A Concept for the EQ Coating System for Nickel-Based Superalloys

K. Kawagishi, A. Sato, and H. Harada

Nickel-based single-crystal superalloys with high concentrations of refractory elements are prone to generate a diffusion layer called a secondary reaction zone (SRZ) beneath their bond coating during long exposure to high temperatures. The SRZ causes a reduction of the load-bearing cross section and it is detrimental to the creep properties of thin-walled turbine airfoils. In this study, a new bond coat system, "EQ coating," which is thermodynamically stable and suppresses SRZ has been proposed. Diffusion couples of coating materials and substrate alloys were made and heat treated at 1,100°C for 300 h and 1,000 h. Cyclic oxidation examinations were carried out at 1,100°C in air and the oxidation properties of EQ coating materials were discussed. High-velocity frame-sprayed EQ coatings designed for second-generation nickel-based superalloys were deposited on fourth- and fifth-generation nickel-based superalloys, and the stability of the microstructure at the interface and creep property of the coating system were investigated.

INTRODUCTION

Nickel-based superalloys, which have excellent high-temperature strength and oxidation resistance, are required for the high output and high efficiency required of gas turbines and jet engines. Advanced-generation nickel-based superalloys, which contain large amounts of strengthening elements and platinum-group metals, provide excellent high-temperature strength and suppression of topologically close-packed (TCP) phase formation.[1–3] However, an oxidation-resistant coating must be applied to the surface of these alloys because they are likely to have lower oxidation resistance than the previous generations of superalloys due to the nature of the alloying elements.

When conventional coatings such as Pt-Al or MCrAlY are applied to rhenium-containing advanced-generation single-crystal superalloys, a harmful layer called a secondary reaction zone (SRZ) is formed at the interface of the coating and substrate.[4–6] The SRZ zone results from interdiffusion during the high-temperature exposure and oxidation resistance of the coating layer, resulting in degradation of the mechanical properties of the substrates.[7] Diffusion barriers[5,8–10] and carburization[6] have been employed to minimize interdiffusion between the bond coat and the substrate, but these techniques require a complicated manufacturing process and long-time exposure in high temperature.

In previous research,[11–17] a new coating system called an EQ coating was developed in which stable phases that are thermodynamically in equilibrium with the substrate, such as γ′ phase, have been used as coating materials. With this coating, SRZ formation between the coating and the substrate is suppressed and interdiffusion is minimized because chemical potentials of the alloying elements in the substrate and coating in equilibrium state are equal. The oxidation resistance of the γ′ phase was evaluated[14] and its oxidation behavior was proven to be superior to the substrate. β-phase EQ coating systems using β-phase coating material in equilibrium with γ/γ′ nickel-based superalloys were also examined[15,16] to obtain higher oxidation resistance than γ/γ′ phase EQ coating. In this article, the concept of EQ coating is summarized and the latest data are presented.

Nickel-based superalloys consist of a regularly arranged γ phase and γ′ phase. These two phases are in thermodynamical equilibrium and so the chemical potential of alloying elements in each phase is equal. γ phase and γ′ phase alloys and γ/γ′ tie-line alloys, which have the same composition as the γ phase and γ′ phase of nickel-based superalloy substrates, can be used as EQ coating material. Figure 1 shows an (Ni, X)-(Al, Y) pseudo-binary phase diagram. The substrate S is a broken line, which means γ/γ′ tie-line consists

How would you…

…describe the overall significance of this paper?

Applying oxidation-resistant coatings to nickel-based superalloys is a technique for obtaining long lifetimes of turbine components in extreme high temperature. This paper proposes a novel concept in designing the coating material for advanced nickel-based single-crystal superalloys. The coating material described provides a durable and low-cost coating system without deterioration of high-temperature strength.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

To maintain the stability of interface between the coating and the substrate, interdiffusion is suppressed by using the equilibrium phase of the substrate as a coating material.

…describe this work to a layperson?

This work concerns a technique to use materials in long-time exposure to high temperatures over 1,000°C without resultant weakness and oxidation.

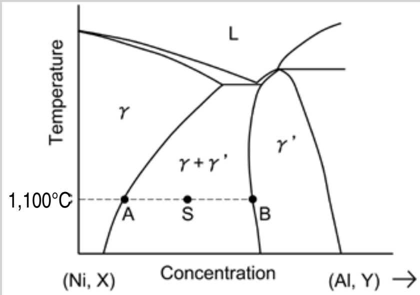


Figure 1. An (Ni, X)-(Al, Y) pseudo-binary phase diagram.

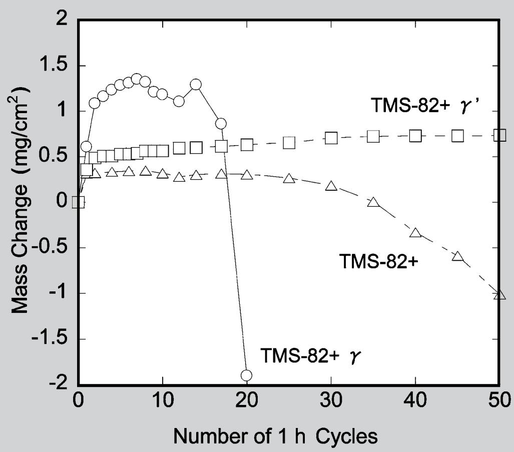


Figure 2. The cyclic oxidation properties of TMS-82+ tie-line alloys at 1,100°C.

of the γ phase of composition A and γ′ phase of composition B. In the microstructure, the γ phase of composition A and γ′ phase of composition B are intermingled and the chemical potential of the alloying element i is equal at all points on the tie-line such as A, B, and S. One can conclude that alloys A, B, and other alloys on the tie-line are in equilibrium with the substrate and there is no driving force of interdiffusion because the difference of the chemical potential of element i is zero between substrate S and these alloys. In other words, using alloys A, B, and other alloys on the tie-line as a bond coat, SRZ formation due to the interdiffusion of alloying elements is expected to be suppressed.

In previous research,[12] oxidation resistance of tie-line alloys for the second-generation superalloy TMS-82+ [18] was investigated. Results of the cyclic oxidation examination performed to evaluate the oxidation resistance of EQ coatings are shown in Figure 2. The examination was performed at 1,100°C in air, using TMS-82+, TMS-82+γ, and TMS-82+γ′. This result shows that alloys of TMS-82+γ show the largest mass increase in the first few cycles and decrease in the following cycles due to fast oxidation and spallation. TMS-82+γ′ shows the most excellent oxidation resistance in 50 cycles' examination and it is obviously improved from that of TMS-82+. The difference of the oxidation property of the γ phase and γ′ phase is due to the structure of oxide.[14]

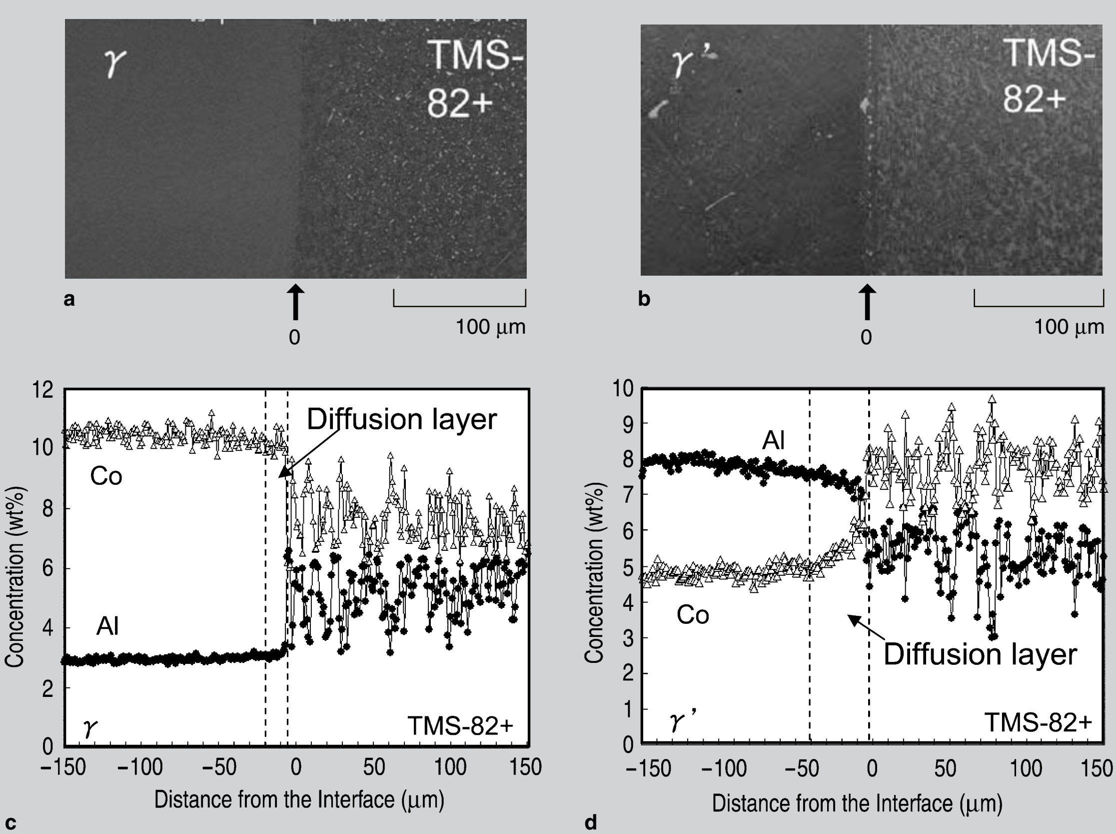


Figure 3. Cross sections of diffusion couples of (a) γ-EQ coating and (b) γ′-EQ coating and concentration profiles (c, d) with TMS-82+ substrate heated at 1,100°C for 300 h.

While the γ′ phase forms a protective Al_2O_3 layer, the γ phase mainly forms a non-protective thick inner oxide layer of NiO and particles of Al_2O_3. Thus, it is concluded that the γ′ phase is a promising material for an oxidation-resistant coating.

In this study, γ′ phases of nickel-based superalloys are designed as coating materials and thermal sprayed on the advanced-generation nickel-based superalloys. The γ′ phase of second-generation nickel-based superalloys are used as coatings for fourth- and fifth-generation superalloys in order to reduce the cost and obtain high oxidation resistance. The microstructure stability at the interface of the substrate and coating material is investigated.

See the sidebar for experimental procedures.

RESULTS AND DISCUSSION

Cross sections of diffusion couples of TMS-82+ and two coating materials, TMS-82+γ and TMS-82+γ′, after diffusion at 1,100°C for 300 h are shown in Figure 3. In both diffusion couples, SRZ was not found and only very thin diffusion layers were observed. In the γ′ phase alloy, a small amount of disk-like TCP phase was found but these particles disperse uniformly throughout the whole sample. It is estimated that this TCP formation is not due to diffusion but to the heat treatment condition. From the concentration profile analysis of aluminum and cobalt in Figure 3c, TMS-82+γ/TMS-82+, and Figure 3d, TMS-82+γ′/TMS-82+, diffusion couples were analyzed by using electron probe microanalysis (EPMA) and the thicknesses of diffusion layers were evaluated as 15 μm and 40 μm, respectively. In the conventional coating system, TMS-82+ is reported to form over 100 μm of the diffusion layer with the Ni-Cr-Al-Y coating.[12] From these results, using the γ and γ′ phase of TMS-82+ as a coating on a TMS-82+ substrate, it is concluded that the thickness of the diffusion layer between the coating and the substrate will be suppressed drastically.

The effect of the γ′ EQ coating on the fifth-generation superalloy was also investigated using the diffusion couple of fifth-generation superalloy TMS-173 and its γ′ phase. As shown in Figure 4b, a 15 μm thick diffusion layer was obtained after the diffusion at 1,100°C for 1,000 h. Thus, it is confirmed that the concept of EQ coating can be applied to a ruthenium-containing fifth-generation nickel-based superalloy.

Figure 5 shows cross sections of (a) Amdry9954 and (b) TMBC-1 coating with the fourth-generation nickel-based single-crystal superalloy TMS-138A. After the heat treatment at 1,100°C for 300 h, a primary diffusion zone (PDZ) about 90 μm thick and an SRZ 140 μm thick were formed at the interface of Amdry 9954. The term "PDZ" can be defined as a diffusion layer between the coating and substrate containing TCP such as granular μ, σ phase, or car-

EXPERIMENTAL PROCEDURE

The concept of an EQ coating was confirmed in the diffusion couple experiment in which a second-generation nickel-based single-crystal superalloy TMS-82+ and fifth-generation nickel-based single-crystal superalloy TMS-173 [19] were used as substrates. The compositions of the γ phase and γ′ phase at 1,100°C were calculated by the Alloy Design Program[20] and these compositions were used for coating materials. Compositions of samples used in this study are shown in Table A. Samples of coating materials were arc melted and after homogenization, each sample was cut to 10 mm diameter and 5 mm thickness. Sample surfaces were polished by 0.05 μm-φ Al_2O_3 particles into a mirror surface and cleaned. After cleaning, coating materials were coupled with the single-crystal superalloy substrates. Diffusion couples of a substrate alloy and a coating alloy were heated at 1,100°C for 300–1,000 h in air. Cross sections of each diffusion couple were observed by scanning electron microscope (SEM) and concentration profiles were analyzed by energy dispersive x-ray spectroscopy (EDX) and electron probe microanalyzer (EPMA). Oxides formed on the surface after the oxidation examinations were observed and oxidation mechanisms were discussed.

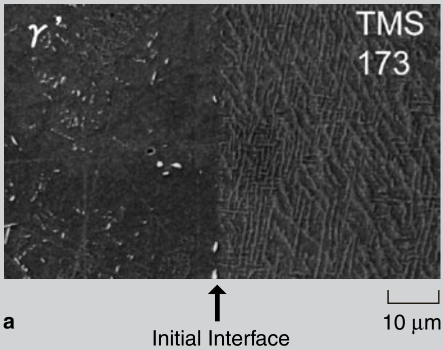
High-velocity frame spray (HVOF spray) powder of the EQ coating (TMBC-1) designed for the second-generation superalloy RenéN5 was prepared. The commercial Co-Ni-Cr-Al-Y coating, Amdry 9954 (Sulzer Metco Ltd.) was also used for the comparison. The substrates were the fourth-generation nickel-based superalloy TMS-138A and the fifth-generation nickel-based superalloy TMS-196. Nominal compositions of coatings and substrates are shown in Table B. TMBC-1 is designed as a γ′ phase of RenéN5 and rhenium was removed, so improvement of the oxidation resistance and reduction of the material cost can be expected in this coating. A 100 μm-thick EQ and Amdry9954 coating was applied to TMS-138A and TMS-196 by HVOF. Samples were heat treated at 1,100°C for 300 h in air. After heat treatment, cross sections of samples were observed by SEM and compositions of phases precipitated at the interface were analyzed by EDX.

Table A. Nominal Compositions of Specimens for Diffusion Couple Experiment (wt.%, Ni-bal.)

Sample	Co	Cr	Mo	W	Al	Ti	Ta	Hf	Re	Ru
TMS82+										
substrate	7.7	4.6	1.8	8.6	5.3	0.5	6.3	0.1	2.4	—
γ	10.5	7.6	2.6	10.0	2.9	0.2	3.4	0.0	4.2	—
γ′	4.7	1.4	0.9	7.2	7.9	0.7	9.5	0.2	0.5	—
TMS-173										
substrate	5.6	3.0	2.8	5.6	5.6	—	5.6	0.1	6.9	5.0
γ′	4.2	1.5	1.5	5.3	7.8	—	8.0	0.2	2.6	3.9

Table B. Nominal Compositions of 4th and 5th Generation Superalloys and Coatings (wt.%, Ni-bal.)

Sample	Co	Cr	Mo	W	Al	Ta	Hf	Re	Ru	Y
TMS-138A	5.8	3.2	2.8	5.6	5.7	5.6	0.1	5.8	3.6	—
TMS-196	5.6	4.6	2.4	5.0	5.6	5.6	0.1	6.4	5.0	—
TMBC-1 (RenéN5γ′-Re+Y)	6.2	4.0	1.0	4.5	8.1	9.9	0.4	—	—	0.1
Amdry 9954	38.5	21.0	—	—	8.0	—	—	—	—	0.5



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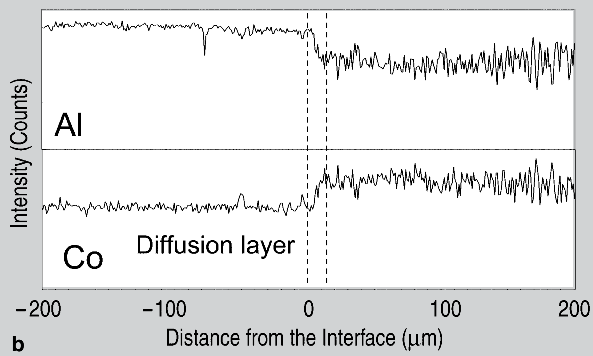

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Figure 4. (a) Cross section and (b) concentration profiles of TMS-173γ′/TMS-173 diffusion couple heated at 1,100°C for 1,000 h.

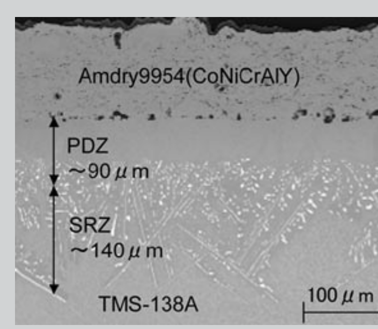
bides, and "SRZ" can be defined as a layer of γ′ matrix containing γ and P phase (TCP) needles formed beneath the PDZ derived from the diffusion.[4] On the contrary, TMBC-1 forms a 40 μm thick diffusion zone but does not form SRZ. We can see from these results that the diffusion of cobalt, chromium, and other elements does not form SRZ by suppressing the interdiffusion of aluminum. Also, the difference of chemical potential for elements with a low diffusion coefficient such as rhenium between the coating and substrate does not affect the driving force of the interdiffusion.

Results of the conventional Co-Ni-Cr-Al-Y coating, Amdry9954, and the EQ coating, TMBC-1, applied to the fifth-generation single-crystal nickel-based superalloy TMS-196 are shown in Figure 6. Heat treatment at 1,100°C for 300 h leads to a PDZ of about 65 μm and an SRZ of 80 μm in (a) Amdry 9954. TMS-196 has higher chromium content so the chemical potential of aluminum and chromium is larger than those of TMS-138A; thus, the differences of the chemical potential of aluminum and chromium from those of Amdry 9954 are smaller than TMS-138A, so that the thickness of the diffusion layer in TMS-196/Amdry 9954 is smaller than TMS-138A/Amdry 9954. (b) TMBC-1 coating produces about 50 μm of the diffusion layer but no SRZ. Therefore, the SRZ suppression effect of EQ coating is also confirmed in the fifth-generation nickel-based superalloy, which contains high ruthenium.

The cross sections of oxides formed at the surface of (a) Amdry 9954 and (b) TMBC-1 after heat treatment at 1,100°C for 300 h are shown in Figure 7. The oxides of both coatings consist of a protective Al_2O_3 layer and $NiAl_2O_4$ spinel layer; the total thickness of oxide was about 8 μm. From this result, it is estimated that the oxidation resistances of both coatings are almost equivalent. Small cracks are observed in the surface of both coatings under the oxide. The delamination of the oxide from the coating surface may be due to low adhesiveness of the oxide. However, there is a possibility that this delamination occurred in the sample-mounting process for SEM observation, and further investigation is necessary.

The results of the cross-section observation clarified that SRZ formation is suppressed in a high-velocity oxy-fuel sprayed EQ coating, designed for the second-generation nickel-based superalloy, when applied to the fourth- and fifth-generation nickel-based superalloys. To minimize the diffusion layer, the design of an equilibrium γ′ phase coating for each substrate is necessary. However, the γ′ phase of the advanced-generation superalloys may incur high production costs and provide oxidation resistance. As proved in this study, if the chemical potential of aluminum in the coating, which has a large diffusion coefficient in the superalloy and contributes to SRZ formation, is brought closer to that in the substrate than the conventional coating system, it is possible to suppress the SRZ formation. However, the coating composition is not equal to the equilibrium composition. Therefore, it is concluded that the oxidation-resistant modified EQ coating can be applied to several generations of nickel-based superalloys without specifying the superalloy substrate.

A. Sato et al. reported that, for the coating layers PDZ and SRZ, no load and creep rupture life decreases result from the decrease in load-bearing cross section of the substrate.[21] The EQ coating does not form an SRZ; thus, this coating does not appear to degrade the creep strength. This expectation has been confirmed in recent work and the results will be published in the near future.



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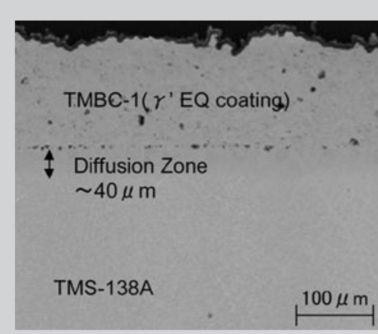

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Figure 5. Cross sections of (a) Amdry 9954/TMS-138A and (b) TMBC-1 /TMS-138A after 300 h heat treatment at 1,100°C.

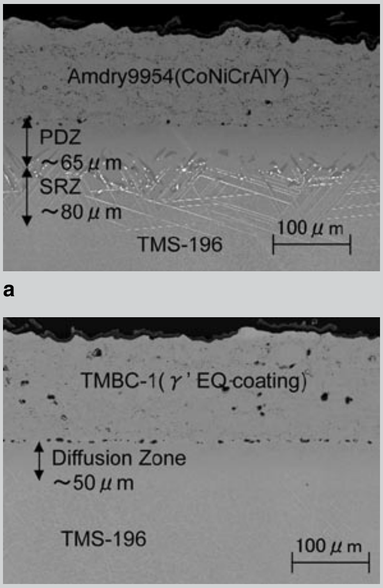

Figure 6. Cross sections of (a) Amdry 9954/TMS-196 and (b) TMBC-1/TMS-196 after 300 h heat treatment at 1,100°C.

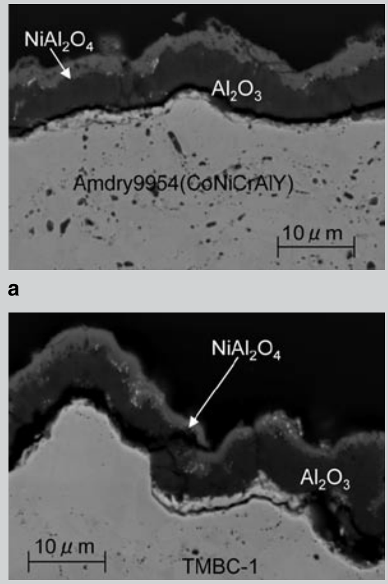

Figure 7. Cross sections of oxides formed on (a) Amdry 9954/TMS-138A and (b) TMBC-1/TMS-138A oxidized at 1,100°C after 300 h.

CONCLUSION

The EQ coating on advanced-generation nickel-based superalloys does not degrade high-temperature strength by using equilibrium compositions. Third- and more-advanced-generation nickel-based superalloys contain a high amount of rhenium, and SRZ formation is not avoidable. Recently, high-pressure turbine blades have been getting thinner and thinner to improve cooling efficiency and decrease engine weight, and so this problem has been serious. The EQ coating provides a new, low-cost technique to solve this problem, and this technique has a benefit in the repair of turbine blades. Usually, only a single re-coating is possible for reuse of turbine blades because the coating layer and the diffusion layer beneath the coating have to be removed before re-coating and the thickness of sound substrate becomes thinner. However, it is not necessary to remove the diffusion layer in the EQ coating system because it suppresses SRZ formation. The EQ coating enables cyclic re-coating and consequently could provide airlines significant cost savings in engine maintenance. It should be reasonably concluded that the EQ coating is an innovative technique for the practical use of the advanced nickel-based superalloys.

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K. Kawagishi and H. Harada are with the National Institute for Materials Science, 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305-0047, Japan; A. Sato is with IHI Corporation, 1 Shin-Nakahara-cho, Isogo-ku, Yokohama 235-8501, Japan. Dr. Kawagishi can be reached at kawagishi.kyolo@nims.go.jp.