ARMY RESEARCH LABORATORY

Platinum-Modified Diffusion Aluminide Coatings on Nickel-Base Superalloys

G. M. Kim, G. H. Meier, and
F. S. Pettit

ARL-CR-50

March 1993

prepared by

Materials Science and Engineering Department
University of Pittsburgh
Pittsburgh, PA

under contract

DAAG46-85-K-0008

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	**2. REPORT DATE** March 1993	**3. REPORT TYPE AND DATES COVERED** Final Report - June 1985 to June 1988

4. TITLE AND SUBTITLE Platinum-Modified Diffusion Aluminide Coatings on Nickel-Base Superalloys	**5. FUNDING NUMBERS** Contract No. DAAG46-85-K-0008
6. AUTHOR(S) G. M. Kim, G. H. Meier, and F. S. Pettit	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials Science and Engineering Department University of Pittsburgh Pittsburgh, PA 15261	**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory Watertown, MA 02172-0001 ATTN: AMSRL-OP-PR-WT	**10. SPONSORING/MONITORING AGENCY REPORT NUMBER** ARL-CR-50

11. SUPPLEMENTARY NOTES

Milton Levy, COR

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited	**12b. DISTRIBUTION CODE**

13. ABSTRACT *(Maximum 200 words)*

Conventional and platinum modified diffusion aluminide coatings on some state-of-the-art single crystal and polycrystalline nickel-base superalloys have been compared in tests designed to establish conditions representative of those existing in gas turbines operating over a range of applications. Resistance of these coatings to oxidation, high temperature hot corrosion, and low temperature hot corrosion have been compared. Platinum has been found to significantly improve the resistance of diffusion aluminides to all of these forms of degradation but the improvement with regard to low temperature hot corrosion is not as great as in the case of the other two forms of attack. Substrate composition has been found to exert a very significant effect on the lives of coatings in the high temperature tests. In the case of high temperature oxidation elements such as Hf are important in that they extend coating lives whereas for high temperature hot corrosion the type and concentration of refractory elements are significant factors affecting coating lives. A limited number of experiments have indicated intermittent hot corrosion exposures degrade the subsequent cyclic oxidation resistance of Pt-aluminide coatings.

14. SUBJECT TERMS Superalloys, Nickel-base superalloys, Oxidation resistance, Platinum coatings, Single crystals	**15. NUMBER OF PAGES** 31 **16. PRICE CODE**

17. SECURITY CLASSIFICATION OF REPORT Unclassified	**18. SECURITY CLASSIFICATION OF THIS PAGE** Unclassified	**19. SECURITY CLASSIFICATION OF ABSTRACT** Unclassified	**20. LIMITATION OF ABSTRACT** UL

Contents

Page

Introduction 1

Experimental

Characterization of Materials Used in This Program 1

The Experimental Tests 4

Other Experimental Tests Used in This Program 7

Results and Discussion

Cyclic Oxidation 7

Cyclic Hot Corrosion (High Temperature Hot Corrosion) 15

Low Temperature Hot Corrosion 15

Effects of Intermittent Hot Corrosion on Cyclic Oxidation Behavior 20

Effects of Other Precious Metals and Variation of Amount of Platinum in Coatings 20

Selection of Coating System for Burner Rig Testing 21

Conclusions 22

References 24

Figures

1. SEM depicting the typical microstructure of a diffusion aluminide coating produced by the Co-Dep process on PWA 1480 2
2. SEM of a diffusion aluminide coating (PWA 73) on PWA 1480 3
3. SEM of a platinum-modified diffusion aluminide coating on PWA 1480 3
4. Weight change versus time curves for various coating substrate combinations during cyclic oxidation in air at 1135°C (one hour cycles) 5
5. Weight change versus time curves for various coating substrate combinations exposed to cyclic hot corrosion conditions in air at 1000°C 5
6. Weight change versus time curves for various coating substrate combinations exposed to low temperature hot corrosion conditions at 700°C 6
7. Weight changes versus time data for the oxidation of the single crystal superalloys in air at 1093°C 7

8. Photographs of (a) PWA 1480 (top), and (b) CMSX-3 (bottom) after 24 hours of oxidation in air at 1093°C. Depleted zones are evident along with an acicular phase in PWA 1480 and coarsened γ' in CMSX-3 8

9. Weight change versus time data for several coating substrate combinations during cyclic oxidation in air at 1100°C 9

10. Cross sections of coated CMSX-3 after cyclic oxidation in air at 1135°C. (a) Pt-modified aluminide after 3414 cycles, (b) PWA 73 after 1007 cycles 10

11. Acoustic emission data obtained during cooling of the coated specimens after 24 hours oxidation in air at 1093°C 11

12. SEM of the surfaces of CMSX-3 (a) with a platinum-modified aluminide coating (top), and (b) a diffusion aluminide coating (bottom). After the acoustic emission tests 12

13. Weight change versus time curves showing the range of behavior observed for the various coating substrate combinations during isothermal oxidation in air at 1100°C 13

14. Cross sections of Co-Dep coated alloys after cyclic oxidation in air at 1135°C. (a) CMSX-3 substrate after 2806 cycles, (b) PWA-1480 substrate after 1706 cycles 14

15. Cross sections of coated PWA 1480 after 300 hours cyclic hot corrosion in air at 1000°C. (a) Pt-modified aluminide, (b) PWA 73 16

16. Cross sections of coated CMSX-3 after 300 hours cyclic hot corrosion in air at 1000°C. (a) Pt-modified aluminide, (b) PWA 73 17

17. Cross sections of coated Rene 80 after cyclic hot corrosion in air at 1000°C. (a) Pt-modified aluminide after 150 hours, (b) PWA 73 after 100 hours 18

18. Cross sections of CMSX-3 after 24 hours isothermal exposure to low temperature hot corrosion conditions at 700°C. (a) Pt-modified aluminide, (b) PWA 73 19

19. Cross section of Co-Dep coated CMSX-3 after 24 hours exposure to low temperature hot corrosion conditions at 700°C 20

20. Weight change versus time data indicating the effect of prior exposure to hot corrosion conditions on the cyclic oxidation behavior of a Pt-modified aluminide coating on PWA 1480 21

Introduction

Advanced designs for gas turbines emphasize higher performance standards which usually require higher operating temperatures and longer lives for turbine hardware. Several advanced nickel-base, single crystal, superalloys have been developed for such turbines. Oxidation and hot corrosion studies [1,2] have been performed on such superalloys. The oxidation resistance of the single crystal alloys is approximately twice that of the contemporary polycrystalline nickel-base superalloys. The better oxidation resistance of the single crystal alloys result from the compositional differences that are possible compared to polycrystalline superalloys since grain boundary strengthening elements are no longer required. The hot corrosion resistance of the single crystal alloys is not significantly different from the polycrystalline versions.

While the single crystal nickel-base superalloys do have improved oxidation resistance, coatings will be necessary to achieve the desired useful lives under operating conditions. It is therefore necessary to compare the behavior of coatings on the different single crystal alloys, as well as on polycrystalline alloys. The present program is concerned with comparing the lives of several diffusion aluminide coatings on some single crystal alloys and on a polycrystalline alloy when such systems are exposed to oxidizing or hot corrosive conditions. Another objective of this program is to examine the effect of platinum on the lives of diffusion aluminide coatings.

Experimental

Characterization of Materials Used in This Program

Specimens of two single crystal alloys and one polycrystalline alloy were obtained from different sources in the heat treated condition. One of the single crystal alloys, PWA 1480 (Ni-9.8Cr-5.1Al-1.5Ti-4.7Co-11.9Ta-4.0W)*, was obtained from Pratt and Whitney. The other single crystal alloy, CMSX-3 (Ni-7.7Cr-5.5Al-0.9Ti-4.86Co-5.8Ta-7.8W-0.6Mo-0.1Hf), was obtained from Garrett Turbine Engine Company. Rene 80 (Ni-14Cr-3.0Al-5.0Ti-9.5Co-4.0W-4.0Mo-0.015B-0.32Zr-0.17C)**, which was supplied by General Electric Company, was used as the polycrystalline alloy. All three of these alloys had been solutionized and aged to produce γ' precipitates in a γ matrix. Both of the single crystal alloys consisted of γ' particles distributed in a γ matrix. Some larger globules of γ' were also evident. The observed microstructures were consistent with the microstructures reported for such alloys [1,2]. The Rene 80 alloy also exhibited γ' particles in a polycrystalline matrix of γ along with carbide particles.

The alloys were coated by two state-of-the-art aluminizing processes; namely, PWA 73 [3] and Co-Dep [4], and by two different procedures for incorporating platinum into diffusion aluminide coatings. The principal method used to incorporate platinum into the coating was that used by Turbine Components, Incorporated; however, near the end of this program platinum modified coatings prepared by Howmet

---

* Percentages are given in weight percent

** EDX analysis indicated the presence of Hf in Rene 80

Corporation were also used. In the case of the platinum modified coating prepared by Turbine Components, Incorporated, the specimens were coated with 5 μm to 10 μm of platinum using an electrolytic plating process. In order to deposit the platinum layer on the coupons, a thin platinum wire was spot-welded to each coupon. This wire was cut from the specimen after the aluminizing process. The platinum-coated specimens were then aluminized (out of the pack) by exposing them to $AlCl_3$ at 1080°C for four hours. This vapor was produced by using NH_4Cl and a 50% mixture of nickel and aluminum powders. The Howmet process for preparing the platinum-modified coating is proprietary and probably consists of the same essential steps but uses different procedures to obtain them.

The as-processed coatings had structures typical of diffusion aluminides, as shown in Figures 1 and 2. When platinum was added to the coating, a platinum-rich phase was evident in the outer portions of the coating (see Figure 3) which was identified as $PtAl_2$. This phase was discontinuous in the coatings formed upon PWA 1480 and CMSX-3 but was continuous on Rene 80. Such results show that the diffusion characteristics of the substrate influence the coating microstructure even when the conditions to develop the coating are the same.

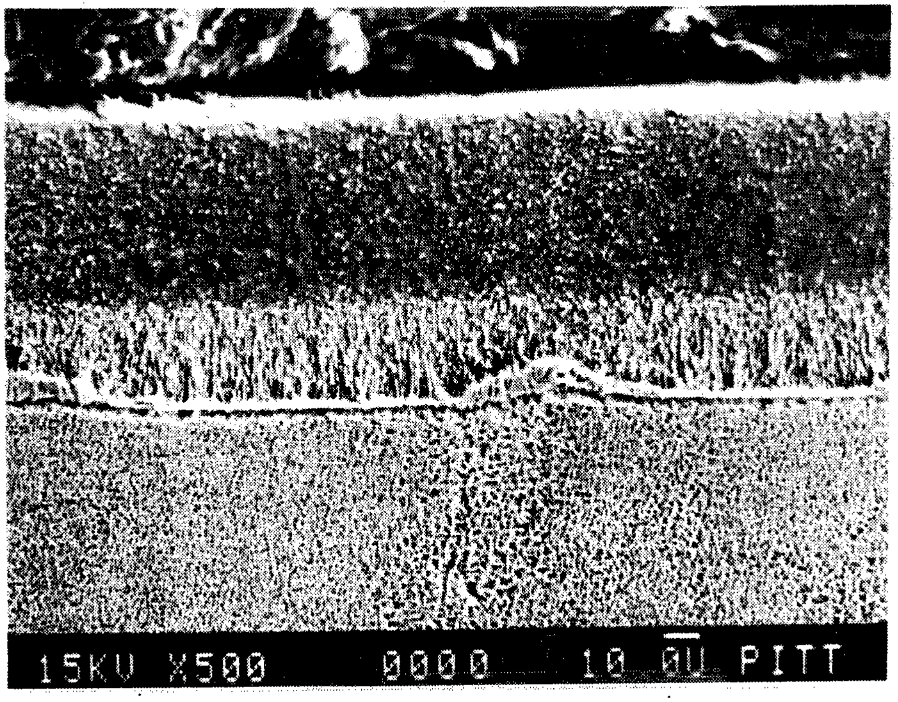

Figure 1. SEM depicting the typical microstructure of a diffusion aluminide coating produced by the Co-Dep process on PWA 1480.

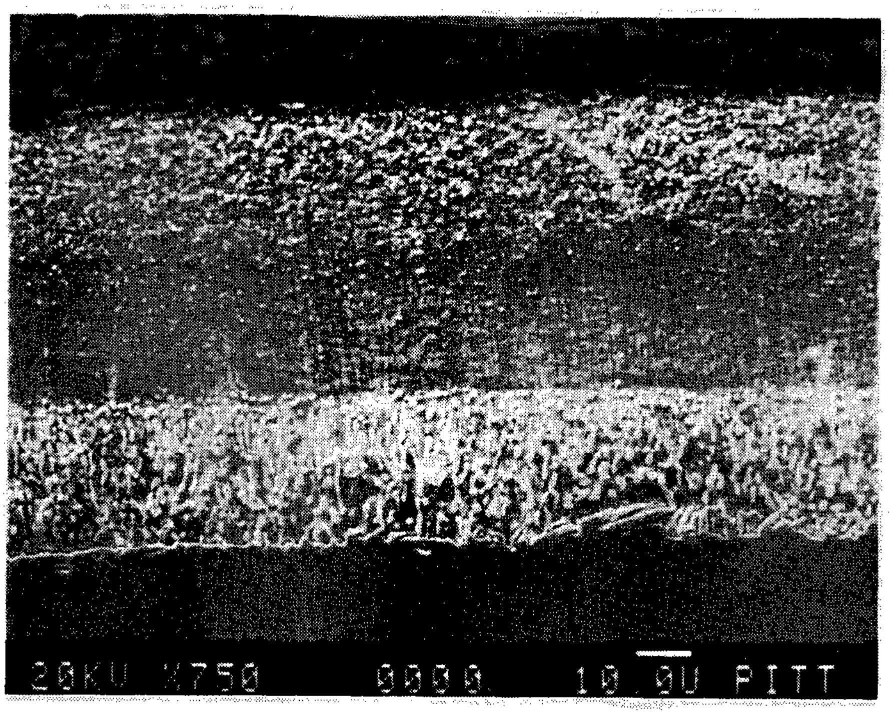

Figure 2. SEM of a diffusion aluminide coating (PWA 73) on PWA 1480.

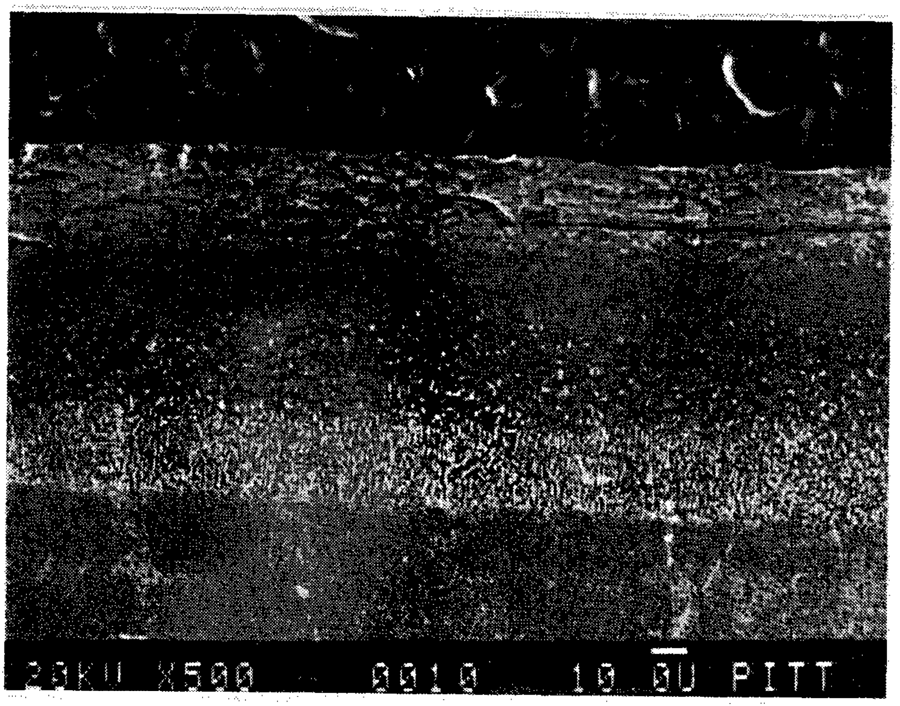

Figure 3. SEM of a platinum-modified diffusion aluminide coating on PWA 1480.

The Experimental Tests

A number of different tests were performed on the coated specimens in order to compare oxidation and hot corrosion properties. All of these tests consisted of laboratory tube furnace tests using coated coupons about 1.5 cm x 1.5 cm x 0.3 cm. Weight change measurements as a function of time were performed during the test as were visual examinations of specimen surfaces upon the conclusion of testing. The exposed specimens were examined using standard metallographic techniques, scanning electron microscopy (SEM), and X-ray diffraction (XRD) to characterize the amounts and types of degradation. The following specific tests are described.

Cyclic Oxidation

An important property of coatings on superalloys is their ability to protect the substrate from oxidation degradation. Very often such tests are performed in dynamic burner rigs. Such tests usually involve high temperature and cyclic conditions to produce thermally-induced stresses. It has been shown [2] that cyclic tube furnace tests can also be used to compare alloys in cyclic oxidation. The same ranking as the burner rig was obtained but with different total exposure lives for the alloys. In this program cyclic oxidation was done at 1135°C in air. Each cycle consisted of 45 minutes of specimen exposure to the hot zone of the furnace (1135°C) followed by 15 minutes in the cold zone which was close to room temperature. The cycling was performed automatically and the exposed specimens were examined and weighed at time intervals that were selected based upon the amount of attack observed in the initial tests. Typical weight change versus time data are presented in Figure 4. It can be seen that the coating systems all exhibit weight changes that are initially small, but eventually much larger weight changes are observed. The onset of the larger weight changes indicates the beginning of failure of the coatings as confirmed by metallographic examination of cross sections of the exposed specimens. Usually these weight changes are weight losses, but if the oxidation products do not spall weight increases can occur. It is always necessary to confirm the onset of coating failure as indicated by the onset of abrupt changes in the slopes of the weight change curves by XRD of corrosion products and metallographic examination of the specimens.

In attempting to study the effects of platinum on the properties of diffusion aluminide coatings, it is necessary to examine the diffusional stability of the coatings. Experiments were, therefore, performed where coated specimens were annealed in argon and the amount of interdiffusion between the coating and substrate was determined using metallographic techniques.

Cyclic Hot Corrosion

It is now well established [5] that there are two important forms of hot corrosion; namely, low and high temperature hot corrosion. To cause these two forms of degradation, different test conditions are required. In the case of high temperature hot corrosion, it is important to apply a Na_2SO_4 deposit regularly to the specimen surface and to cycle the specimen between the test temperature and room temperature. The gas composition is not a critical factor when the temperature is at 1000°C and testing can be performed in air. The data obtained are quite similar to those obtained in cyclic oxidation in that similar shaped curves are obtained. Typical results are presented in Figure 5. The time required to obtain increased rates of degradation are used to compare the high temperature hot corrosion resistance of the coating systems.

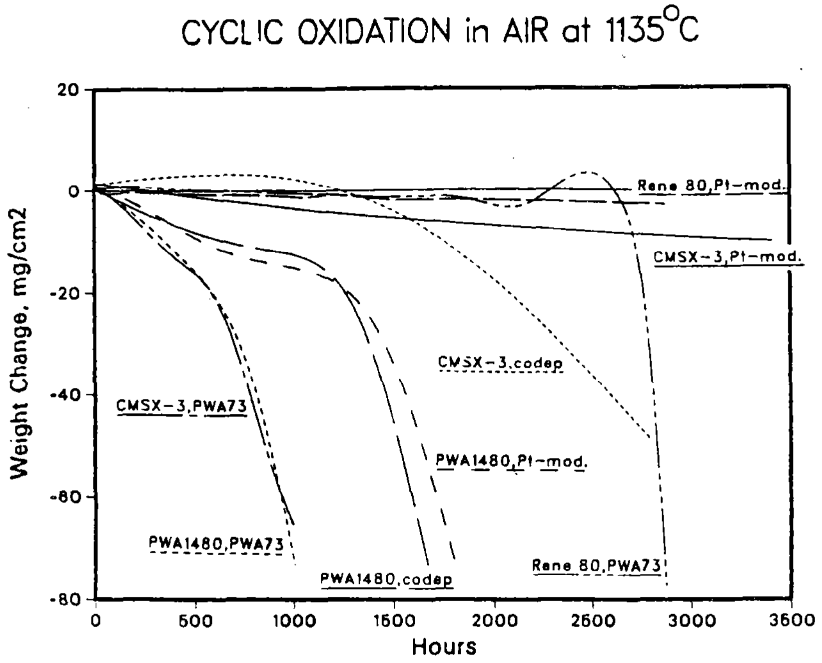
CYCLIC OXIDATION in AIR at 1135°C

Figure 4. Weight change versus time curves for various coating substrate combinations during cyclic oxidation in air at 1135°C. (one hour cycles).

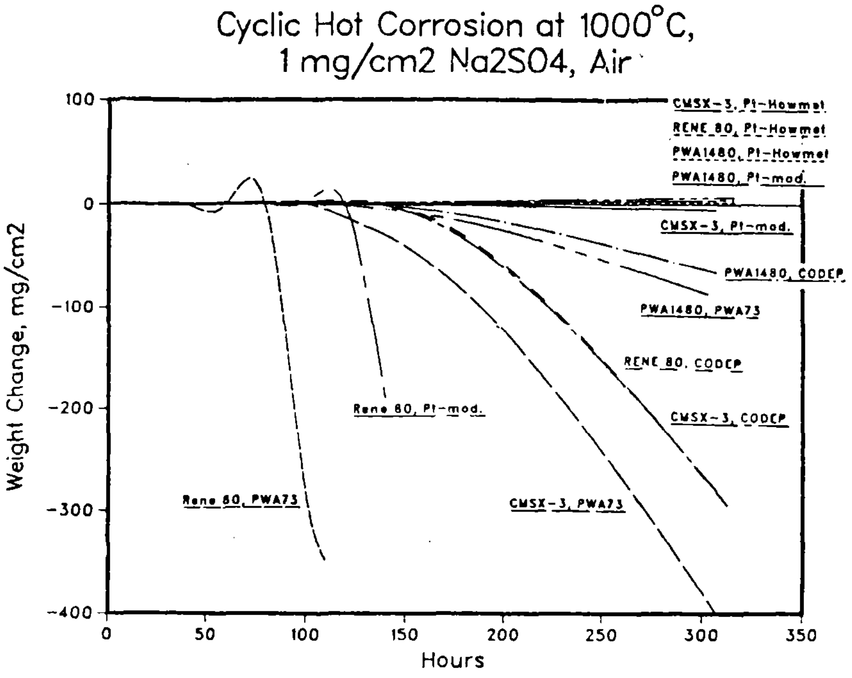
Cyclic Hot Corrosion at 1000°C, 1 mg/cm2 Na2SO4, Air

Figure 5. Weight change versus time curves for various coating substrate combinations exposed to cyclic hot corrosion conditions in 1000°C.

Low Temperature Hot Corrosion

In the case of low temperature hot corrosion it is necessary to have SO_3 present in the gas phase and to apply deposits that are liquid at the test temperature which usually is 700°C. In the present program, deposits of Na_2SO_4-50 mole percent $NiSO_4$ were used in gases with an initial room temperature composition of O_2 with 100 ppm SO_2. These gas mixtures were passed over a platinum catalyst which established an SO_3 pressure at 700°C of about 10^{-4} atm. This test is very severe and it usually is not necessary to cycle the specimens from the test temperature. Isothermal tests are, therefore, usually performed in continuous recording balances to obtain weight changes as a function of time. The magnitude of the weight changes are used to compare the amount of low temperature hot corrosion attack. It is important to emphasize that the amount of attack of these coatings at 700°C in the absence of hot corrosion attack is extremely small and usually not detectable by the current state-of-the-art microbalances. Hence, the observation of weight changes of 0.2 mg/cm^2 or more indicate that hot corrosion attack is occurring. As in the case of the other tests, it is also imperative that the results from all these tests be corroborated by metallographic examination of polished cross sections of the exposed specimens. Typical weight change data obtained from the low temperature hot corrosion test are presented in Figure 6.

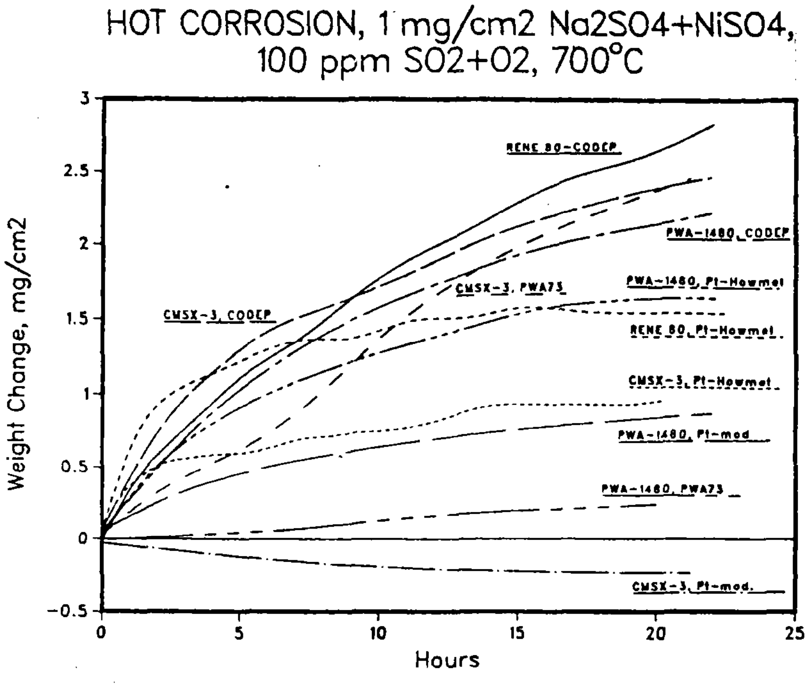

Figure 6. Weight change versus time curves for various coating substrate combinations exposed to low temperature hot corrosion conditions at 700°C.

Other Experimental Tests Used in This Program

It has been shown [6] that alumina scales formed on Pt-Al alloys are very resistant to spalling in a cyclic oxidation test. In order to examine the affects of platinum on the adherence of alumina to the coatings, acoustic emission tests were performed. These tests [7] have been described previously and consisted of oxidizing specimens for 24 hours at 1100°C and then using a wave guide and transducer along with other equipment [7] to measure the energy released upon cooling the oxidized specimens to room temperature. The number of counts above a threshold level was used to estimate the temperatures at which cracking began to occur and to compare the amount of cracking and spalling on different coating systems.

In some applications of gas turbines hot corrosion conditions are not present for long periods of time and failure via this process is not an important factor; however, it is possible that coatings may be subjected intermittently to hot corrosion conditions and the exposure could affect the oxidation lives of the coatings. In order to examine the influence of short exposures to hot corrosion conditions on oxidation, a few specimens were exposed to low temperature hot corrosion conditions and high temperature hot corrosion conditions, and then tested in cyclic oxidation.

Results and Discussion

Cyclic Oxidation

The uncoated alloys were oxidized isothermally at 1093°C to examine their oxidation behavior. Typical weight change data are presented in Figure 7, and photographs showing typical microstructures after oxidation are presented in Figure 8. The weight changes are small and consistent with the Al_2O_3 scales that were confirmed to have been formed on these alloys. The aluminum depleted zones, the acicular precipitates in these zones, and the coarsened γ' are all features reported previously for the oxidation of the single crystal alloys [1,2].

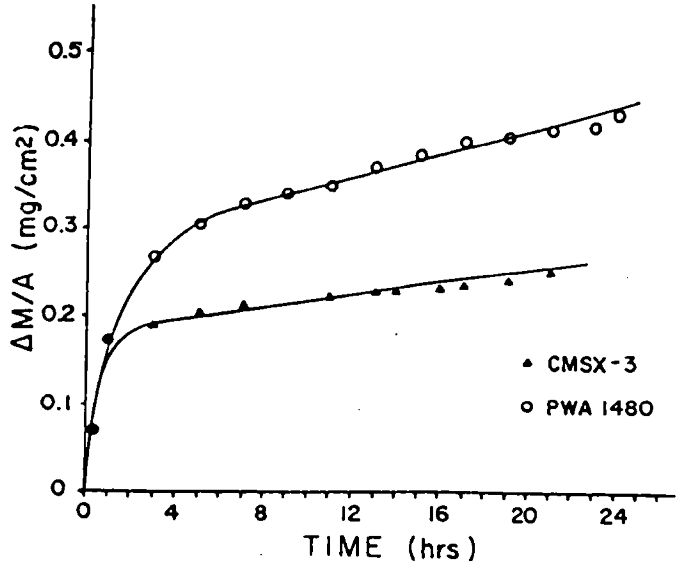

Figure 7. Weight changes versus time data for the oxidation of the single crystal superalloys in air at 1093°C.

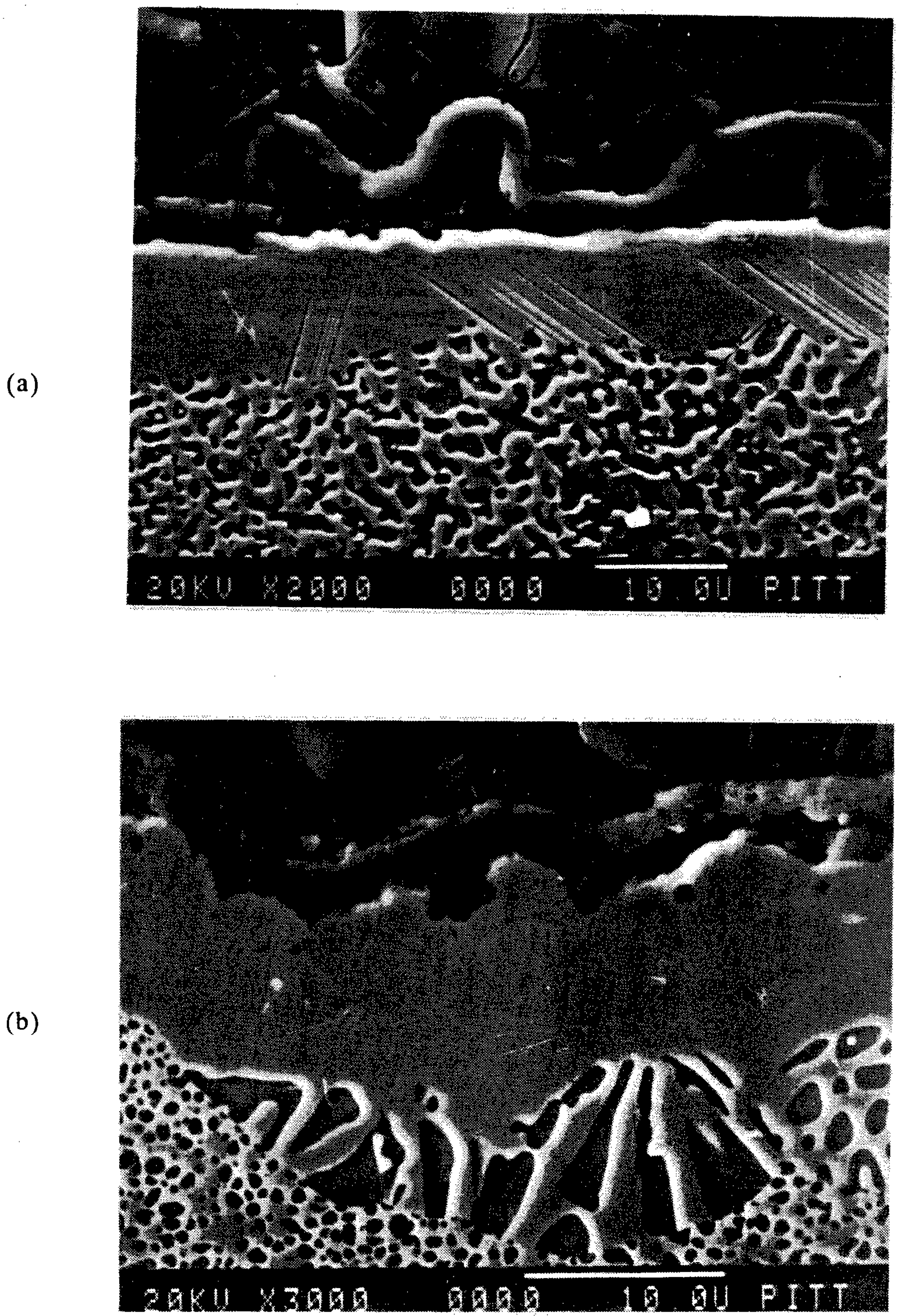

Figure 8. Photographs of (a) PWA 1480 (top), and (b) CMSX-3 (bottom) after 24 hours of oxidation in air at 1093°C. Depleted zones are evident along with an acicular phase in PWA 1480 and coarsened in CMSX-3.

The results obtained in the cyclic oxidation tests are summarized in Figures 4 and 9. These data show clearly that the incorporation of platinum into the coating extends the lives of the coatings. These data also permit some additional significant results to be identified. First, the compositions of the substrates definitely affect the lives of the coatings. The elements in the substrates that exert the most substantial effects on coatings lives are evidently the elements which affect the adherence of alumina, such as hafnium (Hf) [8]. Secondly, the aluminizing process influences coating lives. Co-Dep appeared to outperform PWA 73.

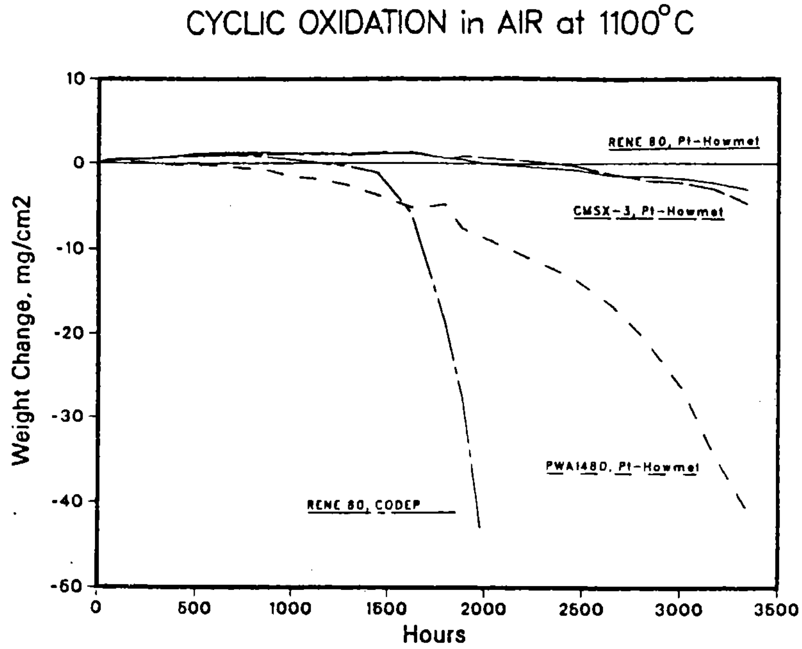

Figure 9. Weight change versus time data for several coating substrate combinations during cyclic oxidation in air at 1100°C.

Every coating that contained platinum performed better on all of the substrates than coatings without platinum. There is no question platinum extends the cyclic oxidation lives of coatings. The reason that platinum produces such effects is not fully understood. As can be seen in Figure 4, CMSX-3 and Rene 80 with platinum-modified coatings have not failed after 3000 hours of testing at 1135°C, whereas failure of the other coatings on these substrates did occur at shorter times. Figure 10 shows the degradation microstructures for a Pt-modified coating and PWA 73 on CMSX-3. The corrosion of the alloy with PWA 73 has penetrated well into the substrate in 1000 cycles, whereas the substrate of the alloy with the Pt-modified coating is only starting to be degraded after 3400 cycles. The platinum-modified coating was least effective in extending coatings lives on PWA 1480 but, as can be seen in Figure 4, this coating on PWA 1480 was better than PWA 73 and as good as Co-Dep. The data presented in Figure 9 are for a slightly lower temperature than those in Figure 4, but the same general results are evident; namely, the platinum-modified coatings provide the longest coating lives, and this type of coating is most effective on substrates containing elements such as Hf.

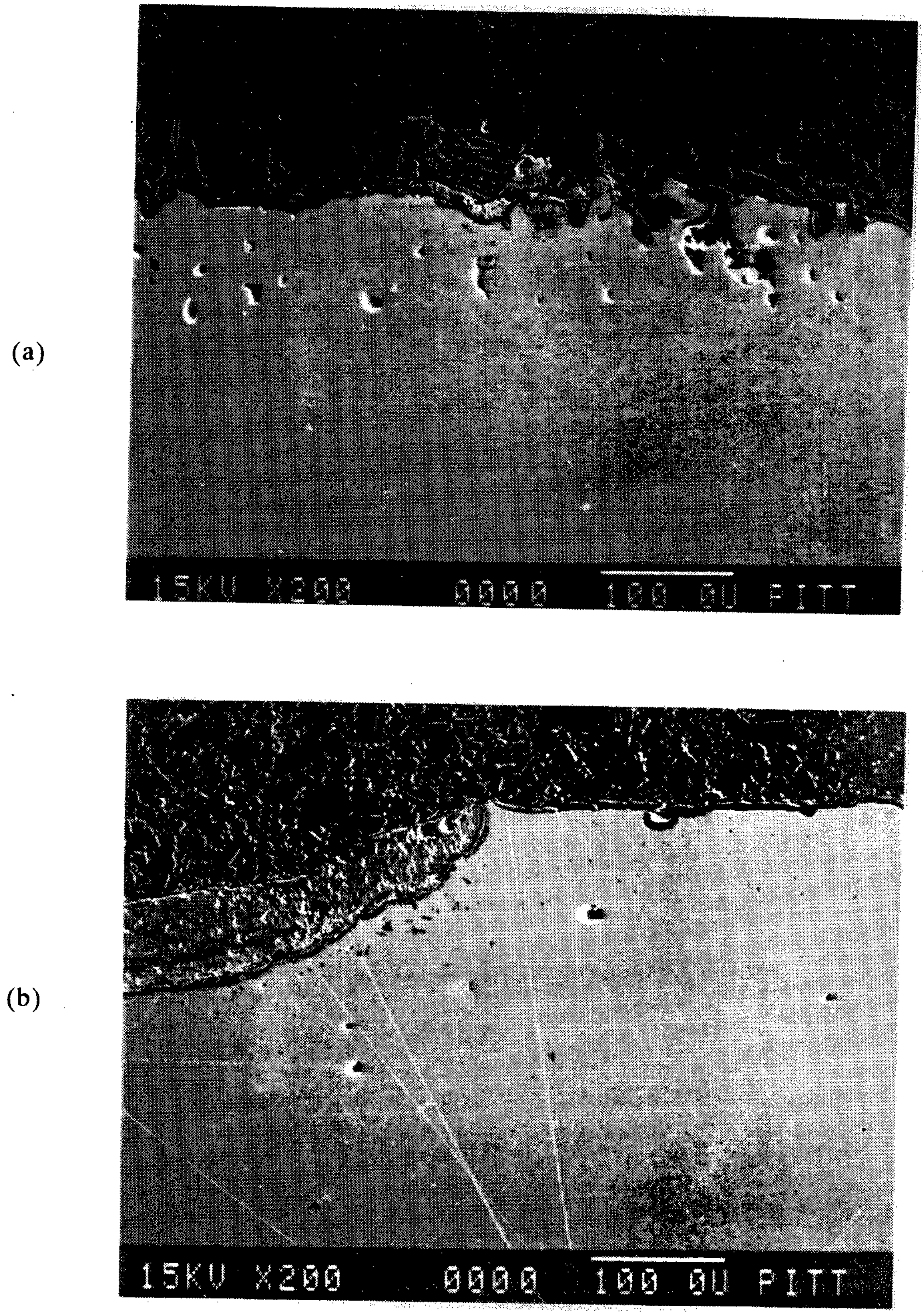

Figure 10. Cross sections of coated CMSX-3 after cyclic oxidation in air at 1135°C. (a) Pt-modified aluminide after 3414 cycles, (b) PWA 73 after 1007 cycles.

There are data in the literature which indicate that platinum can cause the adherence of alumina formed upon alloys to be improved [6,9]. The adherence of alumina on some of the coatings used in the program was compared using acoustic emission. As can be seen in Figure 11, cracking of the alumina scale was detected on coatings with and without the platinum modification. Moreover, the amount of cracking and spalling was sometimes greater on the platinum modified coatings, as shown in Figures 11 and 12. While more extensive testing may have shown that the platinum-modified coatings generally exhibited better adherence of the alumina scales, the observed cracking and spalling was after only one exposure for 24 hours at 1100°C. It is not reasonable to propose that the improvement of oxide scale adherence is a major reason for the extended lives of the platinum modified coatings.

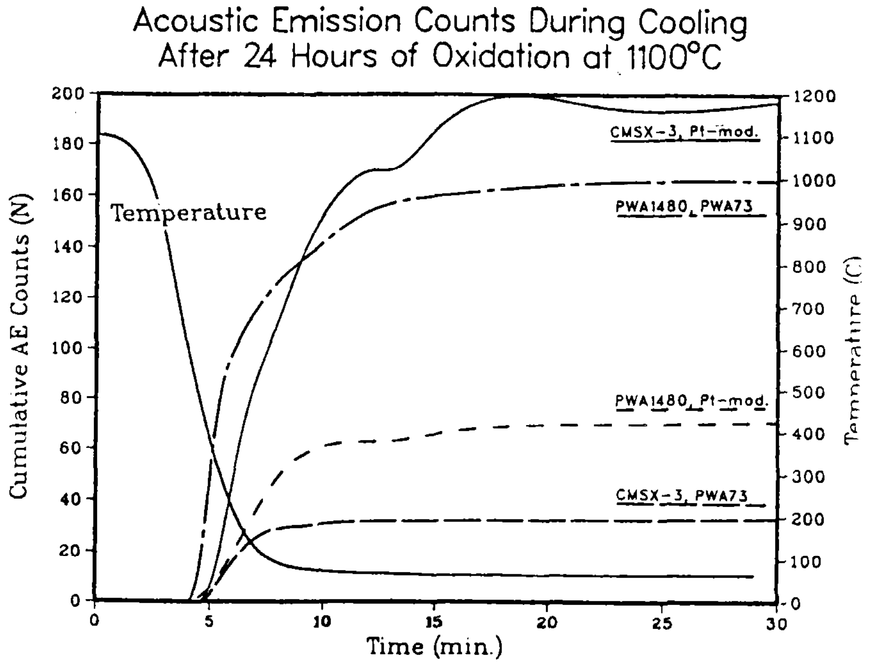

Figure 11. Acoustic emission data obtained during cooling of the coated specimens after 24 hours oxidation in air at 1093°C.

Schaeffer [10] has compared the performances of diffusion aluminide coatings with and without platinum during cyclic oxidation of IN 738 and MAR M200. The major effects of platinum were found to be related to the growth rates of the alumina scales and with the selective oxidation of aluminum in these coatings. Platinum in the aluminide coatings resulted in the formation of a more pure alumina with parabolic rate constants significantly smaller than those for the unmodified coatings. Furthermore, the platinum modified coatings were capable of continuing to have alumina scales reform after cracking and spalling of the alumina. This latter condition was believed to result from a higher concentration of aluminum in the platinum-modified coatings and less competition from other elements in the coatings for oxygen. Coated specimens were oxidized isothermally to compare the weight changes of the coatings with and without platinum. The data for all of the specimens fell in the band indicated in Figure 13. Most of the Pt-modified coatings fell in the lower region of this band, but the results are not conclusive because some of the Pt-free coatings also showed very small weight increases.

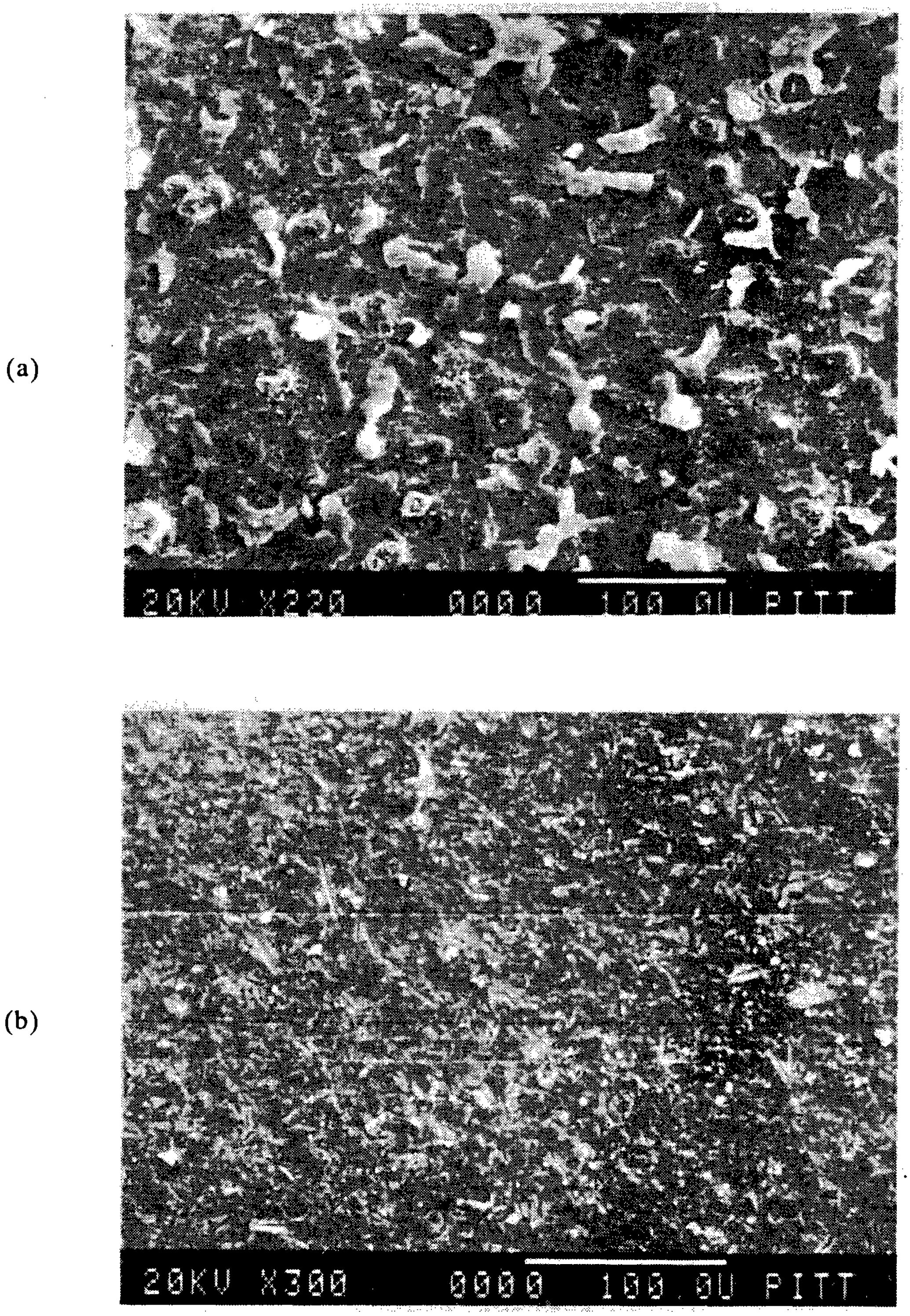

Figure 12. SEM of the surfaces of CMSX-3 (a) with a platinum-modified aluminide coating (top), and (b) a diffusion aluminide coating (bottom). After the acoustic emission tests.

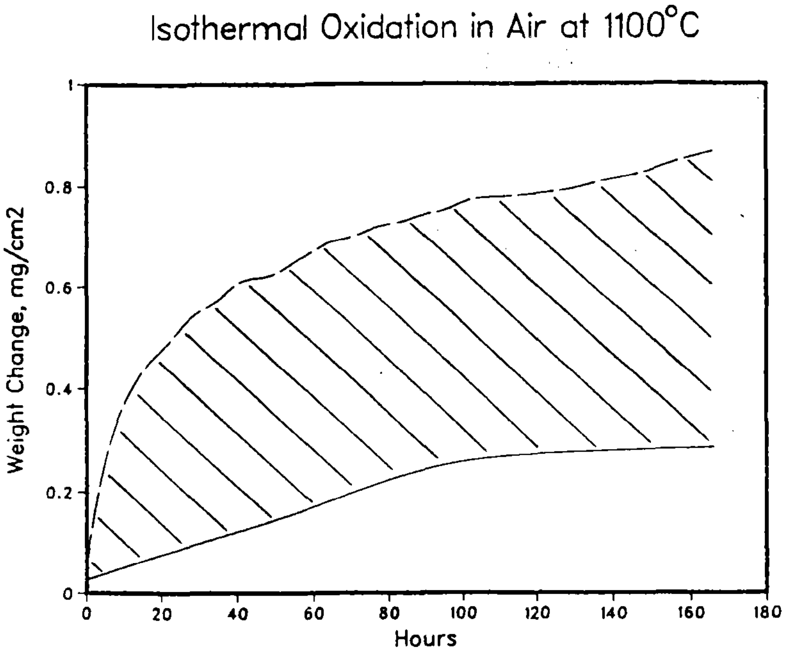

Figure 13. Weight change versus time curves showing the range of behavior observed for the various coating substrate combinations during isothermal oxidation in air at 1100°C.

Coated specimens were annealed for various times in argon and hydrogen to compare the amount of interdiffusion between the coating and the substrate in the absence of large oxidative components. The resulting microstructures did not indicate a substantial difference between the amount of interdiffusion of coatings with and without platinum. The results obtained in this program show very conclusively that platinum extends the lives of diffusion aluminide coatings on nickel-base superalloy substrates. The reason that this occurs has not been conclusively established. The results are in agreement with those of Schaeffer which show the most important effect of platinum is to establish conditions whereby the selective oxidation of aluminum from the coatings can continue to relatively low aluminum concentrations. It is important to emphasize that the lives of the platinum-modified coatings are especially long on substrates that contain approximately 1% Hf. The Hf evidently improves the adherence of the alumina to these coatings and extends the coatings' lives. The effects of Hf may not be apparent during the initial exposure of the coatings, but it becomes apparent after longer times when interdiffusion between the coating and the substrates is more extensive. There does not appear to be a large difference between PWA 73 on CMSX-3 and PWA 1480, but a substantial difference exists for Co-Dep in these two substrates. This difference is illustrated in Figure 14 where it is seen that a Co-Dep coating on CMSX-3 is still intact after 2800 cycles while the degradation has penetrated into the PWA 1480 substrate after 1700 cycles. One may propose that hafnium does not enter the coating to a substantial amount for PWA 73 but it does for Co-Dep (see Figure 4). However, the Co-Dep coating on PWA 1480 has been found to have a longer life than PWA 73. The Co-Dep process does result in some titanium being added to the coating. Titanium has been found to improve the adherence of alumina to FeCrAl substrates [11]. Titanium did not, however, improve the adherence of alumina to NiCrAl [11]. In the present program, it is not possible to state why Co-Dep provides more protection than PWA 73. In fact, the results are such that it has not been shown conclusively why one coating is better than the other.

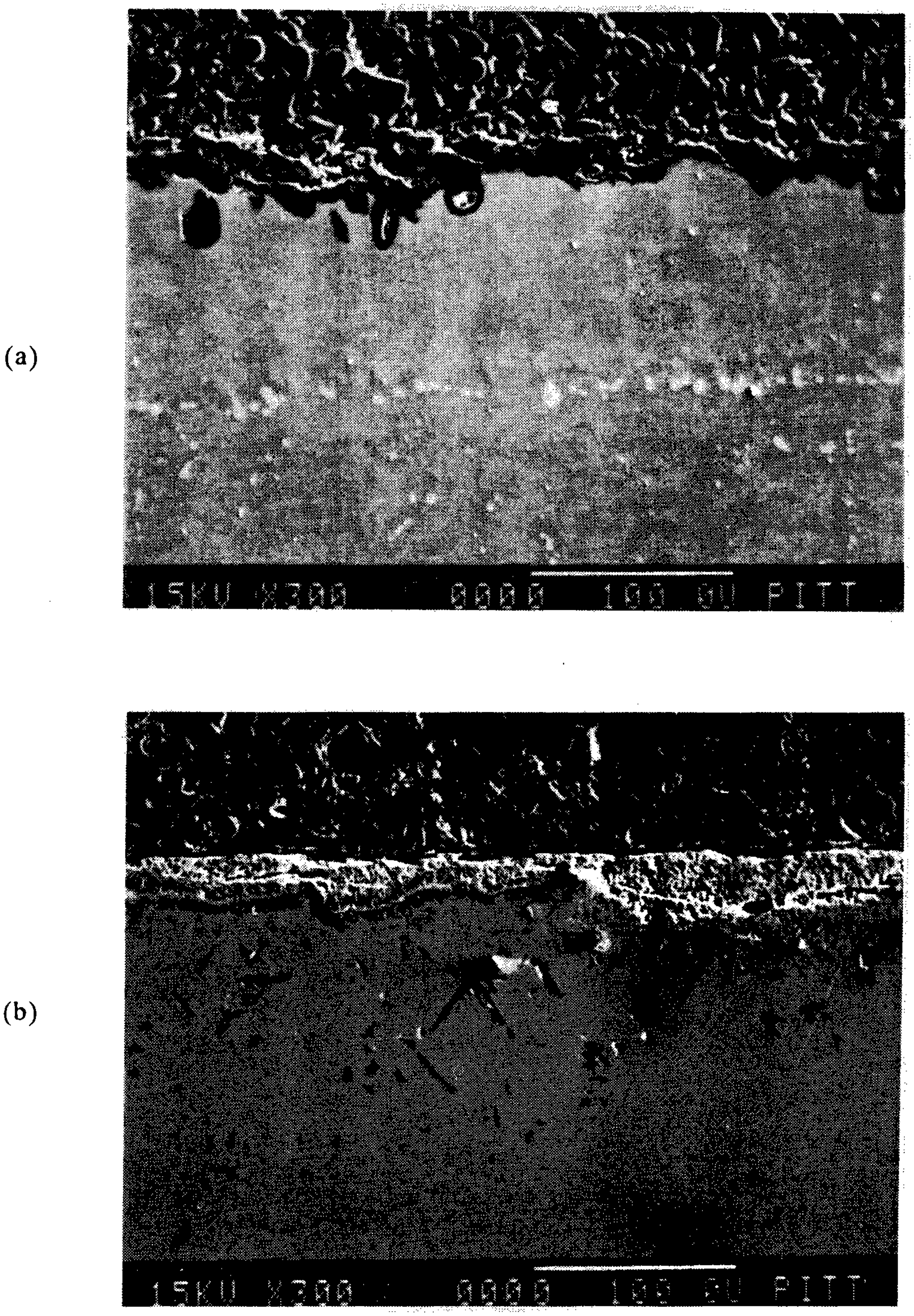

Figure 14. Cross sections of Co-Dep coated alloys after cyclic oxidation in air at 1135°C. (a) CMSX-3 substrate after 2806 cycles, (b) PWA-1480 substrate after 1706 cycles.

Cyclic Hot Corrosion (High Temperature Hot Corrosion)

Results obtained from the high temperature hot corrosion tests are presented in Figure 5. These data show conclusively that the platinum-modified coatings are better than coatings that do not contain platinum. Typical microstructures of specimens exposed to cyclic hot corrosion conditions are presented in Figures 15 through 17. Even though the platinum-modified coatings have been exposed for longer times, the amount of degradation is much more extensive in the coatings that do not contain any platinum. In this program it has not been possible to determine why the platinum-modified coatings perform better. In this test, alumina formation and the capability to reform after spalling is an important parameter. It, therefore, is proposed that good cyclic oxidation properties also result in good high temperature hot corrosion resistance.

Examination of the data presented in Figure 5 shows that there is also an effect of substrate composition. As can be seen in Figure 5, coatings have shorter lives on Rene 80 compared to CMSX-3 which, in turn, are not as good as coatings on PWA 1480. The significant difference between these substrates is the amount and type of refractory elements. Rene 80 contains both Mo and W. CMSX-3 contains mainly W, whereas PWA 1480 contains predominantly Ta. In the hot corrosion literature [12] it is well documented that refractory elements such as Mo and W can have a profound effect upon hot corrosion behavior. The results obtained for the high temperature hot corrosion test show that platinum extends the lives of diffusion aluminide coatings, but for optimum lives the composition of the superalloy substrate is also an important factor.

Low Temperature Hot Corrosion

The weight change data for coatings systems exposed to low temperature hot corrosion conditions are presented in Figure 6. The weight changes are not as large as those of the high temperature hot corrosion test but still very much larger than would have been observed in the absence of a deposit and without any SO_3 in the gas phase. Examination of these results show that the weight changes for the coatings which contain platinum are usually significantly less than those which do not contain any platinum. This observation is also supported by metallographic examination of the exposed specimens. As can be seen in Figure 18, less attack of the coating on CMSX-3 with platinum has occurred than that of the coating with no platinum. The lower magnification micrograph in Figure 19, when compared with Figure 18 (a), also indicates substantially more degradation of Co-Dep than the Pt-modified coating in CMSX-3.

It has not been possible to determine why the platinum-modified coatings perform better than conventional diffusional aluminides in the low temperature hot corrosion test in this program. It has been proposed [13] that the $PtAl_2$ phase is more resistant to hot corrosion than phases such as NiAl which is the major phase in conventional diffusion aluminides. The low temperature hot corrosion mechanism [14] apparently involves fluxing reactions for both aluminum and nickel. In the platinum-modified coatings the replacement of nickel by platinum may cause the nickel fluxing reaction to be decreased and thereby, due to coupling of fluxing reactions, the fluxing of aluminum may be inhibited.

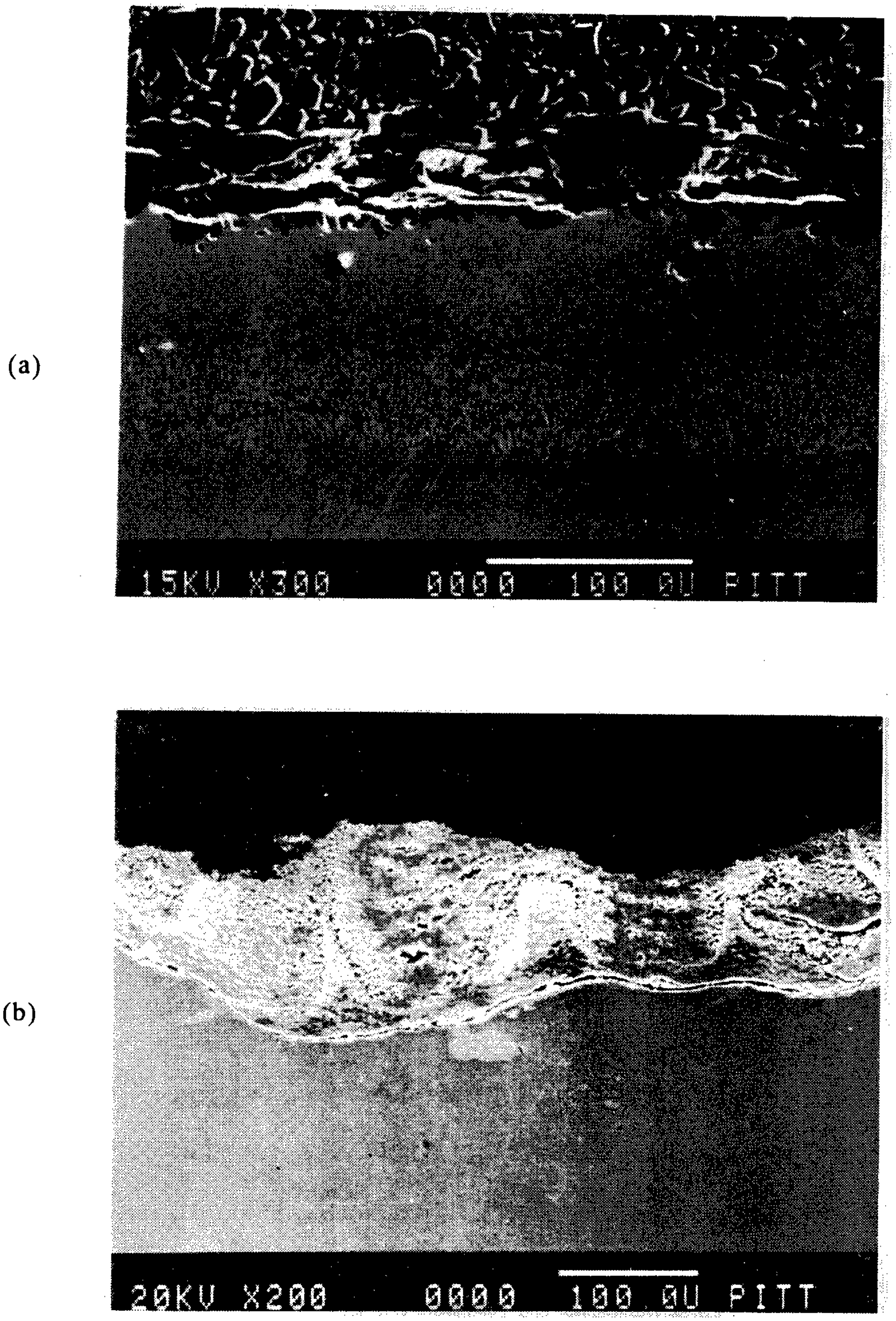

Figure 15. Cross sections of coated PWA 1480 after 300 hours cyclic hot corrosion in air at 1000°C. (a) Pt-modified aluminide, (b) PWA 73.

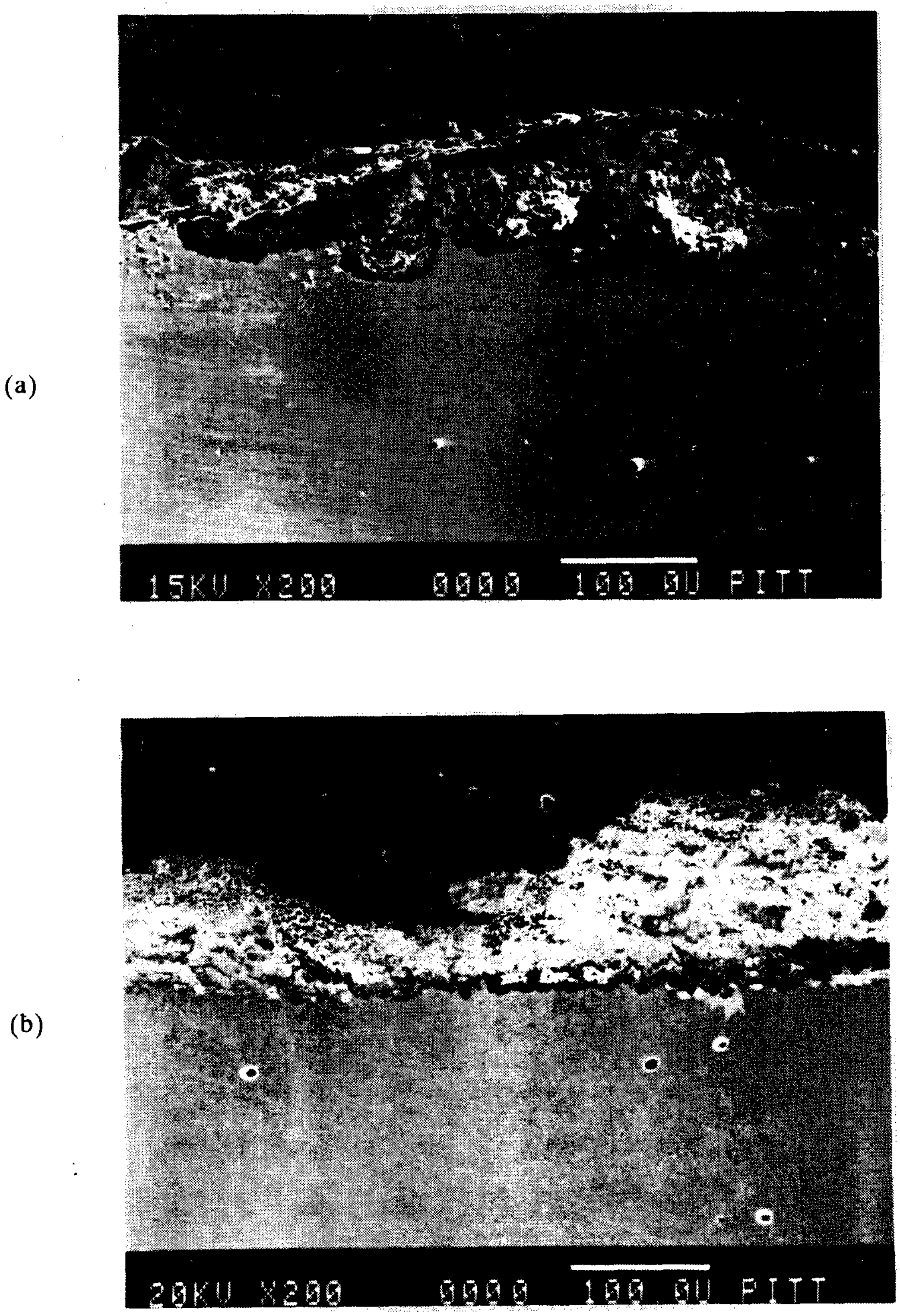

Figure 16. Cross sections of coated CMSX-3 after 300 hours cyclic hot corrosion in air at 1000°C. (a) Pt-modified aluminide, (b) PWA 73.

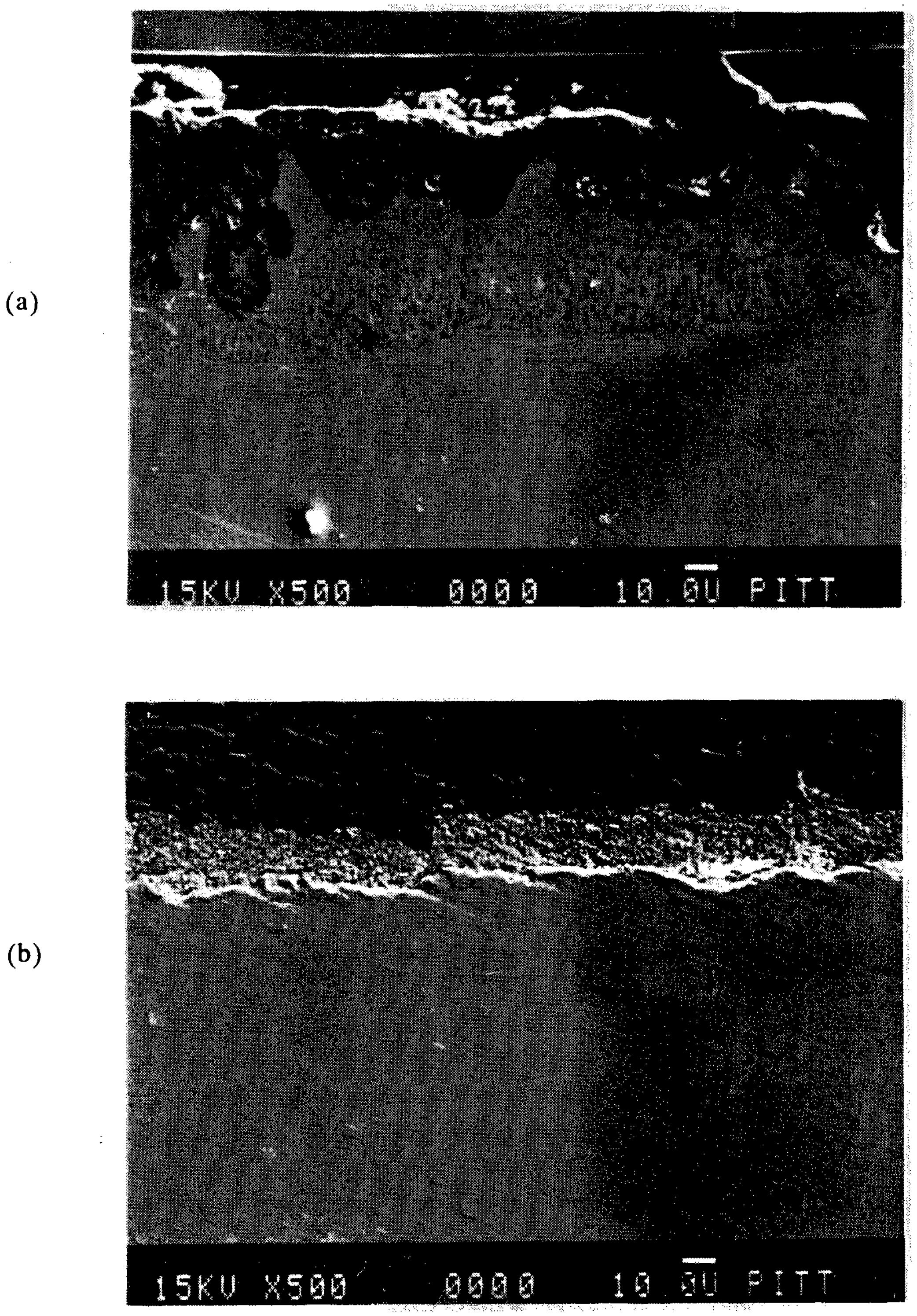

Figure 17. Cross sections of coated Rene 80 after cyclic hot corrosion in air at 1000°C. (a) Pt-modified aluminide after 150 hours, (b) PWA 73 after 100 hours.

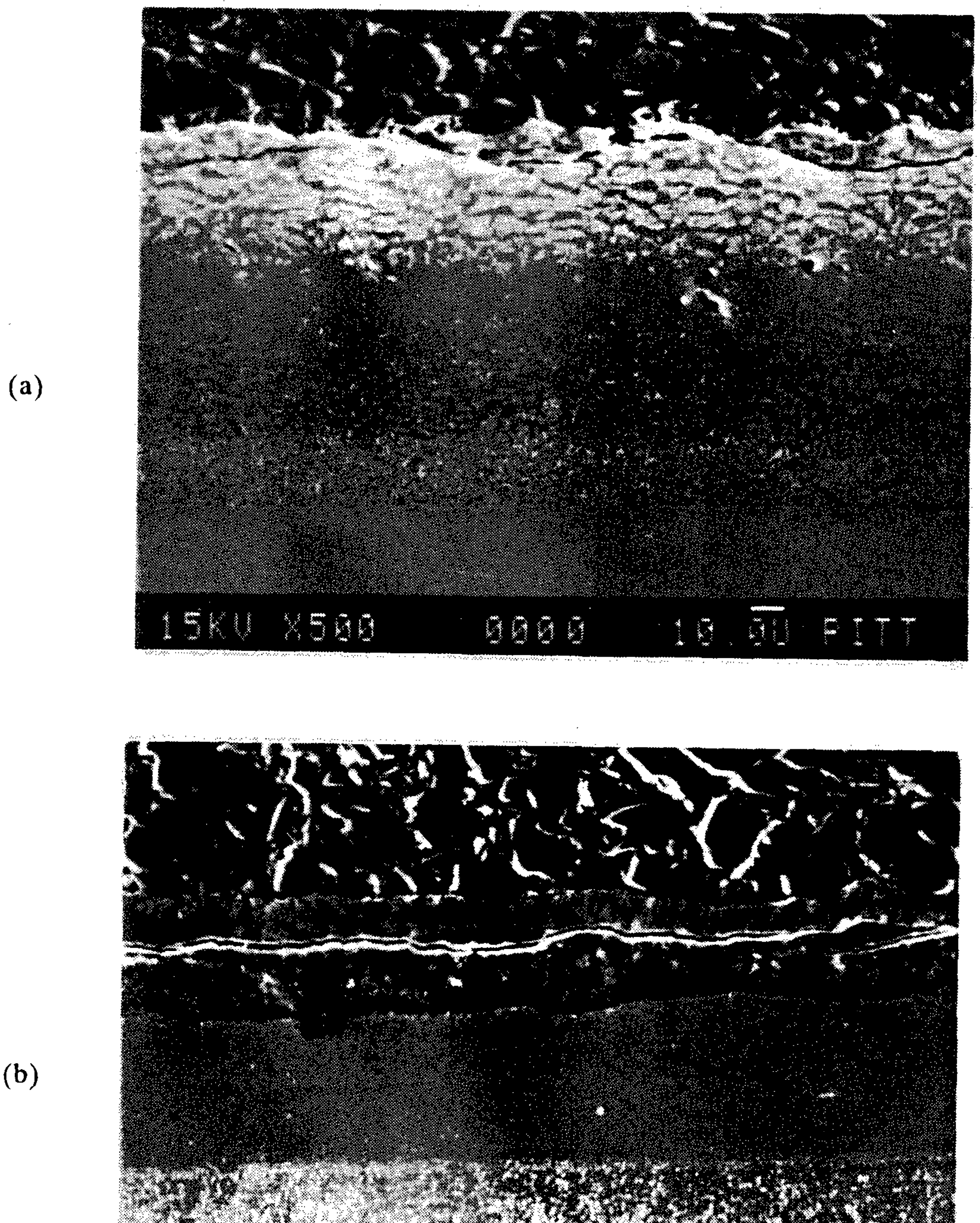

Figure 18. Cross sections of CMSX-3 after 24 hours isothermal exposure to low temperature hot corrosion conditions at 700°C. (a) Pt-modified aluminide, (b) PWA 73.

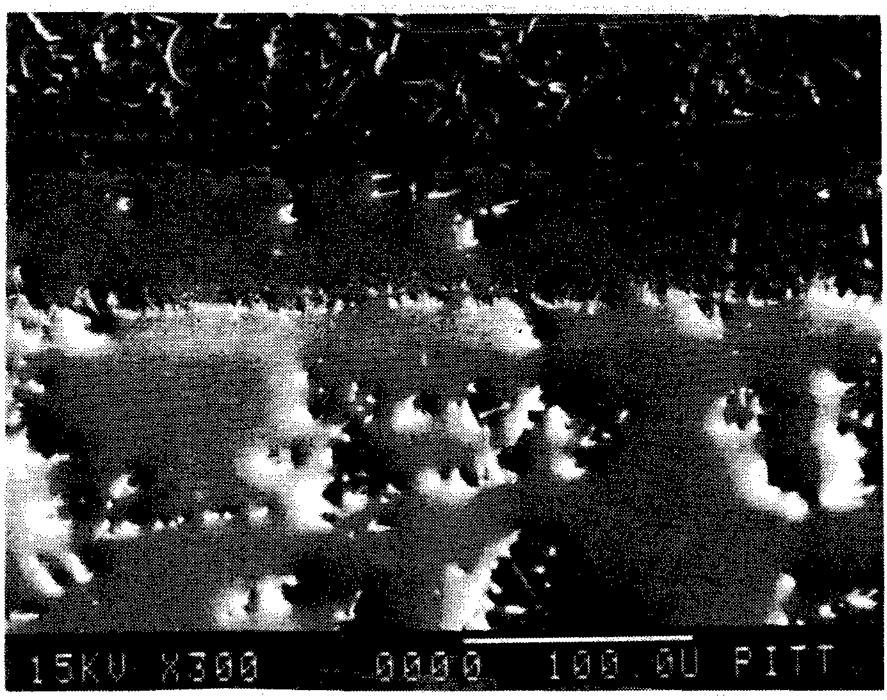

Figure 19. Cross section of Co-Dep coated CMSX-3 after 24 hours exposure to low temperature hot corrosion conditions at 700°C.

Effects of Intermittent Hot Corrosion on Cyclic Oxidation Behavior

The effect of temporary exposure to hot corrosion conditions on the subsequent high temperature oxidation characteristics of Pt-modified aluminide coatings was investigated in a limited number of experiments. The coatings applied by Turbine Components, Incorporated on PWA 1480 were exposed either to low temperature hot corrosion conditions isothermally for 20 hours, or to cyclic hot corrosion conditions for 60 cycles and then put into a cyclic oxidation test in air at 1100°C. The results of this test are presented in Figure 20 which includes the weight changes during both hot corrosion (indicated by arrows) and cyclic oxidation. The shape of the curves is similar for both specimens but weight loss is somewhat more rapid after the low temperature hot corrosion. Unfortunately, the same coating was not tested at 1100°C in the absence of hot corrosion. However, comparison with the data in Figure 9 for the cyclic oxidation of the Pt-modified coating produced by Howmet Corporation suggests that the exposure to either low or high temperature hot corrosion has greatly decreased the cyclic oxidation resistance of the coatings. This phenomenon should be investigated in greater detail since it appears likely that exposure to only intermittent hot corrosion conditions is a rather common occurrence for turbine hardware.

Effects of Other Precious Metals and Variation of Amount of Platinum in Coatings

Specimens which have been plated with different thicknesses of platinum and one thickness of rhodium prior to aluminizing are currently being procured. However, these are not yet available and no comment on the effect of these variables can be made at this time.

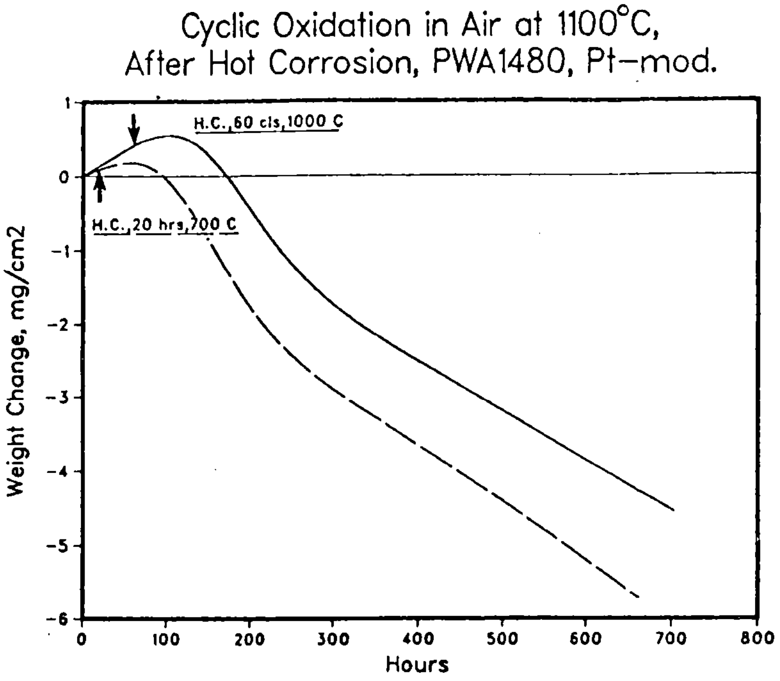

Figure 20. Weight change versus time data indicating the effect of prior exposure to hot corrosion conditions on the cyclic oxidation behavior of a Pt-modified aluminide coating on PWA 1480.

Selection of Coating System for Burner Rig Testing

The results obtained in this program show that platinum in coatings very significantly extends the lives of coatings when exposed to cyclic oxidation and to high temperature hot corrosion conditions. Furthermore, while the effect is less substantial, the platinum-modified coatings also perform better in low temperature hot corrosion conditions. It has not been possible in this program to show that improvements in platinum-modified coatings can be obtained by changing the amount or the type of precious metal. It also has been determined that the substrate composition plays a significant role in determining coating lives. Elements such as Hf extend cyclic oxidation lives, and refractory elements such as Ta are preferable to Mo or W. Pratt and Whitney have modified PWA 1480 considering such factors. It is, therefore, proposed that the burner rig tests be performed using modified PWA 1480 and using Turbine Components, Incorporated's platinum-modified diffusion aluminide coating.

Conclusions

Conventional and platinum-modified diffusion coatings on some state-of-the-art nickel-base superalloys have been compared in tests designed to establish high temperature oxidation conditions, high temperature hot corrosion conditions, and low temperature hot corrosion conditions which are representative of those encountered in gas turbines operating in a wide range of applications. The platinum-modified coatings have been found to be superior to the conventional aluminides in all of these tests. Significant remarks with regard to the performance of the platinum-modified coatings are as follows:

- The platinum-modified coatings always performed better in cyclic oxidation than the conventional aluminide, and the magnitude of the increase in life due to platinum was greater when Hf was present in the superalloy substrate.
- Platinum in the diffusion aluminides improves resistance to high temperature oxidation, apparently because it causes the aluminum in the coatings to be selectively oxidized for longer periods of time.
- Platinum in coatings improves their resistance to high temperature hot corrosion. The magnitude of this effect is also dependent on substrate composition; namely, the type and amounts of refractory elements.
- The means by which platinum extends high temperature hot corrosion lives has not been clearly established, but it is proposed that it results in part from the improved resistance to high temperature oxidation.
- Platinum-modified coatings are more resistant to low temperature hot corrosion, but difference in lives is not as great as the improvement produced by platinum in high temperature oxidation and high temperature hot corrosion.
- Limited data indicate that intermittent exposure to either low or high temperature hot corrosion conditions degrades the subsequent resistance of Pt-aluminide coatings to cyclic oxidation. The mechanism and extent of this degradation should be investigated further.
- More work is required to determine if other precious metals, different amounts of precious metals, or combinations of certain precious metals, and other elements such as Hf, can be used to obtain coatings superior to the current platinum-modified coatings.

References

1. LEVY, M., FARRELL, P., and PETTIT, F. S. *Corrosion*, v. 42, 1986, p. 708; also U.S. Army Research Laboratory, MTL TR 87-40, August 1987.
2. LEVY, M., HUIE, R., and PETTIT, F. S. *Corrosion*, v. 45, 1989, p. 661; also U.S. Army Research Laboratory, MTL TR 89-26, April 1989.
3. Process developed by Pratt and Whitney Aircraft.
4. Process developed by General Electric Corporation.
5. PETTIT, F. S., and GIGGINS, C. S. *Hot Corrosion*. Superalloys II, C. T. Sims, N. S. Stoloff, and W. C. Hagel, eds., John Wiley and Sons, ch. 12, 1987.
6. FELTEN, E. J., and PETTIT, F. S. Oxid. of Met., v. 10, 1976, p. 189.
7. ASHARY, A., MEIER, G. H., and PETTIT, F. S. *Acoustic Emission Study of Oxide Cracking During Alloy Oxidation*. Proceedings of High Temperature Protective Coating, S. C. Singhal, ed., AIME, Atlanta, GA, 1983, p. 105.
8. HITTLE, D. P., and STRINGER, J. Phil. Trans. Roy, Soc., London, v. 309, 1980, p. A295.
9. GOLIGHTLY, F. A., STOTT, F. H., and WOOD, G. C. Oxid. of Met., v. 10, 1976, p. 163.
10. SCHAEFFER, J. M. S. Thesis, University of Pittsburgh, 1987.
11. PETTIT, F. S., and MEIER, G. H. University of Pittsburgh. Unpublished data.
12. WOOD, J. H., and GOLDMAN, E. *Protective Coatings*. Superalloys II, ch. 13.
13. WU, W. T., RAHMEL, A., and SCHORR, M. Oxid. of Met., v. 22, 1984, p. 59.
14. MEIER, G. H., and PETTIT, F. S. *Hot Corrosion of Metallic Alloys and Stabilized Zirconia*. University of Pittsburgh, Annual Report on ONR Contract No. N00014-81-K-0355/P00007, June 1988.

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
	Commander, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: AMSRL-OP-CI-AD, Technical Publishing Branch
1	AMSRL-OP-CI-AD, Records Management Administrator
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22304-6145
2	ATTN: DTIC-FDAC
1	MIAC/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211
1	ATTN: Information Processing Office
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCSCI
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, Director
	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35809
1	ATTN: AMSMI-RD-CS-R/Doc
1	AMSMI-CS, R. B. Clem
	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
2	ATTN: Technical Library
	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1	ATTN: AMSTA-ZSK
1	AMSTA-TSL, Technical Library
1	AMSTA-RCK
1	PEO-ASM, PM-Bradley, SFAE-ASM-BV-SC
1	PEO-ASM, PM-Abrams, SFAE-ASM-AB-S
	Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005
1	ATTN: SLCBR-TSB-S (STINFO)
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: Technical Information Office
	Director, Benet Weapons Laboratory, LCWSL, USA AMMCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
1	AMSMC-LCB-R
1	AMSMC-LCB-RM
1	AMSMC-LCB-RP
	Office of the Project Manager, Tank Main Armament Systems, Picatinny Arsenal, NJ 07806-5000
1	ATTN: AMCPM-TMA
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901
3	ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger

No. of Copies	To
	Commander, U.S. Army Aviation Systems Command, Aviation Research and Technology Activity, Aviation Applied Technology Directorate, Fort Eustis, VA 23604 -5577
1	SAVDL-EU-TAP
	U.S. Army Aviation Systems Training Library, Fort Rucker, AL 36360
1	ATTN: Building 5906-5907
	Commander, U.S. Army Aviation Systems Command, 4300 Goodfellow Boulevard, St. Louis, MO 63166
1	ATTN: AMSAV-GTD
1	AMSAV-E
1	AMCPEO-AV
1	Dr. K. Bhansali
	Naval Research Laboratory, Washington, DC 20375
1	ATTN: Code 5830
1	Code 2627
	Chief of Naval Research, Arlington, VA 22217
1	ATTN: Code 471
	Commander, U.S. Air Force Wright R&D Center, Wright-Patterson Air Force Base, OH 45433-6523
1	ATTN: WRDC/MLLP, D. M. Forney, Jr.
1	WRDC/MLBC, Mr. Stanley Schulman
1	WRDC/MLXE, A. Olevitch
	NASA - Marshall Space Flight Center, MSFC, AL 35812
1	ATTN: Mr. Paul Schuerer/EH01
	Chief of Naval Research, Washington, DC 20350
1	ATTN: OP-987, Director
	Aeronautical Systems Division (AFSC), Wright-Patterson Air Force Base, OH 45433-6503
1	ATTN: ASD/ENFEF, D. C. Wight
1	ASD/ENFTV, D. J. Wallick
1	ASD/XRM, G. B. Bennett
	Air Force Flight Dynamics Laboratory, Wright-Patterson Air Force Base, OH 45433
1	ATTN: AFFDL/FIES, J. Sparks
	NASA - Ames Research Center, Army Air Mobility Research and Development Laboratory, Mail Stop 207-5, Moffet Field, CA 94035
1	ATTN: SAVDL-AS-X, F. H. Immen
	NASA - Johnson Spacecraft Center, Houston, TX 77058
1	ATTN: JM6
1	ES-5
	Naval Air Systems Command, Department of the Navy, Washington, DC 20360
1	ATTN: AIR-03PAF
1	AIR-5203
1	AIR-5164J
1	AIR-530313
	Naval Post Graduate School, Monterey, CA 93948
1	ATTN: Code 57BP, R. E. Ball

No. of Copies	To
	Naval Surface Weapons Center, Dahlgren Laboratory, Dahlgren, VA 22448
1	ATTN: Code G-54, Mr. J. Hall
1	Code G-54, Dr. B. Smith
	Commander, Rock Island Arsenal, Rock Island, IL 61299
1	ATTN: SMCRI-SEM-T
	Armament Systems, Inc., 326 W. Katella Avenue, 4-K, Orange, CA 92667
1	ATTN: J. Musch
	Beech Aircraft Corporation, 9709 E. Central Avenue, Wichita, KS 67206
1	ATTN: Engineering Library
	Bell Helicopter Company, A Textron Company, P.O. Box 482, Fort Worth, TX 76101
1	ATTN: J. R. Johnson
	Boeing Helicopters, P.O. Box 16858, Philadelphia, PA 19142-0858
1	ATTN: N. Caravasos, M/S P30-27
1	Cessna Military, P.O. Box 7704, Wichita, KS 67277-7704
	Fairchild Industries, Inc., Fairchild Republic Company, Conklin Street, Farmingdale, Long Island, NY 11735
1	ATTN: Engineering Library, G. A. Mauter
	FMC Corporation, Central Engineering Labs, 1185 Coleman Avenue, Box 80, Santa Clara, CA 95052
1	ATTN: Gary L. Boerman
	Gruman Aerospace Corporation, South Oyster Bay Road, Bethpage, NY 11714
1	ATTN: Technical Information Center, J. Davis
	McDonnell Douglas Helicopter Co., 5000 East McDowell Road, Mesa, AZ 85205-9797
1	ATTN: Library
1	Mr. A. Hirko
	IIT Research Institute, 10 West 35th Street, Chicago, IL 60616
1	ATTN: K. McKee
	Kaman Aerospace Corporation, Old Winsor Road, Bloomfield, CT 06002
1	ATTN: H. E. Showalter
	Lockheed-California Company, A Division of Lockheed Aircraft Corporation, Burbank, CA 91503
1	ATTN: Technological Information Center, 84-40, U-35, A-1
	Vought Corporation, P.O. Box 5907, Dallas, TX 75232
1	ATTN: D. M. Reedy, 2-30110
	Martin Marietta Corporation, Orlando Division, P.O. Box 5837, Orlando, FL 32805
1	ATTN: Library, M. C. Griffith
	McDonnell Douglas Corporation, 3855 Lakewood Boulevard, Long Beach, CA 90846
1	ATTN: Technical Library, C1 290/36-84
	Northrop Corporation, Aircraft Division, 3901 W. Broadway, Hawthorne, CA 90250
1	ATTN: Mgr. Library Services, H. W. Jones
	Parker Hannifin, 14300 Alton Pkwy., Irvine, CA 92718-1814
1	ATTN: C. Beneker
	Sikorsky Aircraft, A Division of United Aircraft Corporation, Main Street, Stratford, CT 06601
1	ATTN: Mel Schwartz, Chief of Metals

No. of Copies	To
	Teledyne CAE, 1330 Laskey Road, Toledo. OH 43697
1	ATTN: Librarian
	Georgia Institute of Technology, School of Mechanical Engineering, Atlanta, GA 30332
1	ATTN: Mechanical Engineering Library
	Lukens Steel Company, Coatesville, PA 19320
1	ATTN: Dr. E. Hamburg
	Republic Steel Corporation, 410 Oberlin Avenue SW, Massillon, OH 44646
1	ATTN: Mr. R. Sweeney
1	Mr. W. H. Brechtel
1	Mr. T. M. Costello
	Ingersoll Rand Oilfield Products Division, P.O. Box 1101, Pampa, TX 79065
1	ATTN: Mr. W. L. Hallerberg
	SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025
1	ATTN: Dr. D. Shockey
	Illinois Institute of Technology, Metallurgical and Materials Engineering Department, Chicago, IL 60616
1	ATTN: Dr. Norman Breyer
	Corpus Christi Army Depot, Corpus Christi, TX 78419
1	ATTN: SDSCC-QLS
	Naval Air Warfare Center, Warminster, PA 18974-5000
1	ATTN: Dr. Uinod S. Agarwala (Code 6062)
	Ohio State University, Department of Metallurgical Engineering, Columbus, OH 43212
1	ATTN: Dr. B. Wilde
	LRA Laboratories Inc., 18195A East McDurmott, Irvine, CA 92714
1	ATTN: Dr. Lou Raymond
	McDonnell-Douglas Helicopter Co., Mesa, AZ 85205
1	ATTN: J. Hawkins
	U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
2	ATTN: AMSRL-OP-CI-D, Technical Library
1	AMSRL-OP-CI-D, Visual Information
1	AMSRL-OP-PR-WT
16	AMSRL-MA-MA, Milton Levy COR