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Aircraft Materials Technical Memorandum 404

METALLOGRAPHY OF ALUMINIDE COATINGS

by

P. ROHAN

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SUMMARY

Metallographic techniques have been established for the examination of gas turbine blades and their protective coatings. Particular attention was given to edge retention of specimens during polishing and to etchant selection to allow microstructural evaluation of major phases. Edge retention was achieved firstly by depositing a nickel plate over the specimen (by electroless deposition) and secondly, by minimizing the use of cloth polishing pads. Etchants were then evaluated for phase delineation in polished Allison T-56 turbine blades, (IN738 substrate alloy coated with high-activity nickel aluminide). Characteristics of four most useful etchants are described.

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1.0 INTRODUCTION

The Corrosion Control group at ARL has commenced a programme for evaluating protective coatings for gas turbine blades currently used by the RAAF (work previously performed at MRL). To enable examination and evaluation of metallographic specimens (with particular attention given to surface features), techniques have been developed for sample preparation and microstructural etching. In developing these techniques, Allison T-56 turbine engine blades cast from a nickel-based superalloy (IN 738) and coated with nickel aluminide were sectioned. The nickel aluminide coating applied by a high-activity "pack-cementation" process to the outer surface of the blades, imparts oxidation/corrosion resistance to the substrate superalloy. Metallographic procedures were developed with an aim to minimise edge rounding and highlight the detailed microstructure by selective etching. As the coatings are only between 50 and 100 μm thick and attention needs to be given to oxide/corrosion scales produced on the surface, edge retention is essential.

Nickel-based superalloys are composed of FCC γ - Ni solid solution containing γ'- Ni_3Al precipitation phase, carbides and various other precipitates such as η, (hcp, eg Ni_3Ti), σ, (tcp, eg CrCo, CrNiMo), etc.(ref. 1). The coating mainly consists of β - NiAl and may contain precipitate particles and carbides derived from alloying elements contained in the substrate (ref. 2). Various etchants have been used to reveal these features with the most useful being reported here.

The blades used were rejects from routine maintenance performed by the RAAF on Allison T56 turbo-prop engines (from either the C-130 Hercules or P-3 Orion aircraft) and as such showed various defects and coating conditions.

2.0 EDGE RETENTION

In order to minimise edge rounding during (manual) polishing of specimens, 2 steps were taken:

1. A Ni coating is first plated over the sample,
   (Ni electroplating of specimens was previously used by MRL
   for related work)

2. SiC paper was used down to 4000# (5μm) to minimise the use of cloth pads (which exacerbate edge rounding).

2.1 NICKEL PLATING

To avoid loss of corrosion products from the outer surface of samples during immersion in plating solutions and due to handling, entire blades were vacuum impregnated with epoxy resin. The viscosity of the epoxy was sufficiently low to allow penetration of the scale and prevent fragmenting during polishing. After impregnation, the excess resin was allowed to run off leaving only a thin film to cure over the surface. The cured epoxy must have high hardness and minimal shrinkage to prevent scale separation from the coating.

400# SiC paper was later used to roughen the cured epoxy surface to allow mechanical 'keying-in' of the plated coating and avoid flaking.

The procedure for the electroless deposition of nickel is given in Table 1. Firstly, the surface to be plated was cleaned of contaminants by placing the sample in a beaker of acetone and cleaning ultrasonically. After drying, the sample is placed in the sensitizing-nucleating solution where the following reaction takes place (ref. 3):

$$Sn^{2+}_{(aq)} + Pd^{2+}_{(aq)} \Leftrightarrow Sn^{4+}_{(aq)} + Pd_{(s)}$$

ie. palladium chloride is reduced to colloidal Pd metal particles by Sn^{2+}, which then forms hydrolysed Sn^{4+} which in turn stabilises the Pd colloid.

Before the sample can be plated in the electroless Ni bath, the Sn^{4+} ions surrounding the adsorbed Pd must be removed. This 'acceleration' step dissolves the Sn^{4+} without affecting the Pd layer.

The electroless Ni bath itself contains essentially,

a) a Ni salt ($NiSO_4.6H_2O$),

b) a reducing agent (sodium hypophosphite, $NaH_2PO_4.6H_2O$);

and results in the following reaction:

$$2H_2PO_2^-{}_{(aq)} + 2H_2O + Ni^{2+}{}_{(aq)} \Leftrightarrow Ni_{(s)} + H_{2(g)} + 4H^+{}_{(aq)} + 2HPO_3^{2-}{}_{(aq)}$$

Sodium acetate ($NaC_2H_3O_2$) is added to increase the deposition rate and buffer the solution, while the other additive, lead acetate ($Pb(C_2H_3O_2)_2\ 2H_2O$) stabilises the bath to prevent catalytic decomposition (ref. 3).

An alternative to electroless deposition is to sputter a conducting film over the epoxy and then electroplate a Ni coating using the low stress sulphamate bath (ref. 1); this would be useful for a small number of specimens as the electroless bath has a short life (the procedure for electroplating is given in appendix 1).

After plating, the specimens are mounted in epoxy resin for polishing (see figs. 1 & 2).

2.2 POLISHING

When the mounting epoxy had cured, the samples were abraded with SiC paper ranging from 220# to 4000# using ethanol for cleaning and lubrication. Interchangeable SiC paper discs were used which clipped onto a brass polishing wheel. Care was taken to retain the brittle scale during polishing which, besides being lost, would scratch the specimen on breaking free. After 4000#, final polishing was carried out using 1μm diamond paste on a felt pad.

Edge rounding still occurs to some degree; however, for better results, automatic polishing would be required.

3.0 ETCHANTS

Many etchants have been tried, the most useful are those listed in Table 2. Relevant figures (with detailed captions) and microstructures are referenced in the table.

In Table 2, it may appear that the lactic acid etch (etchant (1)) and the iron chloride etch (etchant (2)) perform similarly; however they are quite different. Etchant (1) was used for microstructural observation of both substrate and coating to good effect. Etchant (2) was too severe on the aluminide coating for optical microscopy and was more useful as a macroetchant, as it colour contrasted the dendritic structure of the grains (fig. 8). As a consequence of its preferential attack of Al rich phases, it has been used to strip the coating from a blade leaving the skeleton of the scale, coating grain boundaries and the precipitation region of the substrate (fig. 14).

The electrolytic etchants can be used for phase extraction; ie. electrolyte (1), when used for longer periods, can be used to dissolve the substrate leaving γ' precipitates (fig. 9) and electrolyte (2) can be used for carbide extraction (fig. 11), as little dissolution of these phases occur, compared to the surrounding material.

3.1 CARBIDE STAIN

Figures 15 and 16 show examples of the effect obtained using the carbide stain. Two different superalloys are shown; in figure 15, IN 738 was stained to reveal the blocky matrix carbides of M_6C type; while in figure 16, the matrix carbides are $M_{23}C_6$ in René 80H.

A chain of small discrete carbide particles is developed in superalloy grain boundaries during post-forming aging to improve creep rupture life (ref 1). Due to the presence of these carbides in grain boundaries, the carbide stain can also be used to delineate grains on a polished specimen without destructive etching. (fig.17).

4.0 CONCLUSION

1. Edge retention of polished turbine blade specimens is essential for examination of the aluminide coating applied to the outer surface. This has been acheived by nickel plating an approximately 30 μm thick layer over the specimen before mounting and polishing.

2. Four etchants have been selected for their ease of use and phase delineation:

    i. a microetchant (immersion) for coating and substrate.

    ii. a macroetchant (immersion) for the substrate.

    iii. an electrolytic microetchant for the substrate and for phase extraction of γ'.

    iv. an electrolytic microetchant for substrate and coating, and phase extraction of carbides .

In addition, a carbide stain was used to identify carbide phases by colour contrasting.

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APPENDIX 1.

Instead of the electroless plating procedure, a Ni coating may be applied by electroplating if a conducting film exits on the surface. A conducting film may be applied simply by sputtering techniques; however, of the metals tried, gold performed the best so this was used sparingly.

The electroplating bath that was most satisfactory, by way of solution stability and producing a coating of low stress, was the Sulphamate Bath (ref.1):

$NiCl_2.6H_2O$	0-30g/l
$Ni(SO_3.NH_2)_2$	260-450g/l
H_3BO_3	30-45g/l (or to pH)

Operating Conditions;

pH	3 - 5
temp	38-60°C
current density	100 mA/cm^2
(constant current power supply)	
time	1hr.
constant agitation.	

TABLE 1: ELECTROLESS NICKEL PLATING PROCEDURE.

STEP	ACTION	FORMULA
1	Clean specimen	Acetone & ultrasound.
2	Sensitizing/nucleating (ref. 3)	Stanous chloride 2g/l Palladium chloride 0.2g/l HCl 10ml/l in H_2O Immerse 1 min 20-40°C.
3	Acceleration (ref. 1)	Dilute HCl Immerse 30 sec 50°C.
4	Plating bath (ref. 4)	Nickel sulphate 25 g/l Sodium acetate 9 g/l Lead acetate 0.001 g/l Sodium hypophosphite 23 g/l Immerse 60 mins, 80°C, pH 4-5.

TABLE 2: ETCHANTS FOR NICKEL BASED SUPERALLOYS.

ETCHANT	USE	EFFECT / COMMENTS
1. (ref. 5) 30ml Lactic acid 30ml Acetic acid 20ml HCl 10ml HNO_3	Immerse 5 sec	Dissolves γ' & β, leaves α-Cr in coating; good for microstructure of coating and substrate. (figs. 3 to 5)
2. (ref. 6) 5g $FeCl_3$ 15ml HCl 60ml Ethanol	Immerse 5 sec	Dissolves γ' & β; good macro etch, reveals grain structure of substrate and coating. (figs. 6 to 8)
3. Electrolyte (1) (ref. 5) 1% Citric acid 1% Ammonium-sulphate in H_2O	1V, 10 sec*	Dissolves substrate leaving γ'. (figs. 9 & 10)
4. Electrolyte (2) (ref. 7) 10% HCl 4% Tartaric acid in Methanol	2V, 10 sec*	Dissolves coating & substrate leaving carbides and interdiffusion zone precipitates. (figs. 11 to 13)
Carbide stain (ref. 5): 50/50 Aqueous soln. K_2MnO_4 and 60% NaOH soln.	Swab 3 sec	Stains carbides according to structure: - $M_{23}C_6$ green-pale blue - M_6C brown - MC multicoloured. (figs. 15 to 17)

* For a specimen area of approximately 1.5cm^2 .

Figure 1: Edge and corrosion product retention using the Ni plating procedure.

Figure 2: Retention of corrosion product produced by static laboratory tests; the bright band on LHS is the blade material, RHS is Ni plate.

Figure 3: SEM micograph of the effect of etchant (1) on a high activity aluminide coating. On the RHS of the micrograph, the γ matrix contains voids where γ' has been removed. To the left is the interdiffusion zones which are highlighted due to dissolution of γ' (inner) and β (outer) phases which previously surrounded the precipitates. The coating β phase has been dissolved revealing precipitates arising from substrate alloying elements in two distinct bands; a finer precipitate size close to the outer interdiffusion zone, and a coarser precipitate toward the outer edge. Little oxidation of this coating has occurred as there is no indication of γ' formation due to Al depletion, (ref.7).

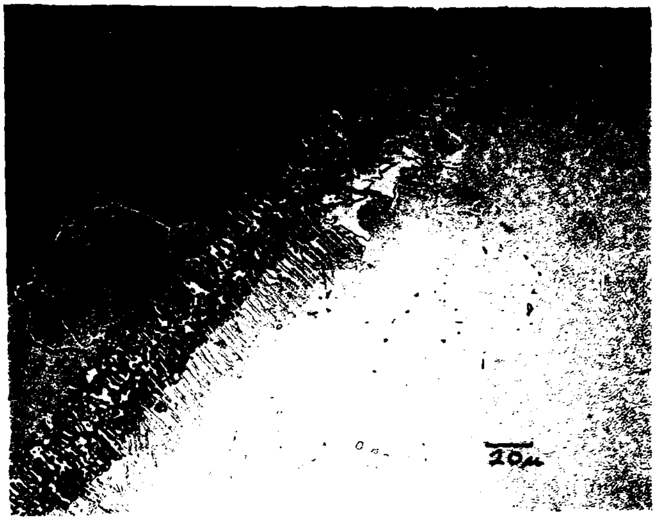


Figure 4: Optical micrograph showing the effect of etchant (1) on the substrate and coating. The coating grain structure is revealed (showing less precipitates than fig. 3 due to solutioning during service) and the substrate γ, γ', carbides and grain boundaries are clearly seen.

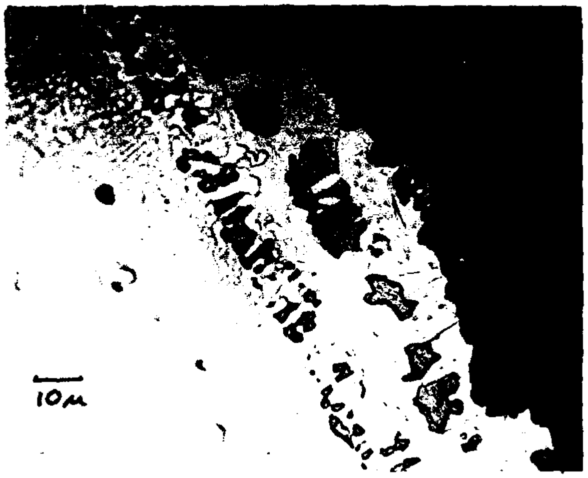


Figure 5: Also etchant (1), but here the coating has undergone Al depletion as the β phase exists only as isolated grains in the coating; the rest of the coating is probably γ' phase.

Figure 6: SEM micrograph obtained using etchant (2). This etchant has revealed more coating structure for a similar coating area to fig. 4 due to preferential attack on Al rich regions. Because of this, etchant (2) is not as applicable for optical micrographs as etchant (1).

Figure 7: A different coating area than in fig. 6 (also etchant (2)) showing greater solutioning of coating precipitates due to longer service exposure. Oxidation is also visible down a coating grain boundary reaching the substrate.

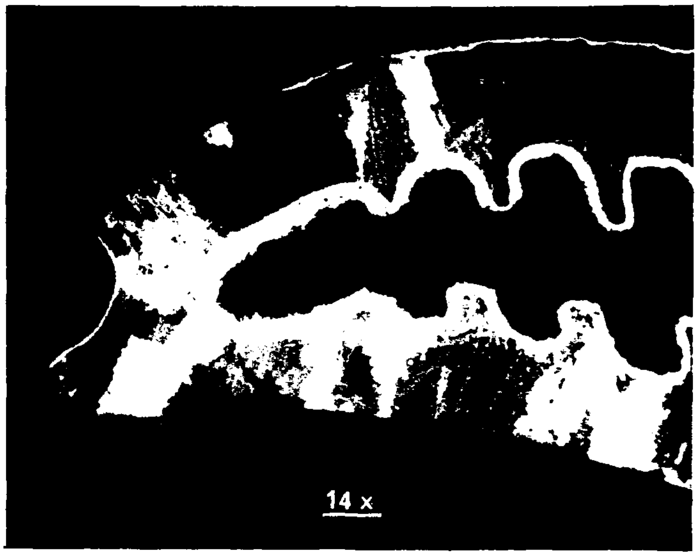


Figure 8: Colour contrasting effect of etchant (2) on macrostructure. The dendritic grain structure and corrosion depleted regions are clearly defined (LHS is leading edge).

Figure 9: In this micrograph, etchant (3) has been used to isolate γ' in the substrate (LHS). The β phase of the coating is intact and the interdiffusion zone precipitates have dissolved.

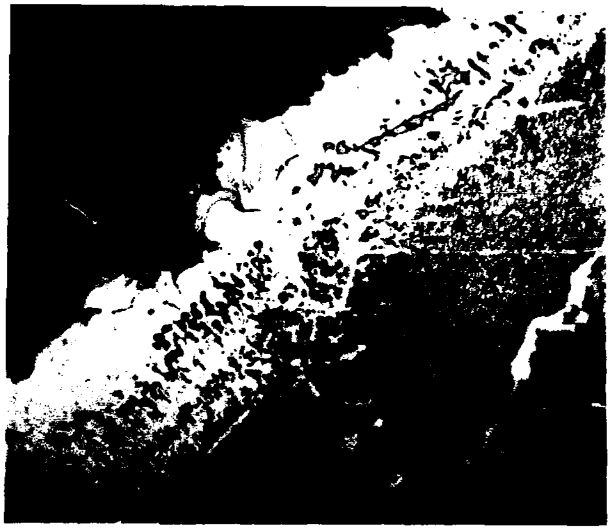


Figure 10: Optical micrograph using etchant (3). The darker phase at the outer edge of the coating is probably γ' formed by Al depletion. Grain-boundary carbides are also visible in the substrate.

Figure 11: Etchant (4); β, γ and γ' phases have been preferentially attacked leaving carbide phases and interdiffusion zone precipitates. Note the plate-like appearance of precipitates projecting into the substrate (RHS).

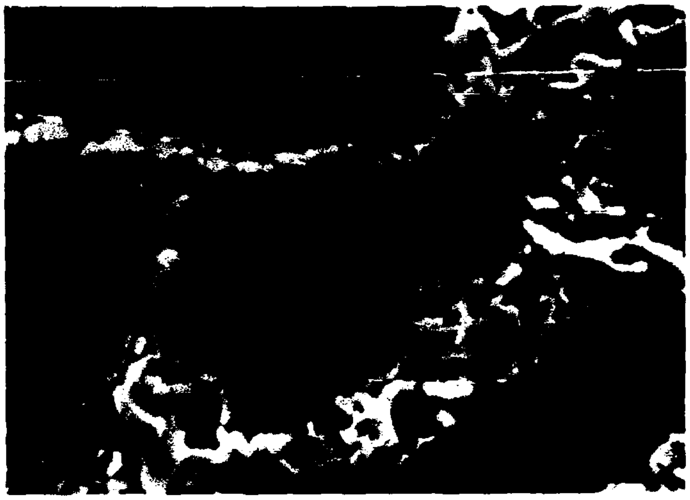


Figure 12: Etchant (4) used to reveal grain boundary carbides. γ' attack has left voids in the matrix and grain boundaries.

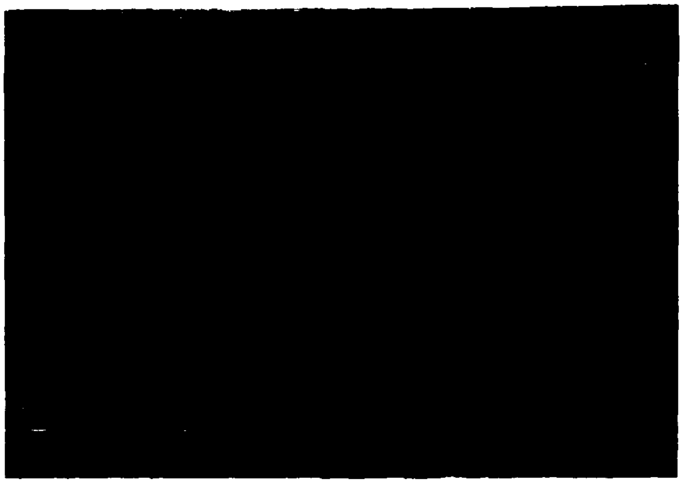
Figure 13: Optical micrograph showing coating and substrate etched with etchant (4) for 10 sec.

Figure 14: SEM micrographs of the outer surface of a turbine blade with NiAl removed by etchant 2;

a) shows the scale (top 1/2), and the interdiffusion zone, (bottom 1/2), connected by coating grain boundaries.

b) magnification of grain boundaries in a),

c) three regions of the coating are revealed here, starting from the LHS bottom,
  -inner and outer interdiffusion zone bands
  -Ni rich region of the coating (smoother diagonal band).



(a)

(b)

(c)

Figure 15: Optical micrograph showing the effects of carbide stain on superalloy IN738. Larger matrix carbides and smaller chain grain boundary carbides have stained brown (M_6C).

Figure 16: $M_{23}C_6$ carbides dispersed in superalloy René 80H.

Figure 17: Carbide stain used to delineate structure without etching. The micrograph reveals a fatigue crack running down a substrate grain boundary.

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16. ABSTRACT

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