Alternative Coatings for Wear and Corrosion: The Electrospark Deposition Process

Roger N. Johnson, Pacific Northwest National Laboratory, Richland, WA, USA

Nearly all of more than 120 commercially available coating materials and process combinations evaluated for severe service in nuclear reactor applications failed one or more of the acceptance criteria. A micro-welding process, termed Electrospark Deposition (ESD), was developed. It replaced the detonation-gun/HVOF coatings that had been used with an ESD coating that provided orders of magnitude increase in wear and damage resistance, a five-fold improvement in corrosion performance, lower friction, and more than a 50 percent saving in cost, using the same coating material. The process was in production for nuclear components for 10 years without a single coating failure or coating reject. ESD is a consumable electrode, micro-welding process that uses electrical pulses that are typically three orders of magnitude shorter than in other pulse welding processes. The process generates no hazardous wastes, fumes or effluents, and requires no vacuum systems, chambers, chemicals or spray booths. Substrates require no special surface preparation and nearly any metal, alloy or cermet can be applied to metal surfaces. The ESD coatings have been found to be among the most damage-resistant coatings known and are particularly suitable for use in the severe environments involving high stresses, high temperatures, thermal cycling, irradiation, wear, corrosion, and erosion. The process is not limited to coatings. Repairs are routinely made to damaged surfaces by restoring dimensions using original (or better) substrate materials. Examples of applications are described.

For more information, contact:
Roger N. Johnson
Senior Staff Scientist
Pacific Northwest National Laboratory
P.O. Box 999, K3-59
Richland, WA 99352
Phone: 509-375-6906
e-mail: roger.johnson@pnl.gov

Introduction

Chrome electroplating is one of the most widely used surface treatment processes in industry, but represents one of the most significant contributions to hazardous, carcinogenic waste generation and pollution control costs. Alternative technologies are being developed and qualified that will reduce or eliminate the dependence on this process while providing equal or superior performance in wear and corrosion protection. The High Velocity Oxygen Fuel (HVOF) process is one alternative technology that is gradually replacing chrome electroplating in some applications[1-4]. Other alternatives are required for applications where HVOF coatings cannot be applied because of geometry constraints or because of service conditions exceeding the damage resistance of the HVOF coating. Cost-effective, pollution-free coating alternatives are needed to achieve environmental goals without sacrificing performance of key components.

Numerous coating technologies have been developed for material protection including HVOF and other thermal spray processes; electrochemical, such as the chrome electroplating; various vacuum processes, such as magnetron sputtering or other physical vapor deposition (PVD) processes; and chemical vapor deposition (CVD). Each has its advantages and limitations and appropriate applications. In recent years, a novel coating technology has been developed that produces some of the most robust, damage-resistant coatings known. In contrast to most of the above-mentioned coatings, which may produce chemical or mechanical bonds with a substrate, the Electrospark Deposition (ESD) process creates a true metallurgical bond, yet does so while maintaining the substrate at or near ambient temperatures. This prevents thermal distortions or metallurgical changes in critical heat-treated metal substrates.

Background

Electrospark Deposition is a consumable electrode, micro-welding process that uses electrical pulses that are typically three orders of magnitude shorter than in other pulse welding processes. Pulse durations of a few microseconds combined with pulse frequencies in the 0.1 to 2-kilohertz range thus allow substrate heat dissipation over ~99% of the duty cycle while heating only ~1%. The result is cooling rates that may approach 10^5 to 10^6 C/sec, depending on material, and the generation of nano-structures in the deposited material that may be amorphous for some alloys. This structure can produce unique corrosion and tribological benefits. Although a true weld (fused surface) is produced to create a metallurgically bonded coating, the total heat input is so low that the bulk substrate material remains at or near ambient temperatures. (Parts may be hand-held while coating.) This eliminates thermal distortions and metallurgical changes in sensitive substrates, and allows parts to be coated in the final heat-treated or thermo-mechanical condition without subsequent treatment.

The process generates no hazardous wastes, fumes or effluents, and requires no vacuum systems, chambers, chemicals or spray booths. Substrates require no special surface preparation and nearly any metal, alloy or cermet can be applied to metal surfaces.

Modern versions of ESD had their start in the U.S. Department of Energy's nuclear program. A metallurgical coating was needed for severe service with stringent requirements of friction, corrosion, wear, thermal cycling, and irradiation performance[5]. Nearly all of more than 120 commercially available coating materials and process combinations failed one or more of the acceptance criteria[6]. We ultimately tried an early version of a process we later termed electrospark deposition, and found promising results. However, the process lacked adequate reproducibility, was frustratingly slow in its application, and unacceptable in achievable surface finishes or adequacy of coverage, particularly for corrosion barrier applications. After several years of development, we succeeded in achieving the required improvement in the process, equipment and deposition rate, and in the quality and coverage of the coating. The process replaced the detonation-gun/HVOF coatings that had been used with an ESD coating that provided orders of magnitude increase in wear and damage resistance, a five fold improvement in corrosion performance, lower friction, and more than 50 percent saving in cost, using the same material. Much of this was attributed to the metallurgical bond achieved and to the nano-structure inherent in most of these coatings. Figure 1 shows a comparison of the damage resistance of the HVOF type coating and of the ESD coating that replaced it. A more detailed history and description of the process is available in prior literature[7, 8].

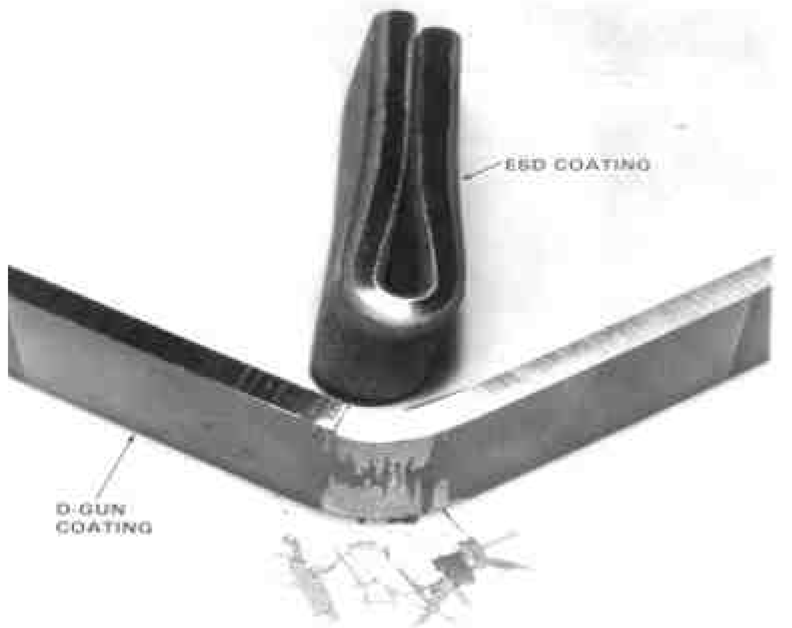


Fig. 1 – Bend tests on detonation-gun/HVOF and ESD coatings of chromium carbide on stainless steel

Process Attributes

The ESD process differs from other welding processes, not only by the exceptionally short duration of the pulse, but also by the contact of the electrode with the substrate. In most welding processes, control of the gap between the electrode and the substrate is a critical parameter. In ESD, the electrode contacts the substrate, and the contact force is the parameter that must be controlled. Direct contact would cause the electrode to weld itself to the substrate if a rapid relative motion were not maintained between the two surfaces. We accomplish this by using rotating, oscillating, or vibrating motion of the electrode, with our best results usually obtained by a rotation of the electrode at several hundred RPM. Figure 2 shows an automated ESD applicator in operation.

The key to the achievement of a commercially viable ESD process was the development of an understanding of the process parameters affecting the deposit and the control of those parameters. The process is basically simple, but as in most new technologies, complex in the details that are important to its success. ESD has the normal parameters that affect most weld processes, but adds a number of parameters that are not immediately apparent. Among the parameters are: electrical (voltage, capacitance, amperes, pulse rate, inductance, pulse duration), environment (cover gas composition, flow rate and geometry, temperature), electrode (composition, density, geometry, rotation speed, traverse speed, orientation, contact force), and substrate (material, surface finish, cleanliness, temperature, geometry).

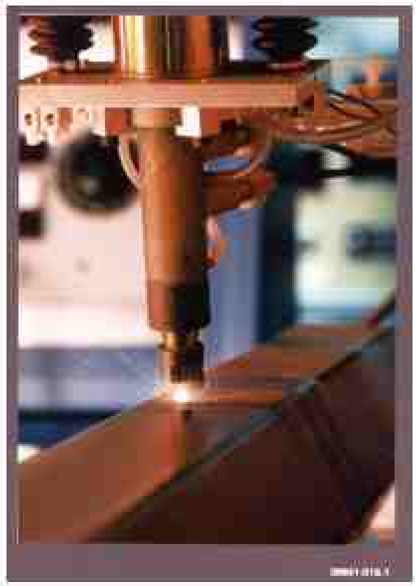


Fig. 2 – Automated ESD applicator with rotating electrode.

The process is very versatile in the number of materials that can be deposited on metal substrates. The primary restriction is that both electrode and substrate must be electrically conductive. An additional requirement is that both materials be capable of being melted in the electric arc without going directly to a gas phase or decomposing. Attempts at depositing bismuth telluride or chromium silicide, for example, were unsuccessful. Presumably the material vaporized or decomposed in the arc without significant transfer of any molten material. Similarly, graphite, which does not have a molten phase at atmospheric pressures, does not transfer from an electrode in any significant quantities. Graphite electrodes have been used, however, to thinly carburize some strong carbide formers such as titanium or zirconium. Table 1 lists some of the materials that have been successfully deposited on metal surfaces using ESD. Table 2 lists the substrates that have been coated by ESD.

Table 1.
ESD Coatings Applied to Date

For Wear Resistance	**For Corrosion Resistance**	**For Build-up or Special Surface Modification**
Hard Carbides[a] (of W, Cr, Ti, Ta, Hf, Mo, Zr, V, Nb)	Stainless steels Hastelloys[b], Inconels[b], Monels[b]	Ni-base and Co-base super alloys,
Hardfacing Alloys (Stellites[b], Tribaloys[b], Colmonoys[b], etc.)	Fe, Ni, & Ti Aluminides	Refractory Alloys (W, Ta, Mo, Nb, Re, Hf)
Cr, Ti, Zr& Ta Borides	FeCrAlY, NiCrAlY, CoCrAlY	Noble metals (Au, Pt, Ag, Pd, Ir)
Intermetallics and Cermets	Al and Al Bronze Alloys	Other Alloys (Fe, Ni, Cr, Co, Al, Cu, Ti, V, Sn, Er, Zr, Zn)

(a) With metal binders, usually 5-15% Ni or Co

(b) Trademarks: Hastelloy – Haynes International, Kokomo, IN
Inconel & Monel – International Nickel Co, Huntington, WV
Stellite & Tribaloy – Deloro-Stellite Co., Goshen, IN
Colmonoy – Wall Colmonoy Corp., Detroit, MI

Table 2
Substrate Alloys Coated by ESD

High and Low Alloy Steels	**Nickel and Cobalt Alloys**	**Refractory Metals (W, Re, Ta, Mo, Nb,)**
Stainless Steels	Titanium Alloys	Chromium
Tool Steels	Aluminum Alloys	Uranium
Zirconium Alloys	Copper Alloys	Erbium

Geometry of the substrate or part to be coated usually does not limit ESD deposits as it can in thermal spray processes. Any surface that can be touched by the electrode, including inside valve bodies, inside diameters and blind holes, can be coated. For example, ESD was used coat the inside diameter of a 9 mm (0.3 in) stainless steel tube, 3.35 m (11 ft) long with an iron aluminide. In another instance, a disk-shaped electrode, as shown in Figure 3, was used to coat another non-line-of-sight geometry. Stress corrosion cracking in the roots of the "Christmas tree" of a steam turbine component was eliminated by an ESD application of a nickel-chrome-molybdenum corrosion-resistant alloy.

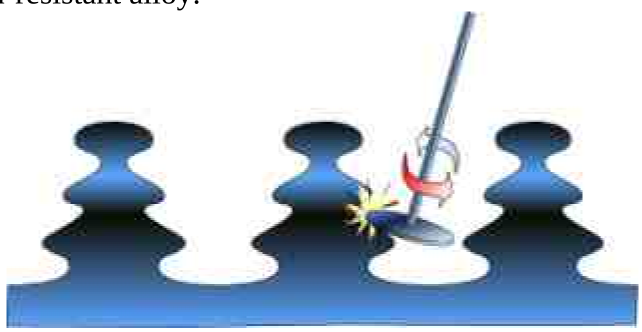


Fig. 3 – Spinning disk electrode used to ESD coat a non-line-of-sight surface on a steam turbine component.

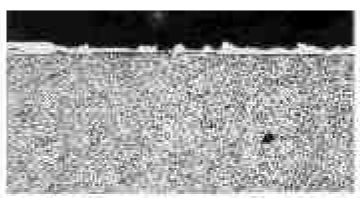
Deposition rates have been increased by over an order of magnitude, to one to 20 cm^2/min for a 25 µm coating. Although the deposition rate is still relatively slow compared to other welding processes and to HVOF, this is mitigated by the minimal time spent in surface preparation, by use of automated coating techniques, by use of multiple applicators, or by the ability to coats parts in-place or in the field. Although further improvements in deposition rate may be possible, there is an inherent limit. At some point, with increasing spark energy and increasing spark frequency, for example, the rapid solidification of the deposit would no longer occur, heat affected zones would become significant, and substrate temperatures would increase to levels that allow metallurgical changes or thermal stress buildup. In other words, the process would become indistinguishable from other arc welding processes.

ESD may still be the lowest cost option for many coating requirements, in spite of its low deposition rate. Ideal applications include those that a) cover or repair small areas, especially those on large or high value parts, or b) involve geometries that cannot be coated by thermal spray or HVOF, or c) require a low heat input to maintain a prior thermo-mechanical condition or to eliminate distortion, or d) require service conditions that exceed the limits of other processes (i.e. high contact stresses, high deformation of coated parts, high temperatures, radiation, thermal cycling, etc.).

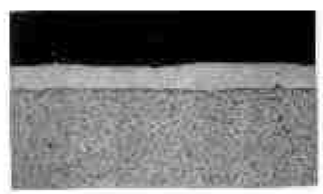
Coating thicknesses achievable by ESD depend strongly on the materials involved, and can range from ~25 µm (~1 mil) for some intermetallics and hard, brittle materials, to 5 mm (0.2 in) or more for some more ductile materials. For most applications, thicknesses of less than 100 µm (4 mils) are most desirable and practical. We usually recommend that thicknesses be kept to the minimum that will meet the service requirements. For example, in wear tests of Tribaloy 800 coatings rubbing against each other, a 25 µm thick coating outwore a 100 µm thick coating by six times. The difference was attributed to higher stresses and fracturing in the thicker, brittle material. More recently, ESD has been used to repair high value parts by rebuilding damaged or out-of-tolerance surfaces, as will be discussed later. The original (or a better) material may be used to build up damaged areas by several mm.

Recent Advances in the ESD Process

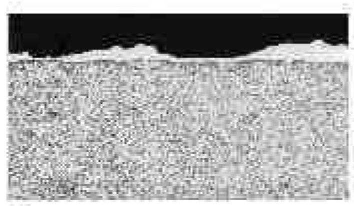
A skilled operator can recognize and control parameters to near optimum conditions when the process is fully visible (the normal case). However, when the surface being coated is not visible to the operator, control is more difficult. Pacific Northwest National Laboratory (PNNL), through support from the U.S. Strategic Environmental Research and Development Program, has developed sensors and systems for the automated control of the process in non-line-of-sight applications. This system focuses on control of the contact force between the electrode and the substrate, which is one of the primary parameters of interest. Developments are in progress to not only enable control in automated coating, but also in manual depositions on non-line-of-sight surfaces. Figure 4 shows an example of the effect of contact force on the deposit characteristics. Figure 5 shows the effect of contact force on the weight gain of equal area coupons coated with Stellite 6 under otherwise identical conditions.



a) 15 g force



b) 100 g force



c) 350 g force

Fig. 4 – Effect of electrode contact force on ESD deposit characteristics, Stellite 6 on 4340 steel. a) 15 g force, b) 100 g force, c) 350 g force

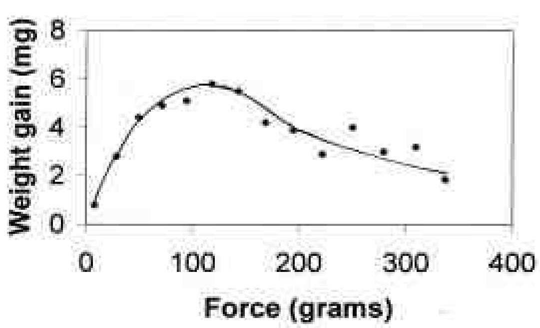


Fig. 5 - Effect of electrode contact force on weight gain of equal area steel coupons during ESD coating with Stellite 6.

Limitations of the ESD Process

Some surfaces are inherently difficult to coat. Because the electrode must contact the surface, any surface geometry that does not allow full contact with the electrode may be coated only on adjacent areas where contact is possible. Figure 6 shows an example of a geometry that is difficult to coat. Internal corners should have a radius proportional to the size of the electrode to assure coverage. Similarly, coating threads on bolts, for example, should not be attempted. Surface waviness with a period less than the electrode diameter may lead to a coating that only builds up on the peaks. Some deposition parameters can result in an initial coverage that leaves some areas uncoated. Since the arc goes to the nearest surface, only the high points will continue to build up with subsequent passes or layers. Figure 7 shows an example of some of the surface textures possible. The rougher surfaces can be desirable where applications require a gripping action, as on some metal handling tools. Generally, the thicker the coating and the higher the deposition rate, the greater will be the as-deposited surface roughness. The minimum as-deposited surface roughness is about 2.5 µm (100 µin) AA.

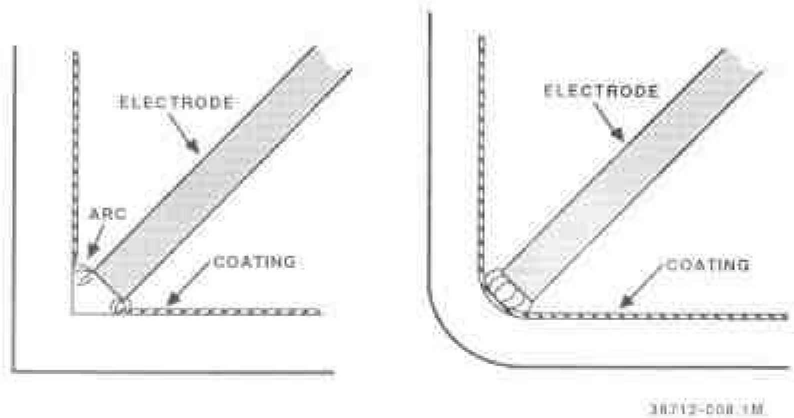


Fig. 6 – Limitation on coating inside corners unless corners are rounded

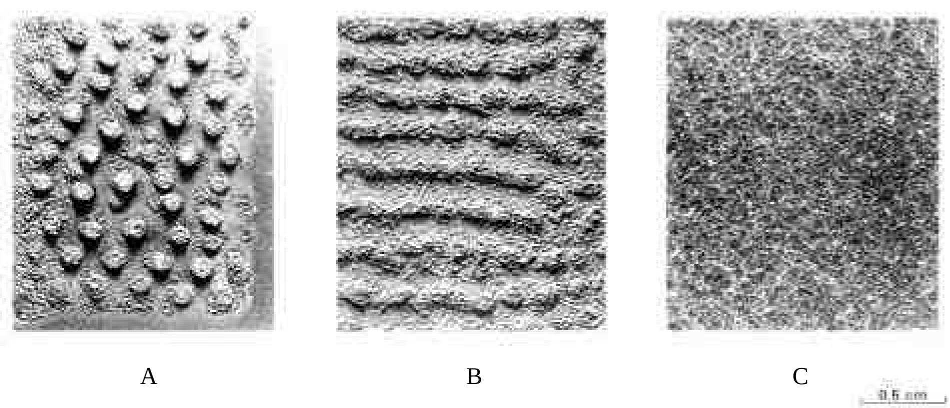


Fig. 7 – Surface textures possible with ESD

The rapid solidification that occurs in the deposit and the volume change that sometimes results from going from the liquid to the solid state can cause some materials to exhibit stress relief cracking. This often can be reduced or eliminated by pre-heating the substrate, as is common with other welding procedures. However, pre-heating may be undesirable, especially when one of the principal reasons for the use of ESD is its low heat input. During the development of ESD chromium carbide coatings, for example, pre-heat of the substrate was not an option because of the requirement for maintaining 20 percent cold work in the substrate. Extensive parameter development succeeded in eliminating the stress relief cracking in the coating, but testing revealed that the resulting crack-free coating no longer exhibited the wear, friction, and corrosion performance required for the service conditions. An optimum crack pattern, as shown in Figure 8, is now specified for chromium carbide used in nuclear applications. (This is the same structure that survived the bend test shown in Fig. 1.)

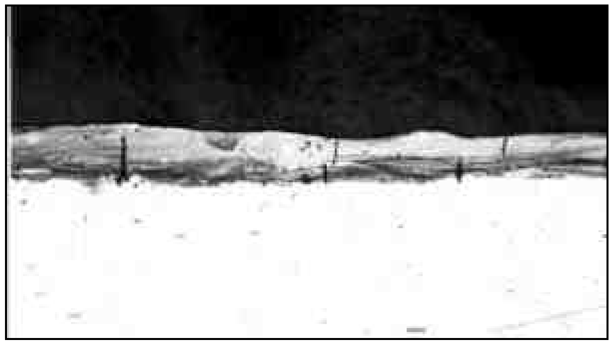


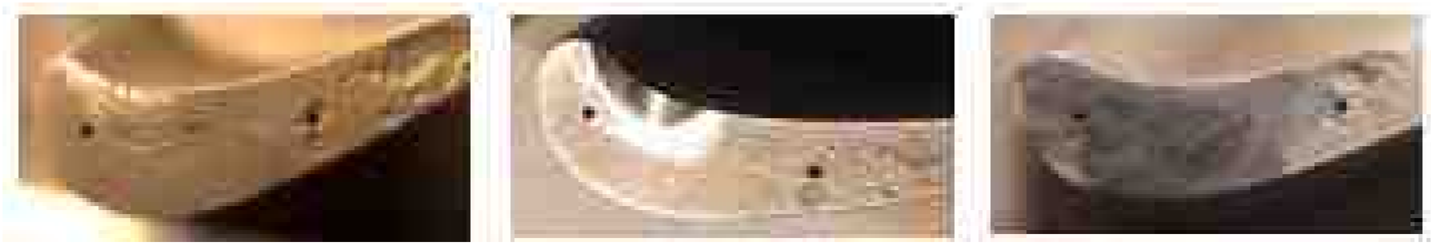
Fig. 8 – ESD Chromium Carbide showing optimum stress-relief crack pattern.

The stress-relief cracking is most frequently observed in the hard carbide deposits (Cr carbide, W carbide, etc.). The wear performance of these materials is still outstanding, as seen in numerous applications (described later). The tough damage resistance of the ESD coatings, including the carbide coatings, has been used to advantage in the final forging of coated parts to achieve geometries that would be difficult to coat otherwise, such as grooves in tools and gun barrels. The forging action not only produces the shape required, without damaging the ESD coating, but also can improve the surface finish of the as-deposited coating. Any coating that exhibits stress-relief cracking, however, may not be a good candidate for protection of surfaces from corrosion, or for use on components subject to fatigue, unless a coating of another appropriate material is applied as a first layer.

Applications

In addition to the nuclear applications previously mentioned, ESD is being increasingly used for coating and repair of high value gas and steam turbine components. Because of its low heat input and freedom from distortion, ESD is used to repair casting defects and mis-machined parts that otherwise would be scrap, often saving thousands of dollars per part. Figure 9 shows a repair of thermal-fatigue cracks in a single-crystal turbine blade accomplished by ESD. Other turbine applications include a) pre-placement of platinum on selected areas of turbine blades for subsequent platinum aluminide diffusion coatings, b) hardsurfacing of blade tips used in ablative seals, c) repair of diffusion coatings, d) pre-placement of braze alloys on difficult-to-wet turbine materials for precision assembly of complex components and e) corrosion and erosion protection of turbine blades in severe environments, such as the corrosive gasses typical of geothermal power plants, and particle erosion from ingestion of sand in military turbines.

Metal working tools frequently are used under severe stresses and temperatures that can challenge the strength and integrity of any coating. The ESD coatings have successfully proven themselves in such applications as cutting tools, dies, drills, shears, forging tools, etc. Improvement in tool life is rarely less than 100%, and frequently approaches an order of magnitude or more. Economic benefits are not just in increased

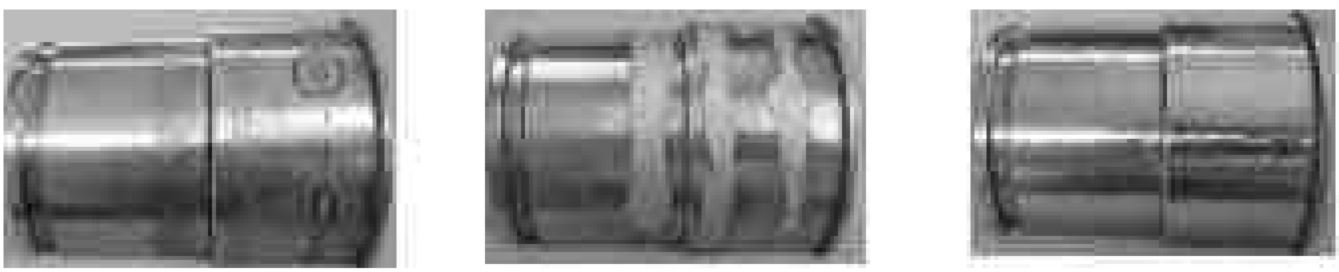


a) b) c)

Fig. 9 – Repair of single-crystal turbine blade by ESD, showing a) as-received blade with thermal fatigue cracks, b) cracks removed by grinding, c) restored by ESD using original material as filler and finished. (Photos courtesy Advanced Surfaces & Processes, Inc.)

tool life, however, but also in production rate increases through higher feeds and speeds for machining tools and drills. Special coatings are in development for end mills to increase speed of metal removal on difficult-to-machine titanium alloys and nickel-base superalloys. Tool steel dies used in the hot extrusion of titanium alloys were ESD coated with a mixture of refractory metal carbides and molybdenum. The normal life of the dies was increased from 300 extrusions to an average of 980 extrusions for the coated dies.

Seawater corrosion is a constant concern in naval components. Figure 10 shows an ESD repair performed on a Cu-Ni alloy bearing on a submarine steering control damaged by pitting corrosion in seawater. The U.S. Navy is qualifying the ESD process for use on shipboard for similar repairs on shafts and bearings in-place, often eliminating the need for expensive disassembly and dry-dock repairs. The small size and portability of the ESD equipment makes such options practical.



a) b) c)

Fig. 10 – Cu-Ni bearing repaired by ESD, a) as-received, b) after filling all pits with the parent metal, c) after finishing to original condition. (Photos courtesy Advanced Surfaces & Processes, Inc.)

Other applications where ESD is replacing hard chrome plate and other processes are:

a) Timber and paper industry – chipper knives, pulp processing doctor blades, plug augers, shredder knives, log debarkers, folder blades, sickle bar guards, and pulp and cement conveyer augers, severe service chain-saw teeth.
b) Automotive industry – titanium carbide coatings on titanium valves for racing engines, metal working and cutting tools,
c) Medical industry – orthopedic drills, orthotic leg and ankle brace components, dental tools, needle holders, hemostats,
d) Nuclear industry – core components, valve guides, steam generator tube supports, electromagnetic pumps, transducers, component positioning hardware, control rods, burnable neutron absorber coatings,
e) Agricultural industry – subsurface hop cutter blades, various harvesting tools and cutters.

Summary

No single process or material, by itself, is likely to replace hard chrome plate. However, the increasing cost of environmental compliance for chromium plating provides a challenge to produce and qualify alternate processes and materials that will provide comparable protection of critical surfaces, and to do so economically. The Electrospark Deposition process offers environmental and performance advantages that make it a candidate for replacement of hard chrome plate in a number of applications. Environmental advantages include no hazardous wastes, fumes, or effluents, no special chambers or sound booths, and minimal surface preparation of substrates. ESD coatings are some of the most robust and damage resistant available, surviving service conditions of high contact stresses, wear, corrosion, deformation, irradiation and thermal cycling that destroy most other coatings. The low heat input and rapid solidification of the deposit result in the nano-structures that contribute to the performance. Complex geometries and non-line-of-sight surfaces can now be coated. Some applications will be limited by the inherently low deposition rates and the limited thicknesses achievable with some materials.

Acknowledgments

This work was supported by the U.S. Government's Strategic Environmental Research and Development Program. We also acknowledge information kindly provided on some of the ESD commercial applications by Advanced Surfaces and Processes, Inc., of Cornelius, OR.

References

1. B. D. Sartwell, P.M. Natishan, K.O. Legg, J.D. Schell, and J.D. Sauer, *Proc. of the AESF Aerospace/Airline Plating Forum*, p. 97 (March 1998).

2. Bruce D. Sartwell and Philip E. Bretz, *Advanced Materials and Processes*, p. 25 (August 1999).

3. B.D. Sartwell, K.O. Legg, and P.E. Bretz, *Proc. AESF Aerospace Plating and Metal Finishing Forum*, p. 131 (March 2000).

4. Jerry D. Schell and Mark Rechtsteiner, *Proc. AESF Aerospace Plating and Metal Finishing Forum*, p. 140 (March 2000)

5. R. N. Johnson, *Proc. Int. Conf. on Liquid Metal Technology in Energy Production*, CONF-76053, US-ERDA, p. 122 (1976)

6. R. N. Johnson, *Thin Solid Films*, **118**, 31 (1984)

7. R. N. Johnson, *Proc. First Int. Conf. on Surface Modification Technologies*, p. 189 (1988).

8. R. N. Johnson, *Elevated Temperature Coatings: Science and Technology I*, p. 265 (1995)