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**COMPARATIVE PERFORMANCE OF A THERMAL BARRIER COATING SYSTEM
UTILIZING PLATINUM ALUMINIDE BOND COAT ON ALLOYS CMSX-4[®] AND
MAR M[®] 002DS**

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Abstract

It is known that the relative performance of thermal barrier coatings is largely dependent upon the oxidation properties of the bond coat utilized in the system. Also, the oxidation properties of diffusion-type bond coats (aluminides and their modifications) are functions of the superalloy substrate used in blade applications. Therefore, the performance of a given coating system utilizing a diffusion-type bond coat can significantly vary from one superalloy to another. Toward the objective of developing coating systems with more universal applicability, it is essential to understand the mechanisms by which the superalloy substrate can influence the coating performance. In this study, we examined the relative performance of yttria-stabilized zirconia/platinum aluminide coating system on alloys CMSX-4 and MAR M 002DS representing single-crystal and directionally-solidified alloy systems respectively using thermal exposure tests at 1150°C with a 24-hour cycling period to room temperature. Changes in coating microstructure were characterized by various electron-optical techniques. Experiment showed that the coating system on alloy MAR M 002DS had outperformed that on alloy CMSX-4, which could be related to the high thermal stability of the bond coat on alloy MAR M 002DS. From a detailed

microstructural characterization, this difference in behavior could be explained at least partially in terms of variation in chemical composition of the two alloys, which was also reflected on the exact failure mechanism of the coating system.

[®]CMSX and MAR M are registered trademarks of Cannon-Muskegon and Martin Marietta Corporations respectively.

1. Introduction

Application of thermal barrier coatings as surface protection systems for gas turbine blades allows the turbine entry temperature to be increased by as much as 200 °C leading to more power output, less fuel consumption, and cleaner environments, e.g. [1]. State-of-the-art technology involves the deposition of a of metallic bond coat (usually a modified aluminide-type) on the superalloy followed by a top coat of yttria-stabilized zirconia acting as a thermal insulator, e.g. [2]. The function of the bond coat is to develop an oxide layer acting as a "glue" to enhance

the adhesion of the ceramic top coat, and provide an additional resistance to oxidation. However, one limitation of these coating systems is the dependence of the overall coating performance on the superalloy substrate composition. To develop coating systems of more universal applicability, it is important to develop an in-depth understanding of coating degradation modes as functions of superalloy substrate composition. In a recent study, we have shown that for a γ - γ' platinum bond, the Ti content of the superalloy substrate can have a significant effect on the coating performance [3].

It is the objective of this study to compare the performance of a thermal barrier coating system utilizing a platinum-aluminide bond coat deposited on commercial grades of the single-crystal alloy CMSX-4[®] and the directionally-solidified alloy MAR M[®] 002. Emphasis has been placed upon: i) microstructural features in the as-deposited condition, ii) thermal stability, iii) oxidation behavior, and failure mechanism.

2. Procedure

Table 1 shows the nominal chemical compositions of the alloys included in the study. All samples were in the form of rods about 10 cm in length and 8 mm in diameter. The bond coat with nominal Pt and Al contents of 55 weight % and 25 weight % respectively was applied by electroplating a 6-8 μm layer of Pt followed by an aluminizing treatment, and pre-oxidation/diffusion heat treatment at 1150 $^{\circ}\text{C}$ to develop the bond coat microstructure as well as a thin layer of aluminum oxide about 1 μm in thickness to enhance the adhesion of the ceramic top coat. In the as-deposited condition, the bond coat on both alloys had a nominal total thickness of about 55 μm including the interdiffusion zone. Subsequently, a layer of the ceramic top coat (zirconia + 8 weight % yttria) about 250 μm in thickness was deposited on the oxidized bond coat using the technique of electron-beam physical vapor deposition [4].

Thermal stability, oxidation behavior, and coating performance were determined from thermal exposure tests at 1150 $^{\circ}\text{C}$ in air with a 24-hour cycling period to room temperature. Additional thermal exposure tests were carried out at 1000 $^{\circ}\text{C}$ and 1050 $^{\circ}\text{C}$ to study the kinetics of interdiffusion between the superalloy substrate and bond coat. Various techniques used to characterize the microstructure included scanning electron microscopy (SEM) combined with energy dispersive x-ray spectroscopy, electron probe microanalysis, transmission electron microscopy (TEM) and diffraction, and x-ray diffraction. Thin-

foils for transmission electron microscopy were prepared by combination of electropolishing and ion beam thinning to observe the bond coat microstructure near the surface. All foils were examined at an accelerating voltage of 200 keV.

3. RESULTS AND DISCUSSION

3.1 Microstructure in the As-Deposited Condition

Qualitatively, the coating microstructure on both alloys exhibited similar features in the as-deposited condition as illustrated in Figure 1. Figures 1a and 1b show backscattered SEM composition images (Z-contrast images) along a cross-section of the coating and into the superalloy substrates. It is observed that for both alloys, the bond coat could be divided into three distinct layers: i) an outer layer about 20 μm in thickness and exhibiting brighter contrast indicating a higher average atomic number, ii) an intermediate layer about 20 μm in thickness and exhibiting darker contrast corresponding to a lower average atomic number, and iii) an inner interdiffusion zone about 15 μm in thickness. However, the interdiffusion zone of alloy CMSX-4 exhibited a finer structure in comparison with alloy MAR M 002DS, which could be related to differences in the chemical composition of the two alloys as described below. An x-ray diffraction pattern representative of outermost coating layer on both alloys is shown in Figure 1c. All diffraction lines were consistently indexed in terms of the structures of β -NiAl (cubic B2-type; $a = 0.2888 \text{ nm}$) and PtAl₂ (Cubic, CaF₂-type; $a = 0.5930 \text{ nm}$). Since Pt can replace for both Ni and Al [5], it is expected some Pt could also partition to the β -phase in the outermost coating layer. Consistent with these results, concentration profiles derived from microprobe analysis along cross-section of the bond coat and into the superalloy substrate showed that most of the Pt was concentrated within the outermost coating layer as shown in Figure 1d. As can be seen, similar results were obtained for both alloys. Therefore, the brighter contrast exhibited by the outermost coating layer on both alloys could be related to the higher Pt concentration (higher average atomic number).

Figure 2 is an example illustrating the microstructure of PtAl₂ as revealed by dark-field TEM imaging. It is observed that PtAl₂ was present as a fine dispersion (bright contrast) within the matrix of β -phase (dark contrast) as illustrated in Figure 2a. A microdiffraction pattern of the respective cubic structure of PtAl₂ in $\langle 001 \rangle$ orientation is shown in the inset. The elemental composition of PtAl₂ is

shown Figure 2b. Although some elements particularly Ni and Co could be present within particles of PtAl₂ in solid-solution replacing for Pt, it is also possible that a portion of these elements as well as Cr observed in the spectrum of Figure 2b could have originated from the surrounding matrix.

Earlier studies of diffusion aluminide coatings such as the bond coat included in this study have shown that the kinetics of interdiffusion between the coating and superalloy substrate during thermal exposure at elevated temperatures are critically dependent upon the concentration of refractory elements in the superalloy as well as their distribution within the interdiffusion zone [6]. Although the nominal refractory element contents of alloys CMSX-4 and MAR M 002DS are about the same as shown in Table 1, two compositional parameters could possibly lead to the difference in the microstructure of interdiffusion zone observed in Figures 1 and 2: i) the absence of C in alloy CMSX-4 and presence of Re, and ii) the presence of C in alloy MAR M 002DS and absence of Re as described below.

Figure 3 illustrates the results of analyzing the structure of the interdiffusion zone corresponding to alloy CMSX-4. A backscattered SEM composition image is shown in Figure 3a. An energy dispersive x-ray spectrum showing the elemental composition of the matrix phase is shown in Figure 3b. Quantitative microprobe analysis indicated that corresponding composition was consistent with that of γ' -phase with a nominal as shown in Figure 3c. It is to be noted that Re is known to have a stabilizing effect on the γ' -phase [7]. Detailed analysis of the precipitates observed within the interdiffusion zone indicated a base composition of Ni-Cr-W as demonstrated in the energy dispersive spectrum of Figure 3d. It is known that σ -phase exists over a wide range of composition in the Ni-Cr-W although it is not thermodynamically stable in any of the respective binary systems [8].

In contrast with the case of alloy CMSX-4, the composition of matrix phase of the interdiffusion zone corresponding to alloy MAR M 002DS was found to be more consistent with that of β -phase as shown in Figures 4a-4c. Because of the higher enthalpy of formation and binding energy of β -phase in comparison with γ' -phase [9], the interdiffusion zone corresponding to alloy MAR M 002DS is expected to have higher stability in comparison with the case of alloy CMSX-4 as confirmed by the results of thermal stability characteristics presented later. Also, the presence of C in alloy MAR M 002Ds can allow the interdiffusion zone to accommodate more refractory elements in the form of carbides as

demonstrated in Figures 4d and 4e in addition to the Ni-Cr-W σ -phase (Figure 4f).

3.2 Comparative Coating Performance: Thermal Stability Characteristics and Oxidation Behavior

Figure 5 shows comparative performance of the coating system on alloys CMSX-4 and MAR M 002DS as determined from thermal exposure tests at 1150 °C with a 24-hour cycling period to room temperature. Failure was indicated by macroscopic spallation of the top coat. It is observed that the coating on alloy MAR M 002DS outperformed that on the alloy CMSX-4, which could be explained in terms of differences in thermal stability characteristics and oxidation behavior as shown below.

As an example, Figures 6a and 6b illustrate the effect of 48 hours of exposure at 1150 °C with a 24-hour cycling period to room temperature on the microstructures along a cross-section of the bond and into the substrate. In case of alloy CMSX-4 (Figure 6a), a considerable growth of the interdiffusion zone was observed. Also, the β -phase in the outermost coating layer was partially transformed into the γ' -phase. However, in the case of alloy MAR M 002DS (Figure 6b), the microstructure remained qualitatively similar to that in the as-deposited condition (Figure 1b), although the thickness of the outermost layer containing PtAl₂ and β -phase was reduced. The presence of γ' -phase in the outermost coating layer of alloy CMSX-4 is demonstrated in the results of TEM experiments shown in Figures 6c-6e. In $\langle 111 \rangle$ orientation, the β -phase in the bright-field TEM image of Figure 6c is distinguished from the γ' -phase by the characteristic superlattice reflections. In the case of β -phase, the diffraction pattern resembles that of a disordered body-centered cubic crystal (Figure 6d), however, in the case of γ' -phase, superlattice reflections appear at every 1/2-position of the fundamental reflection.

The tendency of the β -phase to transform into the γ' -phase could be related to outward diffusion of Ni as well as other substrate elements. Simultaneously, the Pt content in the outermost layer was reduced due to inward diffusion of Pt. These processes were found to occur more rapidly in the case of alloy CMSX-4, which could be related to lower stability of its interdiffusion zone as described. This is further illustrated in Figure 7 showing comparative kinetics of interdiffusion for the two alloys expressed as fractional growth of the interdiffusion zone per unit time. As can be seen, the kinetics of interdiffusion

followed a nearly parabolic rate behavior and the activation energy was about the same for both alloys (290 kJ/mol) suggesting that interdiffusion occurred by the same mechanism for both alloys. However, interdiffusion occurred at a faster rate in the case of alloy CMSX-4 consistent with the expected lower stability of its interdiffusion zone. Since diffusion data for intermetallic compounds is rather scarce, it was difficult to correlate the estimated activation energy with a particular diffusion mechanism. As expected, direct correlation was found to exist between the thermal stability characteristics and oxidation behavior as demonstrated by the results presented below.

Because of the lower thermal stability of the bond coat on alloy CMSX-4 as demonstrated above, less protective oxides would be expected to form during the earlier stages of thermal exposure at a given temperature in comparison with the case of alloy MAR M 002DS. This is consistent with the coating life data shown in Figure 5 and further confirmed by the observed growth rates of the thermally grown oxide as described below.

Figure 8a shows the effect of exposure time at 1150 °C on the thickness of the thermally grown oxide (total oxide thickness - thickness of initial oxide layer present in the as-deposited condition). Although the stage of primary oxidation was followed by a steady state for both alloys, breakaway oxidation occurred earlier in the case of alloy CMSX-4. This suggested that coating failure occurred by the same mechanism in both alloys, however, the corresponding kinetics were accelerated in the case of alloy CMSX-4. As an example, Figures 8b and 8c show the microstructure of the Al₂O₃ oxide layer developed by the bond coat on alloys CMSX-4 and MAR M 002DS respectively after 48 hours of exposure at 1150 °C. It is observed that alloy MAR M 002DS (Figure 8c) differed from alloy CMSX-4 (Figure 8b) in that the oxide layer contained Hf-rich oxide pegs extending into the bond coat and enveloped by Al₂O₃, which is typical behavior of reactive elements such as Hf, e.g. [10]. This is well known to improve the adhesion of the oxide scale.

Based upon the above observations, it could be concluded that the variation in coating performance on alloys CMSX-4 and MAR M 002DS could be related to differences in their chemical compositions influencing both the thermal stability characteristics and oxidation behavior of the bond coat. Although loss of loss of adhesion between the thermally grown oxide and bond coat was the mode of failure for both

alloys, the underlying mechanism was different as shown below.

3.3 Comparative Failure Mechanism of the Coating System

For both alloys, the surface of the ceramic top coat exposed by the failure was covered by the thermally grown oxide indicating that the mode of failure was loss of adhesion between the oxide and bond coat. In the case of alloy CMSX-4, oxide particles enriched in Ta and Ti were observed beneath the thermally grown layer of Al₂O₃. For alloy MAR M 002DS, the presence of Hf-rich oxide was more pronounced. However, the mechanisms leading to spallation of the thermally grown oxide could be identified from examination of the bond coat surface exposed by the failure as demonstrated in Figure 9.

Due to the nature of the mechanism leading to oxide spallation, secondary SEM imaging in the case of alloy CMSX-4 was more revealing. Characteristically, the bond coat surface contained high density of voids as shown in the example of Figure 9a. At higher magnifications oxide particles enriched in Ta and Ti could be detected in some voids. Depending upon their concentrations, Ti and Ta could degrade the adherence of Al₂O₃ by forming Ta and Ti-rich oxide particles near the oxide-metal interface [12,13]. This can lead to oxide decohesion by coalescence of voids formed around the oxide particles. However, it is also possible that the formation of less protective oxides due to interdiffusion with the superalloy substrate could significantly contribute to the observed accelerated oxidation toward the end of the coating life (Figure 8a).

In the case of alloy MAR M002DS, backscattered composition SEM imaging was more revealing in studying the characteristics of the bond coat surface exposed by the failure. Unlike the case of alloy CMSX-4, the bond coat surface contained islands of Al₂O₃ containing particles of Hf-rich oxide as shown in the backscattered image of Figure 9c and corresponding energy dispersive x-ray spectra of Figures 9d and 9e. This observation suggested that fracture of the Hf-rich oxide pegs near the oxide-bond coat interface observed in Figure 8c had played an important role in the loss of adhesion between the thermally grown oxide and bond coat. Usually, this behavior is encountered in Al₂O₃-forming alloy systems containing reactive elements because of the nature of the distribution of growth stress in the vicinity of the oxide pegs [10,13,14]. To summarize, the schematics of Figure 10 illustrate the sequence of

events, which could lead to loss of adhesion between the thermally grown oxide and bond coat on both alloys as depicted from experimental observations. A better understanding of the factors governing the adhesion of the thermally grown oxide and in turn, the useful life of the coating can be developed by considering the influence of key elements in the superalloy substrate as well as in the bond coat as described below.

It was shown that minor amounts of sulfur in the superalloy substrate can degrade the adherence of the oxide scale because of its tendency to segregate at the surface, which could lead to forming voids at the oxide-metal interface and/or weakening of the oxide-metal bond [15]. However, the presence of Pt in aluminide coating was found to eliminate or minimize the detrimental effect of sulfur [15,16]. Other beneficial effects of Pt include purer oxide scale of slower growth rate as well as increasing the diffusional stability of the bond coat [15-18]. Consistent with these results, it is also found that Pt promotes selective oxidation of Al by suppressing the formation of non-protective oxides particularly NiO in the case the Pt+Hf-modified γ' - γ bond coats [19]. Reactive elements such as Hf and Y are well known to improve the protective nature of Al_2O_3 , particularly its adherence to the underlying substrate, e.g. [15,16,19-22]. It is interesting to note that some common beneficial effects of Hf and Y have been reported particularly their effects on the grain morphology of Al_2O_3 scale. Both Hf [15,16,19,20], and Y [21,22] were observed to promote the formation of columnar grains of Al_2O_3 improving their fracture toughness. However, because higher concentrations of reactive elements can produce undesirable effects and in the meantime Pt is found to combat some of these effects, it is important that Pt-modified bond coats contain balanced amounts of Pt and reactive elements to achieve optimum oxidation resistance [20].

4. Conclusion

Experiment showed that the Pt-aluminide bond coat in a thermal barrier coating system on alloy MAR M 002DS outperformed that on alloy CMSX-4 because of differences in chemical compositions of the two alloys influencing the structure of the interdiffusion zone in the as-deposited condition as well as the thermal stability characteristics and oxidation behavior of the bond during thermal exposure at elevated temperatures. Although for both alloys, the mode failure was loss of adhesion between the thermally grown oxide and bond coat, the underlying mechanism was different. In the case of

alloy CMSX-4, oxide decohesion occurred by void formation around Ta, Ti-rich oxide particles near the oxide-bond coat interface and their subsequent coalescence. However, in the case of alloy MAR M 002DS, oxide decohesion was facilitated by fracture of Hf-rich oxide pegs enveloped by Al_2O_3 near the oxide-bond coat interface.

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TABLE 1 Nominal Chemical Compositions of Alloys CMSX-4[®] and MAR M[®] 002DS (weight %)

Element	Ni	Co	Cr	Al	Ti	Mo	W	Ta	Hf	Re	Zr	Fe	C
Alloy CMSX-4 [®]	Bal.	9.5	6.2	5.5	1	0.6	6.5	6.5	0.1	2.9	-	-	-
Alloy MAR M [®] 002DS	Bal.	10	9	5.5	1.5	0.5*	10	2.5	1.25	-	0.055	0.5*	0.15

* maximum

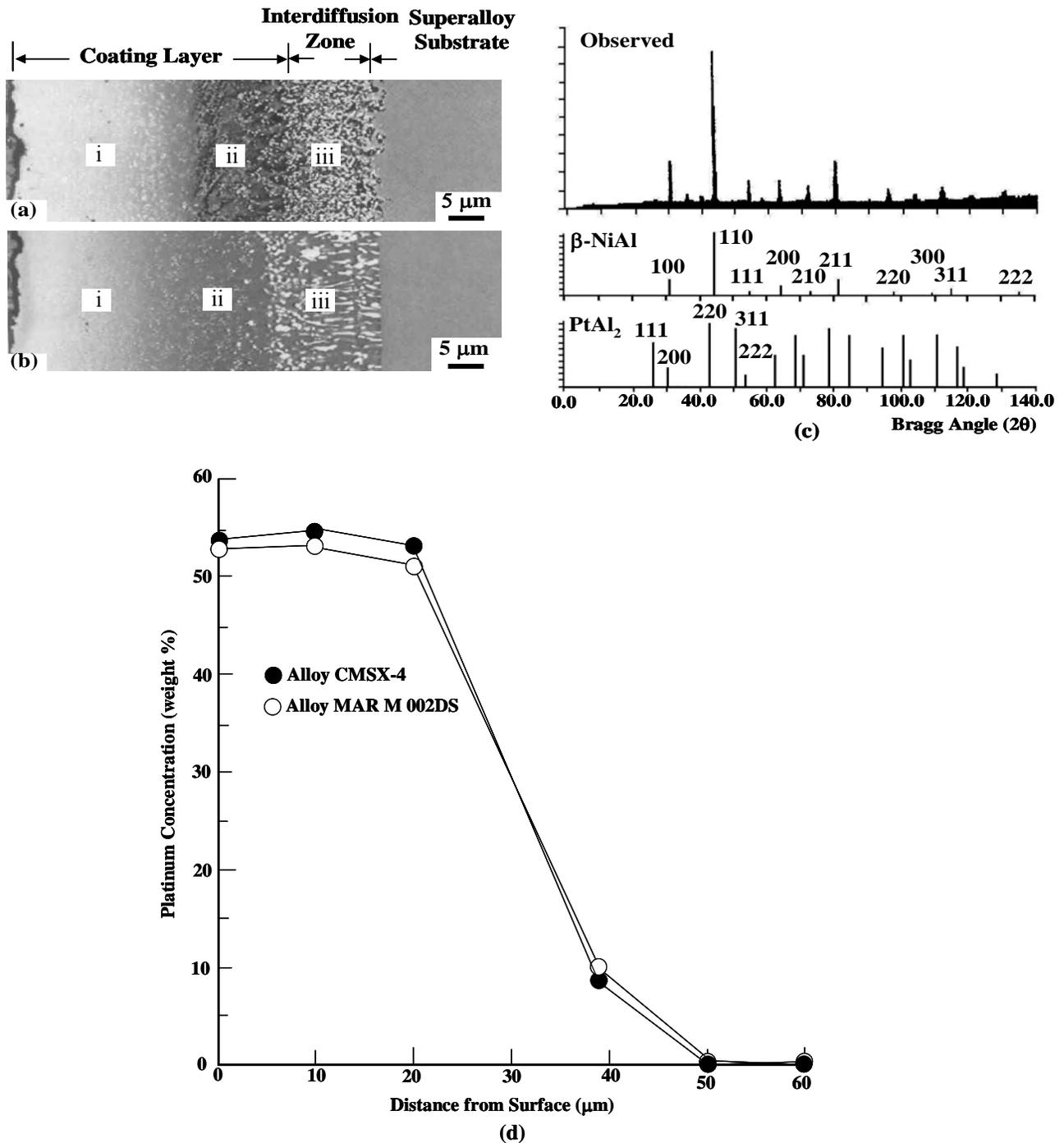


Figure 1 Characteristic microstructural features in the as-deposited condition. (a) and (b) are backscattered SEM composition images along a cross-section of the bond coat and into alloys CMSX-4 and MAR M 002Ds respectively; the three bond coat layers i, ii, and iii are indicated. (c) X-ray diffraction pattern representative of the outermost layer of the Pt-aluminide bond coat on both alloys; standard patterns of β -NiAl and PtAl₂ are also shown. (d) Concentration profiles of Pt along a cross-section of the bond coat and into the substrates.

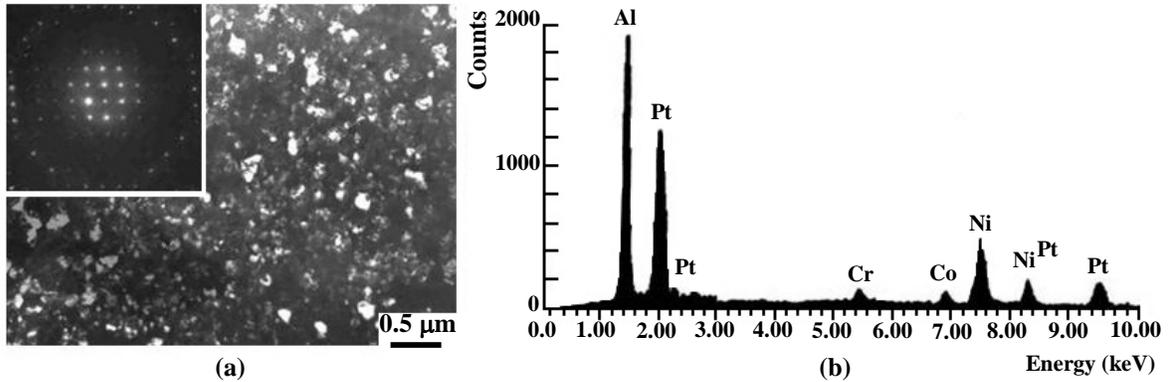


Figure 2 An example derived from the bond coat on alloy CMSX-4 illustrating the microstructure of PtAl₂ in the outermost coating layer in the as-deposited condition (a) Dark-field TEM image formed with the (200) reflection; the inset is a microdiffraction pattern in <001> orientation consistent with the structure of PtAl₂ (b) Corresponding energy dispersive x-ray spectrum illustrating the elemental composition of PtAl₂.

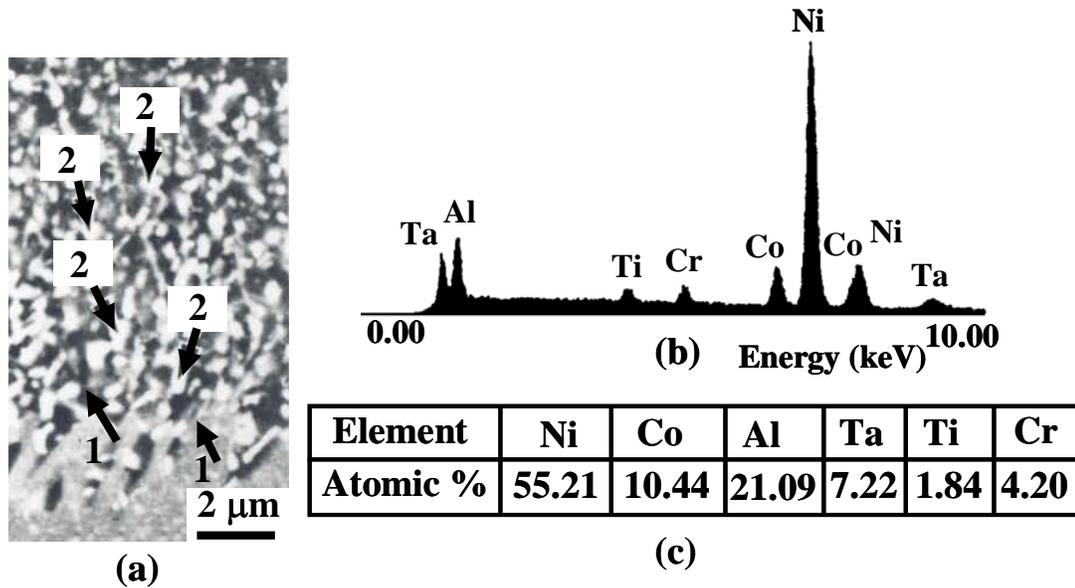


Figure 3 Analysis of the composition of interdiffusion zone of the coating on alloy CMSX-4 in the as-deposited condition. (a) Backscattered SEM composition image showing the microstructure of the interdiffusion zone. (b) Energy dispersive x-ray spectrum showing the elemental composition of the matrix phase (regions marked 1), (c) Composition of the matrix phase as determined by electron probe microanalysis. (d) Energy dispersive x-ray spectrum representative of the precipitates (regions marked 2).

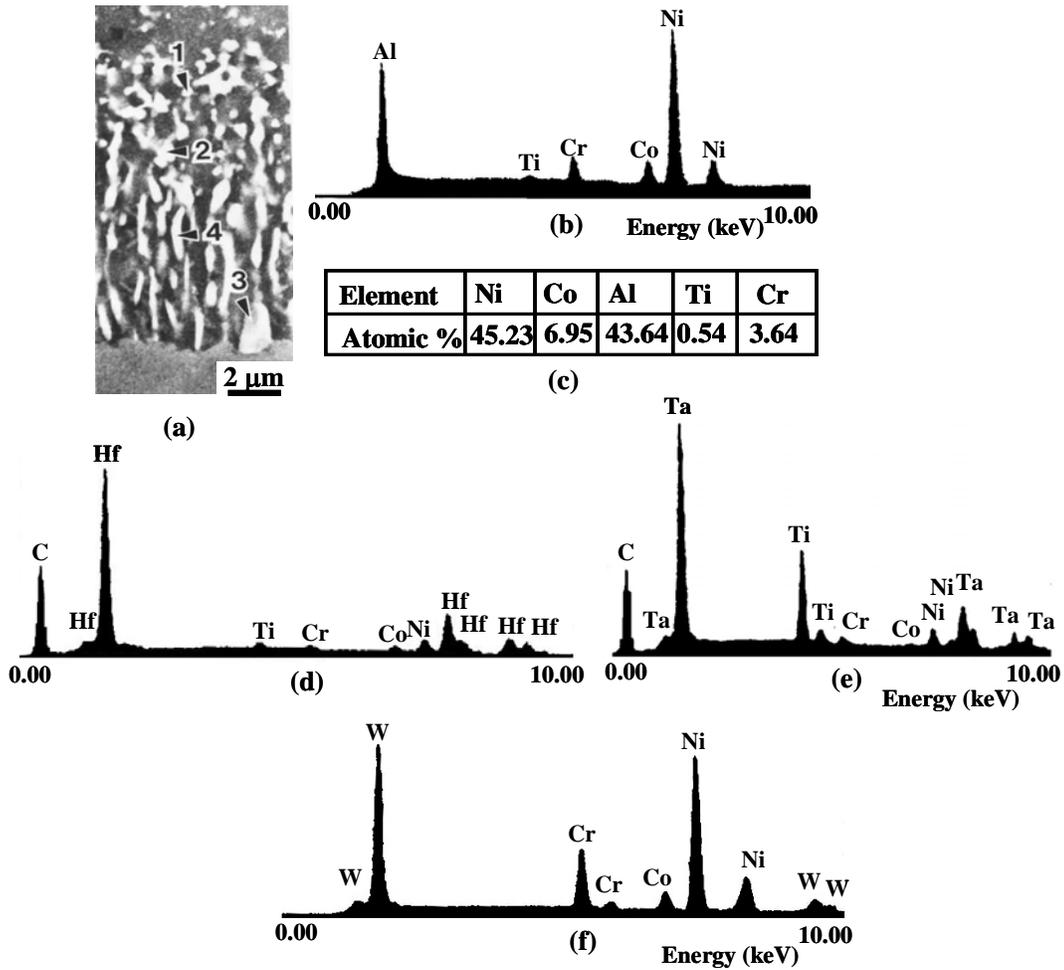


Figure 4 Analysis of the composition of interdiffusion zone of the coating on alloy MAR M 002DS in the as-deposited condition. (a) Backscattered SEM composition image showing the microstructure of the interdiffusion zone. (b) Energy dispersive x-ray spectrum illustrating the elemental composition of the matrix phase (region marked 1), (c) Composition of the matrix phase as determined by electron probe microanalysis. (d), (e), and (f) are energy dispersive x-ray spectra illustrating the elemental compositions of the precipitates marked 2, 3, and 4 respectively in (a).

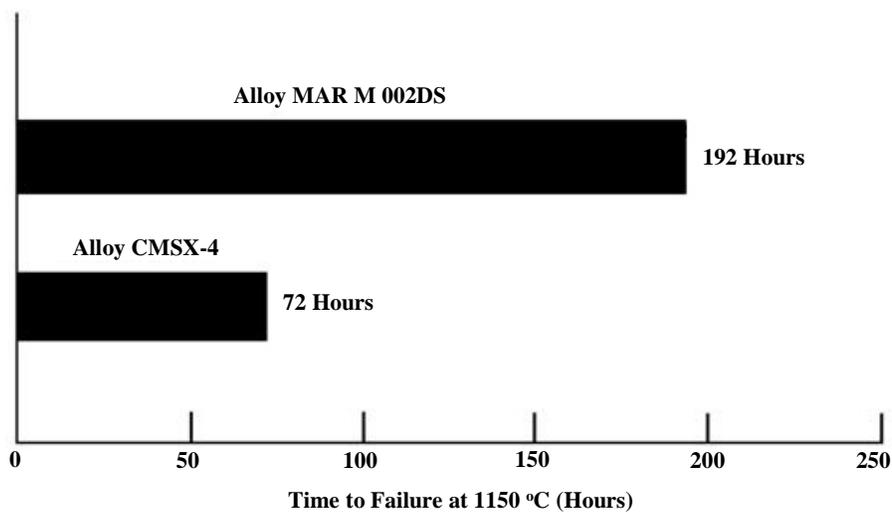


Figure 5 Comparative performance of the coating system on alloys CMSX-4 and MAR M 002DS as determined from thermal exposure tests at 1150 °C in air with a 24-hour cycling period to room temperature.

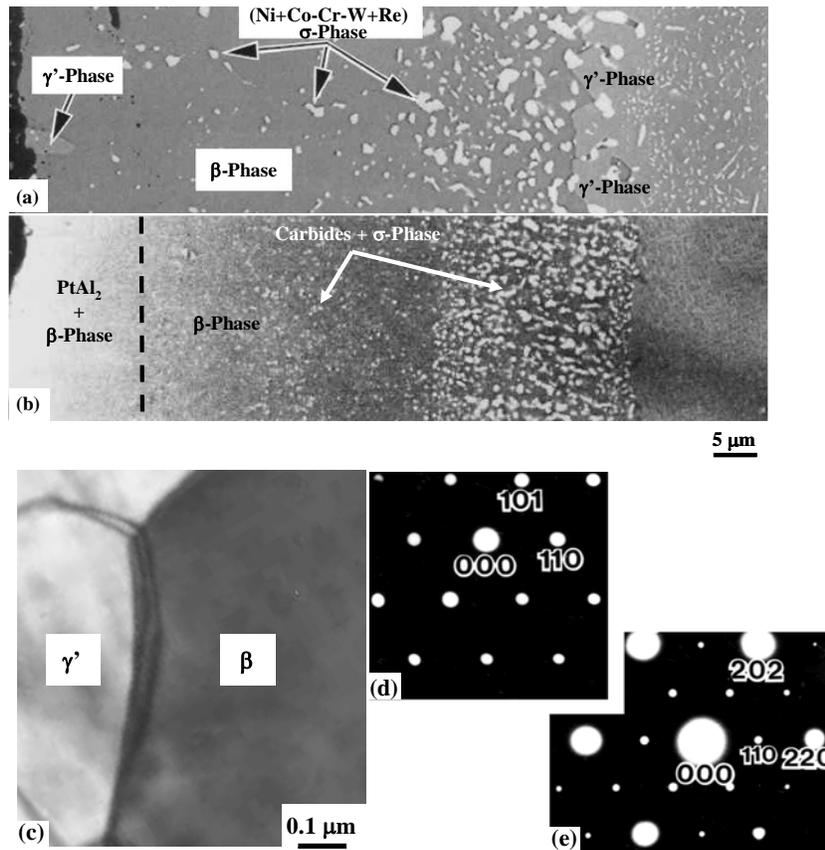


Figure 6 Examples illustrating comparative thermal stability characteristics of the bond coat during thermal exposure at 1150 °C. (a) and (b) are backscattered SEM composition images illustrating the effect of 48 hours of exposure at 1150 °C on the microstructure of the bond coat on alloys CMSX-4 and MAR M 002DS respectively. (c) Bright-field TEM image showing the presence of γ' -phase in the outermost coating layer on alloy CMSX-4. (d) and (e) are characteristic diffraction patterns of γ' -phase and β -phase in $\langle 111 \rangle$ orientation respectively.

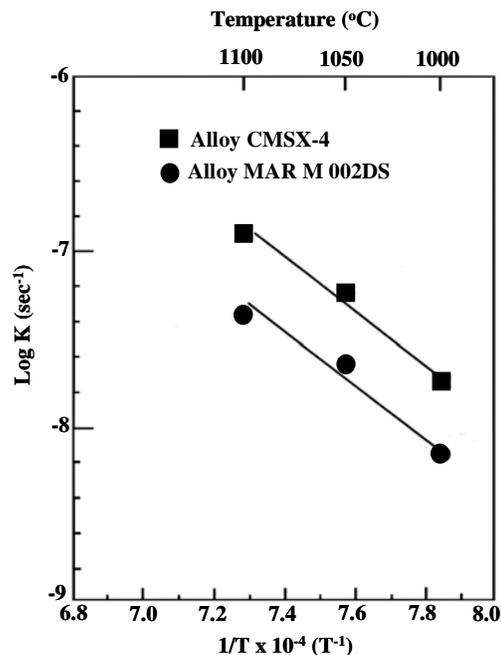
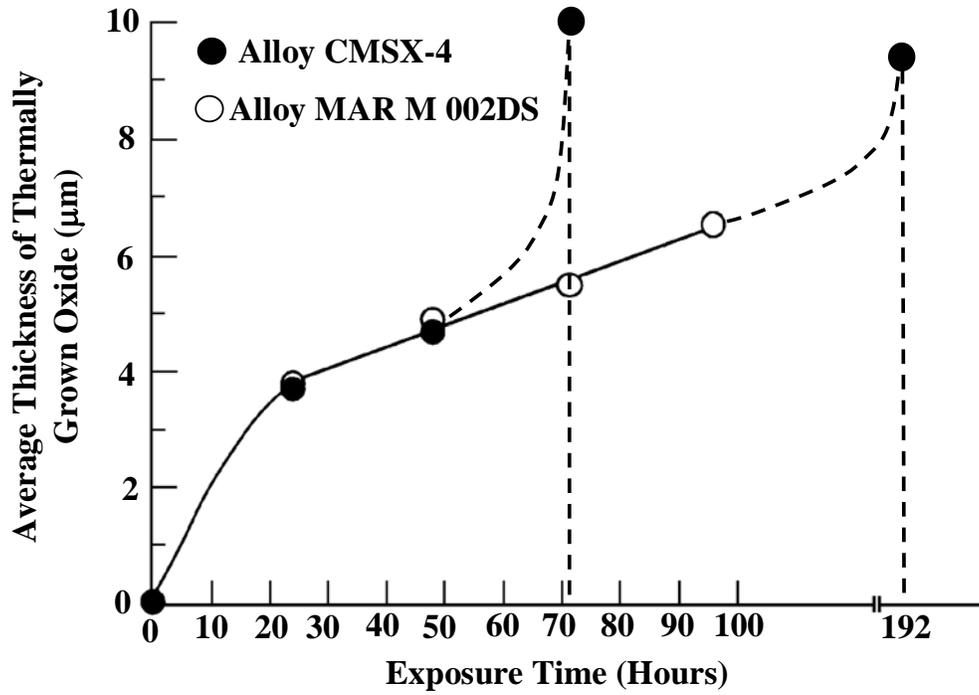
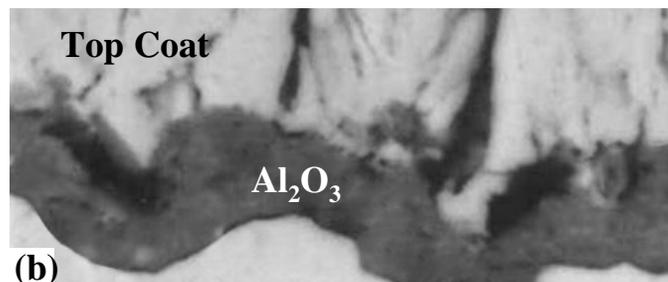


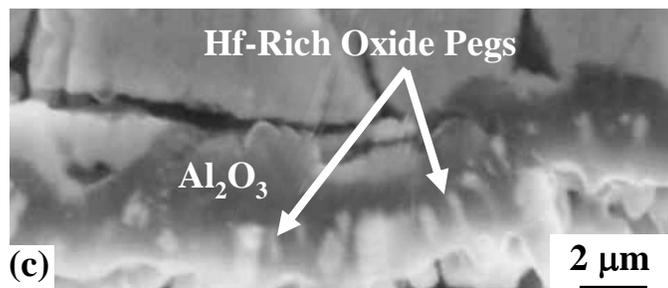
Figure 7 Temperature dependence of the parabolic rate constant (K) of interdiffusion between the bond coat and the superalloy substrates.



(a)



(b)



(c)

Figure 8 Comparative oxidation behavior of the bond coat during thermal exposure at 1150 °C. (a) Thickening rate of the thermally grown oxide. (b) and (c) are backscattered SEM composition image showing the microstructures of the thermally grown oxide corresponding to alloys CMSX-4 and MAR M 002DS respectively after 48 hours of exposure.

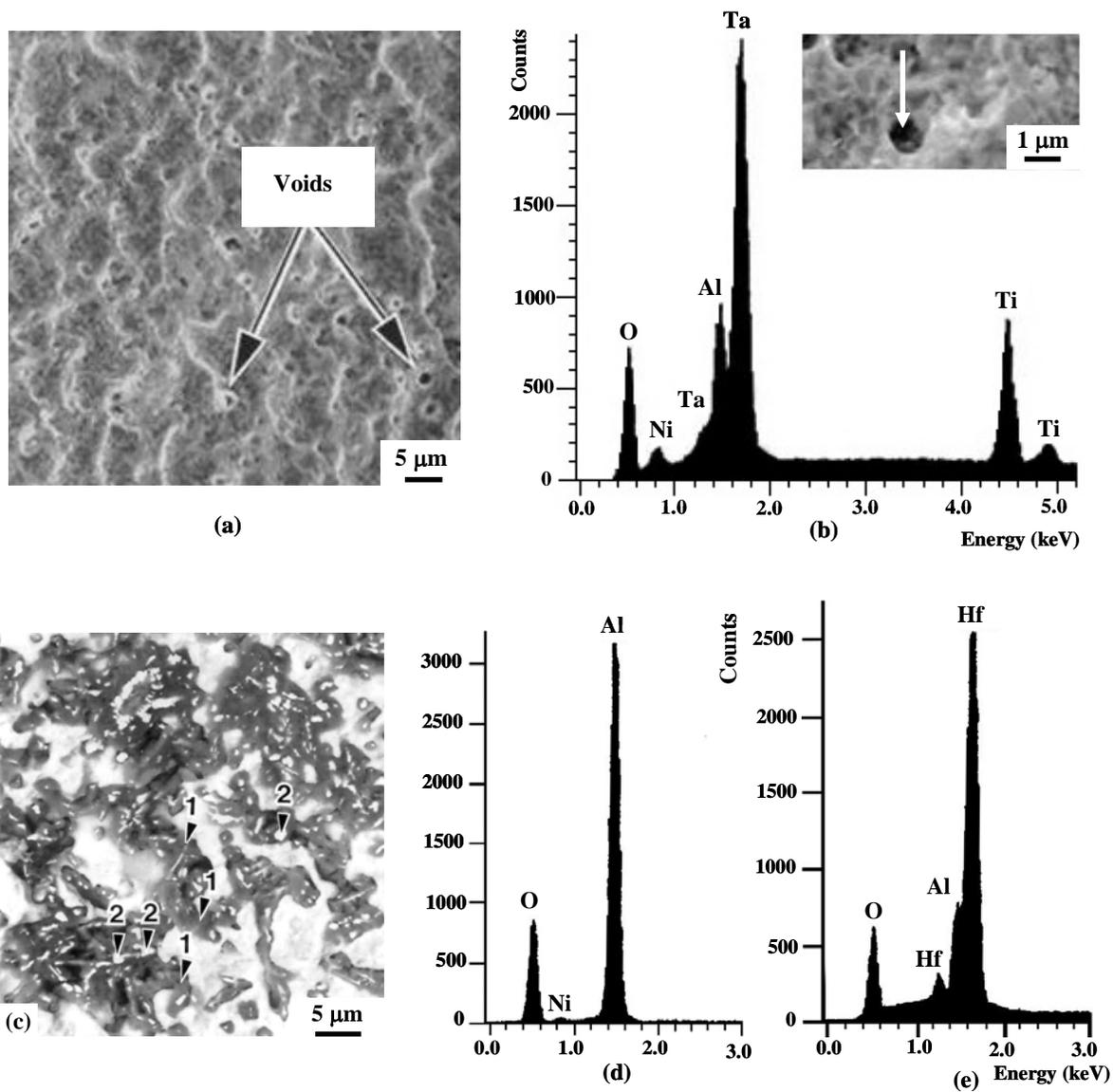


Figure 9 Microstructural features of the bond coat surface exposed by failure of the coating system on alloys CMSX-4 (a,b) and MAR M 002DS (c,d,and e) during thermal exposure at 1150 oC with a 24-hour cycling period to room temperature. (a) Secondary SEM image showing the microstructure of the bond coat surface exposed by failure of the coating system on alloy CMSX-4 after 72 hours of exposure. (b) Corresponding secondary SEM image at higher magnification and energy dispersive spectrum showing the presence of Ta,Ti-rich oxide particles within voids at the coating surface. (c) Backscattered SEM composition image showing the microstructure of the bond coat surface exposed by failure of the coating system on alloy MAR M 002DS after 192 hours of exposure. (d) and (e) are corresponding energy dispersive x-ray spectra showing the elemental compositions of regions a and 2 in (c).

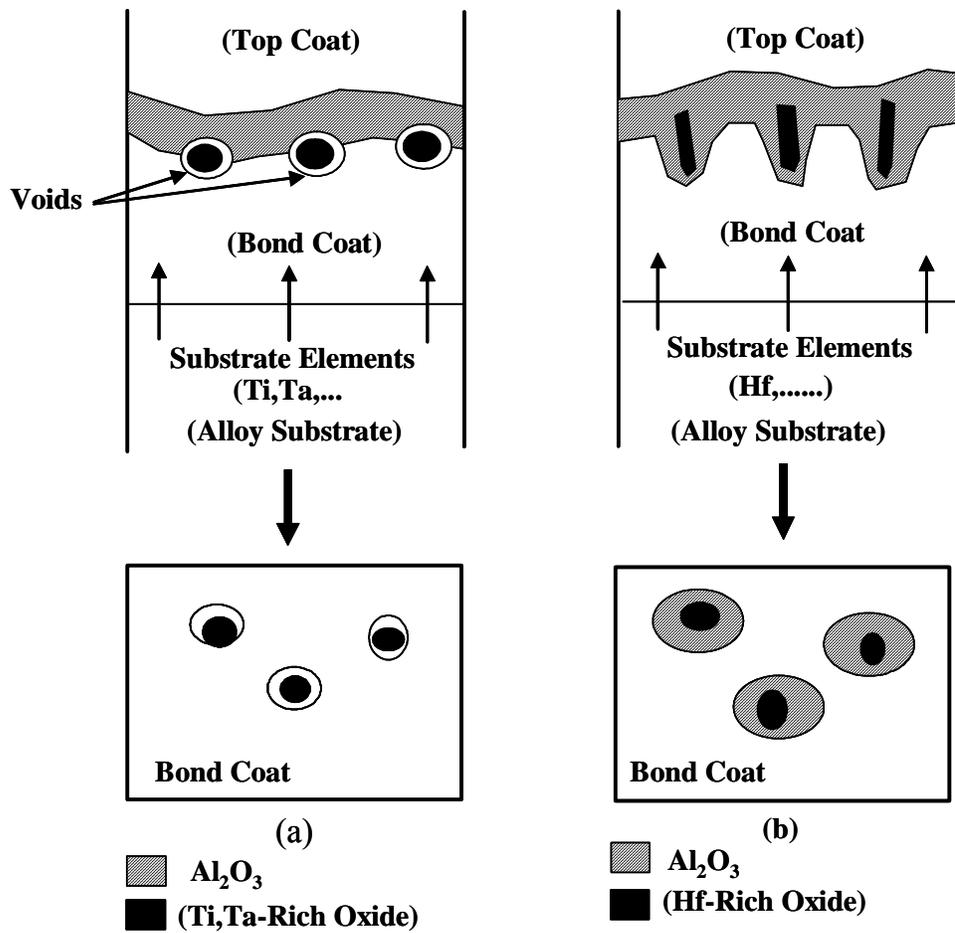


Figure 10 Schematics illustrating possible mechanisms leading to decohesion between the thermally grown oxide and underlying bond coat. (a) Alloy CMSX-4: coalescence of voids formed around Ta, Ti-rich oxide particles near the oxide-bond coat interface. (b) Alloy MAR M 002DS: fracture of Hf-rich oxide pegs.