High Temperature Corrosion Behavior of HVOF, Fe_3Al Coatings

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Abstract

This work evaluates the suitability of iron aluminide coatings for use in high temperature fossil fuel combustion environments, such as boiler applications. The coatings are applied using High Velocity Oxy-Fuel (HVOF) thermal spray techniques. Bulk Fe_3Al coatings are known to exhibit excellent oxidation and sulfidation resistance at high temperatures, however, the behavior of HVOF-deposited Fe_3Al coatings has not been documented. HVOF thermal spray deposition was used to produce free-standing Fe_3Al coatings for high temperature corrosion and oxidation studies. The free standing coatings were then subjected to temperatures up to 1000^oC in various furnace atmospheres during exposure tests exceeding 1000 hours. The furnace atmospheres explored included, dry air, wet air, oxidizing (various ratios of CO_2:CO), carburizing (CO_2, CO, CH_4 mixtures) and a simulated fossil fuel combustion atmosphere (N_2-15CO_2-5O_2-1SO_2-20H_2O, in volume percent). The mass gain was monitored as a function time from which the parabolic rate constant for oxidation of the coating was determined.

Free-standing, HVOF Fe_3Al samples exhibited limited corrosion at the sample surface while Inconel Alloy 600 samples experienced greater mass gain with significant oxidation at the sample surface and internal oxidation during oxidation experiments in air at 1000^oC. Fully dense Fe_3Al coatings exhibited parabolic rate constants for oxidation comparable to those of bulk Fe_3Al reported in literature. However, HVOF Fe_3Al coatings with open porosity exhibited breakaway corrosion after relatively short exposure times (a few hundred hours). Also, during exposure to a simulated, fossil fuel combustion atmosphere, the free-standing, HVOF Fe_3Al samples exhibited mass gain similar to those observed during oxidation in air.

Introduction

Increasing the operating temperature of fossil power plants directly increases plant efficiency and reduces the emissions. There has been a steady increase in fossil fuel-fired power plant operating temperatures – 530-560^oC for many current fossil fuel power plants [1], to 600^oC for some advanced plants [2] and up to 760^oC for the proposed advanced, ultra-supercritical power plant [3, 4]. These systems are limited by the high temperature mechanical properties and corrosion resistance of the materials in combustion environments. High operating pressure (>13 MPa) inside super-critical and ultra-supercritical fossil systems necessarily require creep resistance of structural materials. Often times, materials that satisfy the high temperature, structural requirements do not possess the required corrosion resistance. While bulk Fe_3Al has been shown to be highly corrosion resistant in simulated fossil fuel combustion atmospheres [5,6], its mechanical properties make is unsuitable in high temperature structural applications [7]. Therefore, one option is to use Fe_3Al as a coating on a suitable high temperature, structural alloy. Iron aluminide powder is readily available and can be applied as a relatively thick coating using the High Velocity Oxy-Fuel (HVOF) thermal spray coating technique. This is a versatile deposition technique which is capable of controlling the residual stress in the Fe_3Al coating. Powder particles during HVOF coating application are typically semi-solid and moving at many hundreds of meters/second. These semi-solid particles can cause significant deformation of the substrate surface upon impact, effectively "peening" the surface. This "peening" stress in combination with quenching stresses and Fe_3Al coating/substrate CTE mismatch can be used to control the residual stress in the coating and thereby generate coatings with a high resistance to cracking. (The peening stress that develops during HVOF is absent or insignificant in the various other types of coating techniques, e.g. plasma spray, twin wire arc spraying, aluminizing, CVD, etc.., and manipulation of the stress state in coatings made by these methods is limited.) The relative contributions of the quenching, peening and CTE mismatch stresses sum to give a residual stress state in the coating that can range from tensile to neutral to compressive [8,9] and is largely controlled by the combustion chamber pressure, P_c, in the HVOF thermal spray gun. A compressive stress state is most desirable for iron aluminide coatings exhibiting limited ductility, since tensile stresses in the coating would tend to promote cracking.

HVOF thermal spray deposition incorporates minor amounts of oxides and/or porosity and it must be determined whether these impurities and defects in HVOF Fe_3Al coatings can degrade the excellent oxidation, corrosion and sulfidation resistance typically associated with bulk iron aluminides. This work reports on the degradation behavior of free-standing Fe_3Al material deposited by HVOF thermal spray techniques in various furnace atmospheres at high temperature and compares the results to the behavior of bulk Fe_3Al reported in literature.

Experimental Methods

The composition of the powder used for HVOF coating deposition is shown in Table 1 and corresponds to Fe_3Al with minor additions of chromium and zirconium for enhanced mechanical properties. The particle size of the powder was -270 US Standard Mesh Size with the majority of the powder (>80%) being -400 US Standard Mesh Size.

Table 1 Composition of the Iron Aluminide Powder

Supplier: AMETEK Product: FAS-C (-270) Lot #: 037601					
Element	Fe	Al	Cr	Zr	C
Wt. %	Bal.	15.7	2.4	0.2	0.02

Table 2 HVOF Thermal Spray Parameters

HVOF Thermal Spray Torch	JP 5000, 10.2 cm barrel		
Standoff distance	35.6 cm		
Chamber pressure	P1 620 kPa	P2 720 kPa	P3 340 kPa
Kerosene flow rate	26.5 l/h	16.7 l/h	
Oxygen flow rate	820 slm	520 slm	
Equivalence Ratio	1	1	
Powder	Fe_3Al, Lot #0376601		
Carrier gas flow rate	5 slm		
Rotation	5 rpm		

Free-standing Fe_3Al coatings were made with HVOF thermal spray technique by applying a relatively thick coating (~1-1.5 mm) to a plate of 9Cr-1Mo steel, approximately 19 mm x 25 mm x 100 mm. The plates were prepared by grit blasting followed by grinding with 280 grit sand paper to produce a relatively smooth finish. The HVOF torch parameters are shown in Table 2. HVOF combustion chamber pressures of 620, 720 and 340 kPa were used to generate Fe_3Al coatings and designated P1, P2 and P3, respectively. The surface of the prepared plate was translated in front of the HVOF torch at a rate of 25 mm/sec with 5 mm pitch. Compressed air was applied to the front of all plates to moderate substrate heating during thermal spray deposition. The coatings were then removed from the plates by striking the side of the plate which de-bonded the HVOF Fe_3Al coating from the plate. Samples for testing were then cut from the de-bonded coating.

High temperature, environmental testing was carried out in various furnace atmospheres with the specific conditions given in Table 3. In each case, the atmosphere flowed through the furnace once before exiting the furnace – it was not re-circulated. Mixtures of gases were accomplished through mass flow controllers while the simulated fossil combustion gas mixture was purchased as a pre-mix compressed gas. Water was injected along with the simulated fossil combustion pre-mixed gas to achieve 20% water by volume at 1000°C. “Wet” air was generated by bubbling air through water at room temperature. Samples were cleaned and weighed prior to exposure. The samples were exposed the various furnace atmospheres and removed at intervals and re-weighed. The samples were returned to the furnace and subjected to additional exposure.

Table 1 Exposure Conditions at 1000°C

Furnace Atmosphere	Gas Flow Rates, ml/ minute					P_{O_2}, atm
	Air	CO	CO_2	CH_4	Pre-mix**	
Dry Air	100	-	-	-	-	0.2
Wet Air*	100	-	-	-	-	0.2
Oxidizing	-	1	100	-	-	10^{-10}
Simulated Fossil Combustion	-	-	-	-	70	$5x10^{-2}$
Carburizing	-	1	100	1	-	10^{-18}

* Achieved by bubbling air through water at room temperature prior to entering the furnace.

** The composition was N_2-15CO_2-5O_2-1SO_2 + 20% H_2O. The water content was achieved by injecting water vapor upstream of the hot zone in the furnace.

Experimental Results and Discussion

Mass Change Behavior at 1000°C in Air **-** The mass change behavior of free-standing coatings in both dry and wet air is shown in Fig. 1. Generally, samples P1 and P2 showed relatively small mass gains in both dry and wet air, although the mass gain of both coatings was slightly higher in wet air. Sample P3 showed significantly greater mass gain than either P1 or P2. In fact, P3 exhibited catastrophic or breakaway corrosion in wet air after a relatively short period of exposure, <1000 hrs, Fig. 1b.

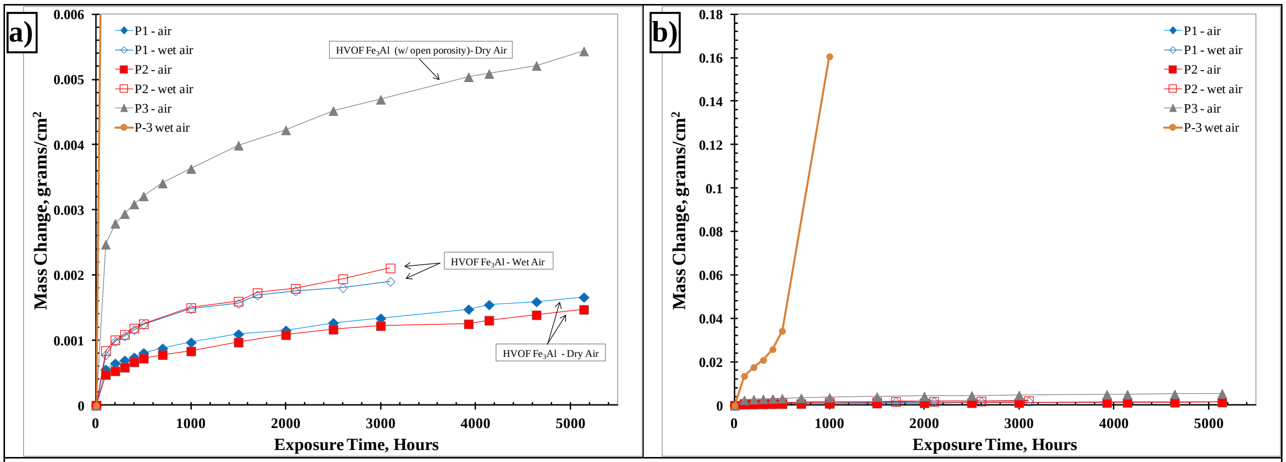


Figure 1. a) The mass change behavior upon being exposed to dry and wet air at 1000°C. The anomalous behavior of P3 in wet air at 1000°C is shown in b).

The anomalous behavior of P3 was further investigated and density measurements, utilizing the Archimedes principle, indicated P3, in the as-deposited condition, contained a substantial amount of open porosity. Further support for this conclusion was obtained by optical metallography of a cross section through sample P3, Fig. 2a. Considerably more porosity is evident in P3 than in either P1 or P2, Fig. 2b & c. The surface corrosion product is completely devoid of any aluminum and consisted exclusively of iron and oxygen, suggesting iron oxide, Fig. 3. This sample also was sectioned and prepared for metallography, Fig. 4. It is evident that extensive oxidation has taken place, Fig. 4a. In the high magnification micrograph of Fig. 4b, taken near the center of the sample, it appears that the remaining

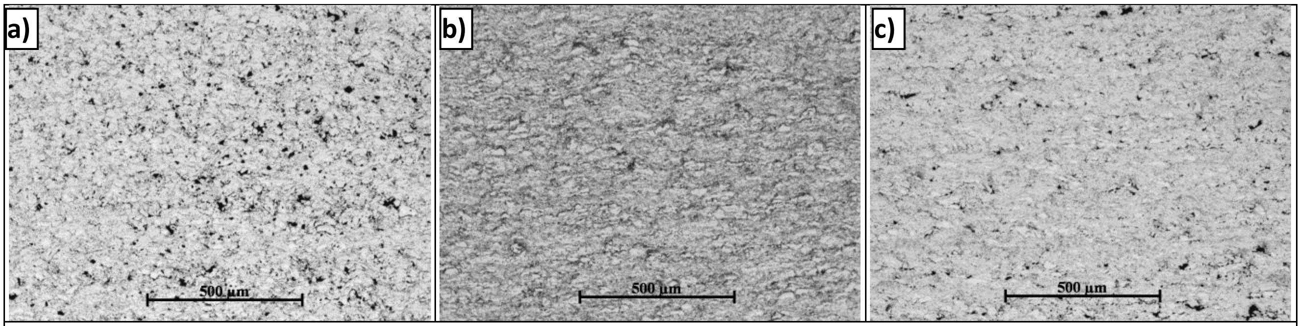
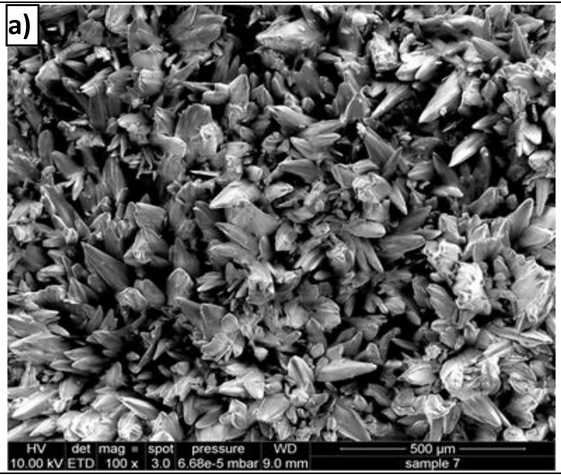


Fig. 2. Optical micrographs of the microstructure of coatings a) P3, b) P1 and c) P2.

Fe_3Al material - the bright phase in this micrograph - contains a network of dark lines and is, in fact, probably a network of oxidized cracks. It is likely that the network of open porosity allowed internal oxidation on the surface of the pores. The volume change associated with the oxidation products resulted in internal stresses and cracking of the Fe_3Al matrix which, in turn, allowed additional oxidation and further cracking. The result is a self propagating mechanism. Repeated fracturing followed by passivation through alumina oxide formation depletes the coating of aluminum and eventually re-passiviation can no longer be supported [10]. At this point, non-protective iron oxide begins to form, Fig. 3, and leads to break away corrosion. Ultimately, it can be concluded that open porosity in these HVOF Fe_3Al coatings is unacceptable, especially since samples P1 and P2 without open porosity perform extremely well even at exposures exceeding 5000 hrs, Fig. 1.



b)

Element	***Wt %***	***At %***
O K	14.33	36.67
AlK	00.65	00.99
CrK	00.52	00.41
FeK	84.49	61.93

Fig. 3 The surface corrosion product of coating P3 in a) is essentially iron oxide, b) as indicated by EDS chemical analysis.

The cause of the porosity can be attributed to the low combustion chamber pressure used to produce sample P3. The chamber pressure determines the velocity of the powder particles during HVOF thermal spray deposition. Coating P3 was deposited at the lowest combustion chamber pressure of 340 kPa, resulting in a particle velocity on the order of 570 m/sec [8]. Coatings P1 and P2 were deposited with higher combustion chamber pressures of 620 and 720 kPa, respectively, resulting in particle velocities of approximately 630 and 650 m/second [8]. These higher velocities were likely sufficient to cause significant deformation of the particles when they impinged on the substrate, allowing them to better conform to the surface topography and, thereby, result in lower porosity in the deposited material.

Therefore, the critical particle velocity resulting in closed porosity must be somewhere between 570 and 630 m/second.

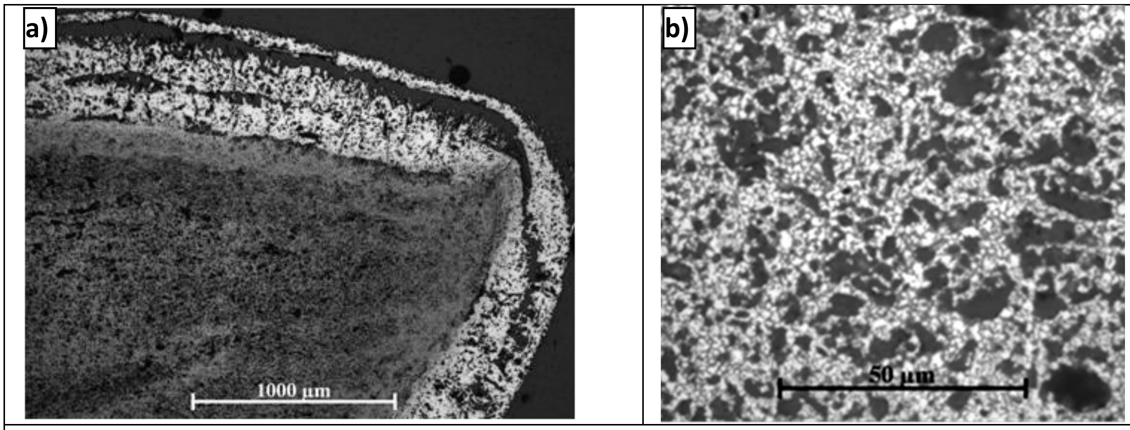


Fig. 4 Optical micrograph through a cross section of the failed sample, P3. The internal microstructure is highly fractured and internally oxidized on a fine scale.

Determination of the Reaction Rate Constants - The mass change data in Fig. 1 can be used to calculate the oxidation rate constant associated with these HVOF iron aluminide coatings. The assumption is made that the oxidation behavior follows a standard parabolic behavior and has the form of:

$$x^2 = K_p t + x_o$$

where

x is the mass change

K_p is the parabolic rate constant

x_o is a constant

t is time

The parabolic rate constants calculated from plots of the square of the mass change versus time are given in Table 4. As expected, the rate constant for sample, P3, is significantly higher than either P1 or P2. Furthermore, the parabolic rate constant in moist air is slightly higher than in dry air, however, both are still relatively low. It is interesting to note that a bare piece of Inconel 600, run in the same oxidation experiments, exhibits an oxidation rate constant in moist air approximately 2 orders of magnitude higher than that of the HVOF Fe_3Al samples. Therefore, an HVOF Fe_3Al coating would offer significant protection to Inconel Alloy 600 in a high temperature, oxidizing environment.

Table 4 Calculated Parabolic Oxidation Rate Constants at 1000°C

Temperature = 1000°C	**Parabolic Rate Constant, g^2/cm^4s**			
Atmosphere	Coating P1 (P_c=0.6 MPa)	Coating P2 (P_c=0.7 MPa)	Coating P3 (P_c=0.3 MPa)	I-600 base metal
Dry air	$1x10^{-13}$	$1x10^{-13}$	$1x10^{-12}$	Not evaluated
Wet air	$3x10^{-13}$	$3x10^{-13}$	$4x10^{-10}$	$2x10^{-11}$

Comparison of HVOF Fe_3Al Oxidation behavior to Bulk Fe_3Al - An ongoing review of the literature has yielded parabolic rate constants for exposures in dry air of cast Fe_3Al at exposure times up to about 200 hours. In one particular study, researchers at ORNL [11] provide a parabolic rate constant for cast Fe_3Al material at both 800 and 900°C. However, their method for the calculation of K_p includes the initial transient behavior of oxidation as opposed to strictly steady state behavior which was used in the determination of the values given in Table 4. If the exposure data in Fig. 1 for the HVOF Fe_3Al samples corresponding to 200 hours at 1000°C are used to calculate the rate constants in the manner of [11], it is found that the constants for the HVOF Fe_3Al samples are about a factor of 20 higher than that given [11] for 900°C. One can extrapolate the data in [11] by use of an Arrhenius-type plot were the log of the rate constant is plotted against the reciprocal absolute temperature, Fig. 5. In this case, the parabolic rate constant of the HVOF Fe_3Al coatings is about a factor of 3 higher than expected by the extrapolation of the data in [11] to 1000°C. In reality however, this is probably within the statistical error, considering the limited amount of data. In fact, if all three data points are used to calculate an activation energy for oxidation they yield a value (~287 kJ/mole) very near that of alumina-formation kinetics on bulk Fe_3Al given by others as ~250kJ/mole [12]. Thus, it would appear that the high density HVOF-deposited Fe_3Al materials are behaving very similarly to bulk Fe_3Al.

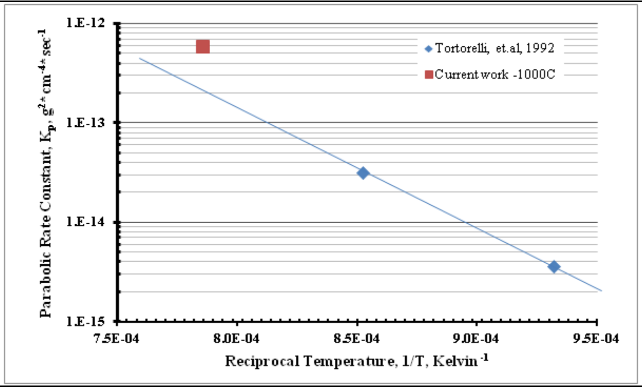


Fig. 5. Comparison of the parabolic oxidation rate constant in this work with the extrapolation of the data by Tortorelli, et. al. [11].

Mass Change Behavior in Simulate Fossil Fuel Combustion, Oxidizing and Carburizing Atmospheres – The degradation behavior of these HVOF-deposited Fe_3Al samples was also investigated in various other potentially aggressive atmospheres at 1000°C. The preliminary results are shown in Fig. 6 where the mass gain behavior in dry and moist air has been included for comparison purposes. Again, sample, P3, performed poorly and exhibited break away corrosion behavior. However, samples P1 and P2 in the

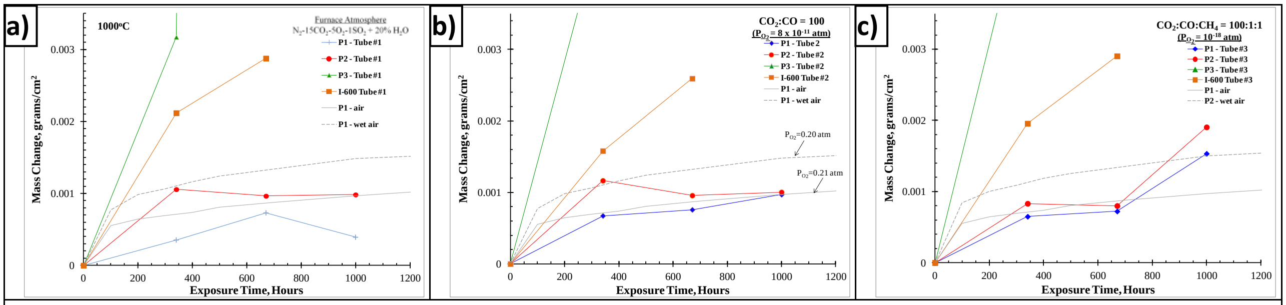


Fig. 6 The mass change behavior of Fe_3Al samples P1, P2 and P3 in a) a simulated fossil fuel combustion atmosphere, b) oxidizing atmosphere (P_{O_2}~10^{-10} atm) and c) carburizing atmosphere (P_{O_2}~10^{-18} atm).

simulate fossil fuel combustion and the oxidizing atmospheres exhibited behavior very similar to that found in dry air. Also, the mass gain is considerably less than that exhibited by alloy Inconel Alloy 600 in these same atmospheres. Representative microstructures of the samples after exposure to the simulated fossil fuel combustion atmosphere are shown in Fig. 7. In the case of both P1 and P2 there is only a thin corrosion layer on the surface of the sample, Figs. 7a and 7b, respectively. The corrosion products in P3, Fig. 7c, extend a considerable distance below the surface of the coating. The Inconel 600 sample also exhibits considerable internal oxidation below the surface of the specimen (~50 microns) as well as a relatively thick corrosion layer on the surface of the sample. Tests with longer exposure times and subsequent metallography with chemical analysis are planned for these conditions to determine the reaction rate constants.

Finally, the HVOF-deposited Fe_3Al samples also exhibit mass gain in the carburizing atmosphere at 1000^{o}C, Fig. 6c. However, it should be pointed out that the mechanism for the weight gain is most likely absorption of carbon into the materials rather than oxidation. Additional metallography and chemical analysis is planned for these samples.

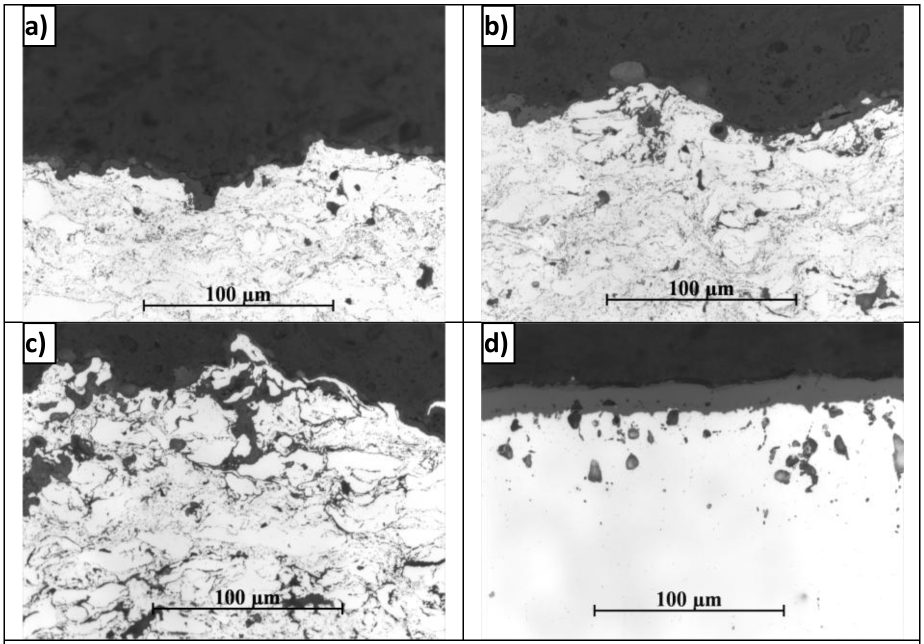


Fig. 7. Microstructure of the coatings a) P1, b) P2, c) P3 and d) Inconel 600 after 341 hrs of exposure to the simulated fossil fuel combustion atmosphere.

Conclusions

The exposure testing of HVOF-deposited Fe_3Al material reported in this work resulted in the following conclusions:

- Oxidation of HVOF-deposited Fe_3Al material is similar to oxidation of bulk Fe_3Al
- Open porosity in HVOF-deposited Fe_3Al coatings results in breakaway oxidation:

  - Open porosity allows internal oxidation and matrix fracturing due to the volume change associated with the oxidation product
  - Excessive oxidation due to matrix fracturing leads to the consumption of aluminum from the HVOF-deposited Fe_3Al material and, upon depletion of the aluminum, the formation of a non-protective iron oxide corrosion product is favored
- A critical chamber pressure/powder particle velocity exists, above which closed porosity is achieved in the HVOF-deposited Fe_3Al materials
- Corrosion of HVOF-deposited Fe_3Al material in simulated fossil fuel combustion atmospheres is low and similar to oxidation in air
- Corrosion/oxidation of HVOF-deposited Fe_3Al material is found to be lower than Inconel Alloy 600 in the environments studied

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