%).

2.5. $CrCl_3 \cdot 6H_2O$ activated Al-W packs

Again, a pack containing W, but no Al, with a composition of 20W-4$CrCl_3 \cdot H_2O$-76Al_2O_3 (wt%) was firstly analysed in order to assess whether W can be deposited from the vapour phase. Fig. 4 plots the vapour pressures of AlCl and WCl_2 as a function of temperature for this W pack. Other chloride species of W such as WCl and WCl_x ($x = 3$ to 6) are also present, but, their vapour pressures are far lower than that of WCl_2 and hence are omitted. It can be seen that the vapour pressure of WCl_2 is more than 10 orders of magnitude lower than

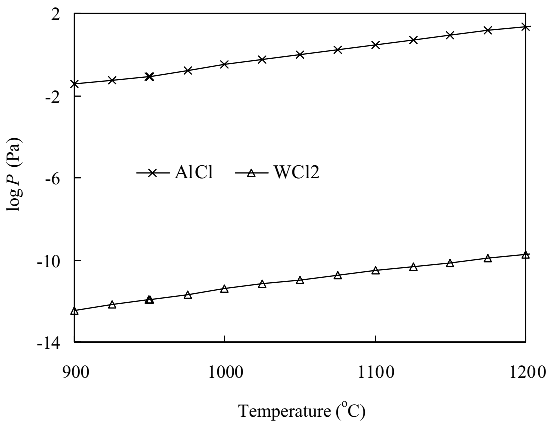

Figure 4 Equilibrium partial pressures of AlCl and WCl_2 as a function of temperature for a pack 20W-4$CrCl_3 \cdot H_2O$-76Al_2O_3 (wt%).

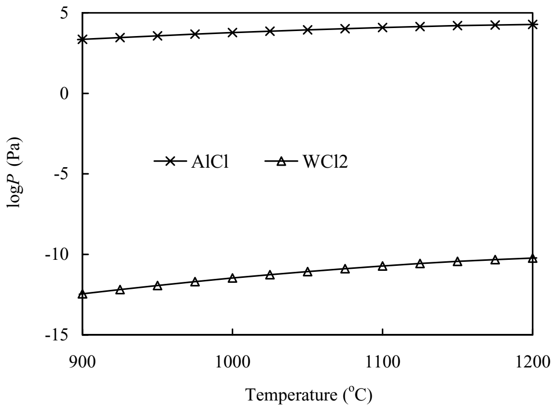

Figure 5 Equilibrium partial pressures of AlCl and WCl_2 as a function of temperature for a pack 1.2Al-20W-4$CrCl_3 \cdot H_2O$-74.8Al_2O_3 (wt%).

that of AlCl, suggesting that not much chloride vapours of W can be generated in the pack. Hence, W may not be deposited from the vapour phase in this pack. As discussed in the previous section, the AlCl species is converted from Al_2O_3 in a chlorine rich environment at high temperatures. It is of major significance to note that its vapour pressure in this W pack is much lower than in a comparable Hf pack (Fig. 2), indicating that Al_2O_3 is much more stable in this W pack than in the comparable Hf pack at high temperatures.

It is expected that adding Al to the W pack would push the vapour pressure of AlCl further apart from those of chloride vapours of W. Fig. 5 shows the vapour pressures of AlCl and WCl_2 for a pack 1.2Al-20W-4$CrCl_3 \cdot H_2O$-74.8Al_2O_3 (wt%). Again, Other W-chlorides are omitted because they are at much lower levels. It is clear that the vapour pressure of AlCl becomes at least 14 orders of magnitude higher than that of WCl_2, indicating that this pack may only depositing Al and no W can be deposited from the vapour phase.

3. Experimental procedures

The substrate used for this study is a commercial alloy CMSX-4 with a nominal composition of 61.7Ni-5.6Al-6.5Cr-9.0Co-6.0W-6.5Ta-3.0Re-1.0Ti-0.6Mo-0.1Hf (wt%). The alloy rod of 16 mm in diameter was sliced into buttons with a thickness between 2 to 3 mm. The specimen surfaces were polished to a 1200 grit finish and then degreased before being placed in pack powders.

Pack powder mixtures were prepared by accurately weighing out and thoroughly mixing appropriate amounts of powders of Al_2O_3, Al, Hf, W and halide salts. The average particle sizes of Al_2O_3, Al, Hf and W powders were less than 50 μm, 75 μm, 5 μm and 1 μm respectively. $CrCl_3 \cdot 6H_2O$ was used as the activator. This chemical was ground using a mortar and pestle, but not sieved, before being weighed out and added into the pack powders.

The cementation packs were prepared by burying the substrates in a powder mixture charged in a cylindrical alumina retort of 30 mm diameter and 40 mm length, which was then sealed with an alumina lid and cement. The cement seal was cured at about 80°C for at least two hours before the pack was loaded into an alumina tube furnace. Once loaded, the furnace was circulated with argon and temperature was raised to deposition temperatures at a heating rate of 10 K/min and was held there for the required duration. The furnace was then cooled to room temperature at its natural rate by switching off its power supply. The deposition times reported in this study were the holding times at deposition temperatures.

The coated specimens were analysed using 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 estimated from the depth profiles of element concentrations in the coating layer measured by EDS.

4. Results and discussions

4.1. Codeposition of Al and Hf

According to the thermochemical calculations presented in Section 2, $CrCl_3 \cdot 6H_2O$ is a more suitable activator for codepositing Al with Hf than both AlF_3 and CrF_3. Therefore, a series of pack powder mixtures were formulated and prepared using $CrCl_3 \cdot 6H_2O$ as the activator with Al varying from 1 to 3 wt%, Hf 3 to 20 wt%, $CrCl_3 \cdot 6H_2O$ 3 to 6 wt% with the balance being Al_2O_3. The specimens were all coated at 1100°C for 8 h. With careful adjustment of the pack composition and precise control of the deposition process, it was found that Al and Hf could indeed be codeposited from the vapour phase.

Fig. 6 shows a cross-sectional SEM image and concentration profiles of major elements in the coating layer measured by EDS for an as-coated specimen. After the deposition process, the specimen showed a weight gain of about 23.4 mg/cm^2. It can be seen that the coating had a multilayer structure consisting of three major distinctive layers with a total thickness of about 62 μm. The top layer contained high concentrations of Hf, Al and Ni, confirming that both Hf and Al were deposited from the vapour phase. However, Ni and other minor elements such as Cr and Co were not deposited from the vapour phase, but diffused into this layer from the substrate. Although this layer is not uniform in thickness, probably as a result of preferential diffusion along the grain boundaries, it can be estimated that the average thickness of this layer is about 12 μm. Fig. 7 shows a XRD pattern measured from the as-coated surface. The major phase detected in this top layer was $Ni_7Hf_6Al_{16}$. This is consistent with the EDS measurements, which showed that the Hf concentration in the surface layer is about 21 at.%.

The middle layer had a thickness of about 22 μm with a uniform phase containing mostly Al, Ni, Cr and Co. Again, it can be certain that Al was deposited from the vapour phase, and Ni, Cr and Co originated from the substrate through diffusion. Ni concentration in this layer was almost constant with an average reading slightly below 48 at.%. Taking into account of Al, Co and Cr concentrations in this layer, it is reasonable to suggest that this middle layer is essentially the hypostoichiometric NiAl phase with all other elements present in its solid solution.

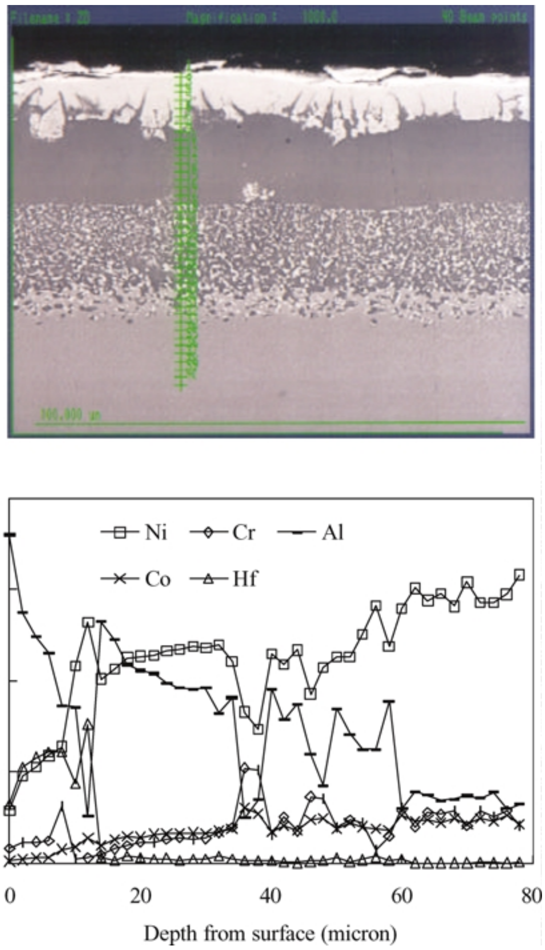

Figure 6 Cross-sectional SEM image and concentration profiles of major elements in the coating layer for a specimen coated by codeposition of Al and Hf.

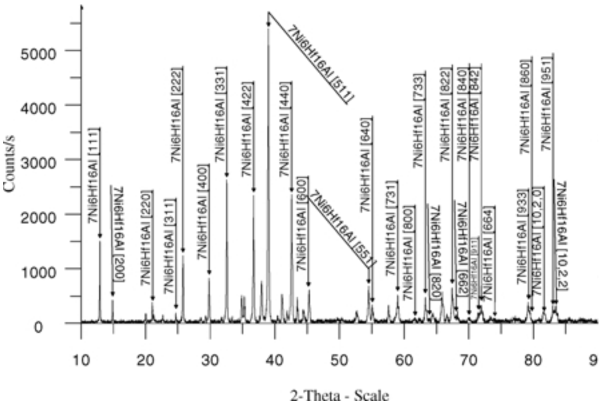

Figure 7 XRD pattern measured from the as-coated surface codeposited with Al and Hf.

The Hf concentration in the middle layer varied between 1.7 to 0.5 at.%, indicating that small amount of Hf was also deposited into this layer from the vapour phase during the deposition process. However, it cannot be certain at this stage about the true Hf concentration level in this layer, since it is known that the EDS results become unreliable when the concentrations of the elements to be measured are below 3 at.% especially in a complex system containing multiple elements with overlapping energy levels. The research efforts are continuing in using other measurement techniques such as WDS (Wavelength Dispersive Spectroscopy), which has better resolutions than EDS, to determine how much Hf was deposited from the vapour phase into this middle layer.

The inner layer in direct contact with the substrate had all the features typical of a diffusion zone containing precipitates of high atomic weight elements of the original substrate, revealing that the coating was formed predominantly through the outward Ni diffusion. No Kirkendall voids were formed at the boundary between the middle layer and this diffusion zone, probably because the outward diffusion flux of Ni, Co, Co and other substrate elements was fully compensated by the inward diffusion flux of Al. The thickness of this diffusion zone was about 30 μm, which is approximately half of the total thickness of the coating, a result consistent with the previous observations for the nickel aluminide diffusion coatings formed by the outward Ni diffusion in pack powder mixtures of sufficiently low Al activity [3, 5–7].

The multilayer structure shown in Fig. 6 probably indicate that the codeposition process occurred in a sequential manner. At the initial deposition process, the element deposited was primarily Al with very little Hf and a layer of NiAl coating was formed through the outward Ni diffusion. As the deposition process continued, the vapour composition of the pack, particularly in the vicinity of the substrate, became progressively more favourable for codepositing Al and Hf, which led to the formation of a $Ni_7Hf_6Al_{16}$ layer on top of the previously formed NiAl layer through continued outward Ni diffusion. A detailed kinetic study on the coating formation process would be useful in providing further evidence to support this hypothesis.

Nevertheless, the observed multilayer structure is very similar to those reported previously for the diffusion coatings formed on Ni and Ti base alloys by codepositing Al and Cr and Si [5, 11–13]. A common feature revealed was that, although the pack powder mixtures were carefully formulated for the codeposition process, Al appeared to be always the element deposited first into the substrate, leading to the formation of an aluminide layer at the initial stage of the codeposition process. This was then followed by the deposition of primarily the second element at a later stage, resulting in a coating structure consisting of at least two distinctive layers. This strong tendency of preferential Al deposition at the initial deposition stage probably indicates that Al could be more easily converted to the Al-chloride vapours than Cr, Si or Hf, which could in turn lead to the formation of an initial transient vapour phase composition favourable for depositing only Al.

It has thus been demonstrated experimentally that Al and Hf can be codeposited from the vapour phase to form diffusion coatings on nickel base superalloys using the $CrCl_3 \cdot 6H_2O$ activated pack powder mixtures containing the elemental Al and Hf powders. This is in good agreement with the results of thermochemical calculations, which showed that sufficiently high vapour pressures of $HfCl_4$ and $HfCl_3$ could be generated in these packs and be brought into a comparable range with that of AlCl by adjusting the pack composition and deposition conditions, inducing a favourable condition for codepositing Al and Hf. However, since the vapour pressures of both $HfCl_4$ and $HfCl_3$ are within the same order of magnitude as that of AlCl, it cannot be certain at this stage which one of these two species acted as the depositing species responsible for releasing Hf on the substrate. At temperatures higher than 1050°C, the vapour pressure of $HfCl_4$ is closer to that of AlCl than the vapour pressure of $HfCl_3$ (Fig. 3), which may favour the suggestion that $HfCl_4$ is the depositing species. However, this cannot be certain at this stage and more research efforts are needed to clarify this issue, which would lead to a considerably simplified thermochemical analysis procedure for identifying the pack compositions and deposition conditions for depositing diffusion coatings with the required alloy composition and microstructure.

4.2. Codeposition of Al and W

The thermochemical calculation results showed that W cannot be deposited from the vapour phase. However, it is considered that, if the fine W powders are brought to intimate contact with the substrates in an aluminising pack of sufficiently low Al activity that induces coating formation through the outward Ni diffusion, a layer of fine W particles might be entrapped into the coating layer, leading to the formation of a composite coating with a sufficiently high volume of W particles evenly distributed in a NiAl matrix.

Feasibility of this approach was investigated using a modified pack configuration as illustrated schematically in Fig. 8. In essence, the substrate to be coated is embedded in a thin layer of a contact pack containing W, Al and an activator, but no inert fillers such as Al_2O_3. The whole pack is then buried in a normal pack of sufficiently low Al activity for aluminising. In order to ensure that W particles can be entrapped in the coating layer, it is essential that compositions of both the contact pack and the normal pack are formulated to induce an outward Ni diffusion process. The particle size of W powders in the contact pack may also have to be sufficiently small so that they can be easily entrapped into the outwardly growing coating layer.

In a previous publication [3], it was reported that the aluminide coatings on nickel base superalloys are formed predominantly by the outward Ni diffusion at 1100°C in the $CrCl_3 \cdot 6H_2O$ activated packs containing 1.2 wt% of Al or less. Thus, in this work, both the contact and normal pack powder mixtures contained 1.2 wt% Al and 4 wt% $CrCl_3 \cdot 6H_2O$ with balance being W and Al_2O_3 in the contact and normal pack powder mixtures respectively. The specimens were all coated at 1100°C for 8 h.

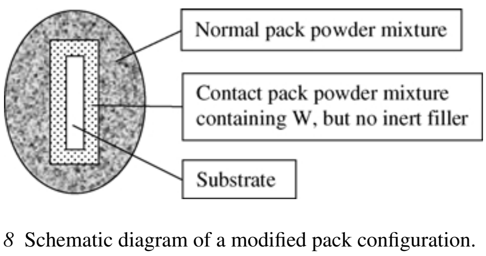

Figure 8 Schematic diagram of a modified pack configuration.

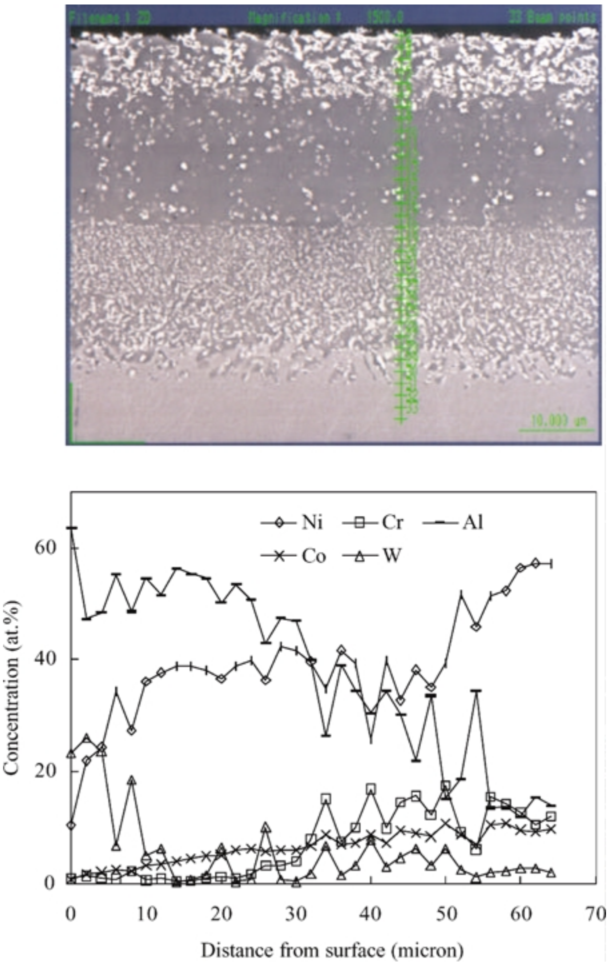

Figure 9 Cross-sectional SEM image and concentration profiles of major elements in the coating layer for a specimen coated using a modified pack configuration for entrapping W particles in the NiAl coating layer.

Fig. 9 shows a cross-sectional SEM image and concentration profiles of major elements in the coating layer measured by EDS for a coating formed under these conditions. As expected, the coating showed a structure typical of the nickel aluminide coatings formed through the outward Ni diffusion—an outer coating layer with a diffusion zone underneath. The major elements present in the coating layer were Al, Ni, Cr, Co and W. Al was deposited from the vapour phase, but Ni, Cr and Co came undoubtedly from the substrate through outward diffusion. The bright spot-like phases in the outer coating layer shown in the SEM image, are the entrapped W particles. There was no evidence to suggest that W was deposited from the vapour phase, which was in agreement with thermochemical calculations. It can be seen that the entrapped W particles were more evenly and densely distributed in a top band of about 10 μm towards the surface. The total thickness of the coating including the diffusion zone was about 58 μm with a thickness of about 32 μm for the outer coating layer.

Fig. 10 shows a XRD pattern measured from the as-coated surface. It can be seen that the major phases present were W and NiAl, confirming that the outer coating layer is essentially a composite with evenly

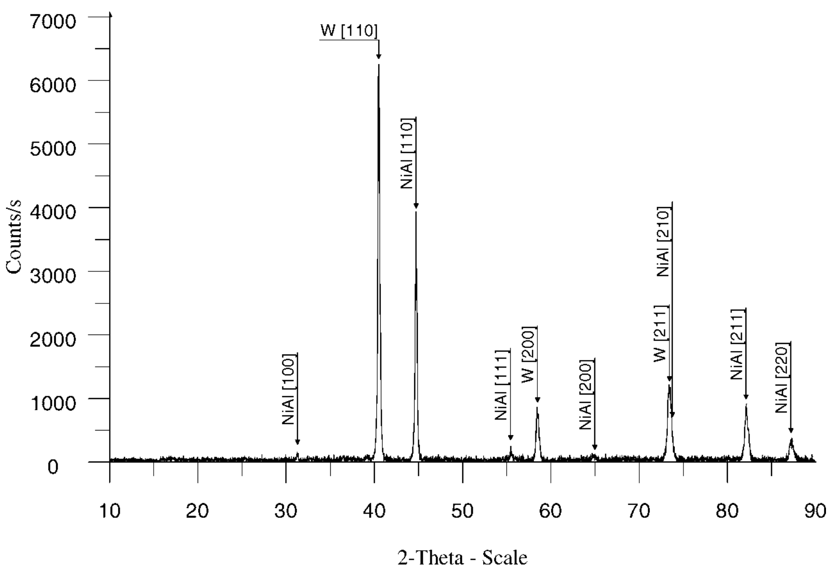

Figure 10 A XRD pattern measured on the as-coated surface containing W particles entrapped in a NiAl matrix formed via outward Ni diffusion.

distributed W particles in a NiAl matrix. It may be possible to homogenise the W concentration in this layer by a further diffusion heat treatment at a suitably high temperature.

It has long been known that nickel aluminide coatings form on nickel-base superalloys primarily through two different mechanisms [14, 15]: the outward Ni diffusion and the inward Al diffusion. It has also been reported that, in the in-pack process, the coatings formed through the outward Ni diffusion often contain randomly distributed pack particles (mostly alumina), which are undesirably, but unavoidably, entrapped into the coating layer during the coating formation process [5, 14, 15]. However, the results obtained in this study demonstrated experimentally that the outward Ni diffusion mechanism could be usefully exploited to develop a diffusion coating containing a high volume of W particles with potentially good sulphidation/erosion or abrasion resistance using the modified pack configuration. It is expected that the same technique can be applied to entrap other refractory metal powders such as Re, Mo, Pt and others in the outer NiAl coating layer, which may be further homogenised by a subsequent heat treatment at a sufficiently high temperature, leading to the formation of a refractory metal modified NiAl coating with properties tailored for protecting the substrate against the sulphidation or other type of environmental degradation at high temperatures.

5. Conclusions

Thermochemical analyses were carried out for a series of pack powder mixtures containing elemental Al and Hf or W powders as depositing source and $CrCl_3 \cdot 6H_2O$ or AlF_3 or CrF_3 as activator for codepositing Al with Hf or W on nickel base superalloys by the pack cementation process. The results suggested that Al and Hf could be codeposited from the vapour phase. Compared with AlF_3 and CrF_3, $CrCl_3 \cdot 6H_2O$ is a more suitable activator for the codeposition. The optimum coating temperature is in the range of 1050°C to 1150°C. However, the results also indicated that W could not be deposited from the vapour phase and hence codeposition of Al and W are not possible with these packs.

The results of coating deposition experiments confirmed that codeposition of Al and Hf could be achieved at 1100°C in the $CrCl_3 \cdot 6H_2O$ activated packs containing elemental Al and Hf powders. The coating formed had a multilayer structure consisting of a $Ni_7Hf_6Al_{16}$ top layer with a NiAl layer underneath, followed by a diffusion zone. These results also confirmed that pack compositions suitable for codeposition of Al and Hf could be effectively identified by comparing the vapour pressures of $HfCl_4$ and $HfCl_3$ with that of AlCl.

It was experimentally demonstrated that a high volume of W particles could be entrapped into the outer NiAl coating layer using a modified pack configuration, leading to the formation of a composite coating layer with W particles evenly distributed in a matrix of NiAl. A critical requirement for the formation of this type of composite coatings is that the compositions of the contact pack and normal pack are suitably formulated to induce an outward Ni diffusion process. This modified pack process could be similarly applied to develop nickel aluminide coatings containing other refractory metals that may not be codeposited with Al from the vapour phase.

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