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Oxidation/Carbonization/Nitridation and In-Service Mechanical Property Degradation of CoCrAlY Coatings in Land-Based Gas Turbine Blades

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This article describes variations in the microstructure/composition and mechanical properties in plasma sprayed CoCrAlY coatings and a modified René 80 substrate of gas turbine blades operated for 21,000 h under liquefied natural gas fuels. Substantial oxidation/carbonization occurred in the near surface region of concave coatings, but not in the convex coatings. Aluminum and nickel/titanium-rich nitrides formed in near interface coatings and substrates of concave side of blades, respectively. Small punch (SP) specimens were prepared from the different blade location to examine the variation of the mechanical properties in the coatings. In SP tests, brittle cracks in the near surface and interface coatings of the concave side easily initiated up to 950 °C. The convex coatings exhibited higher ductility than the concave coatings and substrate and showed a rapid increase in the ductility above 800 °C. Thus it is apparent that the oxidation/carbonization and nitridation in the concave coatings produced a significant loss of the ductility. The in-service degradation mechanism of the CoCrAlY coatings is discussed in light of the operating temperature distribution and compared to that of CoNiCrAlY coatings induced by grain boundary sulfidation/oxidation.

Keywords carbonization, mechanical property degradation, nitridation, oxidation, scanning Auger microprobe, small punch testing method

1. Introduction

Advanced technologies of superalloy casting, coatings, and cooling enable the enhancement of the fuel efficiency of land-based gas turbines by increasing the firing temperature. Advanced performance of gas turbine blades is critical to maintain safe operation and prolong the remaining life of gas turbines (Ref 1, 2). Plasma sprayed coatings have been widely applied to improve the resistance of gas turbine blades to elevated temperature environmental attack. Yet, the degradation of blade coatings inevitably occurs while in service. Microstructure/composition evolution of coatings used in service have been extensively studied. However, the mechanical property degradation of coatings has not been well understood because the standard testing method is not suitable for examining the mechanical properties of coatings localized near the surface in complex shaped blades (Ref 3). In order to overcome the problem, a small punch (SP) testing method has been applied to gas turbines blades used in service in conjunction with scanning Auger microprobe (SAM) analysis on the microstructure/composition (Ref 4-7). It has been shown that in-service mechanical property degradation of CoNiCrAlY coatings is strongly related to grain boundary sulfidation and oxidation resulting from elevated temperature environmental attack. In addition, variations in the ductility in the layered structure of aluminized CoCrAlY coatings have been clearly demonstrated using the SP testing method (Ref 8, 9).

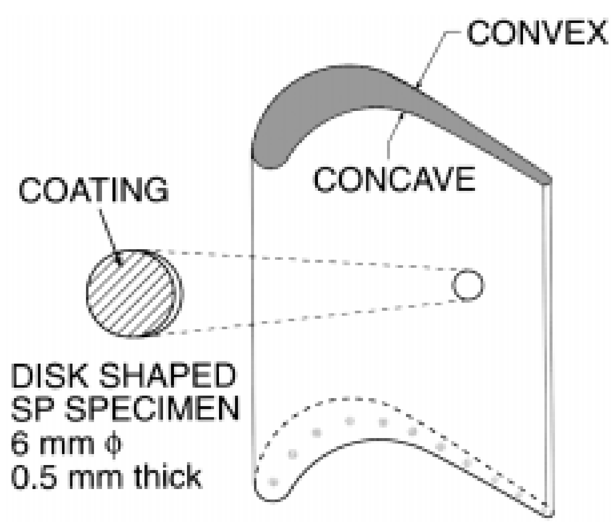

Fig. 1 Extraction of small punch (SP) specimen from gas turbine blade used in service

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In this article, the distribution of the microstructure/composition in CoCrAlY coatings and a modified René 80 substrate of gas turbine blades operated in-service is analyzed by SAM. Changes in the mechanical properties of the coatings depending on the blade location are examined using the SP testing method. The relationship between the mechanical property degradation and microstructure/composition evolution in the coatings is presented, and the result is compared to the in-service degradation of the CoNiCrAlY coatings (Ref 4-7).

2. Experimental Method

This study employed gas turbine blades made of a modified René 80 substrate and low-pressure plasma sprayed CoCrAlY coatings. The gas turbine blades had been retired after 21,000 h operation under the combustion of liquefied natural gas (LNG). The blade had camberline-cooling holes. The coating thickness varied in a range from 120 to 200 μm depending on the blade location.

Disk-shaped SP specimens (6 mm diameter and 0.5 mm thick) were machined from concave and convex sides of the blade using an electrical discharge machine (Fig. 1). Scanning Auger microprobe specimens (3 mm wide, 2 mm thick, and 10 mm long) along the longitudinal direction of blades were also extracted from the concave and convex sides. The coatings were located on one side of the SP and SAM specimens. Substrate SP specimens were prepared from the midsection of the blade. The surface of coated SP specimens was located in the near surface and interface regions of the concave and convex coatings by polishing with emery paper (1000 grit).

The microstructure and composition of the blades were examined by SAM. Mechanically polished sections of the concave and convex sides were ion sputter-cleaned (3 keV) in argon gas atmosphere (5×10^{-6} Pa). Scanning Auger microprobe analysis was made on the sputter-cleaned surface using a cylindrical mirror analyzer (5 keV) of Physical Electronics model 660, (Eden Prairie, MN). The SAM elemental maps were taken that correspond to the secondary image microstructure. The first derivative Auger peak height of elements was acquired at selected points based on the elemental map using a survey or multiplex mode. The concentration of elements, C_e, was estimated from the measured Auger signal intensity and the relative sensitivity factor of elements (Ref 10).

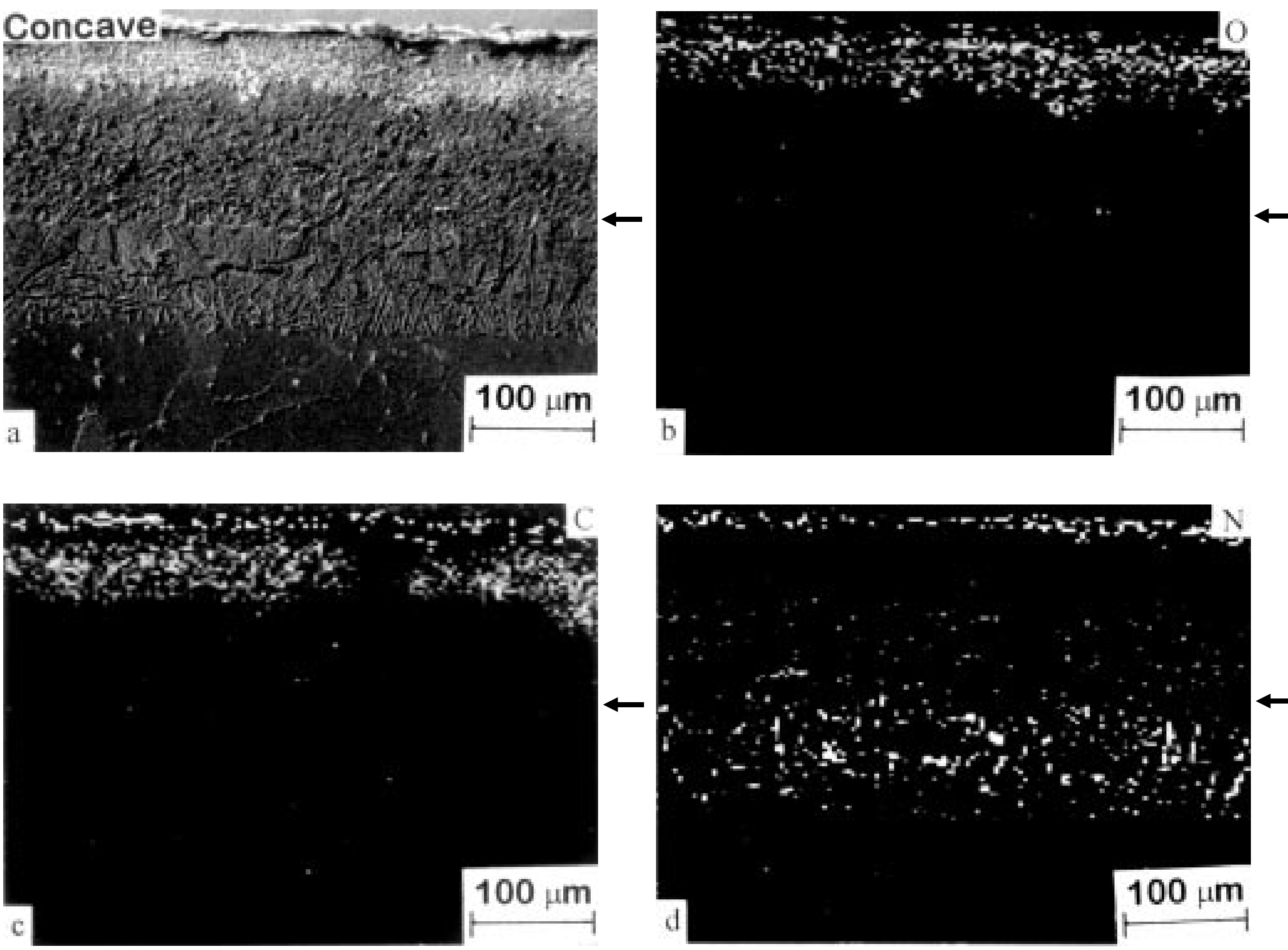

Fig. 2 The specimen is tilted 30° toward coatings for argon-sputtering. Arrows indicate coating/substrate interface. (a) Secondary image micrograph. (b) Oxygen. (c) Carbon. (d) Nitrogen maps on longitudinal section of concave side of blade

Specially designed specimen holders consisting of lower and upper dies and clamping screws were used for SP tests (Ref 4, 11). The SP specimens were placed into the lower die and clamped using the upper die and screws. Biaxial tensile stresses were applied to coatings using a puncher with a hemispherical tip (diameter of 2.4 mm). The SP tests were performed in air at room temperature (RT) and in a temperature range from 800 to 950 °C at the cross head speed of 8×10^{-6} m/s using a screw-driven Instron testing machine (Canton, MA). The SP specimens were heated by an induction coil. The details of the elevated temperature SP testing apparatus are indicated in Ref 4.

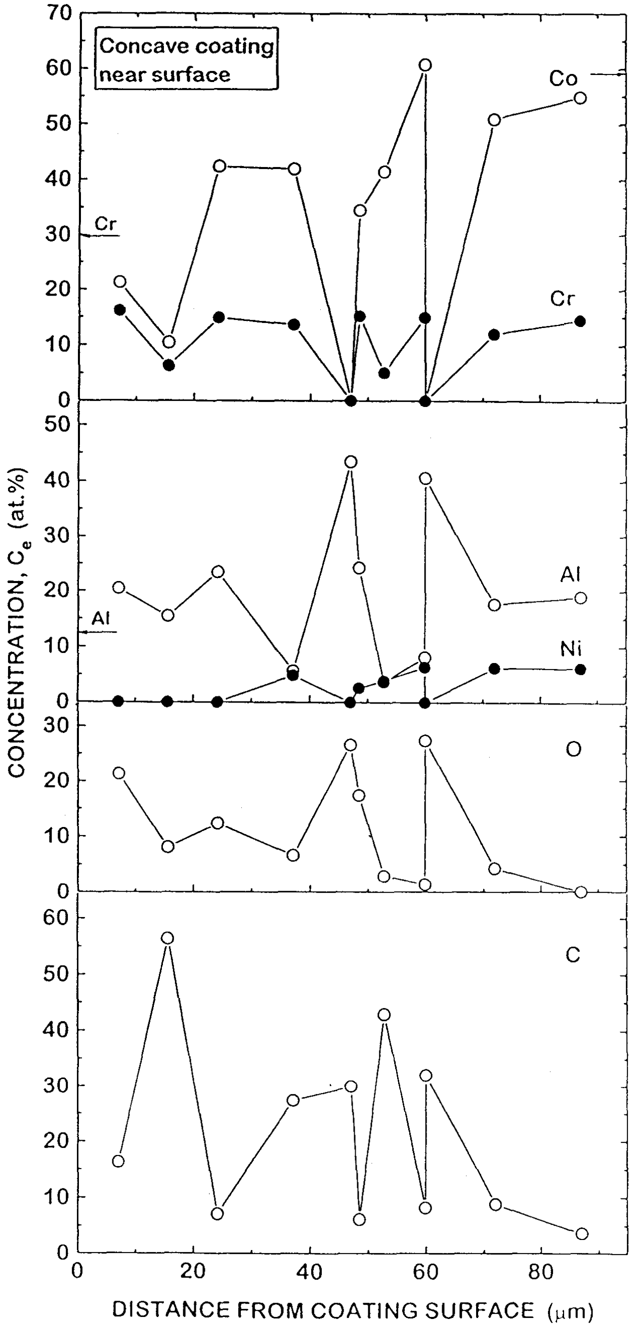

Fig. 3 Profiles of cobalt, chromium, aluminum, nickel, oxygen, and carbon in near surface coating region of concave side. Arrows indicate the nominal content of alloying elements in the coatings.

3. Results

3.1 Microstructure and Composition

The microstructure and composition of the concave and convex sides of the blade were examined using SAM. Figure 2 shows a secondary image micrograph and oxygen, carbon, and nitrogen Auger maps observed on argon-sputtered sections of the concave blade. It is evident that oxidation and carbonization extensively occurred to a depth of 65 μm near surface region of the concave coatings. Figure 3 shows the profiles of oxygen and carbon as well as alloying elements in the near surface coating

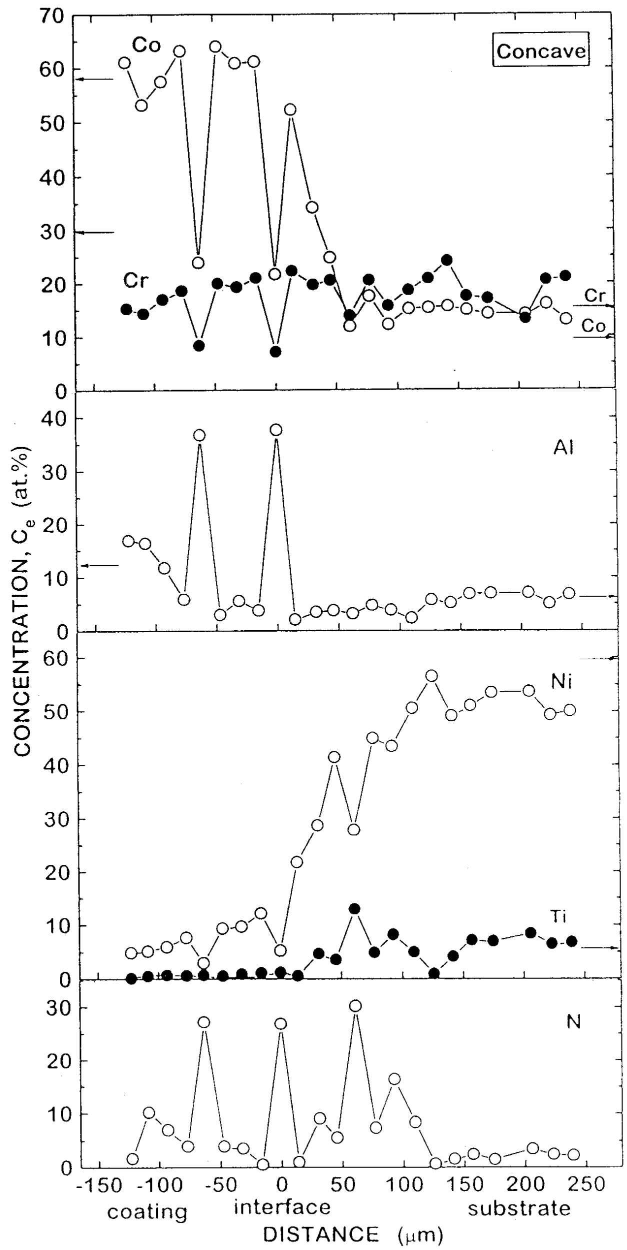

Fig. 4 Profiles of cobalt, chromium, aluminum, nickel, titanium, and nitrogen in near interface coatings and substrate region of concave side. Arrows indicate the nominal content of alloying elements in the coatings and substrate.

region. Arrows indicate the nominal composition of the coatings. As a result of heterogeneous oxidation and carbonization, the amount of cobalt and aluminum largely fluctuated, and the content of chromium decreased by more than 50%. This implies that inward diffusion of oxygen and carbon would have occurred in the concave coatings. The oxidation and carbonization tended to occur concurrently.

As shown in the elemental map (Fig. 2), moreover, nitridation was detected in near interface coatings and substrates of the concave side of the blade. However, it should be noted that the formation of oxide scales produced a charging effect on the top layer of the concave coatings and, therefore, an artificial signal appeared in the nitrogen map (Fig. 2). Figure 4 illustrates the distribution of alloying elements and nitrogen below the oxygen/carbon enriched region in the concave coating and in the near interface region of the substrate. The concentrations of cobalt, chromium, and aluminum varied due to the nitride formation. Aluminum-rich nitrides formed in a coating region where the oxidation and carbonization were absent (Ref 12). The reductions in the chromium content were smaller compared to the near surface, and some nickel diffusion into the concave coatings occurred. A diffusion zone of 90 μm extended from the interface into the substrate. The diffusion zone comprised needle-shaped, nickel/titanium-rich nitrides, which was densely distributed, and some titanium/carbon-rich nitrides (Ref 12). Swaminathan and Lukezich (Ref 13) found similar nitrides in transition ducts made of nickel-base superalloys (IN-617) in gas turbines used in service.

Conversely, microstructure/composition evolution occurred to smaller extents on the convex side of the blade. The oxidation was only observed on the top layer of the convex coatings, and carbonization and nitridation were negligible (Fig. 5) (Ref 12). Comparing the profiles of alloying elements in the concave and convex coatings (Fig. 4 and 6), it is clear that the convex blade exhibited smoother variations in the concentration of alloying elements. Nickel more extensively diffused into the convex coatings than into the concave coatings. A smaller diffusion zone of 50 μm formed in the convex side of the blade. Selected area SAM analysis indicated that the convex coatings contained the dispersion of nickel/aluminum enriched precipitates, and the diffusion zone consisted of the formation of elongated nickel/aluminum- and chromium-rich phases (Ref 12).

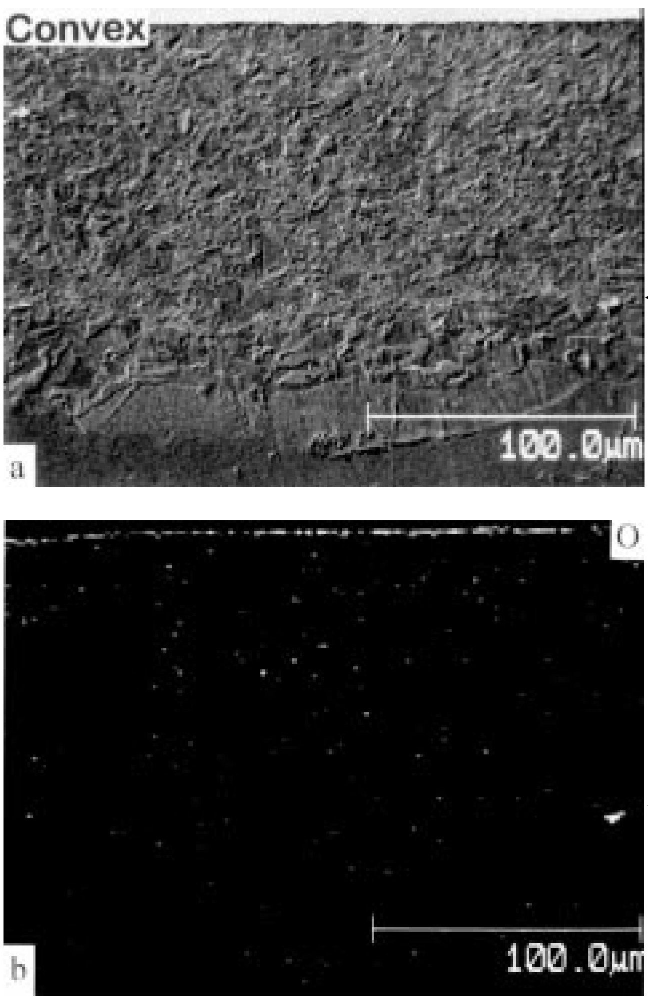

Fig. 5 The specimen is tilted 30 ° toward coatings for argon sputtering. Arrows indicate coating/substrate interface. (a) Secondary image micrograph. (b) Oxygen map on longitudinal section of convex side

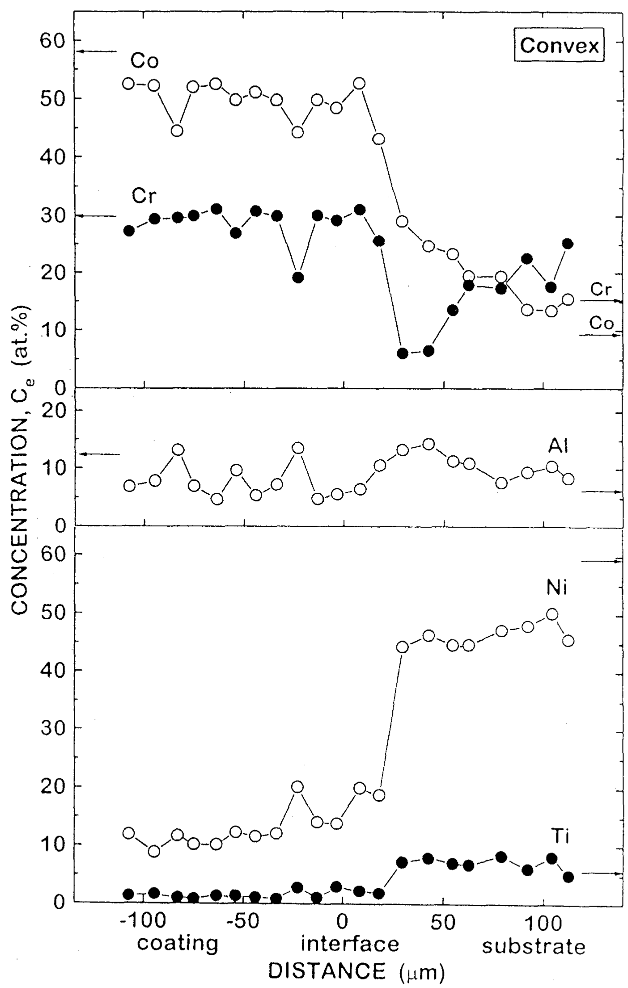

Fig. 6 Profiles of cobalt, chromium, aluminum, nickel, and titanium in coatings and near interface substrate region of convex side. Arrows indicate the nominal content of alloying elements in the coatings and substrate.

3.2 Mechanical Properties

The mechanical properties of the concave and convex coatings and substrate were investigated using the SP testing method. Figure 7 indicates several load vs. deflection curves obtained from SP tests on near surface coated specimens of the concave and convex sides at RT and 900 °C. The yield load, P_y, can be defined at the transition point from the elastic to plastic bending deformation region. The yield strength, σ_y, in the blades was determined from the P_y value and the specimen thickness, t_o (Ref 14). In Fig. 7, brittle crack initiation of the coatings led to a decrease in the loading rate at the critical defection, δ_f (Ref 12). Ductile cracks in the convex coatings formed at elevated temperatures without inducing a loading rate change (900 °C in Fig. 7). In such cases, SP tests were load interrupted at several deformation stages to determine the value of δ_f. The ductility, ε_f, of the coatings and substrate was defined at the initiation stage of cracks and then estimated from δ_f together with t_o (Ref 4-7, 14, 15). The estimate of ε_f for the ductile cracking had less than 10% error.

Figure 8 shows the temperature dependence of σ_y for the concave and convex coatings and the substrate. Coated SP specimens indicated lower yield strength than substrate specimens. The near surface and interface coatings of the convex side exhibited the same temperature dependence of σ_y and higher yield strength than the near interface coatings of the concave side. The near interface coatings of the concave side indicated hardening at 800 °C and a more rapid drop in the yield strength than the convex coatings above 850 °C. Most of the near surface coatings in the concave blade revealed cracking prior to the yielding, thereby not indicating the value of σ_y except at RT and 950 °C in Fig. 8.

Figure 9 illustrates the variations of the ductility to the testing temperature for the near surface and interface coatings of the concave and convex sides and the substrate. The concave coatings showed substantially lower ductility than the convex coatings in all the testing temperature range. The near interface coatings of the concave side had a little higher ductility at RT and 800 °C than the near-surface coatings and depicted a small ductility trough at 850 to 900 °C. The ductility in the convex coatings, which was higher than in the substrate, precipitously increased above 800 °C. The near surface coatings of the convex side slightly exceeded the ductility above 800 °C, compared to the near interface coatings. By comparing the ductility of the used convex coatings to that of unused coatings with the same composition (Ref 8), it was found that the RT ductility in the CoCrAlY coatings was increased while in service. However, the unused CoCrAlY coatings showed a rapid increase in the ductility at 730 °C and two-fold increase in ductility at 800 °C, compared to the used convex coatings. The addition of nickel in the convex coatings, arising from the interdiffusion of cobalt/nickel,

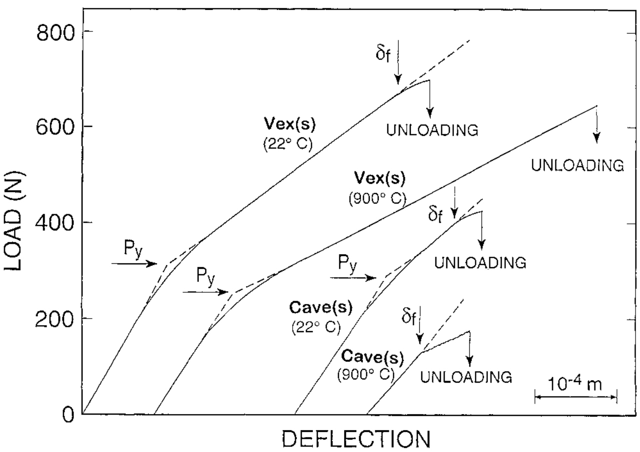

Fig. 7 Load versus deflection curves obtained from SP tests on a near surface coated specimen of concave and convex sides at 22 and 900 °C indicating yield load, P_y, and critical deflection at crack initiation, δ_f. The concave and convex coatings near the surface are designated as cave (s) and vex (s).

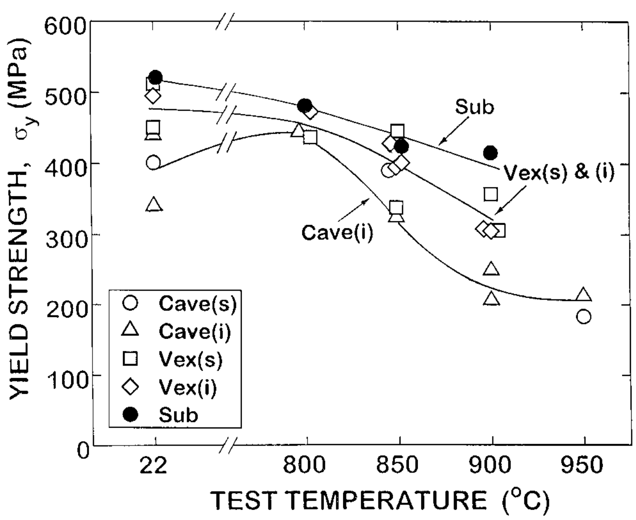

Fig. 8 Temperature dependence of yield strength, σ_y, in near surface and interface coatings of concave and convex sides and substrate. The near surface and interface coatings of the concave side are designated as cave (s) and cave (i) and near surface, and interface coatings of the convex side are designated as vex (s) and vex (i).

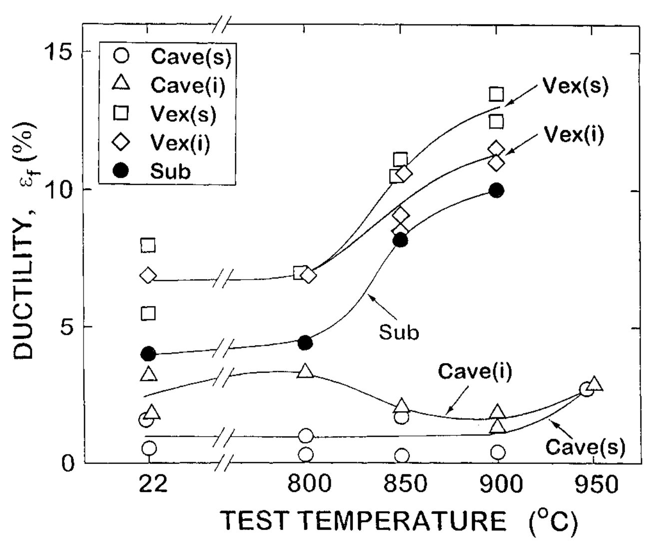

Fig. 9 Temperature dependence of ductility, ε_f, in near surface and interface coatings of concave and convex sides and substrate. The near surface and interface coatings of the concave side are designated as cave (s) and cave (i), and near surface and interface coatings of the convex side are designated as vex (s) and vex (i)

would lead to the ductility improvement and loss, respectively, at lower and higher temperatures (Ref 16).

The cracking morphology of the concave and convex coatings is summarized in Ref 12. Brittle cracks initiated at the center of the concave coatings and predominantly propagated along the radial direction at RT and elevated temperatures. The convex coatings delineated crack propagation along the radial or tangential direction at RT. Elevated temperature cracks heterogeneously nucleated and discretely grew along more random directions in the convex coatings.

4. Discussion

This study examined the microstructure/composition and mechanical properties in CoCrAlY coatings and modified René substrates of gas turbine blades retired after 21,000 h operation under LNG combustion. In this section, the microstructural and mechanical degradation of the coatings used in service are discussed in light of elevated temperature environmental attack.

4.1 Environmental Attack-Induced Microstructure/Composition Evolution

Scanning Auger microprobe analysis has shown significantly different evolution of microstructure and composition for the concave and convex coatings. In the concave side of the blade, oxidation/carbonization in the near surface coatings and nitridation in the near interface coatings and substrate resulted from elevated temperature environmental attack (Fig. 2-4). Nitrogen diffused into the concave side three times farther than carbon and oxygen. Thus the diffusivity of nitrogen would be about one order of magnitude larger than that of oxygen and carbon, although diffusion data is not available. However, it is not clear why the nitridation did not occur at all in the near surface coatings even though the near surface region was discretely oxidized and carbonized (Fig. 2 and 3). On the contrary, oxidation was minimal, and carbonization and nitridation were negligible in the convex coatings. There exists a possibility that oxides would have spalled from the convex coating because of its smaller coating thickness than the concave coating. Nevertheless, the diffusion zone in the convex blade extended to smaller extents, compared to that in the concave coating. The diffusion zone in the concave and convex sides contained nickel/titanium-rich nitrides and nickel/aluminum-enriched phases, respectively. Thus, forming the diffusion zone in the concave and convex sides of the blade would be controlled by the migration of nitrogen and aluminum in nickel, respectively.

Based on the metallurgical study, it is speculated that the concave side would have been subject to higher operating temperatures than the convex side. It is difficult to make a direct measurement, and reasonable computational analysis of the operating temperature in rotating blades. Yoshioka et al. (Ref 17) and Cheruvu et al. (Ref 18) have proposed a metallurgical method of examining the size or density evolution of γ' in the substrate reflected by the temperature to estimate the operating temperature. However, cast blade substrates show heterogeneous distribution and evolution of γ'. Thus, this technique is only applicable for the estimation of relative changes in the operating temperature around gas turbine blades where the γ' morphology has been examined prior to the operation (Ref 17).

4.2 Environmental Attack Effect on Fracture Properties

The SP tests indicated large changes in the mechanical properties of the coatings depending on the blade location. The in-service mechanical property degradation in the CoCrAlY coatings is taken into account from a metallurgical point of view. The oxidation/carbonization and nitridation of the concave coatings gave rise to higher ductile-brittle transition temperature than 950 °C. Note that the oxidation/carbonization exerted a more deleterious effect on the ductility at lower temperatures than the nitridation. In addition, more dispersion of nickel/aluminum-rich precipitates in the near interface coatings of the convex side, resulting from the interdiffusion of alloying elements, produced slightly lower ductility at higher temperatures (Ref 12).

The in-service degradation of the CoCrAlY coatings is compared to that of CoNiCrAlY coatings reported elsewhere (Ref 4-7). In CoNiCrAlY, blade coatings operated under combined fuels of kerosene and LNG, or mainly under kerosene fuels and thermally aged in air, different extents of grain boundary sulfidation and oxidation occurred (Ref 4-7). It has been shown for the CoNiCrAlY coatings that combined effects of grain boundary sulfidation and oxidation produced a stronger embrittlement effect than oxidation alone. Yet the ductile-brittle transition temperature was observed at 950 °C in the most embrittled CoNiCrAlY coatings. Thus, it is evident that the fracture properties in the CoCrAlY coatings were more severely degraded by the oxidation/carbonization and nitridation, compared to those in the CoNiCrAlY coatings affected by the sulfidation/oxidation. Moreover, it is pointed out that the convex CoCrAlY coatings used in service had a better ductility below 850 °C than the unused CoNiCrAlY coatings (Ref 7). This finding would be partly related to the high susceptibility of coatings containing larger amounts of nickel to oxygen-induced embrittlement (Ref 7, 19).

Land-based gas turbines are frequently subject to the startup and shutdown transient operation. The low cycle fatigue (LCF) behavior of coatings plays a critical role in the in-service integrity of gas turbine blades. The extension of LCF coating cracks gives rise to the exposure of the substrate to elevated temperature environments so that the substrate would be degraded by the environmental attack. In this way, the remaining life of gas turbine blades is controlled by the LCF behavior of the coatings. The LCF behavior at RT has been recently studied in the CoNiCrAlY and aluminized CoCrAlY coatings using the SP testing method (Ref 6, 12, 19). The LCF life of the coatings, defined at the crack initiation stage, decreased while in service and thermally aging and depended on the layered structure of the aluminized CoCrAlY coatings. It has been shown (Ref 19) that the LCF life of the coatings would be extrapolated from the ductility. However, the LCF life showed larger data scattering than the ductility because the surface deformation controlling the LCF life is strongly influenced by oxides formed near the coating surface. Consequently, it is concluded that the application of the SP testing method is useful for characterizing in-service mechanical degradation of blade coatings under monotonic and cyclic loading conditions.

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5. Conclusions

The following conclusions can be drawn:

A study on the microstructure/composition and mechanical properties in concave and convex CoCrAlY coatings of gas turbine blades operated for 21,000 h under liquefied natural gas fuels was completed by applying scanning Auger microprobe and small punch (SP) testing methods. A near surface coating region in concave sides was extensively oxidized and carbonized but not in convex sides. Aluminum and nickel/titanium enriched nitrides formed in near interface coatings and substrates of the concave side, respectively. Small punch specimens were extracted from the different blade location to examine the variation of the mechanical properties in the coatings. Small punch tests indicated that the onset of cracks in the near surface and interface coatings of the concave side occurred at low strains (<3%) up to 950 °C. The convex coatings had higher ductility (>6%) than the concave coatings and substrate and showed a rapid increase in the ductility above 800 °C. It is clear that the oxidation/carbonization and nitridation in the concave coatings resulted in a significant reduction in the ductility. The in-service degradation mechanism of the CoCrAlY coatings is discussed in comparison to that of CoNiCrAlY coatings resulting from sulfidation/oxidation.

Acknowledgments

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