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ABSTRACT
There is a need for materials that are highly resistant to corrosion, environmental fracture, cavitation, and liquid droplet impingement, especially within the Navy. Several novel approaches to enhancing the cavitation and impingement resistance of ship and aircraft components are discussed. These approaches include: (1) new ultra-hard amorphous-metal coatings, applied with a hydrogen-fueled HVOF process; (2) coatings with extreme interfacial bond strength, produced with LLNL's new laser-based HVLAD process; (3) nickel aluminide coatings with nano-diamond strengthening and hardening, applied with a combination of cold spray and post-deposition heat treatment with intense diode sources; (4) diode-assisted friction stir processing for the elimination of surface defects in large cast propellars; and (5) laser peening for the elimination of residual tensile stresses, and the associated fatigue and environmental cracking. This paper discusses several novel approaches to the development of such materials, through surface engineering, and the benefits that will be enjoyed if such a developmental effort is successful.

Surface Engineering of Corrosion, Environmental Fracture, Cavitation & Impingement Resistant Materials

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INTRODUCTION

There is a need for materials that are highly resistant to corrosion, environmental fracture, cavitation, and liquid droplet impingement, especially within the Navy. This paper discusses several novel approaches to the development of such materials, through surface engineering, and the benefits that will be enjoyed if such a developmental effort is successful.

Damage Due to Cavitation

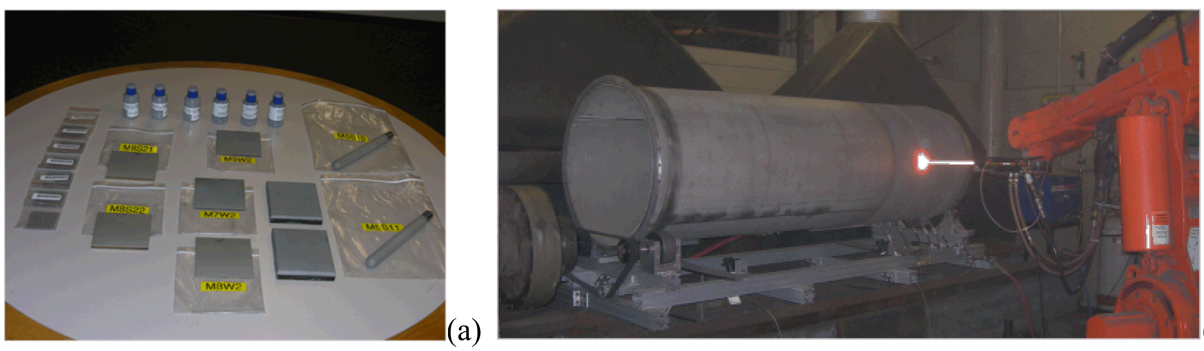
When a liquid enters a low-pressure region, gas-filled cavities can form in the liquid. When these bubbles travel in the flow to regions of higher pressure the bubbles may collapse and generally through the action of asymmetric implosion instabilities generate extremely high velocity jets that can that impinge of materials with dynamic pressures of thousands of atmospheres, which can cause substantial erosion and erosion corrosion damage at the surface of control valves, pumps, impellers, propellers, dams, spillways and other engineered components [1-5]. As discussed in the article on cavitation found in Wikipedia, the noise created by cavitation is a particular problem for military submarines, since it dramatically increases the chances of being detected by passive sonar.

Damage Due to Liquid Impingement – Liquid droplets in high velocity streams of gas and steam will impact solid surfaces in regions where there are abrupt changes in the direction of flow. Kinetic energy transferred to the solid surfaces during impact, which is referred to as liquid impingement, causes substantial erosion of the surface. Liquid impingement is experienced by turbine blades in both fossil-fueled and nuclear power generators.

APPROACHES FOR DEVELOPMENT OF CAVITATION-RESISTANT MATERIALS

The surface engineering of several of advanced materials that promise to be resistant to damage due to cavitation and liquid impingement is discussed. Specific approaches include:

Ultra Hard Amorphous Metal Coatings – Application of ultra-hard corrosion-resistant iron-based amorphous-metal coatings with the high-velocity oxy-fuel (HVOF) process for the protection of underlying substrates. Such amorphous metal formulations, known as SAM2X5 and SAM1651, have been developed and used on an industrial scale. These materials have undergone extensive testing over several years, and have been shown to be more corrosion resistant in near-boiling geothermal brines than nickel-based Alloy C-22 [6-9]. More important for this application, these amorphous metals are much harder. For example, Type 316 stainless steel has a hardness of 150 HVN, Alloy C-022 has a hardness of 250 HVN, where as the amorphous metals that will be investigated for resistance to cavitation and droplet impingement have Vickers hardness numbers ranging from 1100 to 1300 HVN. Through a previous program jointly funded by the DOE RW and DARPA DSO, members of this team assembled a large multi-institutional team, developed the appropriate alloy compositions, and involved a group of industrial partners for gas atomization of amorphous metal powders, and for deposition of amorphous metal coatings from these powders with the HVOF process. These coatings have been made in multi-ton quantities, applied in thicknesses ranging from 15 mils to 12 millimeters, as shown in Figure 1, and promise to be ideal for this application. These materials have been shown to be thermally stable at temperatures between the glass transition temperature, and the crystallization temperature, which is between 600 and 700°C, making them suitable for some steam turbine applications.



(a) (b)

Figure 1 – (a) Samples of amorphous-metal HVOF coatings used for long-term corrosion testing and (b) high-velocity oxy-fuel process at Caterpillar used to coat half-scale containers with SAM1651 amorphous metal. Quality assurance checks of the coating thickness and roughness were made during the coating process.

In Situ Formation of Nickel Aluminide Coatings via Cold Spray & Diode Heating – The application of conformal pre-curser coatings consisting of nickel and aluminum with a cold spray process, with subsequent conversion of this composite coating to nickel aluminide through the use of high-power diode arrays for localized heating. This material is already used for the coating of blades in gas turbines and jet engines. Nickel aluminide includes three intermetallic compounds ($NiAl$, $NiAl_3$ and Ni_3Al), or ordered alloy phases formed between nickel and aluminum, with an unusually high strength-to-weight ratios and thermal conductivity at extreme temperature (5× that of stainless steel at 800°C) [10-13]. It has a density of 7.26 g/cm^3 and a hardness of 12 HRC. One of the most common practical engineering materials based upon nickel aluminide is IC-221M, which consists not only of nickel and aluminum, but also chromium, molybdenum, zirconium and boron, with the boron addition enhancing both ductility and hardness. At a temperature of 800°C the yield strength of this material is in excess of 700 MPa, compared to a yield strength of 250 MPa for nickel-based Alloy 625. According to published articles, the most abrasion-resistant material ever produced was made in 2005 by embedding diamonds in a nickel aluminide matrix. This material was developed by Dale E. Wittmer and Peter Filip at Southern Illinois University Carbondale by materials scientists, the composite consists of a mixture of nickel, aluminum, metal carbide and industrial diamond, and required processing at 1400°C. During testing, engineers at the Robert Bosch Tool Company in Louisville, Kentucky found this composite to be 800 times more wear resistant than the company's toughest carbide now used commercially in making mining tools, drill bits, ceramic tile routers and other such tools.

Use of Friction Stir Processing for Elimination of Cavitation Causing Defects – Friction stir processing (FSP) has been used on large castings of nickel aluminum bronze, for the purpose of eliminating defects on propellers that can give rise to cavitation and noise generation on Naval ships and submarines. As shown in Figure 2, it has been found that in addition to eliminating voids in the surface of these large castings that may cause promote cavitation and noise generation, FSP also enhances passive film stability and corrosion resistance [14]. This team will enhance the rate at which FSP can be used for surface homogenization and defect elimination by using auxiliary diode heating to soften the material being worked, thereby enabling faster traverse speeds.

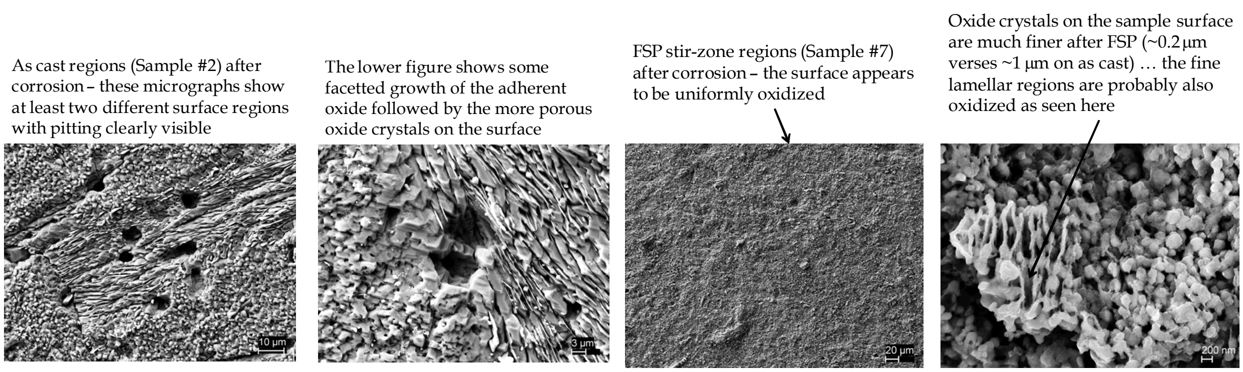
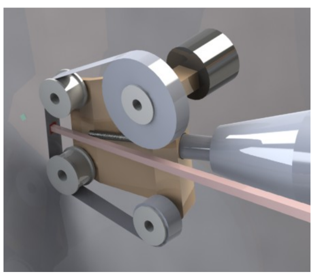


Figure 2 – (two figures on left) Sample #2 is as-cast nickel aluminum bronze, and shows significant porosity and grain-to-grain variability in oxide growth; (two figures on right) Sample #7 is a friction stir processed nickel aluminum bronze, and shows homogenization, the elimination of porosity, and more uniform oxide growth.

Refractory Coatings with Extreme Interfacial Bond Strength – Application of ordinary and dispersion-strengthened refractory-metal coatings with extreme interfacial bond strength onto steel substrates with the team's new High Velocity Laser Accelerated Deposition (HVLAD) process. This process uses the world's most powerful and highest repetition rate production lasers for localized explosive bonding, thus producing a very broad range of advanced high-temperature and corrosion-resistant coatings with extreme interfacial bond strength. These interfacial bonds approach the ultimate tensile strength of the substrate. The HVLAD process can be explained in terms of several discrete steps. During step 1 – the high-performance corrosion resistant film material is advanced with a spool assembly, and bathed with water that serves as a tamper during laser pulse. Step 2 – a special laser pulse with rectangular beam cross-section is imaged onto the advancing high-performance film material bathed with a thin layer of water. Step 3 – the laser pulse generates a high temperature plasma and very large pressure shearing out a section of film accelerating it to hypersonic velocities. Step 4 – patches of ultra-hard and corrosion-resistant film are accelerated and bonded to the substrate in a controlled step-by-step process creating coating. Step 5 – the film patch hits the substrate at an oblique angle, where the high impact velocity induces plastic shear flow at the interface creating a high-strength explosive bond. The HVLAD process is illustrated in Figure 3.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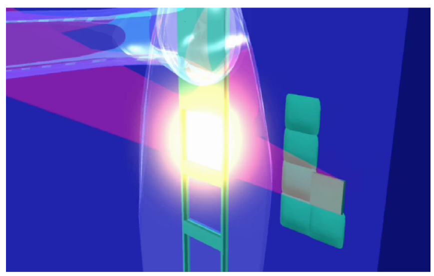
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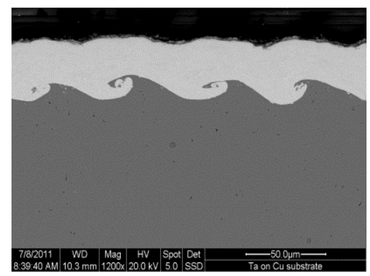

(c)

Figure 3 – (a) A special head is adapted to laser-peening lasers and associated robotics, as shown in the center image, and (b) patches of high-performance corrosion-resistant film are accelerated and bonded to the substrate in a controlled step-by-step process creating coating (c) An actual HVLAD coating showing explosively bonded interface. HVLAD offers a cost-effective means of producing corrosion-resistant coatings, such as Ta and Ta-W alloys, with bonding at the interface comparable to those achieved with explosive bonding processes.

Protective coatings of various types are essential for ensuring long service life for components in high-temperature power plants. These coatings help prevent initiation and propagation of various modes of corrosion: uniform corrosion, pitting, crevice corrosion, erosion–corrosion, fretting corrosion, stress corrosion cracking, corrosion fatigue, and hydrogen-induced cracking. In some cases, special coatings can also provide electrical insulation and enhance high-voltage standoff. Conventional chemical and physical vapor deposition (CVD and PVD) processes, such as high-velocity oxy fuel (HVOF), for the deposition of such protective coatings often require high temperatures and the handling of hazardous powders and chemicals that pose inhalation risks for workers and lead to unacceptable porosity and poor interfacial bond strength. The proposed ambient-temperature HVLAD process, which requires no chemical or powder feed and is capable of producing coatings with no residual porosity and ultra-strong interfacial bonds (Figure 1), could save the U.S. economy billions of dollars every year from corrosion loss. The HVLAD process leverages the laser peening (LP) process originally developed at LLNL, where unique high-performance lasers have been developed and deployed for stress mitigation and the prevention of stress-corrosion cracking [Farmer, Hackel et al. *PVP* **408**, 71–81 (2000)]. In the LP process, an intense laser pulse and tamper work collaboratively to produce a powerful hammer effect that drives deep levels of plasticity into metal surfaces, creating protective layers of compressive stress and thereby reducing crack initiation and growth. By inducing compressive stress, the laser treatment enhances the fatigue lifetime of components. We have recently learned to use these lasers to produce high-integrity coatings.

A highly localized method for producing explosively bonded interfaces, the HVLAD process uses the pressure pulse generated by a high-peak-power laser to accelerate a thin film of dense metal foil to a hypersonic velocity toward the intended substrate, with a controlled shearing angle relative to the interface. Upon impact, the kinetic energy from the accelerated foil colliding with the substrate creates the formation of an alloyed interface, with interfacial deformation and roughening. The interleaving (interlocking) of the coating and substrate materials achieved with this process enable coatings to be produced with a bond strength equivalent to the UTS of either the coating or substrate, whichever is weaker and limiting. The interface evident in the scanning electron micrograph (SEM) shown in Figure 1 is similar to those formed during explosive bonding but here with a highly controlled production amenable process [S. Carpenter, R. Wittman, Explosion Welding Annual Review, Materials Society **5,** 177 (1977)].

HVLAD coatings could make possible the use of high-temperature materials in power plants, leading to an increase in efficiency of up to 20% and resulting in huge savings for the economy and the environment. By making it possible to operate power plants at higher temperature through the use of high-temperature materials, substantial increases in process efficiency can be realized. Increasing the operating temperature of an energy conversion system from 325°C (~600K) to 900°C (~1200K), the efficiency might be increased by as much as 20% in fossil-fuel, solar-thermal, and nuclear power plants. Oxide dispersion strengthened ferritic martensitic (ODS FM) steels have very good high temperature strength and radiation resistance and are leading candidate materials for next-generation nuclear power plants (Figure 4). The use of these advanced materials is discussed in the literature [Ukai et al. (2002); Klueh et al. (2007)]. Such materials were used for the fabrication of nuclear fuel cladding for the BOR-60 sodium-cooled fast reactor, and have shown outstanding performance at irradiations as high as 71 displacements per atom (dpa). These materials have been joined with pressurized resistance welding (PRW and friction stir welding (FSW), both of which have residual weld stresses that can be improved through the use of laser peening.

While ODS FM steels have very good high-temperature strength, these materials lack corrosion resistance in exotic high-temperature coolants such as molten fluoride salts (FLiBe and FLiNaK) and liquid metals such as Li, Pb-Li and Pb-Bi [Farmer, El-Dasher et al, (2010); El-Dasher, Farmer et al. (2011)]. The HVLAD process can be used to deposit high-temperature, corrosion-resistant coatings of very expensive corrosion-resistant alloys such as Ta-10W on less corrosion-resistant structural materials such as ODS steel, with bond strengths limited by the yield strength of the coating or substrate material, whichever is the weaker. Such refractory-metal clad structural materials can enable operation of power conversion equipment in extremely corrosive high-temperature environments, thereby realizing improvements in efficiency (Figure 5).

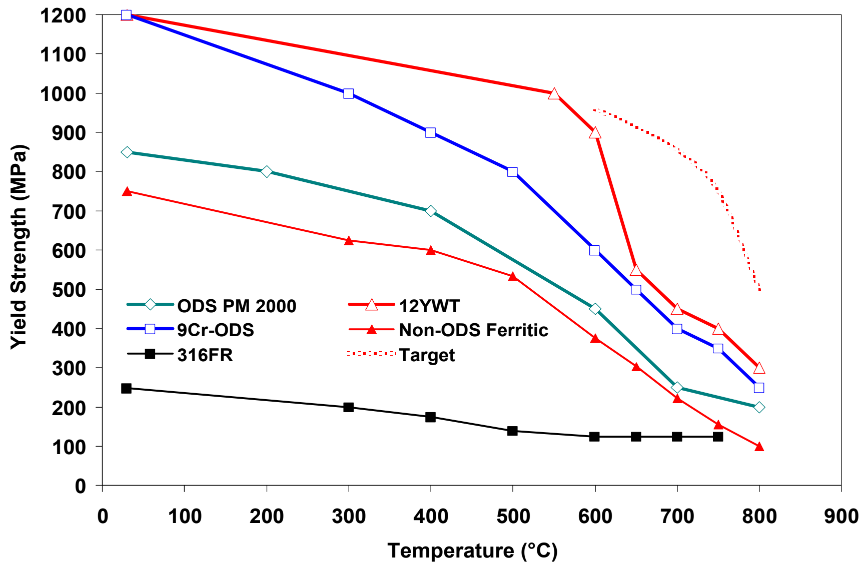

Figure 4 – ODS FM steels have very good high temperature strength and radiation resistance and are leading candidate materials for next-generation nuclear power plants [Ukai et al. (2002); Klueh et al. (2007)]. Such materials were used for the fabrication of nuclear fuel cladding for the BOR-60 sodium-cooled fast reactor, and have show outstanding performance at irradiations as high as 71 displacements per atom (dpa). These materials have been joined with both pressurized resistance welding (PRW), as well as friction stir welding (FSW), both of which have residual weld stresses that can be improved through the use of laser peening. HVLAD will be used to coat this high-temperature radiation-resistant material with refractory metal cladding to protect it from corrosion in extreme environments.

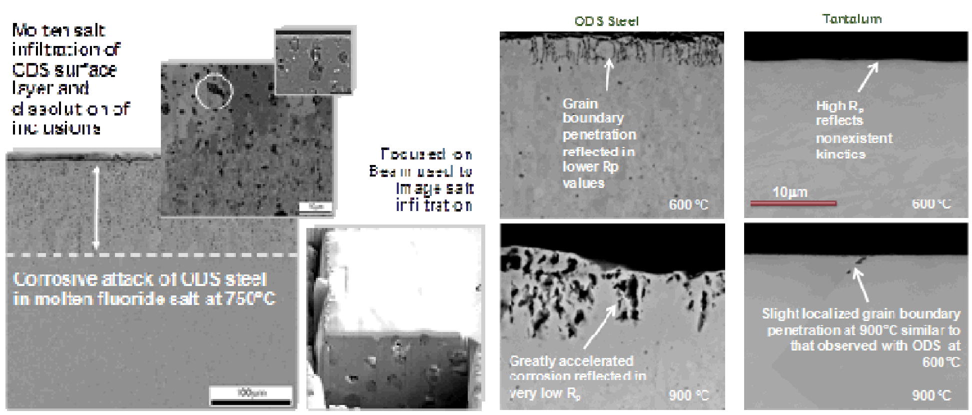

Figure 5 – HVLAD can be used as an effective means of producing coatings such as Ta and Ta-W alloys with true metallurgical bonds with a scanning coating tool. While ODS FM steels have very good high-temperature strength, these materials lack corrosion resistance in exotic high-temperature coolants such as molten fluoride salts (FLiBe and FLiNaK) and liquid metals such as Li, Pb-Li and Pb-Bi. In contrast, Ta and Ta-W have exceptional corrosion resistance in such extreme environments [Farmer, El-Dasher et al, (2010); El-Dasher, Farmer, et al. (2011)]. Other coating materials may be optimal for other applications.

Use of Laser Peening for Elimination of Residual Tensile Stress and Fatigue – Laser peening is a process that has been used to introduce compressive stresses into surfaces near welds, thereby mitigating residual weld stress, and reducing the risk of stress corrosion cracking near these welds [15]. More recently, this laser-based process has been used for stress mitigation in the fan blades in jet engines, as shown in Figures 6 and 7, thereby reducing fatigue, prolonging engine life, and dramatically improving operational safety.

(a) (b)

Figure 6– (a) The beam delivery robot during laser peening of a fan blade from a jet engine, and (b) one of four transportable systems now in operation. Laser Peening (LP) has been used successfully for stress mitigation in gas and steam turbine blades, the airframe of F-22 fighter jets, and arrestment hook shanks for aircraft carriers.

Figure 7 – A transportable laser-peening system located has now been located in Palmdale, CA to support F-22 overhauls. Production setup for processing F-22 wing attachment lugs. Spot placement is adjusted to 0.1 mm accuracy on each laser shot.

SUMMARY

Several novel approaches to enhancing the cavitation and impingement resistance of ship and aircraft components are discussed. These approaches include: (1) new ultra-hard amorphous-metal coatings, applied with a hydrogen-fueled HVOF process; (2) coatings with extreme interfacial bond strength, produced with LLNL's new laser-based HVLAD process; (3) nickel aluminide coatings with nano-diamond strengthening and hardening, applied with a combination of cold spray and post-deposition heat treatment with intense diode sources; (4) diode-assisted friction stir processing for the elimination of surface defects in large cast propellars; and (5) laser peening for the elimination of residual tensile stresses, and the associated fatigue and environmental cracking.

Refractory Metal Coatings with Extreme Interfacial Bond Strength – This process leverages high-energy short-pulse lasers developed by the U.S. inertial confinement fusion process for the localized explosive bonding of continuous refractory metal coatings, including Ta, Ta-2.5 W, Ta-10W, with and without dispersion strengthening and hardening. These materials have melting points ranging from 2995 to 3410°C, and are immune to corrosion in exotic high-temperature coolants, including molten fluoride salts (FLiBe and FLiNaK), and liquid lithium [16-17]. These materials have unparalleled interfacial bond strength, and will provide unrivaled protection from erosion-corrosion, exacerbated by cavitations and liquid droplet impingement at very high temperature.

Ultra Hard Amorphous Metal Coatings – Ultra-hard corrosion-resistant iron-based amorphous-metal coatings have Vickers hardness numbers ranging from 1100 to 1300 HVN, compared to 150 HVN for Type 316 stainless steel, and 250 HVN for Ni-based Alloy C-22. The extreme hardness of these coatings, and their intrinsic corrosion resistance, will provide protection from liquid droplet impingement in steam and gas turbines, as well as in applications where cavitations are problematic at temperatures in excess of 600°C, making them suitable for steam turbine applications.

In Situ Formation of Nickel Aluminide Coatings via Cold Spray & Diode Heating – Like the amorphous metal coatings, the exceptional hardness and wear resistance of conformal nickel aluminide coatings dispersion strengthened with nano-diamond additions will provide exceptional protection from cavitations and liquid droplet impingement in steam and gas turbines at temperatures up to 800°C. These novel coatings will be produced through a combination of cold spray and diode array heating (CSDH).

Use of Friction Stir Processing for Elimination of Cavitation Causing Defects – Friction stir processing (FSP) has been used on large castings of nickel aluminum bronze, for the purpose of eliminating defects on propellers that can give rise to cavitation and noise generation on the propellers of ships and submarines. It has been found that in addition to eliminating voids in the surface of these large castings, that may cause promote cavitation and acoustic noise, FSP also enhances passive film stability and corrosion resistance. This team will enhance the rate at which FSP can be used for surface homogenization and defect elimination by using auxiliary diode heating to soften the material being worked, thereby enabling faster traverse speeds.

Use of Laser Peening for Elimination of Residual Tensile Stress and Fatigue – The application of laser peening will introduce compressive surface stresses into turbine blades and other components at depths as great as 6 millimeters, thereby making the initiation and propagation fatigue, corrosion fatigue, stress corrosion cracking, and hydrogen induced cracking virtually impossible in the peened area. This laser-based materials process has been used effectively to mitigate fatigue and environmental fracture in the fan blades of jet engines, and will now be combined with the other materials and processes discussed here to derive even greater benefit.

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