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The Effects of Oxidation-Induced Failures on Thermal Barrier Coatings with Platinum Aluminide and NiCoCrAlY Bond Coats

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13. ABSTRACT (Maximum 200 words)

This program has been directed at determining the mechanisms by which oxidation causes failure of thermal barrier coatings (TBCs) and developing modified systems with improved resistance to oxidation-induced failures. The thermal barrier coating was yttria stabilized zirconia (YSZ) deposited via electron beam vapor deposition (EBPVD). This TBC was deposited on both platinum aluminide and NiCoCrAlY bond coats which in turn were deposited on superalloy substrates of Rene N5.

The oxidation testing was performed at 1000°, 1100° and 1200°C in air using cyclic exposures. The approach consisted of initially examining state-of-the-art systems and based upon the results obtained to prepare modified TBCs. Emphasis was placed upon bond coat modifications. In the case of the NiCoCrAlY bond coats it was found that defects in the as-processed coatings at the TBC-bond coat interface caused failures. Procedures to prevent the formation of such defects extended TBC lives. The lives of TBCs on platinum-aluminide bond coats were influenced by ratcheting of the bond coat at the bond coat-TBC interface. Polishing of bond coats prior to TBC deposition is proposed to inhibit ratcheting and extend TBC lives.

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ABSTRACT

The objective of this program was to understand the mechanisms controlling the durability of Thermal barrier Coatings (TBCs) and use this understanding to develop new TBCs with improved performance characteristics. The system studied consisted of the single crystal superalloy René N5 as a substrate and yttria-stabilized zirconia as a ceramic topcoat prepared by electron beam physical vapor deposition (EB-PVD). The parameters which were varied were the type and fabrication condition of the bond coat. Two general types of bond coat were studied; a platinum modified aluminide and a NiCoCrAlY overlay.

The degradation behavior of the state-of-the-art systems during thermal cycling was evaluated in the first stage of the study. It was found that the times to failure (TBC spallation) were shorter for the NiCoCrAlY bond coats than the platinum aluminides. The failure mode for the NiCoCrAlY bond coats was found to involve fracture initiation at defects at the bond coat/TBC interface which then propagated along the interface between the bond coat and the thermally-grown aluminum oxide layer (TGO) which formed on the bond coat. Therefore, in the second stage of the study, processing methods to minimize the effects of these defects were investigated. These included overaluminizing and deposition of a thin platinum overlayer on the bond coat prior to TBC deposition. Both techniques improved coating lives with the Pt overlayer having the most dramatic effect. Layers of Pt deposited under the NiCoCrAlY resulted in minimal improvement, which is consistent with the proposed failure mode.

The failure of the Pt aluminide was found to involve a combination of fracture along the TGO/ bond coat interface and a deformation mode of the bond coat known as "ratcheting". A variety of modifications were made to the Pt aluminide bond coats. These included variation of the coating thickness, Pt-content, and surface preparation (grit blasting, media polishing, etc.). Variation of the bond coat thickness and Pt-content did not produce a dramatic increase in TBC life. However, the results indicated that the surface condition of the platinum-aluminide bond coat did significantly affect TBC life.

Finally, the application of the TBC directly on the superalloy (without a bond coat) was studied. In some cases these specimens exhibited significant lives, particularly when a thin Pt layer was deposited on the alloy prior to TBC deposition. The potential of these "no bond coat" systems must be further evaluated.

In conclusion, it is believed that this program has been highly successful, particularly in that it has involved translation of knowledge gained in mechanistic studies to practical improvements in an important engineering system.

INTRODUCTION

The use of thermal barrier coatings (TBCs) has resulted in a significant improvement in the efficiency of aircraft gas turbines(1-3). These types of coatings have been used for many years on combustion liners, but with advanced thermal barrier coatings, vanes, and even the leading edges of blades can now be coated. The use of TBCs can achieve temperature differentials across the coating of as much as 200°C. Typical systems consist of a nickel-base superalloy substrate coated with a MCrAlY or diffusion aluminide bond coat, onto which is deposited a yttria-stabilized zirconia (YSZ) TBC. The bond coats are usually deposited via diffusion aluminizing processes or low-pressure plasma spray (LPPS). The YSZ can be deposited by air plasma spraying (APS) or electron beam physical vapor deposition (EBPVD). Typical microstructures are presented in Figure 1. The EBPVD coatings are used for the most demanding applications, such as the leading edges of airfoils.

The objective of this program was to develop new thermal barrier coatings (TBCs) with improved performance characteristics. The approach consisted of attempting to understand the mechanisms controlling the durability of TBCs and use this understanding to obtain new systems. The development of such coatings is not a straightforward task, since there are a number of different types of TBCs, which can be degraded via oxidation, hot corrosion, and erosion. Another difficulty with such a program is the logistics involved in preparing specimens for testing. Facilities and experience in fabrication procedures must be available to fabricate state-of-the-art TBC systems. The equipment can be expensive, but a more important factor is the experience that is required to prepare TBC systems that are relevant and competitive. In this program the degradation of TBCs by oxidation was emphasized because this mode is most frequently encountered. The logistic, specimen preparation, difficulty has been overcome by working closely with a gas turbine manufacturer (GE Aircraft Engines) and coatings vendors (Praxair and Howmet). All the coatings and coatings' modifications in this program have been made by one of these companies.

The selection of the initial TBC systems to be studied was based upon a number of factors. A substantial amount of data on TBCs is currently available in the literature(3-8). For example, it has been reported for plasma-sprayed TBCs that bond coats which are "good alumina formers" provide the longest lives and result in fracture within the zirconia some distance above the bond coat(3-5). Bond coats which tend to produce significant amounts of spinel in the oxide layer supposedly result in spallation at the zirconia/bond coat oxide interface and generally exhibit shorter lives. Longer lives have been achieved by prealuminizing a NiCrAlY bond coat(5), controlled preoxidation to form alumina(4), and direct deposition of alumina diffusion barriers onto the bond coat(6-9). An indirect, but critical, factor is the adherence of the alumina to the bond coat. It is believed that some results in the literature which ascribe improved TBC performance to changes in aluminum and chromium content of the bond coat(8) are partially the result of yttrium content and, therefore, alumina adherence. The data available on EBPVD TBCs is not as extensive as that for plasma spray TBCs. It is often stated that spallation of the ceramic TBC involves fracture along the TGO-bond coat interface(9-10). Some investigators have proposed that the microstructure of the bond coat plays a significant role in EBPVD TBC failures(10). The available literature, however, does not permit conclusive statements to be made in regard to the performances of different, specific TBC systems. The reasons for this situation are discussed in the following.

The ceramic YSZ coatings have been fabricated using EBPVD and PS processing. Furthermore, such coatings have been prepared by different fabricators. It is often stated that

EBPVD YSZ TBCs outperform PS YSZ TBCs, and that EBPVD TBCs fail at the TGO-bond coat interface, whereas PS TBCs fail at the splat boundaries in the YSZ. However, close examination of the available results shows that comparison of EBPVD and PS YSZ TBCs must be done with care because such coatings have different characteristics. For example PS YSZ TBCs are usually much thicker than EBPVD YSZ TBCs. It has also become evident that the failure modes of TBCs are influenced by test conditions, namely, temperature, gas environment, and cyclic versus isothermal testing. Therefore, failure modes have significance only when coupled with the test conditions.

In view of the current situation, it was decided to initiate the current program by focusing on EBPVD TBCs and to investigate the influences of bond coats on TBCs lives. Plasma sprayed TBCs are not to be ignored, but the lives of such TBCs will be examined in another program subsequent to understanding and improving EBPVD TBCs in the current program. The TBC was 8 wt.% yttria stabilized zirconia since this TBC is the current state-of-the-art.

The bond coats which are currently considered state-of-the-art are platinum modified diffusion aluminides and MCrAlY coatings. In this program, different modifications of MCrAlY coatings and platinum aluminide bond coats have been studied. The approach consisted of starting the program by investigating current state-of-the-art bond coats. As results were obtained on the failures of these TBCs, modifications were made to attempt to obtain new improved systems.

In summary the objectives of this program are,

- To compare the failures of EBPVD YSZ TBCs on platinum aluminide and NiCoCrAlY bond coats after exposure to oxidizing environments
- To develop models to describe the failure of TBCs on each of these bond coats
- To make modifications to the bond coats to extend TBC lives.

EXPERIMENTAL

A large number of TBC specimens have been fabricated and studied in this program. All of the TBCs were deposited upon the single crystal superalloy substrate René N5 (Ni – 7.5Co – 7.0Cr – 1.5Mo – 5.0W – 3.0Re – 6.5Ta – 6.2Al – 0.15Hf – 0.05C – 0.004B – 0.01Y in wt%). The ceramic topcoat was 8 wt% yttria stabilized zirconia deposited via EBPVD using commercial coating equipment operated by Praxair, Howmet and GE. Two types of bond coats were investigated, namely, platinum aluminides and NiCoCrAlY coatings. In this program as shown in Figure 2 the initial TBC systems that were studied were state-of-the-art. As results became available and failure mechanisms began to be developed, TBCs with modified bond coats were prepared and tested. After the modified TBC systems had been evaluated, additional recommendations for improved bond coats were formulated. In Table 1 the state-of-the-art systems and the modified systems are identified.

The state-of-the-art systems consisted of three types of platinum aluminide bond coats identified as A, B and C. One platinum aluminide was prepared by GE, the other two were prepared by Howmet. All three bond coats were fabricated by using electrolytic deposition of about 5 – 7 μm of platinum, followed by an anneal to permit some interdiffusion between the superalloy substrate and the platinum layer, which in turn was followed by chemical vapor deposition of aluminum. The two Howmet aluminides used different electrolytic processes to deposit platinum. One involved a phosphate electrolyte and the other utilized an hydroxide electrolyte. A schematic showing a typical TBC and bond coat is presented in Figure 3. An as-processed TBC with a platinum aluminide bond coat is shown in Figure 4. A typical compositional profile across an as processed platinum aluminide bond coat is presented in Figure 5. The bond coat is usually composed of large columnar grains of β phase (NiPt)Al. The characteristics of the bond coat at the TBC interface are determined by the surface condition of the bond coat prior to TBC deposition. During TBC deposition an alumina scale (thermally grown oxide, TGO) develops between the bond coat and the TGO. The stable form of the TGO is α-Al_2O_3, but depending upon the surface condition of the bond coat, as well as deposition conditions and bond coat pretreatments, other forms of alumina can develop during the early stages of TGO formation. In Figure 6 an as-processed TBC with a platinum aluminide bond coat that was grit blasted prior to TBC deposition is compared to a TBC system where the bond coat was not given any surface preparation. As will become obvious in this report, the surface condition of the bond coat prior to TBC deposition is an important factor affecting TBC lives. In this program two types of grit blasting of bond coat surfaces were used. One type was a heavy grit blast, 8 grit (2mm) Al_2O_3 at 60 – 80 psi. The other was a light grit blast, 220 grit (700μm) Al_2O_3 at 25 psi.

The NiCoCrAlY bond coats (Ni – 22Co – 16Cr – 13Al – 0.05Y) were deposited by Praxair using an argon shrouded plasma spray process (NiCoCrAlY A) and by a detonation process (NiCoCrAlY B). The powder used was of prealloyed composition. The coatings were vacuum heat treated, peened with stainless steel shot and vibratory finished with alumina media to provide a surface roughness of 1.5 μm Ra. Prior to TBC deposition, the coatings were given the heavy grit blast producing a surface roughness of 1.8 – 2.0 μm Ra. These coatings have been used successfully as bond coats for thermal sprayed TBC systems. A purpose of the current research was to determine if these same type thermally sprayed bond coats could be adapted to a mixed process TBC having the EBPVD ceramic topcoat. The natural roughness of the thermal spray bond coat has provided the mechanical bond believed important in the fully thermal sprayed system. For the EBPVD ceramic bonding, different mechanisms may be important and the surface of the NiCoCrAlY bond coat may require modification for optimum performance. The compositions of NiCoCrAlY A and B are presented in Table 2. A typical as processed TBC with a NiCoCrAlY bond coat is shown in Figure 7. The modified TBCs that were prepared based upon the results obtained with the state-of-the-art systems are described in Table 1. The TBCs were deposited by GE, Praxair and Howmet. Modifications were made to both the platinum aluminide and NiCoCrAlY bond coats. The specific modifications will be described subsequently after results from the state of the art systems have been discussed.

Some specimens were prepared with bond coats but without TBCs in order to examine the degradation of the bond coats during cyclic oxidation testing. The oxidation experiments for all specimens were performed in laboratory air in a bottom-loading furnace made by C & M Furnaces. The cycle consisted of: 10 minute heating from room temperature to 1100°C, 45 minutes at temperature, and forced air cooled from 1100°C to room temperature in 10 minutes. A typical cycle is presented in Figure 8. The testing was performed using 20-1 hr cycles after which the specimens were examined visually. The first cycle to temperature consisted of a 20 minute heat to temperature rather than a 10 minute heat. Between 20 hr cycles the specimens were retained in a desiccator. Most experiments were performed at 1100°C but a few experiments were performed in the same furnace but at temperatures of 1000° and 1200°C.

All exposed specimens, including those with TBCs or bond coats without TBCs, were examined as a function of exposure time using XRD, optical metallography and scanning electron microscopy.

RESULTS AND DISCUSSION

Oxidation Degradation of NiCoCrAlY and Platinum Aluminide Bond Coats with No TBCs

Before discussing the results obtained with the state-of-the-art TBC systems the oxidation characteristics of the bond coats without TBCs will be described. Both of the NiCoCrAlY bond coats and the platinum aluminide bond coats were cyclically oxidized at 1100° and 1200°C in the same furnace that was used to test the TBC specimens. The surface of the platinum aluminide bond coat became severely deformed during oxidation, Figure 9a, and voids developed in the bond coat just beneath the TGO. When the TGO above the void cracked, oxide was evident on the surface of the void, Figure 9b. The oxide scale did not spall excessively from the platinum aluminide bond coat but cracks were evident, Figure 10, in the alumina scale after cyclic oxidation. In cases where the alumina did spall it was not unusual to observe a refractory metal rich phase at the coating-TGO interface, Figure 11. Such phases were also observed at grain boundaries in the bond coat Figure 11c.

The oxidation characteristics of the two NiCoCrAlY coatings were similar to one another. On both of these coatings α-Al_2O_3 scales were developed during oxidation but there was also a significant amount of oxide protrusions that developed due to oxidation of yttrium in the coatings, Figure 12. Such oxide protrusions were more pronounced in NiCoCrAlY A compared to NiCoCrAlY B, Figure 13. The formation of these oxide protrusions is caused by the oxidation of yttrium. The yttrium oxide provides for rapid transport of oxygen into the coating. More work is required to completely understand how these protrusions are formed and how the frequency of these protrusions is influenced by the yttrium content of the coating. Spalling of the α-Al_2O_3 scales from these coatings was not excessive but appeared to be greater than that for the platinum aluminide coating, Figure 13a. Refractory metal rich (Re, W) phases were also observed in some of these coatings due to interdiffusion between the coating and the substrate, Figure 13c.

While the initial oxidation degradation of the NiCoCrAlY coatings appeared to be more severe than the platinum aluminide coating, after 3000 hrs of cyclic oxidation both coatings appeared to be close to failure. It is, therefore, believed that the oxidation resistance of these bond coats is about the same.

Results Obtained from the Oxidation Testing of the State-of-the-Art TBCs

The failure times of the state-of-the-art TBCs are presented in Table 3. It can be seen that the TBCs on the NiCoCrAlY bond coats had shorter failure times than TBCs on platinum aluminide bond coats. Also for both types of bond coats, the failure times decreased as the temperature of exposure was increased.

A substantial difference between the failure times for the platinum aluminide bond coats A, B and C was not apparent, Table 3. Furthermore, the failure characteristics were also similar. The TBC failures on the platinum aluminide bond coats occurred in the TBC near the TGO, Figure 14, and at times along the TGO-bond coat interface. When failure was in the TBC near the TGO, ratcheting(11) had occurred during cyclic oxidation, Figure 14. This ratcheting caused pieces of the TBC to become detached as shown in Figure 15. In those areas where ractcheting was not excessive, the failure proceeded along the TGO-bond coat interface, Figure 16.

In the case of the NiCoCrAlY bond coats, the TBC failures occurred predominantly along the TGO-bond coat interface with numerous excursions into the TGO and the TBC, Figure 17. In the as processed TBCs defects at the TBC-TGO-bond coat interfaces were observed. These defects consisted of, areas where the TBC was detached from the TGO and bond coat, Figure 18, areas where cracks initiated at locations where transient oxides had formed in the TGO, Figure 19, oxide protrusions that extended into the bond coat due to reactive element oxidation, Figure 17c, and oxide inclusions that were in the as-processed bond coats. To examine the fracture path of the TBCs as a function of exposure time, an indent test(12) was used to cause failure of the TBC at times shorter than that caused by cyclic oxidation. The results obtained from this test are presented in Figure 20. Failure of the as processed specimen was predominantly along the TGO-TBC interface. This result shows that this interface is weak but sufficient strain energy in the TBC to cause failure is not present. As the specimen is exposed to oxidation the fracture path progressively changes from the TGO/TBC interface to the TGO/bond coat interface as the stored elastic energy in the TGO increases due to TGO growth. It is proposed that the as processed defects initiate failure at the TBC-TGO interface as the TGO thickens with crack propagation through the TGO and along the TGO-TBC interface. When these surface defects along the TGO/TBC interface are of high density failure can occur by buckling of the TBC with the TGO remaining attached to the bond coat.

Modifications to TBC Systems Based Upon Results Obtained with the State-of-the-Art Systems

In the case of the NiCoCrAlY bond coats it appeared that the defects observed at the TBC-TGO interface played a role in initiating TBC failures. It was therefore decided to apply platinum overlayers to these bond coats prior to TBC deposition in order to attempt to remove these defects. These platinum (5 – 7 μm thick) overlayers were applied using electrolytic deposition followed by a 4 hr anneal at 1025°C in vacuum to permit some interdiffusion of the platinum with the NiCoCrAlY coating prior to TBC deposition. The bond coats were grit blasted prior to deposition of the platinum. Since some substrate elements were observed in the NiCoCrAlY bond coats, a platinum layer was also deposited on a separate set of superalloy substrates prior to depositing the NiCoCrAlY bond coats and TBCs to attempt to inhibit interdiffusion between the substrate and bond coat. Since a substantial amount of transient oxidation was observed on the NiCoCrAlY bond coats, some modified TBCs were also prepared using aluminized bond coats prior to TBC deposition. Finally, since the NiCoCrAlY bond coats were deposited by spray processes, the edges of the test coupons often were not completely covered with bond coat. To determine if this condition could lead to early failure of TBCs on NiCoCrAlY bond coats, some test coupons of N5 were coated with an aluminide coating on all surfaces, and this coating was removed from one surface by polishing followed by NiCoCrAlY bond coat and TBC deposition. These modified NiCoCrAlY bond coats are described in Table 1. For comparison during testing TBCs were also prepared with no modifications other than to ensure that good processing practices were followed and these TBCs are described in Table 1 as "optimized compositions". The modified NiCoCrAlY bond coats were coated with YSZ TBCs in EBPVD coaters at Praxair, Howmet and GE. The purpose of having TBCs deposited by three different sources was to determine if deposition of the ceramic TBC affected TBC lives.

In considering the results obtained with the state-of-the-art TBCs with platinum aluminide bond coats, a substantial difference in TBC lives was not observed for the different platinum aluminide bond coats (i.e. A, B, and C). It was decided to modify the platinum aluminide bond coats by varying the thickness of the platinum layers deposited prior to aluminizing, and by varying the thicknesses of the aluminide coating. The different combinations that were prepared are described in Table 1. As in the case of the NiCoCrAlY bond coats, TBCs were deposited on these modified platinum aluminide bond coats by EBPVD coaters at Praxair, Howmet and GE. In the case of TBCs deposited by GE, the bond coats were given a heavy grit blast whereas those prepared by Howmet were given a light grit blast. For TBCs deposited by Praxair the bond coats were not grit blasted.

Results Obtained from Oxidation Testing of the Modified TBC Systems

NiCoCrAlY Bond Coats

In Table 4 the failure times for the various modifications of the NiCoCrAlY A and NiCoCrAlY B TBC systems are presented. It can be seen that the failure times for the unmodified TBCs are similar to those obtained previously with the state-of-the-art systems. Moreover the application of an aluminide coating to the sides of the specimens did not affect the lives of the TBCs with NiCoCrAlY bond coats. On the other hand all of the modifications to the NiCoCrAlY bond coats appeared to improve the performances of the TBCs. The presence of the platinum underlayer did not produce a large increase in TBC lives but all specimens failed consistently after about 160 cycles which is greater than failure times for the unmodified TBCs. Aluminizing the NiCoCrAlY bond coats extended the TBC lives to between 220 to 480 cycles. The largest improvement in TBC lives was observed for the platinum overlayer where failure times ranged between 600 and 1240 cycles with an average of 925 cycles based upon results obtained from four tests. A chart comparing TBC failure times for NiCoCrAlY bond coats and NiCoCrAlY bond coats with platinum overlayers and underlayers is presented in Figure 21. The platinum underlayer may have inhibited substrate elements from entering the coating, but since the effect of the underlayer on TBC performance was not large, this modification will not be considered in this report. The aluminized NiCoCrAlY bond coat performed better than the TBCs on the unmodified bond coats. As shown in Figure 22 the aluminized NiCoCrAlY bond coat appears to have fewer defects in the bond coat-TGO-TBC region compared to the unmodified bond coats, Figures 17, 18 and 19. Nevertheless this modification will not be considered in more detail in this report. The platinum overlayer modification on the NiCoCrAlY bond coats extended TBC lives close to those for the state-of-the-art platinum aluminide bond coats. An as-processed TBC with a platinum overlayer is presented in Figure 23. The platinum layer adjacent to the TBC is uneven because it was deposited on a NiCoCrAlY bond coat that had been grit blasted. However, it can be seen, Figure 23, that a thin TGO of Al_2O_3 has developed between the platinum layer and the TBC. Examination of this TGO revealed that no defects were present. The surface of the bond coat after TBC failure is shown in Figure 24. The failure path is in the TGO and the TBC. There is no failure along the TGO-bond coat interface. In Figure 25 the platinum overlayer, TBC and TGO can be seen prior to failure and at failure. It can be seen that cracks initiate in the TBC and propagate into the TGO. Failure appears to be by cracking in the TGO. Cracking in the TGO near the TBC may reduce the stored elastic energy in the TGO which is the driving force for cracking along the TGO-bond coat interface. Hence, such cracking in the TGO may also be causing TBC lives to be extended. It is necessary to examine TBCs with platinum overlayers where the initial TBC-bond coat interface is more smooth compared to that shown in Figure 23. Patents(13, 14) are available in the literature that propose the use of platinum layers in fabricating TBCs will produce beneficial effects, but no results to document such effects are available in the open literature.

The results obtained with the modified NiCoCrAlY bond coats show defects in the vicinities of the TGO-TBC and TGO-bond coat interfaces, Figure 26, cause the TBCs to fail. When the defect density is high failure may occur along the TGO-TBC interface. When the defect density is lower but still significant, growth of the TGO increases the elastic strain energy in the TGO and failure is initiated at these defects but with the high strain energy in the TGO the cracks propagate through the TGO and proceed along the TGO-bond coat interface.

Platinum Aluminide Bond Coats

In the case of the modified platinum aluminide bond coats the failure times are presented in Table 5. At the present time no trends are evident in TBC lives for the different combinations of platinum thicknesses and aluminide thicknesses. It is apparent, however, that the surface condition of the platinum aluminide bond coats may be important in regard to TBC lives. The shortest lives appear to be the TBCs with as processed bond coat surfaces, followed by a heavy grit blast, and then the light grit blast with the media finish having the longest TBC lives. The 0.5 mil Pt + 3 mil aluminide had a very short TBC life but this may have been caused by a processing problem and an additional specimen of this bond coat is being tested. The media finish also involved a subsequent Howmet proprietary treatment after the media finish.

The failures in the case of the TBCs on the platinum aluminide bond coats were essentially the same as those for the state-of-the-art platinum aluminide TBCs. Ratcheting of the TBC and TGO was evident, Figures 14, 15 and 16. The specimens that were given the light grit blast and the media finish had failure times of 1780 and 2280 cycles, respectively, which are significantly larger than failure times for the state-of-the-art TBCs. In Figure 27, cross sections of the as-processed TBCs with the light grit blast and the media finish are presented. The TGOs on these specimens are more smooth compared to the TGO on heavy grit blasted specimens, Figure 6a. The exposed specimens with the light grit blast and media finish surface conditions that failed have not been examined in detail as yet. Based upon the results available it appears that TBCs on platinum aluminide bond coats fail when the strain energy in the TGO exceeds the fracture toughness of the TGO-bond coat interface. Ratcheting(11) leads to premature TBC failures and smooth bond coat surfaces, Figure 27, result in longer TBC lives because ratcheting is less severe. Void formation was also evident in bond coats after TBC spallation, Figure 28. These voids developed at grain boundaries in the bond coat, Figure 28. At present the role of voids in the bond coat on TBC failures is not understood and more work is required to attempt to understand void development in bond coats.

No Bond Coat Systems

Some TBCs were prepared on N5 substrates where no bond coats were applied. Two types of no bond coat systems were prepared. In one type the N5 substrate was given the media finish and given an oxidation exposure prior to TBC deposition. In the other, a 5 – 7 μm platinum layer was deposited on the N5 substrate followed by an anneal (4 hrs at 1025°C in vacuum). This type of specimen was then given a media finish followed by the preoxidation treatment and then the TBC was deposited. Both of these specimens were tested in the bottom loading furnace at 1100°C. The no bond coat without the platinum layer failed after 140 cycles. The no bond coat with the platinum intermediate layer failed after 500 cycles. Additional specimens of these no bond coat specimens are now in test. The results that have been obtained to date show that TBC-no bond coat systems are possible, and more importantly, that the thin platinum intermediate layer can be used to improve TBC lives in no bond coat systems.

Comparison of the Temperature Dependences of TBC Failures on NiCoCrAlY and Platinum Aluminide Bond Coats

TBC specimens on NiCoCrAlY bond coats have been tested to failure at 1000°, 1100° and 1200°C. The logarithm of the reciprocal of the failure times is plotted versus reciprocal temperature in Figure 29. An Arrhenius relationship is followed with an activation energy of 356 kJ/mole. This activation energy is close to that obtained from the parabolic rate constants for the growth of α-Al_2O_3 scales on Pt-Al alloys(15). Data points for TBC failures on the platinum aluminide bond coats are only available for the temperatures of 1100° and 1200°C. These data points have been placed in Figure 29 and a line having the slope of that obtained with NiCoCrAlY bond coats drawn through these points. It can be seen that the failures of TBCs on the platinum aluminide bond coats are consistent with an activation energy of 356 kJ/mole (85.1 kcal/mole). The curve for the TBC failure on platinum aluminide bond coats has been extrapolated to 1000°C and a failure time of 14,791 hrs has been obtained. TBCs on platinum aluminide bond coats have been tested in a bottom loading furnace at 1000°C and failure had not occurred after 1420 cycles. These tests have been terminated since it was considered impractical to attempt to verify the extrapolated value.

The results that have been obtained with the temperature dependences of the TBC failures indicates that growth of the α-Al_2O_3 TGO is an important factor in TBC failure. However, other factors, such as defects in the case of the NiCoCrAlY bond coats, and ratcheting in the case of the platinum aluminide bond coats, also play a role in determining the actual failure time. A decrease in the growth rate of the TGO should also result in improved TBC performance. The growth of the TGO beneath a TBC on the NiCoCrAlY bond coat with the platinum overlayer conforms to the parabolic rate law, Figure 30, with a rate constant close to that for the growth of α-Al_2O_3 on platinum-aluminum alloys.(15) The α-Al_2O_3 growth on the NiCoCrAlY bond coats appears to be more rapid than on the NiCoCrAlY bond coat with the platinum overlayer, Figure 30, but it is not clear how important this condition is in regard to TBC failures on NiCoCrAlY bond coats.

RECOMMENDED MODIFICATIONS FOR IMPROVED PERFORMANCES OF TBCS ON NiCoCrAlY AND PLATINUM-ALUMINIDE BOND COATS

Based upon the results obtained from testing of the modified TBC systems the following new systems are being prepared and are the recommended new systems for this program.

In the case of the NiCoCrAlY bond coats, it is clear defects in the bond coat and in the TGO near the TBC must be eliminated. Consequently after NiCoCrAlY bond coat deposition it is necessary to modify the surface of these bond coats by polishing. The surface preparations to be considered (Table 1) are the media finish, polishing through 1 μm α-Al_2O_3 and the media finish followed by a preoxidation treatment to stabilize an α-Al_2O_3 TGO.

Since the platinum overlayer significantly improved TBC performance on NiCoCrAlY bond coats, this modification should be optimized, if possible. Several approaches should be considered, namely, a media finish to the NiCoCrAlY bond coat prior to deposition of platinum, and a media finish of the NiCoCrAlY bond coat followed by platinum deposition with a final media finish of the platinum overlayer. Finally, the growth rate of the α-Al_2O_3 TGO may be able to be reduced by subjecting bond coats to pretreatments that could be able to produce a rather coarse grained α-Al_2O_3 scale. Hence, in those modifications with platinum overlayers, preoxidation treatments will be used to attempt to preform coarse-grained α-Al_2O_3 TGOs. These recommended modifications are described in Table 1.

In the case of the platinum aluminide bond coats it is clear that surface modification should be examined as a means to extend TBC lives. As described in Table 1 several approaches are recommended to produce surface conditions appropriate for extending TBC lives. These include the media finish as well as preoxidation treatments to stabilize the α-Al_2O_3 TGO and also to attempt to coarsen the TGO grain size. It is also considered worthwhile to modify the sequence of applying the platinum layers in preparing platinum aluminide bond coats. In Table 1, some heavy grit blast samples for both NiCoCrAlY and platinum aluminide bond are included for base line comparisons.

FUTURE WORK

In this program models have been developed for the failures of TBCs on NiCoCrAlY bond coats and platinum aluminide bond coats. Also modifications have been formulated to improve the performances of TBCs on both of these bond coats. These modified systems are now being prepared and will be tested with funding from another program.

ACKNOWLEDGEMENTS

The authors greatly appreciate the assistance provided by Howmet Corporation (Bruce Warnes), Praxair Surface Technologies (Tom Taylor and Ann Bolcavage) and GE Aircraft Engines (Ram Darolia and Dave Wortman) for specimen preparation and many helpful technical discussions.

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Table 1
Sequence of Bond Coat Modifications for YSZ EBPVD TBCs on René N5 Substrates

State of the Art Systems
(All bond coats given heavy grit blast)
TBCs Deposited by GE
Bond Coats: Pt Aluminide A, Pt Aluminide B, Platinum Aluminide C, NiCoCrAlY A, NiCoCrAlY B

Initial Modifications

TBCs Deposited By Praxair (All bond coats given heavy grit blast)					
NiCoCrAlY A	Optimized composition	Aluminized Coating on Sides	Pt Underlayer	Pt Overlayer	Aluminized
NiCoCrAlY B	Optimized composition	Aluminized Coating on Sides	Pt Underlayer	Pt Overlayer	Aluminized
Platinum Aluminide	.25 mil Pt 1.5 mil Aluminide		.25 mil Pt 3 mil Aluminide		.5 mil Pt 3 mil Aluminide
TBCs Deposited by Howmet (All specimens given light grit blast)					
NiCoCrAlY A	aluminized				
Platinum Aluminide	.25 mil Pt 1.5 mil aluminide	.25 mil Pt 3 mil aluminide	.5 mil Pt 1.5 mil aluminide	.5 mil Pt 3 mil aluminide	.25 mil Pt * 1.5 mil aluminide

* Media finish and preoxidation

TBCs Deposited by GE
(All specimens given heavy grit blast)

NiCoCrAlY A	Optimized Composition	
Platinum Aluminide	.25 mil Pt 1.5 mil aluminide	.25 mil Pt 3. mil aluminide

Recommendations for Improved TBCs
TBCs to be Prepared by Praxair

NiCoCrAlY A	Heavy Grit Blast	Media Finish	1μm α-Al_2O_3 polish	Media finish + Preoxidation	Praxair Surface Treatment
NiCoCrAlY A	Media Finish + Pt Overlayer	Media Finish + Pt Overlayer + Media Finish	Media Finish + Pt Overlayer + Media Finish + Preoxidation		
Aluminide	Media finish + Pt overlayer				
Platinum Aluminide	Media finish + Pt overlayer	Media finish + Pt overlayer + Preoxidation			
Platinum Aluminide	As processed	Heavy grit blast	Howmet Best Practice		

Table 2
Compositions of MCrAlY Coatings (wt%)

COATING	Ni	Co	Al	Cr	Hf	Y	Si	O	C	Fe	Re	Ta
D-Gun LN-72	44.4	22.95	13.82	16.59	-	0.57	-	0.9	0.58			
Shrouded Argon LN-11	48.0	21.78	12.58	16.45	-	0.43	-	0.16				

Table 3
Failure Times for the Current State-of-the-Art TBCs

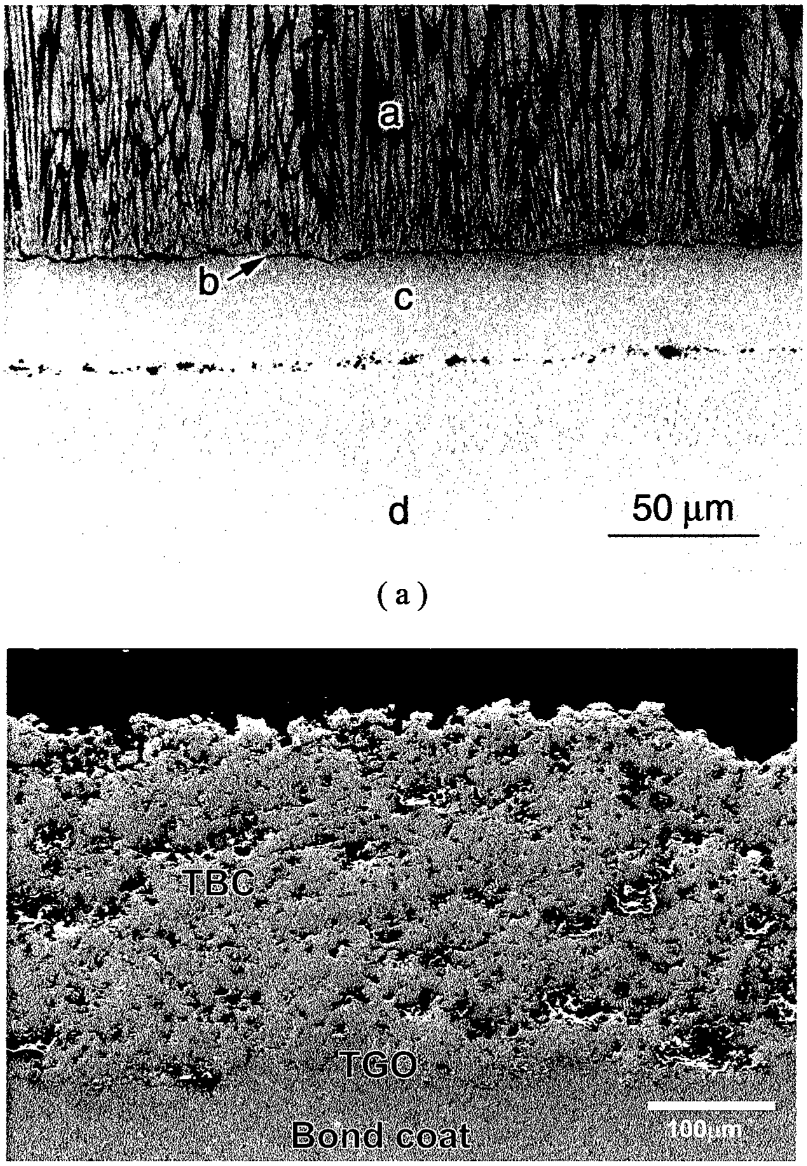
Bond Coat type	Cyclic		Isothermal
	1100°C	1200°C	1200°C
Pt Aluminide A	1005 cyc	132 cyc	-
Pt Aluminide B	1220 cyc	120 cyc	100 hrs
Pt Aluminide C	1280 cyc	132 cyc	100 hrs
NiCoCrAlY A	76,102 cyc	9 cyc	
NiCoCrAlY B	102,139 cyc	5 cyc	

Table 4
Failure Times (cycles) for TBCs on NiCoCrAlY Bond Coats

	1000°C	1100°C
NiCoCrAlY A	560	60
NiCoCrAlY B	780	40
NiCoCrAlY A (Pt Underlayer)		160
NiCoCrAlY B (Pt Underlayer)		160
NiCoCrAlY A (Pt Overlayer)		880, 980
NiCoCrAlY B (Pt Overlayer)		600, 1240
NiCoCrAlY A (Aluminized)	1420+	460
NiCoCrAlY B (Aluminized)	1420+	280, 220
NiCoCrAlY A Pt-Aluminide Coating on Sides		40
NiCoCrAlY A Pt Aluminide Coating on Sides		60

Table 5
Failure Times (cycles) at 1100°C for TBCs on
Platinum Aluminide Bond Coats

	Heavy grit blast	Light grit blast	As processed	Media Finish +
0.25 mil Pt + 1.5 mil Aluminide	1120	1600	1080	
0.25 mil Pt + 3 mil Aluminide		360	1020+	
0.5 mil Pt + 1.5 mil Aluminide		1780		
0.5 mil Pt + 3 mil Aluminide			860	2280



(a)

(b)

Figure 1. Photomicrographs showing the typical microstructures of (a) EPBVD and (b) APS YSZ thermal barrier coatings. In the EBPVD TBC the YSZ topcoat, a, is evident on the bond coat, c, where a thin TGO (thermally grown oxide) has been formed between the TBC and the bond coat during processing. The superalloy substrate is identified as d.

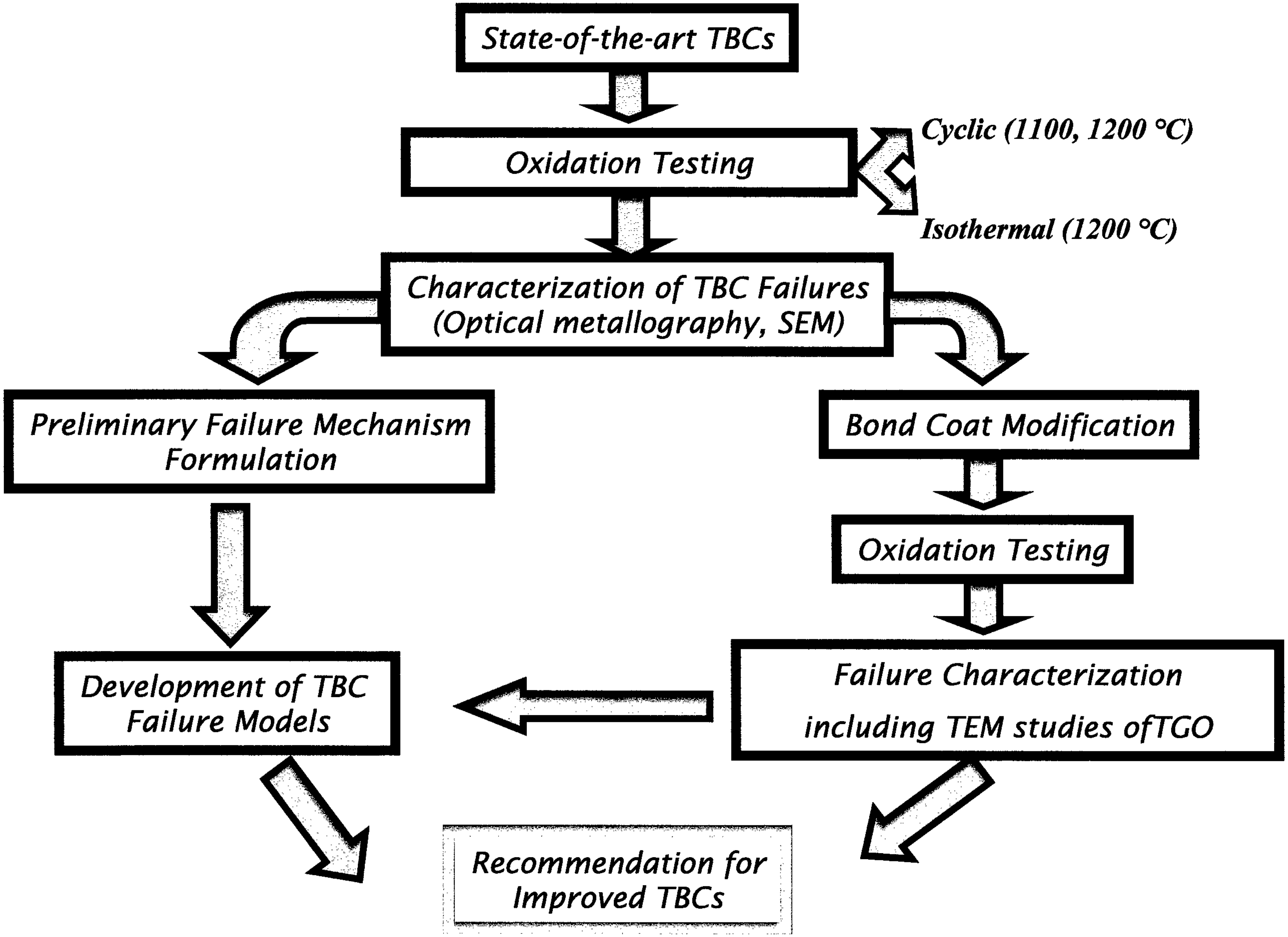


Figure 2. Flow diagram showing the sequence of studies that have been performed in order to formulate recommendations for improved EBPVD TBCs.

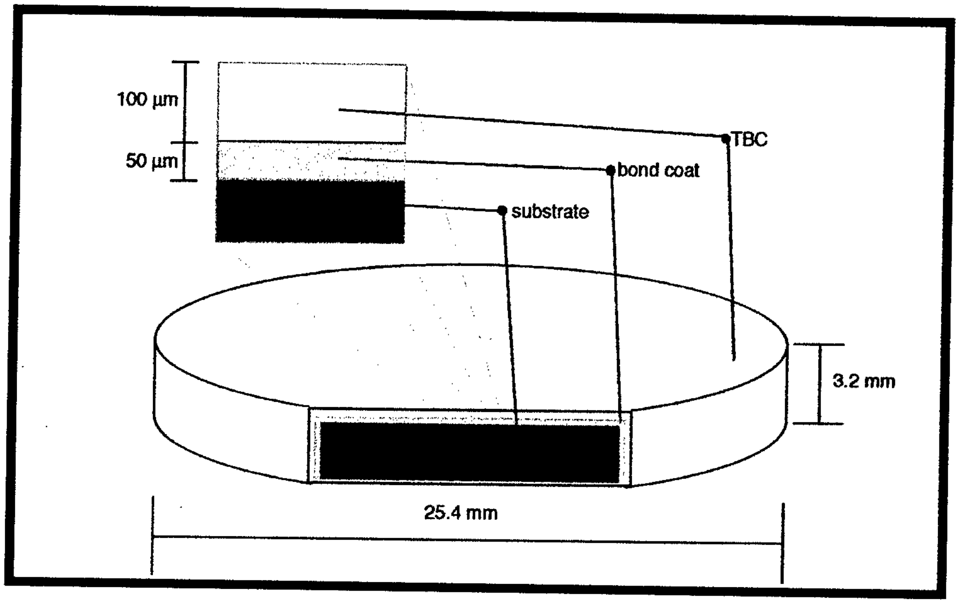


Figure 3. Schematic to show the typical configuration of the specimens used in this study.

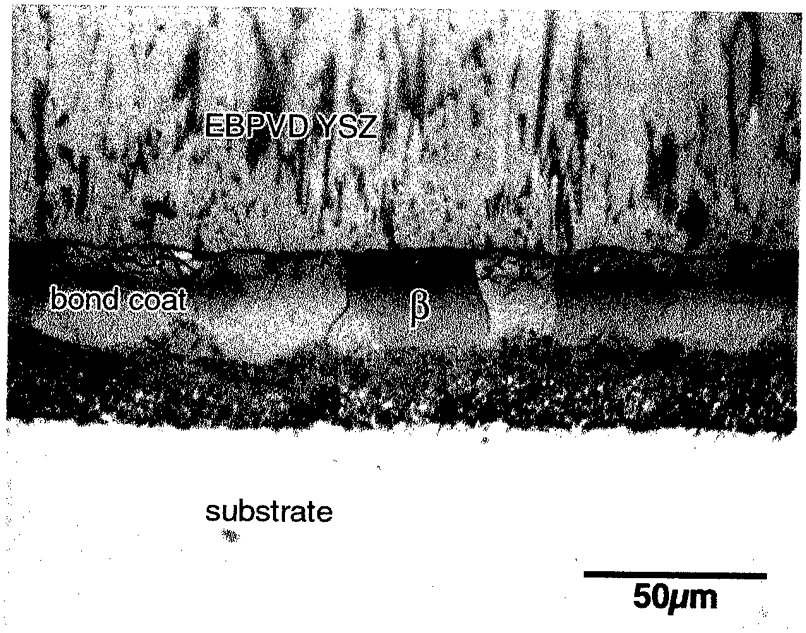


Figure 4. Cross-sectional micrograph showing a typical TBC system with the platinum aluminide bond coat in the as-processed condition. The β-phase is (Ni,Pt)Al.

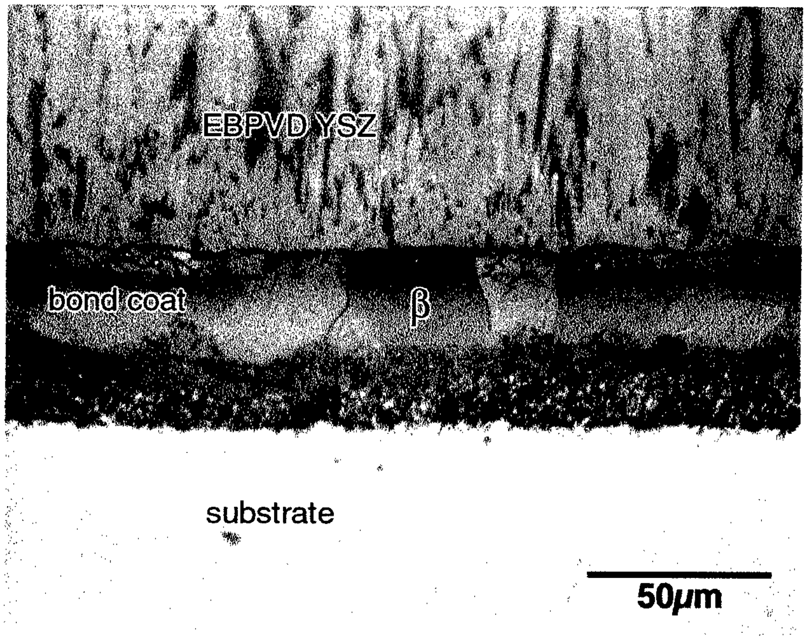


Figure 4. Cross-sectional micrograph showing a typical TBC system with the platinum aluminide bond coat in the as-processed condition. The β-phase is (Ni,Pt)Al.

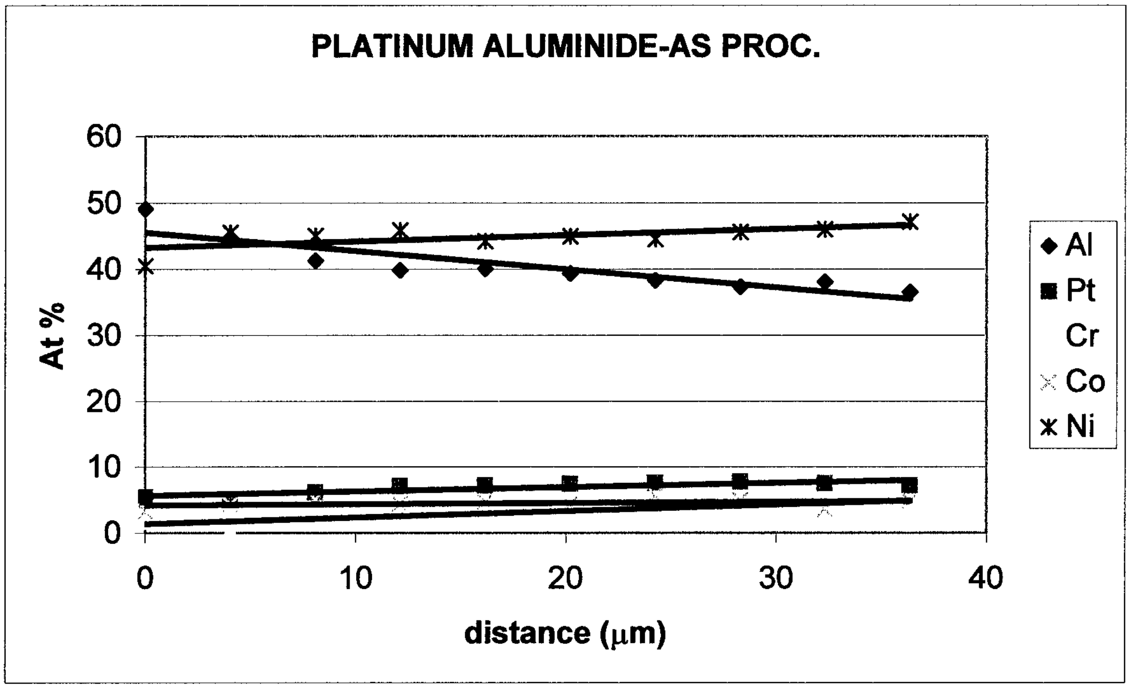


Figure 5. Concentration profiles of Al, Pt, Cr, Co and Ni across an as-processed platinum aluminide bond coat.

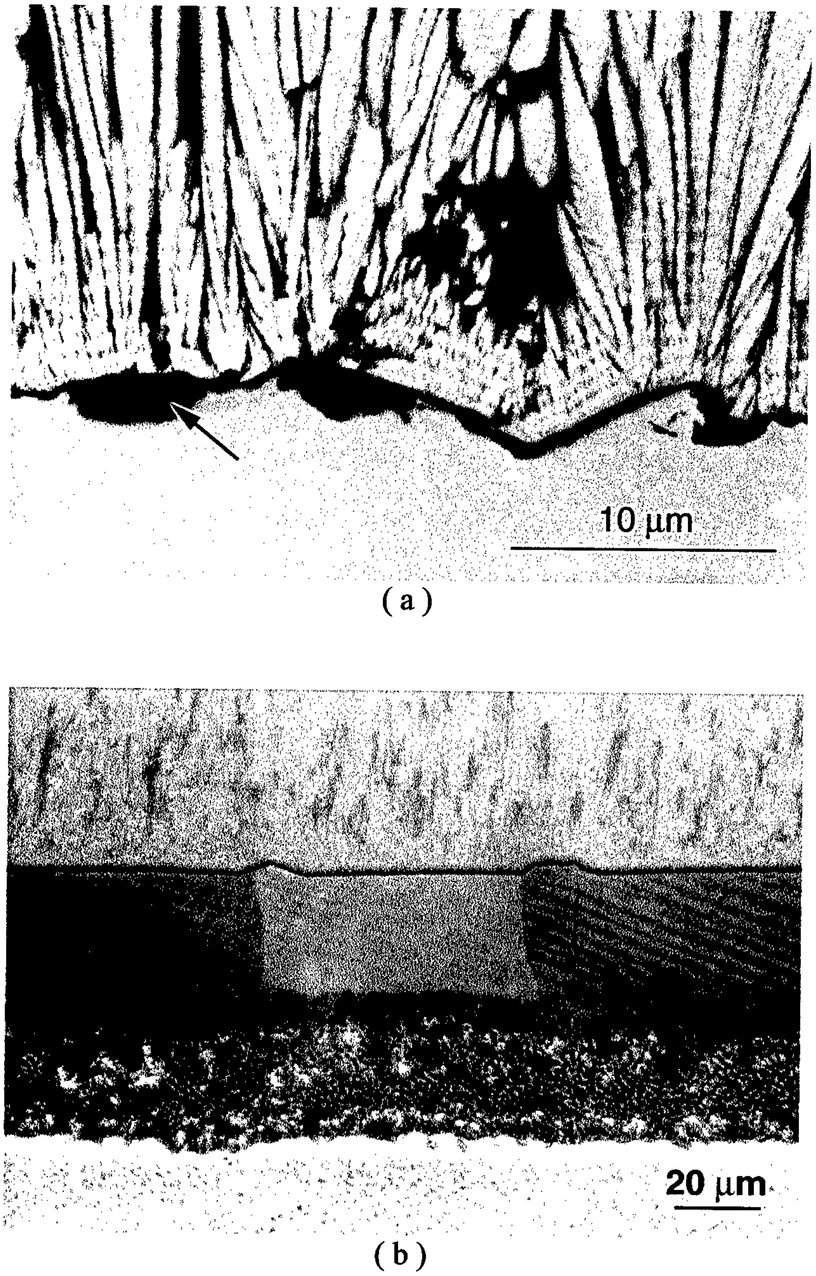


Figure 6. Photomicrographs showing two as-processed bond coats where one bond coat has been grit blasted prior to TBC deposition, (a), and the other bond coat has not been given any surface preparation prior to TBC deposition, (b).

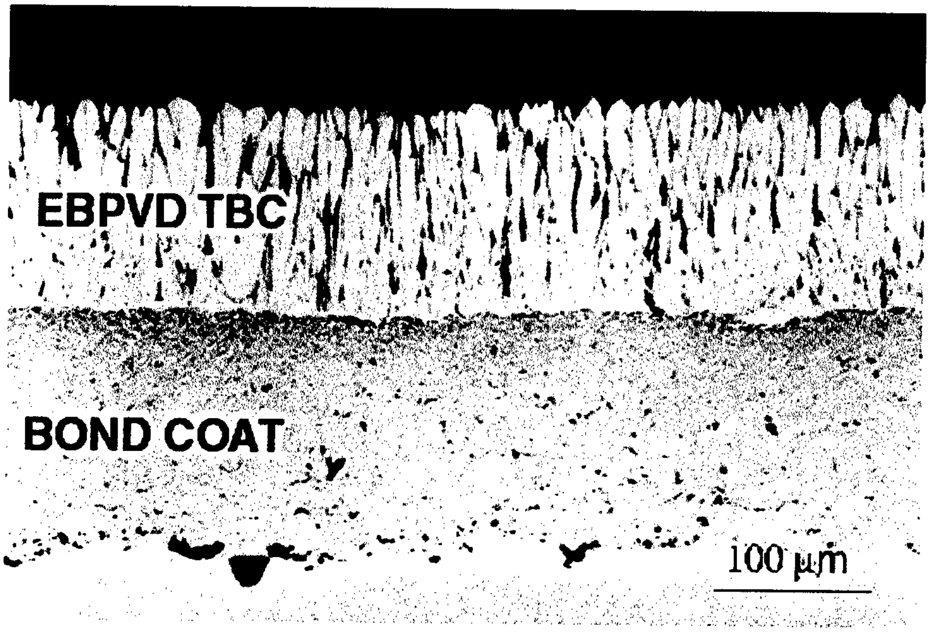


Figure 7. Scanning electron micrographs showing an as-processed TBC with a NiCoCrAlY bond.

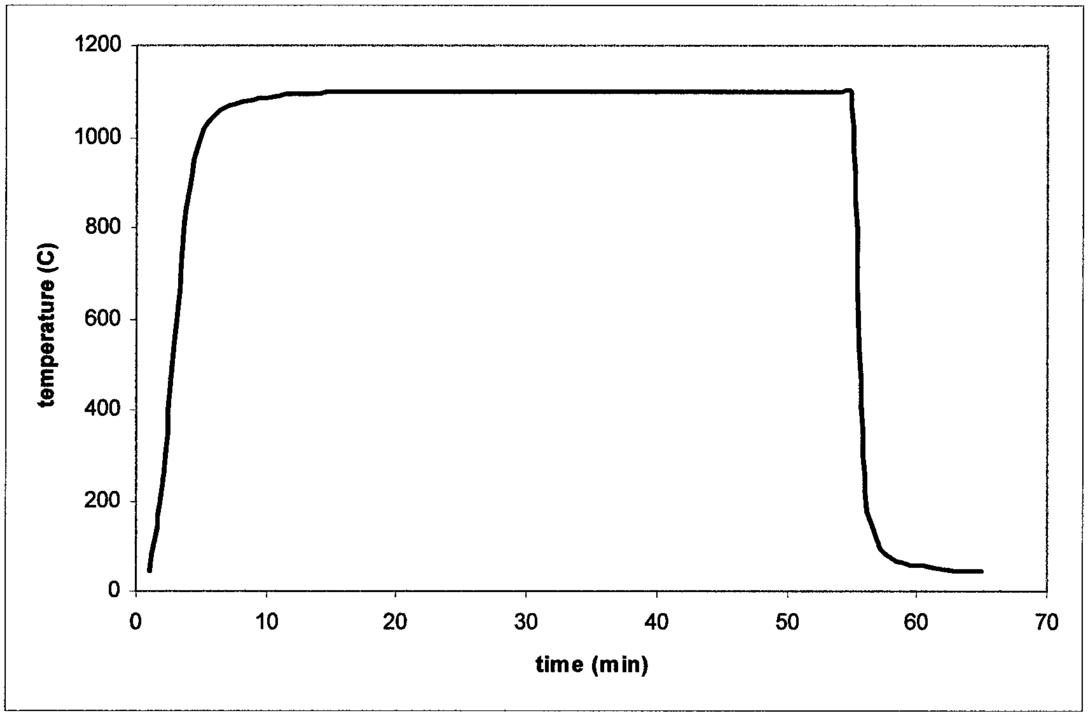
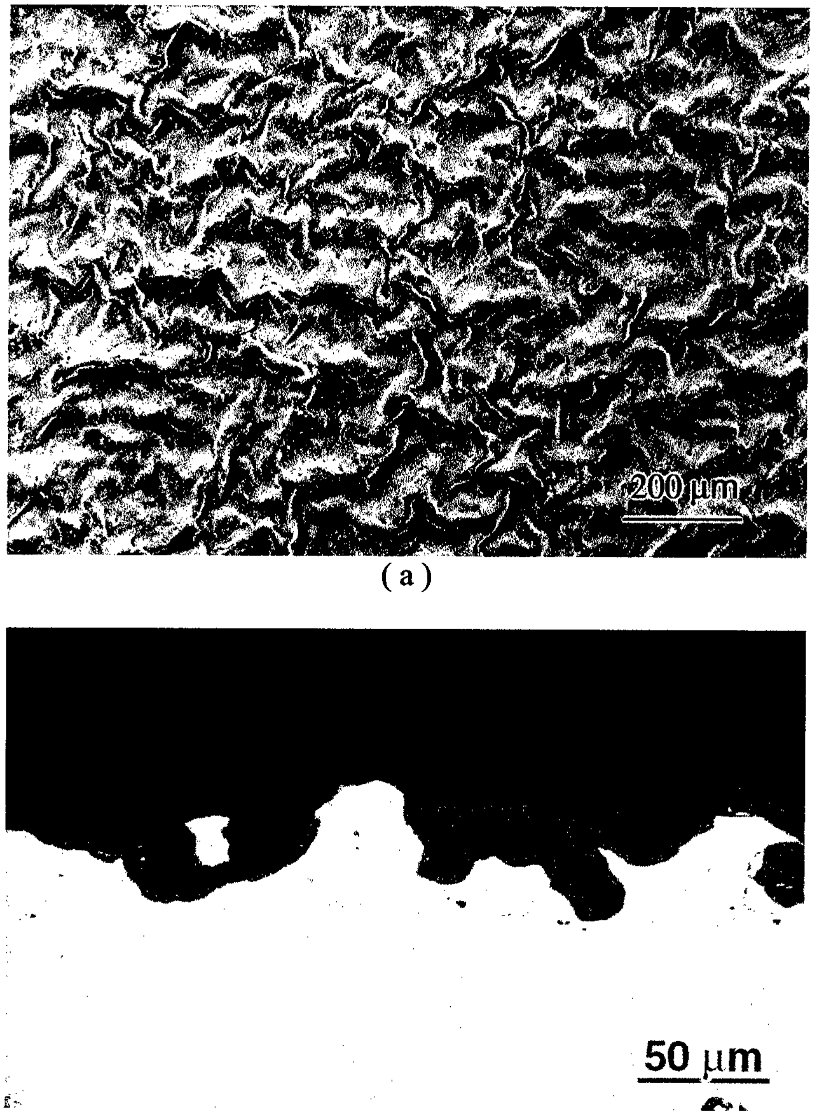


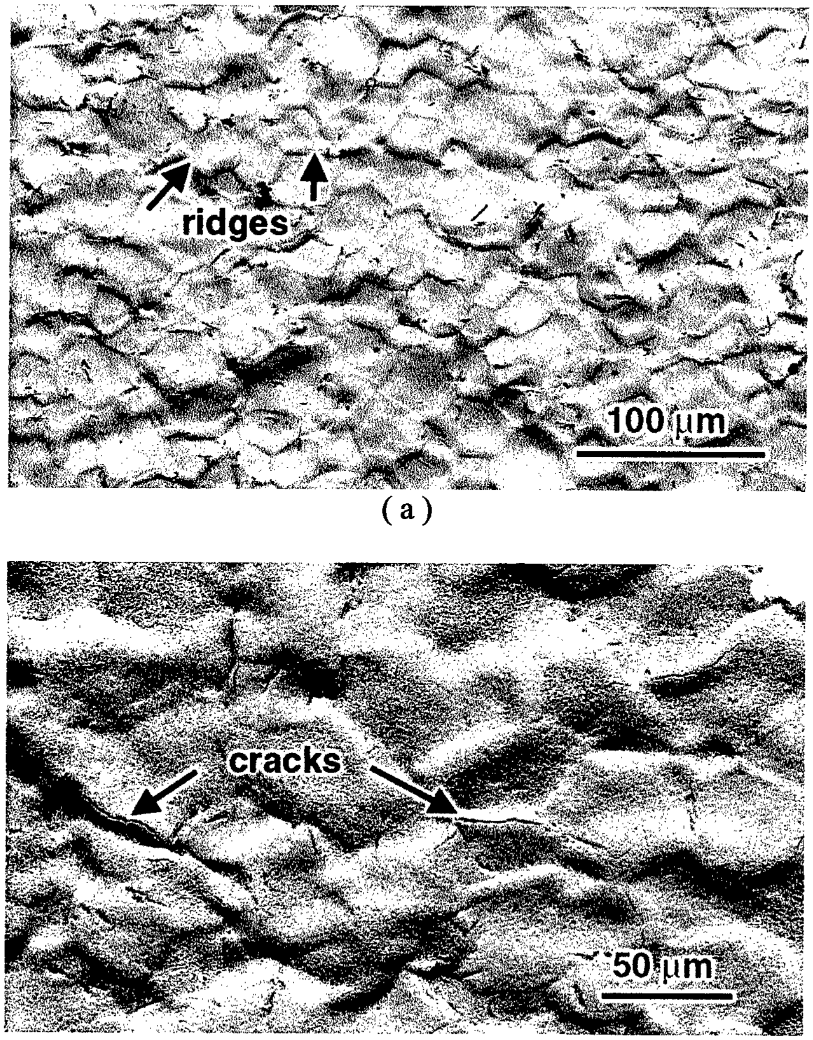
Figure 8. Sketch showing the temperature profile for specimens exposed in the bottom loading furnace.



(a)

(b)

Figure 9. a) Surface micrograph of the Pt-Aluminide bond coat, showing the highly deformed surface that developed during 955 cycles of oxidation at 1100°C. b) Scanning electron micrograph showing the large cavities that formed at the bond coat-oxide interface after exposure at 1100°C for 3031 cycles

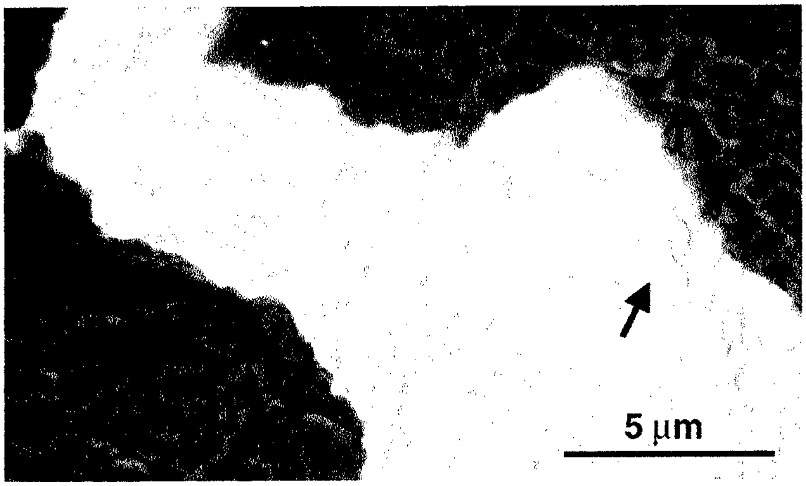


(a)

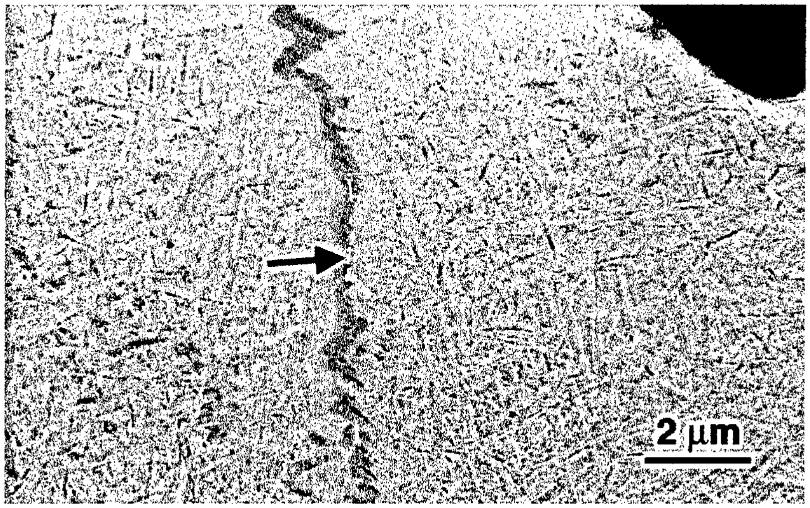
(b)

Figure 10. Surface micrographs showing ridges that developed at the surfaces of platinum-aluminide bond coats during coating formation, (a). During cyclic oxidation of these coatings cracks in the oxide at these ridges were apparent, (b).

(a)

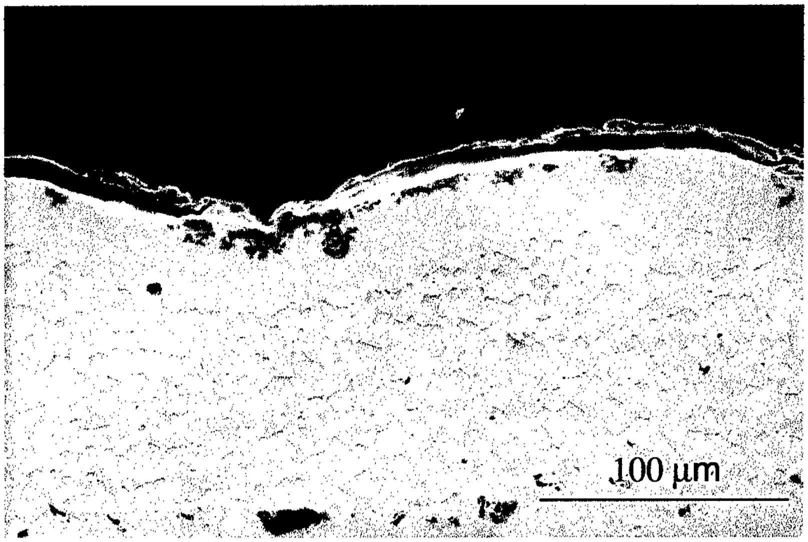


(b)

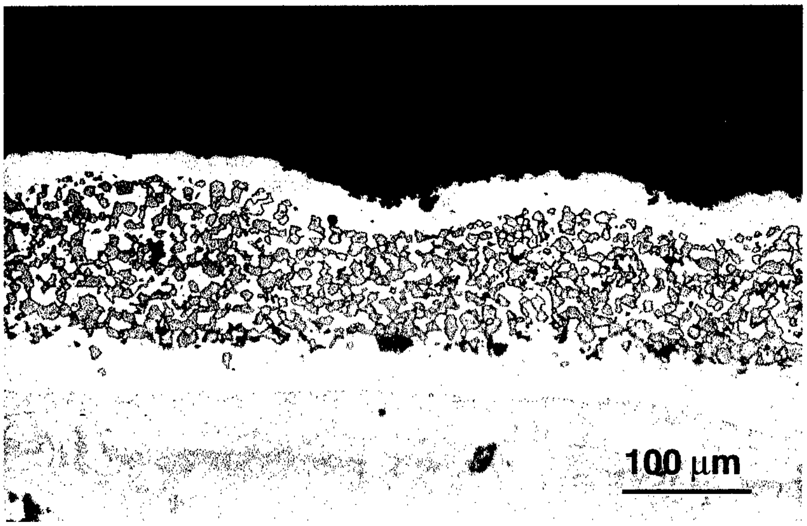


(c)

Figure 11. After cyclic oxidation of the platinum-aluminide coatings, refractory metal rich phases (tantalum and tungsten) were evident at the oxide-coating interface, (a) and (b). Such phases were also observed at grain boundaries in the coating, (c).



(a)



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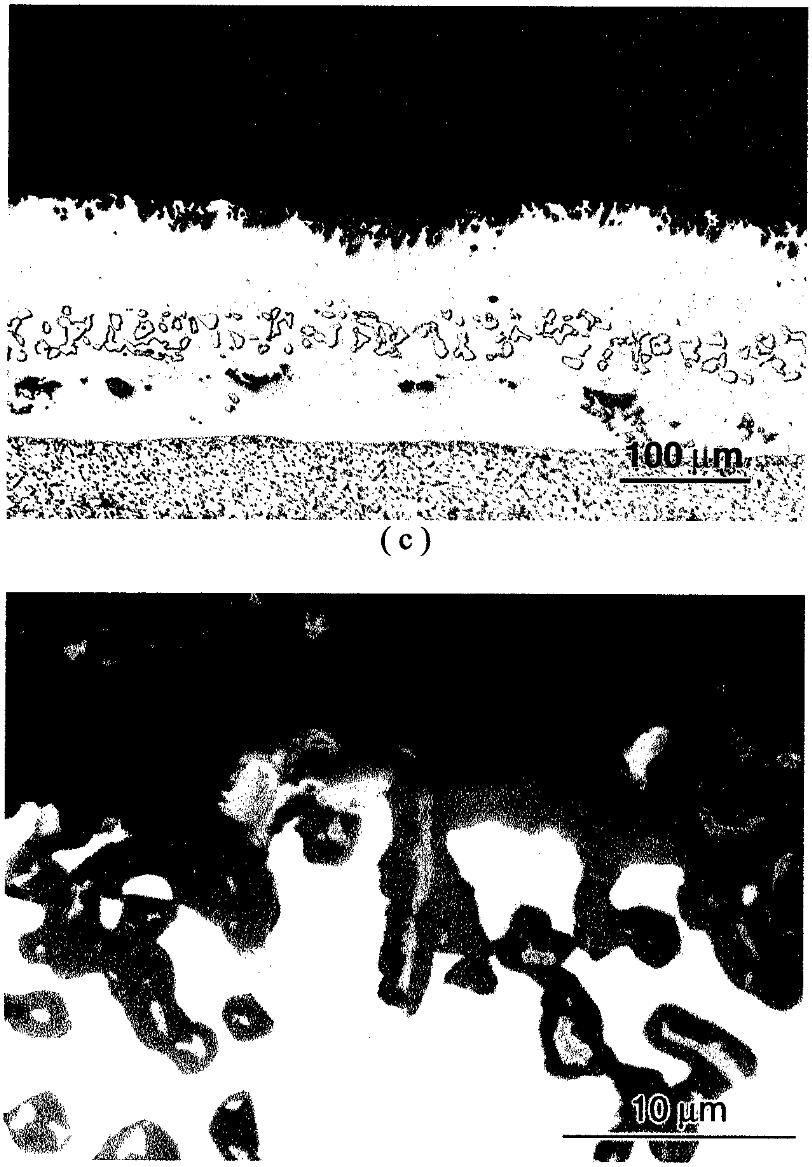
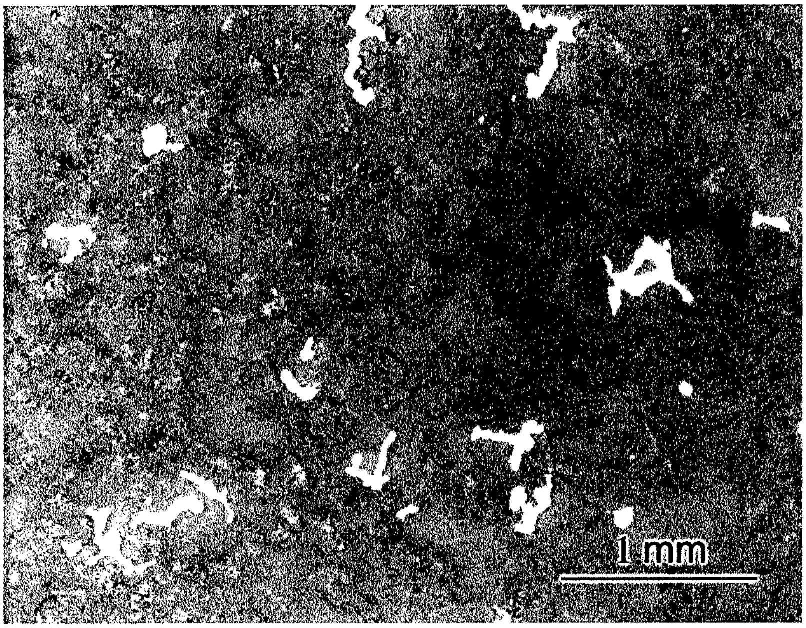


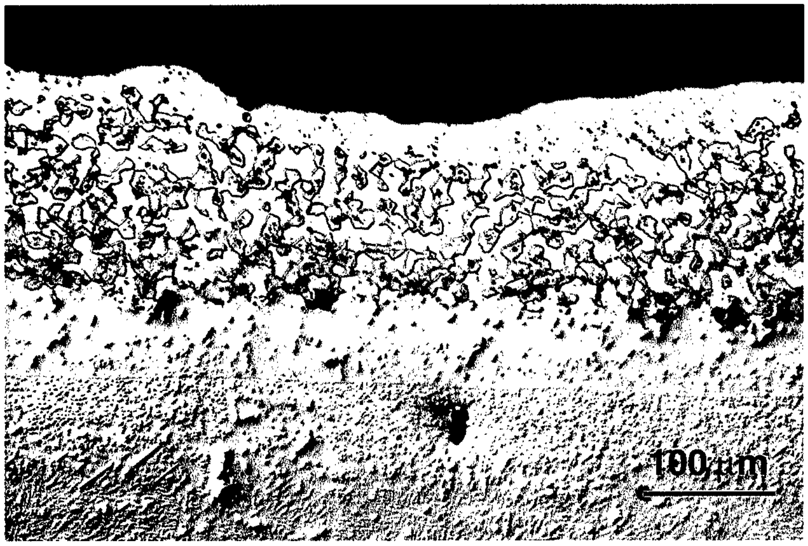
(c)

(d)

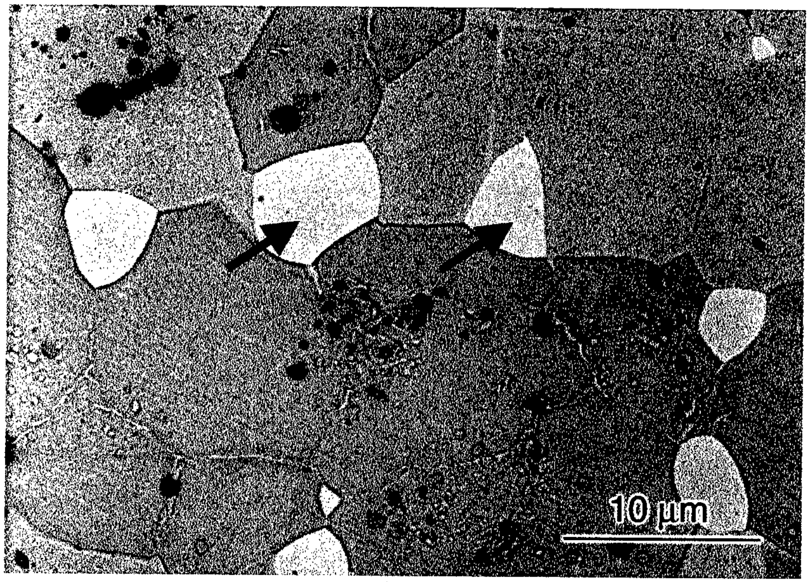
Figure 12. Scanning micrographs of NiCoCrAlY A showing cross sections of this coating after 209, (a) and (b), and 955, (c) and (d), cycles of exposure at 1100°C. Oxide protrusions extended into the coating at locations where yttrium rich oxides had been formed, (d).



(a)



(b)



(c)

Figure 13. Scanning micrographs showing the surface and cross section of NiCoCrAlY B coating after 955 cycles of exposure at 1100°C, (a) and (b). Refractory metal rich phases (arrows) were evident in the bond coat.

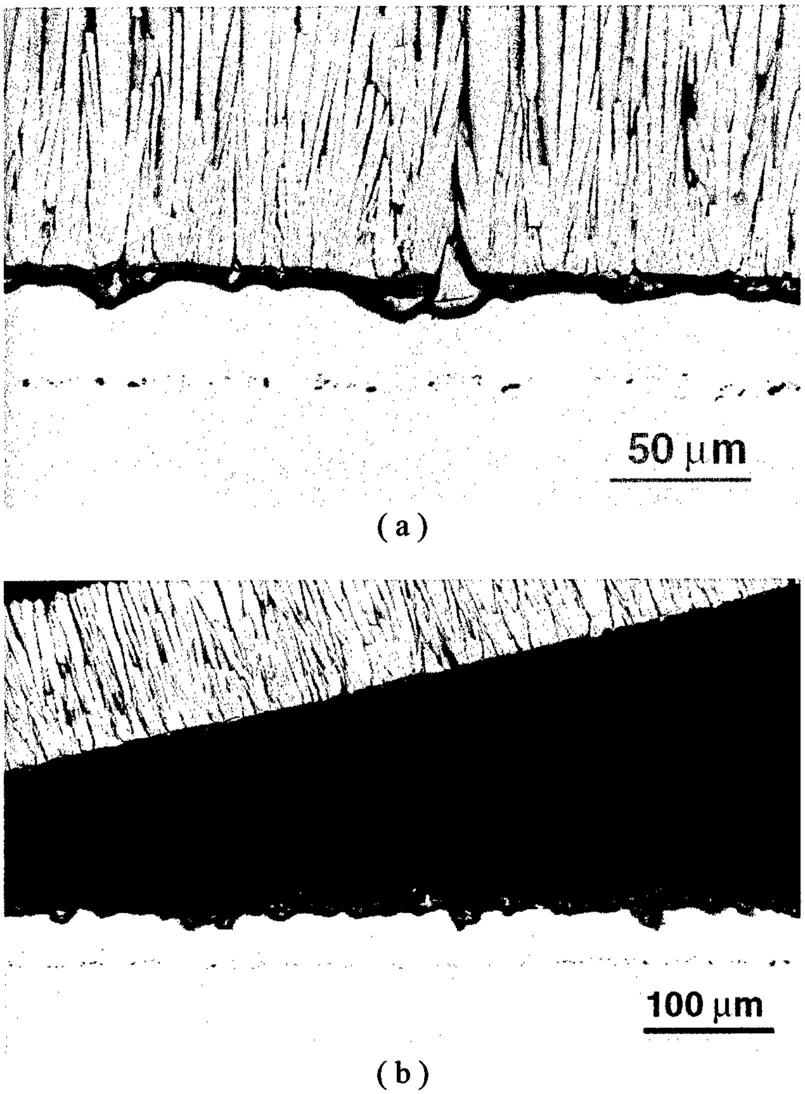


Figure 14. Cross sectional micrographs of the TBC systems with Pt aluminide bond coats after exposure at 1100°C before failure, 758 cycles, (a) and after failure, 1280 cycles, (b). The TBC/bond coat interface became highly irregular due to ratcheting.

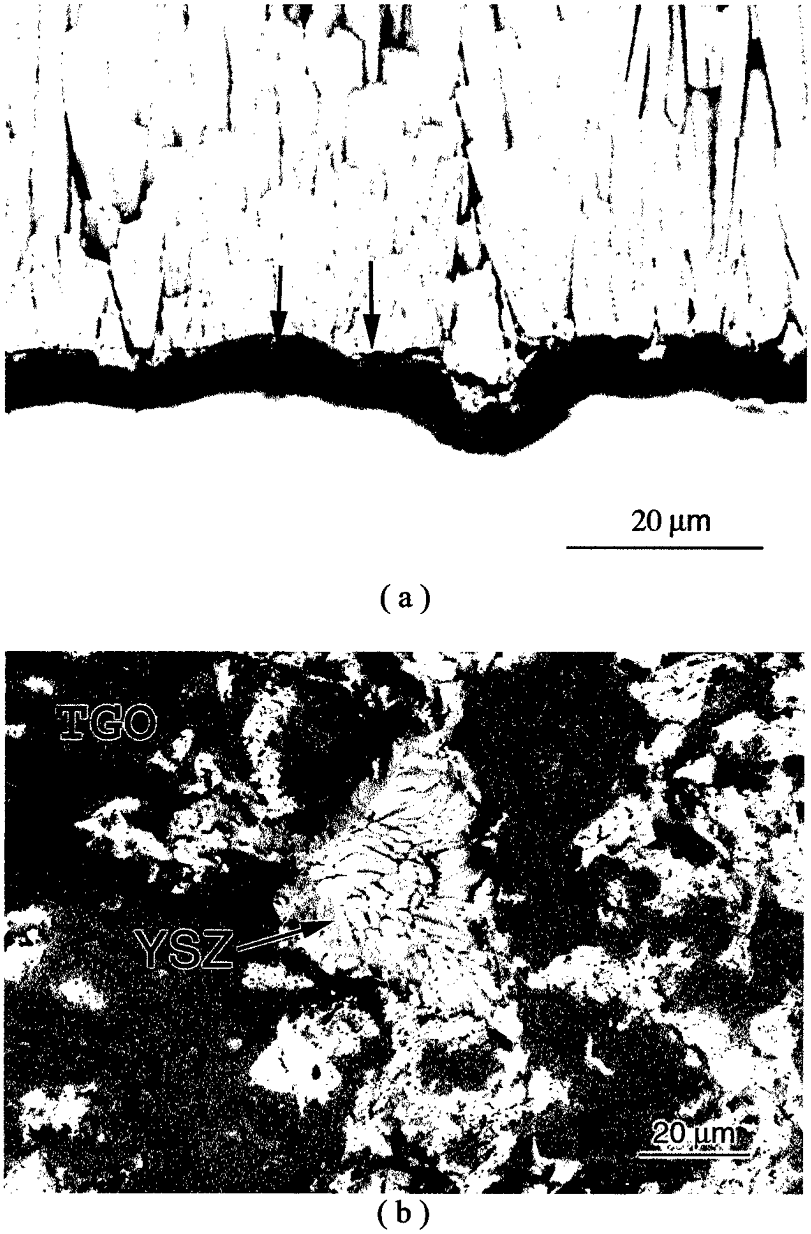


Figure 15. a) Scanning electron micrograph of the TBC system with the Pt aluminide bond coat prior to failure showing cracks that initiated at ratchets in the TBC and propagated into the TGO. b) Scanning electron micrograph of the bond coat after spalling of the TBC where pieces of the TBC were pulled from this coating upon failure. The failure has been predominantly in the TGO and TBC.

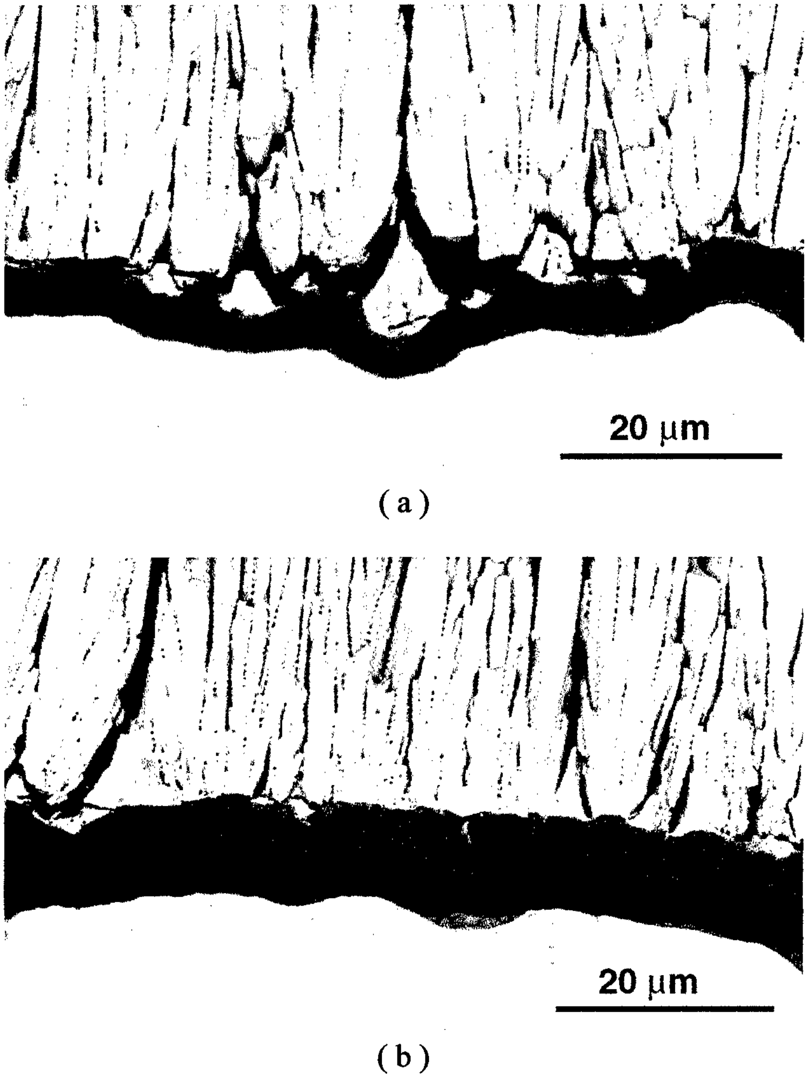
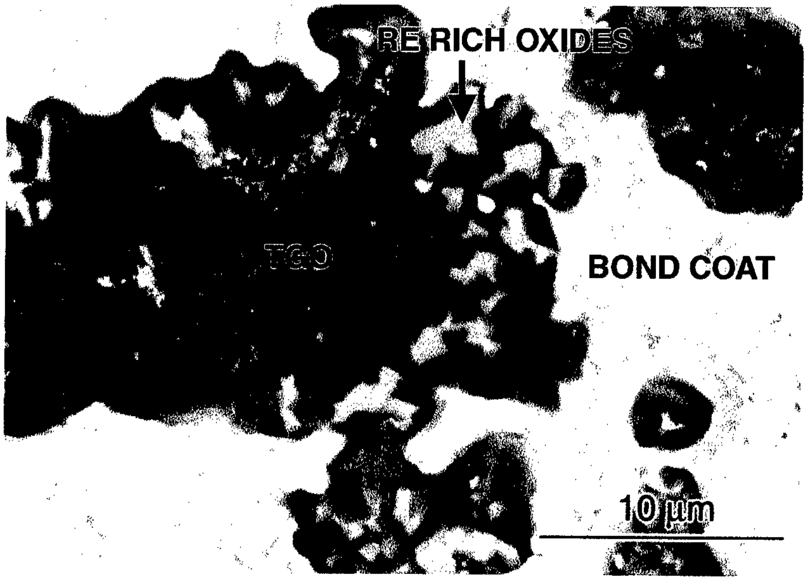
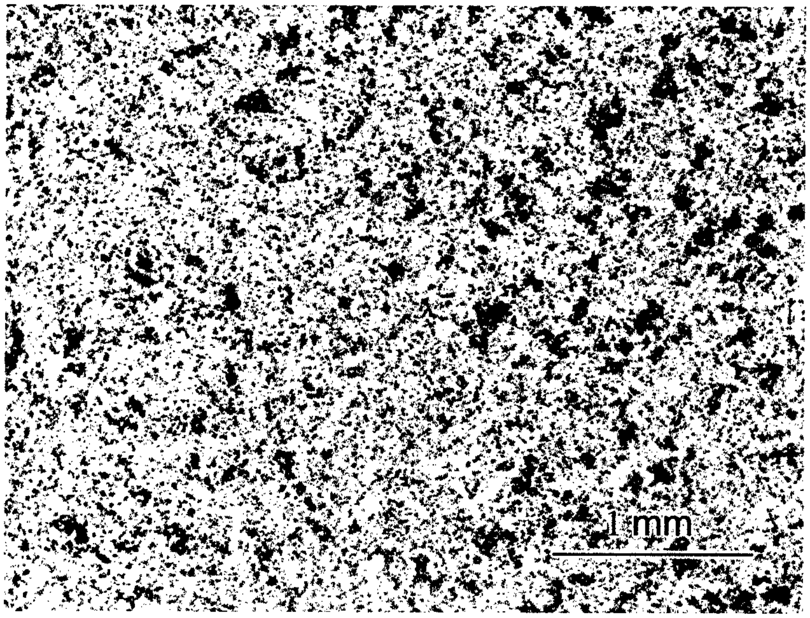


Figure 16. Scanning electron micrographs from the TBC system with platinum aluminide bond coat prior to failure (after 758 cycles of exposure at 1100 °C) The detachment was observed to be in the TBC, TGO or along the TGO/TBC interface when numerous ratchets were present, (a), whereas it was along the TGO/bond coat interface when ratcheting was less pronounced, (b).

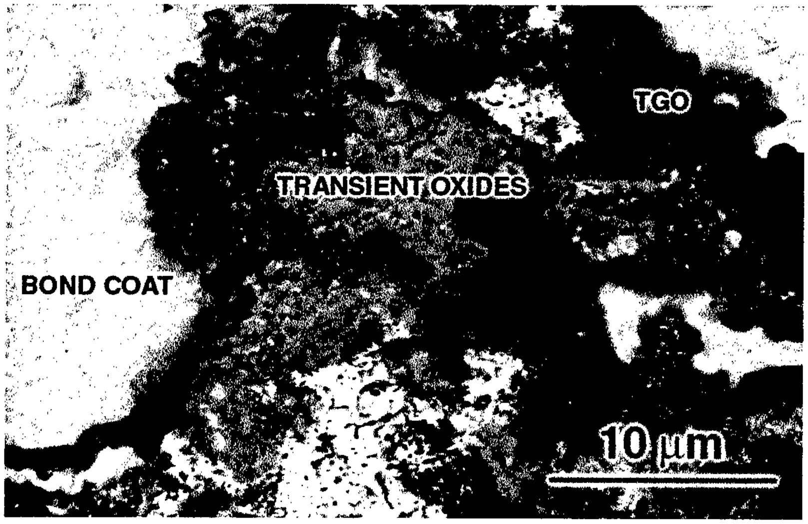


(c)

Figure 17. Surface micrographs of the NiCoCrAlY bond coat after spalling of the TBC showing that fracture was predominantly along the TGO-bond coat interface, (a), with excursions into the TGO and TBC, (b) and (c). At these sites of TGO and TBC, transient oxides, (b), and reactive element oxides, (c), were often evident.



(a)



(b)

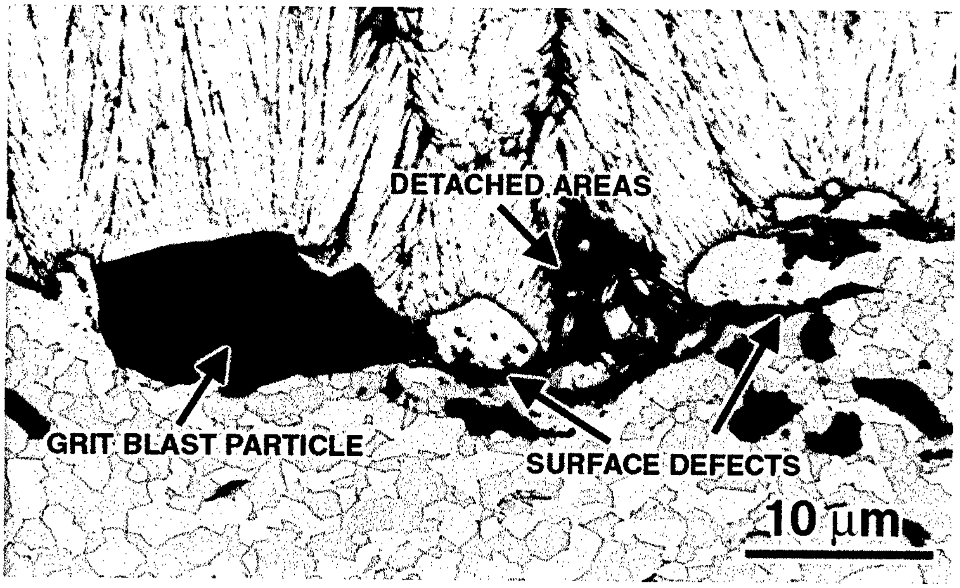
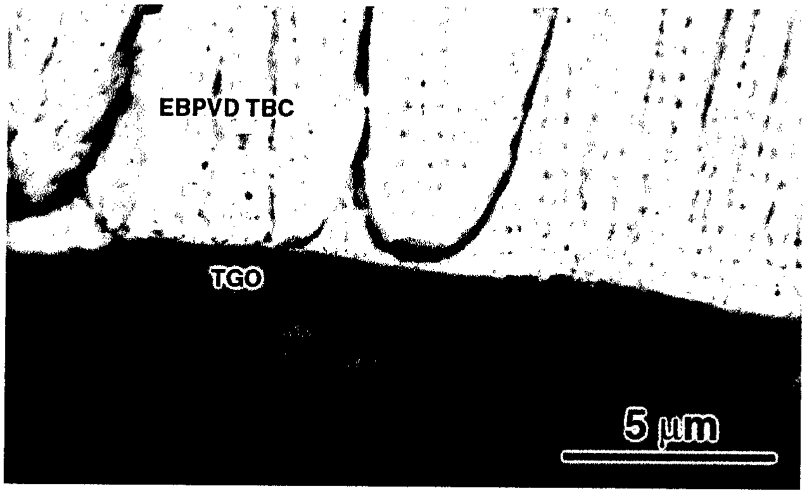
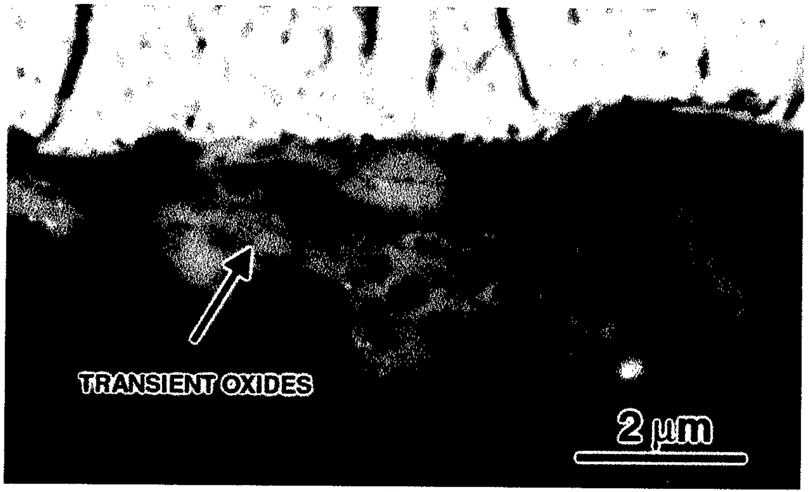


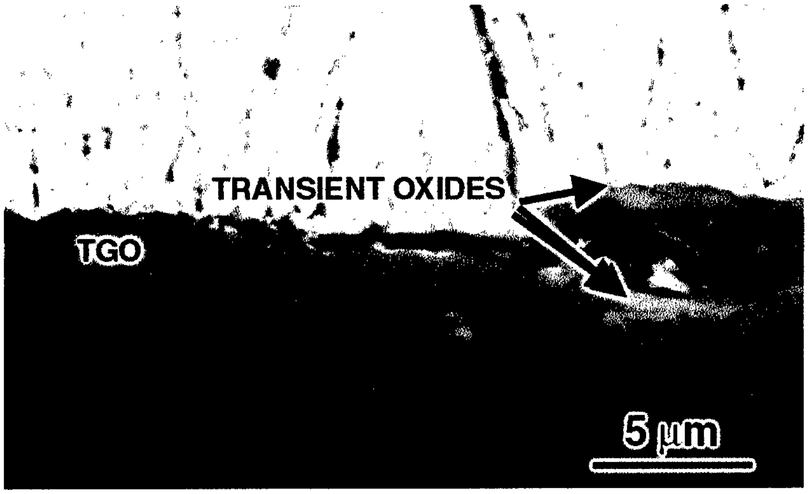
Figure 18. Scanning electron micrograph showing an as-processed TBC on a NiCoCrAlY bond coat where detached areas along the TBC-TGO-bond coat interface are evident.



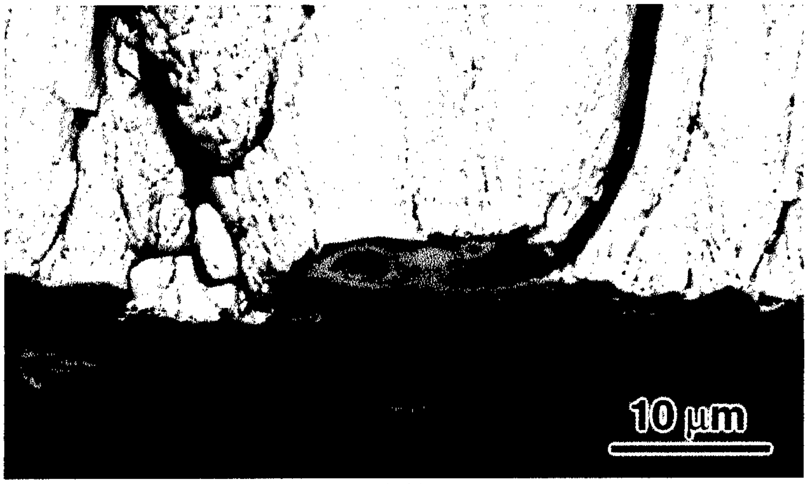
(a)



(b)

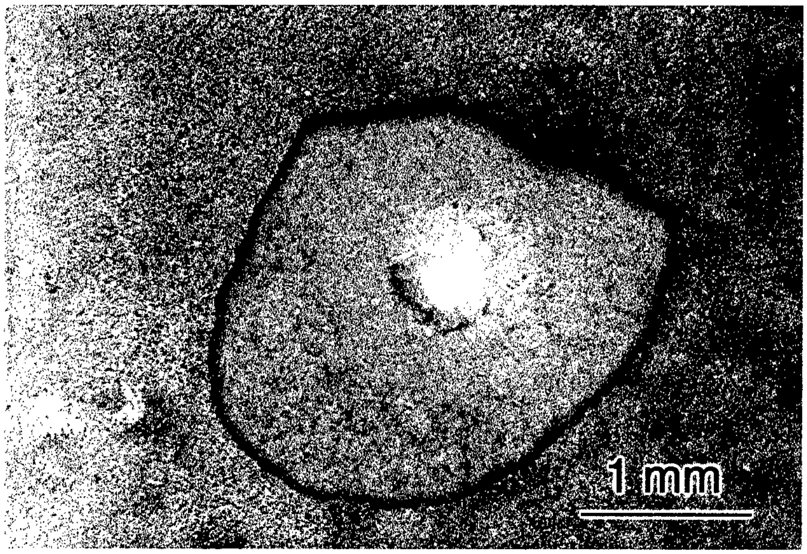


(c)

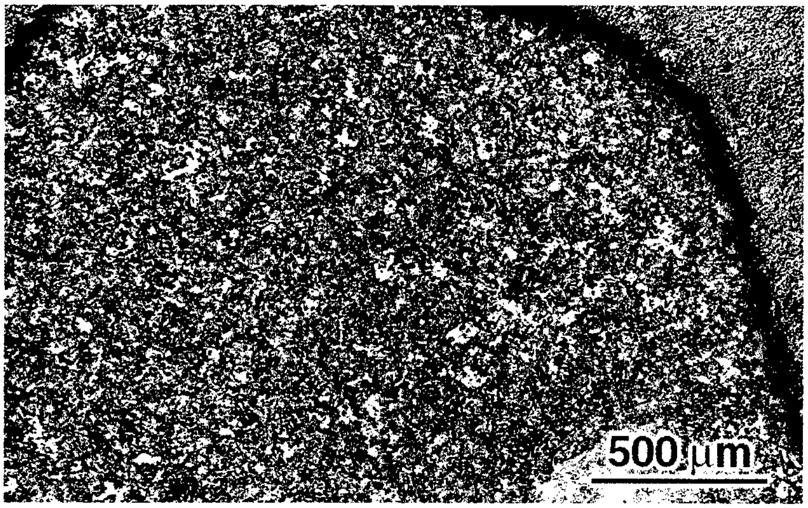


(d)

Figure 19. Scanning electron micrographs showing TBCs and TGOs on a NiCoCrAlY bond coat after failure. In some regions the TGO was uniform and dense where no transient oxides were evident, (a). In regions where transient oxides were present the TGO is porous and nonuniform, (b), and cracks, (c) and (d), were evident indicating that the transient oxides can affect crack propagation and crack initiation.



(a)



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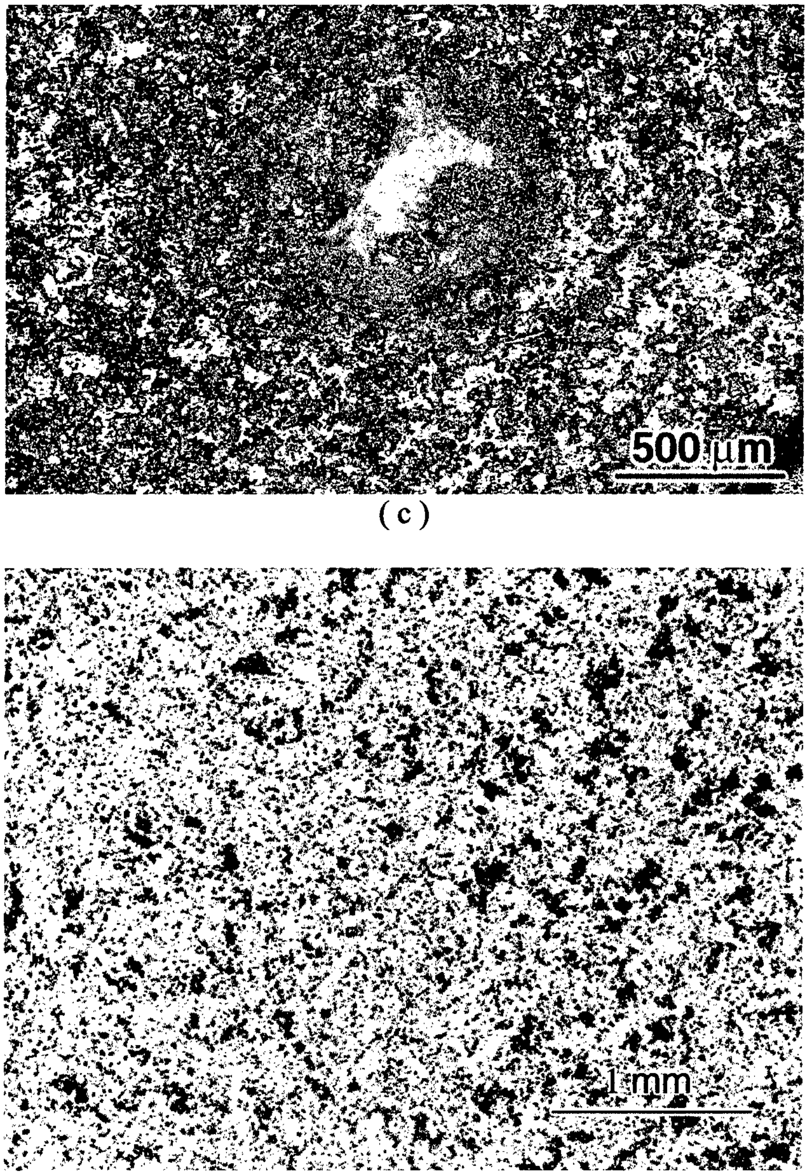


(c)

(d)

Figure 20. Scanning electron micrographs showing the surface of a NiCoCrAlY bond coat exposed after indentation to cause delamination of the TBC as a function of exposure time at 1100°C. In the case of the as-processed specimen, (a), failure has occurred along the TBC-TGO interface and as the exposure time is increased, (b) 10 cycles, (c) 25 cycles, (d) 82 cycles, failure along the TGO-bond coat interface (light areas) progressively increases.

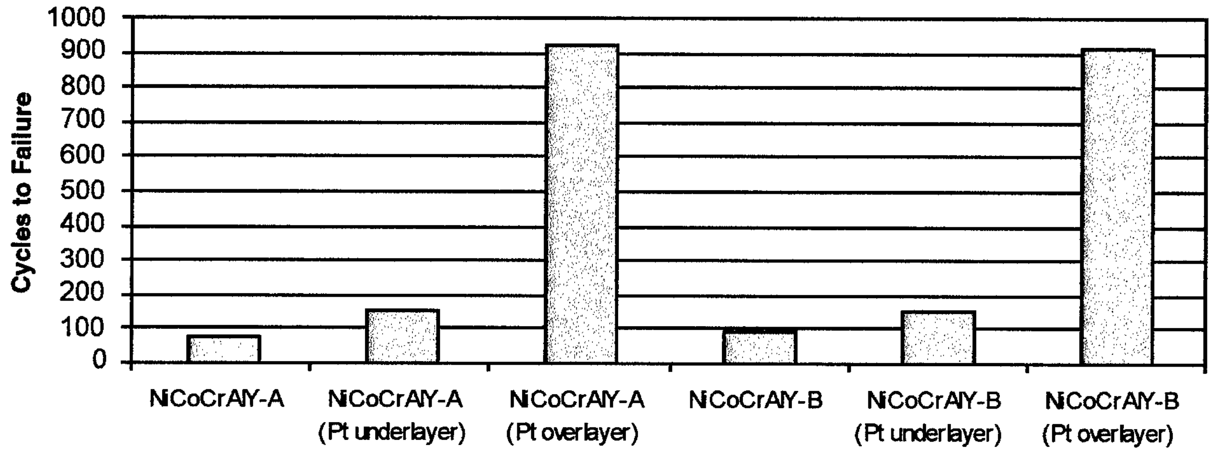


Figure 21. Chart comparing the failure times of TBCs tested at 1100°C in the bottom loading furnace.

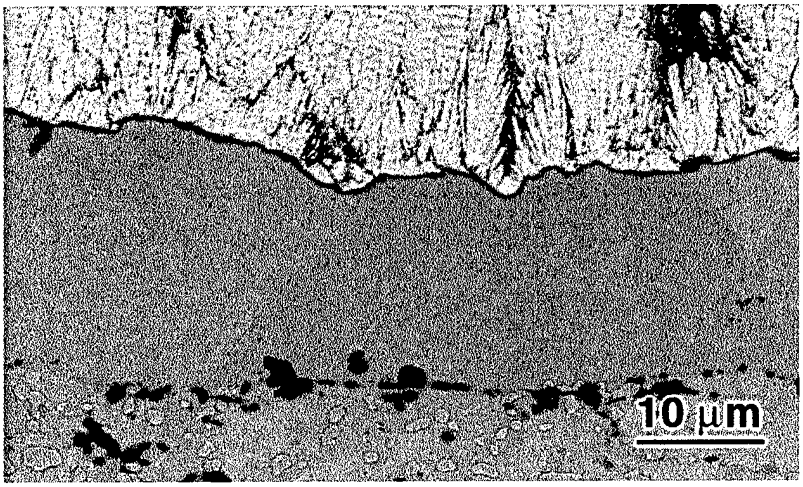
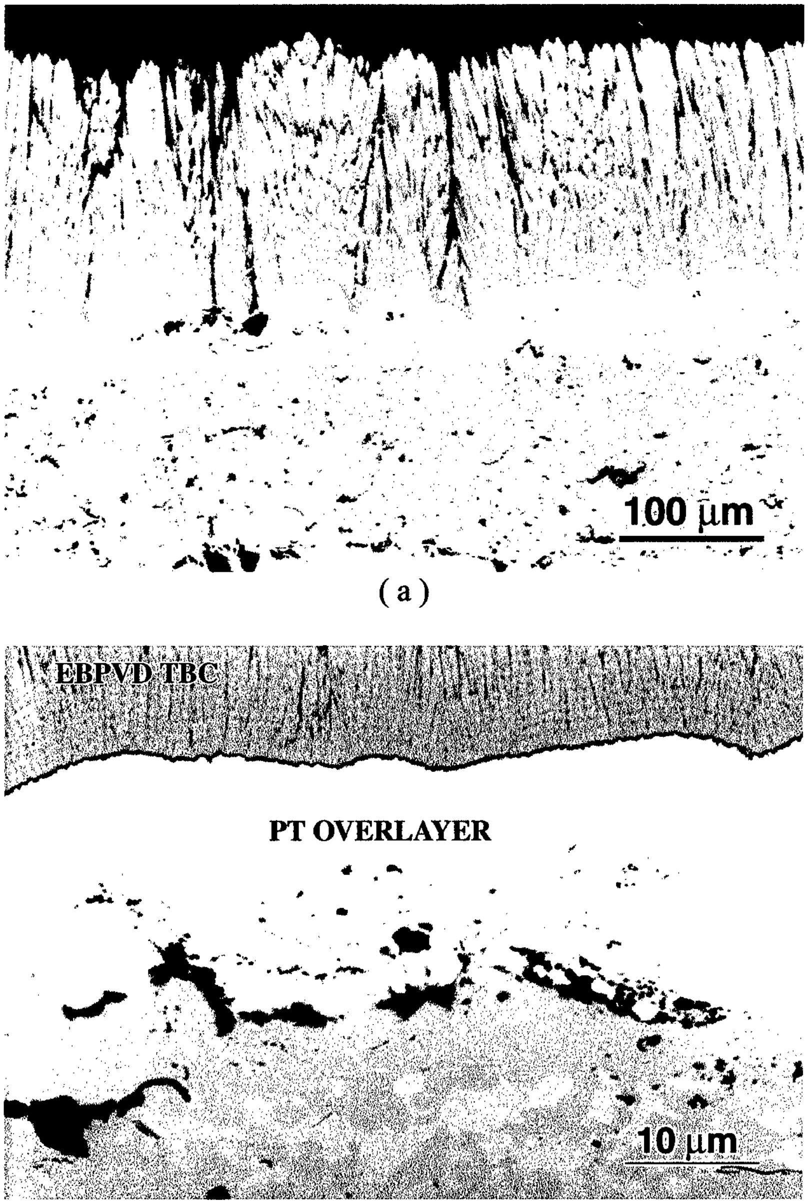


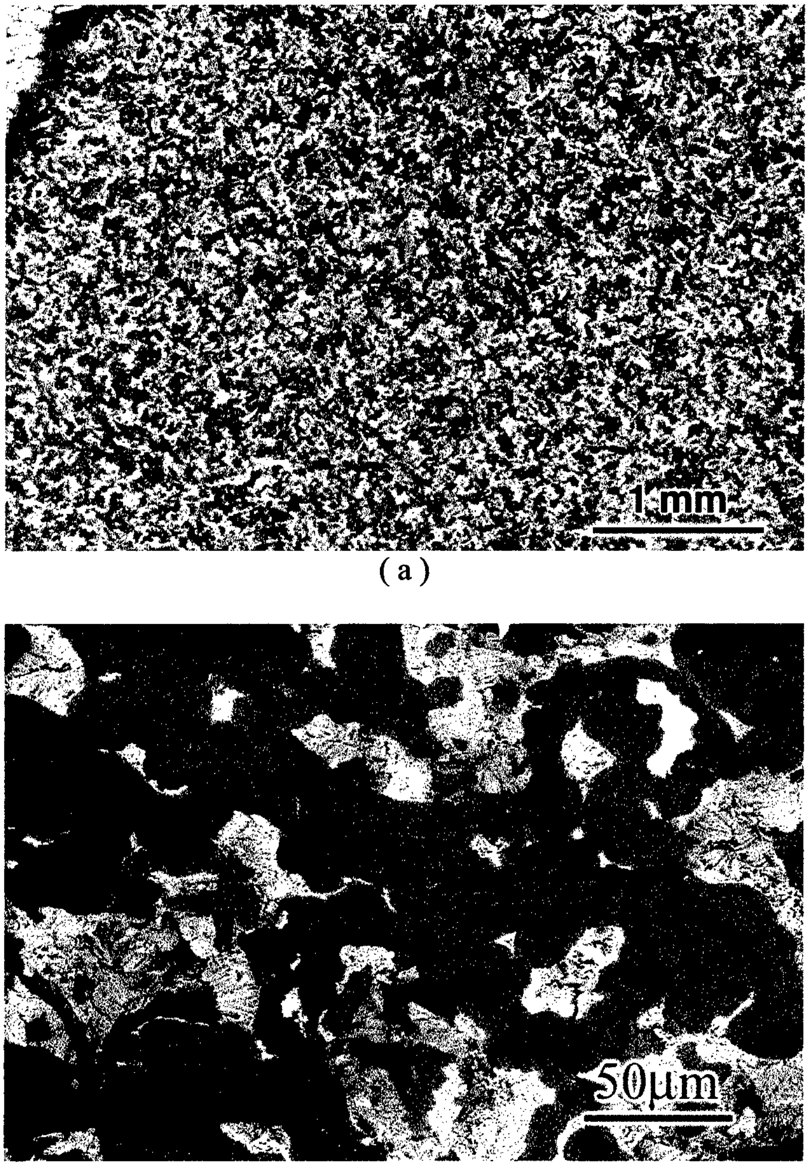
Figure 22. Scanning electron micrograph showing an as-processed TBC with an aluminized NiCoCrAlY bond coat. Fewer defects are evident at the bond coat-TBC interface compared to the as-processed NiCoCrAlY bond coats.



(a)

(b)

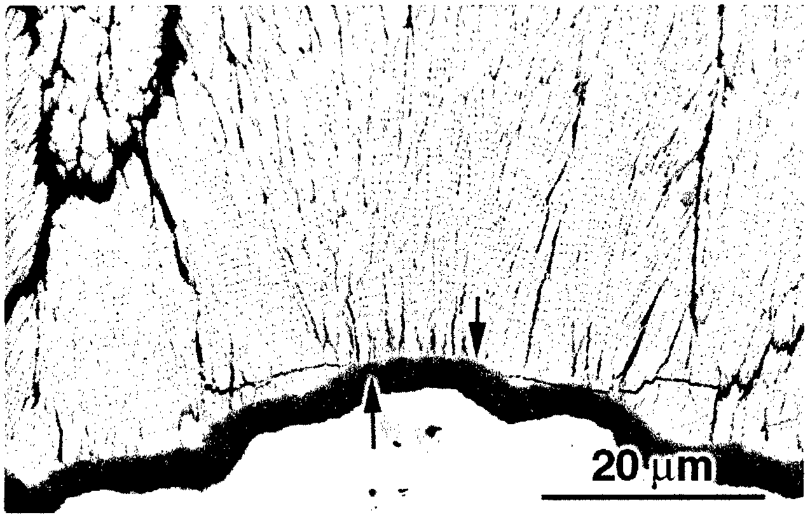
Figure 23. Scanning electron micrographs showing an as-processed TBC with a platinum overlayer on a NiCoCrAlY bond coat. The bond coat-TBC interface is highly irregular, (a), since the bond coat was grit blasted prior to deposition of platinum. No defects are evident in the vicinity of the bond coat-TGO-TBC zone, (b).



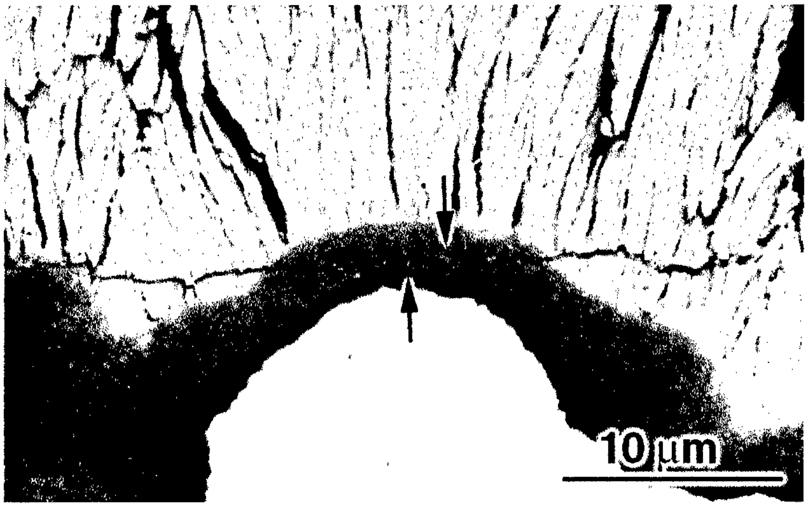
(a)

(b)

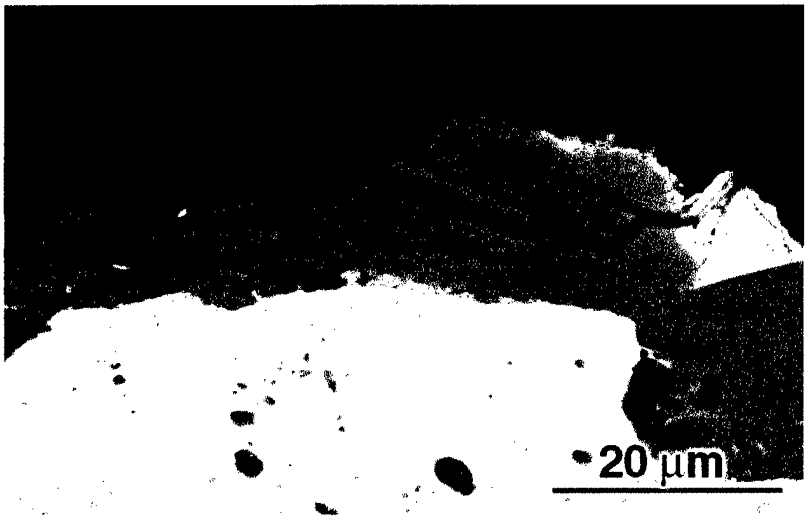
Figure 24. Scanning electron micrographs showing the surface of the platinum overlayer NiCoCrAlY bond coat after spalling of the TBC, 880 cycles at 1100°C, (a) and (b). All of the failure has occurred in the TGO and in the TBC.



(a)



(b)



(c)

Figure 25. Scanning electron micrographs showing the initiation of cracks in the TGO, (a) and (b), after 40 cycles at 1100°C, and after failure, 880 cycles at 1100°C, where numerous cracks in the TGO are apparent, (c)

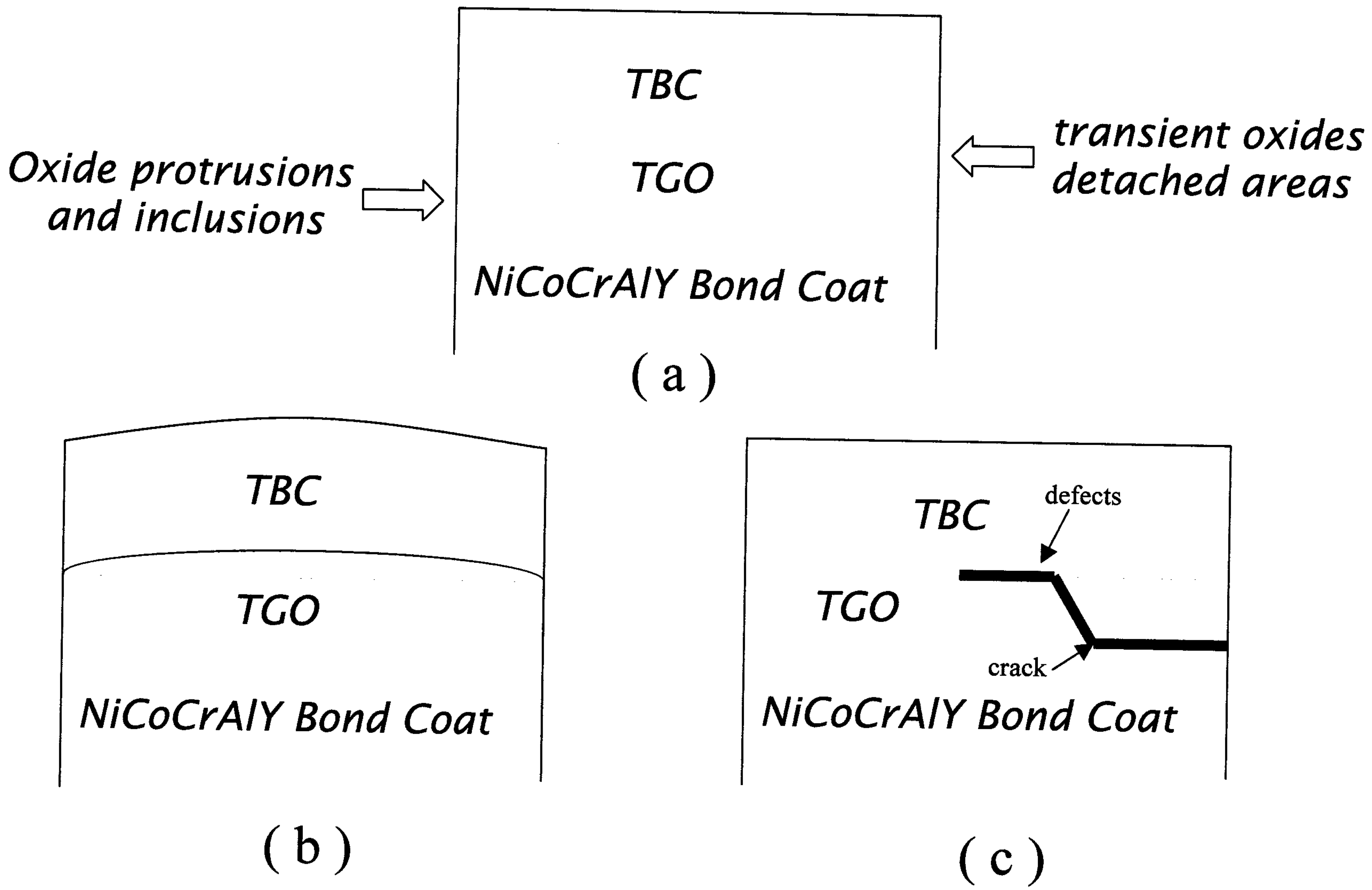


Figure 26. Sketches to describe TBC failures on NiCoCrAlY bond coats. Defects are present in the as-processed TBC, (a). When these defects develop continuous networks the failure is along the TBC-TGO interface, (b), whereas when the defects are isolated the TGO must thicken to provide sufficient strain energy and the cracks initiate at these defects and propagate through the TGO and propagate along the TGO-bond coat interface.

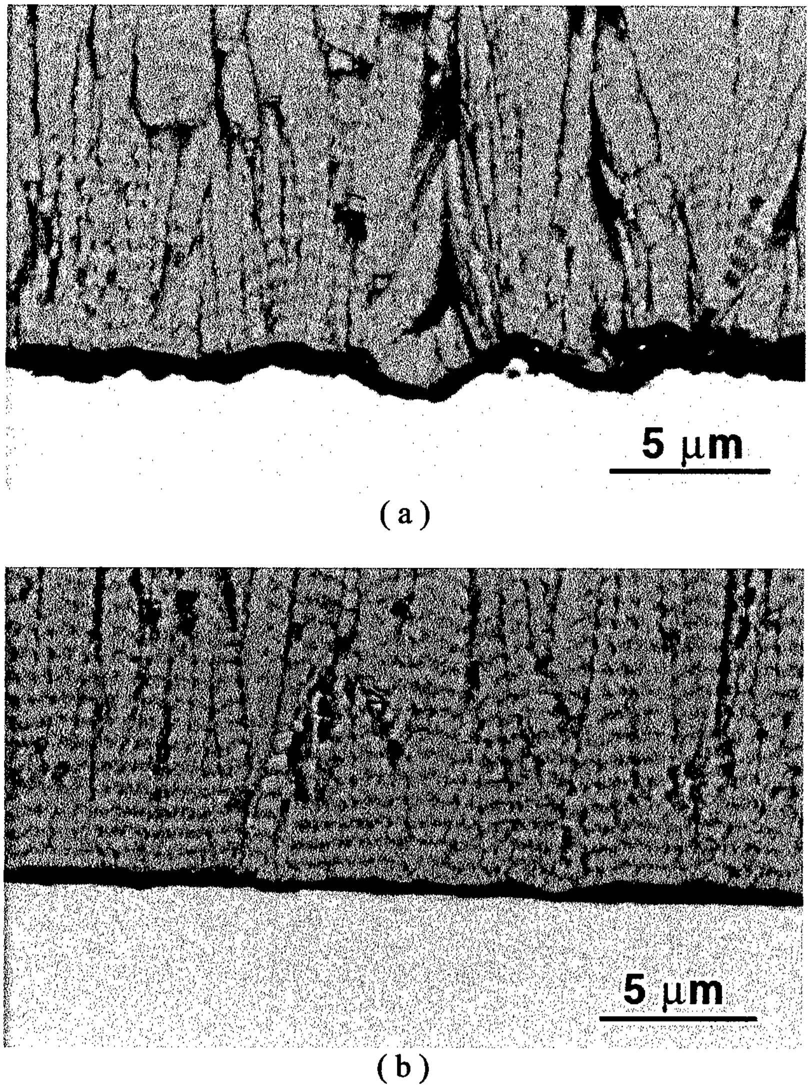
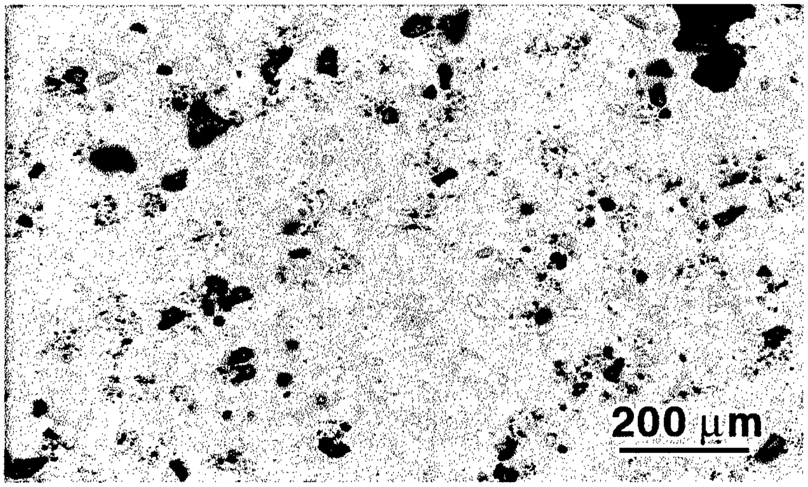
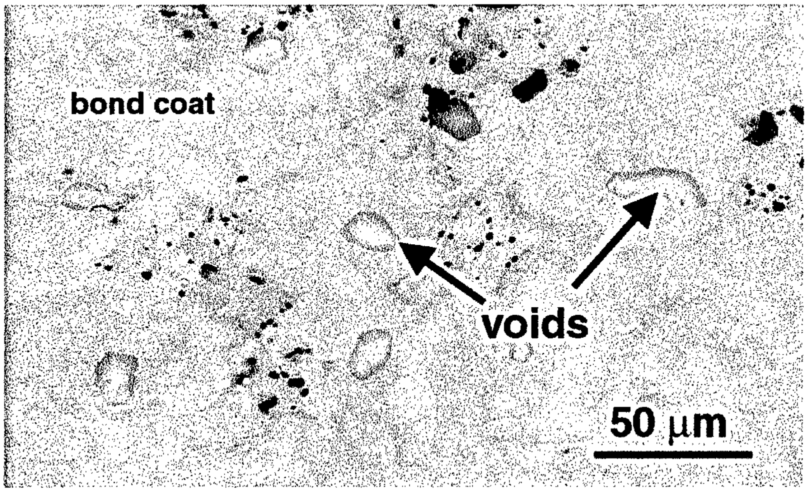


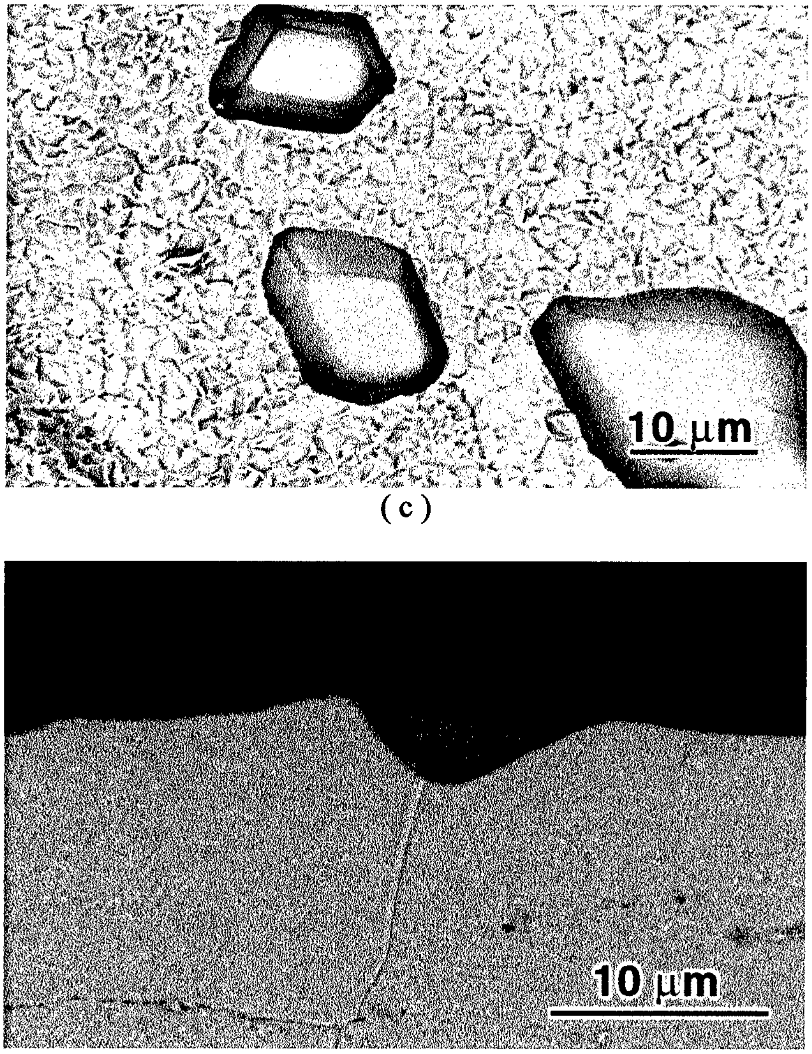
Figure 27. Scanning electron micrographs showing as-processed TBCs for which the platinum aluminide bond coats were given a light grit blast, (a), and a media finish followed by a preoxidation treatment, (b).



(a)



(b)



(c)

(d)

Figure 28. Scanning electron micrographs showing the surfaces of platinum aluminide bond coats after TBC spalling (1600 cycles at 1100°C). These surfaces frequently contained alumina particles, (a), which may have resulted from embedded grit blast particles. Voids were also evident, (b), which always were associated with grain boundaries in the bond coat, (c) and (d).

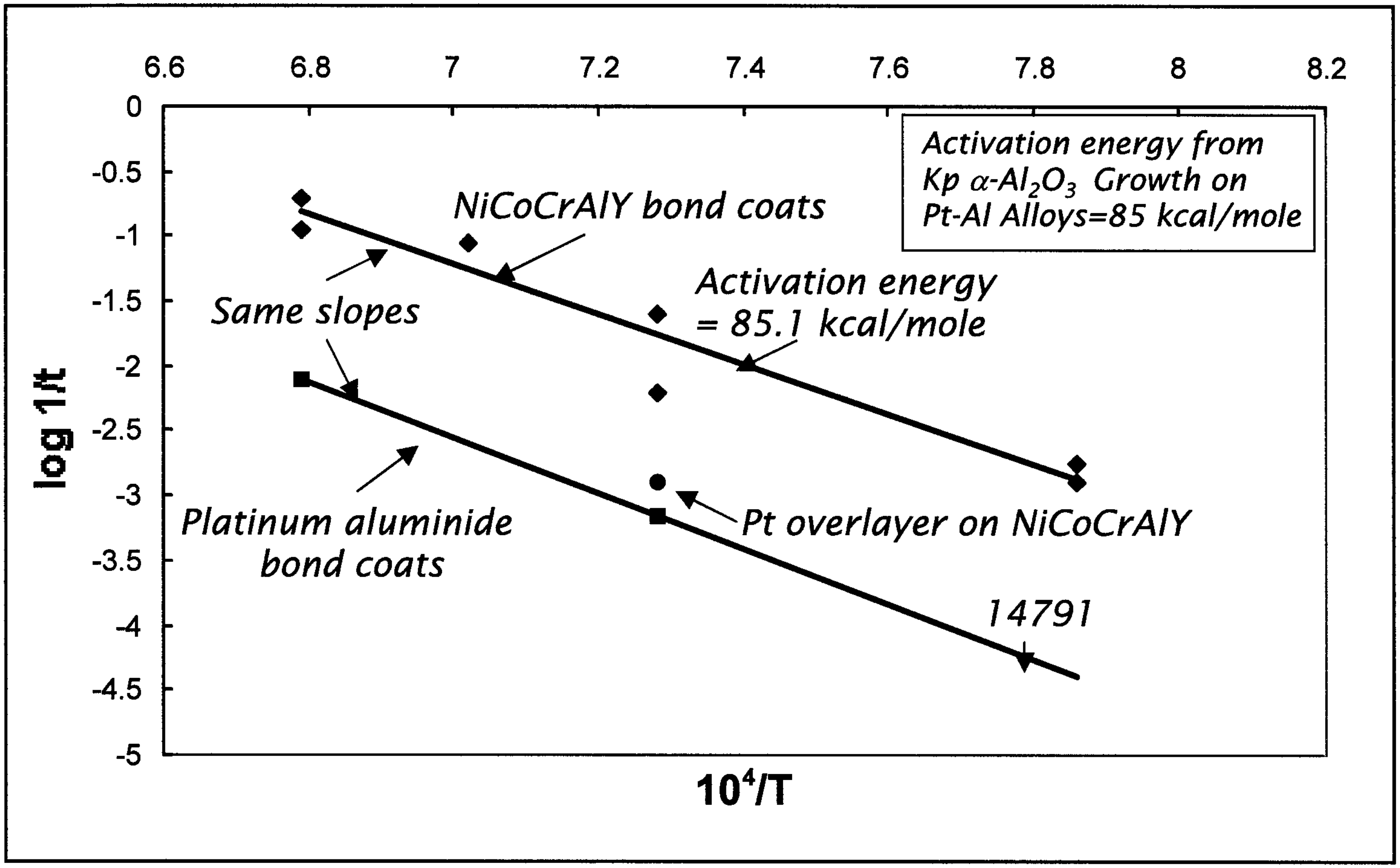


Figure 29. Temperature dependence of the reciprocal of the TBC failure times for NiCoCrAlY and platinum aluminide bond coats where it can be seen that the failure times conform to an Arrhenius-type relationship.

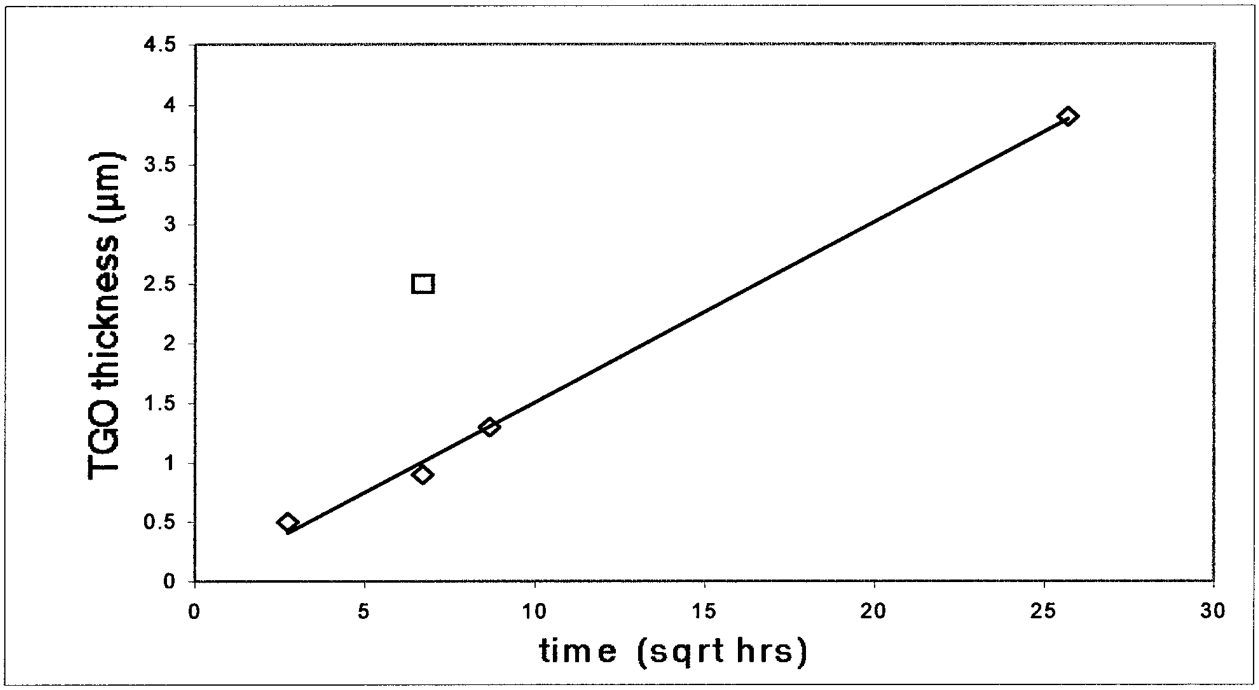


Figure 30. TGO thicknesses formed on the NiCoCrAlY bond coat with a platinum overlayer versus the square root of exposure time at 1100°C where it is evident that the data conform to parabolic rate law. The square data point is the TGO thickness for a NiCoCrAlY bond coat exposed at 1100°C.