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**EFFECTS OF DIFFUSION ON ALUMINUM DEPLETION
AND DEGRADATION OF NiAl COATINGS**

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ABSTRACT

Experiments were performed to critically demonstrate the effects of diffusion on the aluminum depletion and degradation of NiAl coatings on superalloys. Pack aluminized IN 100 and Mar-M200 were diffusion annealed in 5×10^{-3} torr vacuum at 1100°C for 300 hours. Aluminum losses due to oxidation and vaporization were minimal. Metallographic and electron microprobe analyses showed considerable interdiffusion of the coating with the substrate, which caused a large decrease in the original aluminum level of the coating. Subsequent cyclic furnace oxidation tests were performed at 1100°C using 1 hour cycles on pre-diffused and as-coated specimens. The pre-diffusion treatment decreased the oxidation protection for both alloys, but more dramatically for IN 100. Identical oxidation tests of bulk NiAl, where such diffusion effects are precluded, showed no signs of degradation at twice the time needed to degrade the coated superalloys. These results, plus limited tests showing the reduced oxidation resistance of aluminum-poor NiAl, suggest a degradation model whereby the coating is first depleted of aluminum by diffusion, (as opposed to Al_2O_3 spalling),

then rapidly degraded by the formation of spall-prone oxides.

INTRODUCTION

As aircraft gas turbine inlet temperatures have increased, blade materials have been coated to reduce the adverse effects of oxidation. Recent advances in directionally solidified eutectics will allow even higher blade temperatures ($\sim 1100^{\circ}\text{C}$) and require greater protection from coatings. It has been shown, however, that current NiAl coatings fail during cyclic oxidation at 1100°C in times less than ~ 1000 hours.^{1,2}

The failure of the coating is generally assumed to result from the alternate formation and spalling of an Al_2O_3 film during cyclic oxidation.³⁻⁷ Repetition of these processes leads to aluminum depletion and a resultant acceleration of oxidation. That aluminum is removed from the coating is an often demonstrated fact. But that this is a result of the initial oxidation and Al_2O_3 spalling has not been conclusively proven. An alternative process is possible: the aluminum concentration of the coating may first be diluted by interdiffusion with the substrate. This possibility is raised because bulk NiAl does not appear to suffer from cyclic oxidation as severely as NiAl coatings on superalloys.⁸

It is important to determine which mechanism controls coating breakdown if improvements are to be sought. If spalling of Al_2O_3 controls, then coatings research should endeavor to

reduce Al_2O_3 scale formation and improve scale adherence. If, on the other hand, diffusion is the predominant mechanism, then coatings research should be directed towards minimizing diffusion.

The purpose of this investigation was to determine the relative importance of diffusion and Al_2O_3 scale spallation to coating breakdown. To achieve this goal, pack aluminized IN 100 and Mar-M200 were vacuum annealed at 1100°C to allow diffusion to proceed independently of oxidation. As-coated and as-diffused coatings were compared before and after cyclic furnace oxidation at 1100°C . The as-coated specimens were also compared to thin samples of bulk NiAl in 1100°C oxidation. The extent of degradation was judged by specific weight change, metallography, and electron microprobe analyses.

MATERIALS AND PROCEDURE

Cast coupons of IN 100 were cut into $1.3 \times 2.5 \times 0.25$ cm test specimens. A directionally solidified bar of Mar-M200 was cut into $0.6 \times 2.5 \times 0.25$ cm test specimens. Holes 0.3 cm dia. were spark cut in one end of the specimens for subsequent hanging in furnace oxidation tests. The specimens were prepared for coating by vapor-blasting with alumina grit and rinsing in trichloroethylene, then in ethyl alcohol.

Bulk NiAl alloys ranging from 35 to 50 at. pct. aluminum were arc-melted into 50 gm buttons from high purity (99.99

percent) nickel and aluminum. Thin ($\sim 200\mu$) oxidation specimens of stoichiometric NiAl were produced by mounting and hand grinding slices of the button. Specimens of various hypostoichiometric compositions were sectioned into 0.25 cm thick slices.

Coating of the superalloys was accomplished by a pack aluminizing process described elsewhere.⁹ Briefly, the pack process consists of heating the specimens to 1100°C for 16 hours in a pack of 98 wt. pct. Al_2O_3 filler, 1 wt. pct. Al, and 1 wt. pct. NaCl activator. Flushing the pack with argon at 0.5 l/min. prevented oxidation during aluminizing. Three packs were used for IN 100 specimens with an average aluminum pickup of 17.0 mg/cm^2 . Variations in coating weight occurred from specimen to specimen, with the minimum and maximum being 15.9 and 19.5 mg/cm^2 , respectively. Only one pack was used for Mar-M200, with the average coating weight gain being 22.4 mg/cm^2 . Minimum and maximum depositions on this alloy were 19.8 and 23.3 mg/cm^2 , respectively.

Diffusion annealing of the coated specimens was performed in a vacuum tube furnace at 1100°C for 300 hours. The coated specimens were first preoxidized in 1100°C air for 2 hours in order to form an Al_2O_3 film. This was needed to prevent vaporization of the coating during vacuum annealing. A moderate vacuum of 5×10^{-3} torr also prevented gross aluminum depletion of the coating by curtailing both vaporization and oxidation. A weight gain often occurred for both the pre-oxidation and vacuum annealing treatments (0.8 mg/cm^2 total max). Since primarily Al_2O_3

was formed, a mass balance calculation could be performed to determine the actual amount of aluminum lost. This loss was found to be 0.9 mg/cm^2 or only 4 percent of the aluminum deposited during aluminizing.

The possibility of vaporization losses through the Al_2O_3 film during annealing was also considered. The major gaseous species over alumina at these conditions would be AlO_2 , with a vapor pressure less than 10^{-18} atm. and an aluminum loss rate less than $10^{-14} \text{ mg/(cm}^2 \cdot \text{sec)}$, (10^{-8} mg/cm^2 for a 300 hour anneal).

Cyclic oxidation testing was performed at 1100°C and 1200°C in vertical-tube resistance furnaces with a hot zone of 30 cm. Specimens were suspended by platinum wire hangers attached to a pneumatic cylinder. They were automatically lowered into and raised out of the furnaces by means of an electronic timer/solenoid switch/pneumatic pump arrangement described in reference (8). One cycle consisted of 1 hour of heating and 1/3 hour of cooling to room temperature. Another cycle consisted of 1/10 hour of heating and 1/6 hour of cooling. Specimens were weighed every 15 cycles on an analytical balance accurate to 0.2 mg.

Post-test analyses consisted of surface X-ray diffraction, metallography, and electron microprobe. In situ surface scales were identified by diffractometer scans using $\text{Cu K}\alpha$ radiation with a LiF monochromator. Metallographic specimens were copper-plated before standard mounting and polishing. Etching was

accomplished by immersion in a 33 percent H_2O - 33 percent CH_3OOH - 33 percent HNO_3 - 1 percent HF solution. Microprobe analyses of the polished cross-sections were performed with a 15 kv, 30 nA electron beam integrated over a 40μ wide path.

RESULTS AND DISCUSSION

Pack- Aluminized IN 100

Diffusion annealing of pack-coated IN 100 at $1100^{\circ}C$ for 300 hours produced some very definite effects. Figure 1 shows a striking change in coating structure and an increase in overall coating thickness of 65 percent. X-ray diffractometer scans identified β -NiAl as the major coating phase for both as-coated and as-annealed coatings. Other annealed coating phases identified were γ -Ni and/or γ' -Ni₃Al. These phases probably corresponded to the light-etching phases and fine precipitates in the coating, as shown in figure 1(b). Annealing also formed α -Al₂O₃ plus some TiO₂ (rutile) surface scales.

Microprobe profiles for aluminum (fig. 2) showed that the diffusion annealing treatment decreased the maximum aluminum intensity level in the coating by 40 percent of the as-coated value and increased the coating thickness by ~60 percent. (An Al₂O₃ film is indicated by the sharp peaks at the surface.) Similar effects occurred for the specimen cyclicly oxidized (1 hour cycles) at the same temperature for the same amount of time. Here the maximum aluminum intensity level was decreased

by 54 percent of the as-coated value, and a 10μ surface depletion zone occurred due to oxidation. This implies that depletion of aluminum, the accepted cause of failure for NiAl coatings, occurs to a large extent by interdiffusion with the substrate, in addition to the repeated spalling and formation of an oxide film.

The cyclic oxidation behavior of the diffusion annealed specimens was markedly poorer than that of the as-coated specimens (fig. 3). On the average, diffusion annealed specimens showed a negative weight change (an indication of spalling) at 50 hours, compared to 380 hours for specimens with no pre-annealing treatment. The authors admit that considerable scatter in the data exists. Nevertheless, the two scatter bands are separable to a significant extent.

Pack Aluminized Mar-M200

Diffusion also affected NiAl coatings on Mar-M200, though not so adversely in oxidation testing. The microstructures in figure 4 show that the $1100^{\circ}\text{C}/300$ hour diffusion annealing actually doubled the coating thickness. X-ray diffractometer scans showed that β -NiAl was still the only coating surface phase after annealing.

The microprobe profiles in figure 5 show that $1100^{\circ}\text{C}/300$ hour diffusion annealing reduced the maximum aluminum intensity level by 48 percent of the as-coated value and indeed doubled

the coating thickness. Cyclic oxidation (1 hour cycles) at the same temperature for 700 hours had the same effect on the aluminum profile. No additional effects of oxidation, such as a surface depletion zone, were apparent.

The gravimetric data in figure 6 shows that diffusion annealing was not so degrading for coated Mar-M200 oxidation behavior as it was for IN 100. The average oxidation time needed to produce a negative weight change was 270 hours for diffusion annealed specimens compared to 520 hours for as-coated specimens. Thus, while acknowledging the scatter, the effect of pre-annealing was apparent. The improved behavior of annealed Mar-M200 coatings compared to the annealed IN 100 coatings may be due to the 36 percent heavier coatings originally deposited (or 66 percent thicker coatings after annealing). The result was that the coated Mar-M200 was more protective, on the average, than coated IN 100. Thus the 300 hour pre-annealing treatment represented a smaller fraction of the coating "lifetime," and was therefore less harmful, for Mar-M200 than for IN 100.

Comparison of Bulk NiAl with Coated Superalloys

Two thin specimens of bulk stoichiometric NiAl were oxidized under the same conditions as IN 100 and Mar-M200. The thickness used (200 μ) was intended to contain no more aluminum per exposed area than the NiAl coatings on the superalloys; i.e., it approximated two coatings back-to-back. Yet the cyclic oxidation resistance was markedly better than either coated IN 100 or

Mar-M200, as shown in figure 7. The average time for a negative weight change was 800 hours for NiAl compared to 380 and 520 hours for the coated superalloys. Even after 1500 hours of oxidation the bulk NiAl had not yet lost 1 mg/cm^2 . More importantly, the rate of spalling, as indicated by these curves, was only half that for the coated superalloys - even at twice the oxidation time.

X-ray diffractometer scans of the bulk NiAl surface identified only β -NiAl and Al_2O_3 . Whereas on coated IN 100 the identified surface phases were Al_2O_3 , spinel ($a_0 = 8.10 \text{ \AA}$), TiO_2 , and γ and/or γ' ; and coated Mar-M200 surface phases were Al_2O_3 , γ and/or γ' , and some NiAl (800 and 700 hr. data for the least-spalling specimens of IN 100 and Mar-M200, respectively).

No surface depletion or secondary phases were observed metallographically for bulk NiAl, despite considerable efforts at etching (fig. 8). However the most spall-resistant coated IN 100 and Mar-M200 specimens showed transformations of β -NiAl to martensite and γ or γ' , indicating a decrease in the aluminum content of the coating from about 50 at. pct. to at least 37 at. pct.^{6,10}

Microprobe data on these specimens also bears this out (fig. 9): virtually no depletion zone was apparent for the pure NiAl specimen, and the overall aluminum intensity level was reduced by only ~16 percent of its original value. However the aluminum intensity level for the coated superalloys was reduced

by ~49 percent of the original value.

Since the thin NiAl specimens can be considered simply as a coating without the interdiffusional effects of a substrate, it is apparent that significant gains in coating life could be obtained by limiting interdiffusion with the superalloy substrates. This harmful interdiffusion may involve both the inward diffusion of aluminum and outward diffusion of nickel as well as the "contamination" of the coating by the substrate alloying elements.

Degradation Model

At this point it was clear that diffusion processes were effective mechanisms in initiating coating breakdown. The data also suggests that complete conversion to Ni_3Al is not necessary for rapid oxidation and spalling to occur, i.e., accelerated oxidation was noted for aluminum-depleted β -NiAl. In order to confirm this behavior, supplementary oxidation tests were performed on aluminum-poor compositions of bulk NiAl. An accelerated 1200°C test with a high cycle frequency (0.10 hr) was used to provide easy differentiation between alloys. The gravimetric data in figure 10 show that, indeed, spalling was more pronounced for compositions having less than ~40 at. pct. aluminum. No gradual trend with composition was observed, rather the gravimetric curves fell into two bands. Metallographic and X-ray diffraction analyses showed that only Al_2O_3 was formed and no depletion zone occurred for the low-spalling alloys, while Al_2O_3

and spinel oxides formed and a 50μ γ/γ' depletion zone occurred for the high-spalling alloys. Similar compositional effects can probably be expected for $1100^{\circ}\text{C}/1$ hour cycle testing, but the test times needed would be much longer. (These data are consistent with isothermal work in the Ni-Al system (ref. 11). The experiments in this work indicated that the critical amount of aluminum needed for exclusive Al_2O_3 formation lies between 30 and 40 atomic percent at this temperature.)

Taking the above data into account along with the previously discussed effects of diffusion, it appears that aluminide coating degradation follows this sequence: First the aluminum level is significantly decreased due to diffusion and to a lesser extent by repeated Al_2O_3 spalling. Only after the aluminum content of $\beta\text{-NiAl}$ falls below that needed for Al_2O_3 formation does oxide spalling become the predominant cause of aluminum loss. Surface depletion zones of γ/γ' soon follow, with the final stages of degradation being the same as for previously reported models. Thus, while diffusion may not account for most of the aluminum lost in a severely degraded coating, it is responsible for the initiation of coating failure.

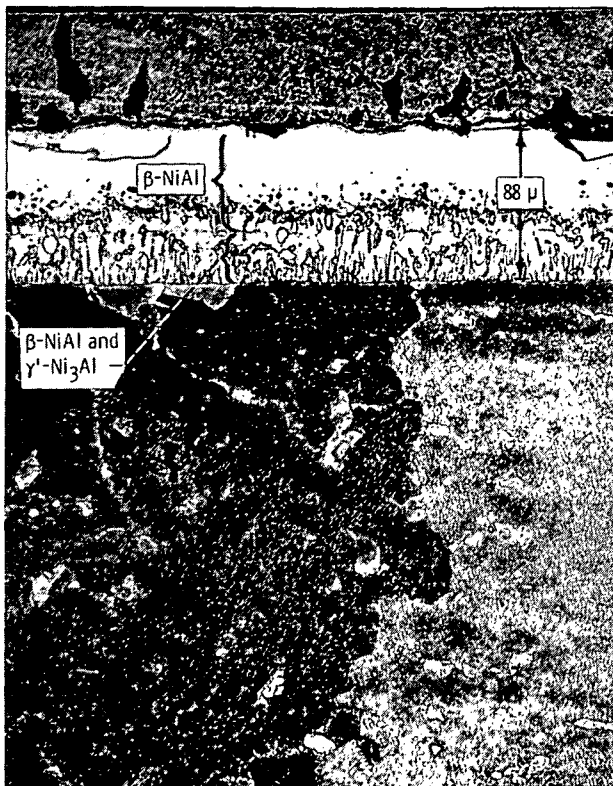
CONCLUDING REMARKS

Based on a comparison of bulk NiAl and diffusion annealed coatings with as-coated superalloys in 1100°C cyclic oxidation, the following conclusions appear justified: (1) loss of aluminum

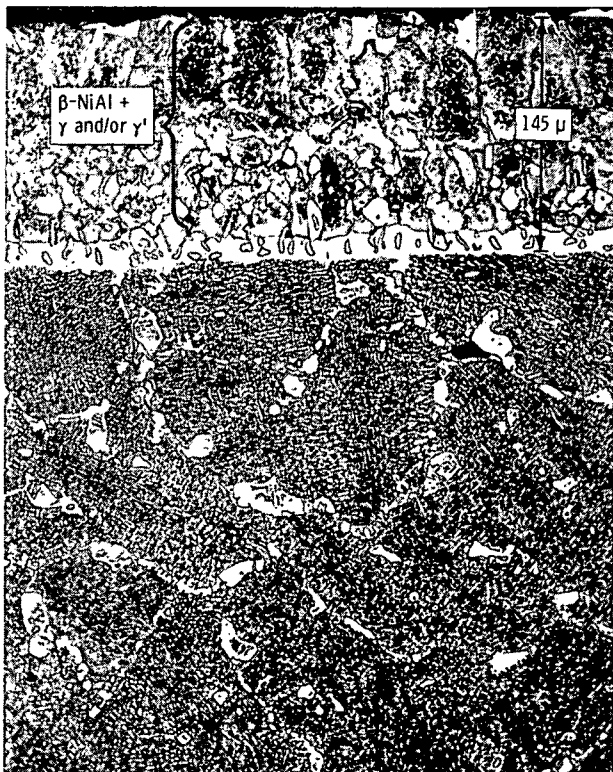
in the coating by diffusion with the substrate triggers coating degradation rather than spallation of Al_2O_3 alone; and (2) this loss of aluminum allows oxides other than Al_2O_3 to form with an increased rate of spalling, which leads to rapid coating failure. Thus the long-time use of NiAl coatings at 1100°C will require a reduction of coating/substrate interdiffusion, possibly by the use of diffusion barriers.

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(a) As-coated IN-100.



(b) Diffusion annealed for 300 hours at 1100°C.

Figure 1. - Effect of diffusion on coating structure of aluminized IN-100; X250.

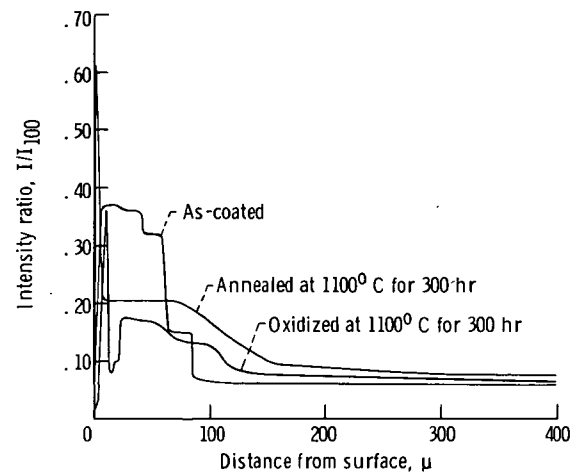


Figure 2. - Aluminum microprobe profiles for pack aluminized IN 100.

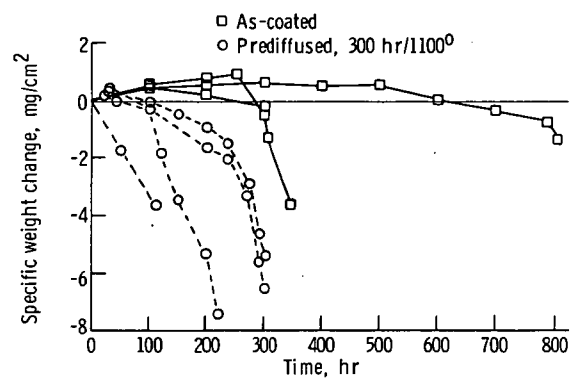
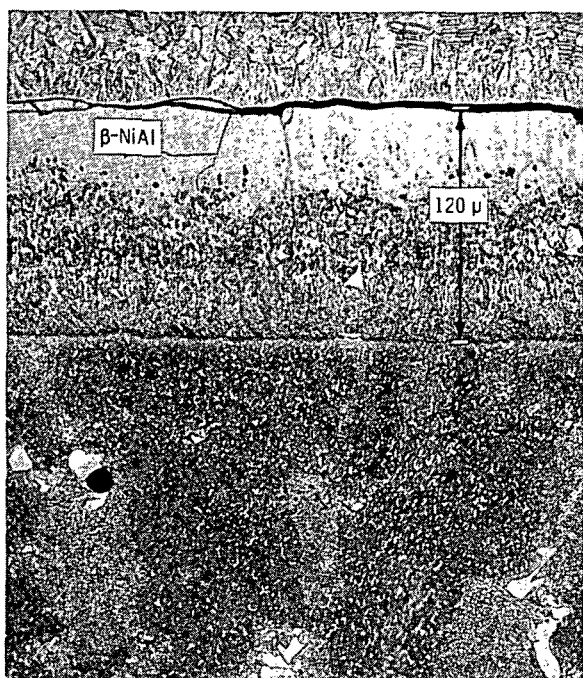
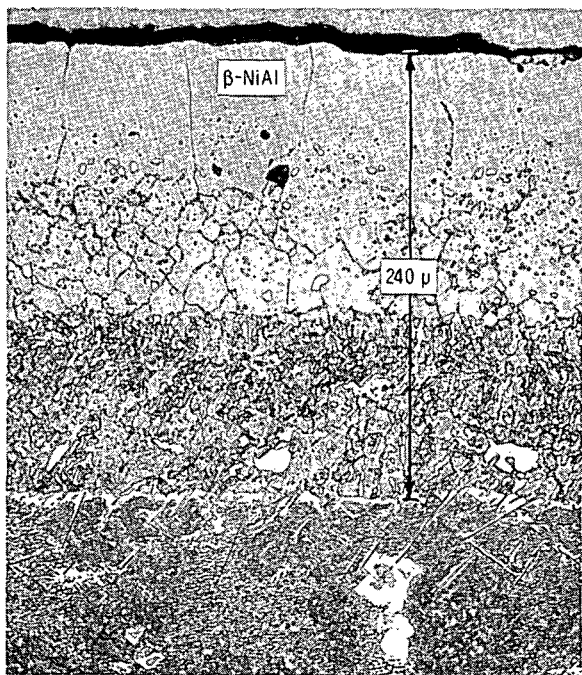


Figure 3. - Effect of diffusion on the oxidation of pack aluminized IN 100. (1100°C/1 hr cycle furnace tests.)



(a) As-coated Mar-M 200.



(b) Diffusion annealed for 300 hours at 1100°C.

Figure 4. - Effect of diffusion on coating structure of aluminized Mar-M 200; X250.

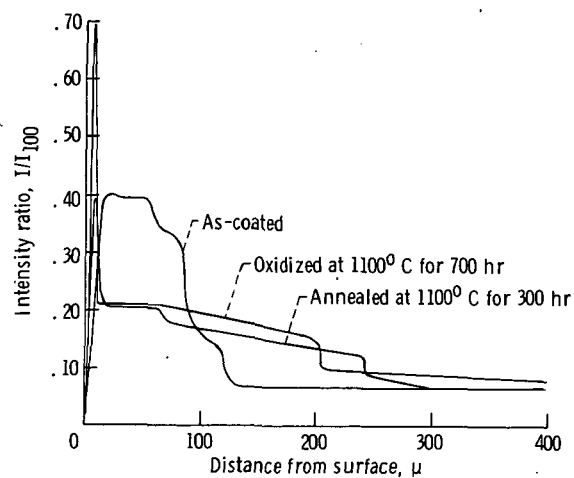


Figure 5. - Aluminum microprobe profiles for pack aluminized MAR M-200.

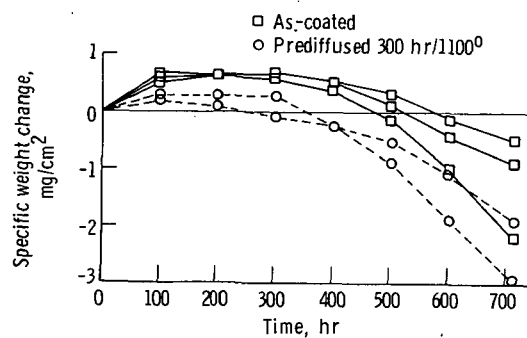


Figure 6. - Effect of diffusion on the oxidation of pack aluminized MAR M-200. (1100°C/1 hr cycle furnace tests.)

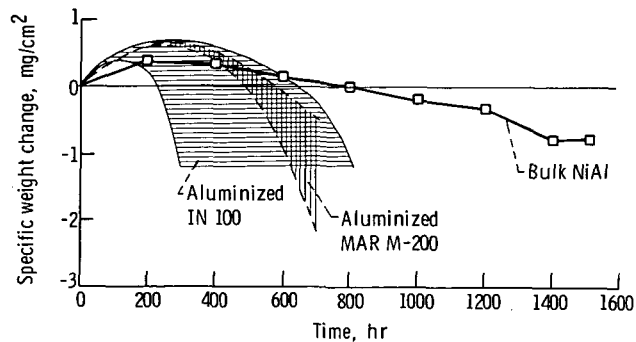
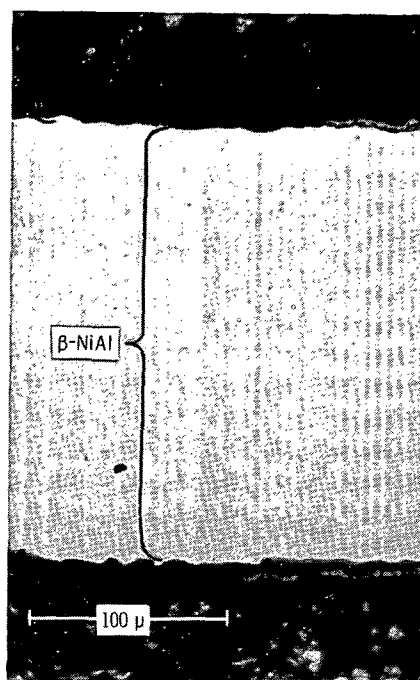


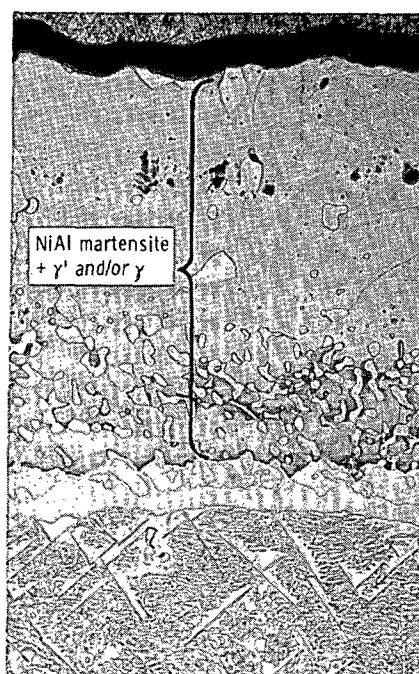
Figure 7. - Comparison of NiAl-coated superalloys with bulk NiAl. (1100°C/1 hr cycle furnace tests.)



(a) Bulk NiAl after 1500 hours.



(b) Pack coated IN-100 after 800 hours.



(c) Pack coated Mar-M 200 after 700 hours.

Figure 8. - Comparative degradation of bulk NiAl and aluminized superalloys, oxidized in 1100° C furnace tests, 1 hour cycles. Etched; X250.

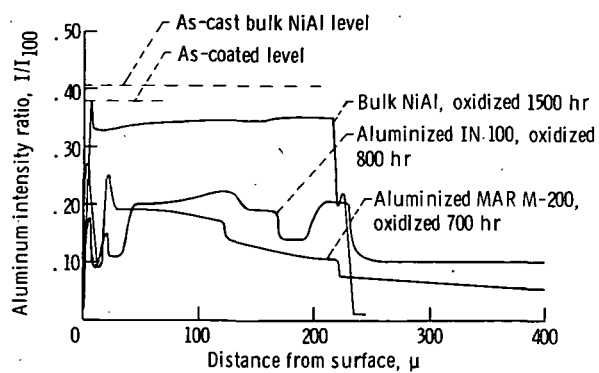


Figure 9. - Comparison of aluminum depletion for bulk NiAl and coated superalloys after cyclic oxidation at 1100°C .

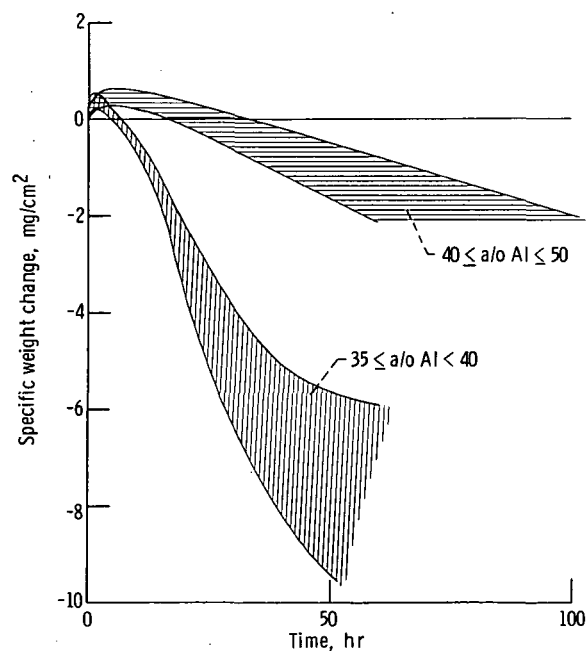


Figure 10. - Effect of composition on cyclic oxidation behavior of bulk NiAl. ($1200^{\circ}\text{C}/0.10$ hr cycle furnace tests.)