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DEVELOPMENT OF A SLURRY ALUMINIDE COATING PROCESS WITH REDUCED ENVIRONMENTAL AND HEALTH IMPACTS

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Abstract

A process has been developed to improve upon the safety and reduce the environmental impact of slurry aluminizing for the protection of gas turbine components. The formulations of traditional aluminizing slurries include undesirable chemicals with respect to toxicity, flammability and the release of volatile organic compounds (VOC's). In the subject development, the chemistry of the slurry binder was designed to produce a safer, more versatile slurry. The chemical composition of the final product (diffusion aluminide coating) was kept constant, in order to maintain effective protection of gas turbine components in high temperature service. Cyclic oxidation testing and field testing in a gas turbine was performed to verify the oxidation resistance of the new coating was the same as that of the oil based formulation. Optical microscopy was used to characterize the uniformity and microstructure of the aluminide coating.

1 Introduction

The hot section of the gas turbine engine require the use of coatings to protect component surfaces from high temperature oxidation and hot corrosion attack. One of the most common protective coatings in the gas turbine industry is the diffusion aluminide coating. First introduced in the 1960's, the diffusion aluminide coating has remained in common use.

The first widely adopted method for applying aluminide coatings to superalloy substrates was a gas phase process known as pack cementation. To form the protective aluminide coating, an aluminum bearing gas was generated by heating an aluminum / salt (pack activator) mixture. The resultant aluminum bearing gas flowed over and diffused into the substrate at an elevated temperature. While this method remains in use today, alternative coating methods have emerged to address some of the disadvantages of pack aluminizing, such as the need for disposal of high

quantities of toxic waste (the spent aluminum pack), high capital costs, and difficulties masking surfaces which are not to be coated [1].

In the 1970's, slurry aluminizing processes entered common usage in the gas turbine industry. These coatings introduced aluminum to the surface of the component at room temperature by applying a slurry of aluminum powder and a liquid. The slurry is most commonly applied by an atomized spray technique. Once dried, the component is heated in vacuum or inert gas retort, to a temperature above the melting point of aluminum. The remains of the liquid binder are driven off during the diffusion heat treatment, while the presence of the molten aluminum film on the surface leads to diffusion of aluminum, forming the protective nickel-aluminide coating [2].

The most widely used slurry aluminizing process is known as Sermaloy J. This coating was a silicon modified aluminide which had increased oxidation and hot corrosion protection compared to the original plain aluminide coatings produced in pack aluminizing processes. One of the major drawbacks of the Sermaloy J coating process was the presence of hexavalent chromium (chromate) in the aluminizing slurry. The chromate additive was used to inhibit reaction of aluminum in the water / phosphate solution [3]. Hexavalent chromium has been shown to increase rates of lung cancer in workers when inhaled [4] which has led to a scaling back of its use.

In 1999, Liburdi introduced a hexavalent chromium-free slurry process known as Liburdi Slurry Repair (LSR®). The oil-based LSR coating has since been successfully applied to 1000's of blade sets and was found in laboratory testing to be superior in oxidation resistance to Sermaloy J [2]. The oil based binder of the original LSR formulation addressed the carcinogenicity of the Sermaloy J product but was also flammable and contained some hazardous materials. The goal of developing the water based LSR coating was to achieve the same performance in service (oxidation protection) but with reduced environmental and health impacts.

2 Toxicity

While the oil-based LSR can be used safely with proper personal protective equipment (PPE) and/or engineering controls, reducing or eliminating the toxicity of materials provides an additional level of protection for users.

Three constituents of the oil-based LSR (ethylbenzene, cobalt bis(2-ethylhexanoate), xylene) are among the 600 substances listed in the EPA's Toxic Release Inventory (TRI) (chemicals which have the potential for harmful human health effects). One of these three chemicals, ethylbenzene, has been found to have carcinogenic properties in testing on animals, but has not been confirmed to be a carcinogen in studies involving human exposure [5].

The water-based LSR is a much simpler formulation, consisting of water as a solvent and a polymer binder. The polymer is chemically inert, non-carcinogenic and is not included on the EPA's TRI list.

3 Volatile Organic Compounds

Volatile organic compounds (VOC's) are defined by the US and Canadian Governments as organic compounds which evaporate readily to the atmosphere and react photochemically to form ground-level ozone. Ground level ozone contributes to smog formation which has adverse effects on respiratory health. VOC's may also have additional, more acute toxic effects on human and animal health.

The surface coatings industry contributed approximately 3.2% of the VOC emissions in Canada in 2015 (down from 4.5% in 1990). Absolute reductions in VOC's have been achieved over this period in part due to the adoption of more water-based coating systems. **Figure 1** shows the VOC emissions in tonnes over the 1990 – 2015 period in Canada by surface coatings [6].

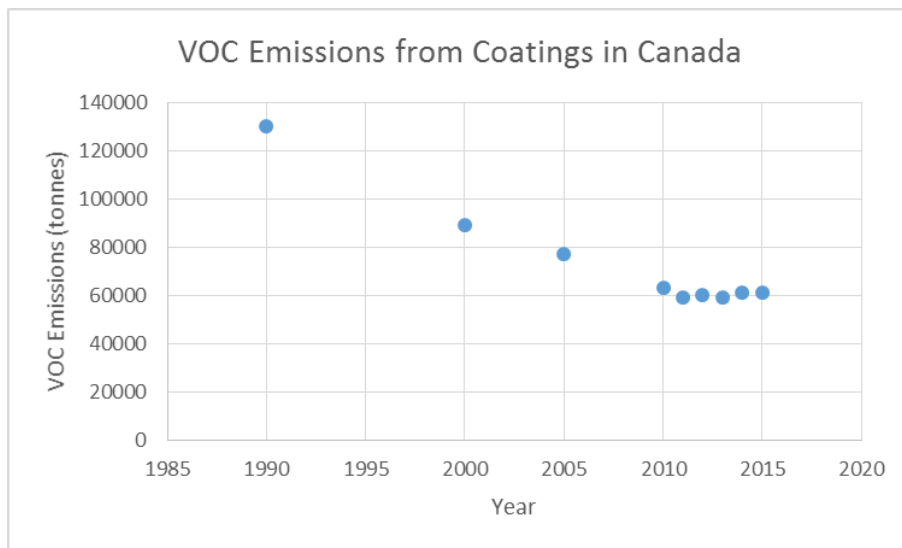


Figure 1: VOC Emissions (in tonnes) from the surface coatings industry in Canada.

In moving from an oil based to a water based binder, the VOC content of LSR was eliminated. The slurry consisting of just water and polymer produced no VOC's (refer to **Table 1**).

Table 1 – VOC's in LSR formulations

Slurry Formulation	VOC Content (g/L)	VOCs [7]
LSR, oil-based	250	ethylbenzene, xylene
LSR, water based	0	n/a

4 Flammability

While all of the LSR products can be used safely, the flammable nature of the oil-based LSR requires that greater safety measures are taken during its use, such as ventilation and the use of explosion proof equipment within the enclosure where the slurry is being applied. While oil-based LSR has a flash point of 110°F [8], the water based formulation of LSR is non-flammable.

5 Coating Green State Characteristics

The development of the water based binder was based on reducing environmental and health impacts while also achieving several functional characteristics in the green (pre-diffusion) coating:

5.1 Surface Wetting

When applied by spray, dip or brush techniques, the slurry should form a continuous film of uniform thickness. Application of both the oil-based and water-based LSR formulations resulted in level, uniform films.

5.2 Drying/Curing:

The wet film should dry to a sufficiently durable state at ambient temperature within a reasonable amount of time such that gentle handling of the component will not damage the coating. Following the initial ambient temperature dry, the coated components are cured at elevated temperature in air to allow for further hardening, and to ensure that the solvents in the green coatings are eliminated prior to vacuum diffusion heat treatment. Insufficient drying of the green coating can lead to defects in the diffused coating.

Drying of the oil-based LSR coating required a temperature of 150°C for a total cycle time of 3.5 hours to produce defect-free diffused coatings, while the water based LSR was sufficiently dried at 75°C (total cycle time: 1 hour). The lower temperature and time of the water-based LSR drying cycle resulted in a 60% reduction in the drying oven's energy consumption¹.

5.3 Particle Cohesion

Once applied and cured, the film should consist of metal particles embedded in a polymer matrix (the green-state of the coating) [2]. The polymer matrix of the green coating should not be friable as green coated components require handling to remove masking, measure coating thicknesses etc...

Scratch tests were performed on green state films (approximately 80 microns thick) using loads of 500g, 750g, 1000g, and 2000g applied to a Rockwell C diamond indenter moving at a constant speed over the coating, **Figure 2**. The water-based LSR was found to be more resilient to scratching as compared to the oil-based LSR. The water based LSR experienced partial exposure of the base material within the 1000g scratch, while the oil-based LSR had full penetration along the scratch at the lowest load (500g). In both cases, there was no damage (delamination, rumpling) adjacent to the scratches.

¹ The full life cycle energy consumption of the binders, including energy usage during manufacture, has not been evaluated.

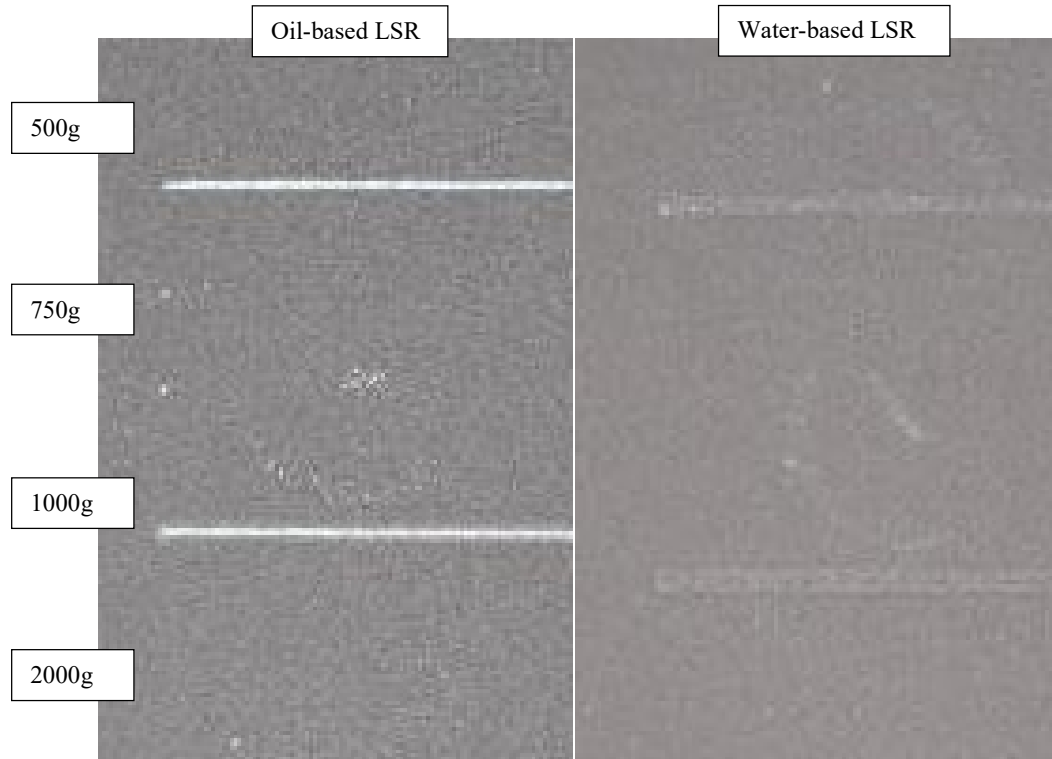


Figure 2: Photographs of green state (pre-diffusion) films after scratch testing.

5.4 Adhesion

The green state coating should be bonded securely enough to the surface such that delamination does not occur spontaneously or with handling.

Tape adhesion tests, per ASTM D3359, were performed on the green state coatings, **Figure 3**. The oil-based LSR rated 4A and 3A (“trace peeling or removal along incisions or at their intersection” and “jagged removal along incisions up to 1.6mm on either side”, respectively) while the water-based LSR rated 4A. On this basis adhesion of the water-based LSR was considered marginally superior to the oil based formulation.

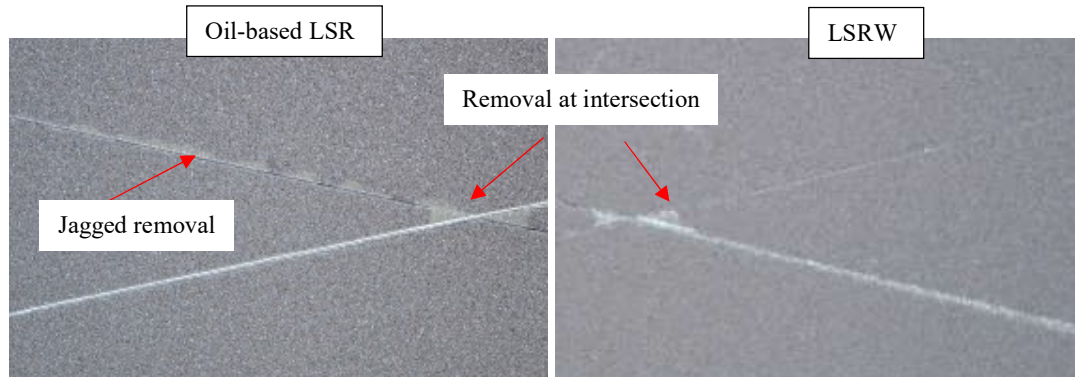


Figure 3: Tape test results of green state (pre-diffusion) films.

5.5 Binder Burn-off Characteristics

During the diffusion heat treatment the polymer matrix undergoes thermal decomposition. A desirable binder would not contaminate or produce discontinuities in the diffusion of the coating. Both the oil-based and water-based LSR produced uniform, contamination-free diffused coatings (refer to Section 6).

A thermogravimetric analysis was performed on the oil-based and water-based binders to determine the temperature necessary for driving off the binder during diffusion heat treatment, **Figure 4**. The binders of both coatings were substantially gone before the onset of aluminum/substrate diffusion (>600°C).

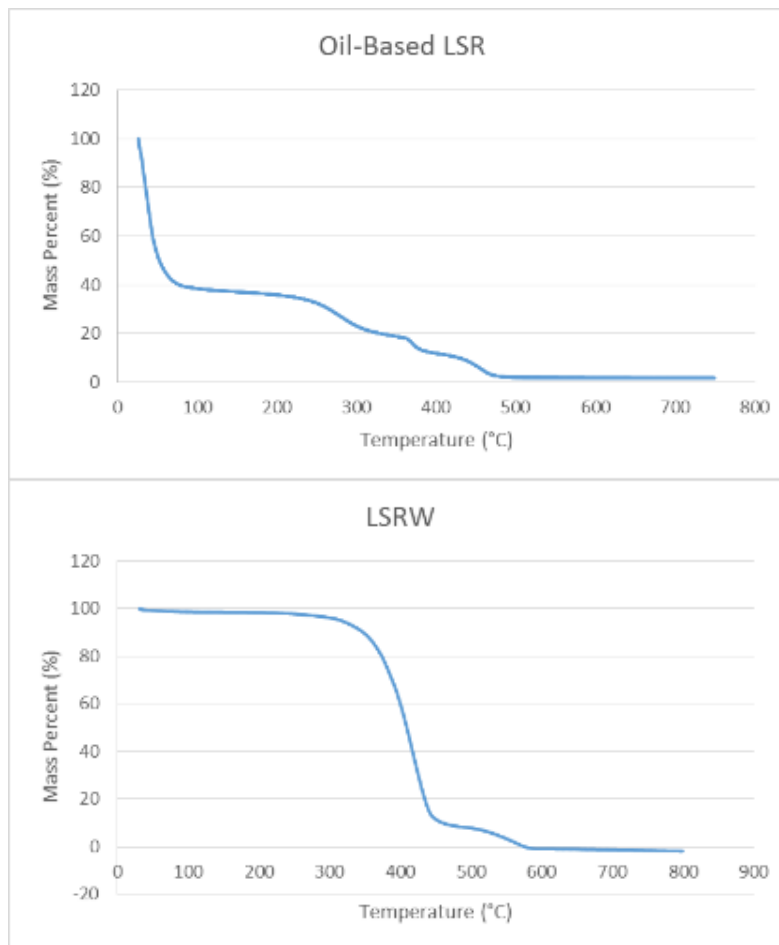


Figure 4: Thermogravimetric Analysis (TGA) of oil based and water based LSR.

6 Diffused Coating

The microstructure, chemical composition and oxidation performance of the diffused water based and oil based LSR coatings was compared.

6.1 Coating Microstructure

X750 coupons were coated with each slurry and diffused in vacuum at 885°C. Cross sections were taken and prepared per ASTM E3. Both coatings consisted of a uniform aluminide layer, **Figure 5**.

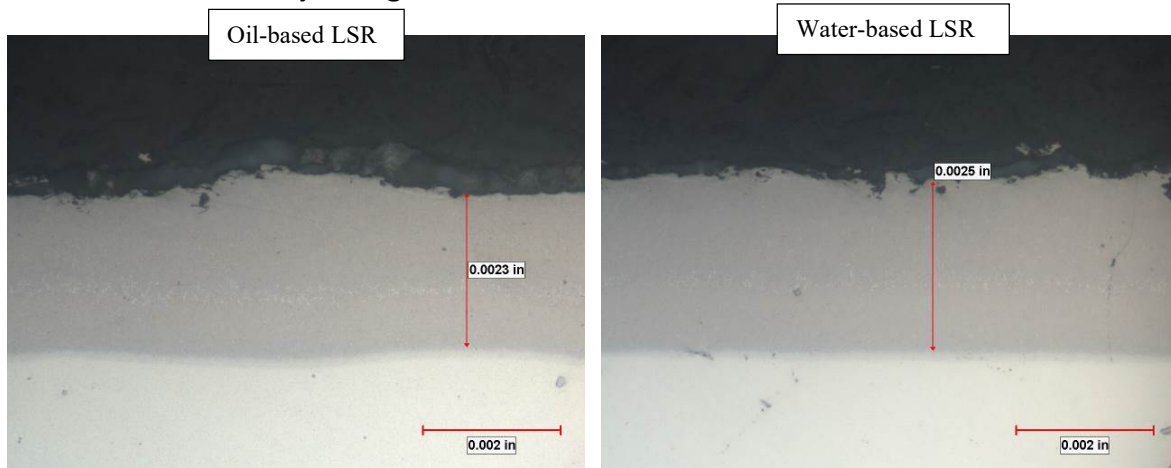


Figure 5: Micrographs showing the LSR coatings.

6.2 Coating Composition

MarM247 alloy coupons were coated with each slurry at comparable thicknesses and diffused in vacuum at 885°C. Cross sections were taken and prepared per ASTM E3. Energy dispersive spectroscopy (EDS) was performed in order to evaluate the compositional profile of each coating, **Figure 6**.

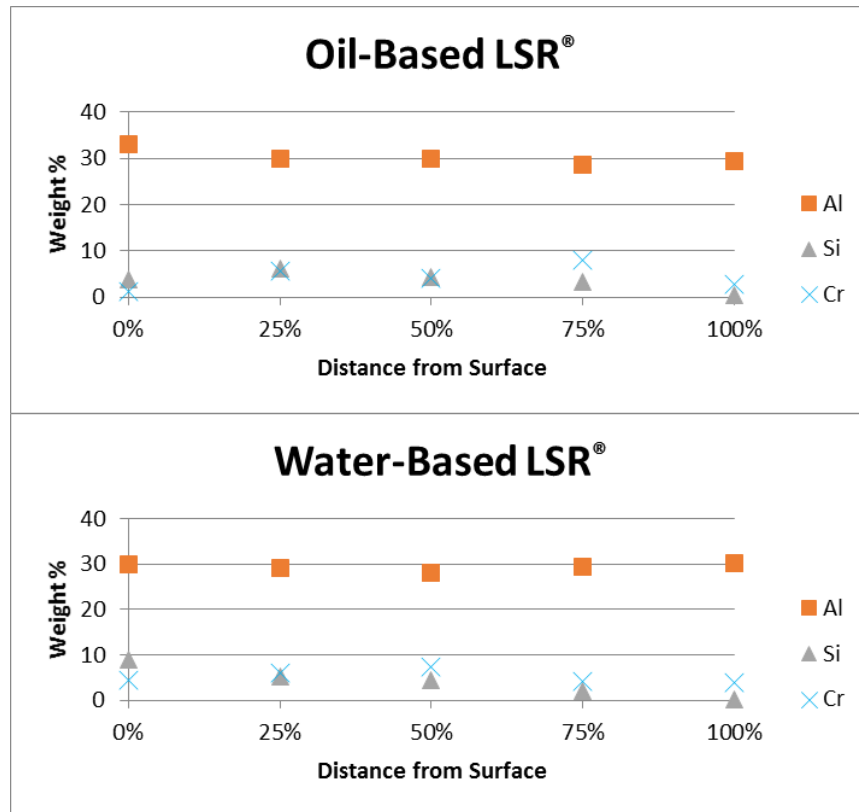


Figure 6: The chemical composition as a function of depth from the surface.

6.3 Cyclic Oxidation Testing

To evaluate and compare the oxidation resistance of the coatings, laboratory cyclic oxidation tests were performed on IN738 coupons coated with each slurry. Each cycle consisted of 50 minutes exposure at 1120°C in air followed by forced air cooling below 400°C in 10 minutes. Four samples of each coating were included in the test. Average weight change, normalized to initial surface area, was monitored every 100 hours. Both coatings experienced similar rates of mass change, and began to lose mass after ~400 cycles of exposure, **Figure 7**.

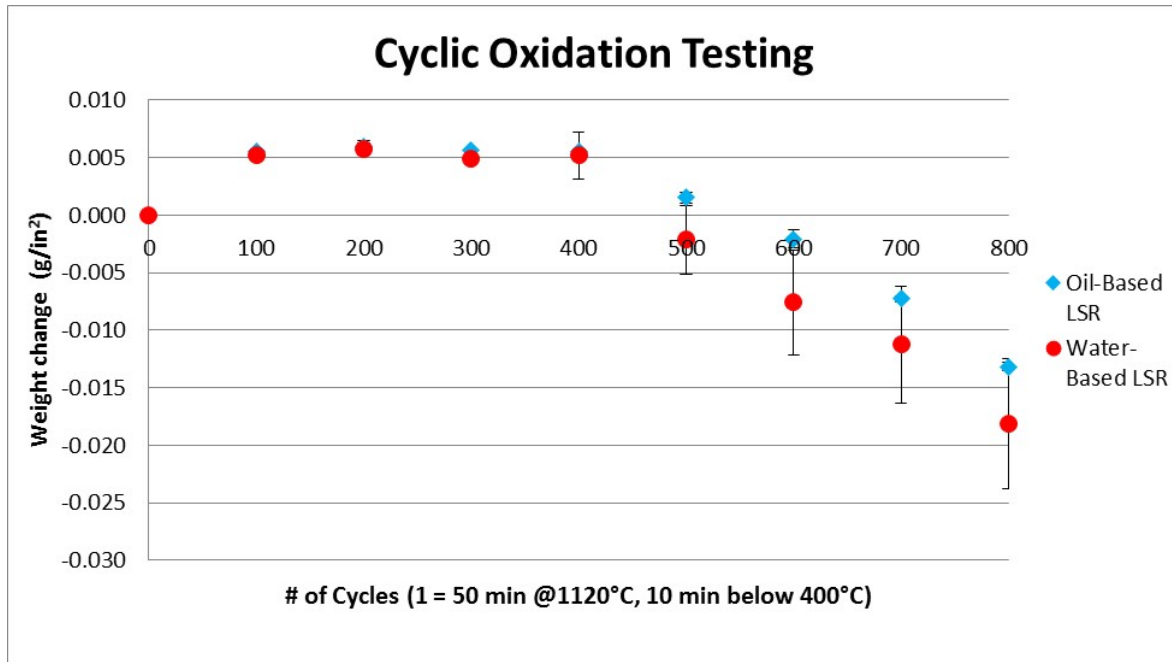


Figure 7: Cyclic oxidation testing results showing weight change over time.

The performance of the coatings was also evaluated by destructive metallurgical examination of randomly selected samples removed after 400 and 600 cycles. **Figure 8** shows the state of each coating after 600 cycles. Approximately 50-60% beta phase remained. Negligible difference in the performance of the two coatings was found.

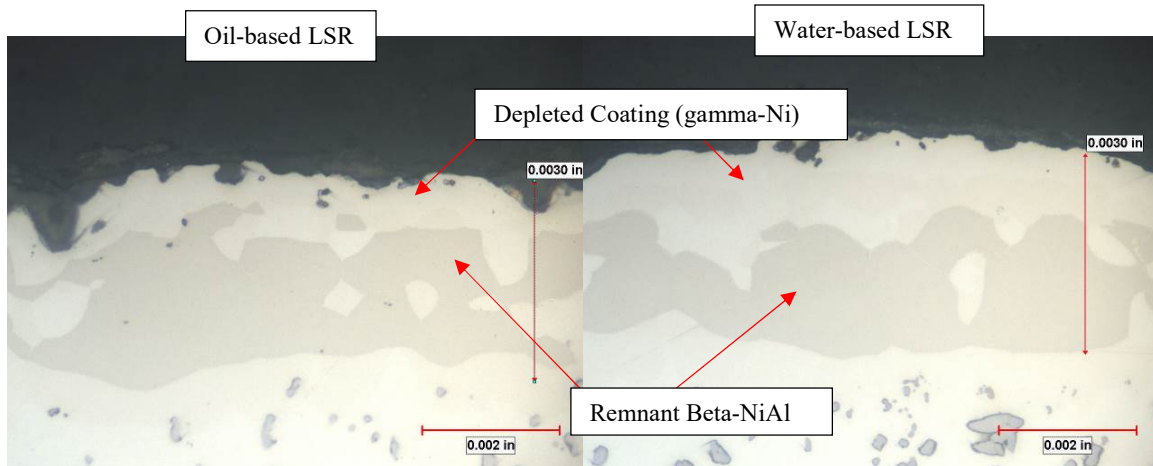


Figure 8: Optical micrographs of the coatings after 600 cycles of cyclic oxidation at 1120°C.

6.4 Evaluation of Service Exposed Coating

An RB211 24C HPT blade was coated with water-based LSR and operated for a 6,000 hour period. No beta aluminate phase depletion was apparent, **Figure 9**. RB211 24C HPT blades typically experience significant beta phase depletion (>80%)

in the hottest regions of the airfoil (mid airfoil, leading and trailing edges) after a full service interval of 24,000 hours.

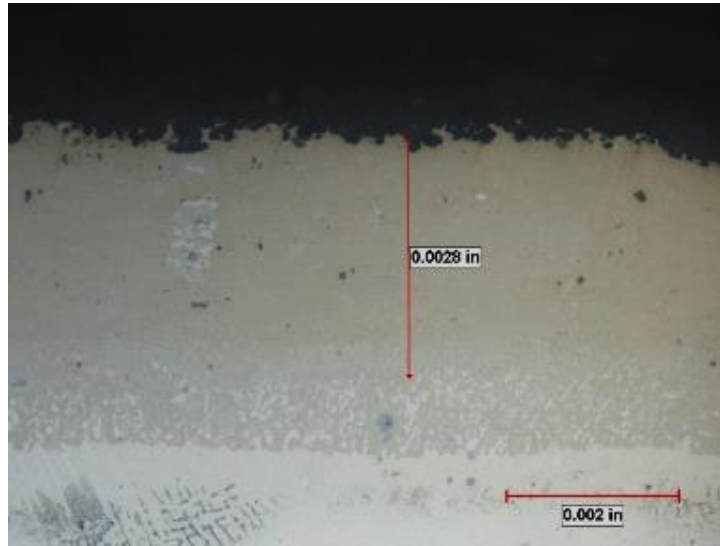


Figure 9: Optical Micrograph showing water-based LSR coating on an RB211 24C HPT blade, mid airfoil trailing edge, after approximately 6,000 hours of service.

6 Conclusions

In converting from an oil-based to a water-based slurry, the diffused LSR coating was kept constant, while the following health, safety and environmental improvements were achieved in the coating process:

- Elimination of volatile organic compounds.
- Conversion to non-flammable process
- Reduced toxicity
- Lower energy usage and shorter process time required to dry the coating.

The properties of the green state (pre-diffusion) coating were also improved upon, specifically the adhesive and cohesive strength.

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