

Aluminization of nickel – formation of intermetallic phases and Ni_2Al_3 coatings

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The occurrence and growth mechanisms of the various intermetallic phases of the Al–Ni system formed during pack aluminization of unalloyed nickel have been investigated with respect to the aluminium activity in the pack. Several types of coatings were obtained: (1) a Ni_2Al_3 coating formed by inward aluminium diffusion in a high activity cement of pure aluminium; (2) a Ni-rich NiAl coating formed by outward nickel diffusion in a low activity pack constituted by an Al–Ni alloy; (3) a mixed type of coating exhibiting the phases Ni_2Al_3 , Al-rich NiAl, Ni-rich NiAl and Ni_3Al in four superposed layers, formed in a pack containing an Al–Cr alloy; (4) a high temperature, high activity type of coating formed above 950°C with an outer layer exhibiting a hypereutectic structure of NiAl₃ grains in a eutectic matrix due to precipitation from the liquid state. The optimum cementation conditions, for the production of maximum thickness and quality Ni_2Al_3 coatings were determined. The influence of surface reactivity and pack activity on the coating quality parameters was investigated.

1. Introduction

The utilization of nickel-base superalloys as structural material in gas turbines, at temperatures usually exceeding 900°C , necessitates their protection by means of coatings to prevent high temperature oxidation and hot corrosion by aggressive environments. A variety of coatings have been developed, based on aluminizing-type diffusion processes. Most of them have as a goal the surface preparation, either by direct reaction or after a diffusion step, of the intermetallic compound NiAl which, in addition to a high melting point (1638°C), exhibits fairly good resistance to oxidation by forming an Al_2O_3 -rich protective scale. Nevertheless, although aluminide coated superalloys have been used for a number of years, very few fundamental investigations on the oxidation of those coatings have been conducted up to now; this led us to undertake a study on the oxidation of the various intermetallic phases of the system Al–Ni involved in aluminide coatings.

We began with the oxidation kinetics of Ni_2Al_3 coating [1, 2], but since the production of the Ni_2Al_3 coatings has not yet been the subject of any published study, we decided to study also the formation and the properties of this type of aluminide coating on pure nickel.

The structure and properties of aluminide coatings depend on their production method. There are numerous and diverse procedures to aluminize metal surfaces. In an exhaustive review Romeo [3] and his collaborators have given a full account of all the processes in use, or only in an experimental stage, to produce high temperature protective metallic coatings on superalloys. Aluminization has to answer two questions concerning the supply of aluminium to the alloy surface and the bonding of the scale at that surface. Romeo [3] has summarized the main features of the following current processing techniques involved in the deposition of aluminium on to the metal: HIP cladding, hot dipping and spraying,

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slurry, electrophoresis, electroplating, metallizing, physical vapour deposition (PVD), pack cementation and chemical vapour deposition (CVD). Among these, pack cementation is the most used and the most investigated process. It has the advantage of permitting effective plating of complicated shape structures and of being easy to carry out both in industrial processing and in the laboratory.

Among the numerous investigations on the pack cementation of nickel-base alloys [4–13] only a few authors have been interested in the cementation of pure metal [4, 10, 11–13] and none in the growth, morphology and quality of Ni_2Al_3 layers on unalloyed nickel.

The purpose of this study is to determine the conditions of the growth of a Ni_2Al_3 coating on pure nickel. The different factors which determine the formation of the coating, their influence on the composition, the morphology and the structural quality of the layers produced are examined.

The variables affecting the thickness and the nature of the phases formed on the substrate, as quoted by Linblad [14] in his review, are:

- the chemical state of the substrate, that is, the composition of the alloys since the growth rate and the morphology of the coatings depend on the rate of Al and Ni diffusion across the phases formed;
- the composition and purity of the powders in the cement;
- the permeability and homogeneity of the pack (not studied in the present work);
- the pressure, the temperature and the time of cementation.

We will also deal with the physical state (polish) of the substrate surface.

As a main result of this investigation, the optimum cementation conditions and pack composition were determined for providing Ni_2Al_3 coatings free from defects, for studying the growth kinetics of these Ni_2Al_3 layers [14] and for oxidation experiments [1, 2].

2. Experimental procedures and techniques

2.1. Coating procedure

The nickel specimens, cut into 10 mm × 10 mm × 2 mm plates, were usually polished on carborundum papers to grit size 600 and with B (3 μm) grade diamond paste, degreased and rinsed.

The coatings were applied using a typical halide-activated pack aluminizing process. The

specimen to be coated was encased in a mixture of powders, placed in a closed retort and heated to the reaction temperature. The pack cement consisted essentially of the aluminium to be deposited, of Al_2O_3 as an inert filler to prevent sintering and of a halide as an active agent, here, CrF_2 . At the treatment temperature, the activator giving rise to aluminium was established by a chemical transport reaction with a volatile aluminium subhalide intermediate (namely AlF) which decomposes at the specimen surface with deposition of aluminium.

The alumina powder used for the cement was preliminarily calcined at 1050°C under flowing pure hydrogen to reduce oxide impurities. The resulting calcine was then screened to powders less than 400 μm , mixed with aluminium powder and annealed for 2 h at 860°C under hydrogen to further eliminate impurities, before adding the CrF_2 activator. This mixture was mechanically homogenized.

The pack cementation was carried out in cylindrical alumina retorts (38 mm diameter, 30 mm height and containing about 20 g cement), closed by a lid and heated in a Kanthal resistance furnace under flowing argon after having been subjected to a vacuum at room temperature for 1 h to degas.

2.2. Investigation techniques

The specimens, sectioned and polished on abrasive papers, were subjected to a final electropolish in sulphuric acid under alternating current at 50 Hz and 1 A for 3 mn.

The phases were identified either by their etching characteristics or under polarized light. Chemical etching was applied with a concentrated acid solution (HNO_3 , H_2SO_4 , H_3PO_4 , 1 : 1 : 1). The grain boundaries of Ni_2Al_3 become observable when electrochemically etched at 3 V in a solution of 20 ml H_2O , 30 ml HCl, 10 ml HNO_3 , 50 ml glycerine and 1 ml HF.

Phase identification was verified by surface X-ray diffraction using $\text{CuK}\alpha_1$ radiation. For inner layers the specimens were subjected to X-ray diffraction of surfaces in the plane of the coating after stepwise removal of the coating by abrasive polishing or electrolytic dissolution.

Distributions of nickel and aluminium in the coatings were determined by a Castaing electron microprobe operating with an incident electron beam at 24 and 10 kV. Qualitative analyses of the phases present were obtained from electron

backscatter and X-ray images over representative areas of the polished cross-sections; quantitative analyses were obtained from intensities of Al- and Ni-K α lines across the coating.

The observations of the surfaces were also carried out using a scanning electron microscope operating with an incident electron beam at 25 kV. The analyses of the surfaces were carried out with the help of an energy dispersive X-ray analysis (EDAX) attachment.

3. The phases in the system Al–Ni

There are, according to Hansen [15], four intermetallic compounds in the Al–Ni system (Fig. 1) with the following structures:

Al	NiAl ₃	Ni ₂ Al ₃
fcc	orthorhombic	rhombohedral
NiAl	Ni ₃ Al	Ni
CsCl type cubic	AuCu ₃ type cubic	fcc.

The last three present a wide composition range, particularly for NiAl, whose composition varies from 42.5 to 69.5 at % nickel.

Bradley and Taylor [17] and more recently Taylor and Doyle [18] have presented a detailed structural study of NiAl and Ni₂Al₃.

NiAl has the CsCl cubic type of structure. This compound extends on both sides of the NiAl composition range with large departures from the stoichiometry. For an excess of Ni in Ni-rich NiAl, aluminium atoms are replaced substitutionally by smaller nickel atoms. The lattice parameter falls in proportion to the excess nickel.

On the other hand for Al-rich NiAl, lattice vacancies exist in the nickel sites with the aluminium sites remaining fully occupied with aluminium atoms. That also involves a diminution of the lattice parameter. That difference in the two non-stoichiometric NiAl compounds results in

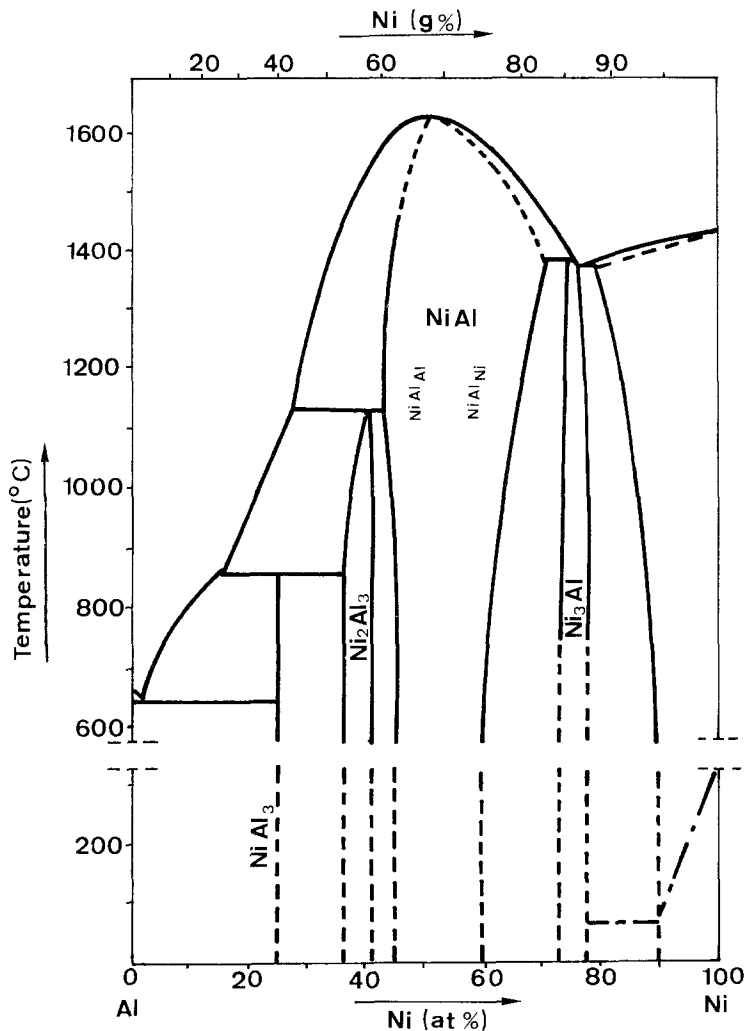


Figure 1 Al–Ni phase diagram.

a great difference in the metallographic structure with a different behaviour on etching. The appropriate perfected etching procedures [19] reveal distinct layers corresponding to the two compositions.

The Ni_2Al_3 structure is closely related to that of NiAl. In this phase 33% of the nickel sites are vacant at the stoichiometric composition but the vacancies are ordered in such a way that every third sheet of nickel atoms perpendicular to one of the three-fold axes of the cube is absent. This ordering reduces the crystal structure from cubic to rhombohedral by unequal diminution of the parameters a and c .

All the phases existing at the cementation temperature formed and were identified in superposed layers depending on the aluminium composition (or activity) of the cement. Ni_2Al_3 was observable by its grain structure under polarized light; Al-rich NiAl appeared as a dull uniform blue, Ni-rich NiAl with a purple granitic aspect and Ni_3Al as bright grey.

4. Results and discussion

4.1. Influence of aluminium activity in the cement on coating structure and classification of the cementation processes

First of all, the structure of the coatings, i.e. the nature and the number of their constituting layers, have been determined as a function of the pack aluminium composition.

Three types of cement were used:

- a cement of pure aluminium mixed with alumina and CrF_2 ;
- a cement with aluminium alloyed with nickel in varying proportions;
- a cement containing a mixture of aluminium and chromium.

The cementation was carried out in the temperature range 760 to 1100° C.

The first cement had the following composition: 40.7 wt % Al, 58 wt % Al_2O_3 , 1.3 wt % CrF_2 .

Between 760 and 950° C, a thick scale of Ni_2Al_3 forms (Fig. 2a) after 20 h of cementation i.e. a very thin underlayer, too thin to be identified with certainty by microprobe analysis (Fig. 3). Thevand [20, 21] has shown that it should be an Al-rich NiAl layer resulting from the interdiffusion in the $\text{Ni}_2\text{Al}_3/\text{Ni}$ couple.

We recall briefly his propositions. From the study of diffusion reactions in the system Al–Ni,

Janssen and Rieck [21] concluded that in NiAl, Ni diffuses predominantly, and that in couples of Ni–Al only Ni_2Al_3 forms by predominant diffusion of aluminium whose diffusion coefficient is higher than that of nickel. This should exclude the possibility of any NiAl underlayer formation. Nevertheless, in the cementation of UDIMET 700 alloy Goward and Boone [8] also observed the formation of NiAl and Ni_2Al_3 layers in the coating. Also, they show by carbide precipitates that aluminium is the species diffusing predominantly throughout the whole scale. An explanation of the contradictory diffusional formation of NiAl can be based on the difference of the NiAl structure on both sides of the stoichiometry and on the similarity of the structures of Al-rich NiAl and Ni_2Al_3 . We have recalled that these two phases have the same structure, derived from b c c, with only a different distribution of the nickel vacancies. In Al-rich NiAl these vacancies are randomly distributed and in Ni_2Al_3 they are ordered in sheets perpendicular to the cube diagonal. From these similarities in the structures, the possibility of predominant aluminium motion in these two phases results, while in Ni-rich NiAl, which has no more nickel vacancies but aluminium atoms substituted by nickel atoms, nickel diffusion is predominant. Given these observations, it can be concluded that the NiAl phase rich in aluminium may form under and between the coating and the nickel substrate by an aluminium interdiffusion process.

In that type of coating, the equiaxial structure of the Ni_2Al_3 grains and their size increasing from metal coating to the surface show that the scale is formed by inward aluminium diffusion. The growth kinetics will follow a parabolic law [15] which confirms that the reaction proceeds from a diffusion regime.

In the second type of cements, the aluminium is alloyed with nickel in proportions equivalent to Ni_2Al_3 and stoichiometric NiAl, or in an Al-rich NiAl alloy with 51.5 at % Al + 48.5 at % Ni (that is 32.8 wt % Al + 67.2 wt % Ni).

The corresponding pack weight compositions are the following:

- 19.9 wt % Al, 28.9 wt % Ni, 49.9 wt % Al_2O_3 , 1.3 wt % CrF_2 ;
- 15.4 wt % Al, 33.4 wt % Ni, 49.9 wt % Al_2O_3 , 1.3 wt % CrF_2 ;
- 48.8 wt % NiAl (Al), 49.9 wt % Al_2O_3 , 1.3 wt % CrF_2 (that is 16 wt % Al + 32.8 wt % Ni).

The Al–Ni alloys in these packs were prepared

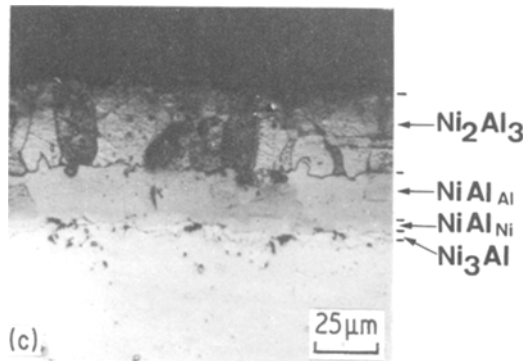
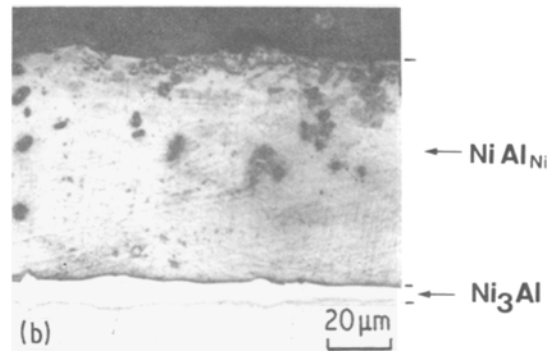
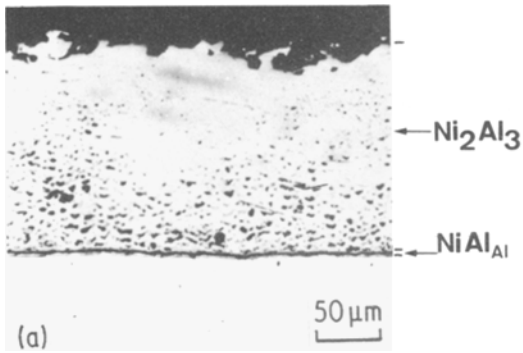


Figure 2 Structure of the coatings: (a) high activity type coating on a specimen subjected to cementation for 50 h at 760°C in a 40.7 wt % pack; (b) low activity type coating on a specimen subjected to cementation for 120 h at 760°C in a pack of 19.9 wt % Al + 28.9 wt % Ni; (c) mixed type coating on a specimen subjected to cementation for 120 h at 760°C in a pack of 34.5 wt % Al + 14.5 wt % Cr.

either during the annealing step of the preparation of the cements from a mixture of aluminium and nickel powders, or by mixing crushed prealloyed aluminium with the NiAl (Al) composition in the pack.

The coatings formed are constituted of a Ni-rich NiAl scale over a Ni₃Al underlayer with an appreciable thickness (Fig. 2b). This structure remains for all cementation conditions between 760 and 1100°C.

This implies lowering of the aluminium activity

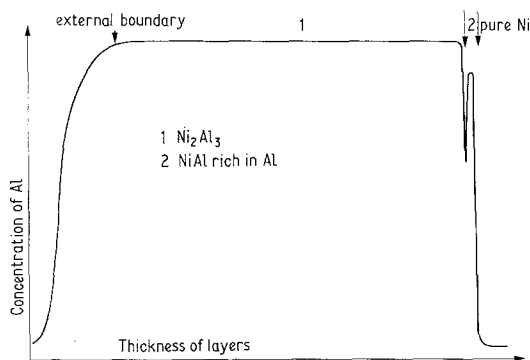


Figure 3 Microprobe analysis of a high activity type coating on a specimen subjected to cementation for 50 h at 760°C in a 40.7 wt % Al pack.

at the reaction surface since the aluminium composition of the external scale is lower than the nominal composition of the cement. In addition, this decrease of the activity involves a diminution of the growth rate of the coating, as shown in Table I which summarizes the thicknesses of scales formed during equal periods of 20 h in the cements used, including pure aluminium.

These results show that the activity naturally varies in the same way as the aluminium content of the alloy in the packs.

A change in the formation mechanism of the scales should be observed. There are inert alumina particles from the cement embedded in the coatings. Therefore their growth is directed by an outward nickel diffusion process.

These two types of coatings consist of Ni₂Al₃ and Ni-rich NiAl corresponding to the two types of cementation processes in the classification proposed by Goward and Boone [8] and specified more recently by Pichoir [23, 24]. This classification is based on the aluminium activity in the cements following the formation mechanism and the structures of the coatings. Thus, there can be distinguished: (1) The “high activity process”, using pure aluminium or high aluminium activity cement at low temperature (700 to 950°C), where the coatings are formed by inward diffusion of aluminium from the surface. Ni₂Al₃ and/or Al-rich non-stoichiometric NiAl are the main constituting phases. (2) The “low activity process” using Al–Ni

TABLE I Coating layer thicknesses for various cement compositions

Cement composition	Time/temperature	Thickness, $e(\mu\text{m})$				
		$e_{\text{Ni}_2\text{Al}_3}$	$e_{\text{NiAl (Ni)}}$	$e_{\text{Ni}_3\text{Al}}$	e_{total}	
					760° C	1000° C
40.7 wt % Al	20 h/760° C	116	—	—	116	—
Pure Al	1 h/1000° C	214	—	—	—	214
19.9 wt % Al, 28.9 wt % Ni	20 h/760° C	—	6	5	11	—
Ni_2Al_3	20 h/1000° C	—	62	7	—	69
16 wt % Al, 32.8 wt % Ni	20 h/760° C	—	5	4	9	—
NiAl (Al)	20 h/1000° C	—	60	6	—	66
15.4 wt % Al, 33.4 wt % Ni	20 h/760° C	—	2	5	7	—
NiAl (stoichiometric)	20 h/1000° C	—	15	8	—	23

alloys or low aluminium content packs, at higher temperatures (1000 to 1150° C), where the coatings are formed by outward diffusion of Ni from the substrate. Ni-rich NiAl and Ni_3Al , are then the main coating phases.

The third type of cement used in this section of our study gives a mixed type of coating. Its weight composition is 34.65 wt % Al, 14.5 wt % Cr, 49.5 wt % Al_2O_3 and 1 wt % CrF_2 . It is derived from a cement perfected at the Onera for the “chromaluminization” process [25].

The lowering of the aluminium activity in the cement by alloying aluminium with chromium involves the interdiffusion of the Ni_2Al_3 coating with the nickel from the substrate which may occur simultaneously with the formation of the cement. Therefore, the coating formed by 50h cementation at 760° C consists of the four phases: Ni_2Al_3 , Al-rich NiAl, Ni-rich NiAl and Ni_3Al (Fig. 2c). These compounds were identified by microprobe analysis (Fig. 4). On the other hand the microprobe did not reveal any trace of chromium in the coating.

The formation and growth of this mixed type of coating may be briefly explained as follows. The aluminium activity of the cement is high enough to allow the formation and the growth of an initial layer of Ni_2Al_3 by aluminium diffusion. But during its growth a concentration gradient is established due to the aluminium diffusion being too fast compared with the aluminium supply at the surface by the transport reaction. This involves a lowering of the aluminium activity at the aluminate substrate interface. This means that the growth of the external Ni_2Al_3 and Al-rich NiAl layers by diffusion of the aluminium is no longer fast enough to oppose the formation of the inner Ni-rich NiAl and Ni_3Al phases which grow by nickel diffusion.

4.2. Determination of the optimum conditions for the formation of Ni_2Al_3 coatings

We have determined the conditions required for the formation of coatings of maximum thickness and quality in a cement of high activity containing about 40 wt % Al. This investigation was made at 760° C for cementation periods of 20 h.

The factors influencing the coating formation are the cement activity and the surface reactivity of the sample to be coated.

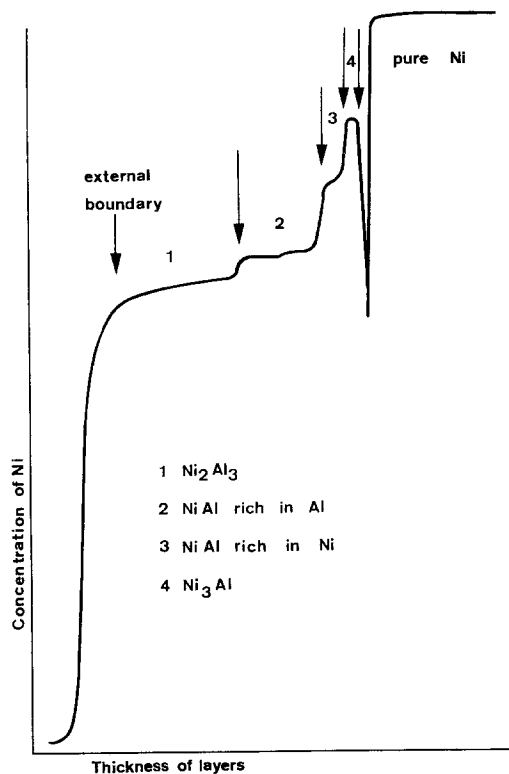


Figure 4 Microprobe analysis of a mixed type coating on a specimen subjected to cementation for 120 h at 760° C in a pack of 34.5 wt % Al + 14.5 wt % Cr.

TABLE II Effect of the surface treatment*

Parameters at final polish	Paper grit 600	Diamond paste				Chemical polish
		7 μ m	A	B	C	
Thickness $e(\mu\text{m})$	79	78	76	95	76	74
Thickness regularity, $\Delta e(\mu\text{m})$	10	9	13	7	10	11
NiAl thickness, % of e	< 2	< 2	< 1	< 1	< 1	< 2
†Interface regularity	2	2	1	1	1	2
†Number of pores	2	2	1	1	1	2
†Pore size/detachments (+)	3(+)	1	2	1	1	2(+)
Figure	5b	—	—	5c	—	5a

*For a pack composition of 41.2 wt % Al, 58.4 wt % Al_2O_3 , 0.4 wt % CrF_2 .

†This corresponds to a comparative classification: the quality of the interface increases when the number decreases; the quantity and the size of pores increase when the number increases.

The parameters used for evaluating the quality of the coatings are: the thickness; the regularity of the thickness, given by the mean error; the existence and the thickness of the NiAl underlayer; the regularity of the coating—substrate interface and the adherence; the number and the size of the pores. Their evolution was determined following the composition and the quantity of the cement

and the physical state of the surface, i.e. the polish of the samples. The results are summarized in Tables II and III and in Fig. 5.

The thickness of the coating is related to the activity of the cement, the regularity of the interface and the morphological quality of the scale to the surface state.

The activity of the cement passes through a

TABLE III Effect of the pack composition*

Parameter	Pack quantity, number of samples per 20 g †		Chromium bifluoride content (wt %) ‡						Aluminium content (wt %) ‡	
			0.4	0.5	1.3	1.7	2	4.3 (annealed §)	41.2 wt % Al	49.3 wt % Al
	1	4							58.4 wt % Al_2O_3	50.3 wt % Al_2O_3
Thickness $e(\mu\text{m})$	140	95	140	159	164	59	56	30	140	90
Thickness regularity, $\Delta e(\mu\text{m})$	6	7	6	12	13	11	9	12	6	10
NiAl thickness, (% of e)	< 1	< 1	< 1	< 1	< 1	< 3	< 3	< 1	< 1	< 2
¶Interface regularity	1	2	1	2	1	2	1	1	1	1
¶Number of pores	1	2	1	1	1	1	1	1	1	2
¶Size of pores	1	2	1	1	1	1	1	1	1	2
Figure	5e	—	5e	—	5f	—	—	—	5e	5d

*For specimens polished up to diamond B paste.

†With a pack composition of 41.2 wt % Al, 58.4 wt % Al_2O_3 , 0.4 wt % CrF_2 .

‡For one specimen per pack box.

§Annealing of cement with prealably mixed activator.

¶This corresponds to a comparative classification: the quality of the interfaces increases when the number decreases; the quantity and the size of pores increase when the number increases.

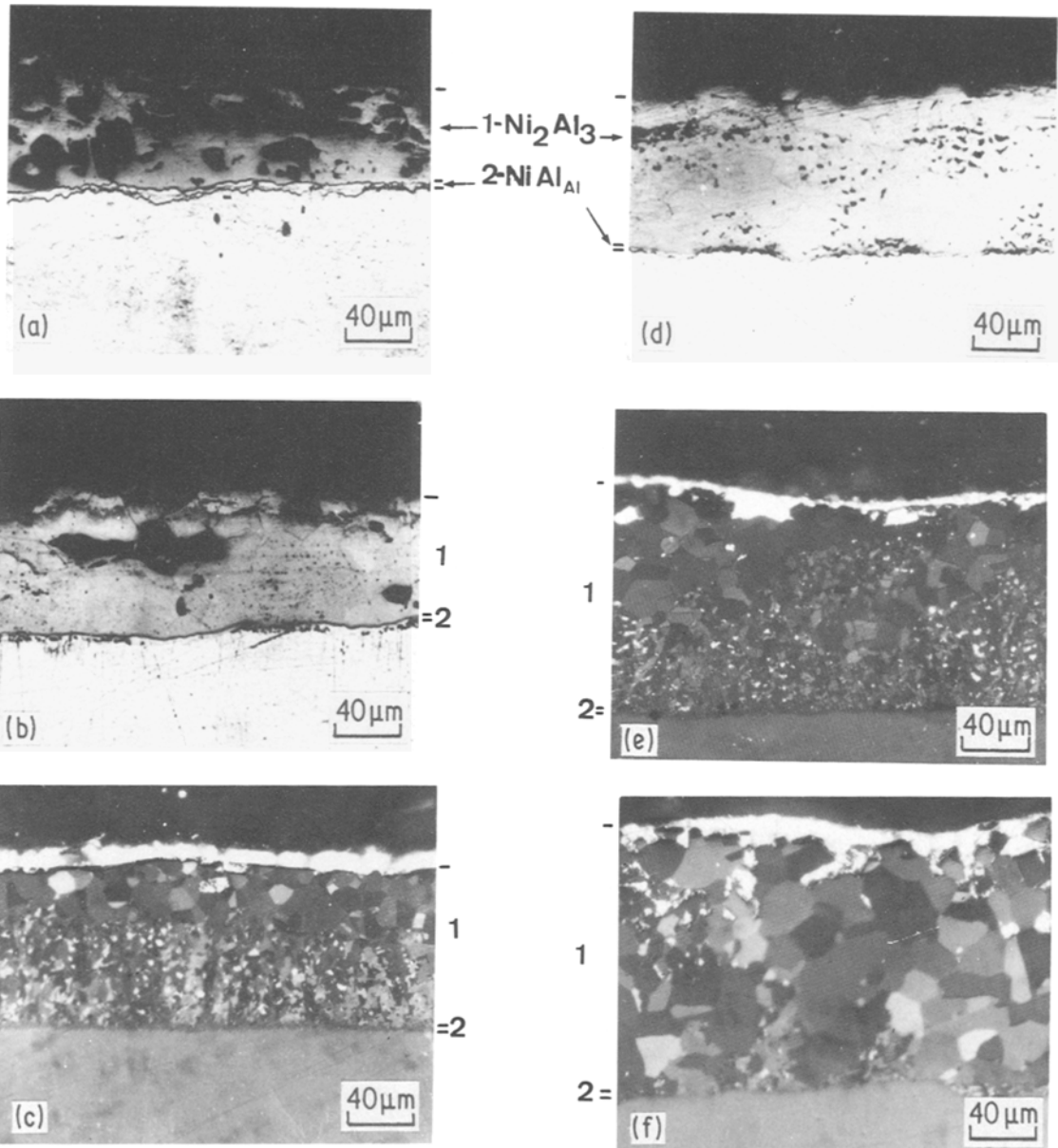


Figure 5 Surface treatment and pack composition effect on the quality of Ni_2Al_3 coatings. All these specimens were subjected to cementation for 20 h at 760°C . (a) After chemical polish, in a pack of 41.2 wt% Al + 0.4 wt% CrF_2 ; (b) after abrasive polish with 600 grit paper, in a pack of 41.2 wt% Al + 0.4 wt% CrF_2 ; (c) after polishing with diamond B paste, in a pack of 41.2 wt% Al + 0.4 wt% CrF_2 ; (d) with same surface preparation, in a pack of 49.3 wt% Al + 0.4 wt% CrF_2 ; (e) with same surface preparation, one specimen per box, in a pack of 41.2 wt% Al + 0.4 wt% CrF_2 ; (f) with same surface preparation and same cementation conditions, in a pack of 41.2 wt% Al + 1.3 wt% CrF_2 .

maximum with a weight composition of 41 wt% Al and 1.3 wt% CrF_2 (Fig. 5e and f). The surface treatment giving the best quality coatings is a final grade B diamond polishing.

The diminution in the surface reactivity after a polishing perfected up to the grade C diamond may be due to a preoxidation film which develops

preferentially on the best-polished surfaces. This also exists on the surfaces prepared by chemical polish and it causes in this case the irregularities and the detachments observed in the coatings (Fig. 5a). The interface is also very perturbed after an insufficient polishing, with grade 600 paper only (Fig. 5b), which shows that the aluminization

reaction proceeds partially from the mechanisms of a heterogeneous gas/metal reaction.

The scale formed is thinner when there is more than one sample in the pack box i.e. for about 20 g cement in the pack. This is due to an impoverishment in the aluminium around the sample. Levine and Caves [9] have elaborated a model for the cementation kinetics of IN100 nickel-base alloys, based on the transfer of the aluminium from the pack to the coating by the diffusion of aluminide halides through an aluminium depleted zone in the pack, adjacent to the specimen. It is assumed that the thickness of this zone increases as the aluminium is transferred to the specimen surface. There ensues a decrease of the cementation rate. Brills-Edwards and Epner [5] have observed such an aluminium depleted zone in the pack, so did Shivakumar and Seigle [12] who obtained a photograph of it. When three or four samples are placed in the box, and whatever their respective arrangement may be, the depleted zones in each sample rapidly interfere with the others involving an important impoverishment of each of them; a decrease of the cementation rate and a thinner

scale formed on those specimens results. Moreover, it is noteworthy to record an unequal growth of the coatings which are less thick on the faces of the samples arranged in front of each other.

The NiAl underlayer is the most important on the less reactive surfaces (Fig. 5a and b). The decrease of the surface reactivity involves, indeed, a diminution of the aluminium supply and then a diminution of its concentration at the reaction interface and an interdiffusion between coating and substrate occurring earlier.

Finally, systematic relations between the thickness uniformity of the scale and its porosity, and the surface state or the pack composition could not be established. They seem rather to depend on the homogenization and the packing of the cement in the box.

To conclude, this part of our study enabled us to determine the cement composition (41 wt % Al, 57.7 wt % Al_2O_3 , 1.3 wt % CeF_2) and the surface treatment (polishing with grade B diamond paste) required to form coatings of maximum thickness and quality. We shall follow these experimental conditions in the study of the growth kinetics

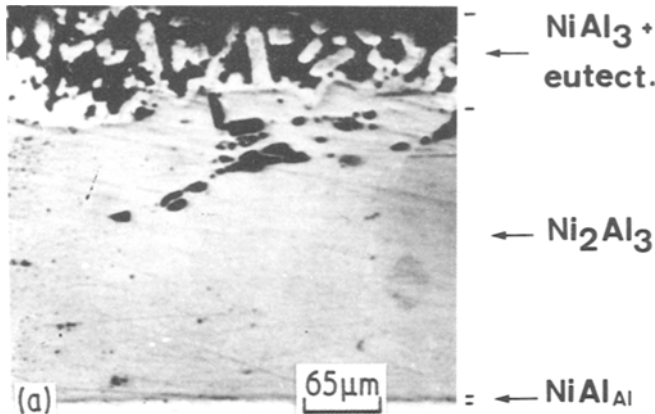
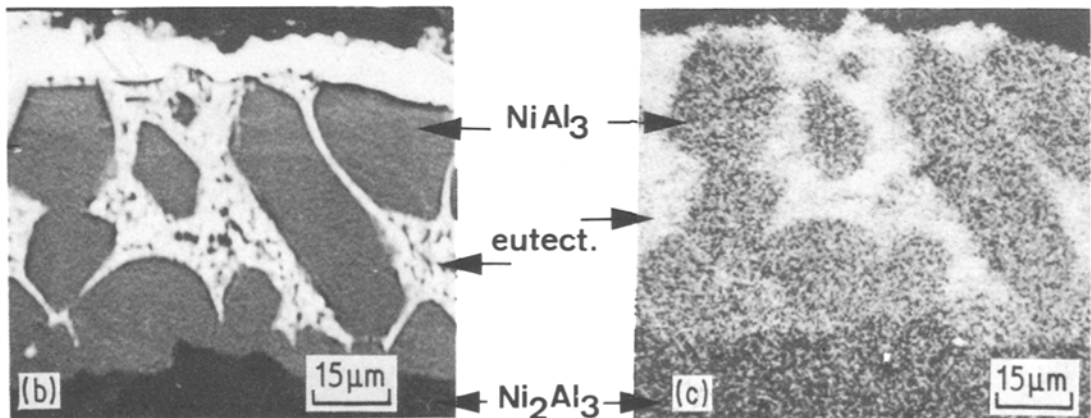


Figure 6 Structure of the high temperature eutectic coating on a specimen subjected to cementation for 1.5 h at 1000°C in a 41 wt % Al pack. (a) cross-section optical micrograph; (b) electron image; and (c) Al X-ray image.



of Ni_2Al_3 coatings [15] and for the production of those used for the study of their oxidation kinetics [1, 2].

4.3. Influence of temperature on the structure of high activity type coatings

Two different structures were distinguished for these high activity type coatings in the temperature range investigated.

Between 760 and 960°C, the structure is unchanged from that described before, that is, essentially a thick Ni_2Al_3 scale within a thin underlayer of NiAl whose thickness slightly increases with temperature to reach about 2% of the total coating thickness.

At temperatures exceeding 950°C the coating exhibits an outer region with a typical hyper-eutectic structure (Fig. 6a) over the Ni_2Al_3 layer. Microprobe analysis demonstrated that this part of the scale is constituted of large NiAl_3 grains in the eutectic matrix containing 5.7 wt% nickel (Fig. 7). The electron and Al X-ray images confirm qualitatively that composition (Fig. 6b and c). The cementation having been carried out at a temperature exceeding the decomposition temperature of NiAl_3 (854°C), this layer is formed by precipitation from a liquid state during the cooling of the specimen at the end of the experiment. The formation of this liquid phase is due to the increase of the sub-halide concentration by displacement to the right hand side of the formation equilibrium with temperature increase. An increase in aluminium activity results in the liquid domain above NiAl_3 .

The coatings are dull grey and lustreless below 950°C and bright grey with a metallic lustre above 950°C. The surface of the low temperature coatings, as revealed by scanning electron microscopy analysis (Fig. 8a and b), appears rough and irregular with an irregular grain relief and widely open grain boundaries; this is typical of a scale formed by inward diffusion and the same aspect will be found for Al-rich NiAl coating surfaces also formed by inward diffusion of aluminium [19]. The surface of high temperature coatings exhibits a reticulated structure (Fig. 8d) characteristic of a precipitated state, on which NiAl_3 globules are stuck (Fig. 8c).

Moreover, we have observed by microfractography [26] on those coatings that the NiAl_3 grains are simply stuck on the surface and that the fracture lines may pass under a grain without

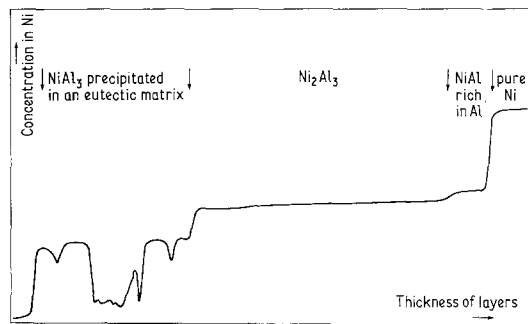


Figure 7 Microprobe analysis of a eutectic structure coating on a specimen subjected to cementation for 1.5 h at 1000°C in a 40 wt% Al pack.

shearing it (Fig. 8e and f). This confirms the formation of those globules by solidification during a process subsequent to the formation of the underlying Ni_2Al_3 scale.

4.4. Influence of temperature on the quality and morphology of Ni_2Al_3 coatings

A comparative study of equithickness Ni_2Al_3 coatings (100 and 180 μm) produced under the formerly defined experimental conditions at temperatures in the range 760 to 1100°C led to the following observations on their morphology and protective qualities.

The coating uniformly covers the surface with coherent bonding at the nickel interface at most temperatures. The quality nevertheless is poorer at the edges, in particular for sharp edges and large thicknesses at high temperatures. Thus, 100 μm thick coatings show complete covering at all temperatures, but with a thickness of 180 μm a slight fissuring just perceptible over a sharp edge at 760°C (Fig. 9a) becomes catastrophic at 900°C (Fig. 9b). This fissure is open and reaches the metal surface. The expanding aspect of the coating in that crack shows that it formed in the course of cementation treatment and that the aluminide developed more rapidly through that fissuring. This may be avoided by rounding the edges during polishing. The coating can then remain up to the highest temperatures (Fig. 9c). Nevertheless, some breaking off of rounded edge coating may appear as in the case of the specimen in Fig. 9d; but the clear break of this fissuring shows that it was formed during the cooling of the sample, since the aluminide did not reform on the bare metal of the substrate. This breaking is due to the constraints

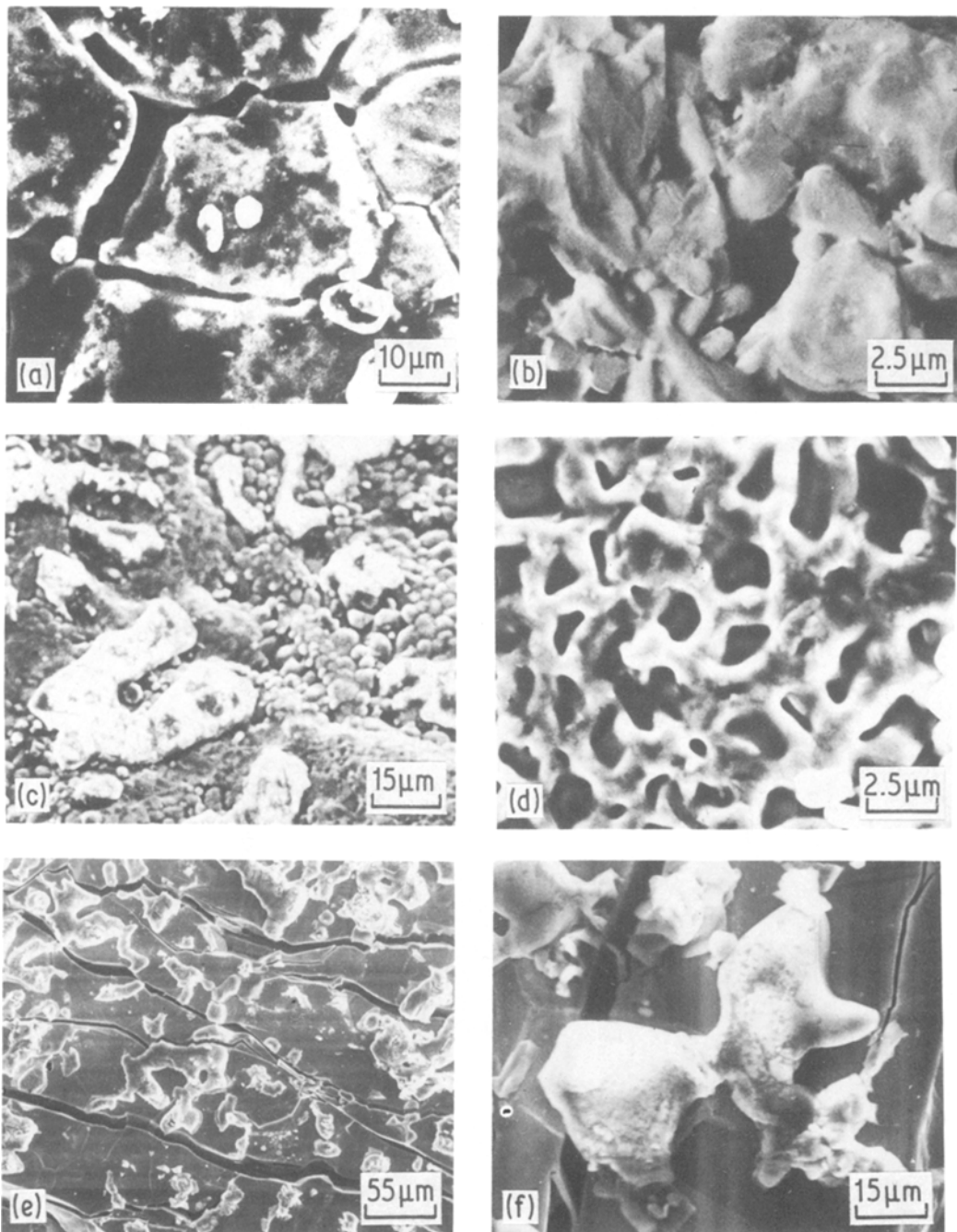


Figure 8 Surfaces of the coatings. (a) and (b) High activity Ni_3Al_3 coating on a specimen subjected to cementation for 5 h at $850^\circ C$ in a 40.1 wt% Al pack. (c) and (d) high temperature eutectic coating on a specimen subjected to cementation for 1 h at $1000^\circ C$ in a 40.1 wt% Al pack. (d) is a detail of (c) showing the reticular precipitation of the surface; (e) and (f) strained eutectic coating by tensile test interrupted before sample rupture, on a specimen subjected to cementation for 10 min at $1050^\circ C$ in a 40 wt% Al pack.

arising in the coating for these large thicknesses and whose relaxation did not occur in the course of cooling.

The occurrence of macroscopic defects such as

holes, open fissures or large closed pores is rare. Their occurrence frequency is aleatory and not directly related to temperature or cementation time. A fine closed porosity appears in some

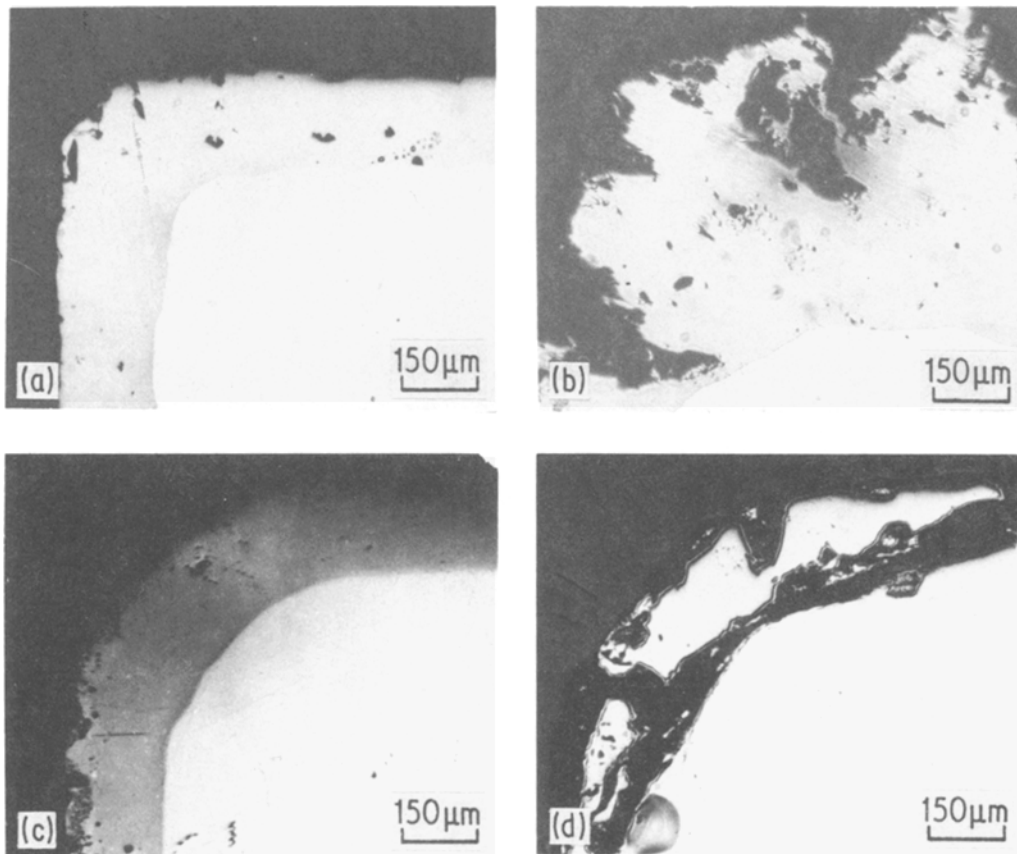


Figure 9 Morphology and quality of the Ni_2Al_3 coatings. $180\ \mu\text{m}$ equithickness high activity coatings on specimens subjected to cementation in 41 wt % Al pack. (a) 49 h at 760°C with an undamaged sharp edge; (b) 4 h at 900°C with a fissured sharp edge; (c) 2.25 h at 950°C with an undamaged rounded edge; (e) broken off rounded edge of the same sample.

specimens (Fig. 10) but in a partial way and also aleatory with temperature and thickness. It may be due to the polishing procedure.

It has been shown that owing to their growth by inward diffusion of aluminium, the high activity Ni_2Al_3 coating presents an equiaxial grain structure with a grain size increasing from the coating–substrate interface to the outer surface of the coating (Fig. 5c and e). With increasing temperature and for equivalent thicknesses this grain size increases throughout the whole scale (Fig. 10) and its structure loses the equiaxial regularity it exhibited at lower temperatures.

5. Conclusions

The occurrence and growth of the various intermetallic phases in the system Al–Ni have been investigated with respect to the aluminium activity of the pack. Two basic types of coatings were distinguished: a Ni_2Al_3 high activity process

coating, which forms by predominantly inward aluminium diffusion; a Ni-rich NiAl low activity process coating, formed by predominantly outward diffusion of nickel.

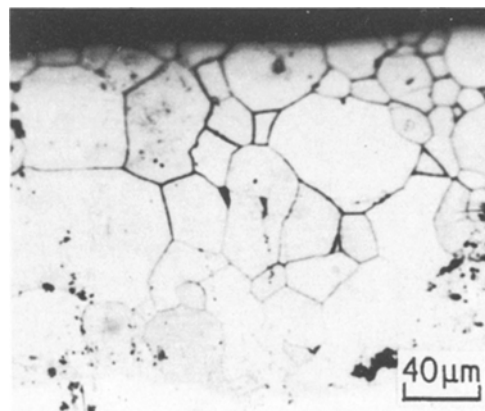


Figure 10 Grain structure of a Ni_2Al_3 coating on a specimen subjected to cementation for 9 h in a 41 wt % Al pack at 850°C .

In an activity lowered cement a mixed type of coating grown by both inward aluminium diffusion for the outer part, namely, Ni_2Al_3 and Al-rich NiAl, and outward nickel diffusion for the inner part, namely, Ni-rich NiAl and Ni_3Al , was observed.

At temperatures above 950°C the occurrence of a higher aluminium content phase in the high activity process was established. There appears a hypereutectic structure of large NiAl_3 grains in the eutectic matrix of Ni in Al, formed by precipitation from a liquid state on the Ni_2Al_3 coating.

In addition, the optimum conditions for the preparation of Ni_2Al_3 coatings of maximum thickness and quality in a high activity pack were determined. The influence of the surface reactivity and the cement activity on the formation, the morphology and the protective qualities of these Ni_2Al_3 coatings were investigated.

Finally, this study gives an overall view on the occurrence of the various phases of the Al-Ni system in the pack cementation of unalloyed nickel. The preparation conditions for Ni_2Al_3 coatings might be extended by a similar investigation on the formation of NiAl coatings. A study is in progress on the influence of the cement activity on the structure of the NiAl type coatings.

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References

1. C. MASSIANI-SECHAUD, J.-P. CROUSIER and R. STREIFF, *Ann. Chim. Sci. Mater.* **3** (1978) 221.
2. *Idem, ibid.* **8** (1979) 665.
3. D. CHATTERJI, R. C. DEVRIES and G. ROMEO

- in "Advances in Corrosion Science and Technology," Vol. 6, edited by M. Fontana and R. W. Staehle (Plenum Press, New York, 1976) p. 82.
4. G. W. GOWARD, D. H. BOONE and C. S. GIGGINS *Trans, ASM* **60** (1967) 228.
5. H. BRILLS-EDWARDS and M. EPNER, *Electrochem. Tech.* **6** (1968) 229.
6. M. J. FLETWOOD, *J. Inst. Met.* **98** (1970) 1.
7. J. MARGALIT, G. KIMMEL and S. NIEDZWIEDZ, *J. Inst. Met.* **98** (1970) 126.
8. G. W. GOWARD and D. H. BOONE, *Oxid. Metals* **3** (1971) 475.
9. S. R. LEVINE and R. M. CAVES, *J. Electrochem. Soc.* **121** (1974) 1051.
10. A. J. HICKL and R. W. HECKEL, *Met. Trans.* **6A** (1975) 431.
11. R. SHIVAKUMAR, N. B. NEMON and L. L. SEIGLE, *Met. Trans.* **4** (1973) 396.
12. R. SHIVAKUMAR and L. L. SEIGLE, *Met. Trans.* **7A** (1976) 1073.
13. L. L. SEIGLE, B. K. GUPTA, R. SHANKAR and A. K. SARKHEL, NASA Contractor report 2939 (1978).
14. N. B. LINBLAD, *Oxid. Metals* **1** (1969) 143.
15. A. THEVAND, J.-P. CROUSIER, R. STREIFF and S. POIZE, *CR Acad. Sci.* **289C** (1979) 25.
16. M. HANSEN, "Constitution of Binary Alloys", 2nd edn. (MacGraw Hill Book Company, New York, 1958) p. 118.
17. A. J. BRADLEY and A. TAYLOR, *Proc. Roy. Soc. (London)* **A159** (1937) 56.
18. A. TAYLOR and N. J. DOYLE, *Appl. Cryst.* **5** (1972) 201.
19. J. M. N'GANDU MUAMBA and R. STREIFF, in "III Euro CVD 1980", edited by H. E. Hintermann (Laboratoire Suisse de Recherches Horlogeres, Neufchâtel, 1980) Ch. 17, p. 124.
20. A. THEVAND, Thèse: Marseille 1975.
21. A. THEVAND, J.-P. CROUSIER and R. STREIFF, *CR Acad. Sci* **280C** (1975) 721.
22. M. M. JANSSEN and G. D. RIECK, *Trans. Metall. Soc. AIME* **239** (1967) 1371.
23. R. PICHOR in "Materials and Coatings to Resist High Temperature Corrosion", edited by Holmes and Rahmel (Applied Science Publishers, 1978) Ch 17, p. 271.
24. *Idem*, in "High-temperature Alloys for Gas Turbines", edited by Coutsouradis (Applied Science Publishers, 1978) Ch 8.
25. P. GALMICHE, *Metals Mater.* **8** (1968) 241.
26. R. STREIFF, unpublished work (1980).

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