

ALUMINIDE COATING ON DIRECTIONAL γ' - δ EUTECTICS *

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The relations between the process variables and the coating microstructure were studied for aluminide-coated γ' - δ directional eutectics. A spectrum of coating microstructures was obtained depending on the choice of the process variables. The process variables were the aluminizing and homogenizing temperatures, the homogenizing time and the activity of aluminum in the coating pack. The microstructures were described with reference to the Ni–Al–Nb ternary phase diagram and the diffusion of the aluminum and the nickel atoms.

1. INTRODUCTION

Recent studies on turbine blade materials have resulted in the development of *in situ* composites. These materials possess an aligned second phase produced by the directional solidification of a eutectic. One system of interest is the directional Ni₃Al–Ni₃Nb (γ' - δ) eutectic¹. Although the environmental behavior of such systems is important, only recently has the oxidation behavior of directional eutectics been studied^{2,3}. These studies have recommended the use of oxidation-resistant coatings for long term, high temperature service^{1,2,4}.

Aluminide coatings on turbine blade materials have been used for a number of years as an efficient and low cost protection system. While an extensive background on aluminide coatings exists in the literature^{5–10}, the process variables–structure–property relationships are not adequately understood. A comprehensive study was therefore undertaken to examine the effects of the aluminide coating process variables on the oxidation behavior of γ' - δ eutectics, through the control of the coating microstructure. In general, the coating microstructure can be altered by the following process variables: the aluminizing and homogenizing temperatures, the homogenizing time and the activity of aluminum in the coating pack. The homogenizing treatments were performed to determine the extent of coating degradation due to the high temperature exposure of the coating, uncomplicated by the effects of oxidation. The ternary diffusion path^{11,12} was used to monitor the

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changes in the coating microstructure since each of the above process variables affects one of the terminal compositions (the surface composition) of the coated substrates.

This paper presents the results of a shorter study on the effects of the aluminide coating process variables on the microstructure of the coated substrates. It deals with the mechanisms of coating formation (aluminization) and degradation in an inert environment (homogenization). The sequence of the phase layers in the coating microstructure is explained with reference to the appropriate Ni–Al–Nb ternary isotherms, and the structural aspects are discussed with the aid of diffusion kinetics. Although only one coating–substrate system was used, the conclusions drawn from the present study are expected to be common to most, if not all, aluminide-coated directional eutectics.

2. EXPERIMENTAL PROCEDURES

Specimens for aluminization were sectioned from a directionally solidified γ' – δ alloy (of nominal composition 15.1 at. % Nb, 75 at. % Ni, 9.9 at. % Al) so that the growth direction was parallel to the plane of the section. After grinding on 600 grit SiC paper, the specimens were degreased and aluminized using the pack cementation process^{7,8,10}. The details of the aluminizing treatment are given in Table I. Temperatures of 900 and 1140 °C were chosen because of the availability of ternary isotherms^{13,14}.

TABLE I

ALUMINIZING TIMES, TEMPERATURES AND THE COMPOSITION FOR HIGH AND LOW ALUMINUM ACTIVITY PACKS

	<i>High aluminum activity pack</i>		<i>Low aluminum activity pack</i>
Aluminizing temperature (°C)	900	1140	1140
Aluminizing time (h)	0.33	0.5	1.0
Pack composition (wt. %)			
Inert filler (Al ₂ O ₃)	72.0	94.0	72.0
Activator (NH ₄ Cl)	3.0	3.0	3.0
Pure aluminum	25.0	3.0	—
Aluminum alloy (45 at. % Ni–55 at. % Al)	—	—	25.0

Homogenizing treatments were performed in an argon atmosphere at 900 and 1140 °C for times ranging from 1 to 150 h. These times provided sufficient coating degradation to permit the formulation of degradation mechanisms.

A combination of metallography, electron microprobe analysis (EMPA) and X-ray diffraction techniques (for the surface phases) was used for phase identification. Microprobe intensities from three line emissions (Nb L α , Ni K α , Al K α) were recorded by point and line counting at successive steps parallel to the diffusion direction; raw intensities were corrected for background and dead times and were converted to concentration values using the alpha coefficient method¹⁵. Diffusion paths along each of the original γ' and δ lamellae were determined by plotting concentration values on the ternary isotherms.

3. RESULTS

3.1. *Aluminization of the substrates*

Figure 1(a), (b) shows the as-aluminized microstructure of a directional γ' - δ

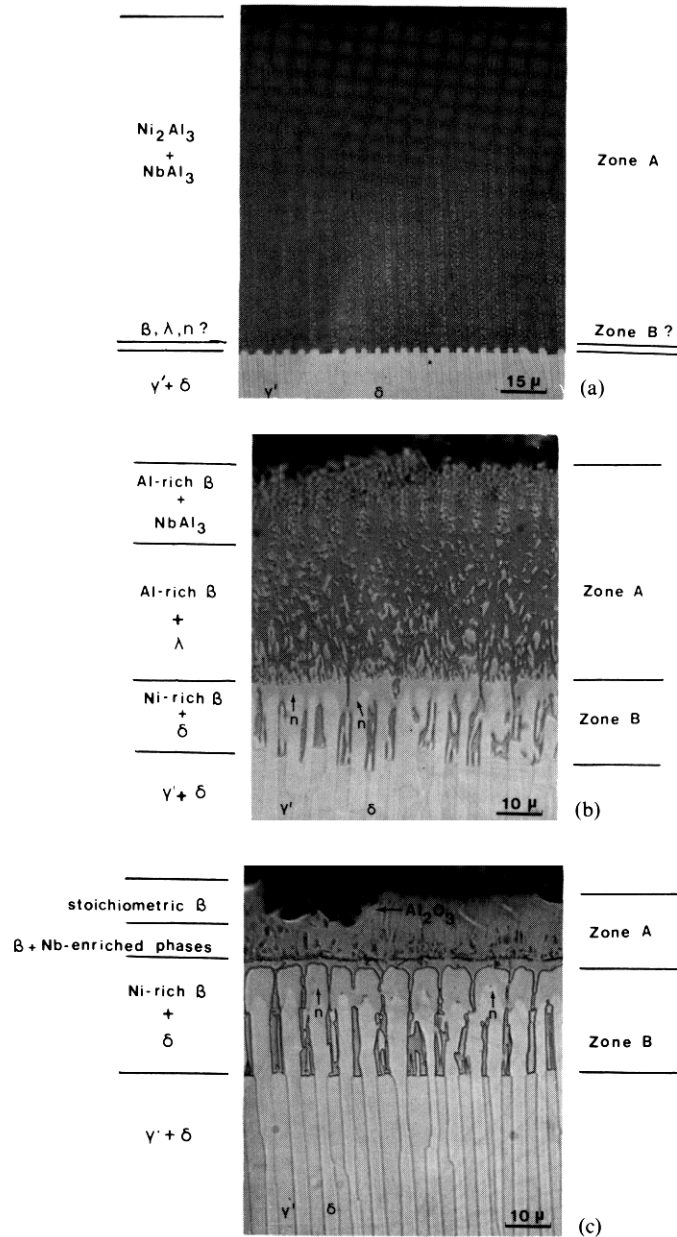
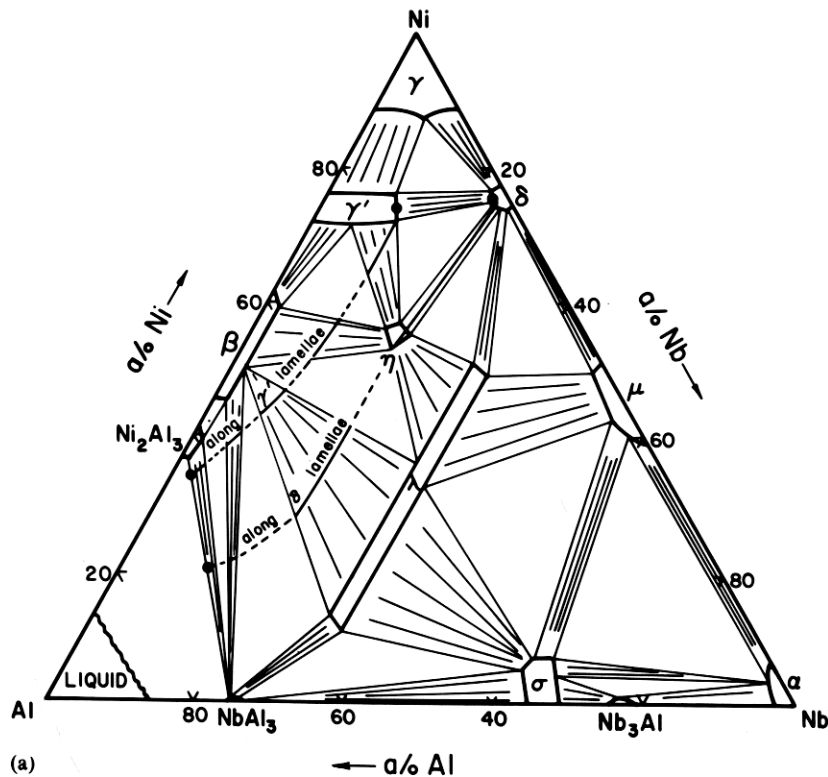


Fig. 1. The microstructure of the as-aluminized coating (a) at 900 °C for 20 min (high aluminum activity pack), (b) at 1140 °C for 30 min (high aluminum activity pack), (c) at 1140 °C for 1 h (low aluminum activity pack).

eutectic at 900 and 1140 °C, respectively, formed by pure aluminum in the coating pack (high aluminum activity pack). Basically, both the microstructures show evidence of the original lamellar morphology, as seen in Fig. 1(a), (b), zone A. However, the phases present in that zone differ at the two temperatures. At 900 °C Ni_2Al_3 and NbAl_3 are present, whereas at 1140 °C a layer of Al-rich β and NbAl_3 is formed above a layer of Al-rich β and $\text{Nb}(\text{Ni}_x\text{Al}_{1-x})_2$ (λ). In addition, at 1140 °C (Fig. 1(b)) another region (zone B) is prominent. It consists of a layer of Ni_2NbAl (η) at the positions marked by arrows and extensions into the γ' lamellae. EMPA data show the latter to consist of two-phase regions of Ni-rich β and δ . (At 900 °C zone B was barely resolved; no conclusions could be reached regarding its composition.)

Figure 1(c) shows the microstructure of an as-aluminized substrate at 1140 °C formed by an alloy of aluminum and nickel in the coating pack (low aluminum activity pack, see Table I for pack composition). As for the high aluminum activity packs, the coating microstructure can be divided into zones A and B. Zone B is very similar to that in Fig. 1(b) and consists of the η phase (denoted by arrows) and coating extensions of Ni-rich β and δ into the γ' lamellae. Zone A, however, differs from that in Fig. 1(a), (b) by the absence of the original lamellar morphology. Particles of aluminum oxide trapped in this zone serve as diffusion markers and indicate the relative motion of the aluminum and nickel atoms.

Figure 2 shows the diffusion paths plotted on the appropriate ternary isotherms for each of the microstructures in Fig. 1.



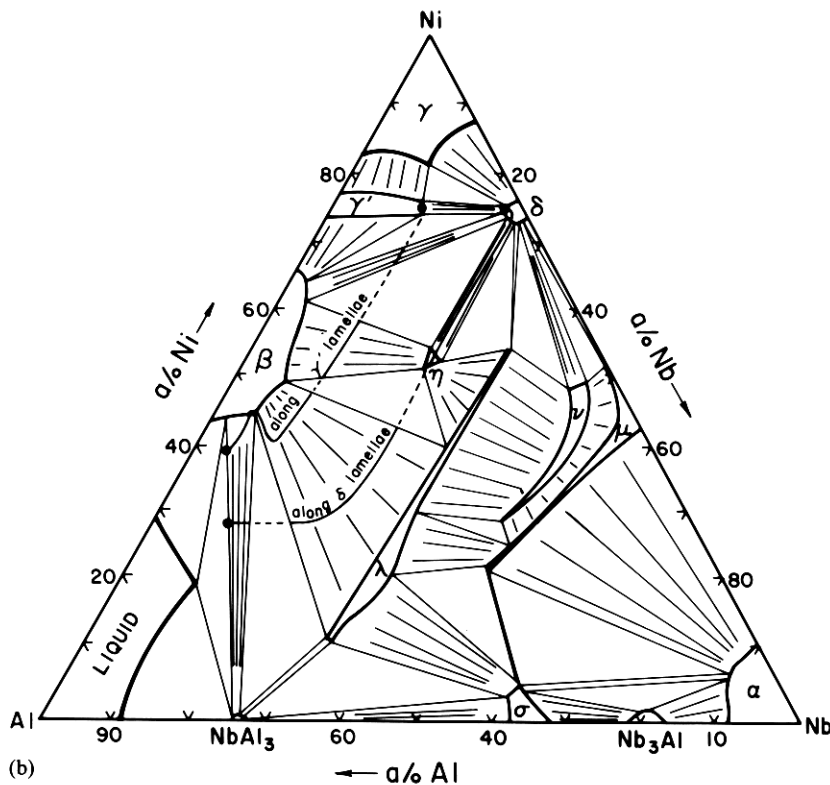


Fig. 2. (a) The Ni-Al-Nb ternary isotherm at 900 °C showing the diffusion paths along the original γ' and δ lamellae for the microstructure in Fig. 1(a); (b) the Ni-Al-Nb ternary isotherm at 1140 °C showing the diffusion paths along the original γ' and δ lamellae for the microstructure in Fig. 1(b).

3.2. Homogenization of the coated substrates

Figure 3 shows the homogenization sequence for the aluminized substrate of Fig. 1(b). The first significant change to occur is the formation of an integral layer of the η phase in zone B (Fig. 3(a)). At a later time a layer of Ni-rich β , containing no secondary phases, forms above the η phase (Fig. 3(b)). At the end of 50 h of homogenizing (Fig. 3(c)) the Al-rich phases of the surface have disappeared, exposing the Ni-rich β layer of composition 3.3 at. % Nb, 59.7 at. % Ni, 37 at. % Al.

The sequence of homogenization of high activity packs at 900 °C is similar to that at 1400 °C but has slower kinetics. The coating layers after 150 h at 900 °C are sequentially similar to those in the as-aluminized microstructure at 1140 °C. This is at variance with what was expected since the 900 °C isotherm shows the existence of a two-phase region of γ' and η instead of the Ni-rich β and δ that appears on the coated substrates. The existence of the $\gamma' + \eta$ region on the 900 °C isotherm is therefore inconsistent with the results of the present study.

Figure 4 shows the stages of homogenization of a substrate aluminized with a low aluminum activity pack at 1140 °C. The first stage involves the disappearance of the η phase (Fig. 4(a)) and the consequent joining of the Ni-rich β in zones A and B (Fig. 4(b)). At the end of 150 h, zone A is separated from the γ' - δ substrate by a layer of γ' .

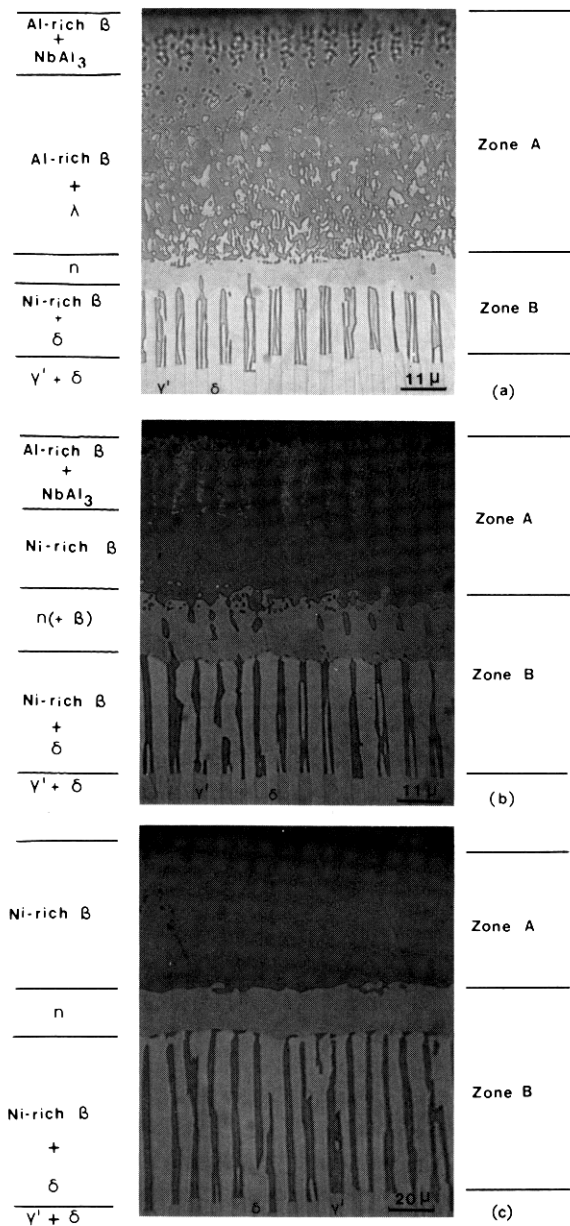


Fig. 3. The microstructure of the coating in Fig. 1(b) after homogenization at 1140 °C for (a) 1 h, (b) 3 h, (c) 50 h.

4. DISCUSSION

4.1. The mechanism of coating formation

In Section 3 several similarities and differences between the microstructures in Fig. 1 were indicated. Zone A in Fig. 1(a), (b) possesses the original lamellar

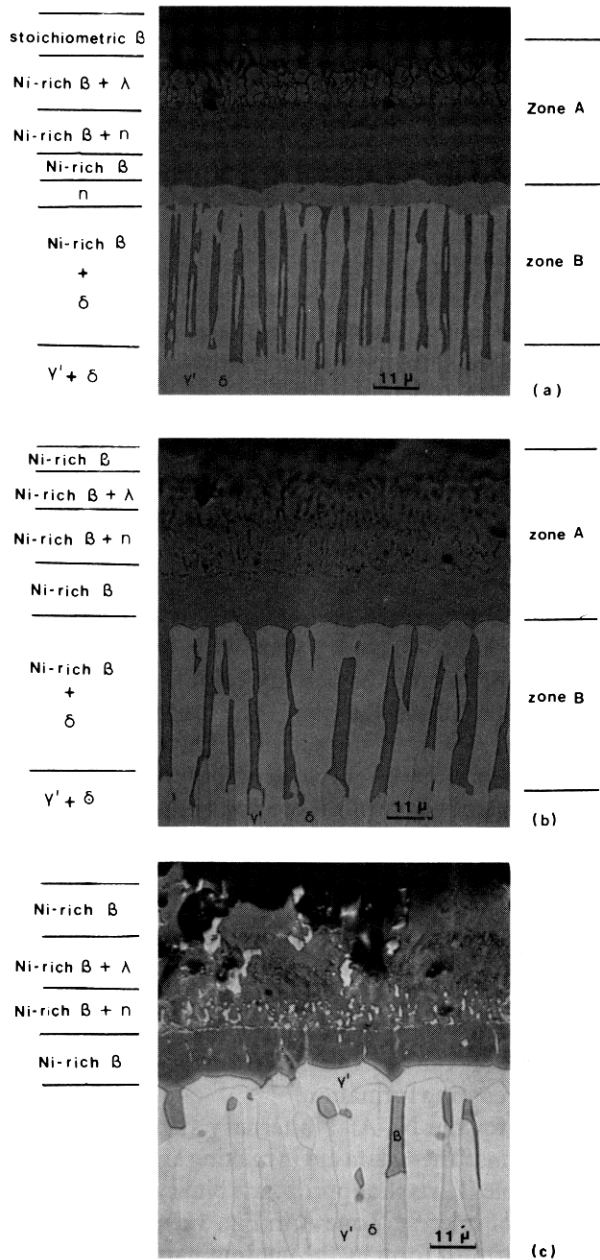


Fig. 4. The microstructure of the coating in Fig. 1(c) after homogenization at 1140 °C for (a) 1 h, (b) 50 h, (c) 150 h.

morphology, whereas this is not evident in Fig. 1(c). Zone B is very similar in Fig. 1(b), (c), whereas it is not resolved in Fig. 1(a). A spectrum of coating microstructures can therefore be obtained by altering the aluminizing process variables, limited at one end by low aluminizing temperatures and high aluminum

activity packs and at the other by high aluminizing temperatures and low aluminum activity packs.

In general, the surface phases present on the coatings are determined by the constitution of the Ni–Al–Nb ternary isotherm or, more precisely, by the aluminizing temperature and the activity of aluminum in the coating pack. In high activity packs, the phases with the highest aluminum content form along the original γ' and δ lamellae. These are Ni_2Al_3 at 900 °C and Al-rich β at 1140 °C (above the melting point of Ni_2Al_3) along the γ' lamellae and NbAl_3 at both temperatures along the δ lamellae. However, the ternary isotherm indicates that both Ni_2Al_3 and Al-rich β have lower solubilities of niobium than the original γ' phase. Thus Nb-enriched secondary phases must precipitate. These phases precipitate along the original δ lamellae since NbAl_3 is almost stoichiometric. Consequently, in high activity packs the surface layers consist of two-phase regions along each of the original γ' and δ lamellae. This is observed in the diffusion paths in Fig. 2.

The diffusion paths originating from the surface phases alternately have to reach the composition of the substrate (γ' and δ). In doing so they have to cross various single-phase, two-phase and three-phase fields. At 1140 °C these are Al-rich $\beta + \lambda$, $\beta + \eta$, Ni-rich $\beta + \delta$ and γ' along the γ' lamellae and Al-rich $\beta + \lambda$, η and δ along the δ lamellae. At 900 °C the identity of the two-phase fields could not be determined.

The sequence of phase layers in low aluminum activity coatings can also be explained with reference to the ternary phase diagram. The surface phase of stoichiometric β forms because it corresponds to the activity of aluminum being transported to the surface of the substrate. However, because of the low solubility of niobium in the β phase, an Nb-enriched secondary phase precipitates. The diffusion path in Fig. 2(b) traverses the two-phase Ni-rich $\beta + \delta$ region and terminates in the γ' phase along the γ' lamellae and passes through the η and δ phases along the δ lamellae.

The structural aspects of the coating layers can now be discussed with the aid of appropriate diffusion data. Clearly, the manner in which zone A formed in Fig. 1(a), (b) is different from the manner in which it formed in Fig. 1(c). Also, the structural similarity at zone B in Fig. 1(b), (c) suggests that it formed in a different way from in Fig. 1(a). These similarities and differences can be explained from the relative rates of motion of the mobile species during coating formation.

Although no diffusion data exist for the Ni–Al–Nb ternary system, data are available for the respective binary systems. These data aid in making assumptions as to which species is the most mobile. Table II lists the appropriate binary systems and the most mobile species in the phases of interest. Zone A in Fig. 1(a), (b) contains Ni_2Al_3 , Al-rich β and NbAl_3 and hence must form by the predominant diffusion of aluminum atoms along the original γ' and δ lamellae. The lamellar morphology of the zone is consequently retained. In Fig. 1(c), zone A consists of stoichiometric β , and in this phase nickel atoms are more mobile than aluminum atoms are (Table II). The nickel atoms move outwards and react with aluminum on the external surface. In doing so, the layer of stoichiometric β which forms loses the original lamellar morphology of the substrate. The outward motion of nickel is evidenced by the entrapment of aluminum oxide particles within the outer coating layers.

Zone B in Fig. 1(b), (c) consists of Ni-rich β and δ . In these phases nickel is the mobile species (Table II). Nickel atoms move out of the γ' phase, making it rich in aluminum and niobium and resulting in the formation of Ni-rich β and δ . This zone is not evident at 900 °C (Fig. 1(a)) because of combination of the high interdiffusion coefficient of the Ni_2Al_3 phase and the low aluminizing temperature, which retards the formation of Ni-rich phases.

TABLE II
THE MOBILE SPECIES IN THE Ni-Al, Al-Nb, Ni-Nb AND Ni-Al-Nb SYSTEMS

	Ni-Al	Al-Nb	Ni-Nb	Ni-Al-Nb
<i>Phases</i>				
NiAl ₃ (ϵ)	Al	—	—	⁶³ Ni diffuses
Ni ₂ Al ₃	Al	—	—	faster in γ'
Al-rich β	Al	—	—	than in δ
Stoichiometric and Ni-rich β	Ni	—	—	
γ'	Ni	—	—	
γ	Al	—	—	
δ	—	—	Ni	
NbAl ₃	—	Al	—	
<i>References</i>	5, 16–18	19	20	21

In general, the diffusion rate of nickel out of the original γ' and δ lamellae will not necessarily be the same²¹; lateral diffusion across the original γ' - δ interphase boundary might be expected. This effect is observed during the formation of the η phase layer in Fig. 1(b), (c). At the positions denoted by arrows, the δ lamellae would be juxtaposed with a layer of β containing about 5 at. % Nb, 54 at. % Ni, 41 at. % Al. However, such a situation cannot occur owing to the phase equilibria on the 1140 °C isotherm, and so an intervening layer of the η phase must form. This occurs by transverse dissolution of the β phase.

4.2. The mechanism of coating degradation in an inert environment

Once the coating layers have been formed with Al-rich phases on the surface of the substrate, the inward diffusion of aluminum continues until its concentration gradient cannot support significant inward aluminum diffusion. At this stage a reversal of interface motion occurs²², and the growth of Ni-rich phases is gradually promoted. This involves a change in the mode of diffusion from predominant aluminum motion to predominant nickel motion. Figure 3(b) shows a layer of Ni-rich β (in zone A) formed by the simultaneous diffusion of aluminum inwards through the Al-rich phases at the surface and nickel diffusion outwards from the substrate and the reaction of this nickel with aluminum. The fact that this Ni-rich β layer does not possess the original lamellar morphology and secondary phases indicates that it was formed by the above mechanism. Eventually, the inward motion of aluminum atoms ceases because of the removal of the Al-rich phases at the surface by the outward growth of the Ni-rich β (Fig. 3(c)), and only the motion of nickel atoms through the Ni-rich phases occurs.

In low aluminum activity pack coatings, since Al-rich surface phases are not present, inward diffusion of aluminum does not occur; homogenization continues only by the diffusion of nickel atoms from the substrate into the coating layers.

5. SUMMARIZING REMARKS

The present study shows that a spectrum of microstructures can be obtained in aluminide coatings on γ '- δ directional eutectics by proper selection of process variables. A complete description of the coating microstructures requires reference to the appropriate ternary isotherm as well as to kinetic data (relative mobility of the aluminum and the nickel atoms). Process variables that form Al-rich phases on the surface promote the inward diffusion of aluminum, whereas those which form Ni-rich phases on the surface promote the outward diffusion of nickel atoms from the substrate. The presence of two aligned phases of different compositions in the eutectic substrate allows for diffusion across the interphase boundaries, since the diffusion rates along the γ ' and the δ lamellae are not the same. The above conclusions are expected to be similar for most aluminide-coated directional eutectics.

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REFERENCES

- 1 E. R. Thompson and F. D. Lemkey, *Trans. Am. Soc. Met.*, 62 (1969) 140.
- 2 E. J. Felten and F. S. Pettit, in J. N. Fleck and R. L. Mehan (eds.), *Failure Modes in Composites II*, American Institute of Mining, Metallurgical and Petroleum Engineers, Institute of Metals Division, New York, 1974, p. 220.
- 3 J. G. Smeggil and M. D. McConnell, *Oxid. Met.*, 8 (1974) 309.
- 4 E. J. Felten, T. E. Strangman and N. E. Ulion, Coatings for directional eutectics, *Pratt and Whitney Aircraft, East Hartford, Conn., NASA contract. Rep. CR-134735*, 1974.
- 5 G. W. Goward and D. H. Boone, *Oxid. Met.*, 3 (1971) 475.
- 6 G. W. Goward, D. H. Boone and C. S. Giggins, *Trans. Am. Soc. Met.*, 60 (1967) 228.
- 7 T. K. Redden, *Trans. Am. Inst. Min., Metall. Pet. Eng.*, 242 (1968) 1695.
- 8 *High Temperature Oxidation-Resistant Coatings*, Commun. on Coatings, Natl. Materials Advisory Board, Natl. Acad. Sci./Natl. Acad. Eng., Washington, D.C., 1970.
- 9 S. J. Grisaffe, in C. T. Sims and W. C. Hagel (eds.), *The Superalloys*, Wiley, New York, 1972, p. 341.
- 10 S. R. Levine and R. M. Caves, *J. Electrochem. Soc.*, 121 (1974) 1051.
- 11 J. B. Clark and F. N. Rhines, *Trans. Am. Soc. Met.*, 51 (1959) 199.
- 12 J. S. Kirkaldy and L. C. Brown, *Can. Metall. Q.*, 2 (1963) 89.
- 13 J. S. Benjamin, B. C. Giessen and N. J. Grant, *Trans. Am. Inst. Min., Metall. Pet. Eng.*, 236 (1966) 224.
- 14 V. Ya Markiv, M. F. Matushevskaya and Yu. B. Kuz'ma, *Russ. Metall.*, 6 (1966) 72.
- 15 D. Laguitton, R. Rousseau and F. Claise, *Anal. Chem.*, 47 (1975) 2174.
- 16 M. M. P. Janssen and G. D. Rieck, *Trans. Am. Inst. Min., Metall. Pet. Eng.*, 239 (1967) 1372.
- 17 M. M. P. Janssen, *Metall. Trans.*, 4 (1973) 1623.
- 18 A. J. Bradley and A. Taylor, *Philos. Mag.*, 23 (1937) 1049.
- 19 G. Slama and A. Vignes, *J. Less-Common Met.*, 29 (1972) 189.
- 20 Y. Muramatsu, *Trans. Natl. Res. Inst. Met.*, 17 (1975) 21.
- 21 S. Z. Bokshsteyn, M. A. Gubareva, S. T. Kishkin and L. M. Moroz, *Phys. Met. Metallogr.*, 37 (1974) 104.