INL/CON-09-15875
PREPRINT

Microstructure, Processing, Performance Relationships for High Temperature Coatings

23rd Annual Conference on Fossil Energy Materials

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May 2009

MICROSTRUCTURE, PROCESSING, PERFORMANCE RELATIONSHIPS FOR HIGH TEMPERATURE COATINGS

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ABSTRACT

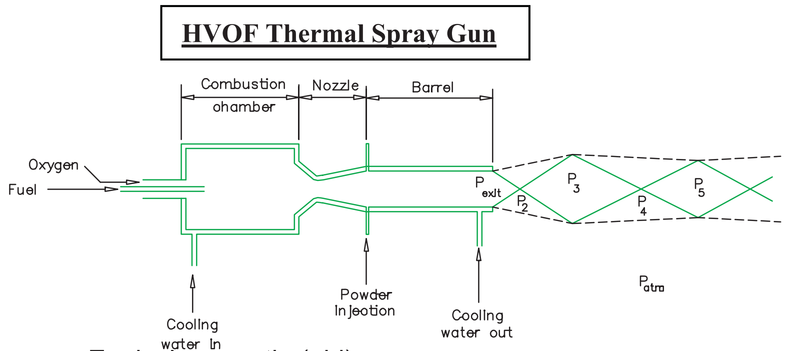
Iron aluminide coatings applied by High Velocity Oxy-Fuel (HVOF) thermal spray methods have shown high resistance to corrosion in fossil energy applications and it is generally accepted that mechanical failure, e.g. cracking or spalling, ultimately will determine coating lifetime. The use of HVOF thermal spray to apply coatings is one of the most commercially viable and allows the control of various parameters including powder particle velocity and temperature. These parameters influence coating properties, such as residual stress, bond coat strength and microstructure. In this work the durability of iron aluminide coatings applied to carbon steel or Grade 91 (9Cr-1Mo steel) substrates by HVOF was assessed during thermal cycling experiments. Two methods were developed – one involving real time interrogation of the coating using an ultrasonic NDE method and another that used traditional thermal cycling in a furnace followed by frequent coating inspection with dye penetrant chemicals to reveal cracking. The second method was developed to rapidly screen various combinations of torch parameter and coating/substrate combinations. Coating thickness was found to affect the cracking behavior of the coating with thick coatings (~250 microns) producing distinct cracks while thinner coatings (~160 microns) produced a fine network of cracks. Thinner coatings of FeAl coating applied to carbon steel survived more thermal cycles than thicker coatings for a given cycle temperature. Increasing thermal cycle temperature resulted in fewer thermal cycles-to-failure at both coating thicknesses, presumably due to the mismatch in the coefficient of thermal expansion (CTE) of the coating and substrate. Future investigations will study the more durable Fe_3Al HVOF coating applied to relevant substrates (Grade 91, various austenitic stainless steels and Ni-based alloys, like alloy 600 and 617). The HVOF process parameter will be systematically varied to understand what is needed to optimize the coating on various substrates.

INTRODUCTION

Typically, materials with the high temperature strength and creep resistance required for fossil fuel boilers and other components lack the necessary corrosion resistance in the process atmosphere to provide a long service life. Conversely, materials with the needed corrosion resistance often are not suitable for the high temperature structural requirements or they are difficult to thermomechanically form into useful shapes. One way of satisfying all the requirements is to apply a coating with the necessary corrosion resistance to a substrate material that satisfies the high temperature structural requirements. The functionality of the system is dependent on attaining a high relative density, which prevents corrosive gases from reaching the underlying substrate material, and the coating being resistant to cracking or delamination, which, again, prevents corrosive gases from reaching the underlying substrate. Due to these issues, there has been reluctance to utilize coatings in high temperature, aggressive environments. However, the need to increase operating temperatures to increase efficiency is driving research to understand the coating process and the factors that contribute to coating failures. Therefore the current work is focused on understanding the relationship between coating parameters and coating durability with the goal of optimizing those parameters to produce reliable coatings with long operating lifetimes.

BACKGROUND

Thermally sprayed coatings as thermal barrier and/or corrosion resistant coatings have long been of interest. Coating/substrate systems can be chosen to satisfy both the structural and corrosion resistance requirements of specific applications in high temperature, highly aggressive environments. The High Velocity Oxy-Fuel (HVOF) thermal spray method, Fig. 1, can be manipulated to control various characteristics of the applied coating[1,2].



- Equivalence ratio (phi)- $\Phi = \dfrac{Fuel / Oxygen}{(Fuel / Oxygen)_{Stoich}}$
- Combustion chamber pressure

P_C – Determined by total mass flow of O_2 and fuel

Figure 1. Schematic of the HVOF thermal spray process.

A mixture of fuel, for example kerosene and oxygen, is fed into a combustion chamber at a predetermined ratio, Φ, while the coating, in powder form, is injected downstream where it is heated, at least partially melted and accelerated at a target (substrate). Particle temperature is controlled, to a large extent, by the oxygen/fuel ratio[3] which also controls whether the atmosphere is oxidizing, neutral or reducing, while the pressure in the combustion chamber, as determined by the fuel and oxidizer feed rates, strongly influences the particle velocity[3,4]. These parameters, along with the CTE of particle and substrate, interact to control the residual stress within the coating[4,5], which can range from compressive to tensile. Manipulation of these variables results in control of the stress state of the coating. The substrate surface condition, coating strength and the residual stress ultimately control the durability of the coating – whether it cracks, delaminates and/or spalls. Since the corrosion resistance of coating materials is only slightly lower than that of wrought material[6], the failure of the coating/substrate system typically is attributable to the mechanical failure of the coating. Elucidation of the interactions between the various HVOF parameters and material parameters is critical in developing high integrity coatings.

TECHNICAL APPROACH

This work focuses on studying the relationship between HVOF processing parameters and the mechanical durability of the resulting coating. Unfortunately, characterization of the coating durability is difficult since it is not an inherent materials property and can vary with substrate preparation and HVOF process parameters. The mechanical stresses and strains under service conditions can be difficult to characterize and simulate under laboratory conditions. Therefore, characterization of coating durability is being limited to the cracking behavior of coatings during rapid thermal cycling and room temperature cracking behavior of coatings applied to round tensile bars. Under both conditions it is necessary to identify when cracking occurs – preferably detecting the first crack to form in each type of test. (In this work, cracking is used to define coating failure.) To this end, work is focused on developing methods for detecting crack formation in real time.

The coating material is limited to iron aluminide, either Fe_3Al or FeAl, since these materials have shown acceptable corrosion resistance in previous work[6]. Substrates include plain carbon steel (1018) as a baseline material as well as other, higher temperature materials, such as grade 91 steel (9Cr-1Mo steel) and nickel-based materials, that are more relevant to fossil energy applications.

The parameters of interest in this work can be divided into those inherent to the coating/substrate system and those that can be varied during HVOF coating deposition. Powder particle velocity, temperature and melted fraction will be controlled with HVOF parameters for a given coating/substrate system. These factors will be manipulated to generate coatings with different residual stresses which will then be related back to the durability of the coating.

THERMAL CYCLING

Rods, nominally 12.7 mm in diameter and 127 mm long, were coated with iron aluminide using HVOF thermal spray methods. Coatings of 160 microns and 250 microns were made. Additionally, plates of 1018 carbon steel (12.7 mm thick) and Grade 91 steel (19.1 mm thick) were coated with iron aluminides of the same thickness. Durability testing for each type of sample was slightly different and outlined below.

Durability Testing of Coated Rods

The Gleeble 3500 Universal Testing System was used to hold and quickly heat the coated rods. The rods were heated to the desired temperature, held there for 2 minutes and allowed to cool. Heating rates were limited to about 350^{o}C/minute, although faster or slower rates were easily obtainable. The cooling rate was somewhat slower (~200^{o}C/minute) but still fairly high due to heat conduction through the water-cooled sample grips. Temperature was tracked by a Type K thermocouple spot welded directly to the coating. Real time crack detection was accomplished using NDE techniques. Specifically, a water-cooled, eddy current coil surrounded the sample and interrogated the coating integrity during thermal cycling. (Eddy current measurements are highly sensitive to cracking perpendicular to the coating surface which disrupts the eddy currents. However, delaminations at the coating/substrate interface have less influence on the eddy current signal.) Previously it was found that a single eddy current coil was inadequate to definitively detect cracking of the coating[7]. Therefore, modifications were made and a second eddy current coil was added to the set up. This enabled a differential signal to be produced, Fig. 2. Although, the signal from each individual coil does not reveal cracking, the differential signal is more sensitive to differences between the signals, caused by differences in cracking beneath each coil. The Gleeble and eddy current data acquisition equipment were setup to perform a number of thermal cycles without further operator input. The thermal cycle during which cracking occurred was then determined from the differential signal.

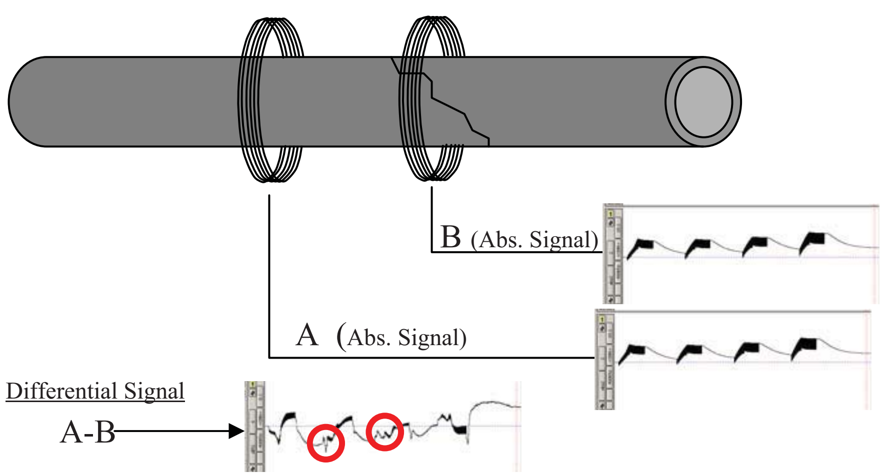


Figure 2. Schematic of the dual eddy current coil arrangement for real time crack detection during thermal cycling. The differential signal reveals cracking, red circles, not evident in either of the absolute signals.

Durability Testing of Coated Plates

Cylinders, approximately 16 mm in diameter, were cut from the individual coated plates using electric discharge machining (EDM) to avoid damaging the coating or coating/substrate interface. The cylinders were then thermally cycled in a standard laboratory furnace (CM Rapid Temp Furnace, model 1720 SM (C)). The furnace was heated to the desired temperature in 5 minutes, held 5 minutes and allowed to cool naturally. Temperature was monitored with a Type K thermocouple in contact with the coating surface. Although the heating and hold times were similar to the rod-type samples thermally-cycled in the Gleeble, the cooling time of these samples was considerably longer, on the order of 1 hour, than that in the Gleeble work. (The hold time was also slightly longer to account for radiant heating in the furnace versus resistive heating of the Gleeble specimens.) The furnace controller was programmed to perform a set number of thermal cycles, after which the coating was evaluated for cracks using the dye penetrant technique. The advantage of this technique is that multiple samples can be tested at once versus only a single specimen in the Gleeble. The disadvantage is that the samples are not evaluated for cracks after every thermal cycle and the number of cycles-to-failure cannot be determined exactly - only within a range. Therefore, thermal cycling in a laboratory furnace is used as a rapid screening tool while testing in the Gleeble is reserved for testing of the most promising specimens.

RESULTS AND DISCUSSION

DURABILITY TESTING OF COATED RODS

Figure 3 shows the results of thermal cycling coatings of 160 microns and 250 microns on carbon steel rods using the Gleeble set up. The behavior of differential eddy current signal during successive thermal cycles is significantly different for the two coating thicknesses. Cracking in the thick coating results in a well defined signal (red circles in Fig. 3) while cracking in the thin coating results in a gradual decrease in the amplitude of the differential signal. The differences can be attributed to distinct cracking events (and relatively large cracks) in the thick coating while cracking is relatively uniform and relatively fine in the thinner coating. Cracking occurs under both eddy current coils in the thin coating, while only under one in the thick coating. The degradation in the differential signal (red lines/arrow) for the thin coatings results from slight differences in the cracking pattern under each eddy current coil.

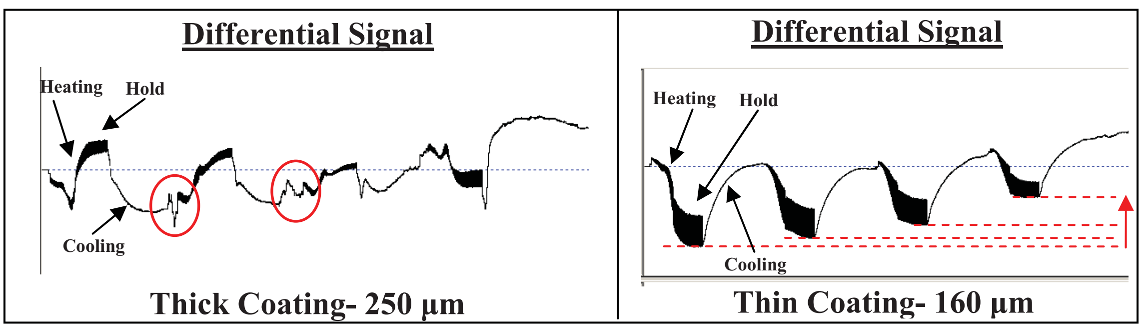


Figure 3. The differential eddy current coil signal for coatings of different thickness.

The surface of each sample after thermal cycling was scanned with an eddy current coil to map the cracking patterns across the surface. The resulting images are shown in Fig. 4. The vertical axis is the distance along the rod while

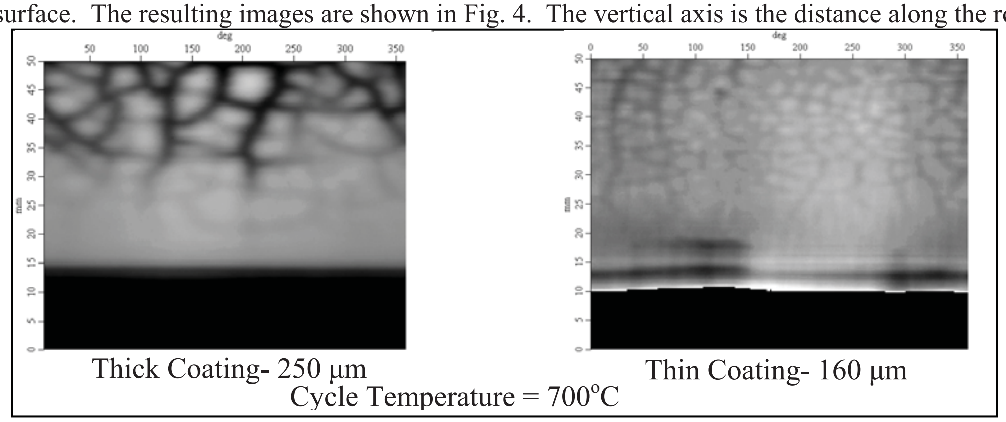


Figure 4. A map of the coating surface using a scanning eddy current coil to reveal cracks.

the x-axis is the angular rotation around the sample, from 0° to 360°. The cracks are larger and more distinct in the thicker coating than in the thinner coating. Also, the cracking pattern is coarser in the thicker coating.

Samples with 250 micron and 160 micron coatings of FeAl on carbon steel were thermally cycled in the Gleeble to different cycle temperatures. The number of cycles-to-failure was determined for each coating thickness and cycle temperature. The results are plotted in Fig. 5. Thinner coatings are more durable at all thermal cycle temperatures, although the difference is small at higher cycle temperatures. As yet, the exact cause of this observation is not fully understood, although it likely arises from differences in residual stress, thermal stresses and/or substrate temperature during coating.

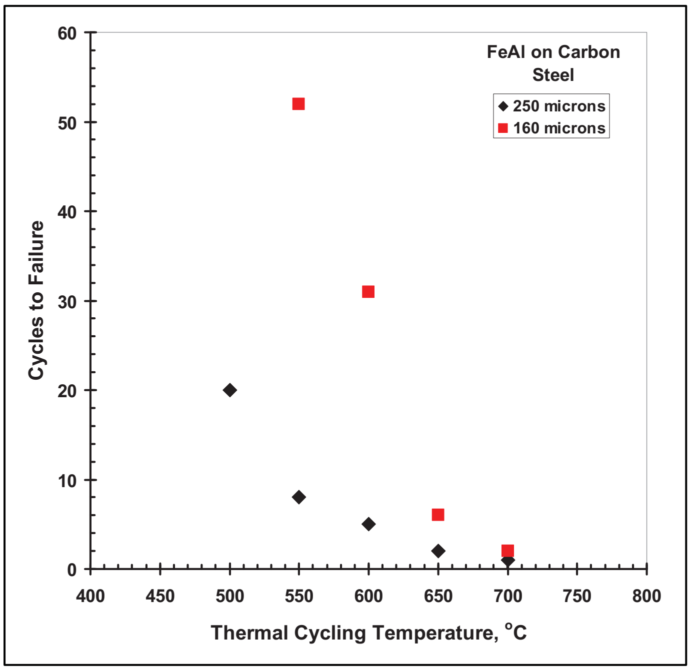
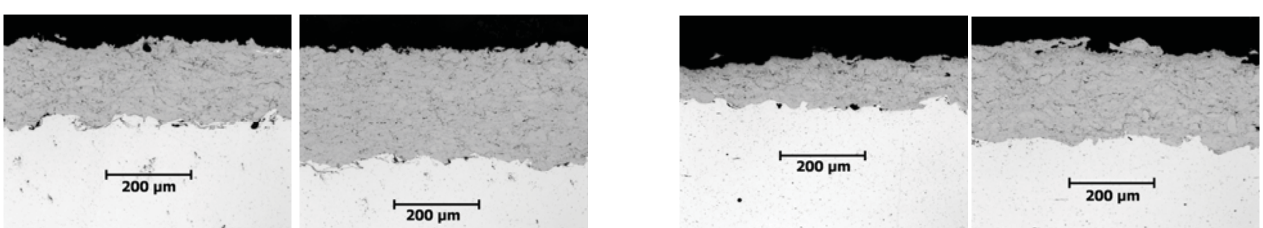


Figure 5. Dependence of the number of cycles to failure on thermal cycle temperature for two different coating thicknesses.

DURABILITY TESTING OF COATED PLATES

Evaluation of the durability of the coatings on plate substrates has just begun and the results, thus far, are preliminary. So far HVOF FeAl coatings have been applied to 19 mm thick Grade 91 steel plates and 12.7 mm thick carbon steel plates. Fig. 6 shows the microstructure of the coating and coating/substrate interface. In general, the



Grade 91 Steel **Carbon Steel (1018)**

Figure 6. Microstructure of thick and thin coatings of FeAl on Grade 91 and carbon steels.

coating looks the same whether it is applied to carbon steel or Grade 91. Porosity, both in the coating as well as at the interface, is minimal.

Currently, thermal cycling of these samples to approximately 480°C has been performed. The results are shown in Fig.7. The cracks in these images are revealed by the dye penetrant. It is evident that the coatings on the Grade 91 steel have cracked, although the thinner coating required more cycles to crack the coating, 10 cycles for the thin coating versus 4 cycles for the thicker coating. It is noted again that the cracking pattern in the thicker coating is much coarser than that observed in the thinner coating on Grade 91. So far the FeAl coating on carbon steel has not failed after a total of 42 thermal cycles.

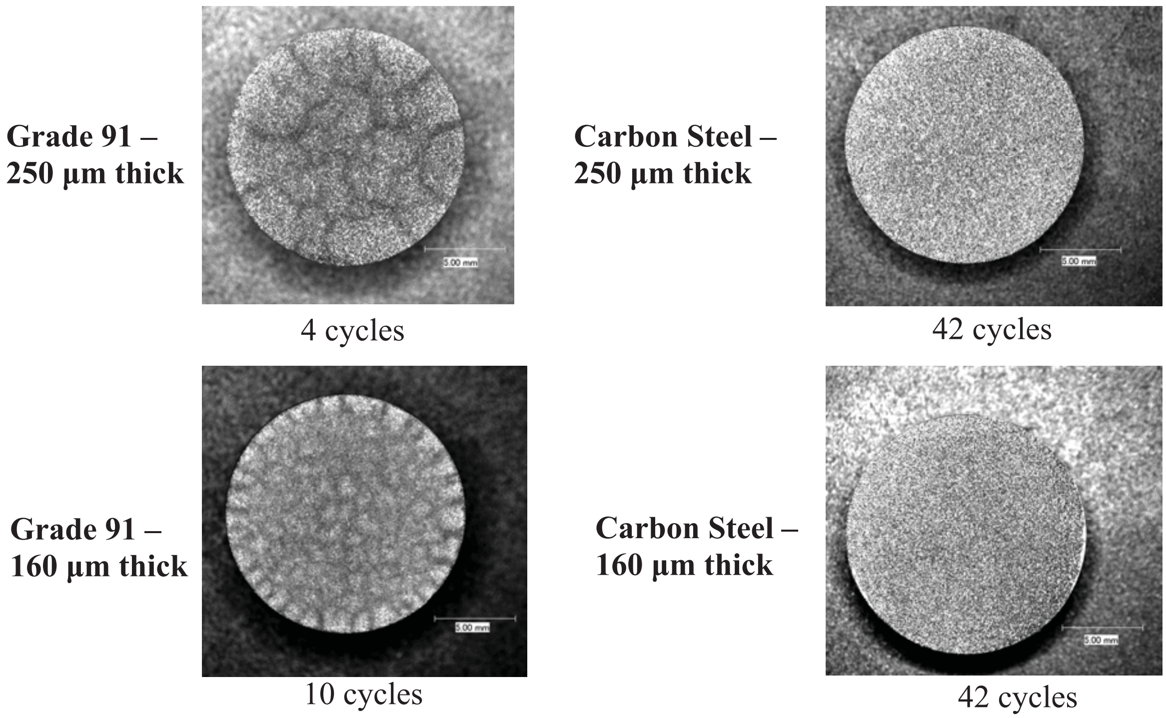


Figure 7. Cracking, as revealed by dye penetrant, in FeAl coatings of different thicknesses on Grade 91 and carbon steel substrates subjected to thermal cycling to 480°C.

The difference in durability exhibited by different substrate materials may be due to the difference in the coefficient of thermal expansion (CTE). The FeAl coating nominally has a CTE of around 23 µm/m·°C. Grade 91 steel has a lower CTE of ~11 µm/m·°C compared to carbon steel, 14 µm/m·°C, which is somewhat closer to the coating. Also, the carbon steel plate is only 12.7 mm compared to the 16 mm thick Grade 91 plate. Even though cooling air was applied to all plates during deposition, the difference in plate thickness undoubtedly resulted in different substrate temperatures, resulting in a different residual stress state for the two different plate thicknesses.

FUTURE WORK ON THERMAL CYCLING

The work to date raises a variety of issues and future work will focus on the following to explore these issues and develop optimized HVOF parameters and coatings:

- The substrate temperature during deposition and the stress state in the coating after deposition will be evaluated to better understand the influence of CTE differences on durability. Ultimately, the substrate temperature may be actively controlled to generate the proper stress state during thermal cycling.
- Manipulation of the HVOF parameters to adjust the CTE of the coating to match that of the substrate. Basically HVOF parameters affect the amount of porosity in the coating which, in turn, decreases the CTE of the coating. The CTE may be able to be tailored to that of the substrate; provided the porosity exists as closed porosity (open porosity would allow the corrosive furnace atmosphere to reach the substrate).
- Further study the affect of coating thickness on cracking pattern of the coating. The cracking network is determined by the stress state in the coating. This study may result in a way to evaluate the stress state at the onset of cracking.

ROOM TEMPERATURE DURABILITY (CRACKING) OF COATINGS

Resistance to cracking due to tensile loading is one way of evaluating relative coating performance and can be used as a screening test for the development of optimum coating systems and parameters. Tensile specimens of substrate material are coated using HVOF and then loaded in tension until a crack is formed. Again, crack detection becomes the main obstacle for evaluating coating durability. Previously, acoustic emission was used to detect cracking. However, very thin coatings did not produce clearly audible cracking events. As found above in the Gleeble thermal cycling work, the cracking pattern of thin coatings under an applied tensile load is relatively fine and the cracks quite small. `Cracking in thicker coatings (>150 microns thick) is quite easy to detect using acoustic emission techniques. Since the behavior is similar to the thermal cycling work, we are designing eddy current coils to detect cracking in these tensile tests. The coil design needs to be slightly different since cracking will be mainly perpendicular to the tensile axis, unlike in the thermal cycling work where cracking occurred in both the transverse and longitudinal directions.

CONCLUSIONS

Dual coil eddy current coils were used to interrogate FeAl coatings on carbon steel rods during thermal cycling. Thicker coatings (~250 microns) exhibited distinct cracking events that resulted in relatively large cracks while thinner coatings (~160 microns) exhibited uniform cracking that resulted in fine cracks. The geometrical cracking pattern was also coarser in thick coatings. Thinner coatings exhibited a greater number of thermal cycles-to-failure than thicker coatings at all thermal cycling temperatures, although this difference decreased as the thermal cycle temperature was increased. Finally, FeAl coatings applied to Grade 91 steel (9Cr-1Mo steel) were not as durable as those applied to carbon steel, presumably due to residual stresses. Future work will need to monitor substrate temperature during deposition and evaluate the residual stress state to optimize coatings for specific applications.

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ACKNOWLEDGMENTS

The authors would like to acknowledge the contributions made by W.D. Swank and D.C. Haggard to prepare the HVOF thermal spray samples, Dr. D.C. Kunerth for designing the eddy current coil and making the eddy current measurements and D.E. Clark for setup and operation of the Gleeble 3500 for the thermal cycling experiments. This report was prepared for the U.S. Department of Energy, Office of Fossil Energy, under DOE Idaho Operations Office, Contract DE-AC07-05ID14517.