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DIFFUSION COATINGS DURING 1100 C CYCLIC TESTING(U)
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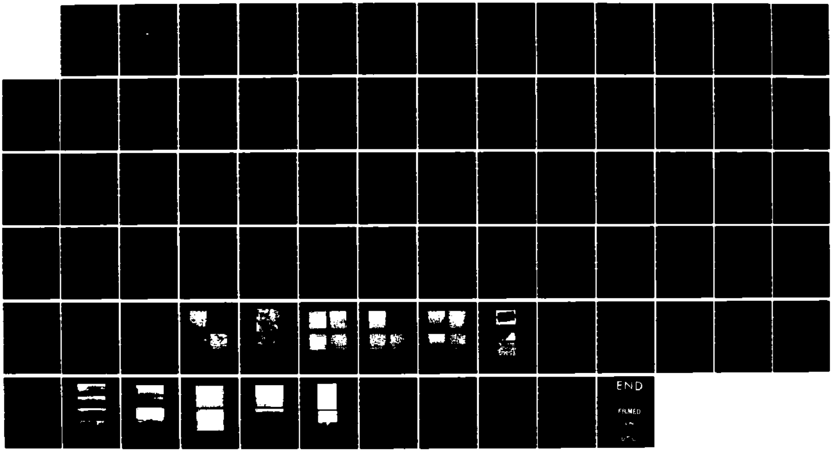

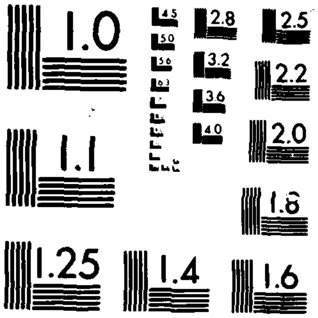

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THESIS

PLASTIC INSTABILITY OF ALUMINIDE AND PLATINUM MODIFIED DIFFUSION COATINGS DURING 1100°C CYCLIC TESTING

by

Thomas F. Manley, II

December 1985

Thesis Advisor: D. H. Boone

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS
AD-A164 526

2a. SECURITY CLASSIFICATION AUTHORITY

3 DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution is unlimited

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Naval Postgraduate School

6b. OFFICE SYMBOL (*If applicable*)
69

7a. NAME OF MONITORING ORGANIZATION
Naval Postgraduate School

6c. ADDRESS (*City, State, and ZIP Code*)
Monterey, California 93943-5100

7b. ADDRESS (*City, State, and ZIP Code*)
Monterey, California 93943-5100

8a. NAME OF FUNDING/SPONSORING ORGANIZATION

8b. OFFICE SYMBOL (*If applicable*)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c ADDRESS (*City, State, and ZIP Code*)

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (*Include Security Classification*)
PLASTIC INSTABILITY OF ALUMINIDE AND PLATINUM MODIFIED DIFFUSION COATINGS DURING 1100°C CYCLIC TESTING

12 PERSONAL AUTHOR(S)
Manley, Thomas F., II

13a TYPE OF REPORT
Master's Thesis

13b TIME COVERED
FROM ________ TO ________

14 DATE OF REPORT (*Year, Month, Day*)
1985 December

15 PAGE COUNT
78

16 SUPPLEMENTARY NOTATION

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
Turbine Blade Coatings; Platinum-Aluminides; Diffusion Coatings; IN-738; Coating Plastic Instability; Rumpling; (Continued)

19 ABSTRACT (*Continue on reverse if necessary and identify by block number*)

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(Continued)

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a NAME OF RESPONSIBLE INDIVIDUAL
D. H. Boone

22b TELEPHONE (*Include Area Code*)
(408) 646-2551

22c OFFICE SYMBOL
69Bl

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

18. (Continued)

Cyclic Oxidation Testing; Coating-Substrate Thermal Expansion Mismatch; Coating Surface Morphology

19. (Continued)

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Accession For
NTIS GRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Avail and/or
Dist Special
A-1

Plastic Instability of Aluminide and Platinum Modified Diffusion Coatings During 1100°C Cyclic Testing

by

Thomas F. Manley, II
Captain, United States Marine Corps
B.S., Virginia Military Institute, 1979

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN ENGINEERING SCIENCE

from the

NAVAL POSTGRADUTE SCHOOL
December 1985

Author: Thomas F. Manley II
Thomas F. Manley, II

Approved by: Donald H. Boone
D. H. Boone, Thesis Advisor

PJ Marto
Paul J. Marto, Chairman,
Department of Mechanical Engineering

JN Dyer
J. N. Dyer, Dean of Science and Engineering

ABSTRACT

Platinum modified and unmodified aluminide diffusion coatings, on a nickel base superalloy (IN-738), were prepared to test the pre-aluminizing surface roughness effect on coating oxide scale adherence. A preliminary study of coating microstructure and surface structure changes during cyclic oxidation at 1100°C was begun. During this testing, significant surface deformation described as rumpling was observed and attributed to plastic instability produced during the cycling. Rumpling is found to be a function of the number and type of thermal strain cycles, thermal expansion mismatch, coating strength, and coating thickness. The role of oxide adherence observed for the Pt modified coatings cannot be determined from the data. Previous mention of this effect was not found in the literature. A similar surface rumpling phenomena, however, has been observed in overlay coating systems under similar conditions. The mechanical and protectivity impact of rumpling can only be inferred due to the limited available data.

[illegible] T[illegible] blade coatings [illegible] Coatings [illegible]

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ACKNOWLEDGEMENT

To Dr. Donald H. Boone, for whom I reserve the highest of professional admiration, I wish to express my deepest gratitude for the privilege of working under your guidance.

For their generous support in the area of coating production and heat treatment, my sincere gratitude goes to Dr. S. Shankar of the Turbine Components Corporation and to Mr. J. S. Smith and C. Thomas of Howmet Corporation.

I wish to extend my appreciation to Dr. Prabir Deb, Tom McCord, Tom Christian, Tammy Ellis, and Tom Kellogg, who collectively supported me both in the conduct of this work and with their comraderie.

Special thanks goes to Darlene Kelley for her instrumental help in putting it all together.

For my wife, Annette, and son, Tommy, words cannot adequately express my gratitude for your loving devotion and support over the past two and a half years. To the two of you I dedicate all I have done.

I. INTRODUCTION

Gas turbines have found extensive use in propulsion of high performance aircraft and for industrial power generation. In military applications, the utility of gas turbine engines is expanding to meet main propulsion requirements for marine craft such as; the Navy Landing Craft, Air Cushion (LCAC), powered by four (TF40B) marine gas turbines; and armored fighting vehicles such as; the M1 Abrams, main battle tank powered by a 1500 horsepower, AVCO Lycoming (AGT 1500) engine.

Coatings for hot section superalloy components are essential for improving performance, efficiency and reducing life cycle costs of gas turbines. Coatings and their processing technology have essentially evolved to provide protection against high temperature oxidation and hot corrosion without degrading a component's mechanical properties.

The protectivity of a coating is derived from its ability to form a stable reaction barrier to the environment, such as Al_2O_3 protective oxide scales, and sustain this barrier for extended periods under severely degrading environments. The ability of a coating to form protective barriers is a function of its chemical constitution, coating system thermo-mechanical compatibility, service environment extremes, and metallurgical structure.

Aluminide diffusion coatings have been the industry mainstay for high temperature application over the past thirty years. However, they have had increasing problems reaching required lifetimes for modern high performance, military application, gas turbines.

Platinum modified aluminide diffusion coatings have shown improved coating protectivity over unmodified aluminide coatings, through enhanced protective oxide scale adhesion and oxide mechanical properties (resistance to cracking). To date, the mechanism(s) by which protective oxide scale (Al_2O_3) properties are improved by platinum addition, has not been established.

The study of platinum modified aluminide coating composition, structural effects and physical-mechanical properties (such as strength, ductility and thermal expansion) are considered central to the understanding of their improved protectivity. The study of these coatings and their properties has been the major thrust of an ongoing research effort at the Naval Postgraduate School, Department of Mechanical Engineering.

The purpose of this thesis is to contribute to the present knowledge of why platinum modified aluminide coatings are effective. Specific goals were established to: 1) improve and expand program cyclic oxidation testing facilities, 2) to study the dynamic effect of 1100°C cyclic exposure on the IN-738 platinum aluminide coating system (with respect to microstructure and surface morphology), and 3) to advance a study of the pre-aluminizing surface roughness effect on Al_2O_3 oxide scale adherence during cyclic high temperature exposure.

II. BACKGROUND

A. THE IMPORTANCE OF SUPERALLOY COATINGS

The advent of superalloy technology in the United States has been dated to the early 1930's as a development response to provide heat-resistant materials for early aircraft turbosuperchargers [Ref. 1]. With the inception of gas turbine engines during the 1940's, it was realized that a major limitation to turbine performance was the maximum attainable temperature and pressure of the associated gas turbine thermodynamic cycle (Brayton Cycle), and in particular, the working gas fluid temperature and pressure of the turbine section inlet.

Ensuing years brought significant improvements in superalloy high temperature mechanical properties. These developments are attributed to improved processing techniques in vacuum melting and casting along with an increased understanding of the high temperature strengthening and hardening mechanisms associated with $\gamma'(Ni_3Al)$ second phase formation and carbide precipitation [Ref. 2]. From these advances, the iron, nickel, and cobalt based superalloy families evolved and grew progressively to meet the ever increasing temperature and mechanical property demands of the military and industry. In fact, the advances in gas turbine design were often a measure of the advancement level in high temperature materials technology.

The continued drive for increased gas turbine performance, without compromise in efficiency, reached a level during the early 1960's where it became apparent that alloying practices to attain improved high temperature mechanical properties, in particular those requiring reductions to Cr and additions of refractory metal elements, seriously degraded a component's ability to thwart high temperature environmental surface degradation [Ref. 3]. To combat this problem engineers turned to the use of elaborate turbine component cooling schemes and high temperature corrosion resistant coatings. These developments led to quantum improvements to gas turbine performance and efficiency.

Over the past twenty years turbine technology has become increasingly reliant on coating systems to meet design performance criteria. Coatings have proven to be the key to improved gas turbine component environmental surface stability. In some cases, use of coatings has even improved substrate mechanical properties such as thermal fatigue resistance [Ref. 4].

Today, virtually all high temperature dynamic, load bearing gas turbine components are coated.

B. COATING SYSTEM DESIGN

In early coating application, high temperature components were designed to meet mechanical requirements first and coated as on afterthought often referred to as the 'Band-Aid' approach. When early coating systems worked, they were dubbed successful. Currently, edisonian techniques are being replaced by extensive basic research and testing of coating systems prior to service implementation.

To maximize component material properties requires a system engineering design approach. This demands that coatings and alloy selection for components must be considered during initial project development stages. Selection of a coating system must take into account many critical factors, other than simply how well it protects against environmental degradation. As higher temperature, pressure and velocity turbine environments are sought (exceeding inlet temperatures of 1370°C and compression ratios of 25:1 [Ref. 1:pp. 3-5]), other factors may even become the component life limiting consideration.

In addition to high temperature oxidation and hot corrosion, discussed in the next section, the following factors must be considered in the design of coating systems [Ref. 5].

1. Coating Constitutional Stability

Coatings are, by nature, of different chemical constitution than the substrates they protect. These compositional variations establish chemical diffusion gradients. During high temperature exposure diffusion rates are always increased. Unacceptable interdiffusion of coating elements with a substrate during service can both degrade the coating's ability to maintain a continuous environmental protective barrier and degrade substrate properties through dilution effects.

2. Mechanical Strength and Ductility

Coatings must be strong enough at high temperatures to withstand loading from vibration, component creep and high velocity airstream forces. In addition, coatings must retain sufficient ductility to resist cracking during thermo-mechanical loading, over the range of their operational cycle. In this respect coating design has generally keyed on development of ductile coating systems which afford good corrosion resistance [Ref. 3:p. 249]. To date, brittle coatings (ceramics) have been unacceptable for use on cyclicly loaded turbine components because of their susceptibility to cracking.

3. Thermally Induced Strains

The combined effects of strains from thermal shock, $\varepsilon(dT/dx)$, and thermal expansion mismatch, $\varepsilon(\Delta\alpha, \Delta T)$, can result in mechanically induced cracking, plastic deformation and thermal fatigue of the coating-substrate system [Ref. 6]. Anticipated service cycle temperature and pressure fluctuation, as well as coating phase thermal expansion and conductivity properties must be evaluated for compatibility with substrate properties.

4. Substrate Property Effects

The application of coatings should be conducted so as not to degrade component properties such as creep resistance, fatigue resistance, and high temperature strength. Improper heat treatment during coating application can result in growth or re-solution of superalloy strengthening phases and a mechanically defective component.

5. Component Function Impairment

Modern turbine blade cooling schemes use elaborate networks of air passages, channels and vents. If a coating blocks or constricts these cooling systems, hot spots can develop and perpetrate a failure [Ref. 7]. Coatings can also impair component dimensional tolerances. For instance, blades are designed to elongate and fit precisely at maximum performance levels. Excessive blade tip coating can constrain expansion tolerances. Aerodynamic efficiency of a coated airfoil is also of major concern. Excessively coating thin foil sections can change the camber and therefore efficiency of a blade. In addition, coating roughness can impair component boundary layer flow conditions.

6. Repairability and Cost Benefit

With increasing turbine component complexity and cost, repair and rebuilding have become a paramount concern.

Coatings must be considered not only on the basis of their cost savings with respect to component service life extension, but also from the standpoint of their ability to be reconditioned. This aspect of total life cycle cost benefit is important and could result in selection of initially more expensive coating systems to reap savings down the line.

C. CORROSION PROTECTION

Two forms of corrosion have proven most devastating to gas turbine components. They are high temperature oxidation and hot corrosion.

Superalloy components exposed to hot gas streams, which invariably contain significant levels of oxygen, are subject to attack by constituent metal conversion to metal oxides. This attack, referred to as high temperature oxidation because of its increased significance at temperatures in excess of 600°C, becomes the major mode of turbine component environmental surface degradation at temperatures in excess of 1000°C [Ref. 8].

Susceptibility of a metallic surface to oxidation is dependent upon the free energy of metal oxide formation and the properties of the resulting oxide. The free energy of oxide formation is reduced (facilitating oxidation) by increased temperatures and oxygen partial pressures. Surface oxidation of a metal is difficult to prevent because oxide formation is thermodynamically favorable for most metals even at extremely low oxygen partial pressures. Oxidation rates, fortunately, can be reduced to acceptable levels through slowing or impairment of the metal reaction by the very formation of a selected oxide layer.

Initially during high temperature oxidation, surface oxides, representative of the exposed metal surface chemical composition, compete in formation until the most thermodynamically stable oxide dominates. This dominant stable oxide can form dense, 'protective' oxide scales which grow laterally and cover the entire metal surface. Upon formation of protective scales, oxidation rate kinetics are lowered and can be physically measured as a parabolic decrease in rate of component (specimen) weight gain. If, on the other hand, the dominant stable oxide forms low density, discontinuous, non-protective scales, oxidation rates will not slow and weight gain from metal reduction will increase linearly [Ref. 8:pp. 603-604].

Most superalloys initially form protective oxide scales of Al_2O_3 or Cr_2O_3. High temperature cyclic exposure (often used to test coating oxidation resistance through specimen weight gain analysis), and oxide growth stresses tend to crack these protective scales which can then separate from the surface (spallation), leaving behind exposed patches of unoxidized metal. Protective oxide scales will again reform until the protective oxide producing alloy elements (Al or Cr) reach a level of critical depletion in the substrate. At this point, less protective oxides, such as NiO or CoO, begin to dominate, accompanied by accelerated rates of oxidation degradation and actual loss of coating substrate metal [Ref. 8:p. 605].

Hot corrosion, the other major form of high temperature corrosion, refers to the enhanced gaseous corrosion obtained when impurities (such as sulfur, vanadium and inorganic salts) from both the environment and low grade fuels, form surface deposits on hot gas path exposed metallic surfaces. These condensed phase deposits serve to wet protective oxide scales and provide conditions ammendable to their localized break down [Ref. 9].

Hot corrosion can be viewed as a two stage process of initiation and propagation. During initiation the rate of surface degradation is slow, as a result of the initial formation of a reaction product barrier at the wetted surface-deposit interface. With increased time in operational service and continued wetting, reaction product barrier effectiveness degrades, leading into the second stage of hot corrosion--propagation. It is this mode of propagation which serves to distinguish between the two generally accepted classes of hot corrosion: high temperature hot corrosion (HTHC) and low temperature hot corrosion (LTHC) [Refs. 9 and 10:pp. 665-669].

HTHC generally occurs at temperatures in the range of 800°C to 950°C. HTHC corrosively propagates via: alloy induced acidic fluxing, basic fluxing, sulfidation or by chlorine induced effects [Ref. 9:pp. 671-674].

LTHC is associated with lower temperatures of exposure, 650°C to 750°C, and is, in general, more severe in nature. LTHC propagates by a gas phase induced acidic fluxing, which results in its characteristic strong pitting mode of attack [Ref. 9:p. 680].

The greatest concern with dynamic turbine component surface degradation by high temperature oxidation and/or hot corrosion is in the reduction of load bearing cross-section and development of stress concentration regions [Ref. 11]. An additional concern can be associated with corrosion related burn through of static sheet metal components, such as combustion liners, with the associated turbine failure [Ref. 12].

The protection coatings afford to superalloys for high temperature corrosion depends on the stability and effectiveness of the protective metal oxides, or reaction products, as a barrier to further attack under service conditions. In this respect, the coating proper simply provides the active element reservoir for maintenance of protective oxide or reaction product barriers [Ref. 13].

D. HIGH TEMPERATURE COATINGS

The three most widely used high temperature coatings are the overlay, thermal barrier and diffusion types [Ref. 8: p. 613].

Overlay coatings are essentially metallic claddings, applied by line of sight plasma spray, electron beam evaporation or sputtering techniques. These coatings, because of their low degree of substrate interaction, do not significantly degrade component mechanical properties. Their non-interactive nature allows for the variation of chemical compositions to match substrate properties and service requirements. However, the higher cost of these coatings associated with vacuum processing, and quality control often make them less attractive [Ref. 14].

Ceramic thermal barrier coatings are used to increase the life of non-load bearing, generally more corrosion resistant alloy, sheet metal components, such as combustion liners and exhaust ducts. These coatings are essentially used for their insulative qualities by which they serve to effectively lower substrate metal temperature. The use of thermal barrier coatings on loaded components, such as turbine blades and vanes, is being actively pursued but has thus far met only limited success, due to their brittle cracking nature [Ref. 8:p. 613].

Diffusion coatings have been the most widely used and cost effective coatings over the years. They are generally applied by inexpensive chemical (halide) vapor deposition processes, such as pack cementation, but have also been successfully applied in slurry form. The bulk of these coatings enrich the component outer surface with aluminum through diffusional processes and rely on formation of Al_2O_3 as a protective scale.

E. ALUMINIDE DIFFUSION COATINGS

Diffusion aluminide coatings were the first coatings to be used extensively in protection gas turbine airfoils because of their excellent resistance to oxidation [Ref. 8: p. 613].

Two basic microstructures characterize aluminide coatings on nickel-base superalloys. These two archetype coating structures have been classified as 'inward' and 'outward' diffusion coatings in reference to the method of aluminum incorporation during their formation.

Inward diffusion coatings are formed through a low temperature high activity process (LTHA). This simply means that processing diffusion temperatures were maintained relatively lOW ($\approx 700^{\circ}C/1$ hr) and the activity or diffusive gradient of aluminum at the component surface was high. These LTHA parameters result in the incorporation of aluminum at the component surface via 'inward' diffusion of aluminum. This type of coating is followed by an incorporating post coating diffusion heat treatment ($\approx 1040^{\circ}C/4$-6 hrs) [Ref. 15].

Inward (LTHA) coatings form a typically three zonee microstructure. The outer two zones, comprising two-thirds of the coating system, are of an Al-rich hyperstoichiometric β(NiAl) phase composition [Ref. 16]. The interdiffusion zone is considered non-protective because its finger-like phase intermeshing often provides a ready avenue for corrosive attack on the underlying diffusion depleted substrate.

Outward aluminide coatings form through a high temperature ($\approx 1000^{\circ}$C/4-10 hrs), low component surface aluminum activity process (HTLA). Aluminum incorporation proceeds by way of outward diffusion of Ni from the substrate through the β(NiAl) phase. Post-coating substrate interdiffusion is not generally required for these type coatings [Ref. 15].

A characteristic two zone microstructure results for outward (HTLA) coatings on nickel base superalloys. The outer zone representing half the coating system, is of a Ni-rich hypostoichiometric β(NiAl) phase [Ref. 16:pp. 476-495]. Again, the interdiffusion zone of β(NiAl) and substrate phase is considered non-protective.

Use of aluminide diffusion coatings for present day military high performance gas turbine application is limited by their susceptibility to degradation from deposit modified hot corrosion and the inherent brittleness associated with their β(NiAl) phase [Ref. 13:pp. 92-96]. Improvement to these coatings has been attempted through modification by Cr or noble metal (Pt, Rh) deposition on component surface prior to inward or outward aluminizing.

F. PLATINUM MODIFIED DIFFUSION COATINGS

Platinum modified aluminide diffusion coatings were orignally conceived and developed by Dr. Günter Lehnert, who published the original British patent in 1970, although some earlier work has been recently identified [Refs. 17, 18 and 19]. The concept behind these coatings was to estabish a diffusion barrier for preventing aluminum transport into the substrate. This concept was proven incorrect as aluminum was found to freely interdiffuse through the platinum layer with platinum concentrating at the aluminized coating surface in the forms of $PtAl_2$ and Pt_2Al_3 [Ref. 17:pp. 100-102].

Further coating development and testing led to commercial marketing of platinum aluminide coatings such as JM-1, LDC-2, and RT-22, and established their greatly enhanced resistance to high temperature cyclic oxidation and HTHC. Improvements of four times the oxidation resistance and six times the hot corrosion resistance times have been noted [Refs. 7:p. 189 and 20].

Platinum aluminide microstructures exhibit a wide range of variation related to processing factors such as: substrate composition, platinum plating technique, plating thickness, pre-aluminizing platinum diffusion, and aluminizing processes to include subsequent substrate heat treatment [Ref. 21].

On the nickel base alloy IN-738, structures have been reported to range between those that form a continuous $PtAl_2$ surface layer with minimal substrate interdiffusion to structures of two-phase $PtAl_2$ + NiAl (Pt in solution) with platinum phase and interdiffusion variations, to structures of a single phase NiAl(Pt) layer [Ref. 21].

In addition to microstructural variations, a wide range of surface morphologies have been noted for the as-formed platinum modified coating systems. A tight oxide scale (Al_2O_3) adhesion and conformity to the typically rough convoluted, as-formed coating surface was also observed [Ref. 21].

Study of the platinum plated surface morphology on IN-738 revealed an exaggerated 'cauliflower' surface topology, characterized by a fine crystalline-facet micro-roughness [Ref. 21]. This study noted that with increasing platinum diffusion the as-plated surfaces tended to roughen. This increased roughening was shown accompanied by an increase in sub-surface Kirkendall porosity and selected phase formation. These diffusional roughening variations were postulated to be responsible for the range of surface roughness observed on the aluminized, as-formed coating systems [Ref. 21].

Improvements in oxidation and HTHC for platinum aluminide coatings have been ascribed to the effect of platinum on improving Al_2O_3 oxide scale adhesion and resistance to cracking [Ref. 22]. The exact mechanism by which oxide adhesion is improved by platinum has not conclusively been established.

Processing differences, and thereby surface structural variations, have been demonstrated to affect the protectivity of these coatings under HTHC testing [Ref. 20]. In other coating systems (MCrAlY overlay; M = metal) surface roughness has been shown to be beneficial to oxide scale adherence [Ref. 21]. The role of surface structure in platinum aluminide protectivity has yet to be established.

It has been postulated that the increased surface roughness of platinum modified coatings provides for an enhanced keying-on of Al_2O_3, similar to the effect of the active element Yittrium on oxide adherence [Ref. 22:pp. 166-180]. Others have suggested that platinum increases oxide adhesion through reduction of mechanical growth stresses [Ref. 23]. In any event, the further study of platinum aluminide surface dynamics and oxide adherence is required to establish an answer.

III. EXPERIMENTAL PROCEDURE

Experimental work was performed in four major areas; apparatus fabrication, specimen preparation, testing and data analysis. Details on each of these areas is presented in the following text.

A. APPARATUS FABRICATION

To set up high temperature cyclic oxidation experiments, two separate experimental furnace configurations were developed. These units are shown in Figures 1 and 2. The designations of horizontal and vertical cyclic oxidation furnace rigs are related to the furnace orientation with respect to ground.

The horizontal rig uses a three zone, 6.0 cm diameter tube, furnace. Specimens are moved automatically in and out of the 14.0 cm calibrated hot zone by means of a chain drive. The cycle is variable and controlled by a timer with the number of cycles documented by a counter. For this experimental program, the furnace was calibrated to maintain a hot zone temperature setting of $1100^{\circ}C \pm 10^{\circ}C$ and cycle frequency was adjusted to achieve a one hour hot, ten minute air cool, exposure. The resultant temperature time curve for one cycle is also shown in Figure 1.

The vertical furnace rig is configured around a 7.5 cm diameter, ceramic tube, furnace suspended five feet above ground by a metal framework. Cycle time, piston and temperature controls were mounted in a standing cabinet. The cycle timing mechanism was wired to activate an 18 inch throw, pneumatic piston. An Inconel ram rod and copper cooling fin assembly attach directly to the piston throw rod. Ceramic specimen holders are supported by 5.0 mm diameter crosspins which slip through pre-drilled holes in the same rod. This furnace configuration vertically cycles specimens in and out of the calibrated hot zone. The specimen ascent and descent rate (and hence heating and cooling rate) can be controlled by adjustment of the piston pressure valve settings. The digital cycle timers used are adjustable and were set to the same frequency as previously described for the horizontal rig. The resultant thermal cycle curve for this configuration is shown in Figure 2.

Material selection for hot zone exposed components of these rigs was complicated by the extreme operating requirements of high temperature (1100°C), length of testing (hundreds of hours) and cyclic thermally induced stress. The useable life of specimen holders posed the greatest problem. After unacceptable performance experience with stainless steel materials, a relatively inexpensive, high temperature castable ceramic was identified and selected for use. Flexible molds were designed and developed to enable local fabrication. The end result produced a specimen holder capable of continuous cyclic heating for periods upwards of one-hundred cyclic hours before required change.

B. SPECIMEN PREPARATION

Two sets of specimens were prepared for experimental purposes. The first set of specimens was selected for the preliminary study of microstructure and surface topology changes during cyclic exposure. The second set was prepared to study the pre-aluminizing surface roughness effect on Al_2O_3 oxide scale adherence by measurement of gravimetric changes during cyclic oxidation. Both sets of coating specimens were prepared using a commercial nickel-base superalloy substrate, IN-738, with nominal composition outlined in Table I. This substrate was obtained in a cast and ground, pin configuration. Pin diameters varied from 0.6-0.8 cm and section lengths were generally on the order of 8.0-9.0 cm.

For the preliminary effects study, substrate pins as described were sent out for commerical platinum electroplating to a thickness of 7.0-8.0 µm. Upon return each pin was encapsulated in quartz tubing and vacuum sealed. They were then heat treated in accordance with one of the adopted standard pre-aluminizing heat treatments noted in Table II. These pins were subsequently sent for commercial aluminizing by one of two processes adopted as standards for this program. As previously discussed, one process, designated as LTHA is a method of inwardly diffusing aluminum onto a substrate and results in production of an inward type aluminide coating system. The second process, HTLA, incorporates aluminum through outward diffusion of nickel from the substrate. Similarly, this process results in the formation of an outward type aluminide coating system. Additional unplated substrate pins were aluminized by these processes to serve as a baseline for comparison. In conjunction with aluminizing, it was required that all specimens be given post aluminizing diffusion treatments of four hours at 1080°C (1975°F). After specimen return, they were cut to test lengths of approximately 2.5 cm. A commercial, brush-on, aluminum slurry repair coating was applied to uncoated surfaces to inhibit excessive localized oxidation attack. Specimens were then coded and categorized as outlined in Table III.

The preliminary run experimentation was conducted in two phases. Phase 0 was comprised of initially available specimens and served to evaluate both the apparatus and testing procedures. Phase 1 specimens were prepared for the specific purpose of this initial study. Table IV lists the Phase 0 and Phase 1 specimens of the preliminary study.

The gravimetric specimens, for weight change measurement, were coated using the same procedure. However, more careful and extensive preparation was required. The as-ground substrate pins were sectioned into approximately 3.0 cm lengths. These pins were then tumbled, in a mix of water and ceramic beads, for three hours to smooth sharp edges and thereby reduce variable coating edge effects. In order to support the samples, a hole, 0.88 mm in diameter, was spark machined (EDM) through one end of each specimen. The specimens were numbered, degreased, sonically cleaned and sent out for commercial platinum plating. The amount of platinum plating deposition was noted by weight change measurement. Specimens were then vacuum sealed and heat treated as previously described.

In order to study the effect of pre-aluminizing surface roughness, the polishing of half the heat treated specimens was required. This was accomplished through step buff polishing of specimens, through a series of abrasive finishes from ≈ 125 μm down to a 1 μm grit, using a hand polishing tool with assorted felt buffing tips and diamond past abrasive compounds.

Specimens were then cleaned, weighed and sent for one of the two previously discussed aluminizing processes. Again, unplated gravimetric substrate pins were included to provide a baseline for comparison. Specimens were inspected and weighed to determine the extent of aluminum incorporation into the coating system. Scanning electron (SEM) micrographs were taken at each step of this processing to document surface morphology changes during preparation. The data obtained on these specimens will be presented in a follow-on report containing the gravimetric experimental results and in a published technical note. The prepared gravimetric specimens are listed in Table V.

C. EXPERIMENTAL TESTING

Cyclic oxidation testing was initiated on the preliminary study specimens (Phase 0 and Phase 1) using the horizontal cyclic oxidation furnace rig. Specimens were loaded into the specimen boat and cycled under normal atmospheric conditions. Representative specimens were removed at approximately fifty cycle intervals (50 hr exposures) and physically examined for signs of oxide spallation and color change. Cross-sectional cuts and low magnification surface photomicrographs were used throughout testing to record coating microstructural and surface morphological change. Cyclic testing of these specimens was performed for up to two hundred and fifty cycles.

D. DATA ANALYSIS

Changes in coating system profiles were characterized using lineal roughness measurements taken from coating cross-section photomicrographs at 250x. Lineal roughness is defined as the ratio of the actual surface profile trace length to the normal surface projection length [Ref. 24].

Figure 3 graphically defines lineal surface roughness. A standard curvimeter (a commercially available instrument for curvelinear measurement) was used to measure the profile trace length. Lineal roughness measurement accuracy was estimated to be within ± 0.02 for each micrograph reading. When more than one micrograph was taken, lineal roughness measurements were averaged.

IV. RESULTS AND DISCUSSION

A. GENERAL OBSERVATIONS

The following observations, made during fabrication and specimen preparation, are peripheral in nature but of significance to follow-on studies and evaluation.

The cyclic oxidation rigs performed well throughout testing. It was noted that the horizontal rig, used for preliminary testing, has a steeper heating and cooling gradient than the vertical rig, see Figures 1 and 2. This is attributable in part to conductive contact of the specimen boat with the furnace tube and cooling mount support. In the vertical rig there is no such conductive contact and heating is convective and radiative in nature. Future experimentation might incorporate these differences in exploration of cyclic thermal gradient effects on coating behavior.

During pre-aluminizing heat treatment, delamination of platinum plating posed a problem with specimens diffused for a short time. This separation was likely the result of thermal gradient strains which arose when the hot encapsulated specimens were placed on room temperature conductive ceramic tiles to air cool. These strains were apparently enhanced by brittleness and coefficient of thermal expansion mismatch between these electrodeposited layers and the specimen substrate. These compatibility problems were the first indications on the sensitivity of these systems. This problem was aleviated, to a great extent, by a reduction of the cooling gradient through elevation of cooling specimens above the ceramic tile with small notched insulative pieces of porous ceramic.

In observation of the preliminary study specimens (Phase 0 and Phase I) initial attention was focused on coating microstructural change, surface oxide formation, oxide adherence and associated surface morphology changes, as previously mentioned. Microstructural change, in particular the observation of $\gamma'(Ni_3Al)$ formation within the predominantly $\beta(NiAl)$ coating layers was of prime interest. The underlying importance of γ' precipitation is that it signals aluminum level reduction within the coating system. Loss of aluminum in a coating system degrades the renovative capacity of protective Al_2O_3 scales. However, γ' formation is strongly dependent on the initial volume fraction of aluminum. Thicker coatings, with an inherently higher volume fraction of aluminum, are generally more sluggish in the formation of γ'. Localized loss of aluminum, at grain boundaries and through other short-circuit diffusion paths, with ensuing γ' formation seriously weakens both coating strength and protectivity. Therefore, the mode of γ'

formation, uniform or penetrating, is also important. Platinum is presumed to reduce Al loss and hence delay γ' formation by reducing Al_2O_3 spallation. However, it may also promote uniform aluminum loss through interference with diffusion path aluminum loss. Strang, et. al., notes this effect in some isothermally exposed platinum aluminide coatings for times up to 16,000 hrs [Ref. 3]. Significantly, the platinum aluminides tested displayed no major γ' formation or oxide spallation during this preliminary 250 hours of cycling. Further analysis is required in this area and is planned.

Figure 4 shows the initial as ground surface roughness of an IN-738 pin, representative of substrate specimens used. This figure also shows the structure of an as received platinum plated pin. As previously noted, Boone and Deb [Ref 21] have extensively reported on the surface morphology of platinum modified aluminide coatings and the typical cauliflower structure produced by electrodeposition, shown in Figure 4. In their work, a wide range of pre-aluminizing topologies were found to be generated through variation of diffusion temperatures and times. They also established the occurrence of two levels of surface roughening. A macro-roughening on the order of 20 μm was observed to occur, after aluminizing, with diffusion. This roughening, as depicted in Figures 4 and 5, appears strongly related to pre-aluminizing surface contours. Additionally, a micro-roughening effect, from Pt-substrate interaction, on the order of one micron in size is found superimposed on the aluminized and diffused macro-roughness. See Figure 5.

Initial observation of the previously mentioned roughness effects during cyclic thermal exposure revealed a previously undocumented surface macro-roughening occurrence with peak to peak distances upwards of 100 μm. This roughness displayed a characteristic 'rumpled' or kneaded surface texture appearance and will be referred to as rumpling throughout this thesis. This term has been used elsewhere to describe similar surface structures [Ref. 25].

B. SURFACE RUMPLING

Previous documentation of surface rumpling occurrence on aluminide or platinum modified aluminide diffusion coating systems has not been located. A similar surface effect has been noted to occur with certain overlay coating systems subjected to intermediate temperature dwell periods, during cyclic oxidation burner rig testing. Strangman reported this effect during a comprehensive study of thermal fatigue failure with overaly coatings [Ref. 6]. Strangman attributes the roughening he observed to thermal expansion mismatch strain, between the coating layer and the substrate, which produce coating cyclic-reversed creep deformation. Others have suggested that the rumpling observed in some tests may be the result of subcoating substrate melting.

Figure 6 presents a low magnification view of four program standard platinum aluminide coatings prior to cyclic testing. In Figure 7, these same four coatings are shown after 200 hours of cyclic testing. As can be seen, all exposed samples display a measure of surface rumpling. Surface rumpling was also observed to occur, to a measurable extent, on the cycled baseline (unmodified aluminide) coatings, see Figure 8.

In addition to the limited rumpling shown, an inspection of the micrographs reveals patches of shiny exposed metal, indicative of oxide scale spallation. Spallation, as previously noted, did not occur on any of the platinum modified aluminide coated specimens during this initial testing and is further confirmation of other reports on the platinum effect in promoting oxide adherence.

To gain further insight into the cause of rumpling and to explore substrate melting effects, specimen types shown to exhibit rumpling were both isothermally tested and exposed to incremental increases in temperature. Figure 9 shows that surface roughening can occur with substrate melting, but on a much grosser scale and at significantly higher temperature (1200°C) than that of the surface rumpling under investigation. The isothermally exposed specimens, as anticipated, did not exhibit rumpling, also shown in Figure 9. Clearly, surface rumpling was found to be dependent on thermal cycling. This observation strongly supports Strangman's hypothesis and suggests thermal expansion mismatch induced cyclic reversed creep plays a major role in the rumpling of diffusion aluminides and platinum modified coatings.

Modeling of this surface plastic instability effect (rumpling) in diffusion coatings is extremely complex. Diffusion coatings are dynamic in nature and inhomogeneous in structure and composition. Thermo-mechanical fatigue testing of similar platinum modified coating systems was conducted, for NASA-Lewis Research Center, in the search of promising coating systems for directionally solidified cast eutectics [Ref. 26]. Some substrate and average coating constituent phase thermal expansion data are available, see References [27] and [28]. However, this data is only of limited value because the coating system is dynamic and occurring constituent phases cannot be considered continuous. Numerical modeling of rumpling is, therefore, not presently considered feasible. Only thermo-mechanical testing and conceptual modeling are presently possible.

Figures 10 and 11 phenomenologically portray the two basic factors; thermal expansion mismatch and thermal gradients, which are believed to govern the strains leading to rumpling. The proposed effect of thermal expansion mismatch during cycling, Figure 10, is shown for two possible cases: α (coating) > α (substrate) and α (coating) < α (substrate). In each case the resultant stress in the coating is shown for portions of thermal cycling, neglecting edge effects and under equilibrium heating and cooling conditions. Figure 11 depicts the expected effect of thermal gradients on an uncoated pin during cyclic heating and cooling. The thermal gradient effect is greatest upon initial heating and cooling exposure of test specimens. These gradient stresses are reduced as uniform temperatures are attained throughout the specimen mass. Cyclic stress reversal is apparent in both the thermal expansion and gradient stress producing mechanisms. Specimen geometry and heating and cooling rates are also considered important factors in the actual magnitude of the produced strains.

Vogel's data on ductile to brittle transition temperatures (DBTT) and ductilities of platinum-aluminide coatings clearly shows these coating systems to be in a state of compression at room temperature, [Ref. 14]. This observation suggests that the diffusion coating systems being tested have a lower coefficient of thermal expansion than the substrate, IN-738 ($\alpha \approx 15.9 \times 10^{-6}/^{\circ}C$, $20^{\circ}C$ - $982^{\circ}C$), [Ref. 30].

Variation in rumpling magnitude was apparent among the different coatings tested. This variation appears related to the ability of the coatings to plastically deform under the stress magnitudes encountered. These stress magnitudes are directly related to high temperature physical properties such as ductility, yield strength, and thermal expansion coefficient which, in turn, are affected by aluminum and platinum concentrations in the coatings. Therefore, variations in coating constitution would be expected to explain in part these observations.

C. ROUGHNESS CORRELATION

The lineal roughness data obtained is listed in Table VI. This data, presented graphically as a function of cyclic exposure is shown in Figures 12, 13, and 14. These figures present a wide variation of roughening patterns. It is clear that all tested specimens increased their surface roughness with increased thermal cyclic exposure.

An apparent roughness plateau is reached by baseline specimens at 100-150 test cycles. This plateau occurs at approximately the same number of cycles as observed for the onset of the previously addressed oxide scale spallation. Douglas in his article on the exfoliation and mechanical behavior of scales, addresses the stress related aspects of high temperature oxide film growth [Ref. 30]. In particular, he notes that if an oxide is stronger than the substrate on which it grows, thermal stress and growth stress can be relieved by plastic flow in the substrate.

The role of oxide induced stress in rumpling is not known but it is suggested as a possible factor. If so, oxide spallation would relieve this stress and reduce further surface ratcheting.

The platinum modified coatings increased in roughness over a much broader cyclic exposure range, with no associated oxide spallation. This data is a strong verification of the beneficial effect of platinum in promoting oxide adherence, irrespective of pre-aluminizing heat treatment parameters or coating structure, at least in the early stages of testing. While it is probable that oxide film formation plays some role in high temperature coating plastic instability, at this point, it is difficult to isolate and quantify this effect.

Further analysis of roughness data for the platinum modified aluminides, with respect to initial coating thickness is presented in Figure 15. Although this analysis includes variations in structural types, a strong trend indicates that initially thinner coatings show greater tendency to rumple than the thicker coatings. Figure 16 shows a cross-section of two similarly treated and developed coating systems of type 4IIB, one initially thicker than the other. Both were thermally cycled 150 hours. The thinner coating clearly experienced a higher degree of rumpling.

Discernment of differences in rumpling between inward (LTHA) and outward (HTLA) coating systems was not readily established. Only one set of coatings, shown in Figure 16, were of close enough initial thickness to allow a comparison to be made. From these two specimens, it was noted that the outward, lower Al content and lower strength coating, rumpled more. However, the structural differences between the two make any conclusions difficult at this point.

As previously noted, coating thickness, structure and composition cannot be varied independently. In general, thicker platinum aluminide coatings have higher aluminum content, greater volume fraction of $PtAl_2$ and a higher concentration of platinum in the surface layer. All these factors seem to increase the strength of the coating and its ability to resist plastic deformation.

D. COATING SYSTEM PROTECTIVITY

The formation of large voids or blisters in the coating layer and their rupture was found to occur. This voiding was only observed to occur with initially thin platinum aluminides, exhibiting a high degree of surface plastic instability, see Figures 17 and 19. This effect on platinum aluminides has not been reported previously in the literature. These voids appear to form under tensile stress and rupture under compressive stress during thermal cycle loading. The significance of this voiding has not been established. However, voiding displays many undesirable characteristics with respect to protectivity, increased surface area, localized thinning and the creation of stress raisers.

In general, thicker coatings would be expected to afford increasing protectivity, discounting thin section or critical tolerance considerations. This presumption is based on their tendency to incorporate a much greater elemental volume of, the protective oxide forming element, aluminum. However, in testing, thicker platinum modified coatings, with demonstrable lower tendency to rumple, exhibit much greater susceptibility to cracking. Figures 18 and 19 are a comparison between a thin rumpled coating with voiding and a thick coating with cracking. This cracking might be explained in part from Vogel's data [Ref. 14], which suggests thick coatings, with higher aluminum levels, would have a DBTT above 800°C and might be expected to behave in a brittle manner over a larger portion of its thermal operation range. A closer review of crack morphology shows cracking appears to originate near the coating interdiffusion zone and propagate outward. Figure 20 clearly demonstrates both a cyclic crack propagation directionality change and an increasing amplitude of propagation in the outward direction. This cracking is not typical of, a single event, brittle failure, propagating from the surface through the coating and sometimes reinitiating in the substrate, as observed by Vogel, also shown in Figure 20. Instead, this cracking exhibits a multi-cycle (fatigue) propagation which can be attributed to thermal cyclic exposure and resulting strains.

The significance of the previous observation lies in the suggestion that an optimum coating thickness design criteria for platinum aluminides may exist between thin coatings (with excessive plastic deformation) and thick coatings (with associated thermal cracking). In addition, the use of surface roughness measurement data from cyclicly exposed specimens could prove useful in future gaging of platinum aluminide protectivity.

Like many systems there are often compromises and regions of property optimization. Coatings are no different. Since protection is provided through formation of adherent Al_2O_3, increasing Al content and volume (coating thickness) should result in a longer time span of protection.

However, in the Pt-Al system, increasing aluminum tends to increase the thermal expansion mismatch induced strains but with a concommittant increase in coating strength. This increased strength apparently serves to reduce the incidence of rumpling, at least under the thermal cycles explored in this investigation. As found in other studies, this results in an increase in DBTT and, hence, a decrease in the ability to plastically relieve the higher stress build-up during cycling, as a result of the increased thermal expansion mismatch. Higher room temperature residual compressive stresses are also present which can result in handling problems. At some point these stresses are relieved by crack initiation and cyclic propagation, outward down the stress gradient in the coating.

On the other hand, decreasing coating aluminum level and thickness results in a lower strength, more ductile coating with the ability to relieve these strains plastically over a wider temperature range. However, excessive plastic deformation which occurs from the combination of high strains and low yield strength can produce other problems, i.e., rumpling. The ability to live with lower aluminum levels is possible in these systems because of the strong oxide adherence effect imparted by platinum. A properly designed platinum modified aluminide coating will therefore require a judicious compromise between these factors.

V. CONCLUSIONS AND RECOMMENDATIONS

The results and discussion support the following conclusions:

1) Plastic instability in the form of surface rumpling can occur in aluminide and platinum aluminide diffusion coating systems subjected to high temperature cyclic exposure.

2) Rumpling is postulated to be a function of thermally induced differential strains and thermal expansion mismatch strains, which would be affected by coating strength and coating thickness. The effect of substrate and initial surface micro-roughness on rumpling has not been established.

3) Rumpling is not attributable to sub-coating (substrate) melting.

4) Adherent aluminum oxide scale contribution to rumpling is not known. However, the occurrence of oxide scale spallation on aluminide coated specimens corresponded to a plateau in surface roughening. Oxide scale spallation did not occur with the platinum modified specimens and rumpling was apparent on a much grander scale.

5) The relation of rumpling to coating system mechanical and protectivity performance is not known. Rumpling can, however, lead to local thinning, increased exposed coating surface area, coating system voids and creation of stress raisers. These contributions of rumpling are considered detrimental to protectivity and mechanical properties in general.

6) Thicker coatings showed a lower propensity to rumple but a greater occurrence of trans-coating cyclic cracking. This suggests an optimum coating thickness design criteria.

7) The complex structural interaction and combination of factors associated with rumpling makes quantitative analysis difficult to perform and interpret.

The following research areas are proposed for further study:

1) The role of oxide adherence in platinum modified diffusion coatings and their effect on surface plastic instability.

2) The effect of thermal cycle rates and coating thickness on surface rumpling of platinum aluminide coatings.

3) The use of rumpling magnitude as a coating strength and compatibility design criteria.

APPENDIX A: TABLES I-VI

TABLE I

IN-738 NOMINAL COMPOSITION (WEIGHT PERCENT)

Ni	Cr	Co	Mo	W	Ti	Al
bal.	16.0	8.5	1.75	2.6	3.4	3.4

Nb	Ta	C	B	Zr	Fe
0.9	1.75	0.17	0.01	0.10	0.5 max

Mn	Si
0.2 max	0.3 max

TABLE II

NPS STANDARD PRE-ALUMINIZING HEAT TREATMENTS*

CODE	TREATMENT
1	1/2 hour @ 870°C (1600°F)
2	2 hours @ 980°C (1800°F)
3	3 hours @ 1040°C (1900°F)
4	4 hours @ 1080°C (1975°F)

* All heat treatments were followed by static air cooling to room temperature

TABLE III

CODING SYSTEM FOR PLATINUM ALUMINIDE AND ALUMINIDE SPECIMENS

R 1 II A

- A — Aluminizing Process (A - Inward, B - Outward)
- II — Coating Modification (II - Platinum Modified; BL - Baseline)
- 1 — Heat Treatment (see Table II)
- R — Pre-aluminizing Surface Condition (S - Smooth, R - Rough)

TABLE IV

PRELIMINARY STUDY SPECIMEN LISTING

PHASE 0		PHASE 1	
Specimen No.	Code	Specimen No.	Code
7	1IIA	1	1IIA
8	2IIA	2	2IIA
10	4IIA	3	3IIA
12	2IIB	4	4IIA
13	4IIB	7	3IIB
16	BLA	8	4IIB
17	BLB	9	1IIA
18	BLA	10	2IIA
19	BLB	11	3IIA
		12	4II1
		15	3IIB
		16	4IIB

TABLE V

GRAVIMETRIC STUDY SPECIMEN LISTING

Specimen No.	Code	Specimen No.	Code
1	R1IIA	10	S3IIA
2	S1IIA	11	R3IIB
3	R1IIB	12	S3IIB
4	S1IIB	13	R4IIA
5	R2IIA	14	S411A
6	S2IIA	15	R4IIB
7	R2IIB	16	S4IIB
8	S2IIB	17	BLA
9	R3IIA	18	BLB

TABLE VI

CYCLIC EXPOSURE SURFACE LINEAL ROUGHNESS DATA

PHASE 0

Specimen No.	Coating Code	Lineal Roughness 0	50	100	150	200	250 [Test Cycles]
7	1IIA	1.01	1.03	---	1.20	1.17	1.20
8	2IIA	---	1.02	---	---	1.12	1.08
10	4IIA	1.01	1.02	---	1.10	1.12	1.14
13	4IIB	1.03	1.12	---	1.25	1.21	1.22
16	BLA	1.01	---	1.08	1.11	1.09	---
17	BLB	1.02	---	1.09	1.08	1.08	---

PHASE 1

Specimen No.	Coating Code	Lineal Roughness 0	50	100	150	200 [Test Cycles]
1	1IIA	---	---	1.04	1.09	1.15
2	2IIA	1.05	---	---	1.10	1.19
3	3IIA	1.02	---	---	1.15	1.17
4	4IIA	---	---	1.06	1.08	1.12
7	3IIB	1.02	---	---	1.08	1.12
8	4IIB	---	1.04	---	1.03	1.04

APPENDIX B: FIGURES 1-20

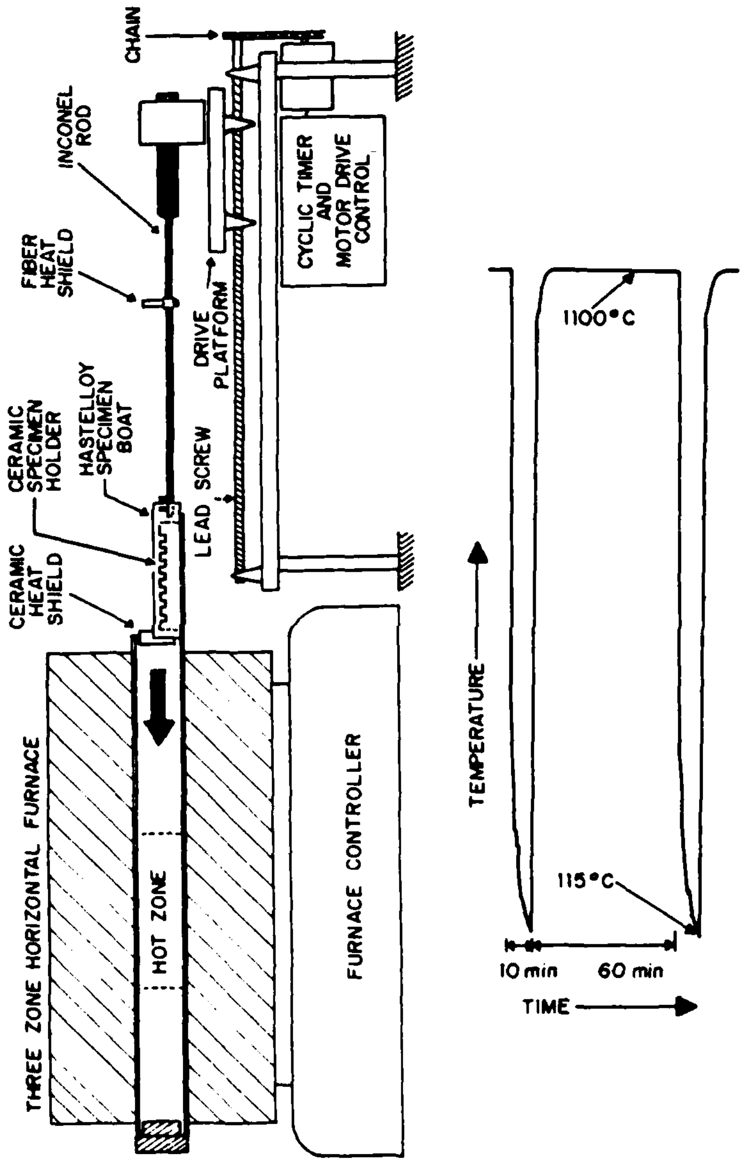

Figure 1. Horizontal Cyclic Oxidation Rig and Associated Thermal Cycle

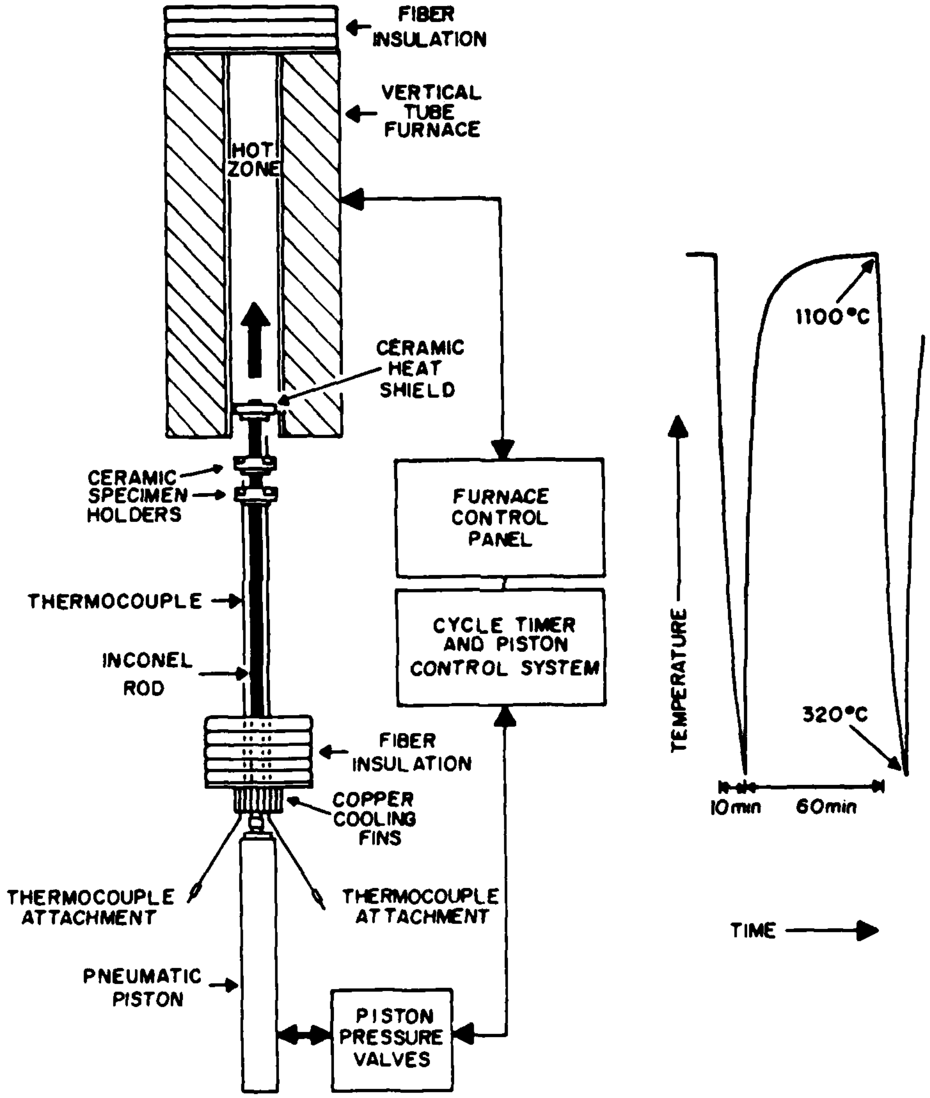

Figure 2. Vertical Cyclic Oxidation Furnace Rig and Associated Thermal Cycle

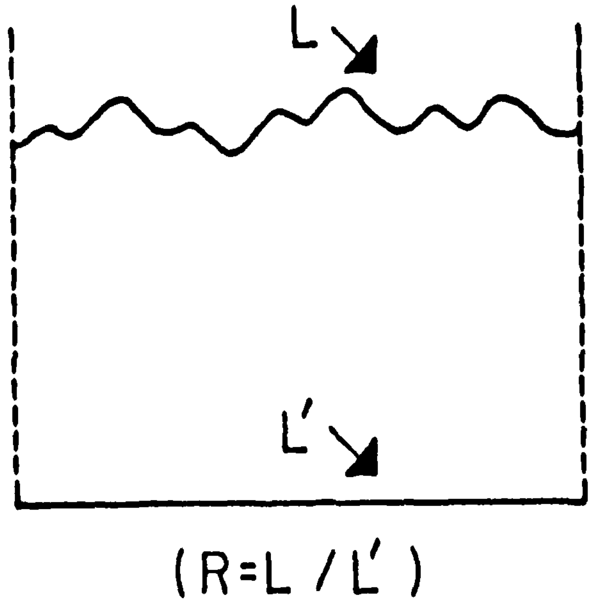

Figure 3. Lineal Surface Roughness Measurement

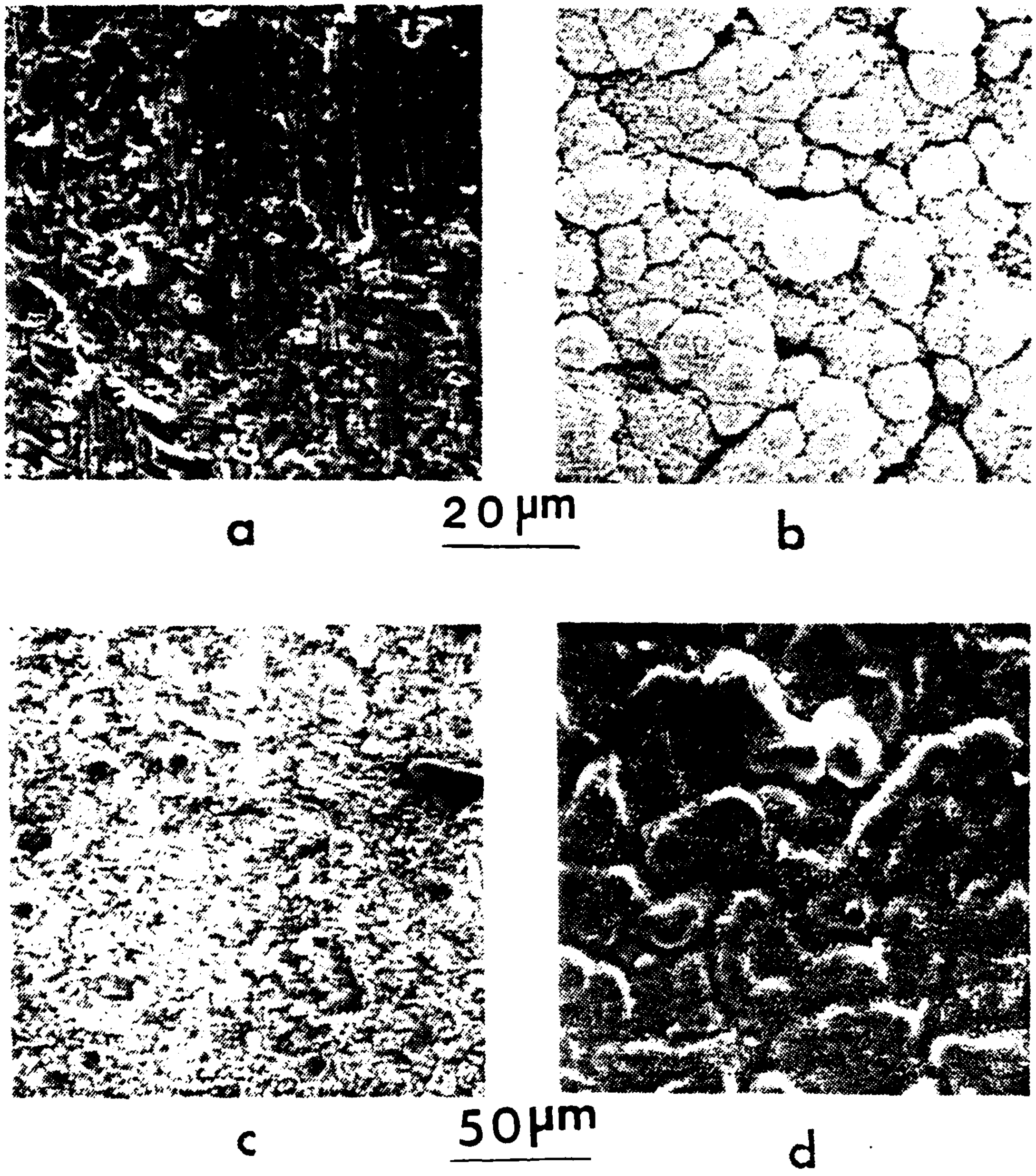

Figure 4. Typical Processing Stage Surface Morphologies: a) IN-738 Ground Pin Surface (1Kx); b) IN-738 with 7.0-8.0 μm Pt Plating (1Kx); c) As-Aluminized, 3IIB Coating (425x); d) As-Cycled 25 hrs, 3IIB Coating (425x)

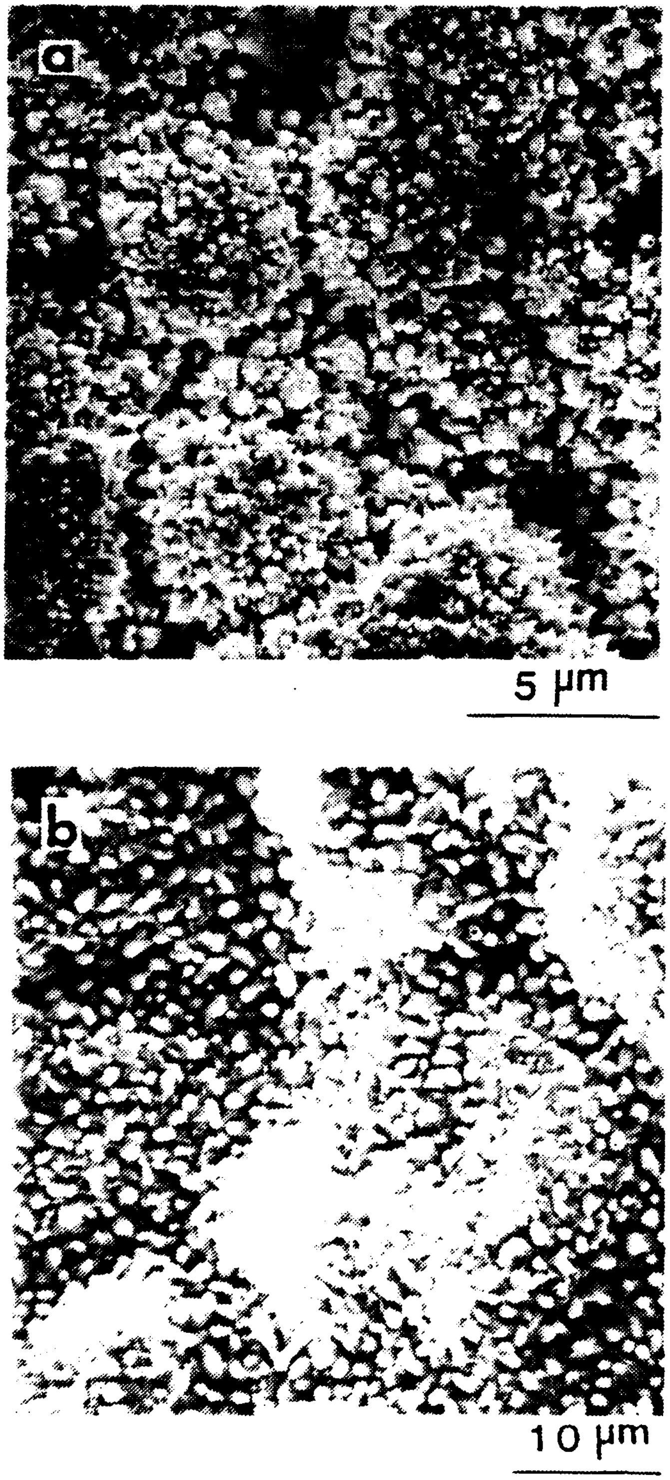

Figure 5. Micro and Macro Roughness Variations:
a) IN-738 with 7.0-8.0 μm Pt Plating (5Kx);
b) As-Cycled 25 hrs, 3IIB Coating (2Kx)

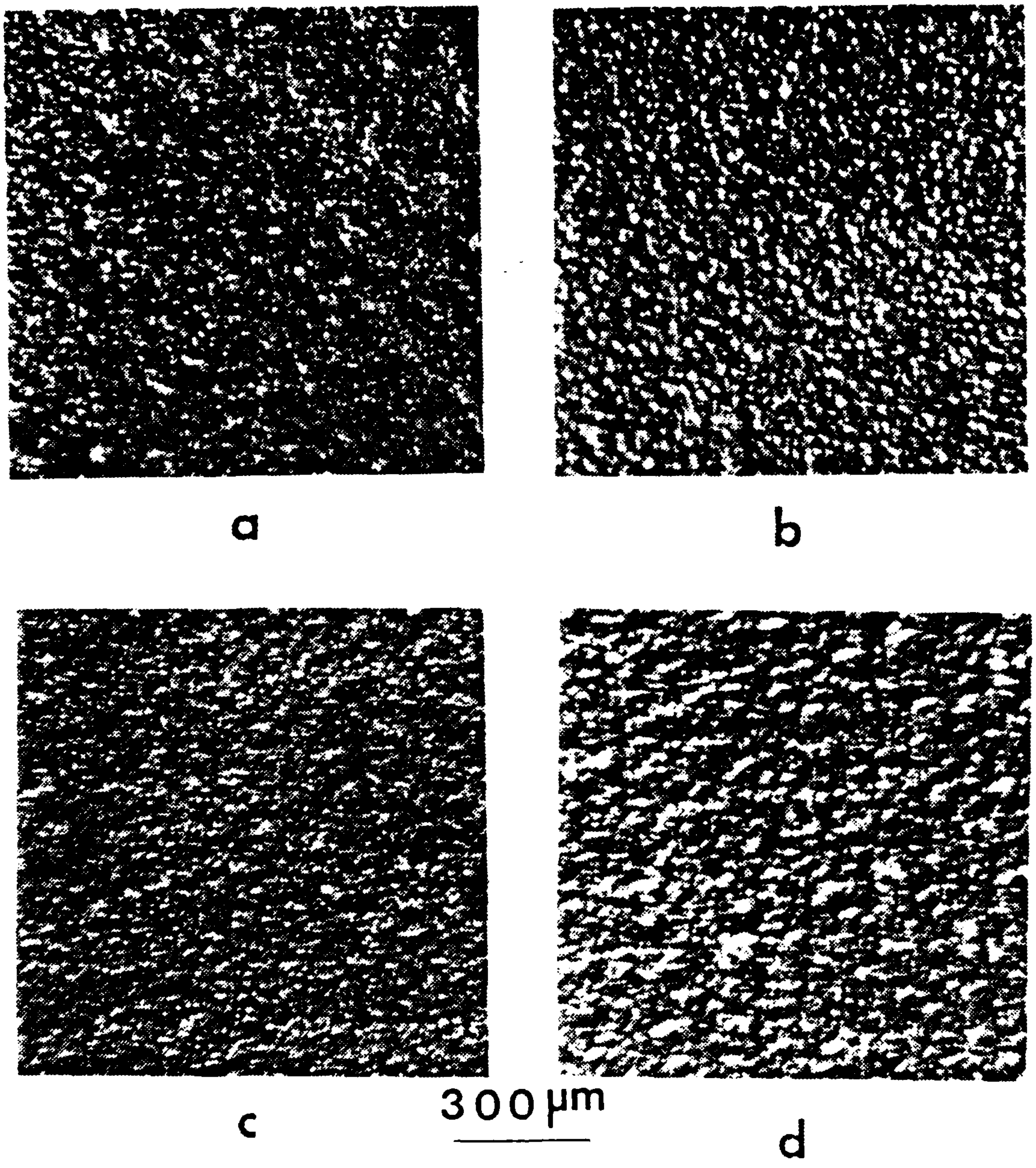

Figure 6. As-Formed Platinum Aluminide Specimen Surfaces (64x): a) 3IIA; b) 3IIB; c) 4IIA; d) 4IIB

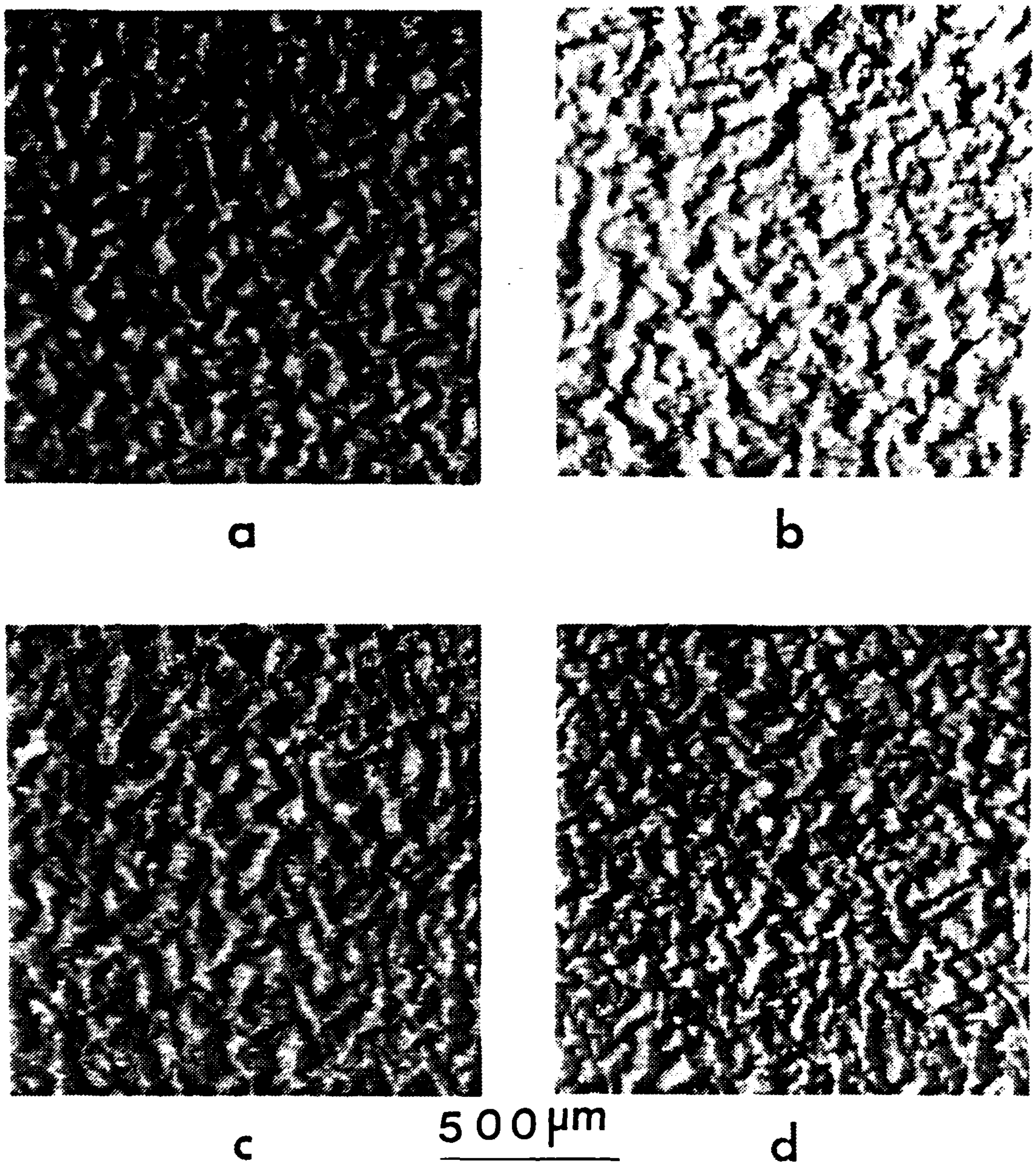

Figure 7. Rumpled Platinum Aluminide Specimen Surfaces, Cycled 200 hrs (52x): a) 3IIA, b) 3IIB; c) 4IIA; d) 4IIB

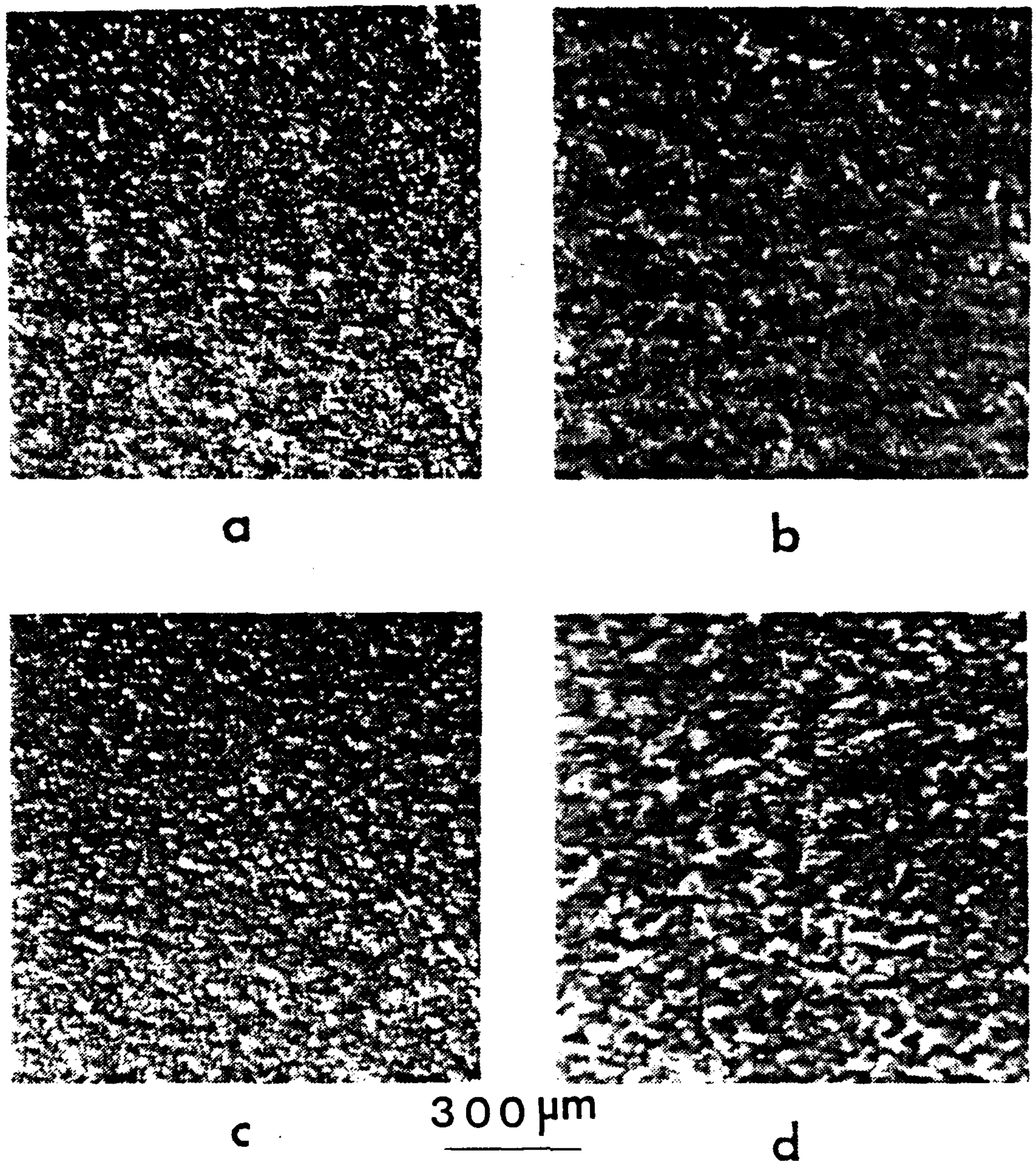

Figure 8. Aluminide Baseline Specimen Surfaces (64x):
a) BLA, As-Formed; b) Rumpled BLA, Cycled 110 hrs;
c) BLB, As-Formed; d) Rumpled BLB, Cycled 110 hrs

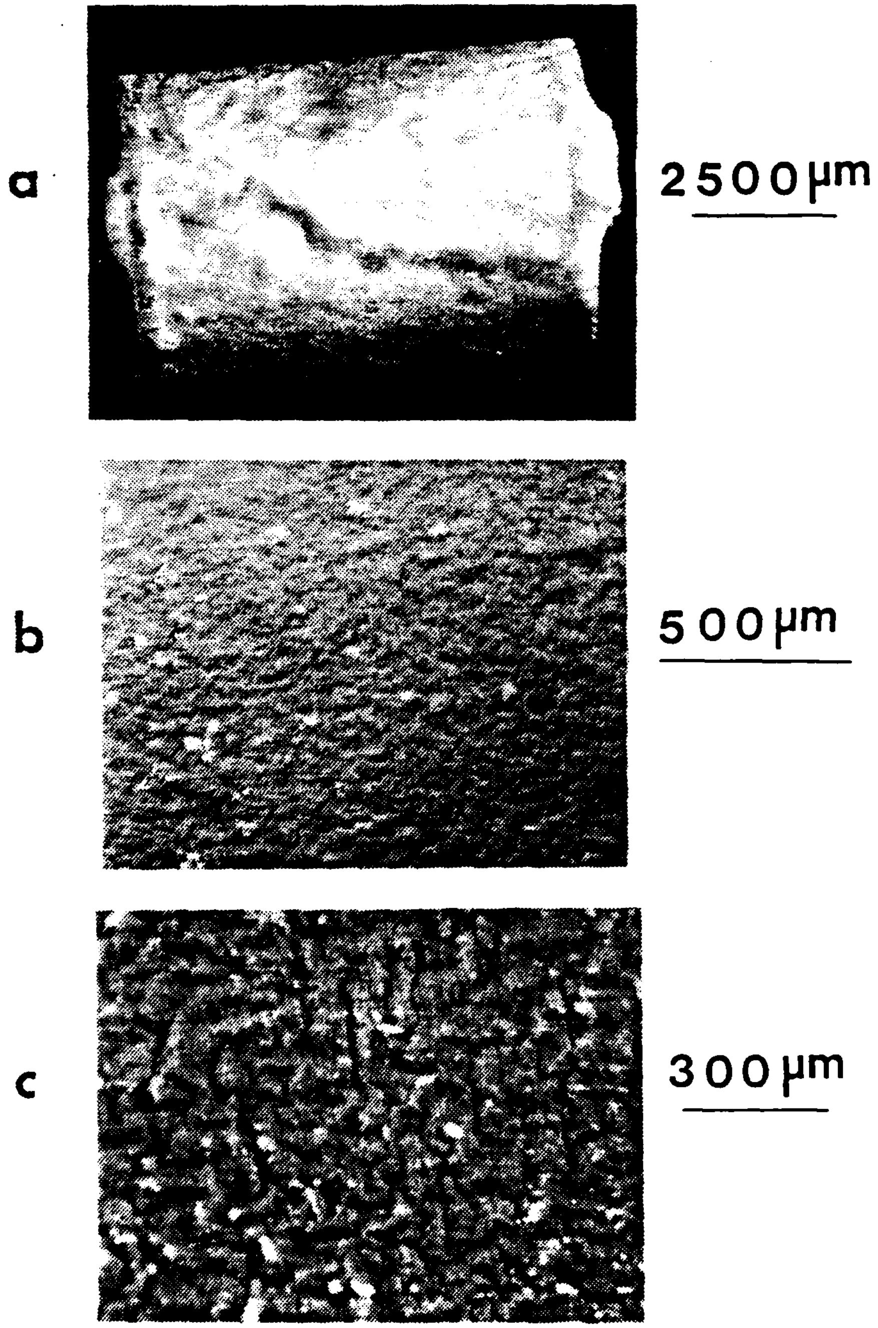

Figure 9. Surface Effects of Platinum Aluminide Specimen 2IIA: a) Roughening Due to Melting at $T > 1200^\circ C$ for 15 min (8x); b) Isothermally Heated for 145 hrs (52x); c) Rumpled Surface, Cycled 110 hrs (64x)

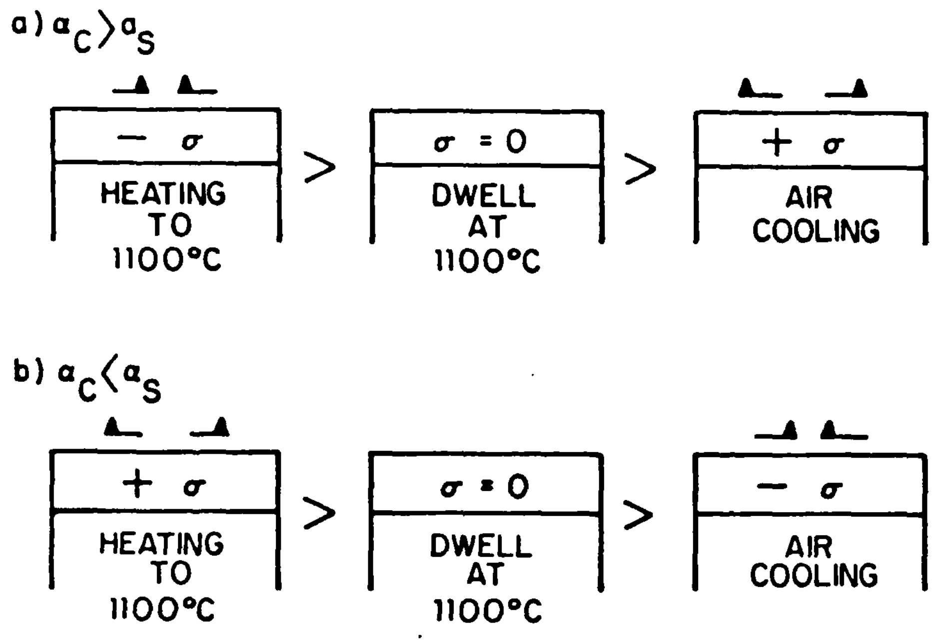

Figure 10. The Effect of Coating-Substrate Thermal Expansion Mismatch During Equilibrium Heating and Cooling for: a) α (Coating) > α (Substrate) and b) α (Coating) < α (Substrate)

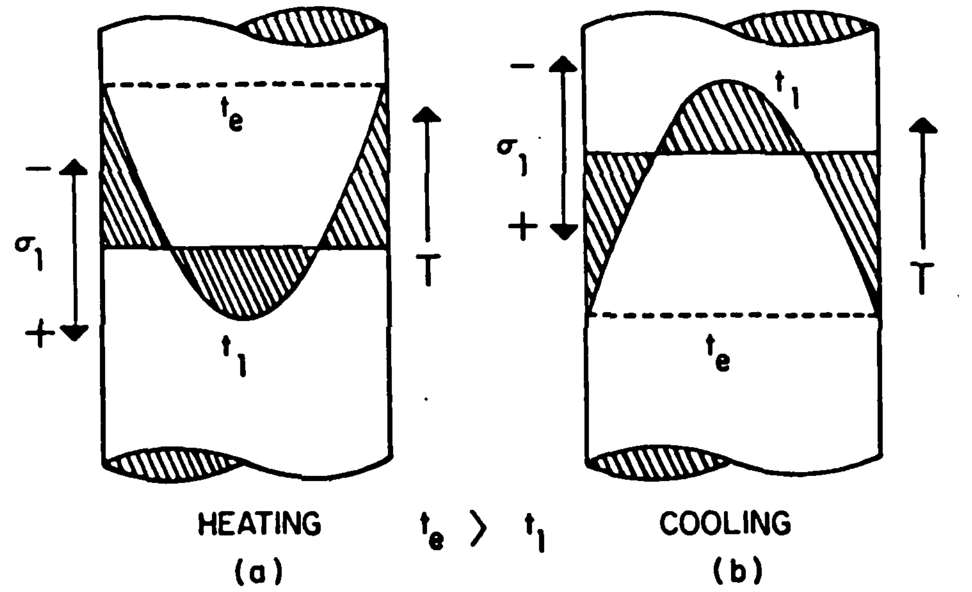

Figure 11. The Effect of Temperature Differential on an Un-coated Pin During:
a) Heating and b) Cooling

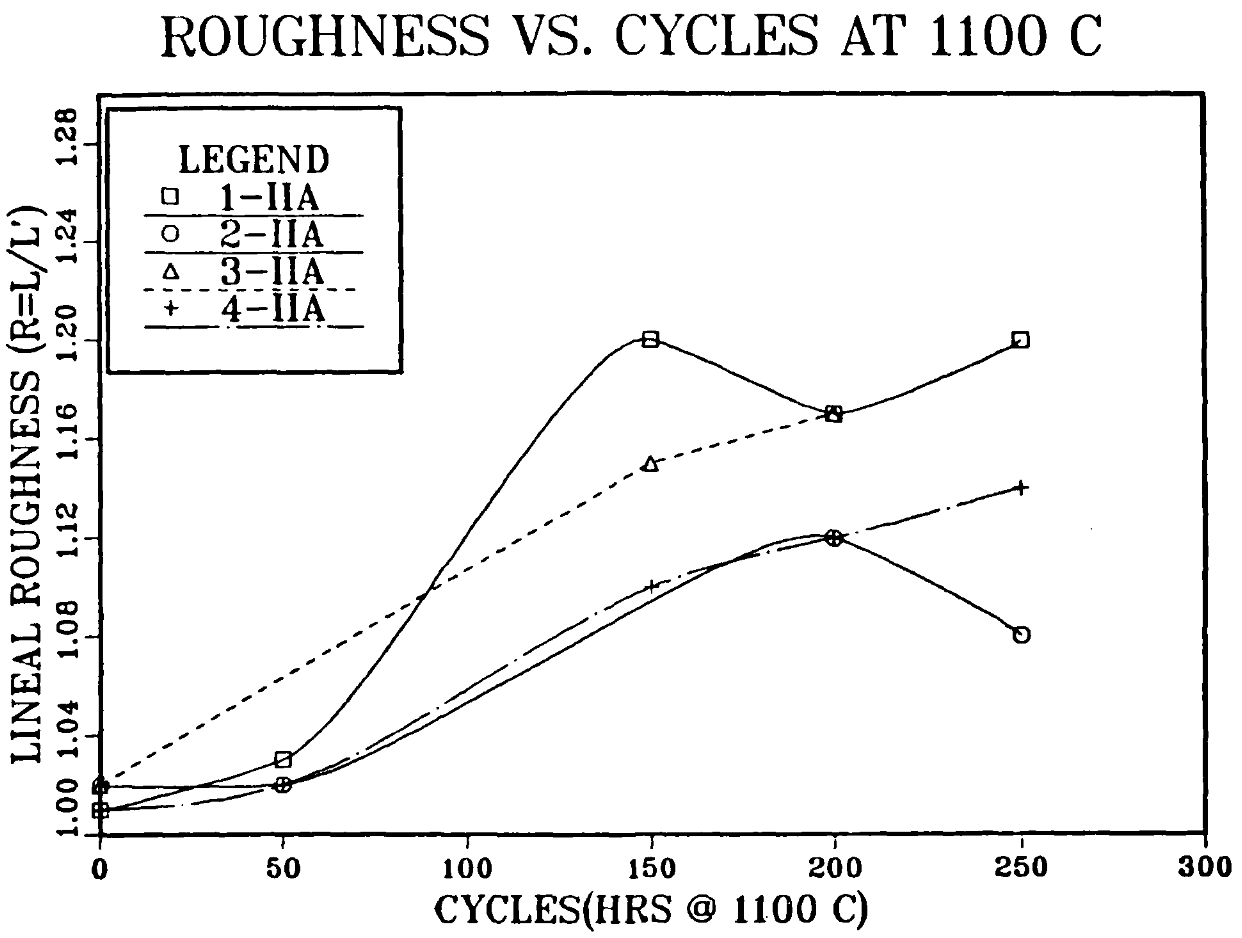

Figure 12. Plot of Lineal Roughness versus Cyclic Exposure for Inward Platinum Aluminide Coating Specimens

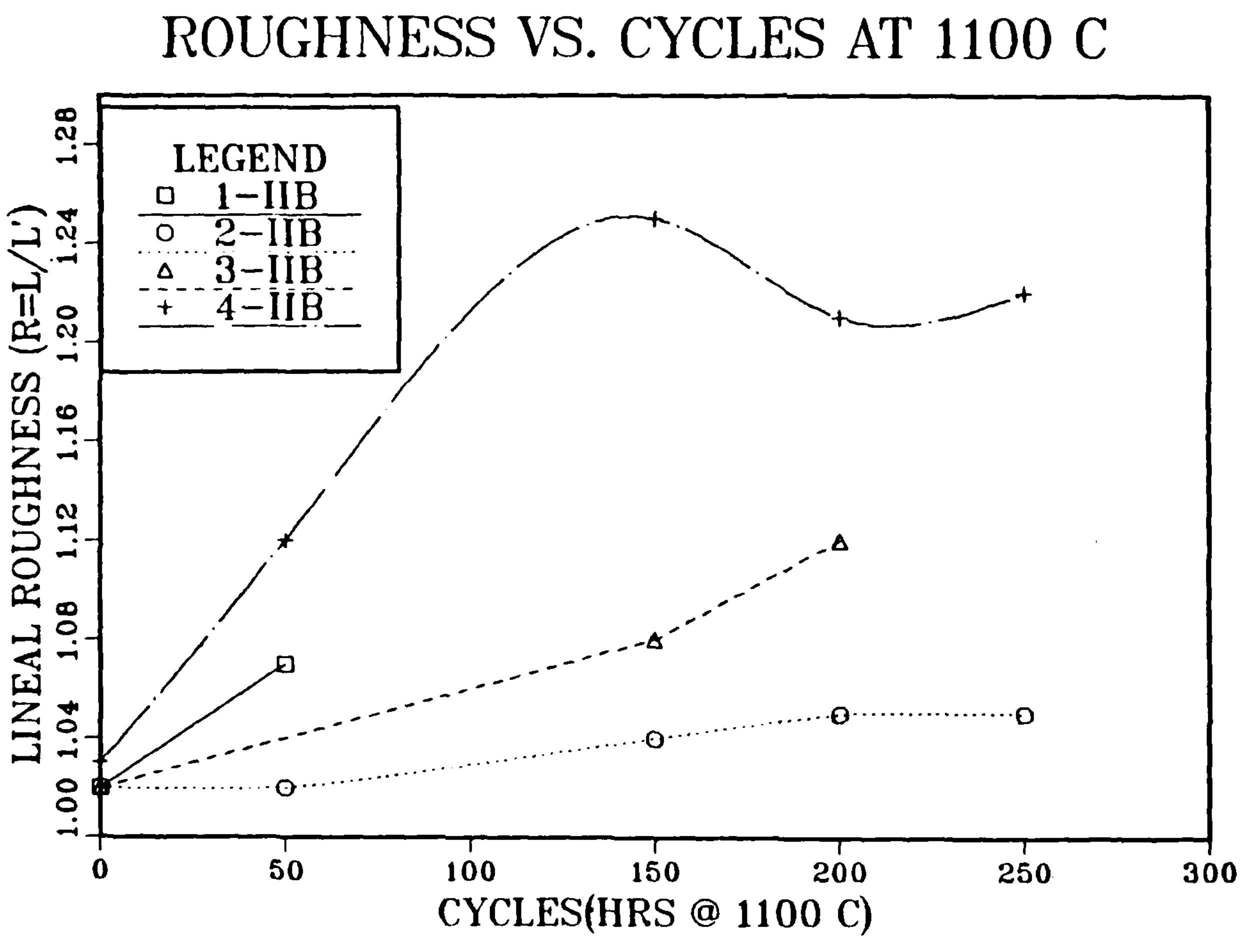

Figure 13. Plot of Lineal Roughness versus Cyclic Exposure for Outward Platinum Aluminide Coating Specimens

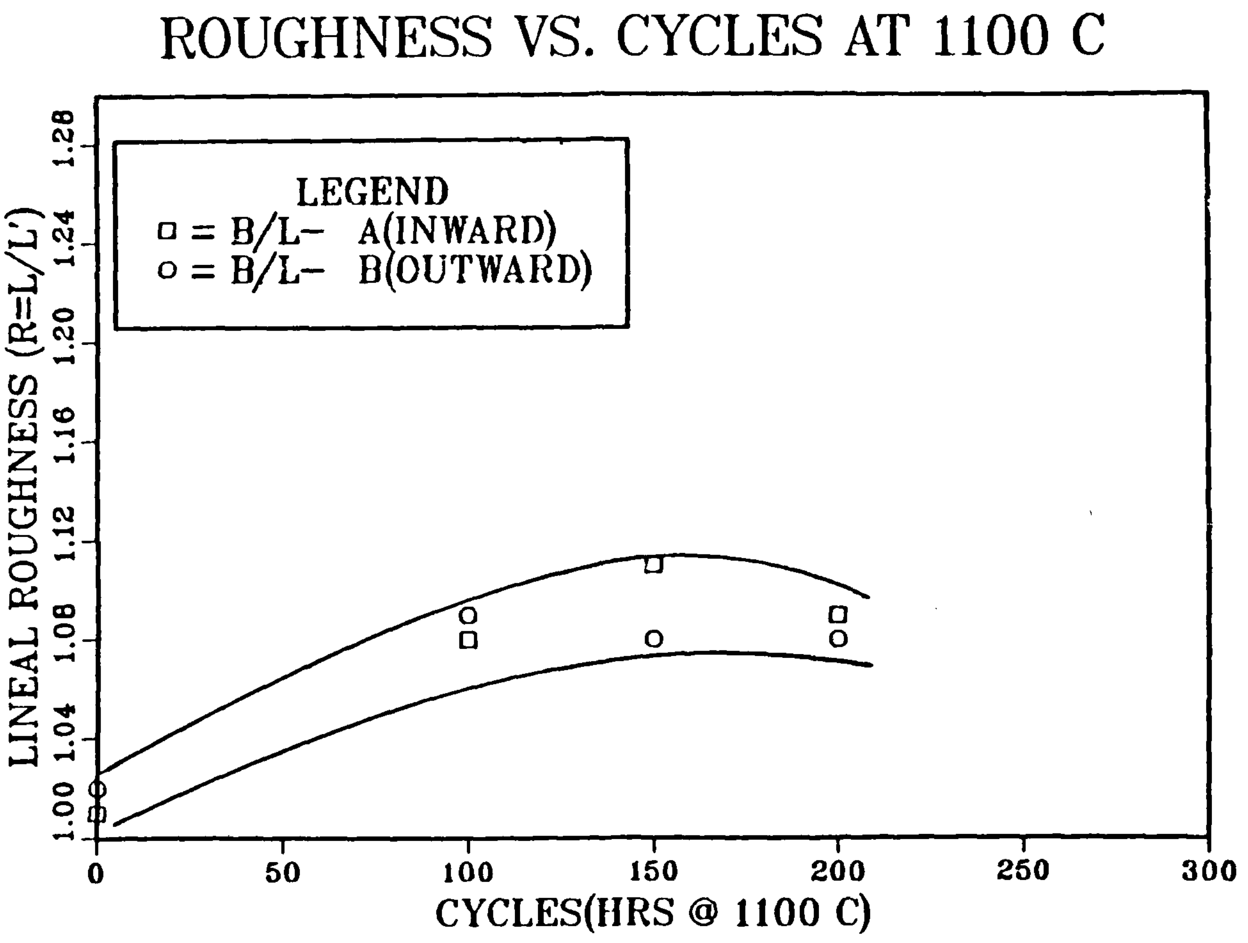

Figure 14. Plot of Roughness versus Cyclic Exposure for Inward and Outward Baseline Specimens

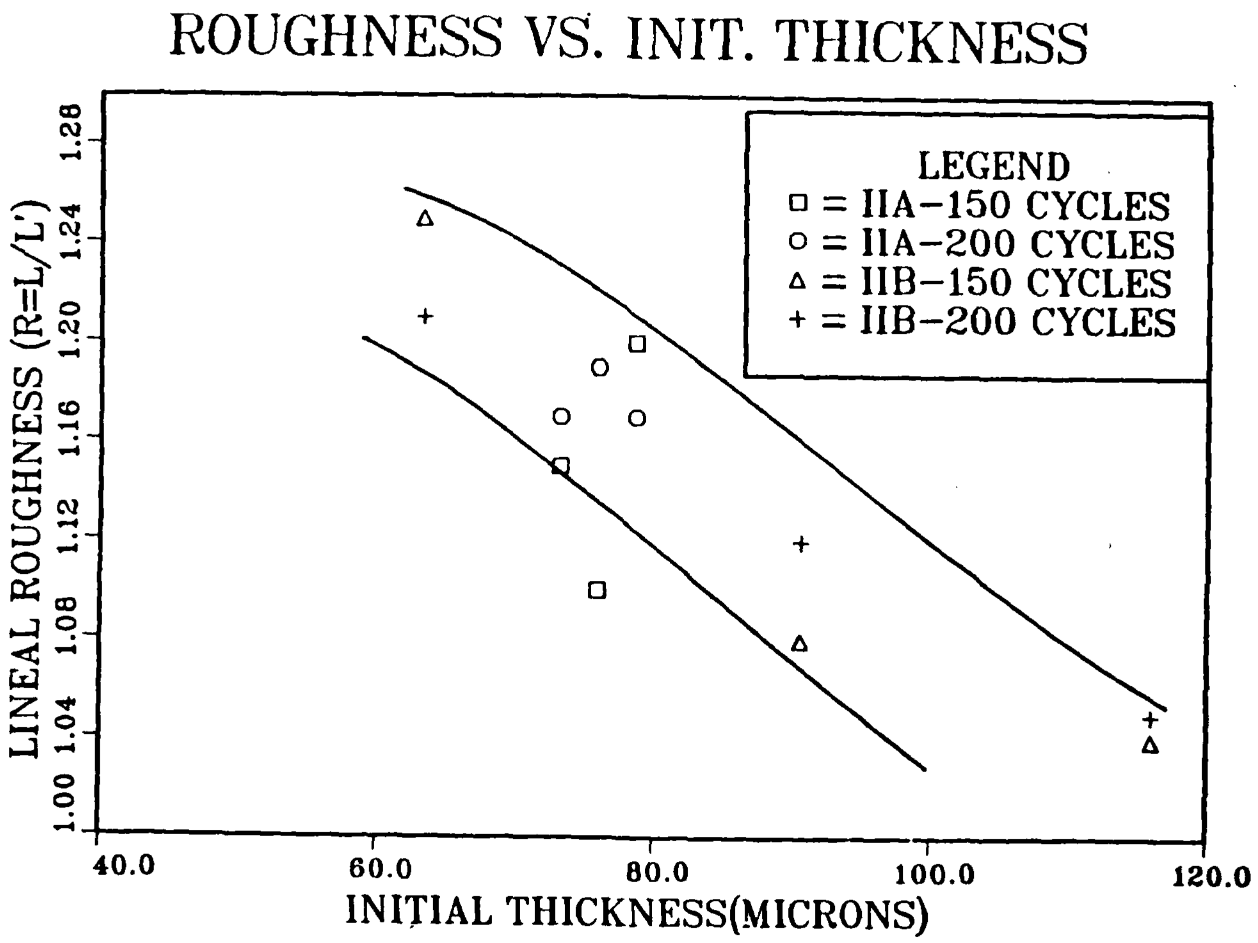

Figure 15. Plot of Lineal Roughness versus Initial Platinum Aluminide Coating Thickness

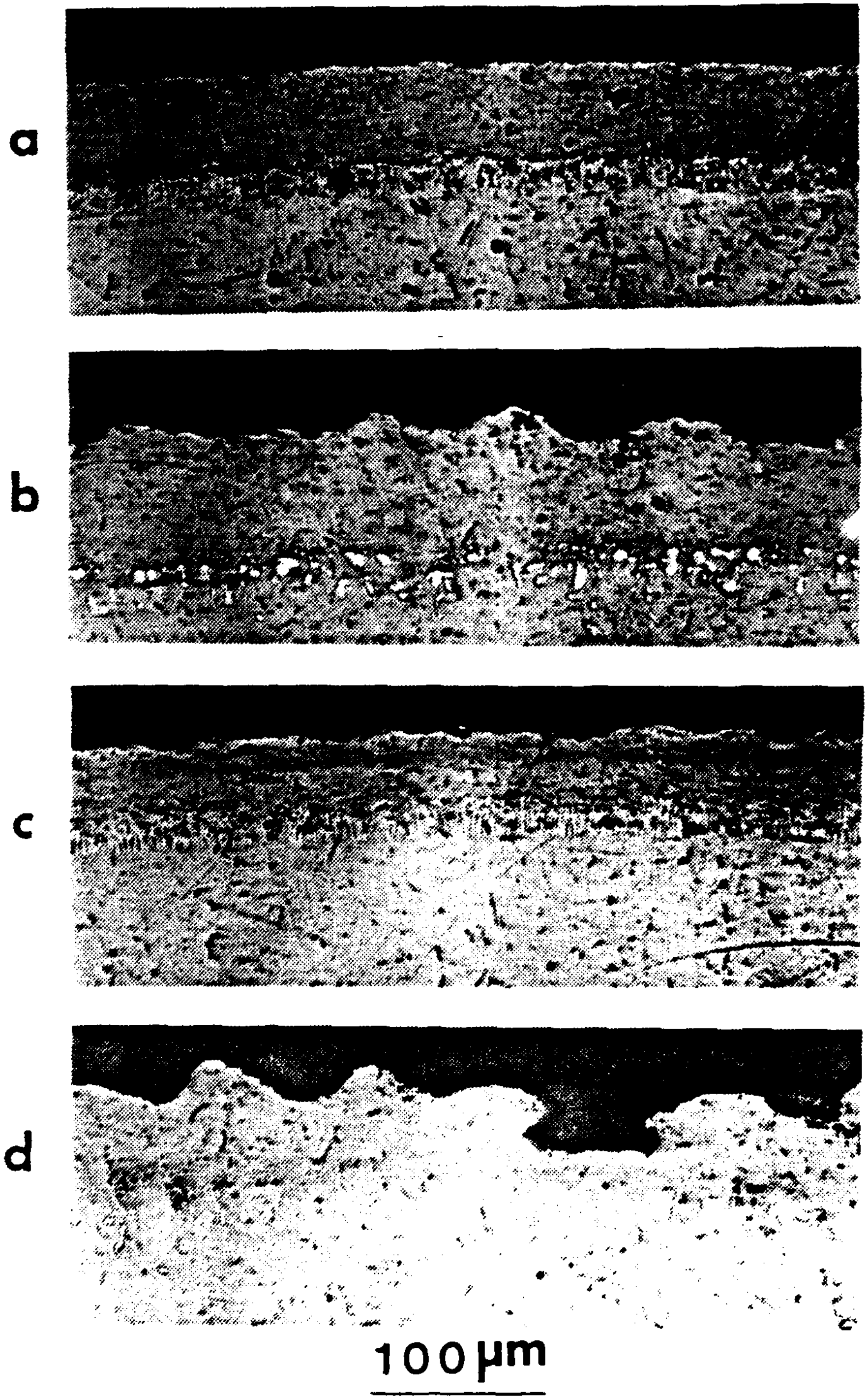

Figure 16. Rumpling Comparison Between Inward and Outward Platinum Aluminide Coatings (x250): a) 4IIA-Un-cycled; b) 4IIA-Cycled 150 hrs; c) 4IIB-Un-cycled; d) 4IIB-Cycled 150 hrs

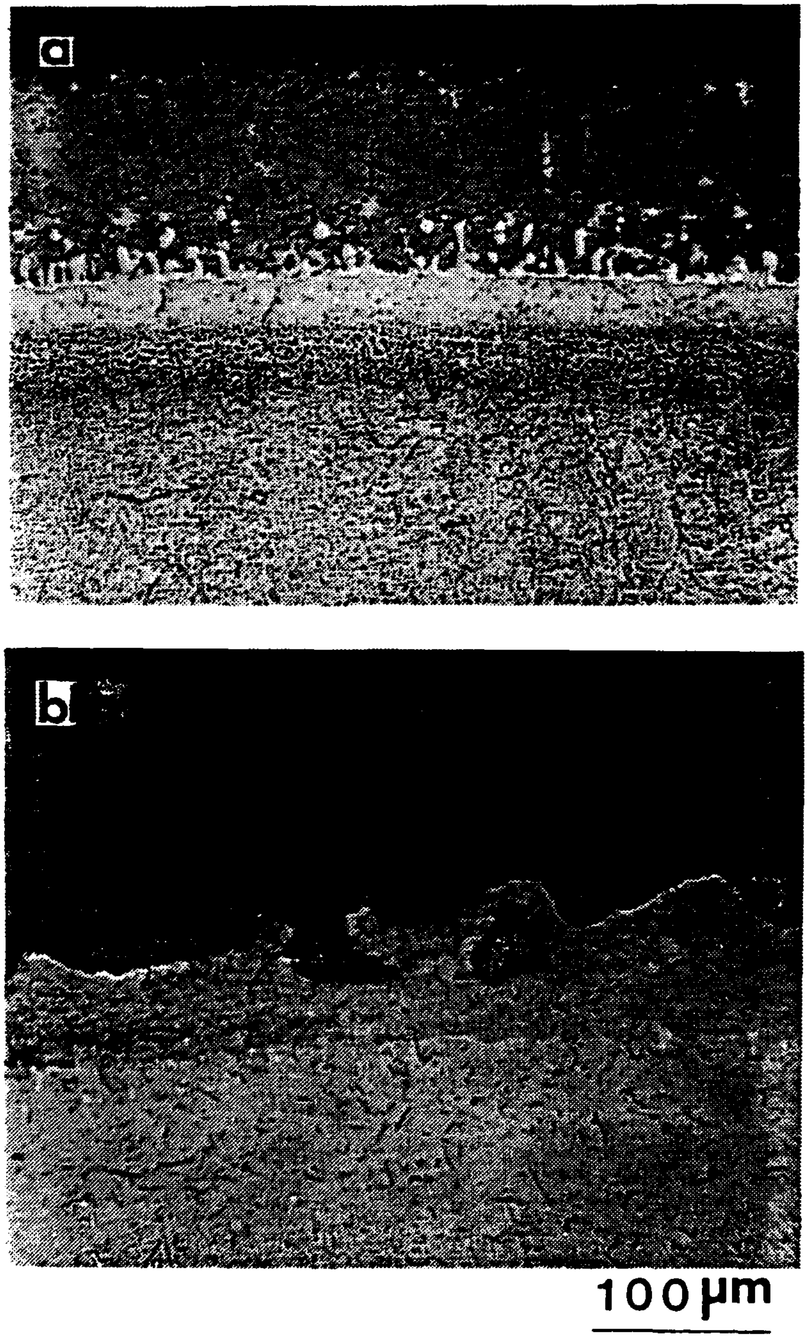

Figure 17. Thickness Rumpling Effect for Similarly Processed Platinum Aluminide Coatings (250x): a) 4IIB, Thick Coating, Cycled 150 hrs; b) 4IIB, Thin Coating, Cycled 150 hrs

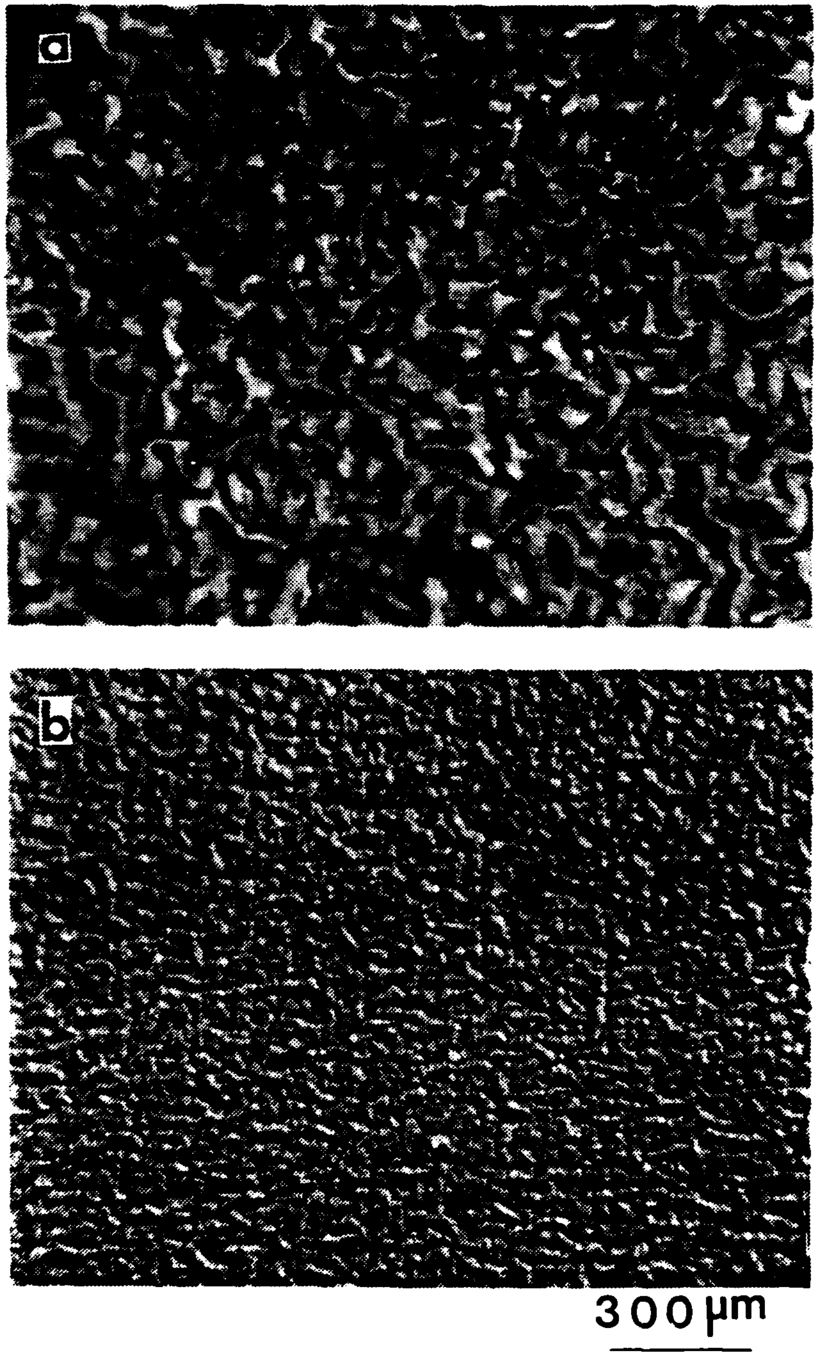

Figure 18. Surface Rumpling Magnitude Thick and Thin Platinum Aluminide Coatings Cycled 160 hrs (250x): a) 4IIB, Thin Coating; b) 2IIB, Thick Coating

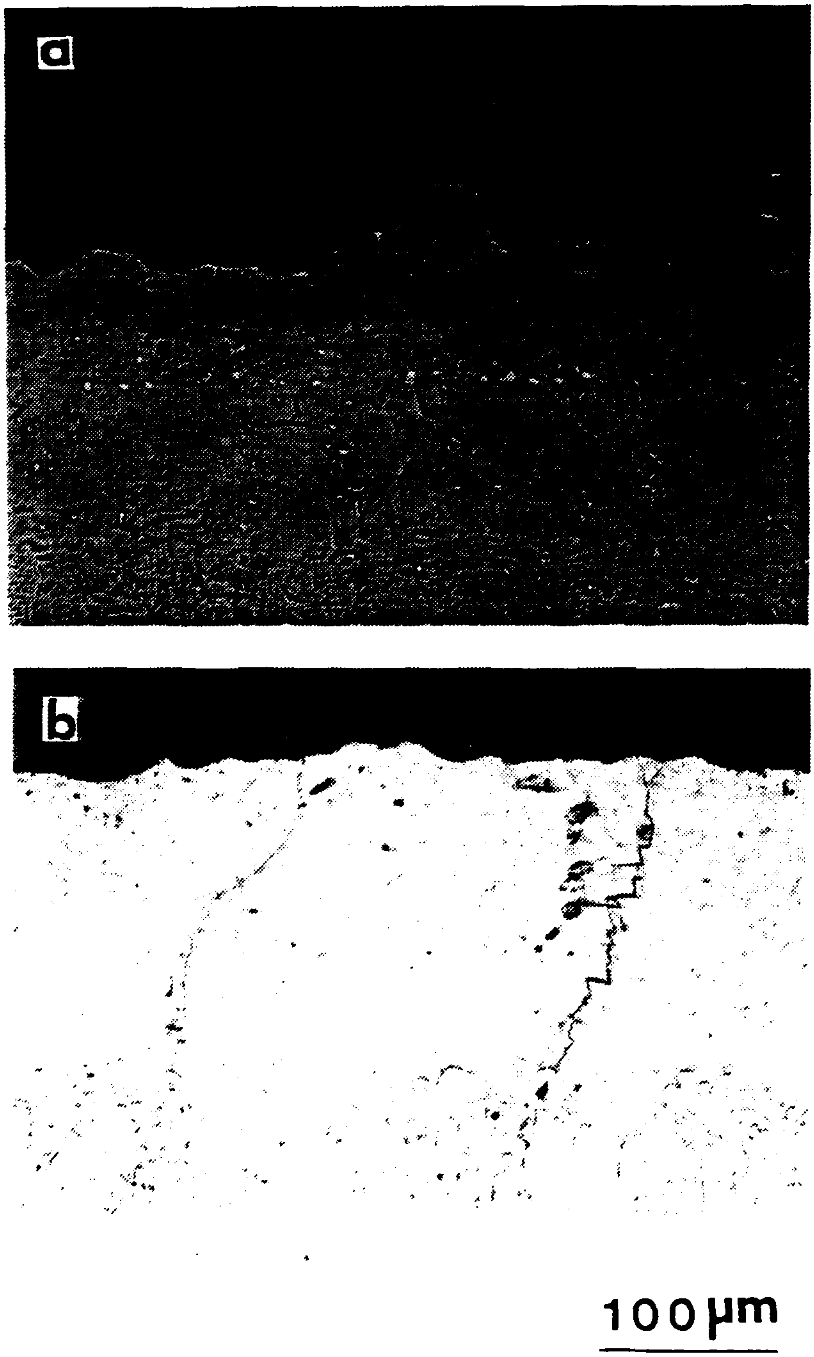

Figure 19. Cross-section Microstructural Comparison of Thick and Thin Platinum Aluminide Coatings Cycled 250 hrs (250x): a) 4IIB, Thin Coating with Void Formation; b) 2IIB, Thick Coating with Cracking

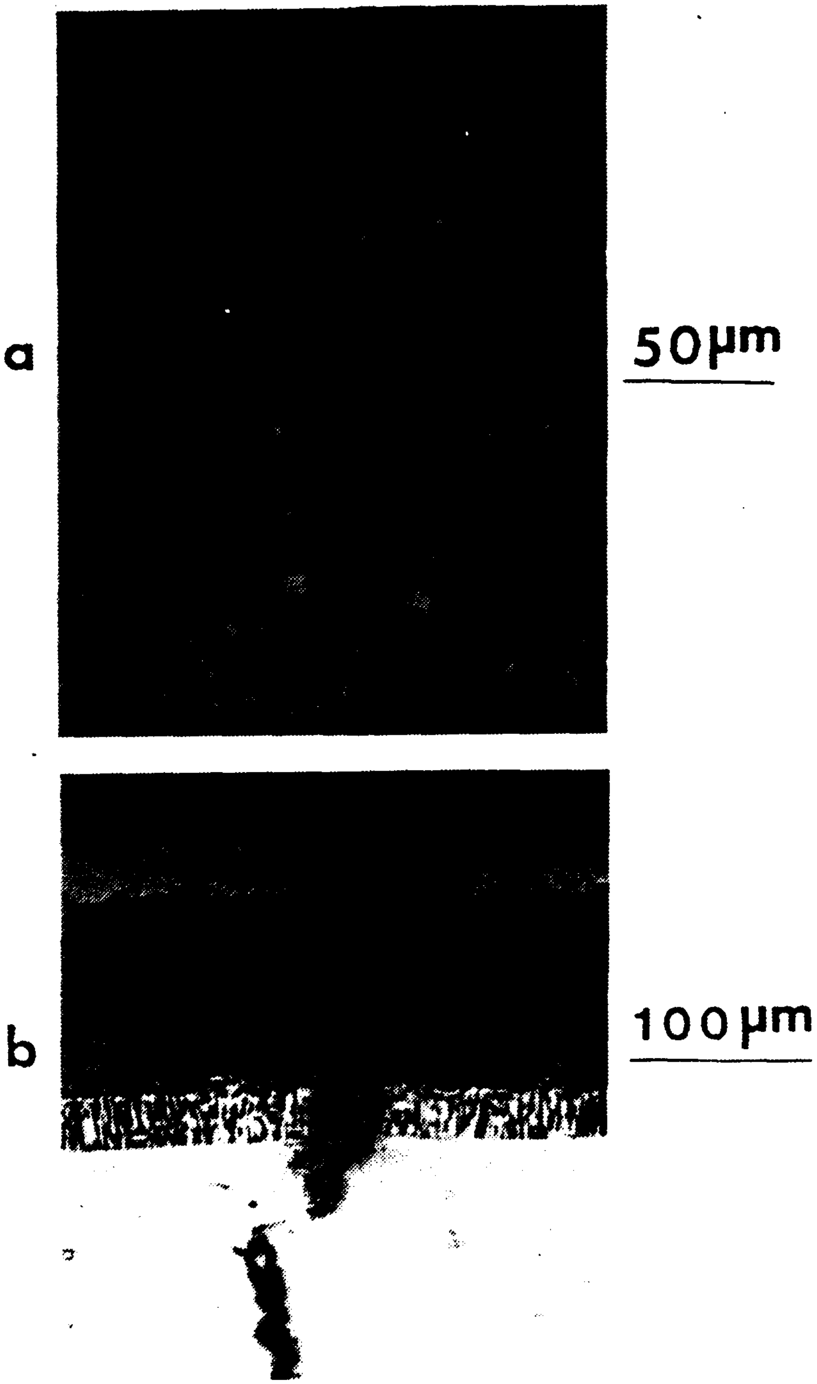

Figure 20. Platinum Aluminide Cracking: a) Cyclicly Induced Thermal Cracking, 2IIB, Cycled 250 hrs (425x); b) Single Event, Brittle Platinum Aluminide Cracking (250x), Courtesy of Vogel

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