MICROSTRUCTURE, PROCESSING, PERFORMANCE RELATIONSHIPS FOR HIGH TEMPERATURE COATINGS

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ABSTRACT

High velocity oxy-fuel (HVOF)coating 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 which influence coating properties, such as residual stress, bond coat strength and microstructure. Methods of assessing the mechanical durability of coatings are being developed in order to explore the relationship between HVOF spraying parameters and the mechanical properties of the coating and coating bond strength. The room temperature mechanical strength, as well as the resistance of the coating to cracking/spalling during thermal transients, is of considerable importance. Eddy current, acoustic emission and thermal imaging methods are being developed to detect coating failure during thermal cycling tests and room temperature tensile tests. Preliminary results on coating failure of HVOF FeAl coatings on carbon steel, as detected by eddy current measurements during thermal cycling, are presented. The influence of HVOF coating parameters of iron aluminides - applied to more relevant structural steels, like 316 SS and Grade 91 steel, - on coating durability will be explored once reliable methods for identification of coating failure have been developed.

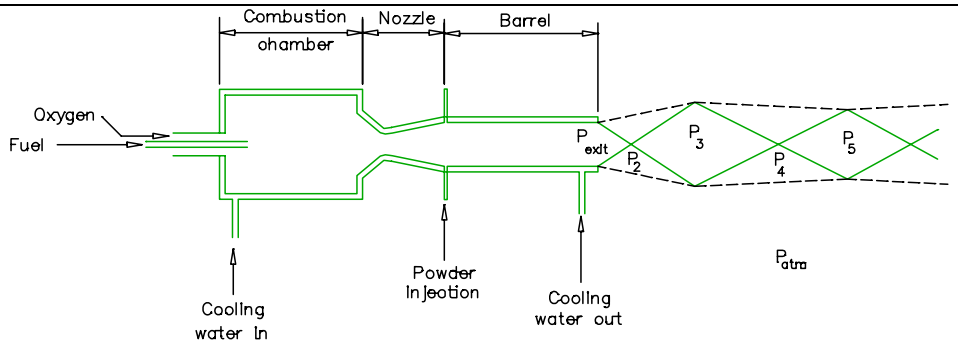
INTRODUCTION

Typically, materials with the high temperature strength and creep resistance required for fossil fuel boilers lack the necessary corrosion resistance 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 will satisfy the high temperature structural requirements. The functionality of the system is dependent on the coating being devoid of open porosity, which would allow corrosive gases to reach the underlying substrate material, and the coating being resistant to cracking or delamination, which would, again, allow corrosive gases to reach 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 oxygen fuel (HVOF) thermal spray method can be manipulated to control various characteristics of the applied coating[1,2]. Figure 1 shows a schematic of the HVOF technique. A mixture of fuel, for example kerosene and oxygen are fed into a combustion



- **Combustion chamber pressure - P_C *determined by total mass flow of O_2 and fuel***
- **Equivalence ratio (phi) -** $\Phi = \dfrac{Fuel/Oxygen}{(Fuel/Oxygen)_{Stoich}}$

Figure 1. Schematic representation of the HVOF thermal spray gun.

chamber. The coating in powder form is injected downstream where it is heated and accelerated at a target (substrate). The powder particles are at least partially melted by the time they impact the substrate where they spread out over the surface. 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. The pressure in the combustion chamber, as determined by the feed rate and pressure of the fuel and oxygen, has a strong influence on 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], Figure 2. By active manipulation of these variables, the stress state of the coating can be engineered. The

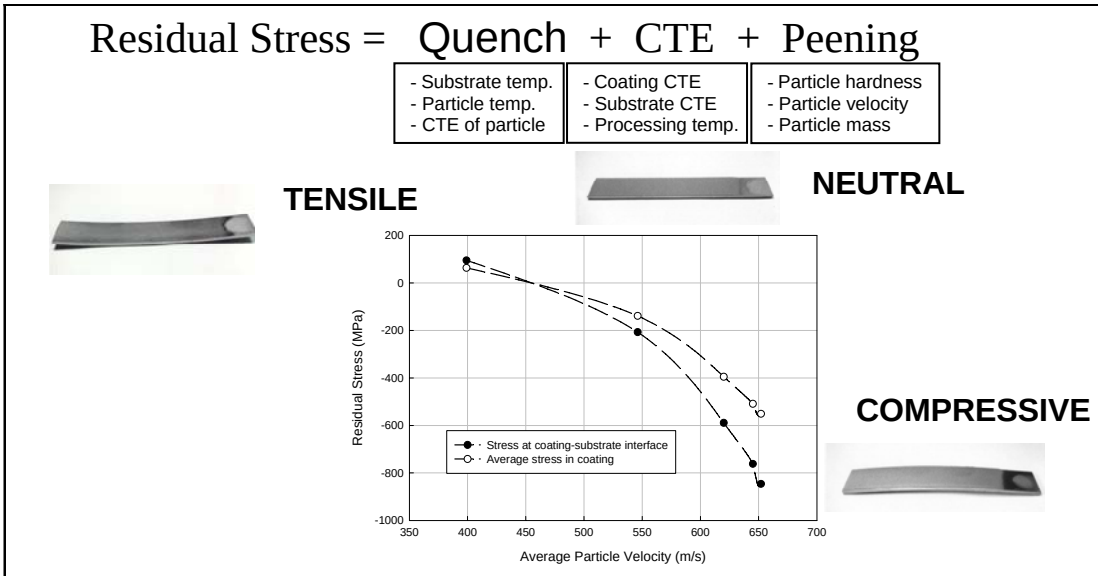


Figure 2. HVOF parameters can be used to control residual stress in the coating.

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 of the various HVOF system and materials 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 durability is being limited to room temperature cracking behavior of coatings applied to round tensile bars and the cracking behavior of coating/substrate systems during rapid thermal cycling. Under both conditions it is necessary to identify when cracking occurs – preferably detecting the first crack to form in each type of test. To this end, work is focused on developing methods for detecting crack formation in real time.

The coating material is limited to iron aluminide since this material has shown acceptable corrosion resistance in previous work[6]. Carbon steel substrates are being utilized to generate coating/substrate systems with low durability so that the detection methods and methodology can be more quickly developed. Other, higher temperature materials, such as grade 91 steel and the nickel-based materials, are more relevant and will be the focus of future work after the crack detection methods have been refined.

The parameters of interest in this work can be divided into those inherent to the coating and substrate materials and those that can be varied during HVOF coating deposition. Powder particle velocity, temperature and melted fraction will be controlled with HVOF parameters which, in conjunction with the CTE of the coating and its mismatch with the substrate, determine the residual stress, whether it be tensile, neutral or compressive, in the coating. 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

Experimental Set Up

The coating/substrate system will be subjected to thermal cycling over the course of its lifetime. In general there will be a difference in the CTE between the coating and the substrate materials. This difference can exceed the strength of the coating and result in crack formation. Furthermore, high operating temperatures may result in relaxation of the residual stress and even recrystallization which can change the stresses, sign and magnitude, during thermal cycling. To document this behavior HVOF coatings applied to rods (to eliminate stress risers that would otherwise occur at sharp corners on a flat dogbone type tensile specimen) have been thermally cycled to failure (cracking). The rods are nominally 12.7 mm in diameter and 127 mm long. The coating is FeAl and is approximately 250 microns thick. Figure 3 shows the experimental set up for thermal cycling experiments. The Gleeble 3500 is used to hold the sample and resistively heat it. Heating rates are currently limited to about 450^{o}C/ minute, although faster or slower rates are easily obtainable. The cooling rate is somewhat slower (~200^{o}C/minute) but is still fairly high and determined by heat conduction through the water-cooled sample grips. Temperature is tracked by a type K thermocouple spot welded directly to the coating. A water-cooled eddy current coil surrounds the sample to detect crack formation during thermal cycling. (Eddy current measurements are highly sensitive to through thickness cracking which disrupts the eddy currents.)

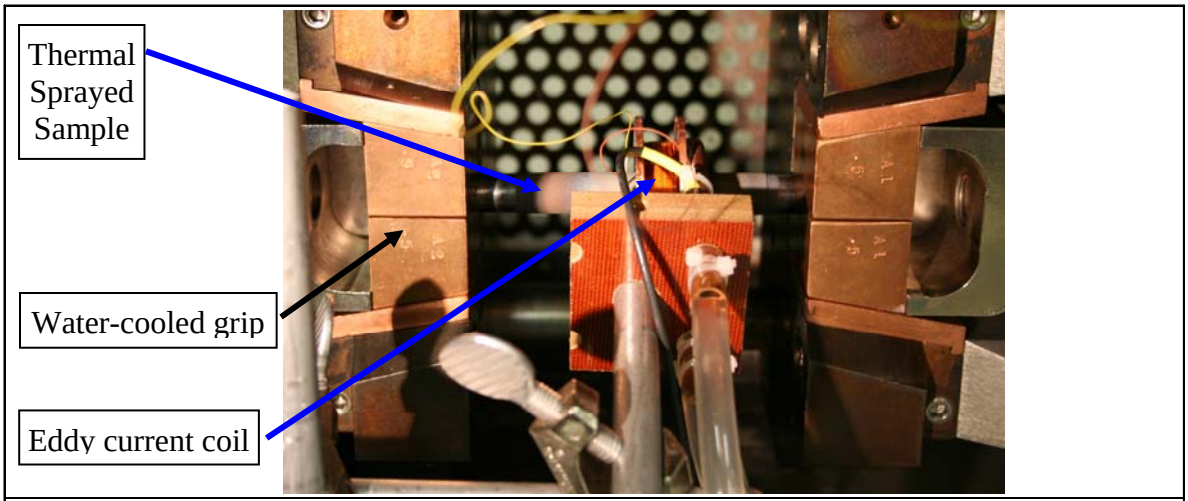


Figure 3. Experimental set up in the Gleeble 3500 for thermal cycling tests.

Results and Discussion

The Gleeble 3500 can be programmed for multiple thermal cycles to a given temperature followed by cooling. Figure 4 shows information that can be obtained using eddy current coils. The images on the left side in this figure are generated by scanning an eddy current coil over the surface and plotting the response in shades of gray. Defects appear bright. The coating appears defect-free in the as-sprayed condition shown in Fig. 4a. During thermal cycling, however, the eddy current coil is held stationary and designed to interrogate one area of the coating and

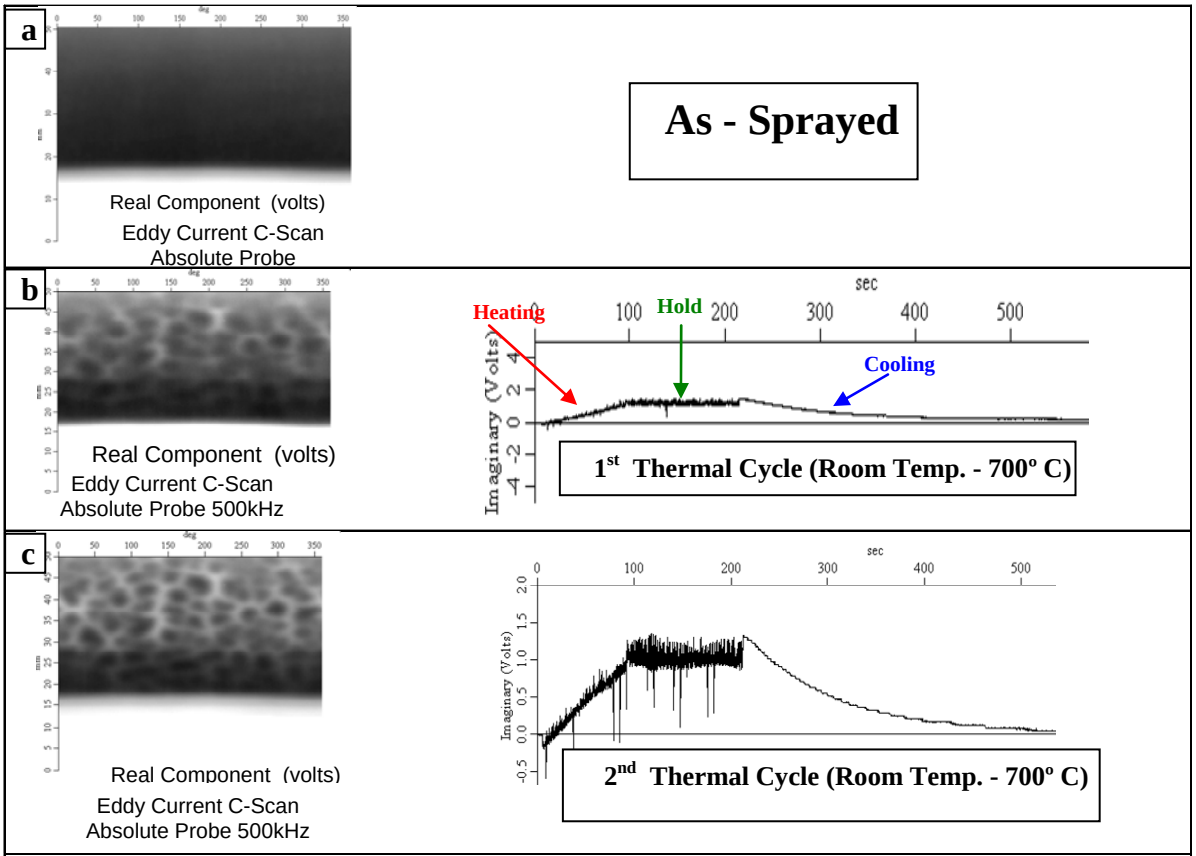


Figure 4. Image of the coating using an eddy current probe is shown at the left while the response of the in situ eddy current coil during thermal cycling is shown on the right.

only the output of the coil is of interest. The response of the eddy current coil during thermal cycling is shown for the first and second thermal cycles on the right side of Fig. 4b and 4c. The shape of the profile is dependent on the coating (eddy current is a relatively near-surface technique) and the effect of heating/cooling on the magnetic and electrical properties of the coating, including phase changes. Heating to 700°C causes the coil output to increase over the first ~2 minutes. The response is steady during a 2 minute hold at 700°C and then decreases as the sample is cooled back to room temperature. Crack formation is expected to be manifested as an abrupt change in the plot of coil response with time. However, nothing is evident in the response/time plot even though the eddy current scan, performed after the thermal cycle, shows numerous cracks (image on the left of Fig. 4b). The response during a second thermal cycle is very similar to that recorded during the first thermal cycle (note the difference in the vertical scale between the two plots). The lack of a clear cracking event in these plots is thought to be due to the averaging effect of the stationary eddy current coil – the coil interrogates an area and the output is an "average" over this area. A small crack may result in a very small, to the point of being insignificant, change in the output response. Fabrication of a coil that interrogates a much smaller area is expected to produce a more definitive change in the output.

A second issue is shown in Fig. 5 in which the sample was thermally cycled up to 800°C for 10 cycles. In this case, heating resulted in a decreasing output (voltage) up to the temperature where the underlying substrate, a low carbon steel, begins to transform to austenite. This triggers a dramatic step in the plot of output versus time since electrical and magnetic properties of austenite are significantly different than the low temperature ferrite phase. The austenite transforms back to ferrite during cooling and again results in a large step in the output plot. This indicates that the substrate is having a significant influence on the eddy current coil output – the coil is probing too deep and is beyond the thickness of the coating which really is the only region of interest. Operation of the coil at higher frequencies will reduce the depth of penetration and the behavior of the eddy currents and their interaction with defects (cracks) in the coating will more strongly influence the coil output. (Conversely, if the depth of penetration is too small then surface roughness of the coating will interfere with crack detection.) Higher frequency operation may require a new eddy current coil to be designed and fabricated.

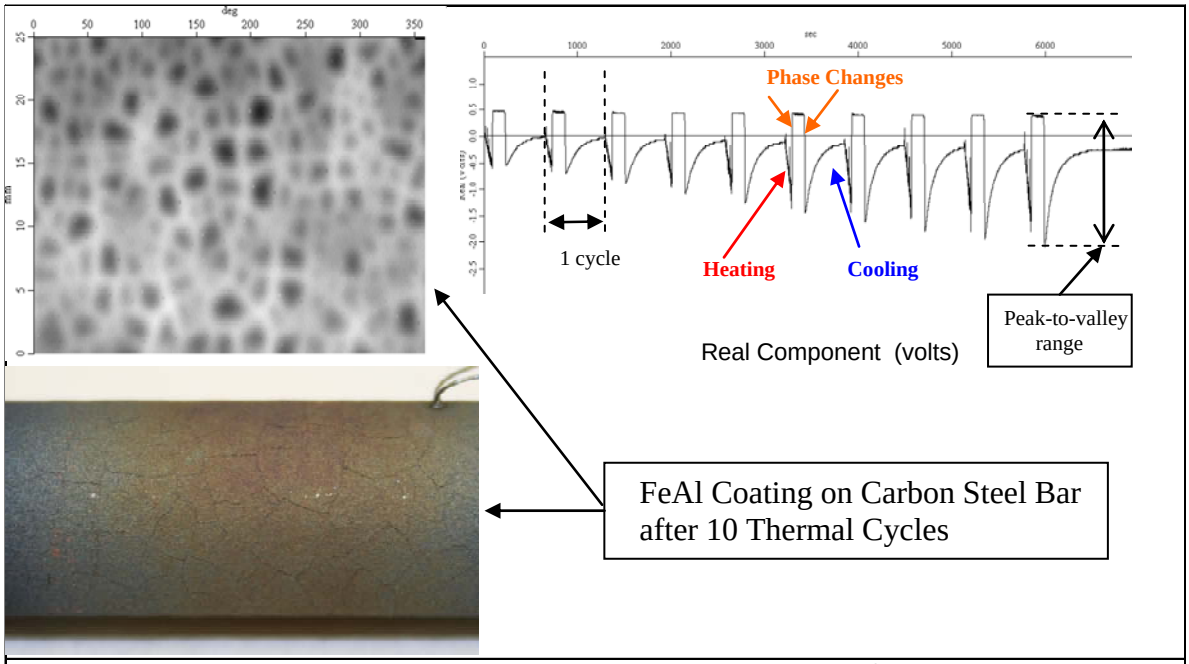


Figure 5. FeAl coating on carbon steel rod after thermal cycling 10 times to 800°C. The substrate transform from ferrite to austenite and back to ferrite again during the thermal cycle.

Figure 5 also shows the peak-to-valley distance for each thermal cycle increases with an increasing number of cycles. During the first cycle the output voltage ranges from 0.5 to -0.5 volts. After the tenth cycle this peak-to-valley distance ranges from 0.5 volts to approximately -2.0 volts. Efforts will be made to see if there is a correlation between the peak-to-valley range and the crack length per unit area and whether it can be used to identify

degradation of the coating. (The other cause for the change in the peak-to-valley range may be microstructural coarsening.) Once degradation can be reliably detected, much more durable coatings will be studied. It is possible that a large number of thermal cycles will be needed to induce cracking and automated thermal cycling/data collection will have to be implemented. The data then can be analyzed offline to determine when cracks started to form.

Finally Figure 6 shows that delamination of the coating from the substrate may also be significant. However, it cannot be determined whether the delamination happened before cracking or as a result of cracking. Although delamination is undesirable, it is not as critical if it occurs without through thickness cracking since there is no path for the corrosive atmosphere to reach the substrate. Delamination may lead to spalling of the coating, however, and increased rates of attack on the substrate. Unfortunately, eddy current techniques are not as sensitive to delaminations in contrast to through thickness cracking. Therefore, delamination detection will be attempted using thermal imaging. Delaminations are expected to result in "hot" and "cold" spots on the coating surface which hopefully can be detected in real time using thermal imaging.

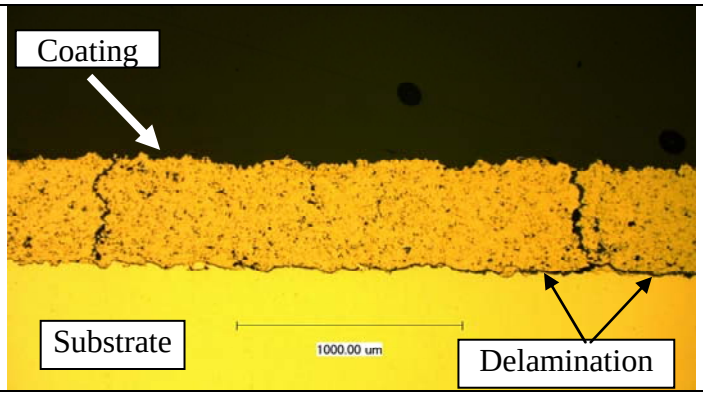


Figure 6. Optical micrograph of a FeAl coating on carbon steel subjected to 2 thermal cycles to 700°C showing delamination of the coating from the substrate.

Conclusions

The results of the thermal cycling tests indicate that eddy current measurements may be a viable method for detecting coating failure by cracking. However, refinement of the eddy current coil design, which increases the sensitivity to cracking in the coating, is indicated. Also, if the extent of cracking, as indicated by the crack length per unit area, can be linked to the peak-to-valley range of the eddy current coil output then an automated program can be implemented to run tests to a high number of thermal cycles on highly durable (crack resistant) coatings. Finally, thermal imaging will also be implemented in an effort to detect delamination during thermal cycling. Once the crack and delamination detection methods are developed, comparisons of the durability of HVOF coatings to commercial coatings, such as weld overlays, will be made.

ROOM TEMPERATURE 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. Testing is relatively straightforward. Tensile specimens of substrate material are coated using HVOF and then loaded in tension until a crack is formed. Crack formation is quite easily detectable in relatively thick coatings (>150 microns thick) using acoustic emission techniques, Fig. 7a and 7b. However, the cracking event in thin coatings is not as easily detected using acoustic emission methods. Spalling of the coating is evident in visual observations, Fig. 7c, and cracking must be occurring. In future work, eddy current methods will be used in addition to acoustic emission methods to detect cracking in coating of intermediate thickness (~150 microns) to relatively thin coatings (<100 microns).

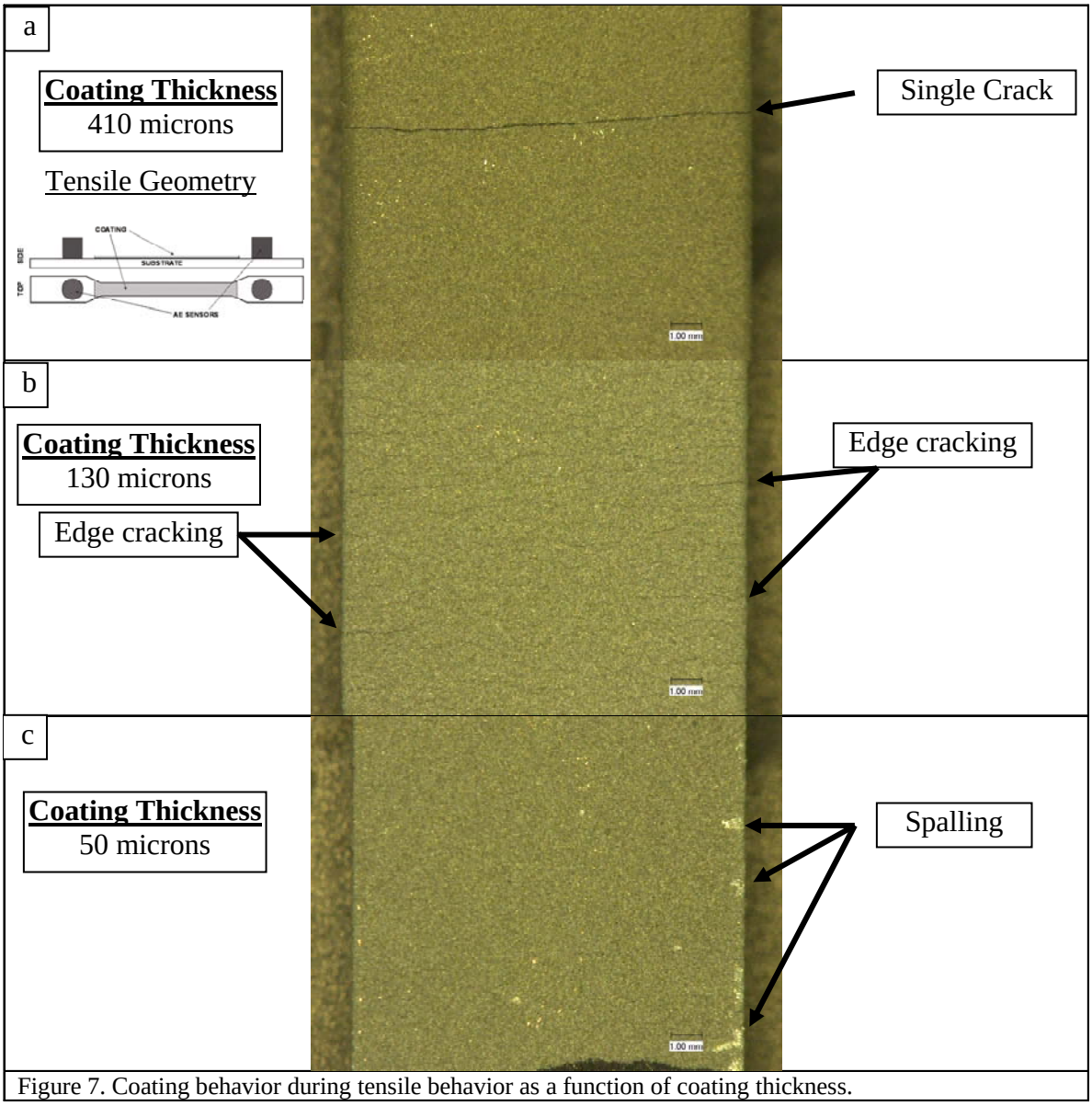


Figure 7. Coating behavior during tensile behavior as a function of coating thickness.

Figure 7b and 7c also indicates that cracking in these flat tensile samples initiated at the sharp corner of the tensile specimen. To eliminate crack initiation at corners, the flat, dogbone style tensile specimens will be replaced with round tensile samples.

CONCLUSIONS

Crack detection methods, based on eddy current techniques, are being developed to assess the durability of iron aluminide coatings. Work has focused on detecting cracking during thermal cycling of rods that have been coated with iron aluminides using HVOF. Crack detection should be possible after slight modifications to the eddy current coil and the frequency of operation. Coating durability testing during thermal cycling will be automated and the influence of coating/substrate materials combinations and thermal spray parameters will be determined. Crack detection by eddy current measurements and acoustic emission methods will be further developed to assess cracking behavior of coating/substrate combinations at room temperature under an applied tensile load, especially in relatively thin coating where acoustic emission methods alone have been found to be inadequate to detect crack

formation. The influence of various HVOF parameters on cracking behavior will be determined once suitable crack detection methods are developed.

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