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DIFFUSION BARRIERS TO INCREASE THE OXIDATIVE LIFE OF OVERLAY COATINGS

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Abstract

Currently, most blades and vanes in the hottest section of aero gas turbine engines require some type of coating for oxidation protection. Newly developed single crystal superalloys have the mechanical potential to operate at increasingly higher component temperatures. However, at these elevated temperatures, coating/substrate interdiffusion can shorten the protective life of the coating. Diffusion barriers between overlay coatings and substrates are being examined to extend the protective life of the coating. A previously-developed finite-difference diffusion model has been modified to predict the oxidative life enhancement due to use of a diffusion barrier. The original diffusion model, designated COSIM, simulates Al diffusion in the coating to the growing oxide scale as well as Al diffusion into the substrate. The COSIM model incorporates an oxide growth and spalling model to provide the rate of Al consumption during cyclic oxidation. Coating failure is predicted when the Al concentration at the coating surface drops to a defined critical level. The modified COSIM model predicts the oxidative life of an overlay coating when a diffusion barrier is present eliminating diffusion of Al from the coating into the substrate. Both the original and the modified diffusion models have been used to predict the effectiveness of a diffusion barrier in extending the protective life of a NiCrAl overlay coating undergoing cyclic oxidation at 1100°C.

Experimentally, thin alumina films were deposited by evaporation and by RF magnetron sputtering on a Ni-base superalloy substrate. The effectiveness of the films in limiting interdiffusion was evaluated by forming diffusion couples with Ni by hot pressing and annealing at 1200°C for 100 hrs. The evaporated alumina films have been shown to be an excellent diffusion barrier at this elevated temperature. However, it was found that the presence of the sputtered films decreased interdiffusion but allowed limited transport of Al and Cr across the film.

Introduction

Currently, many turbine components (e.g., blades and vanes) in advanced aero gas turbine engines require some type of coating for environmental protection. The most common type of coating is a diffusion aluminide which is applied by pack cementation or gas phase aluminizing. The coating consists primarily of the high-Al β NiAl phase at a typical thickness of 60-70 μm . For both pack cementation and gas phase aluminizing processes, Al is transported to the surface of the component and diffusion occurs to produce an Al-rich outer layer. Where environmental conditions are more severe, a more expensive Pt-aluminide may be used. These latter coatings are typically fabricated by electroplating a thin Pt layer on the surface of the component prior to aluminizing. Overlay coatings may also be employed in more demanding environments where simple aluminides are inadequate. The most common overlay coatings are referred to as MCrAl's, where M stands for either Ni, or Co, or a combination of these two elements. Most MCrAl's also contain reactive elements such as Y, Zr, or Hf (i.e., MCrAlY, MCrAlZr). MCrAl overlay coatings generally contain the high-Al β NiAl phase embedded in a more ductile γ Ni solid solution phase and are typically applied by either low pressure plasma spraying (LPPS) or by electron beam physical vapor deposition (EB-PVD) to thicknesses nearly twice that of aluminides (i.e., $\sim 120 \mu\text{m}$). A ceramic layer may be deposited onto any of these metallic coatings to form a thermal barrier coating (TBC). A general discussion of protective coatings is given in reference 1.

At high temperatures in an oxidizing environment, Al from the coating is selectively oxidized to form a protective Al_2O_3 scale which generally thickens parabolically with time (2). However, when the component is cooled, parts of the protective Al_2O_3 layer can crack and spall due to differences in thermal expansion between the oxide and metallic coating. Fortunately, as the component is reheated, Al diffuses within the coating to the surface where it is again selectively oxidized and the protective scale is healed, or reformed. The consequence of this scale loss during thermal cycling is that Al is consumed at a higher rate from the coating than when the scale is allowed to grow isothermally with time (2,3). The reactive elements which are added to the coatings (i.e., Y, Hf or Zr) increase the adherence of the Al_2O_3 scale and thereby decrease the extent of oxide spallation during thermal cycling (2,4). Decreased spalling equates to a lower rate of Al consumption, i.e., a lower rate at which Al is depleted from the coating (3). The significance of a lower rate of Al consumption is that the coating provides protection for a greater period of time.

In addition to loss of Al from the coating by oxidation, the coating is further degraded by interdiffusion with the substrate (1,5). Since the purpose of the coating is to provide an Al reservoir for alumina formation, coatings are by nature higher in Al than the substrate to which they are applied. This difference in Al content between the coating and substrate results in a driving force for diffusion from the coating into the substrate. Simultaneously, elements in the substrate can diffuse into the coating (1,5). Some of these elements, such as Ti or Mo, can have a deleterious effect on oxidation behavior. As scale adhesion continues to improve with various reactive element additions, degradation of the coating by interdiffusion becomes more important. Consequently, there have been numerous efforts in the past to develop diffusion barriers to reduce or eliminate this interdiffusion between the coating and substrate. Unfortunately, by the nature of their formation, diffusion aluminides are not amenable to the use of diffusion barriers. Although there has been substantial recent work involving diffusion barriers to reduce or eliminate diffusion or reactions between fibers in various matrices at elevated temperatures, the remainder of this paper will focus on application of diffusion barriers

to reduce or eliminate interdiffusion between superalloy components and MCrAl overlay coatings.

One early study examined the use of a thin W layer to limit diffusion between a NiCrAl coating and a high-temperature, Ni-base eutectic alloy (6). Although the W layer substantially reduced the diffusion of Cr and Nb between the coating and substrate, the thickness of the W layer greatly decreased with time as the W diffused into both the coating and substrate. More recently, Leverant and Page have applied either a Re (7), or a Ni-Re (8) layer to reduce interdiffusion between an MCrAlY coating and substrate. These researchers observed a significant reduction in the extent of interdiffusion with the presence of a 0.5 μm Ni-Re layer at the coating/substrate interface. The extent of interdiffusion was indicated by the amount of β recession after annealing at 926°C for periods up to 2000 hrs. Lastly, in the area of metallic diffusion barriers, Deakin and Nicholls have patented a diffusion barrier based on PtAl_2 (9). Although the patent refers to use of the barrier between overlay coatings and Ni-base substrates, recent publications (10,11) only show application of this barrier on Ti-base substrates with test temperatures of 900°C or below.

Knotek and co-workers (12,13) have shown a significant reduction in interdiffusion after depositing thin, amorphous Al-O-N oxide coatings. The coatings were deposited by magnetron sputtering with O_2 and N_2 reactive gasses. The best coatings remained amorphous and crack-free at temperatures as high as 1100°C, whereas when N_2 was not used, the resulting alumina film was unstable and began to recrystallize and crack at 800°C. At temperatures of 1200°C, even the Al-O-N coatings began to recrystallize. However, at 1100°C for up to 400 hrs, the 1-1.5 μm thick amorphous alumina coatings proved to be good barriers to interdiffusion.

Finally, Luthra (14) provided a theoretical basis for reducing interdiffusion with a dispersed oxide layer between the coating and substrate. This analysis quantified the life improvement for various thicknesses and volume fractions of dispersed oxide. Luthra predicted that the life of the coating could be improved by a factor as high as 2.5 with an oxide volume fraction of 0.7 (70% oxide).

As the temperature capabilities of newly developed superalloys increase, degradation of the coating by interdiffusion increases in importance. The purpose of the present work was two-fold; firstly, to predict the extension in the oxidative life of an overlay coating with a diffusion barrier, and secondly, to examine the ability of alumina layers deposited by two different techniques to function as diffusion barriers at the elevated temperature of 1200°C.

Predicted Life Extension With Diffusion Barriers

A previously-developed finite difference diffusion model (5,15) was modified to predict the oxidative life of a NiCrAl overlay coating on a Ni-base substrate. The model, designated COSIM for coating oxidation and substrate interdiffusion model, simulates diffusional transport of Al both to the growing oxide scale and into the substrate. The COSIM model incorporates an oxide growth and spalling model, designated COSP (16), to predict the amount of Al consumed in forming and growing the protective alumina scale. Operation of the COSP model requires the growth rate of the oxide scale, input as either a parabolic rate constant or parameters fit to a power law rate, and a spalling parameter, Q_0 , which controls the extent of

oxide spalling each thermal cycle. The rate of Al consumed predicted by the COSP model is taken as the boundary condition for the COSIM model. Operation of the COSIM model requires the starting concentrations of the coating and substrate, the coating thickness, and appropriate diffusivities. The COSIM model predicts Al and Cr concentration profiles in the coating and substrate after various oxidation exposures. Details of the COSIM model are given elsewhere (15). The COSIM model was modified to accommodate a diffusion barrier by eliminating any diffusion across the coating/substrate interface (i.e., a "perfect barrier"). This feature was accomplished in the program by establishing a zero flux plane at this interface by use of a virtual node in the substrate. The concentration at this virtual node was continually set equal to that of the node in the coating adjacent to the interface such that the calculated flux at the interface was always zero.

Predicting coating life with the COSIM model requires definition of a failure criterion. As previously stated, the rate of Al consumption during oxidation accompanied by thermal cycling (i.e., cyclic oxidation), is greater than that during isothermal oxidation due to the oxide spallation. During isothermal oxidation, the Al concentration at the surface of a coating would eventually decrease with time due to the finite thickness of the coating. However, this Al concentration decreases more rapidly during cyclic oxidation due to the higher rate of Al

consumption (3,5). Consequently, a minimum Al concentration of 3 at.%[†] at the surface of the coating was arbitrarily chosen as the failure criterion for this study.

The oxidative life of a coating was predicted using oxide growth and spalling parameters for two MCrAl-based alloys which exhibited very different cyclic oxidation behaviors. Both materials were thermally cycled with 1 hr exposures at 1100°C. A cast NiCrAlZr alloy exhibited excellent cyclic oxidation behavior (17) while an LPPS NiCoCrAlY coating on a Ni-base superalloy showed relatively poor behavior (5). Weight change curves for these two alloys, predicted by the COSP model, are shown in Fig 1. The isothermal growth rates and oxide spalling parameter used with the COSP model are also given for each curve. The greater oxide spallation of the LPPS NiCoCrAlY alloy is reflected in the negative weight change and the larger COSP spalling parameter ($Q_0=0.0075$). This increased spalling results in an increased rate of Al consumption.

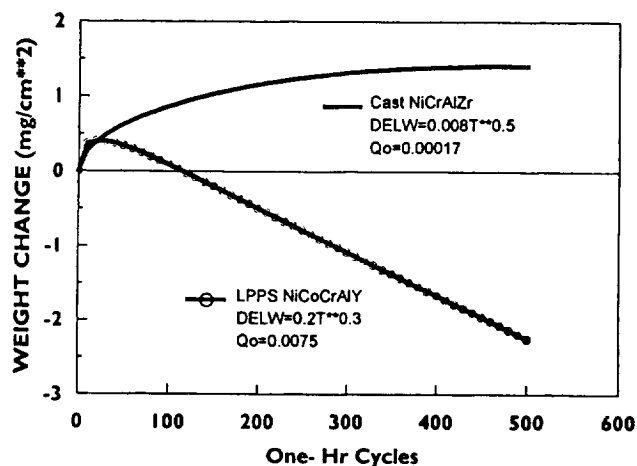


Figure 1. Weight change during cyclic oxidation (1 hr cycles) at 1100 for a cast NiCrAlZr alloy and an LPPS NiCoCrAlY overlay coating on a Ni-base superalloy.

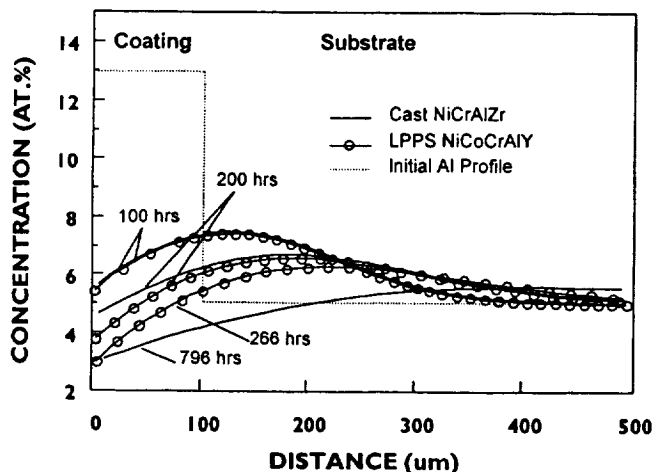


Figure 2 Al concentration profiles predicted by the COSIM model for the two materials shown in Fig 1. Times on curves refer to the number of 1-hr cycles at 1100C.

Al concentration profiles were

[†] All compositions are given in atomic percent unless otherwise noted.

predicted for a 100 μm thick, Ni-20Cr-13Al overlay coating on a Ni-10Cr-5Al substrate. The oxide growth and spalling parameters are as given in Fig 1. Ternary diffusion coefficients for 1100°C were taken from reference 18. Predicted Al concentration profiles for the LPPS NiCoCrAlY material with the higher rate of oxide spalling ($Q_0=0.0075$) are shown in Fig 2 for cyclic oxidation exposures of 100, 200 and 266 hrs. During the 266th cycle, the Al concentration at the surface of the coating decreased to 3 %, the defined failure criterion. The concentration profiles show that significant Al has diffused into the substrate at this time. In comparison, Al concentration profiles for the NiCrAlZr material with the lower rate of oxide spallation ($Q_0=0.00017$) are also shown in Fig 2. With this better oxide spalling behavior, it is predicted that nearly 800 hrs elapse before the surface concentration decreases to 3 %. Although Al is being consumed more slowly due to the reduced oxide spalling, more Al has been consumed by oxidation after 800 hrs leaving less Al in the coating and in the substrate.

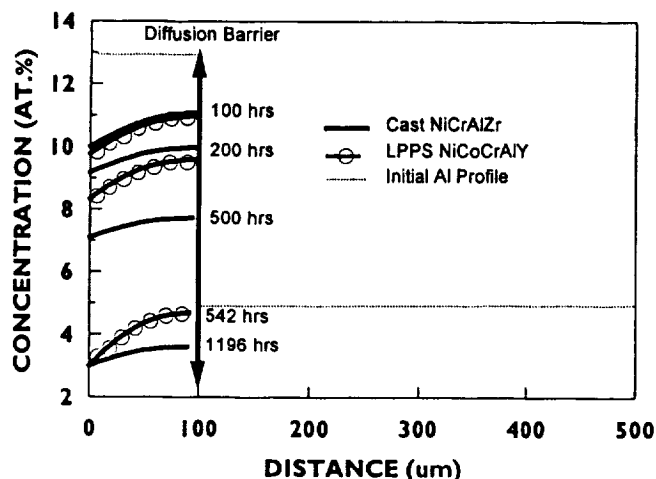


Figure 3 Al concentration profiles predicted by the modified COSIM model except with a diffusion barrier between the coating and substrate. All other conditions as shown in Fig 2.

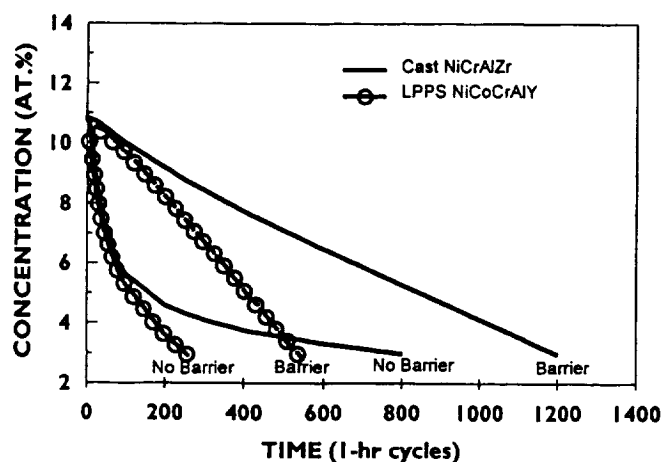


Figure 4 Al concentration at the coating surface predicted by the COSIM model for the two materials shown in Fig 1, with and without diffusion barriers.

For the conditions specified (coating thickness, initial concentrations, failure criterion, etc.), the better spalling behavior of the NiCrAlZr material results in a three fold increase in the oxidative life of the coating.

Al concentration profiles for the two cases above but with a perfect diffusion barrier were also predicted with the modified COSIM model. Profiles after 100, 200 and 542 hr are shown for the LPPS NiCoCrAlY material with the higher spalling rate in Fig 3. Obviously, no change occurs in the substrate. Profiles after 100, 200 and 500 and 1196 hrs are also shown for the NiCrAlZr material in Fig 3.

It is easier to see the differences between the two oxide spalling behaviors with and without diffusion barriers by viewing the time dependence of the Al concentration at the surface of the coating. This Al concentration is shown for the two oxidation behaviors (Fig 1) for identical coatings with and without diffusion barriers in Fig 4. For the LPPS NiCoCrAlY material with the poorer spalling behavior, the diffusion barrier increases the life of the coating by a factor of two (266 to 542 hrs). For the NiCrAlZr material with the better

spalling behavior, the presence of a diffusion barrier increases the life of the coating from 800 to 1200 cycles, an increase of 50%. The data for the NiCrAlZr material highlights the significance of the choice of the failure criterion. For example, if a failure criterion of 5% had been chosen rather than 3%, the lifetime of the coating without a diffusion barrier would have been less than 200 hrs whereas that with the diffusion barrier would have exceeded 800 hrs, an

increase in life of a factor of 4. The explanation for this observation is related to the rate at which the Al concentration at the surface of the coating decreases with time. With the diffusion barrier, this Al concentration decreases almost linearly after approximately 100 hrs. However, without a diffusion barrier, the Al concentration at the surface decreases quickly in the first 100 hrs as Al flows rapidly from the coating into the substrate due to the large concentration difference. Thereafter, the surface Al concentration decreases much more slowly, due to the almost steady loss of Al by oxidation.

Experimental Studies

Thin alumina films were deposited by both sputtering and evaporation on CMSX-4 single-crystal Ni-base superalloy substrates.[†] The coated substrates were diffusion bonded to Ni and annealed at 1200°C for 100 hrs. Nickel was used, rather than a NiCrAl alloy, to simplify the detection of any Al or Cr diffusion across or through the alumina film. It was assumed that any barrier that eliminated diffusion of Al and Cr from the superalloy into the Ni would be equally effective in eliminating Al and Cr diffusion from a NiCrAl coating into the substrate. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to determine the interdiffusion into the Ni. As a baseline, uncoated CMSX-4 was diffusion bonded and annealed for 100 hrs at 1200°C. For this baseline, concentration/distance (C/X) profiles for all elements were measured in the Ni by electron microprobe (EPMA). The concentration measurements showed that Al penetrated farther into the Ni than other elements with easily detectable concentrations at a depth of more than 400 μm from the Ni/CMSX-4 interface.

Alumina films approximately 2 μm thick were deposited on prepared CMSX-4 substrates by either RF magnetron sputtering or electron beam (EB) evaporation. For the evaporation technique, Al_2O_3 was melted by EB heating and deposited onto substrates intentionally heated to approximately 900°C. Further details of evaporated coating deposition are given in reference 19. For sputtering, an alumina target was used with Ar gas at 10 mtorr. No intentional heating of the substrate was used (the substrate temperature increases somewhat due to energetic Al_2O_3 molecules or Ar atoms impacting the substrate). Various surface roughnesses of the CMSX-4 substrate were examined. The roughness of the as-ground surface, measured perpendicular to the grinding marks, was 0.27-0.31 μm Ra. This surface was roughened to 0.5-0.6 μm Ra by glass bead blasting and 1-2 μm Ra by alumina grit blasting. The as-ground surface was also smoothed to 0.02-0.04 μm Ra and 0.01 μm Ra by polishing through 600 grit and 2400 grit SiC paper, respectively. Sputtered alumina films on the polished surfaces were nearly featureless. However, small regions where the film spalled on the as-ground surface indicate how the thin film reproduced the fine surface features (Fig 5). Due to space constraints, only the effectiveness of the alumina films deposited on the smoothed surfaces will be discussed.

X-ray diffraction of the as-sputtered films indicated no crystalline phases; i.e., the film appeared amorphous. However, annealing the sputtered films in Ar for 100 hrs at 1200°C caused the films to become crystalline with an $\alpha\text{-Al}_2\text{O}_3$ structure. The as-deposited evaporated films were not examined by x-ray diffraction. However, after an exposure of nearly 40 hrs in

[†] Nominal composition Ni-9.3Co-7.6Cr-12.6Al-2.2Ta-2.0W-1.0Re-1.3Ti-0.4Mo-0.03Hf at.% (Ni-9Co-6.5Cr-5.6Al-6.5Ta-6W-3Re-1Ti-0.6Mo-0.1Hf wt.%)

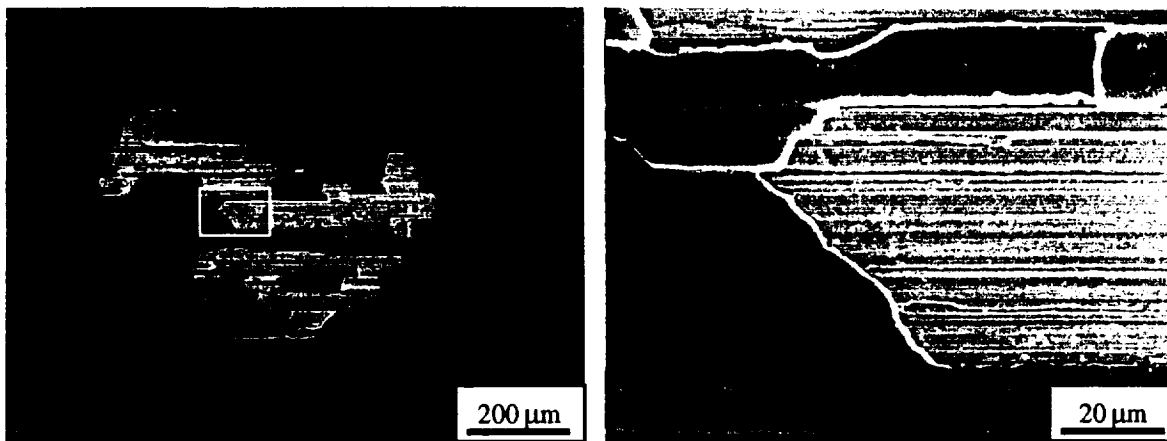


Figure 5 Sputtered alumina film on as-ground CMSX-4. Bright area is bare metal where film has spalled

air at 1150°C, x-ray diffraction also indicated that the films were crystalline with an $\alpha\text{-Al}_2\text{O}_3$ structure. All evaporated films were diffusion bonded after this short anneal in air. Sputter deposited films were diffusion bonded in the as-deposited condition.

The alumina-coated substrates were diffusion bonded with thin Ni slabs by placing them in sandwich fashion in a Mo canister threaded at each end. Threaded Mo bolts were screwed in each end to squeeze the coated substrates and Ni together. The Mo canister containing the diffusion couples were placed in a tube furnace and annealed at 1200°C for 100 hrs in flowing Ar. At the elevated temperature, the diffusion couple samples expand more than the Mo canister causing a compressive force to diffusion bond the samples together. After the bonding anneal, the diffusion couples were sectioned perpendicular to the alumina film and polished by standard metallographic techniques.

The CMSX-4/Ni diffusion couple with the evaporated Al_2O_3 diffusion barrier after a 100 hr anneal at 1200°C is shown in Fig 6. The film appears in intimate contact with the CMSX-4 but with some voids at the Al_2O_3 /Ni interface. The alumina deposited first, adjacent to the

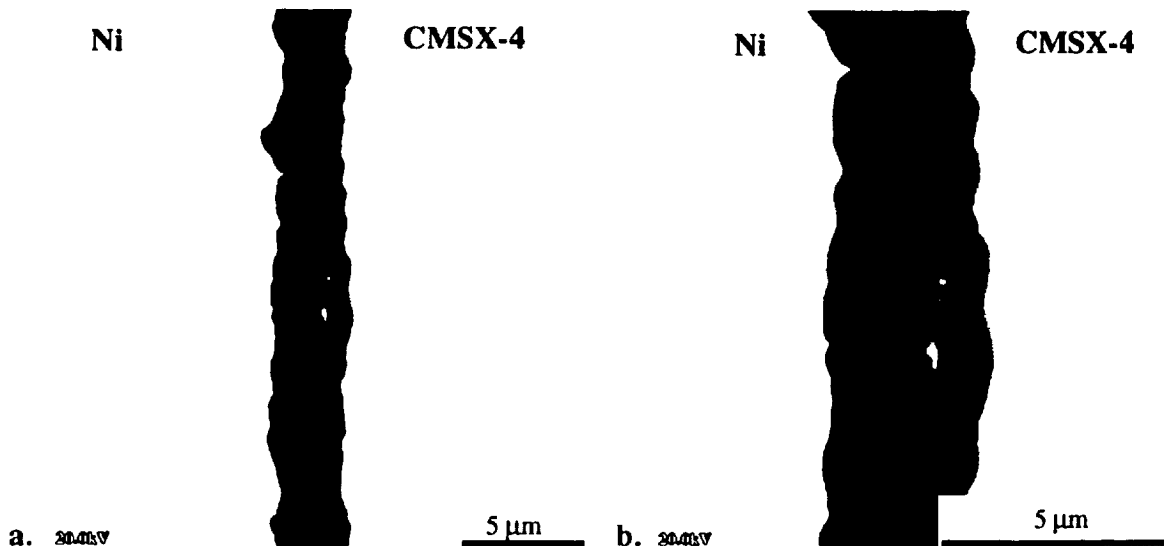


Figure 6 CMSX-4/Ni diffusion couple with evaporated alumina film after 100 hrs at 1200°C.

CMSX-4, appears dense but rapidly transitions to a non-uniform columnar grain structure with gaps between some columns. At higher magnification (Fig 6b), it appears that the Ni has been extruded, or grown, into some of the gaps between the columns. Very few defects were observed, most which appeared to be associated with pre-existing pores at the surface of the CMSX-4 (Fig 7). EDS spectra taken in the CMSX-4 and in the Ni near the alumina film are shown in Fig 8. It is clear that no measurable amounts of alloying elements in the CMSX-4 have diffused into the Ni. Hence, the evaporated alumina film appears to act as a good diffusion barrier at 1200°C for up to 100 hrs.

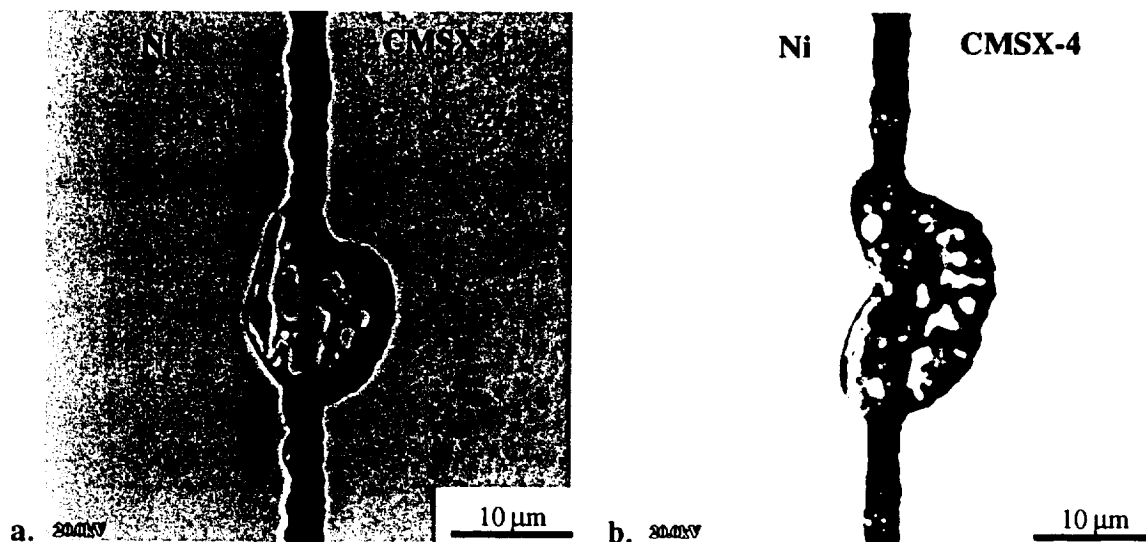


Figure 7 Defects in the evaporated alumina film. (Couple annealed for 100 hrs at 1200°C).

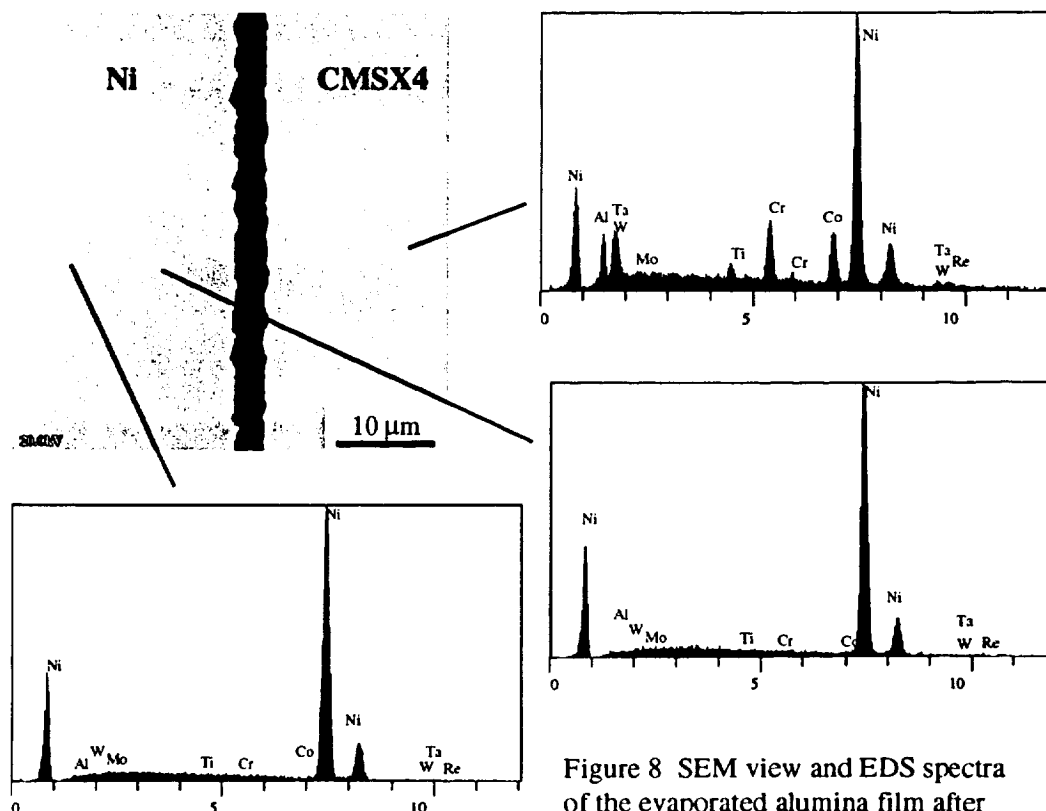


Figure 8 SEM view and EDS spectra of the evaporated alumina film after annealing at 1200°C for 100 hrs.

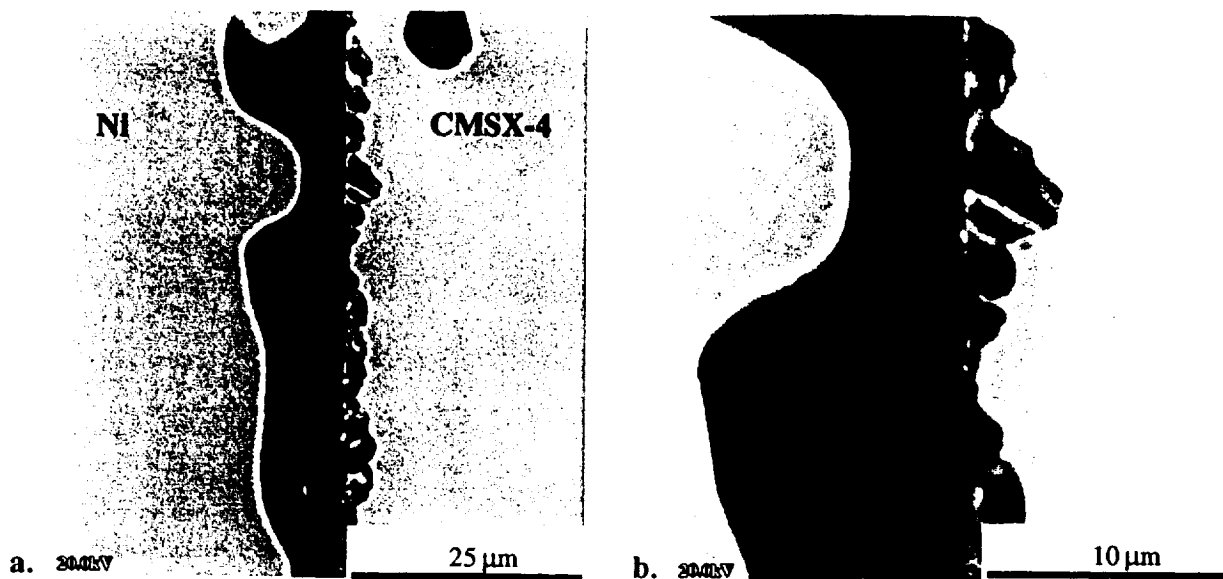


Figure 9 CMSX-4/Ni diffusion couple with sputtered alumina film after 100 hrs at 1200°C. Surface of CMSX-4 polished through 2400 grit SiC paper.

Cross-sectional views of the CMSX-4/Ni diffusion couple with the sputtered Al_2O_3 diffusion barrier are shown in Fig 9. A significant amount of smooth porosity has formed at the Ni/alumina interface. This type of porosity has previously been observed where significant interdiffusion had occurred, as with the CMSX-4/Ni diffusion couples without diffusion barriers. This "Kirkendall" porosity is the result of unequal diffusion fluxes between the diffusing elements. The unequal fluxes result in excess vacancies which coalesce into the served pores. In samples without diffusion barriers which exhibited extensive porosity, the presence of the pores did not appear to significantly reduce interdiffusion possibly due to vapor transport across, or surface transport around, the pores. A small amount of porosity is also apparent in Fig 9 at the alumina/CMSX-4 interface. Unlike the evaporated film, the structure of the sputtered film appears uniform without apparent columnar formation although some cracks in the film are obvious.

The ability of the sputtered film to limit diffusion is indicated by the EDS spectra in Fig 10. EDS spectra taken in the Ni show a small peak for Al and Cr indicating some transport of these elements through the alumina film. Al and Cr were detected in similar amounts regardless of whether the Ni appeared in intimate contact with the alumina or was separated by the pores. No significant peaks were observed for other alloying elements in the CMSX-4, specifically, Ta, W, Ti or Mo.

Summary and Future Work

Diffusion modelling to predict the protective life of an overlay coating shows that a significant increase in coating life can be achieved with diffusion barriers. Hot evaporated alumina films have been shown to be effective diffusion barriers for 100 hrs at 1200°C. Cold sputtered films decreased interdiffusion but allowed some transport, especially Al and Cr, across the film.

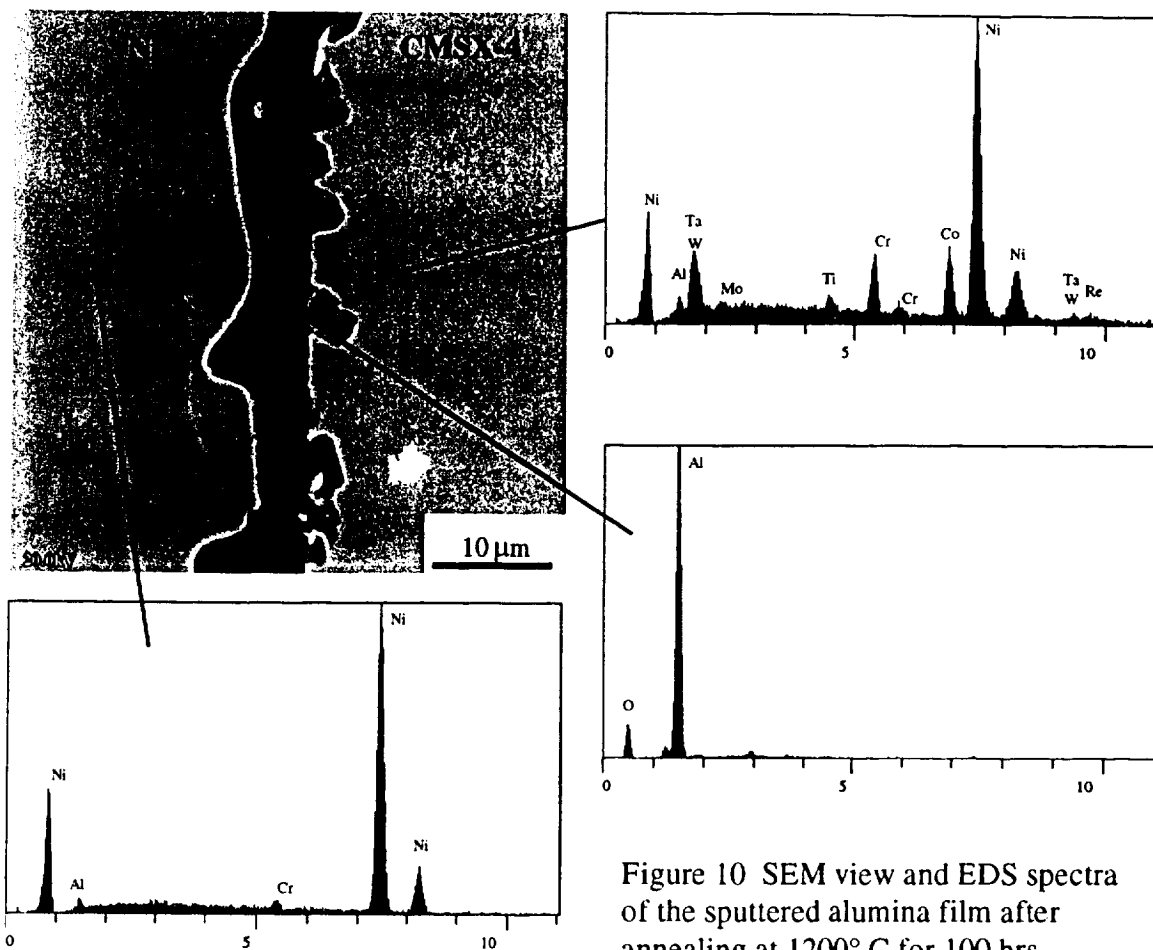


Figure 10 SEM view and EDS spectra of the sputtered alumina film after annealing at 1200° C for 100 hrs.

Work is ongoing to modify the COSIM diffusion model to predict the life enhancement for partial diffusion barriers. A barrier that allows limited interdiffusion could allow a much stronger bond between the coating and substrate than for a continuous barrier film. Further work to characterize the films and the effect of various deposition parameters will also be performed. Diffusion couples using NiCrAl overlay coatings coupled to coated superalloy substrates will also be fabricated and examined.

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