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ENHANCING PERFORMANCE OF SILICON-MODIFIED SLURRY ALUMINIDES ON TURBINE COMPONENTS OPERATING IN MARINE ENVIRONMENTS

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A variety of coatings have been designed to protect turbine components from corrosion due to the combined effects of environmental contaminants, fuel impurities and elevated temperatures. The most effective of these systems rely upon formation of a protective alumina scale to act as a barrier between the gas path environment and the component.

Protection offered by these alumina-forming high temperature coatings is increased by a number of additive elements, including platinum and chromium, but silicon (Si) is found to be especially beneficial in coatings exposed to high concentrations of sulfur in marine environments. Silicon-modified slurry aluminides are shown to resist to both high temperature and low temperature hot corrosion on both nickel and cobalt alloys in marine service.

Laboratory tests show this corrosion resistance can be further enhanced by redistributing critical elements (particularly silicon) within the microstructure of the silicon-modified aluminide. The benefits of these changes are demonstrated in field engine trials.

INTRODUCTION

Background

Long term performance of turbines depends upon protective coatings. Without protective coatings, nickel and cobalt alloys rapidly degrade in the turbine hot section environment. Coatings of ß-NiAl have long been used to limit high temperature corrosion and oxidation of turbine components made of nickel alloys. In service, aluminum in the intermetallic layer preferentially oxidizes to form a thin film of aluminum oxide, Al_2O_3. The oxide scale protects the substrate from corrosive elements in the turbine. In service, thermal cycling and combustion by-products cause the protective scale to spall or weaken, gradually depleting aluminum in the ß-NiAl. Adding platinum improves durability of the oxide scale, increasing coating life. Platinum-modified aluminides have become the standard diffusion coating used on many current turbines.[1,2,3]

Silicon has also been found to improve hot corrosion resistance of high temperature coatings.[4] A silicon-modified slurry aluminide-SermaLoy® J - has proven a cost effective alternative to platinum aluminides. Formulated twenty-five years ago as a touch up for pack aluminides, SermaLoy J resists both Type 1 and 2 (high temperature and low temperature) hot corrosion.[5] The coating has been particularly effective on marine and industrial engines derived from Rolls-Royce flight (aero) turbines. Marine versions of these engines were championed by the British Ministry of Defense (MOD) and have subsequently been introduced to other industrial markets.

History of SermaLoy J at Rolls-Royce

Rolls-Royce's experience with SermaLoy J silicon-modified aluminide began in an engine trial early in the 1980s. To sort coatings for its marinized engines, Rolls-Royce conducted a rainbow test on HP turbine blades made of IN738LC in an RM1C (Tyne) engine rated at 5340 brake horsepower (4MW). Because this turbine was derived from a flight design, coating thickness was limited to 38 to 63 microns (0.0015 - 0.0025") on blades and vanes.

The test compared diffusion and overlay coatings, including some containing platinum. SermaLoy J performed as well as any other, including the best platinum-modified coating. The silicon-containing aluminide was one of the few judged to have "good resistance to high temperature sulphidation and even better resistance to low temperature sulphidation".[6] This observation was subsequently confirmed by others.[7] Since both forms of hot corrosion could occur on the same part in the Tyne design, this capability was judged a unique advantage for the coating.

SermaLoy J is a slurry aluminide. In the process, an aluminum/silicon slurry is applied to the part, then heated in a protective at

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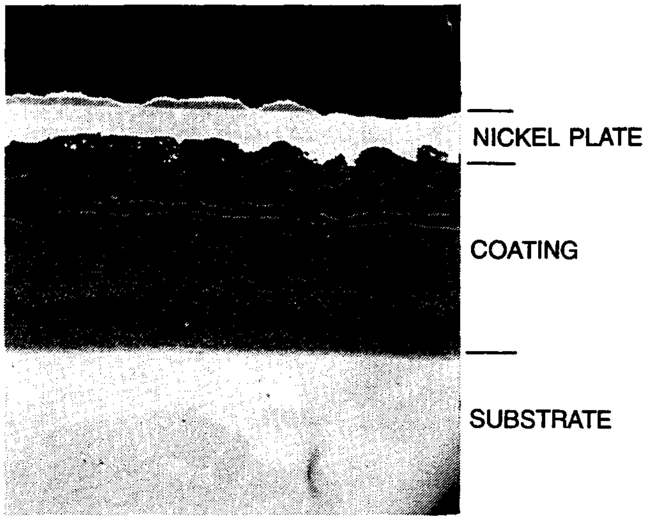

FIGURE 1. SERMALOY J COATING
SUBSTRATE: WASPALOY 500X

mosphere until the aluminum and silicon melt and react with the substrate. As the coating forms by inward diffusion, aluminum selectively reacts with nickel in the substrate, silicon reacts with chromium, and a composite layer of ß-NiAl and $CrSi_2$ forms (Figure 1).

Rolls-Royce confirmed the performance of the silicon-modified aluminide in the Tyne engine test with subsequent testing. A 300 hour salt ingestion trial compared a conventional pack aluminide, platinum-modified aluminide and SermaLoy J on high pressure (HP) and intermediate pressure (IP) turbine nozzle guide vanes (NGVs) in an industrial RB211 turbine. SermaLoy J performed better than the pack aluminide.

A cyclic endurance test of HP1 NGVs on a Spey SM1A demonstrated that SermaLoy J slurry aluminide improved component life. The coating also proved more effective than any other on NGVs made of C242 (21% Cr, 10 Co, 10 Mo, 0.4 C, 0.45 Si, 0.5 Mn, bal. Ni) in a 3500 hour rainbow trial in an Avon engine. In 1990, Rolls-Royce finished its analysis of a 3,000 hour rainbow test on a marine Spey SMIA engine. This unit had run for 3,000 hours on the RAE Pyestock test bed and included eight different turbine blade coatings.

Of the coatings tested, SermaLoy J was best overall. Though cracks were seen in the aluminide after the test, none penetrated the substrate. The platinum aluminide deteriorated so badly in the course of the 3,000 hour test that it was not included in the final comparison of candidate coatings.

Success of the SermaLoy J in the Pyestock SM1A test prompted Rolls-Royce to use the silicon-modified slurry aluminide on production hardware. To date, components coated with the material have accumulated almost 4 million hours in various Rolls-Royce Spey, Tyne and RB211 engines without a coating related failure, operating at temperatures in the range 860-1070°C.

Rolls-Royce is now developing an InterCooled Recuperated (ICR) gas turbine derived from its highly successful RB211 Trent family of Aero engines in conjunction with Westinghouse Electric

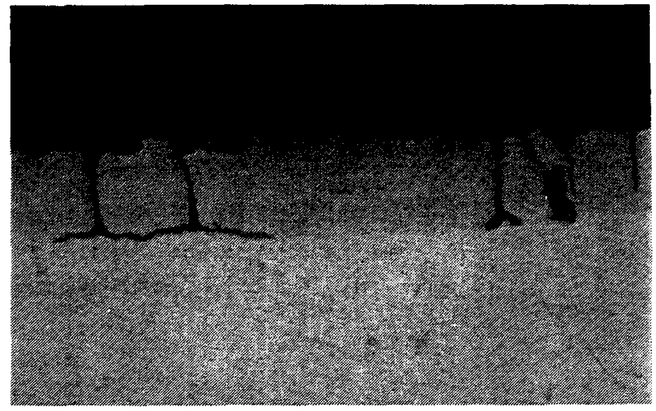

FIGURE 2: CORROSION AT THE BASE OF CRACK IN SERMALOY J ALUMINIDE ON RB211-24C HP TURBINE ROTOR BLADE. SUBSTRATE: MARM002DS. 200X

Corporation's Marine Division of Sunnyvale CA. Several of these units—designated WR-21 engines—are being built for the US Department of Defense as part of a funded development contract to produce a new propulsion engine for the US Naval fleet. SermaLoy J is being used on blades and vanes on these units.

Projected Performance Improvements

Higher operating temperatures and higher speeds demand new materials and technology for these new Rolls-Royce engines. Columnar-grained and single crystal alloys have emerged as alternatives to conventionally cast nickel alloys for turbine blades and vanes. New manufacturing systems are being designed and proved, including a new silicon-modified aluminide.

Rolls-Royce had discovered cracks in SermaLoy J aluminide on engine run parts. Though the population of these cracks was greater than that observed with conventional pack aluminides, none penetrated the base metal. When a crack approached the interface of SermaLoy J and the substrate, it turned to follow that interface (Figure 2).

Rolls-Royce nevertheless concluded that cracks in SermaLoy J were a possible threat to the integrity of hardware, acting as potential sites for crack propagation and short cuts for corrodants to reach the substrate. Corrosion was seen along the walls of the cracks, reducing the thickness of the protective layer. It was decided that a silicon-modified aluminide with a reduced propensity to cracking should also be a more corrosion-resistant coating.

New engine designs in quest of improved efficiency also require coatings with improved temperature capabilities as operating temperatures approaching 1100°C(2012°F). SermaLoy J slurry aluminide is stable to about 1000°C(1832°F). At higher temperatures, the fine layered silicides coalesce and coarsen and the aluminide phase thickens significantly. Coating microstructure had to be stabilized at these temperatures if the benefits of the silicon-modified coatings were to be incorporated into these new engines. In 1988, Rolls-Royce enlisted Sermatech International to help develop a more stable silicon-modified coating that was also more resistant to cracking.

Silicon has been used to modify both diffusion and overlay coatings for some time. Two phase NiCrAlSi overlays containing 8% silicon do not crack in Rolls-Royce engines. SermaLoy J, a single phase aluminide, also contains about 8% silicon, with much of this in the outer third of the coating where local content can exceed 20% (Figure 1). While two phase coatings are generally more ductile than single-phase coatings, it was suggested that this concentration of silicides in the outermost region of the diffusion coating made it more prone to crack. Aluminum concentration in SermaLoy J also plays a role in the mechanical behavior of the coating. The slurry aluminide can contain as much as 35% aluminum by weight. Aluminides containing more than 30% aluminum are relatively brittle.[8]

Conversely, Rolls-Royce had determined that silicon and aluminum contents of the J aluminide were key to the hot corrosion resistance of the coating.[9] Through the joint development effort, Sermatech and Rolls-Royce developed a method to redistribute these key elements and structures within the coating layer. The result was a silicon-modified aluminide more resistant to cracking and stable to a higher temperature than SermaLoy J. This coating has been designated SermaLoy 1515.

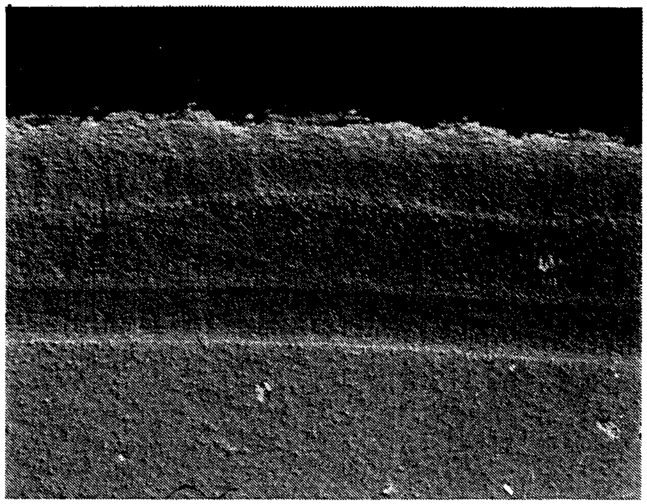

FIGURE 3: SERMALOY 1515 SILICON-MODIFIED ALUMINIDE ON CMSX-4. BANDS OF CORROSION RESISTANT CHROMIUM SILICIDE PHASES ARE DISTRIBUTED THROUGHOUT THE COATING LAYER. 500X, DIFFERENTIAL INTERFERENCE CONTRAST

COATING DEVELOPMENT

Laboratory Trials

An initial screening exercise weighed the effect upon coating microstructure of:

- increasing the ratio of aluminum or silicon in the slurry precursor
- additions of Cr, Ti, Ta, and B to the slurry
- diffusion temperatures (760 to 1120 degrees C)
- diffusion time (2 to 8 hours)

The Taguchi method was used to design an experiment to distinguish the effect of these variables. Optical metallography was used to sort those microstructures on IN738LC (nickel alloy) coated with candidate slurries and diffused by various schedules. Compositional variations were sorted with Electron Probe Micro analysis (EPMA).

Hot corrosion resistance of the variants were evaluated in a laboratory burner rig. Coatings of the most promising candidates, all about 85 µm thick, were applied to IN738LC pins (75mm long by 7mm diameter).

The pins were tested in a burner rig at the Sermatech Materials Laboratory (SML). The rig uses two propane/compressed air burners to heat pins rotating in a spindle. Pin temperature is measured by optical pyrometry. At regular intervals the spindle shifts from above the burner to quench the pins in a fine spray of salt brine. This spray may be doped with sulfates or other contaminants. The rig can deposit up to 0.5 milligram of salt per square cm of pin surface per hour, though deposition rates are typically maintained between 0.045-0.270 $mg/cm^2/hr$. Sodium sulfate deposition in this range simulates conditions in turbines operating on aircraft or land based and marine applications.[10]

To screen silicon-modified aluminides, pins were heated to 950°C (1740°F) within 60 seconds. Every ten minutes, they were quenched in a mist of a solution of 1% Na_2SO_4 plus 10% NaCl in water. Every eight hours, the pins were removed, ultrasonically cleaned in deionized water, weighed and visually examined.

After 500 hours in test, the pins were evaluated by optical metallography. Most coating variants proved less resistant to hot corrosion in laboratory rig tests than did SermaLoy J. One exception was a system formed by a multi-coat technique with interstage diffusion to control the segregation silicon within the final aluminide layer. This multi-stage coating subsequently was designated SermaLoy 1515. Unlike SermaLoy J aluminide, silicon content is limited on the outer surface of 1515 and layers of fine silicides are distributed throughout the aluminide (Figure 3). Sulphidation slows dramatically when it reaches to these layers of silicon phases in the middle of 1515. These initial tests proved redistributing silicon to improve mechanical properties need not compromise corrosion resistance of the silicon-modified aluminide.

In a second iteration, SermaLoy J and 1515 were evaluated on MARM002DS, a columnar-grained nickel base alloy, and CMSX-4 single crystal alloy. (MARM002DS and CMSX-4 are high temperature/high strength alloys that are representative of those that are replacing equiaxed nickel superalloys like IN100 and IN738LC in the next generation of turbines.) Rolls-Royce supplied pins made of MARM002DS which had been coated with a platinum-modified aluminide for a baseline.

Pins were tested at 900°C and cycled over a spray mist of sodium sulfate in water in the burner rig every 10 minutes. The cycle was timed so sulfate deposition was 0.120-0.170 mg/cm2/hr. Pinswere removed when base metal corrosion products became visible or after 750 h of testing. Then two sections were taken from each pin at the locations of maximum Type I hot corrosion attack.

Metallographic measurements of coating thickness were made at 15 degree intervals over the 180 degree region of maximum at-

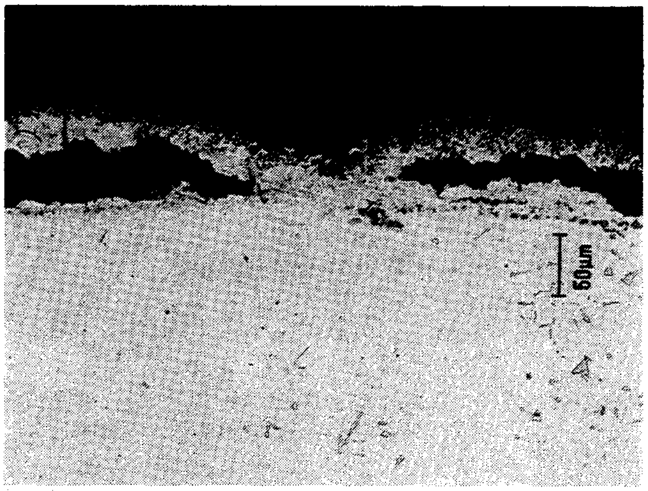

FIGURE 4: "RUMPLING" OF PtAl COATING ON MARM002DS. 200X, UNETCHED

tack on each section. Six measurements were made at 500X at each location for a total of 156 individual measurements per pin. The additive zone of the coatings was used as a measure of coating thickness to eliminate interdiffusion effects which occurred during the tests. Duplicate pins were analyzed for each coating. A cumulative distribution function (CDF) was plotted showing corrosion depth as a function of probability of corrosion exceeding that corrosion depth for each coating. This method is detailed elsewhere.[11]

The platinum-modified aluminide coating was approximately 50 µm (0.002") thick, and had a continuous white layer of $PtAl_2$ on the surface. While optimizing hot corrosion resistance, this phase compromises mechanical properties. That layer "rumpled" and delaminated from the lower part of the coating on two pins during hot corrosion testing (Figure 4). SermaLoy J was 60-70 µm (0.0024-0.0028") thick. SermaLoy 1515 was approximately 100 µm (0.004") on CMSX-4 and up to 125 µm (0.005") thick on MARM002DS.

CDF plots for the various coatings on MARM002DS and CMSX-4 are given in Figures 5 and 6. Condition of the protective coatings on these pins are shown in Figures 7, 8 and 9. SermaLoy J failed at 580 h and 500-540 hr on the two alloys, respectively. All other data were read from pins that had been tested for 700-750 h. Data from platinum-modified aluminide coatings which "rumpled" in test were not incorporated in this analysis.

The hot rig testing showed the corrosion resistance of SermaLoy J depended upon substrate chemistry. CMSX-4 pins coated with J were significantly more corroded after 500-540 hr than MARM002DS pins coated with the same aluminide removed at 580 hr. SermaLoy 1515, on the other hand, provided equivalent protection for both alloys. Moreover, its performance was equivalent to that of platinum-modified aluminide on MARM002DS.

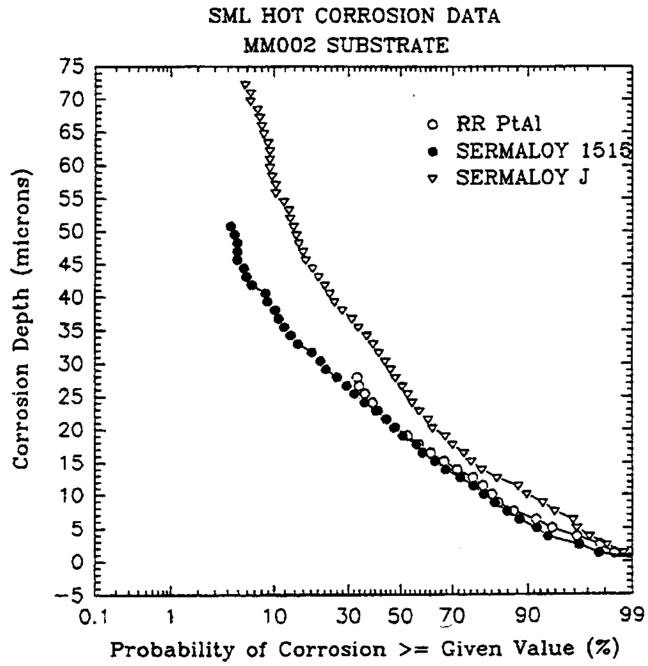

FIGURE 5: CORROSION DISTRIBUTION FUNCTION (CDF) OF PROTECTIVE COATINGS ON MARM002DS

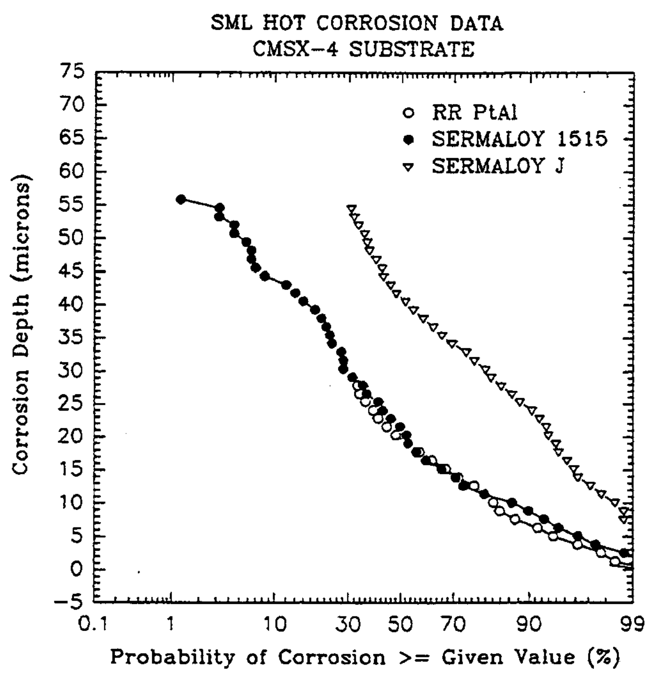

FIGURE 6: CORROSION DISTRIBUTION FUNCTION (CDF) OF PROTECTIVE COATINGS ON CMSX-4

Rainbow Engine Trial

An SMIC (marinized Rolls-Royce Spey turbine) was prepared for a rainbow trial at TE&E Pyestock. Hot section HP 1 blades made

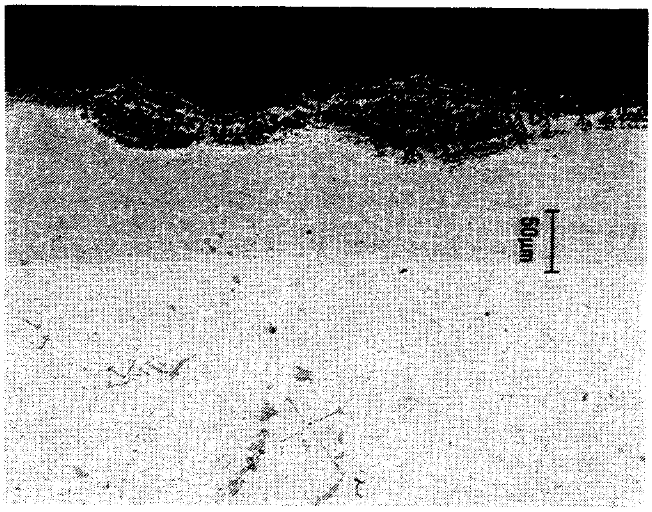

FIGURE 7: MORPHOLOGY OF HOT CORROSION OF SERMALOY 1515 SILICON-MODIFIED ALUMINIDE ON MARM002DS AFTER 750 HR IN HOT RIG TEST. 200X, UNETCHED

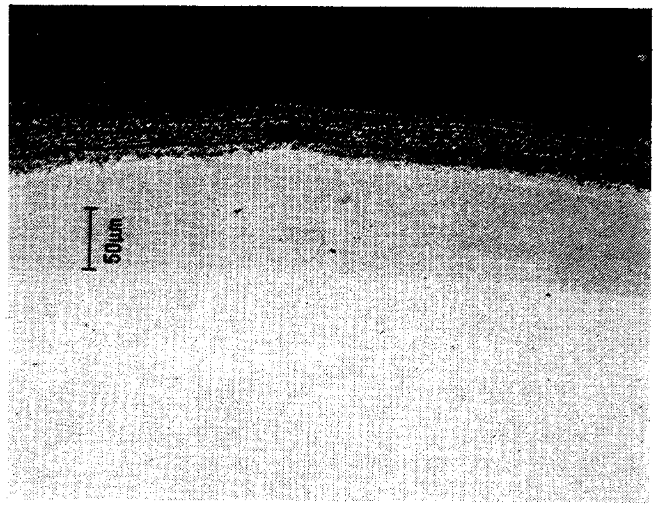

FIGURE 8: MORPHOLOGY OF HOT CORROSION OF SERMALOY 1515 ON CMSX-4 AFTER 750 HR IN HOT RIG TEST. 200X, UNETCHED

of IN792 and MAR-M-002 nickel based alloys were coated with SermaLoy J, CoCrAlY + pack aluminizing, MCrAlY + pack aluminizing, NiCrAlSi overlay and SermaLoy 1515.

After 3,000 hours this engine was returned to Rolls-Royce Ansty for evaluation. Blades coated with typical examples of each coating variant were sectioned transversally at locations equivalent to 1/4 mid and 3/4 airfoil heights. Because attack occurred primarily by high temperature hot corrosion, residual coating thickness measurements were taken as a valid measure of residual coating life. These measurements were made at equidistant positions (12 on blades and 20 on vanes), ignoring diffusion that had occurred in service. These were used to calculate coating service parameters according to the following equations:

$$\text{Mean parameter} = \frac{\text{Mean value of remnant coating}}{\text{Maximum applied coating thickness}}$$

$$\text{Variation parameter} = \frac{\text{Maximum deviation of remnant coating}}{\text{Maximum applied coating thickness}}$$

Metallographic evaluation showed SermaLoy 1515 provided greater protection than SermaLoy J. Based upon this evaluation, SermaLoy 1515 was put into a production engine test.

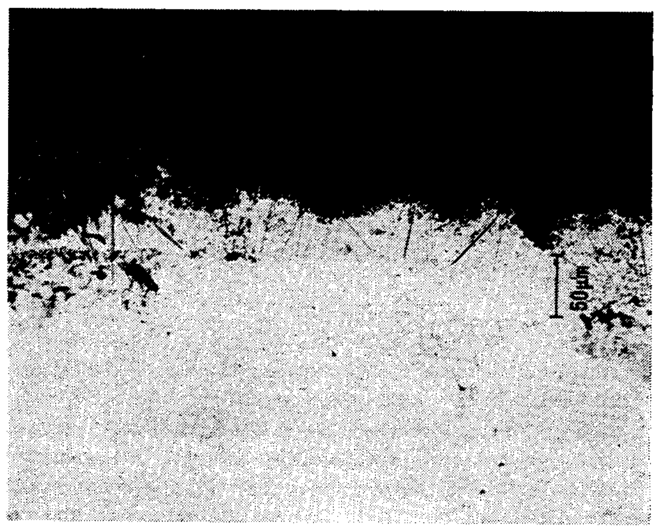

FIGURE 9: MORPHOLOGY OF HOT CORROSION OF PtAl ON MARM002DS AFTER 700 HR IN HOT RIG TEST. 200X, UNETCHED

Field Engine Test

One set of HP turbine rotor blades made of MARM002DS (102 pieces) were coated with SermaLoy J and SermaLoy 1515 by Sermatech Materials Lab and installed in an RB211 by Rolls Wood in February 1991. From July 1991 through November 1993, this unit ran 450 hours on diesel fuel and 11,050 hours on natural gas generating electricity on the coast of the North Sea at Norsk Hydro Oseberg (Platform A in set B). Though rated at 24 MW, the turbine ran at 20MW constant power accumulating 5,500 hours per year with a total of 209 starts.

The intent was to remove these blades from the engine after 8,000 hours of operation on diesel fuel. However, since the engine was converted to natural gas after only 450 hours on diesel fuel, the operator ran the engine beyond this limit. An early boroscope inspection revealed serious hot corrosion of the bare shroud (only gas washed surfaces had been coated). Later boroscope inspection showed shroud corrosion so severe that blades had to be removed from the engine after 11,500 hours.

In December 1993 the engine was stripped for inspection. Each coating had been breached at the leading edge of the blades near the shrouds. The blades coated with SermaLoy 1515, however, showed

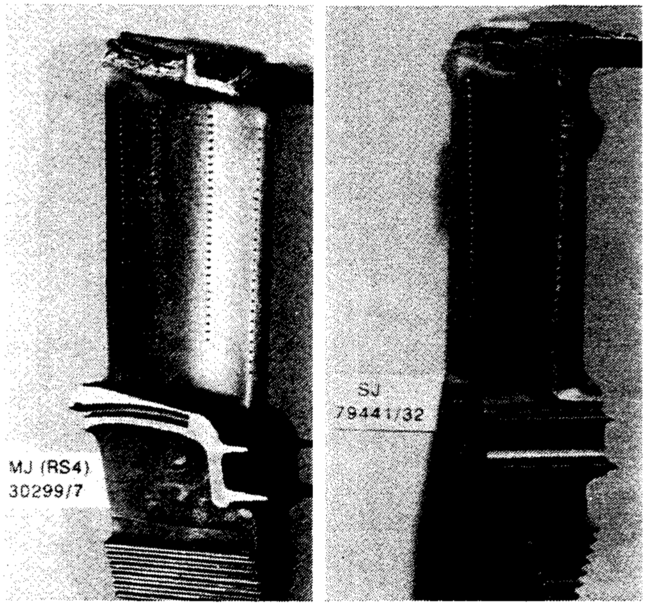

FIGURE 10: RB211-24C HP TURBINE BLADES FROM THE NORSK HYDRO TEST ENGINE AFTER 11,500 HOURS. THE BLADE ON THE RIGHT WAS COATED WITH SERMALOY J, THAT ON THE LEFT WITH SERMALOY 1515. SHROUD SURFACES, WHICH WERE NOT COATED, HAVE SUFFERED EXTENSIVE CORROSION. EROSION HAS ALSO DAMAGED LEADING EDGES.

significantly less distress at this critical region, which experiences a combination of oxidation, hot corrosion, and erosion. Two blades from this test engine are shown in Figure 10.

A careful metallurgical evaluation was done to determine the relative performance of SermaLoy J and SermaLoy 1515 coatings. Cracking of the coatings and associated corrosion was observed on some airfoils. On blades coated with SermaLoy J, cracks initiated at the surface propagated through the coating. None of the cracks in 1515 propagated into the substrate. Rolls-Royce and Sermatech independently concluded that operating life of the hardware would be considerably improved by the application of SermaLoy 1515 over SermaLoy J.

Conclusion

Silicon-modified slurry aluminide coatings protect hardware from both high temperature and low temperature hot corrosion in aeroderived marine and industrial turbines. A multi-stage diffusion process has been developed which further improves performance of a silicon-modified aluminide. The process redistributes silicon throughout the coating structure, improving mechanical properties and corrosion resistance. The new coating has been proven in laboratory and engine tests to be a cost effective alternative to platinum-modified aluminides.

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