

High Performance Nanoscale Composite Coatings For Boiler Applications

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ABSTRACT

In this paper, we will show how revolutionary nanoscale composite coatings can be formed using conventional wire-arc thermal spray systems. The as-sprayed SHS717 wire-arc coatings are found to develop an amorphous matrix structure containing starburst shaped boride ((FeCrMoW)₂B) and carbide (FeCrMoW)₂₃C₆) crystallites with sizes ranging from 60 to 140 nm. After heating to temperatures above the peak crystalline temperature (566°C), a solid state transformation occurs which results in the formation of an intimate three phase matrix structure consisting of the same complex boride and carbide phases along with α -iron phases interdispersed on a structural scale from 60 to 110 nm. The nanocomposite microstructure contains 'clean' grain boundaries which are found to be incredibly stable and resist coarsening throughout the range of temperatures found in boilers. The sprayability, "forgiveness", and repairability of the SHS717 wire-arc coatings are explained in detail with the emphasis on field applicability in boiler environments. Additionally, the properties of the coating are presented including the bond strength, hardness, bend resistance, and impact resistance. The revolutionary performance of the SHS717 coatings in boiler environments are measured via elevated temperature erosion experiments conducted at 300°C, 450°C, and 600°C using bed ash from an operating CFBC boiler and the results are compared with existing boiler coatings.

INTRODUCTION

Erosive high temperature wear in boilers is one of the main causes of downtime and one of the principle engineering problems in these installations. As a result of the combustion process, the oxide particles produced have much higher melting point than the boiler operating temperature. Thus, these particles remain intact and then get entrained into the exhaust gas resulting in a constant bombardment of particulate matter. Maintenance costs for replacing worn pipes are very high and the downtime associated with unscheduled breakdowns caused by the failure of exchange tubes is a source of lost revenue. The environment is also very corrosive due to a number of sources and corrosion rates are found to increase when protective scales are removed by flowing particles.¹ The electrochemical resistance of the coating must be protective in a wide range of conditions since in some boilers, regions exist in which complete combustion occurs resulting in oxidizing conditions and other regions exist where partial combustion leads to reducing environments. High sulfur content creates additional corrosion problems for coal fired boilers, especially in boilers where lower grades of coal are utilized.

There are several approaches which have been used to keep boilers operating for a wide variety of applications. Weld overlays have been used on new pipe, in an attempt to increase their lifetime with some success but this process adds considerable up-front expense. Thermal spray coatings are an alternate approach which offer advantages because they allow in-situ recoating of the boiler tubes with the additional ability to repair localized defects inside the boiler. The ability to recoat boilers during a scheduled outage is especially attractive since down time can be minimized which translates into significant operational cost savings.

Several types of thermal spray coatings are commonly used in boilers today including nickel chrome^{2,3}, iron chrome³, TAFE 95MXC, and Inconel 625. In the thermal spray industry, there has recently been a significant effort towards the development of nanostructured coatings, although none of these materials have matured to the point where they can be economically used in boilers. Two approaches have been commonly used; the first approach is to start with heavily deformed mechanically milled micron sized powder that has a nanoscale structure⁴⁻¹⁰ and the second approach relies on direct spraying of either nano-size powders¹¹ or nano-powder precursors¹²⁻¹⁴. Both approaches rely on maintaining the existing nanoscale structure during spraying and subsequent impact on the substrate. However, the mechanically alloyed powder contains a high amount of internal stress, which results in rapid coarsening through recovery and recrystallization mechanisms and the nanopowder contains an extremely high amount of external surface area that rapidly combines and sinters into coarse structures. Excessive grain growth is a limiting factor in both of these approaches and occurs at low temperatures ($< 0.4 T_m$).

In this paper, we introduce a revolutionary new iron based cored wire, SHS717, which readily forms nanocomposite coatings when sprayed using the wire-arc process and which exhibits a combination of properties which are superior to existing available materials for elevated temperature boiler applications. Development of nanoscale SHS717 coatings was achieved through a novel route involving processing through a solid/solid state transformation which can occur either during spraying or during a secondary post heat treating anneal. This route to nanoscale coatings was enabled by developing alloys that readily form metallic glass structures at cooling rates in the range of thermal spray processes (10^4 to 10^5 K/s).^{15,16} During the devitrification process, the glass precursor when heated to its crystallization temperature readily transforms into a nanoscale composite structure. This refinement is due to the uniform nucleation and extremely high nucleation frequency during crystallization, resulting in little time for grain growth before impingement between neighboring grains. By this route it is possible to develop very stable nanostructures which resist coarsening at elevated temperatures.¹⁷ The chief advantage of this approach, in contrast to other approaches as outlined previously, is that the feedstock material, whether wire for wire-arc spraying or specific powder cuts for HVOF and plasma spraying

is physically identical to conventional feedstock which eliminates all of the spraying problems normally associated with nanoscaled particulate materials and also bypasses the high cost of these materials.

This paper will show how nanocomposite microstructures can be developed while spraying SHS717 cored wire in air with commercially available wire-arc gun systems. Additionally, in analyzing the suitability of thermal spray coatings for boiler applications, we have identified several characteristics / performance criteria which are necessary to increase the lifetime of the boiler pipes while reducing maintenance and repair costs in order to extend the time interval between scheduled outages. These criteria cover the gamut from ease of application and “forgiveness” of the coating during spraying, the integrity of the coating during service, the reparability of the coating along with its elevated temperature erosion performance. We have evaluated these characteristics in detail for the SHS717 alloy and will present the results of this research in the sections below.

EXPERIMENTAL PROCEDURE

The SHS717 alloy is a proprietary eight element glass forming alloy containing chromium (20 to 25), molybdenum (<10), tungsten (<10), boron (<10), carbon (<5), silicon (<5), manganese (<5), and the balance iron. It was designed after extensive research over a multiyear period and contains specific atomic ratios of elements to maximize glass forming ability, hardness, erosion resistance, and corrosion resistance.

Twin roll wire-arc spraying was done using a Praxair Tafa 8835 arc gun with and without ArcJet attachments under a wide variety of spray parameters (see Field Applicability Section). To deposit the 0.020” coatings for the elevated temperature erosion studies, the following optimized parameters were used; spray distance 5”, traverse velocity 24”/s, overlapping spray pattern of 0.35”, voltage 33V, current 200A, green air cap, primary air pressure 65 psi, and spray head pressure of 19 to 20 psi. The erosion tests were carried out on a laboratory scale elevated temperature erosion tester using bed ash from an operating CFBC boiler as the erodent material.¹⁸ Samples of the same lot of feedstock bed ash were used for all of the tests and consisted of particles which were mainly angular in shape with a particle size ranging from 63 to 1700 μm , a mean particle size of 566 μm and a mean particle density of 2522 kg/m^3 . Using Energy Dispersive Spectroscopy (EDS) analysis, the particles of bed ash were found to contain oxide particles with high concentrations of Si and minor concentrations of Al, Ca, S, Fe, K, Ti, and Cl. This compositional analysis is consistent with the normal constituents of ash (SiO_2 , Al_2O_3 , CaO , SO , Fe_2O_3 , KO_2 , TiO_2) identified elsewhere.¹⁹ Note that while fly ash contacts with higher velocity, it is smaller in size than bed ash and it is generally less erosive than bed ash. The hot erosion tests were carried out at three temperatures (300°C, 450°C, and 600°C) under identical test conditions using the more erosive bed ash with a particle velocity of

60 m/s and a 375 gram particle loading. For each sample, erosion tests were conducted at both 30° and 90° impact angles and at a total test time at the targeted temperature of 5 hours.

Bond strength data were obtained on samples sprayed onto 1" diameter bond slugs which were 1" in height according to the ASTM C633-01 standard for measuring the cohesion / bond strength of thermal spray coatings. Impact testing was done using a Gardner Impact testing machine using a 12 lb weight which was dropped at 40" in height and which impacted on a ½" diameter impacter punch. Differential scanning calorimetry (DSC) was done using a Perkin Elmer DTA-7 system at a heating rate of 10°C/minute with samples protected by oxidation through the use of flowing ultrahigh purity argon. X-Ray diffraction was employed by a Philips. Transmission Electron Microscopy (TEM) was performed on a JEOL JEM 2010 analytical electron microscope attached with an EDAX energy dispersive spectrometer (EDS) using an ultra thin window detector. TEM samples of the coatings were made by first slicing with a diamond saw, dimpling and then ion milling from two directions until perforation. Convergent beam electron diffraction (CBED) was employed to analyze the crystal structure and identify the nano-sized phases.

RESULTS AND DISCUSSION

Coating Microstructure

As-Sprayed Microstructure

Since it has not previously been shown that nanoscale structures could be developed through the low tech wire-arc process, detailed microstructural analysis was conducted on both the as-sprayed and heat treated SHS717 coatings. A qualitative measure of the structure of the as-sprayed coupon can be achieved by using X-ray diffraction (Figure 1). The X-ray diffraction diagram showed that ?. DSC analysis verified that the as-sprayed SHS717 wire-arc coatings contain a significant fraction of glass which exhibits a crystallization onset temperature of 561°C, a peak crystallization temperature of 566°C, and a glass to crystalline transformation enthalpy of -112 J/g.

In Figure 2b, the as-sprayed microstructure is revealed using TEM microscopy. In the TEM micrograph, the glass content is roughly estimated to be 70% based on the area fraction imaged. The as-sprayed microstructure is characterized by a glass matrix containing starburst crystallites ranging in size from 60 to 140 nm. The precipitate phases have been identified using convergent beam electron diffraction as an Fe_{23}C_6 type phase and a Fe_2B type phase which is consistent with the X-ray diffraction results (see Figure 1). In the selected area diffraction pattern of Figure 2a, the circular rings of the amorphous phase can be seen along with isolated diffraction spots from the crystallites embedded existing in the glass.

Heat Treated Microstructure

One concern with conventional nanoscale materials is that they contain a high fraction of 2-dimensional defect phase boundaries, which given enough activation energy will coarsen to larger size scales due to their excessive interfacial free energy. Since boilers operate continuously at elevated temperatures, this potential for coarsening and the resulting deleterious changes in properties is a serious concern. To study this effect, the SHS717 coatings were heat treated at 700°C, which represents a temperature high enough to cause complete crystallization and one which is greater than the maximum operating temperature experienced by boilers. The X-ray diffraction diagram for the heat treated wire-arc coating is shown in Figure 3. It can be seen that the alloy has fully crystallized during the heat treatment. The phases have been identified through Rietveld refinement of the X-ray diffraction diagram and are???

The microstructure of the heat treated SHS717 wire-arc coatings is revealed by TEM analysis (Figure 4b). During the heat treatment, consistent with the X-ray diffraction results, the glass content was found to completely crystallize. The starburst morphology of the crystallites seen previously has transformed into a uniform equiaxed nanocomposite microstructure with refinement of the Fe_{23}C_6 type phase during the transformation. The complexity of the devitrification transformation in iron based systems has been recently described.²⁰ Consistent with the X-ray results, the resulting microstructure was a three phase matrix consisting of α -Fe, Fe_{23}C_6 type phase, and Fe_2B type phases with phase sizes between 60 and 110 nm. The microstructure was found to consist of 2/3 volume fraction of nanoscale carbide and boride phases intermixed with the α -Fe phase. EDS results revealed that that transition metals are dissolved (possibly show table) ????? In Figure 4a, the selected area diffraction diagram reveals, the uniform and the nanoscale nature of the microstructure.

As shown after the 700°C anneal, the microstructure of the SHS717 wire-arc coating was found to remain nanoscale with the absence of grain coarsening. This is a characteristic of the glass devitrification process and the formation of very stable and clean phase boundaries. Thus, one would expect that the hardness of the coating, which results to a significant extent from the achievement of the nanoscale structure, would be maintained after exposure to elevated temperatures.²¹ For the specific samples studied, the as-sprayed Vickers hardness (HV300) was found to be 1105 kg/mm² and after heat treatment, the hardness increased to 1210 kg/mm². Thus, consistent with its microstructural stability, after being exposed to elevated temperature, the hardness of the SHS717 wire-arc coatings is not reduced. Furthermore, the hardness of the coating increases due to the transformation of the glass, since the hardness of the glass state is generally found to be lower than the hardness of the nanocomposite structure.^{15,16,20}

Field Applicability

Boilers are very large integrated power components which cannot be easily disassembled, moved, or taken apart. Thus, the coating of boiler components

necessitates utilizing portable spray systems and applying the coatings in the field ideally during the short time window of a scheduled maintenance, or shut-down cycle. Often the conditions inside a boiler are far from ideal with low light, tight corners, sooty conditions and with the additional necessity to coat the large surface area of the boiler heat exchange pipes with a rapid turnaround. All of this makes quality and quality control a real problem which can result in premature coating failure leading to an unexpected boiler shutdown. Therefore, it is very important that the spray materials and processes exhibit very good forgiveness toward application conditions and variations in spraying parameters. While good quality coatings can be created in many materials in the laboratory, field applications, especially in boilers, can often result in poor coatings. To study the “sprayability” of the SHS717 cored wire, a study was launched to show the influence of spray distance and spray angle on the coating properties.

Spraying Angle Influence

Using a constant 5” stand-off, 30 mil coatings were sprayed onto 1018 steel substrates at four different angles; 90°, 75°, 60°, and 45°. Micrographs of the cross sections of the 75°, 60°, and 45° as-sprayed coatings are shown in Figures 5a, 5b, and 5c and show very little difference in structure as a function of spray angle. For each sample, the porosity, microhardness, superficial hardness and deposit efficiency was determined and the results are summarized in Table 1. The changes in properties of the coatings as a function of spray angle are found to be insignificant.

Spraying Distance Influence

Using a constant 90° spray angle, 30 mil coatings were sprayed onto 1018 steel substrates at four different spray distances; 3”, 4”, 5”, and 6”. Micrographs of the cross sections of the as-sprayed coatings at 3”, 4”, and 6” stand-off are shown in Figures 5d, 5e, and 5f and show very little difference in structure as a function of spray distance. For each sample, the porosity, microhardness, superficial hardness, and deposit efficiency was determined and the results are summarized in Table 2. The changes in properties of the coatings as a function of spray distance are found to be inconsequential.

Coating Repairability

Thermal spray coatings are sacrificial and even when performing well in boilers, they will still need to be reapplied during the lifetime of most boilers. Thus, the ability of a coating to be repaired and recoated is crucial to the success of the protection “system” during the lifetime of the particular application. To study this, two separate studies were done on 20 mil thick SHS717 wire-arc coatings to mimic both a repair procedure and a “tie in” procedure. The experimental process used for these studies are described in Table 3. Note that the masking line was placed in the midpoint of the coupon in a direction parallel to the long end of the 1” by 3” 1018 steel coupons.

During both the repair and tie-in procedures, no delamination, cracking, or other specific defects were observed. Examples of the cross section of both the repaired and tie-in coatings are shown in Figure 6 respectfully. Both the repaired and “tie in” areas exhibit similar structures and interfaces as observed in the “as sprayed” SHS717 coating. During analysis of these areas, only a local thickness increase near the masking line allows for finding the edge of the stripped coating. The ability to repair the 20 mils thick coating is superior to what is commonly found in other wire-arc materials.

Coating Properties

Porosity / Oxide Content

As indicated in Tables 1 and 2, the porosity of the SHS717 wire-arc coatings is generally from 2 to 4 wt% over a wide variety of spray conditions with a maximum of less than 5 wt%. This represents a very low value for a wire-arc coating and one which maximizes boiler protection due to minimization of permeability and interconnected porosity. One of the main reasons for this low porosity is the inherent ability of the SHS717 alloy to resist oxidation during the spray process, thus minimizing particle splashing and related voids and porosity. Note that the alloy was designed specifically to resist oxidation during spraying through a proprietary alloy design approach. The oxide content in the coatings is very low and is typically < 1 volume percent. This low value is significant since oxides present in metallic coatings reduce the mechanical soundness of the coating including the structural integrity and cohesive strength

Note that this prevention of oxide formation is entirely the key to the development of nanoscale coatings since the formation of oxides in the liquid melt can result in heterogeneous nucleation sites. Once nucleation is initiated, crystallization is extremely rapid and the resulting crystallization at low undercooling will result in the formation of phases which are several orders of magnitude larger (i.e. microscale). Only by going through the solid/solid state glass devitrification transformation or just missing this regime while undercooling to very low temperatures can nanoscale structures be developed.

Bond Strength

The bond strength of the SHS717 wire-arc coatings were measured using ASTM C633-01 bond pull tests. The bond strength onto 1018 steel bond slugs was measured on coatings from 20 to 100 mils thickness. Only glue failure at 12,500 to 13,000 psi was observed for the coatings with less than 20 mil thickness. The results for the coatings 20 to 100 mil thick are shown in Table 4. It can be seen that the bond strengths are remarkable for wire-arc coatings and represent some of the best published values. Note that the bond strength value of the very thick 100 mil sample is higher than most conventional materials sprayed at 15 mil thickness. This is even more significant when one considers that the coatings were applied directly to the targeted base metal and no intermediate bond coat was used. While carbon steels have a wide application in

boilers, for elevated temperatures boilers greater than 600°C, austenitic stainless steel boiler pipes are sometimes utilized.²² The bond strength of SHS717 wire-arc coatings were additionally measured on 316 austenitic stainless steel bond slugs and for a 20 mil thick coating, the bond strength was found to be very high at 10,180 psi.

To further test the bond strength of the coatings, bend testing was conducted. During the bend test, the outside of the coating is put into tension which can easily exceed the bond strength causing cracking or delamination. The SHS717 coatings were bent 180°C over an anvil and examples of two SHS717 wire-arc 10 mil thick coatings are shown in Figure 7. No cracking or delamination was observed which underscores not only the high bond strength of the coating but the high resiliency of the coating, which is remarkable considering its hardness.

Residual Stress

In conventional materials, the tensile stresses, which arise due to thermal contraction during solidification, increase as a function of coating thickness and ultimately reach a magnitude whereby the tensile stresses exceed the bond strength resulting in coating failure from delamination. It has been found that the SHS717 wire-arc coatings have extremely low residual stresses and no measurable bending was observed on 1/8" thick carbon steel 1" x 3" coupons when 125 mils thick coating was applied. This unique ability to spray coatings with a neutral stress condition is especially helpful for minimizing spalling during normal thermal cycles. The combination of low residual stress and very high bond strength of the SHS717 wire-arc coatings allows the unique ability to spray very thick coatings if necessary. In Figure 8, an 800 mils ($\approx 20,000 \mu\text{m}$) thick coating is shown which was deposited onto a 1/4" thick 1018 carbon steel substrate.

Impact Resistance

The impact resistance of both as-sprayed and heat treated SHS717 wire-arc coatings sprayed 30 mils thick onto 1018 steel plate was determined using a Gardner Drop impact test machine. The heat treatment was done by placing the wire-arc coating in a hot furnace at 600°C, holding for 10 minutes at 600°C, and then removing it from the furnace and allowing it to air cool down to room temperature. This cycle was repeated for a total of 10 times to mimic thermal cycling. In Figure 9, optical pictures are shown of both the as-sprayed and thermally cycled SHS717 wire-arc coatings after impact testing with 480 inch pounds of impact energy. The impact from the punch can be seen near the center of each coupon indicating that the coating had the ability to deform during impact. On both samples, no cracking or delamination was observed which was remarkable considering the high impact energy absorbed during the test.

Elevated Temperature Erosion

Elevated temperature erosion studies were done on SHS717 wire-arc coupons at three different test temperatures (300°C, 450°C, and 600°C). Examples of the

bed ash which was used for the erosion tests can be seen in Figure 10. Additionally, comparative data is presented on some existing commercial wire-arc coatings including TAFE 95MXC and nickel based 625, and compared to 1018 steel plate measured under identical test conditions. For each sample, erosion tests were conducted at both 30° and 90° impact angles and thickness loss and weight loss were measured on all specimens. Since the weight measurements included the material erosion wastage (-) along with the remaining oxide scale (+) and ash deposition (+), the thickness change was found to be the more valid measurement of material wastage. This was especially true at 600°C, where extensive oxidation occurred in the base 1018 steel material which often resulted in a net positive weight gain.

The results of the 300°C, 450°C, and 600°C elevated temperature erosion tests are given in Tables 5, 6, and 7 respectively. The results show that the SHS717 wire-arc coatings generally exhibit better erosion resistance at low impact angle. This is consistent with the high hardness of the coating and its ability to resist the cutting or ploughing mechanism of impinging particles impacting at low angles. At high angles, the kinetic energy of the impinging particles is transferred directly to the coating and material removal occurs by the formation of cracks which occur through plastic deformation. Note that in contrast to ceramic coatings which perform far better at low impact angles or ductile metals which perform better at high angles, the SHS717 wire-arc only shows a small angular dependence on erosion. This universal ability to resist erosion almost independently of contact angle is important for real world boiler applications where the angle of impact changes depending on the area of the boiler, its design, and the amount of turbulent /lamellar flow. Additionally, it is found that roughly 20% to 30% increase in erosion rate occurs when the erosion temperature increases from 300°C to 450°C but only a 4% to 12% increase occurs on increasing the temperature from 450°C to 600°C. This beneficial increase in performance at elevated temperatures is probably due to the glass content of the coating crystallizing and becoming harder with increasing temperature. Thus, the SHS717 nanocomposite coatings provide significant erosion resistance and protection over a wide temperature range. Note that this ability is a result of the temperature stability of the very stable nanocomposite structure which is formed as a result of the glass devitrification transformation.

At 300°C, the comparison between the SHS717 wire-arc coatings and the base 1018 steel plate, clearly shows the increase in lifetime performance from using this type of coating over an uncoated plain carbon steel pipe which is from 227% to 740% over the base steel depending on impact angle. Since coatings can be recoated in-situ while damaged steel pipe will need to be replaced, the advantages of using SHS717 wire-arc coatings are compelling especially when considering both the costs of replacing the base steel heat exchange pipes and the extended downtimes resulting from an unexpected shutdown. At all temperatures the SHS717 wire-arc coatings were found to be superior and to have less erosion thickness loss compared to the 95MXC wire-arc coatings,

which is commonly used for low temperature boilers. At elevated temperatures, due to the more severe corrosion environment, often 625 nickel superalloy wire-arc coatings are used. At 600°C, the 625 nickel wire-arc coatings were found to exhibit a 150 to 290% increase in thickness loss depending on contact angle compared to the SHS717 wire-arc coatings.

CONCLUSIONS

In this paper, results are clearly presented showing the advantages of using the newly developed SHS717 wire-arc coatings to provide elevated temperature erosion protection for boilers in corrosive environments. The ability to develop nanoscale composite microstructures in air using conventional wire-arc spray guns is revolutionary and results in a coating with compelling properties. The ability to spray the SHS717 wire-arc coatings in the field has been demonstrated as the coating is found to be easy to apply with a wide processing window with very good spray “forgiveness” and once coated is easily recoated and repaired. While there are many different types of coating materials with different combinations of properties, all coatings can only provide protection to a component as long as they remain bonded to the component. The SHS717 coatings are found to excel in the respect and exhibit revolutionary bond strength along with extraordinary toughness and resiliency. The elevated temperature erosion resistance of the SHS717 wire-arc coatings was found to be superior based on thickness loss compared to existing wire-arc coatings which have been tested. The universal ability of the SHS717 coatings to resist erosion almost independently of contact angle and at temperatures at least up to 600°C is important for real world boiler applications and is one result of its unique and stable nanoscale structure which is uniform on bulk length scales.

REFERENCES

- [1] S.C.Stultz and J.B.Kitto, Steam its Generation and Use, 40th edition, Babcock & Wilcox, p.22-42.
- [2] V. Higuera Hidalgo, J. Belzunce Varela, J. Martinex de la Calle, and A. Carriles Menendez, “Characterization of NiCr Flame and Plasma Sprayed Coatings For Use in High Temperature Regions of Boilers”, *Surface Engineering*, 16(2000), 137-142.
- [3] V. Higuera Hidalgo, F.J. Belzunce Varela, and E. Fernandez Rico, “Erosion Wear and Mechanical Properties of Plasma-Sprayed Nickel- and Iron-Based Coatings Subjected To Service Conditions In Boilers”, *Tribology International*, 30(1997), 641-649.
- [4] T. Grosdidier, H.L. Liao, and A. Tidu, Thermal Spray Surface Engineering via Applied Research, Proceedings of the 1st International Thermal Spray Conference, May 8-11, 2000, 1341-1344.
- [5] M.L. Lau, E. Strock, A. Fabel, C.J. Lavernia, and E.J. Lavernia, *NanoStructured Materials*, 10(1998), 723-730.
- [6] V.L. Tellkamp, M.L. Lau, A. Fabel, and E.J. Lavernia, *NanoStructured Materials*, 9(1997), 489-492.

- [7] M.L. Lau, V.V. Gupta, and E.J. Lavernia, *NanoStructured Materials*, 12(1999), 319-322.
- [8] B.H. Kear and G. Skandan, *NanoStructured Materials*, 8(1997), 765-769.
- [9] H.G. Jiang, M.L. Lau, and E.J. Lavernia, *NanoStructured Materials*, 10(1998), 169-178.
- [10] M.L. Lau, V.V. Gupta, and E.J. Lavernia, *NanoStructured Materials*, 10(1998), 715-722.
- [11] Ying Chun Zhu and Chuan Xian Ding, *NanoStructured Materials*, 11(1999), 319-323.
- [12] J. Karthikeyan, C.C. Berndt, J. Tikkanen, J.Y. Wang, A.H. King, and H. Herman, *NanoStructured Materials*, 9(1997), 137-140.
- [13] J. Tikkanen, K.A. Gross, C.C. Berndt, V. Pitkänen, J. Keskinen, S. Raghu, M. Rajala, and J. Karthikeyan, *Surface and Coatings Technology*, 90(1997), 210-216.
- [14] N. P. Rao, H.J. Lee, M. Kelkar, D.J. Hansen, J.V.R. Heberlein, P.H. McMurry, and S.L. Girshick, *NanoStructured Materials*, 9(1997), 129-132.
- [15] D.J. Branagan, W.D. Swank, D.C. Haggard, J.R. Fincke, "Wear Resistant Amorphous and Nanocomposite Steel Coatings", *Metallurgical and Materials Transactions A*, 32A(2001), 2615-2621.
- [16] D.J. Branagan, "Devitrified Nanocomposite Steel Powder", *Powder Metallurgy Alloys and Particulate Materials for Industrial Application*, St. Louis, MO, 2000, ed., David E. Alman and Joseph W. Newkirk, TMS, 111-122.
- [17] D.J. Branagan, M.J. Kramer, and R.W. McCallum, "Transition Metal Carbide Formation in the Nd₂Fe₁₄B System and Potential as Alloying Additions", *J. Alloys. and Compounds*, 244(1996), 27-39.
- [18] A.V. Levy, Y.F. Man, "Erosion-Corrosion of Chromium Steel", *Corrosion-Erosion-Wear of Materials at Elevated Temperatures*, NACE, 1986, p168-203.
- [19] V. Higuera Hidalgo, F.J. Belzunce Varela, and E. Fernandez Rico, "Erosion wear and mechanical properties of plasma-sprayed nickel- and iron-based coatings subjected to service conditions in boilers", *Tribology International*, 30(1997), 641-649.
- [20] B.B. Kappes, B.E. Meacham, Y.L. Tang, and D.J. Branagan, "Relaxation, Recovery, Crystallization, and Recrystallization Transformations in an Iron Based Amorphous Precursor", *Nanotechnology*, 14(2003), 1216-1222.
- [21] D.J. Branagan and Yali Tang, "Developing Extreme Hardness (> 15 GPa) in Iron Based Nanocomposites", *J. Composites Part A*, 33 (2002), 855-859.
- [22] S. Gutierrez, *Metal. Electr.*, 658(1993) 31-37.

Tables

Table 1 Influence of Spraying Angle on Properties

Property	90°	75°	60°	45°
Porosity, %	4.8	3.9	3.0	3.6
HV300	1045	1084	1166	1037
Superficial 15N	81.4	81.3	81.2	82.8
Deposit Efficiency	66 to 69%	66 to 69%	66 to 69%	62 to 65%

Table 2 Influence of Spray Distance on Properties

Property	3"	4"	5"	6"
porosity, %	3.2	3.0	4.8	3.5
HV300	1058	1072	1045	1035
Superficial 15N	84.2	83.8	81.4	81.9
Deposit Efficiency	66 to 69%	66 to 69%	66 to 69%	66 to 69%

Table 3 Experimental Procedure for Repair and Tie-In

Repair Procedure	
Step #1	20 mils coating sprayed on entire coupon
Step #2	Half of the coating starting from the masking line was stripped
Step #3	20 mils thick coating was re-sprayed on the stripped area
Tie-In Procedure	
Step #1	Half of the coupon was masked
Step #2	20 mils thick coating was sprayed on the unmasked half
Step #3	Masking was removed and 20 mil thick coating was applied on the previously masked half

Table 4 Bond Strength of SHS717 Arc- Coatings as a Function of Thickness

Thickness (mils)	20	40	70	100
Bond Strength (psi)	12,040	9,800	8,250	6,450

Table 5 Elevated Temperature Erosion at 300°C

Material	Weight Loss (g)		Thickness Loss	
	$\alpha = 30^\circ$	$\alpha = 90^\circ$	$\alpha = 30^\circ$	$\alpha = 90^\circ$
SHS717 Wire-Arc	4.0	6.1	26	36
95MXC Wire-Arc	6.3	6.5	35	47
1018 Steel Plate	44.5	18.3	218	118

Table 6 Elevated Temperature Erosion at 450°C

Material	Weight Loss (g)		Thickness Loss	
	$\alpha = 30^\circ$	$\alpha = 90^\circ$	$\alpha = 30^\circ$	$\alpha = 90^\circ$
SHS717 Wire-Arc	2.8	6.7	32	47
95MXC Wire-Arc	6.7	9.1	36	49

Table 7 Elevated Temperature Erosion at 600°C

Material	Weight Loss (g)		Thickness Loss	
	$\alpha = 30^\circ$	$\alpha = 90^\circ$	$\alpha = 30^\circ$	$\alpha = 90^\circ$
SHS717 Wire-Arc	+4.6	+4.4	36	49
95MXC Wire-Arc	+5.6	+4.1	42	53
Inconel 625 Wire-Arc	6.2	4.2	142	123

Figures

Figure 1 X-ray diffraction diagrams of the as-sprayed SHS717 wire-arc coatings.

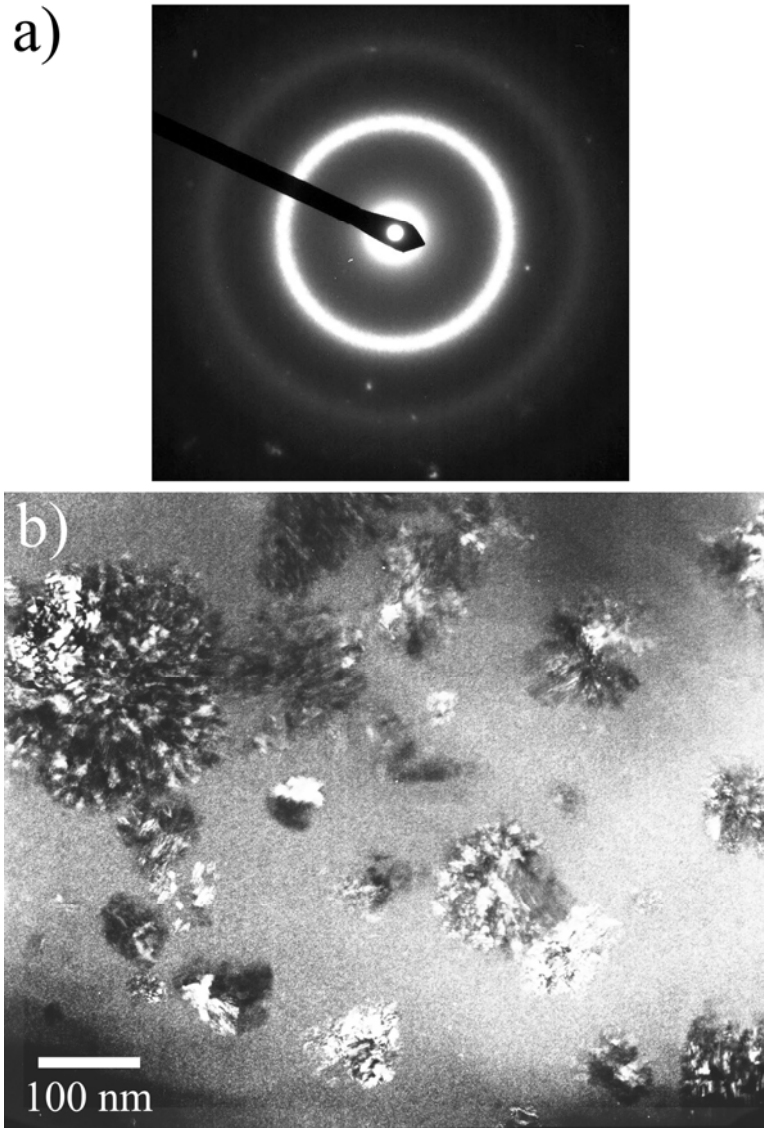


Figure 2 Selected area diffraction (a) and TEM Micrograph (b) of the as-sprayed wire-arc microstructure.

Figure 3 X-ray diffraction diagrams of the SHS717 wire-arc coatings which has been heat treated at 700°C for 10 minutes.

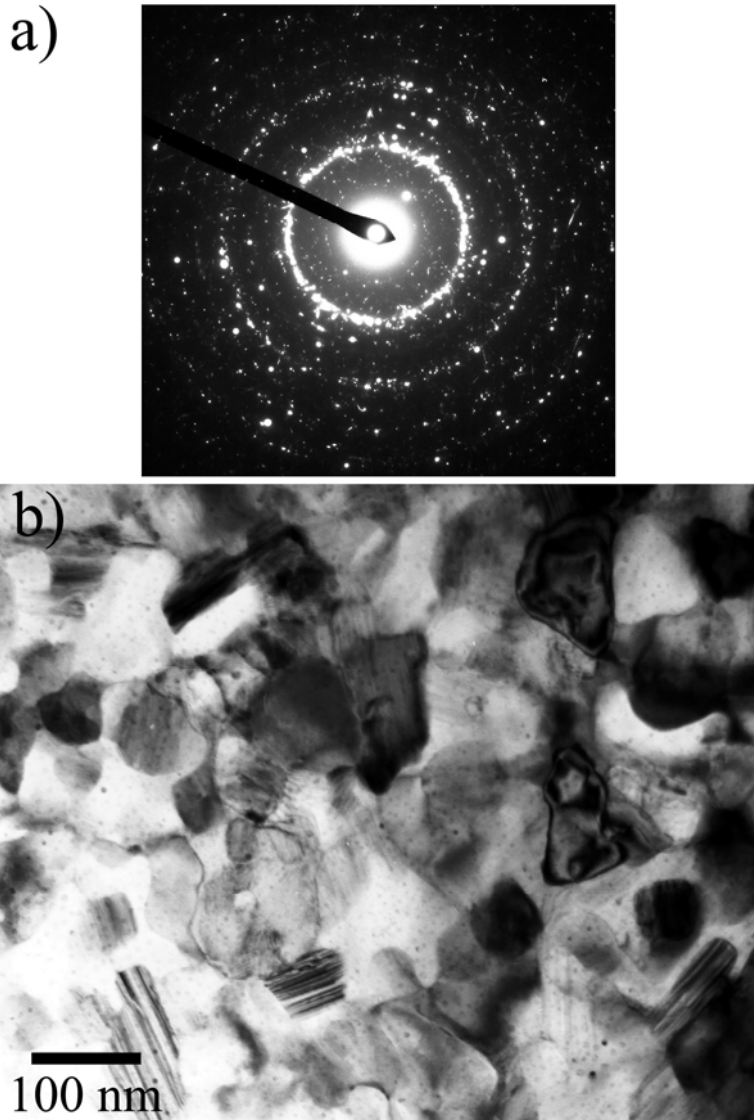


Figure 4 Selected area diffraction (a) and TEM Micrograph (b) of the SHS717 wire-arc coating which was heat treated at 700°C for 10 minutes.

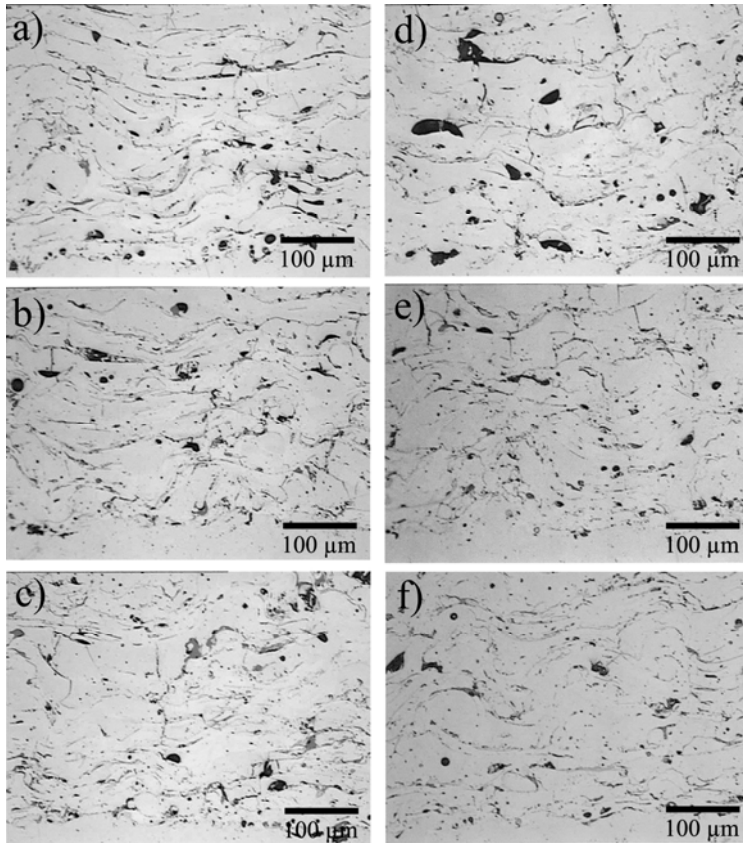


Figure 5 Optical micrographs showing the change in macrostructure of the coating as a function of spray conditions; a) 75° at a 5" stand-off, b) 60° at a 5" stand-off, and c) 45° at a 5" stand-off, d) 90° at a 3" stand-off, e) 90° at a 4" stand-off, f) 90° at a 6" stand-off.

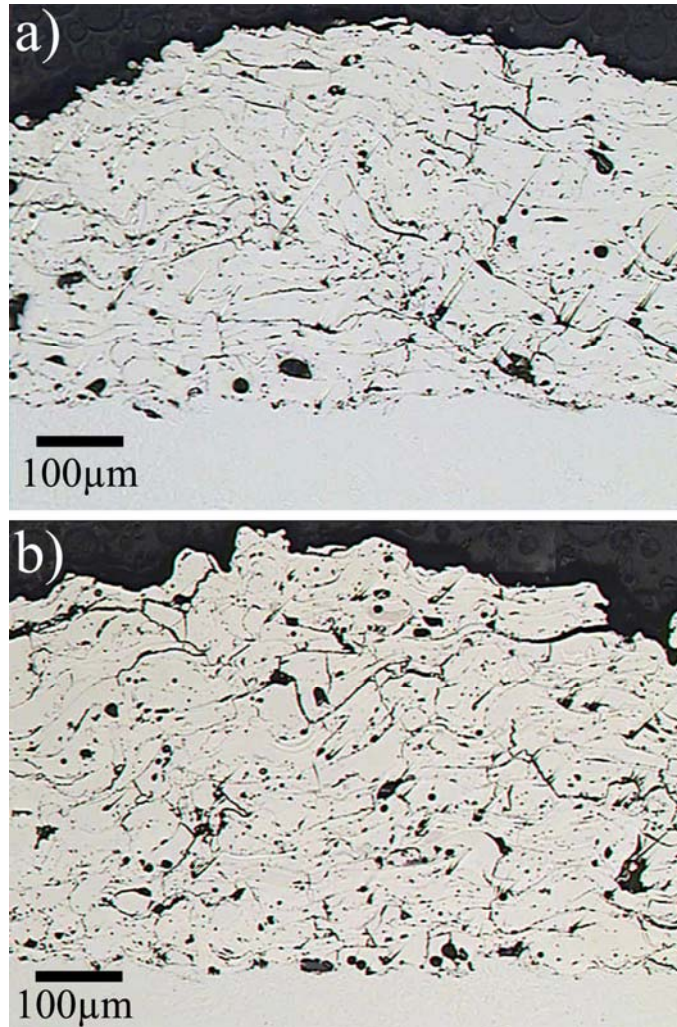


Figure 6 Optical micrograph showing the repaired (a) and "tie in" (b) cross section of the SHS717 coatings.

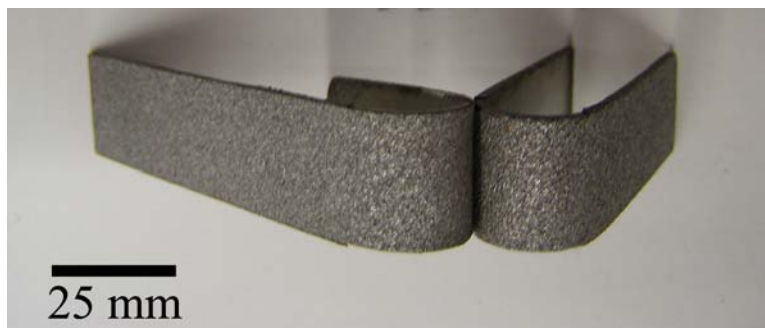


Figure 7 Two separate wire-arc coupons with 10 mil thick SHS717 coatings which have been bent 180°C. Note that no delamination or surface cracking was observed.



Figure 8 Optical micrograph of 800 mil thick SHS717 wire-arc coating deposited onto a ¼" thick 1018 plain carbon steel.

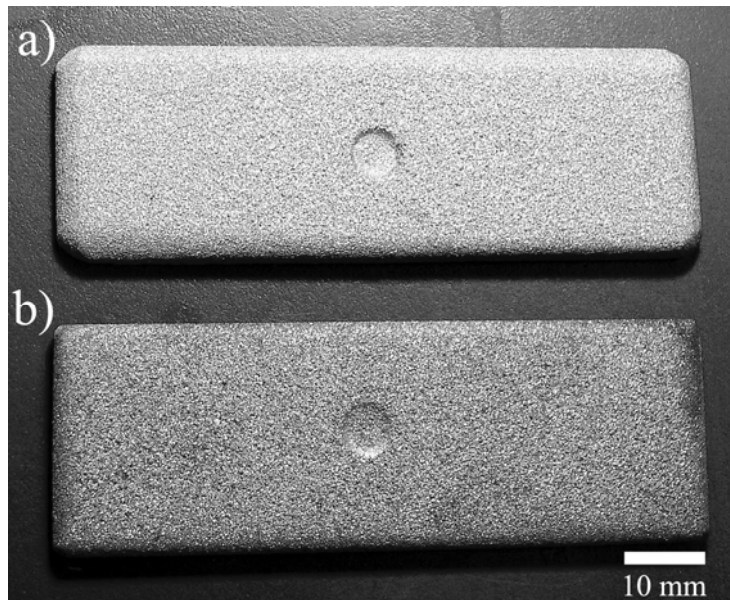


Figure 9 Example SHS717 wire-arc coupons which have been impacted with 480 in/lbs of impact energy during Gardner drop impact testing. Note the impact from the punch near the center of each coupon and the absence of cracking and delamination.

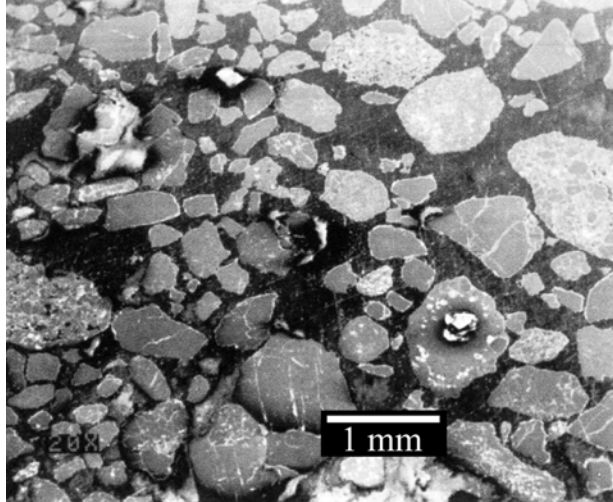


Figure 10 SEM micrograph representative of the bed ash used for the elevated temperature erosion experiments.