Effects of pack composition on the formation of aluminide coatings on alloy steels at 650°C

Z. D. XIANG, P. K. DATTA

Advanced Materials Research Institute, School of Engineering and Technology, Northumbria University, Ellison Building, Ellison Place, Newcastle upon Tyne, NE1 8ST, UK

This is a detailed study aimed to understand the effects of pack composition on the formation and growth of aluminide coatings on alloy steels by pack aluminisation at 650°C, a temperature below the melting point of AI (660°C), using pack powders consisting of AI as depositing source, a halide salt as an activator and Al₂O₃ as inert filler. The packs activated by AICI₃, NH₄CI, AIF₃ and NH₄F were used to investigate the effects of the type of halide salt on the coating formation and growth process and subsequently to identify the most suitable activator for pack aluminising alloy steels at 650°C. The effects of pack Al content on the rate of coating growth were then studied by varying the pack Al content from 1.4 wt% to 10 wt% whilst fixing the pack activator content at 2 wt%. It was observed that among the halide salts studied, AICl₃ is the only suitable activator for pack aluminising alloy steels at 650°C and the rate of coating growth increases with the pack Al content. The equilibrium partial pressures of vapour species generated at the deposition temperature in packs activated by different types of halide salts were calculated and the results were discussed in relation to the observed deposition tendency of packs activated by different types of activators. A vapour phase transportation model was applied to elucidate the relationship between the rate of coating growth and the pack Al content. It was also demonstrated that by combining the low temperature pack aluminising parameters identified in this study with electroless or electro Ni plating, coherent nickel aluminide coatings free of microcracking can be produced on alloy steels at 650°C. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Cost effective materials capable of long-term operation in high pressure steam at or above 650°C are required to further increase the thermal efficiency of steam turbine powder plants and consequently reduce the level of gas emissions from them without incurring a significantly higher additional cost. There has been steady progress in the past two decades in improving the high temperature mechanical strength and creep/fatigue resistance of alloy steels containing typically 9-12 wt% Cr and 1 wt% Mo through alloy composition modification and microstructure control [1, 2]. However, due to relatively low Cr content, these types of steels oxidise and corrode readily in high temperature steam environment. One of obvious ways to enhance the high temperature steam oxidation resistance of these types of alloy steels while preserving their mechanical properties is to deposit a protective surface coating that can effectively insulate the bulk steel from the high temperature steam environment. Recent studies [3, 4] have shown that alloy coatings such as FeAl, FeCrAl and NiAl, which are capable of forming a stable Al₂O₃ scale at high temperatures, are promising coating candidates. These types of alloy coatings are normally deposited by using thermal spray processes such as high velocity oxy-fuel process (HVOF) [3], which are line-of-sight by nature and hence difficult to be applied to coat components of complex geometries. Another approach is to chemically modify the steel surface by enriching it with Al to form aluminide intermetallic compounds. This can be accomplished by pack aluminisation, which is a low cost thermochemical surface treatment process without any line-of-sight restrictions. It is a process conventionally used to aluminise nickel base superalloys [5-7]. Indeed, a number of investigators have used the pack process to aluminise alloy steels and studied the oxidation resistance of the coatings so formed [8, 9]. However, this process requires thermal activation. And as a consequence, in nearly all these studies, the temperatures used to perform the pack process was at or above 800°C, which could fatally degrade the mechanical properties of the alloy steels [2]. To avoid such degradation, pack process needs to be carried out at temperatures below 700°C. A recent study [10] had shown that with a carefully chosen halide salt as an activator, the pack process could indeed be applied to aluminise alloy steels at temperatures below 700°C. It was also observed that the coating formation kinetics was strongly influenced by pack composition. This study aims to understand the effects of pack composition on the aluminide coating formation process and to establish conditions suitable for the stable growth of aluminide coatings at 650°C on the commercial P92 steel containing 9 wt% Cr and 1 wt% Mo. The processing parameters identified were subsequently applied to demonstrate the viability of forming nickel aluminide coatings on the alloy steel by a two-step process of electroless Ni plating followed by pack aluminising at 650° C.

2. Experimental procedures

The commercial P92 steel (Fe-9Cr-1.0Mo-0.1C) was cut to a dimension of approximately $20 \times 10 \times 2$ mm and then manually ground using SiC abrasive paper to a 600-grade finish. The specimens were then degreased with organic solvent and weighed using an electronic balance (Sartorius MC 210 S). The specimens so prepared were then ready for pack aluminising.

Chemicals used for pack aluminising were powders of Al, Al₂O₃, AlCl₃, NH₄Cl, AlF₃ and NH₄F. The average particle sizes of Al and Al₂O₃ powders were 75 and 50 μ m respectively. Powders of the halide salts were prepared by manual grinding with a mortar and pestle, but were not sieved.

An in-pack process was used to aluminise the specimens [6]. Briefly, the specimens were buried in the pack powder mixture, which was charged into a cylindrical alumina crucible of 30 mm diameter and 40 mm length. The crucible was then sealed with an alumina lid and cement, which was cured in an oven at temperatures up to 80°C. The whole pack was loaded into a tube furnace, which was subsequently circulated with argon and heated to and held at 150°C for about 1 h to further cure the cement. The furnace was then heated to 650°C at 10 K/min. After dwelling at this temperature for a required duration, it was cooled to room temperature at its natural rate by switching off its power supply while maintaining the argon gas flow. The weight gains in mg/cm² of the coated specimens were calculated from the specimen weight measured before and after aluminising and the surface area of specimens.

Scanning electron microscopy (SEM) (Hitachi S-2400) with energy dispersive spectroscopy (EDS) was used to analyse the cross-sectional microstructure and chemical composition of the specimens. X-ray diffraction (XRD) (Siemens D5000 diffractometer with Cu-K α source radiation) was used to identify phases formed in the surface layer of the coatings. The coating thickness was estimated from the Al depth profile measured by EDS.

3. Results

3.1. Effects of different activators

The packs containing 4 wt% Al, 2 wt% Halide salt (= AlCl₃, AlF₃, NH₄Cl and NH₄F) and 94 wt% Al₂O₃ were used to carried out the initial series of aluminising experiments to identify the most suitable activator for pack aluminising the steel at 650°C. The deposition time used in all these experiments was 8 h. After the pack deposition process, the specimen weight gains were measured and the phases in the surface layer were determined by XRD. Table I summaries the results obtained. The results show clearly that the specimen's weight gain in the AlCl₃ activated pack was far higher than those in packs activated by all other halide salts.

TABLE I Weight gains and phases in the surface layer of the coatings formed at 650° C for 8 h

Activator	Weight gain (mg/cm ²)	Phase in surface layer
AlCl ₃	5.4	Fe ₁₄ Al ₈₆
AlF ₃	2.2	Fe ₂ Al ₅ , AlF ₃
NH ₄ F	0.9	Fe ₂ Al ₅ , AlF ₃
NH ₄ Cl	-2.7	Fe ₂ Al ₅

The specimen aluminised in the NH₄Cl activated pack actually showed an significant weight loss. These results suggest that among the halide salts studied, AlCl₃ is the most suitable activator for pack aluminising the steel at 650° C.

Although the specimen incurred a weight loss after aluminising in the NH₄Cl activated pack, XRD measurement showed that the major phase in the surface of this specimen was Fe_2Al_5 , indicating that the surface was enriched with significant amount of Al. Thus, two competing processes took place simultaneously during aluminising in the NH₄Cl activated pack, one being the formation and another the dissolution of the coating layer. This is consistent with the results of other investigators who observed that the latter process could be particular severe at longer deposition times in a fluidised bed reactor activated by NH₄Cl [11].

A significant feature for the specimens aluminised in the NH₄F and AlF₃ activated packs was the presence of the AlF₃ phase in the surface layer of the specimen as detected by XRD. Fig. 1 presents a XRD pattern for the specimen aluminised in the NH₄F activated pack (for the specimen aluminised in the AlF₃ activated pack, it showed almost identical features). It shows strong AlF₃ diffraction peaks, revealing that considerable amount of the AlF₃ phase was present in the specimen surface layer. This was later confirmed by the results of SEM/EDS analysis on the cross section of these specimens (see Section 3.2.3), which showed that there was indeed a relatively thick, but not uniform, AlF₃ layer on the specimen surface. AlF₃ was one of the products of the reactions between Al and NH₄F at the deposition temperature. The formation of this solid phase in the substrate surface is a strong indication that AlF₃ is not a depositing species responsible for releasing Al at the substrate surface in the pack aluminising process.

For the specimen aluminised in the AlCl₃ activated pack, the as-coated surface was very smooth with a light-grey metallic appearance without any entrapped pack particles. These are the typical features suggesting that the coating was formed predominantly through the inward Al diffusion. The major phase in surface layer as determined by XRD was $Fe_{14}Al_{86}$.

3.2. Microstructure of the coatings

3.2.1. Coatings formed in the AICl₃ pack

Fig. 2 presents the cross-sectional SEM image and element depth profiles measured by EDS in the coating. On appearance, it shows a single layer coating with a uniform thickness of approximately 33 μ m. However, as revealed in Fig. 3, the atomic Al/Fe ratio in the coating decreased from about 11 at the surface to about 3 at



Figure 1 XRD pattern measured from the as-coated surface aluminised in the NH₄F activated pack at 650°C for 8 h.



Figure 2 Cross-sectional SEM image and element depth profiles in the coating formed in the AlCl₃ activated pack.

a depth of 8 μ m and then remained almost constant at depths beyond 8 μ m, indicating that the coating consisted of two phase layers: an outer Al rich Fe₁₄Al₈₆ layer and an inner FeAl₃ layer. It is also clear that there was an abrupt interface between the coating and substrate at which the Al concentration dropped suddenly to essentially zero. This is a typical feature signifying that the coating was formed via a reaction-diffusion controlled mechanism.



Figure 3 Al/Fe atomic ratio as a function of coating depth for a coating formed in the AlCl₃ activated pack at 650° C for 8 h.

3.2.2. Surface aluminised in the NH₄Cl pack As shown in Table I, the major phase present in the surface layer of the specimen aluminised in the NH₄Cl pack was Fe₂Al₅ despite the fact that the specimen showed a significant weight loss after aluminising treatment. Fig. 4 presents the cross-sectional microstructure and element concentration profiles in the surface layer of the specimen. It shows that the coating was not uniform. The thickest part was only about 8 μ m and the thinnest part 1–2 μ m. However, it can be seen that the Al and Fe concentrations across the coating depth were essentially constant with an atomic Al/Fe ratio close to 2.5, indicating a Fe₂Al₅ phase, which is consistent with the XRD result (Table I).

3.2.3. Surface aluminised in the AIF₃ and NH₄F pack

The surface microstructures at the cross-section were very similar for the specimens aluminised in both AlF₃ and NH₄F activated packs. Fig. 5 shows the microstructure and element concentration profiles at the cross section of a specimen aluminised in the NH₄F activated



Figure 4 Cross-sectional SEM image and element depth profiles in the surface layer of the specimen aluminised in the NH₄Cl pack.

pack. It is clear that there were two layers in the surface. The top layer was AlF₃ with irregular features in thickness. No substrate elements could be detected in this layer by EDS. Underneath the top layer was a thin layer of diffusion coating with a thickness of about $1-2 \mu$ m. The element concentration profiles measured in this thin diffusion coating layer revealed that it was essentially a Fe₂Al₅ coating. These results are consistent with those determined by XRD (Table I).

3.3. Effect of AI content on coating growth

The results presented in the preceding sections suggest that among the halide salts studied, AlCl₃ is the only suitable activator for pack aluminising the steel at 650°C. Thus, a series of experiments were subsequently undertaken to investigate the effect of pack Al content on the coating growth kinetics in the AlCl₃ activated packs by varying the Al content from 1.4 wt% to 10 wt% while keeping the pack AlCl₃ content constant at 2 wt%. All the specimens were aluminised at 650°C for 8 h. After this thermochemical treatment, they were cross-sectioned and the Al depth profiles in the coatings were measured using EDS. Fig. 6 presents the typical results obtained. It shows that the coating thickness increased with the pack Al content, suggesting that the rate of coating growth increased with the





Figure 5 Cross-sectional SEM image and element depth profiles in the surface layer of the specimen aluminised in the NH₄F pack.



Figure 6 Al depth profiles in the coating layers formed at 650° C for 8 h in the AlCl₃ activated packs of different Al content.

pack Al content. This effect is further illustrated in Fig. 7 by plotting the coating thickness as a function of pack Al content. It shows clearly that the coating thickness increased from about 19 μ m to 53 μ m as the pack Al content increased from 1.4 to 10 wt%. Fig. 6 also shows that within the error of the measurement, Al concentration at the surface and characteristics of Al depth profile in the coatings formed in packs of differing Al content remained essentially unaffected by the



Figure 7 Effect of pack Al content on growth of coating thickness at 650°C.

pack Al content. The microstructure of all the coatings were also of essentially the same features as in Fig. 2, indicating that all the coatings were formed via essentially the same mechanism. The phase in the surface layer of all the coatings also remained to be $Fe_{14}Al_{86}$ as determined by XRD. Thus, pack Al content only affected the growth rate of the coating. This effect can be conveniently applied in coating deposition practice to control the coating growth rate or the coating thickness under a set of specified deposition conditions. Nevertheless, more development work is needed to determine whether there is a pack Al content limit at which the coating growth rate reaches a plateau.

4. Discussions

4.1. Effects of activators

The common approach pursued to understand the deposition tendency and kinetics of coating formation in the packs activated by different types of halide salts is through thermochemical calculations of partial pressures of different vapour species generated at high temperatures [12–15]. Such calculations were attempted by a number of investigators to correlate the observed coating growth kinetics to pack compositions [13–15]. For aluminising packs, the vapour species normally included in these calculations were aluminium fluorides or chlorides AlX₃, Al₂X₆, AlX₂ and AlX (X = F or Cl). More recently, it has been pointed out that among these vapour species, only AIX is directly responsible for depositing Al on the substrate surface [5, 6]. Thus, for packs of comparable compositions, the activating strength of different types of halide salts and hence the depositing power of packs can be characterised by the partial pressure of the AlX vapour species (P_{AlX}) generated at different temperatures. A higher value of P_{AIX} is expected to induce a higher rate of coating growth. Fig. 8 compares the calculated P_{AIX} values in the temperature rang of 600 to 800°C for packs of composition 4Al-2Halide salt(= AlCl₃, NH₄Cl, NH₄F and AlF₃)- $94Al_2O_3$ (wt%). The techniques and procedures used to perform these calculations were the same as reported previously [5, 16]. The results in Fig. 8 suggest that the activating strength of NH₄Cl is the highest among



Figure 8 Comparison of the equilibrium P_{AIX} in packs activated by different types of halide salts.

halide salts studied and NH₄F and AlF₃ and AlCl₃ possess almost equal activating strength at 650°C. Thus, the coating growth rate in the NH₄Cl activated packs is expected to be the highest and those in the NH₄F, AlF₃ and AlCl₃ activated packs should be about the same. These theoretical predictions differ substantially from the experimental results presented in the preceding sections, which showed that among these salts, AlCl₃ is the only activator suitable for pack aluminising the alloy steel at 650°C and stable growth of the diffusion coating on the steel surface is not achievable in the NH₄Cl, NH₄F and AlF₃ activated packs at 650°C. However, it is important to keep in mind that NH₄Cl, NH₄F and AlF₃ are far more effective activators than AlCl₃ at temperatures higher than 800°C and are often used to pack aluminise steels or nickel base superalloys at these temperatures [14, 17].

The discrepancies between the theoretical analyses and experimental observations on the deposition tendencies can be attributed to the specific adverse processes taking place at the steel surface that disrupted the coating formation and growth process in packs activated by different types of halide salts at 650°C. In the NH₄Cl activated pack, the experimental results suggested that two opposite processes, i.e. coating formation and dissolution, took place simultaneously at the substrate surface. Only a thin layer of Fe₂Al₅ was present on the specimen surface after aluminising at 650°C for 8 h, during which the specimen showed a weight loss of 2.7 wt%, indicating that the coating growth rate in the NH₄Cl activated pack was only marginally higher than the dissolution rate at 650°C. The specimen also showed a weight loss of about 3 wt% after aluminising in the same pack at 650°C for only 1 h. Thus, coating dissolution resulting in a substrate weight loss is a typical feature of aluminising steels in the NH_4Cl activated pack at 650°C. It is probably caused by the corrosive HCl vapour species generated in the pack at high temperatures. Fig. 9 shows the results of a full analysis of the major vapour species generated in the NH₄Cl activated pack in the temperature rang of 600°C to 800°C. It shows that the partial pressure of HCl is significantly higher than that of AlCl₂, although it is much lower than that of AlCl. The most predominant



Figure 9 Equilibrium partial pressures of the major vapour species in the $4Al-2NH_4Cl-94Al_2O_3$ (wt%) pack.

vapour species in the NH_4Cl activated pack are H_2 and $AlCl_3$. However, $AlCl_3$ is not a vapour species responsible for releasing or depositing Al at the substrate surface.

The process that disrupted coating formation and growth in the NH₄F or AlF₃ activated packs at 650°C differs fundamentally from that in the NH₄Cl activated pack. The evidences shown in Figs 1 and 5 clearly suggest that it was caused by the formation of the solid AlF₃ phase on the substrate surface. This solid AlF₃ layer insulated the substrate surface from the pack vapours containing the AIF species, which is responsible for depositing Al on the substrate surface, and hence hindered the coating growth process. AlF₃ is one of the reaction products at high temperatures in packs activated by fluoride salts. Fig. 10 presents the calculated partial pressures of the major vapour species in the NH₄F activated pack. The results for the AlF₃ activated pack is similar, except that it does not contain H₂ and HF vapour species. It is interesting to note that the calculated partial pressure of AlF₃ is significantly lower than that of AlF in the pack. However, unlike AlF, which can exist only in the vapour phase, AlF₃ has a melting point of 1291°C and can exist both in the vapour phase and in the solid phase at 650°C. The formation of the solid AlF₃ phase on the substrate surface may be regarded as a direct experimental evidence proving that the gaseous



Figure 10 Equilibrium partial pressures of the major vapour species in the $4Al-2NH_4F-94Al_2O_3$ (wt%) pack.

AlF₃ is not responsible for depositing Al on the substrate surface in the pack aluminising process.

4.2. Effects of pack Al content

Figs 6 and 7 clearly illustrate that in the AlCl₃ activated packs, coating thickness increased from 19 to 53 μ m as pack Al content was increased from 1.4 to 10 wt% whilst all other deposition parameters were kept constant. They also demonstrate that the pack Al content affected neither the Al concentration at the coating surface nor the characteristics of the Al depth profile in the coatings formed in packs containing different amount of Al. Thus, the pack Al content changed the coating's growth rate, but not its formation mechanism. These findings are consistent with the observations made previously by the present and other investigators for nickelbase superalloys and carbon steels [6, 9], which also showed that the coating thickness and hence coating growth rate increased with the pack Al content when other deposition conditions remained constant. A number of investigators [13–15], Levine and Caves in particular [13], had attempted to develop analytical models to predict the effects of pack composition on the kinetics of coating growth in the pack aluminising process, which was observed to be parabolic in feature. These analyses were normally based on observation that there always existed an Al depletion zone in the pack powders surrounding the substrate. It was thus assumed accordingly that the coating growth rate is controlled by the vapour phase transport of aluminium halides from the bulk pack through the depletion zone to the substrate surface. It can then be shown [13, 14] that the relationship between the amount of Al deposited (m) and deposition time (t) is:

$$m = kt^{1/2} \tag{1}$$

$$k = \left(\frac{2\rho\varepsilon M}{lRT}\sum D_{\rm i}(p_{\rm i} - p_{\rm i0})\right)^{1/2}$$
(2)

where ε and l are correction factors for pack porosity and pore length, ρ pack Al concentration in g/cm³, Matomic weight of Al, R the gas constant, T the absolute temperature, D_i the diffusivity of the vapour species in pack, p_i and p_{i0} are the partial pressures of the vapour species in the bulk pack and at the coating surface. For coatings of the same microstructure, the relationship between coating thickness (h) and the amount of Al deposited (m) has been shown to be linear [6, 10]. Thus, Equation 1 can be written as:

$$h = C_1 k t^{1/2} (3)$$

where C_1 is a constant. For packs of a specified activator and other ingredients and under constant deposition conditions, by combining Equations 2 and 3, it can be easily shown that the relationship between the coating thickness (*h*) and pack Al content in weight percent (*W*) would be

$$h = CW^{1/2} \tag{4}$$



Figure 11 A plot of h against $W^{1/2}$.

where *C* is a constant. Thus, a plot of *h* against $W^{1/2}$ should be a straight line. Fig. 11 shows such a plot. It confirms that the relationship between h and $W^{1/2}$ is indeed linear. The straight line in Fig. 11 is the least squares fit to the data points, which gives

$$h = 17.4 \ W^{1/2} - 3.0 \tag{5}$$

It is noted that when W = 0, $h = -3 \mu m$, which can be regarded as a small deviation from 0 attributable to experimental error. Thus, there appears a good agreement between theoretical analysis and experimental observations, which seems to support the hypothesis that the vapour phase transport determines the rate of coating growth in the pack aluminising process.

4.3. Formation of novel coatings on steels below 700°C

The results presented in the preceding sections confirm that it is technically feasible to pack aluminise alloy steels at temperatures below 700°C by carefully choosing a suitable halide salt as an activator. It is anticipated that the processing parameters identified can be applied to produce novel diffusion coatings on steels at these low temperatures. One of such coatings is the nickel aluminide compound Ni₂Al₃ or NiAl, which has proved to be resistant against high temperature steam oxidation and thus can protect alloy steels operating in a high temperature steam environment. With the low temperature aluminising parameters identified in this study, it is considered that such coatings can be relatively easily formed on steels by a two step process of firstly electroless or electro Ni plating and then pack aluminising at 650°C. To confirm the viability of such an approach, the alloy steel substrate was firstly plated with a layer of electroless Ni, which contained a trace amount of B, but no P. The specimen was then pack aluminised at 650°C for 8 h using packs containing 4 wt% Al and 2 wt% AlCl3 or NH4Cl and 96. wt% Al2O3. It was observed that the microstructure was similar for coatings formed in both AlCl₃ and NH₄Cl packs and there was no evidence of coating dissolution in the NH4Cl pack as occurred when aluminising the un-plated steel at 650°C



Figure 12 Cross-sectional SEM image and element concentration profiles in a coating formed on an alloy steel by a combination of electroless Ni plating and pack aluminising at 650°C.

(Section 3.1). Fig. 12 presents the cross-sectional microstructure and element concentration profiles for a coating produced in the NH₄Cl activated pack. It shows a coherent coating consisting of an outer Ni₂Al₃ layer (16 μ m) and an inner Fe₂Al₅ layer (17 μ m) with no spallation or microcracking. The XRD measurement from the as-coated surface confirmed that the phase in the outer layer was Ni₂Al₃.

It has thus been demonstrated that the approach outlined for producing nickel aluminide coatings on steels at temperatures below 700°C is indeed technically viable. It can also be easily demonstrated that the microstructure of the coatings produced by the demonstrated process need not to be limited to the one shown in Fig. 12. Instead, it can be made to consist of an outer Ni₂Al₃ layer and an inner Ni layer by varying the initial Ni plating thickness and/or adjusting the pack aluminising parameters. Further research is in progress to investigate the growth kinetics of this type of coatings in packs of varying compositions and the corresponding microstructures of the coatings formed.

5. Conclusions

1. Among the halide salts studied (AlCl₃, NH₄Cl, AlF₃ and NH₄F), AlCl₃ is the only suitable activator for inducing stable growth of aluminide coatings on alloy steels at 650°C. Formation of the solid AlF₃ phase on

the substrate surface hinders the coating growth process in the AlF₃ or NH₄F activated packs at 650°C whereas simultaneous processes of coating formation and dissolution destabilise the coating growth process in the NH₄Cl activated pack at 650°C.

2. With the AlCl₃ activated packs, coatings form at 650° C through an inward Al reaction-diffusion mechanism. Increase in the pack Al content would increase the rate of coating growth, but would not affect the level of Al concentration at the surface or characteristics of the Al depth profile in the coating layer or the formation mechanism of the coatings.

3. It is technically feasible to form nickel aluminide coatings on alloy steels at temperatures below 700°C using a two step process of electroless or electro Ni plating followed by pack aluminising.

Acknowledgement

The authors wish to express thanks to the European Commission for funding this research under the contract ENK5-CT-2002-00608 (SUPERCOAT). They also wish to thank Mr. B. Best for his assistance in the EDS measurements.

References

- 1. R. VISWANATHAN and W. BAKKER, *J. Mater. Engng. Perform.* **10**(1) (2001) 81.
- 2. P. J. ENNIS, A. ZIELINSKA-LIPIEC, O. WACHTER and A. CZYRSKA-FILEMONOWICZ, *Acta Mater.* **45**(12) (1997) 4901.

- A. AGUERO, J. GARCIADE BLAS, R. MUELAS, A. SANCHEZ and S. TRIPAS, *Mater. Sci. Forum* 369-372 (2001) 939
- 4. R. STREIF, J. Phys. IV (1993) 17.
- 5. Z. D. XIANG and P. K. DATTA, Surf. Coat. Tech. 179 (2003) 95.
- 6. Z. D. XIANG, J. S. BURNELL-GRAY and P. K. DATTA, *J. Mater. Sci.* **36** (2001) 5673.
- 7. R. MEVREL, C. DURET and R. PICHOIR, *Mater. Sci. Technol.* **2**(3) (1986) 201.
- L. LEVIN, A. GINZBURGE, L. KLINGER, T. WERBER, A. KATSMAN and P. SCHAAF, Surf. Coat. Technol. 106 (1998) 209.
- 9. H. M. SOLIMAN, K. E. MOHAMED, M. E. ABD EL-AZIM and F. H. HAMMAD, J. Mater. Sci. Technol. 13 (1997) 383.
- 10. Z. D. XIANG and P. K. DATTA, Surf. Coat. Tech. 184 (2004) 108.
- 11. F. J. PEREZ, F. PEDRAZA, M. P. HIERRO, J. BALMAIN and G. BONNET, *Oxid. Met.* **58**(5/6) (2002) 563.
- P. N. WALSH, "Chemical Aspects of Pack Cementation," in Proc. Fourth International Conference on Chemical Vapour Deposition, edited by G. F. Wakefield and J. M. Blocher, (Electrochemical Society, Penington, New York, 1973) p. 147.
- 13. S. R. LEVINE and R. M. CAVES, J. Electrochem. Soc. 121(8) (1974) 1051.
- 14. R. SIVAKUMAR and L. L. SEIGLE, *Metall. Trans. A* 7A (1976) 1073.
- 15. T. H. WANG and L. L. SEIGLE, *Mater. Sci. Eng.* A108 (1989) 253.
- 16. Z. D. XIANG, J. S. BURNELL-GRAY and P. K. DATTA, *Surf. Engng.* **17** (2001) 287-294.
- 17. X. Y. WANG and D. Y. LI, Surf. Coat. Technol. 160 (2002) 20.

Received 9 September and accepted 25 October 2004