

Nanoceramic Coatings Exhibit Much Higher Toughness and Wear Resistance than Conventional Coatings

*Dr. Lawrence T. Kabacoff
Materials Science and Technology Division
Office of Naval Research*

Introduction

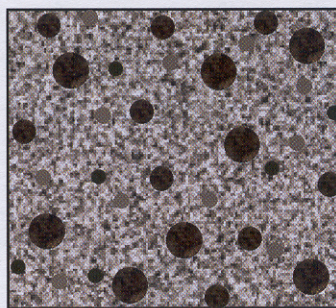
Modifying material surfaces to enhance wear and corrosion resistance is a common practice for both military and commercial applications. Electrodeposited hard chrome is one of the most widely used protective coatings. Ceramic coatings, both single phase and composite types, are also common and they are frequently applied using plasma spray. In this process, the coating material (usually in the form of a powder) is injected into a plasma stream where it is heated and accelerated toward the substrate surface. After impacting the surface the ceramic rapidly cools thus forming a coating layer.

Both hard chrome and ceramic coatings have serious deficiencies that can limit their use. Chrome electroplating uses closely regulated hazardous materials. Compliance with the various environmental safety regulations has made hard chrome increasingly expensive to use. Plasma-sprayed ceramic coatings are somewhat less expensive than chrome (when clean up costs are included), but are generally brittle and have limited success adhering to substrates, which is also a problem for hard chrome. The need for better coating materials has been recognized and considerable effort has recently gone into finding replacements.

Over the last five years, a consortium of companies, universities and Navy personnel have been developing a new generation of wear resistant "nanostructured" ceramic coatings. The consortium is lead by Inframat, Inc. and the University of Connecticut, and team members include the A&A Company, Rutgers University, Stevens Institute of Technology, the Naval Surface Warfare Center (Carderock Division) and Puget Sound Naval Shipyard. It is funded by the Office of Naval Research and its objective has been to achieve mechanical and wear properties unobtainable from more conventional materials (i.e. materials with structural aspects at the micron scale or larger).

Nanostructured materials are characterized by an ultra-fine microstructure with some physical aspect less than 100 nanometers in size. This feature can be grain size, particle or fiber diameter, or layer thickness (Figure 1). There are two reasons why reducing the scale of a material's microstructure can significantly alter its properties. First, as grain size gets smaller, the proportion of atoms at grain boundaries or on surfaces increases rapidly. In a polycrystalline material with a grain size of 10nm, as many as 50% of its atoms are at grain boundaries, resulting in a material with properties far different than nor-

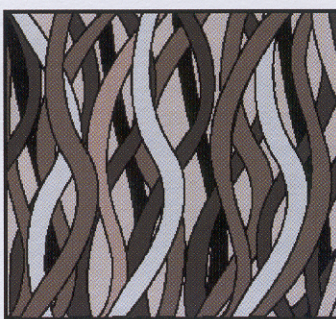
Figure 1. Nanostructured Materials are Characterized by the Inclusion of One or More Types of Features with Dimension Below 100 Nanometers



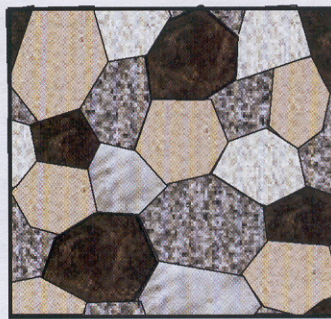
Particle Diameter



Layer Thickness



Fiber Diameter



Grain Size

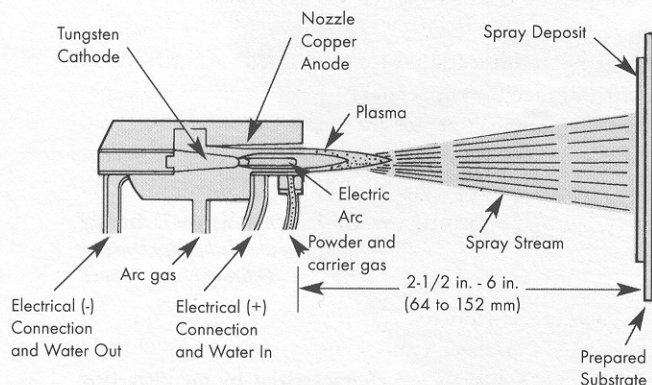


Figure 2. Schematic Diagram of Typical Plasma Torch (Courtesy of R.W. Rigney)

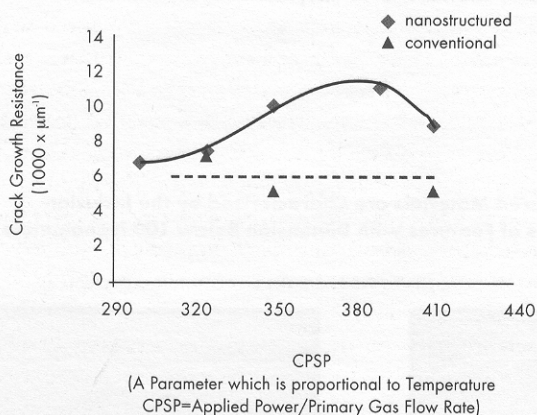


Figure 3. Indentation Crack Growth Resistance vs. Critical Plasma Spray Parameter (proportional to plasma temperature) [3]

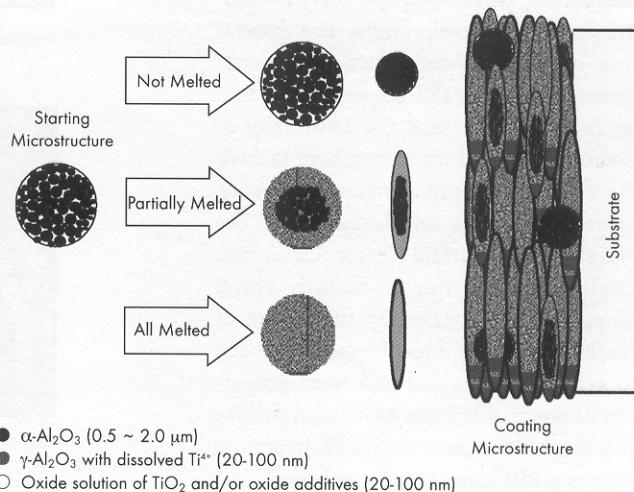
mally seen. The other reason is related to the fact that many physical phenomena (such as dislocation generation, ferromagnetism, or quantum confinement effects) are governed by a characteristic length. As the physical scale of the material falls below this length, properties change radically. Until recently, these changes in deformation behavior and modes of failure have not been well understood due to the inability to consistently fabricate high quality materials. This situation is changing rapidly, with considerable progress now being made in the fabrication of nanomaterials, as well as and the understanding of the interrelations between nanoscale processing, structure, and macroscale properties.

Fabrication of Nanoceramic Coatings

The strategy employed to develop nanostructured coatings concentrated on compositions similar to currently available conventional coatings and to use existing deposition equipment to fabricate them. As only the microstructure of the coatings was changed, it greatly simplified the process of implementing the new technology in both military and commercial applications. One of the coatings under development, a plasma sprayed nanoceramic composite with a composition of $\text{Al}_2\text{O}_3 - 13 \text{ TiO}_2$, has exhibited wear resistance, bond strength, and toughness unprecedented in a ceramic, and is now in use aboard Navy surface ships and submarines, reducing maintenance costs due to wear and corrosion.

Plasma spray, the process used to fabricate ceramic coatings, is very simple in concept, but very complex in practice. An inert gas is passed through a region of electrical discharge, where it is heated to very high temperature (typically 10,000 to 20,000 K). The rapidly expanding plasma is forced out through a nozzle at velocities between 1,200 and 1,500 m/sec and directed toward a substrate. Particles are injected into the plasma, where they are heated and accelerated. Although the plasma and particle temperatures are high, substrate surface heating is minimal. A schematic of a typical plasma spray gun is shown in Figure 2. The complexity arises from the large number of parameters that must be selected and which can affect the structure and properties of the coating. The temperature and velocity of the plasma depend on the power applied to the gun and the type and flow rate of the gas used. Usually, two gasses are used, an inert gas such as helium or argon, and a secondary gas, such as hydrogen. Other factors include the morphology of the powder particles, distance from the gun to the substrate, position and orientation of the powder injection ports, and surface preparation of the substrate. Taken all together, these

Figure 4. Effect of Nanoparticle Agglomerate Melting on Coating Microstructure [3]



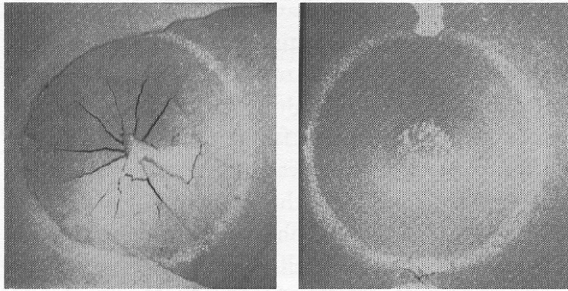


Figure 5. Cup Test Performed on Conventional (Left) and Nanostructured (Right) Al_2O_3 - 13TiO_2 Coatings
(Courtesy of R.W. Rigney)

parameters determine the thermal history of the injected particles, velocity of impact, and flow and solidification characteristics after impact, thus dictating the resultant microstructure.

As compared to traditional plasma spray processes, plasma spraying nanostructured materials introduces a number of complications. The first is that nanoparticles cannot be sprayed by particle injection into the plasma. Very small particles lack the momentum necessary to penetrate into the plasma, or to impact the surface while the plasma sweeps to the side near the substrate. To be sprayed, the particles must be formed into agglomerates approximately 30-100 microns in diameter. For an Al_2O_3 - TiO_2 nanocomposite, this is usually accomplished by dispersing alumina and titania nanoparticles in a fluid with a binder and spray drying [1]. If necessary, the agglomerates are partially sintered to improve structural integrity.

The next problem is forming a nanostructured coating on the substrate. This is not trivial since the agglomerates are greatly heated (promoting rapid grain growth) and are at least partially melted. There are three mechanisms for creating or retaining a nanoscale microstructure: avoiding melting or grain

growth of the feedstock (very difficult), inclusion of nanoscale particles with very high melting temperature that remain solid while the rest of the material melts, or formation of a nanostructure during solidification of the sprayed material upon impact. The last mechanism occurs in composites consisting of two or more immiscible phases (as is the case for Al_2O_3 and TiO_2) and results from solid state decomposition of a single, metastable phase formed by rapid solidification during impact. The metastable phase formed by Al_2O_3 and TiO_2 is a highly defected Spinel [2].

The microstructure and properties of nanostructured Al_2O_3 - 13TiO_2 coatings depend strongly on the temperature of the plasma [3]. This is in sharp contrast to the conventional coating, as illustrated in Figure 3, which shows a plot of indentation crack resistance as a function of a parameter (applied power divided by primary gas flow rate) which is proportional to the plasma temperature. Data is shown for both the nanostructured and conventional coatings. One can see that the crack growth resistance for the conventional material is virtually independent of plasma temperature while the nanostructured coating exhibits a strong dependence.

The reason can be found by following the thermal history of the injected particles. In the plasma spraying of conventional Al_2O_3 - 13TiO_2 , the feedstock consists of large fused and crushed particles that are fully melted prior to impact. Full melting is achieved over a wide range of temperature because of the high thermal conductivity of fused and crushed particles (relative to nanoparticle agglomerates). The coatings typically have grain sizes greater than one micron. When the nanoparticle agglomerates are sprayed at relatively high temperature (under conditions that result in full melting), the "nano" structure consists entirely of grains formed from the decomposition of the metastable Spinel phase.

The difference between the micro-grained material formed from fused and crushed feedstock and the nanostructure formed from the agglomerates arises from the degree of homogeneity in the melted particles. Because of the short residence time, the liq-

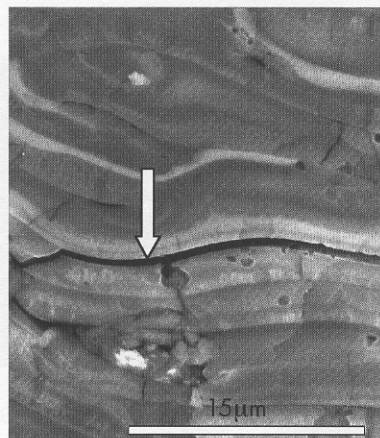
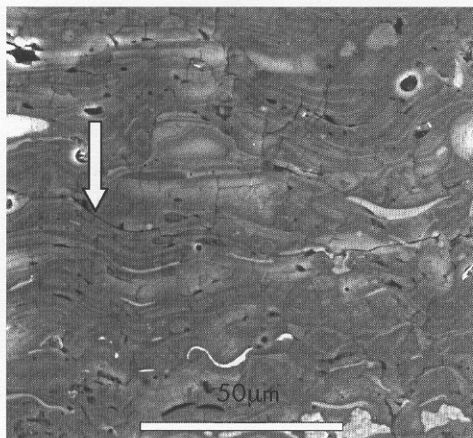


Figure 6. Cross-Sectional Views of Crack Propagating in Conventional Al_2O_3 - 13TiO_2 Coating [3]

liquid formed from melting the fused and crushed particles will contain alumina and titania rich regions. When this liquid solidifies rapidly, the grains formed will be larger than would be obtained from a homogeneous liquid. When plasma spray is carried out at a relatively low temperature, little melting occurs and the structure consists of incompletely sintered particles that have undergone some degree of grain growth. The middle temperature range gives partial melting of the agglomerates and results in regions of micron sized grains (from unmelted particles that have experienced grain growth) surrounded by nanoscale grains from the fully melted material and is illustrated in Figure 4. It is this “duplex” structure that gives the best properties, not a homogeneous nanoscale structure.

Properties of Nanostructured Al_2O_3 - 13TiO_2 Coatings

The obvious parameter by which to judge a “wear resistant coating” is wear rate. Wear can be termed as either sliding or abrasive. Both are measured by running a “wearing” medium over the surface and measuring weight loss. For many coatings, and particularly for brittle materials such as ceramics, this parameter can be misleading. The wear resistance of coatings in use today is outstanding, with wear rates orders of magnitude less than the uncoated surface. Brittle coatings usually do not fail by “wearing out”, but rather suffer from cracking, delamination and spallation. At least as important as wear resistance is bond strength (adhesion to the substrate) and toughness (the ability to withstand an impact or applied strain). It is in these properties that the nanoceramic coatings excel to a remarkable degree.

The bond strength of the nanostructured coatings, as measured by tensile pull tests on coatings applied without a bond coat, is about double that of a conventional coating. The toughness of the nanostructured Al_2O_3 - 13TiO_2 coatings is extraordinary, as is dramatically illustrated in Figure 5. This shows a “cup test” in which a coated coupon is forced down onto a one-inch diameter steel ball (coated side away from the ball), causing it to deform. The deformation is greatest in the center decreasing to zero at the edges. The conventional coat-

ing shows the typical cracking and spalling observed in a ceramic. The nanostructured coating actually deforms along with the substrate and no macroscopic cracking is observed. A blow from a hammer severe enough to deform a steel substrate would not be sufficient to cause failure in the coating. This toughness translates into greater wear resistance, which is two to four times greater than that of the conventional coating [4].

Another important benefit of enhanced coating toughness is improved grindability as almost all ceramic coatings must be ground and polished after spray deposition. Nanostructured ceramic coatings can be ground and polished in about half the time required for conventional ceramic coatings. Since grinding and polishing operations represent about forty percent of the total cost of the coating (compared to about five percent for the cost of the feedstock powder), nanostructured coatings are actually less expensive to apply.

The performance of the conventional and nanostructured coatings can be better understood by examining how cracks propagate in these materials. In the conventional coating, cracks follow the “splat boundaries” which mark the borders between the materials deposited from each droplet (Figure 6). The arrows in this figure point towards a splat boundary. A crack can be seen following another splat boundary [3]. In the nanoceramic composite, the cracks do not follow the splat boundaries, but instead propagate through the nanostructured material that formed during solidification until they encounter a region of larger grains formed from partially melted feedstock. Here, the cracks are either deflected or stop inside the “coarse grained” region. This can be clearly seen in Figure 7, which illustrates that cracks terminate inside regions (see arrows) of large grains formed from unmelted feedstock [3]. Any strain imposed upon a nanostructured coating is accommodated by the creation of microcracks in the normal way, but these cracks are blunted before they can propagate very far or link up with other cracks. The result is a ceramic material that can deform to a degree much greater than in a more conventional, brittle ceramic.

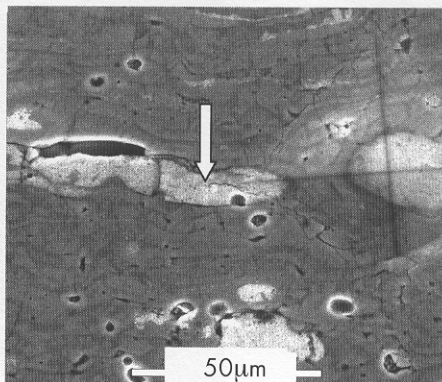
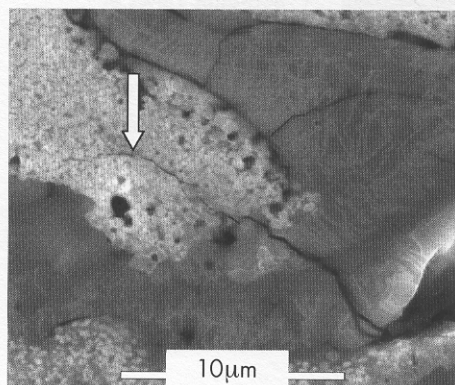
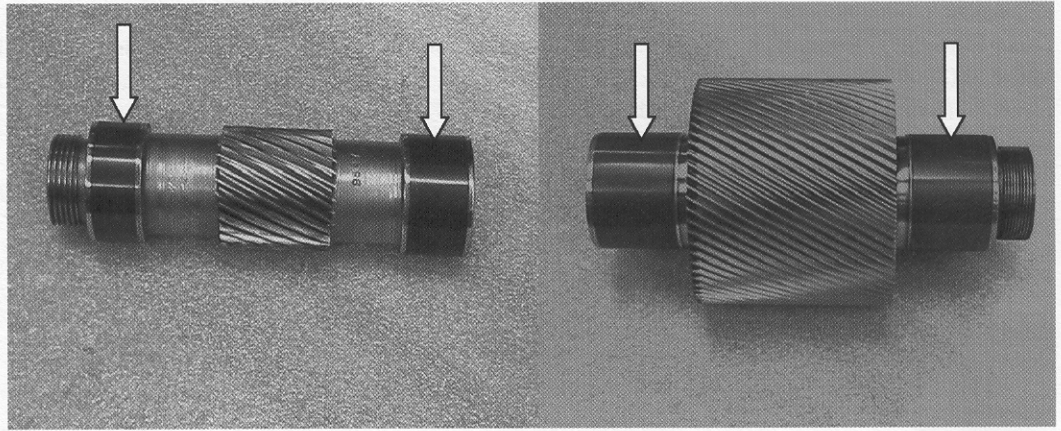


Figure 7. Cross-Sectional Views of Crack Propagating in Nanostructured Al_2O_3 - 13TiO_2 Coating With “Duplex Structure” [3]

Figure 8. High Speed Reduction Gear Set From 80 Ton Air Conditioning Unit. Coated Areas are Marked with an Arrow (Courtesy of R.W. Rigney)



Applications

The applications for nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings can be grouped according to the properties to be exploited. The simplest applications are those in which the nanostructured coatings replace existing conventional ceramic coatings. In such cases, the advantage is greater longevity and reliability. The second case is as a replacement for hard chrome coatings. Here, the advantages are lower cost, elimination of toxic hazardous materials and in some cases, improved performance. The improved performance comes from the non-metallic nature of ceramics. Metallic surfaces in contact with seawater for long periods of time experience buildup of calcareous deposits. Actuator rods with such buildups can severely damage seal areas when the rods are retracted. Electrically non-conducting coatings experience no such buildup. Also ceramics do not promote galvanic corrosion, which occurs when two dissimilar metals are in contact with an electrical conductor such as seawater. In spite of these advantages, conventional ceramic coatings frequently cannot be used over metallic coatings because they lack sufficient bond strength and toughness. Nanostructured ceramics overcome this limitation. In fact, nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings are now being used to coat titanium components on seawater-exposed portions of submarines specifically to eliminate galvanic corrosion on nearby steel structures. The most unique applications are in circumstances where no coatings could previously be employed. For example, many shafts used aboard ships, such as propulsion shafts, undergo sufficient torsional strain to cause failure in a conventional coating. Nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings exhibit sufficient strain tolerance to be a viable candidate for coating of severe wear areas on certain types of shafts.

The qualification of a new material for military applications can be a fairly involved process. This process has been greatly simplified for nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ coatings because the coatings are similar in composition to existing approved coat-

ings and are applied using the same equipment and procedures. They have now been approved under MIL STD 1687A, which governs use of thermal spray coatings on shipboard machinery. The number of applications in use aboard surface ships and submarines is rapidly expanding. There are literally thousands of potential applications and the impact on the cost of maintaining ships, aircraft, and ground vehicles can be very large. This can be demonstrated by examining a typical example.

The component illustrated in Figure 8 is a reduction gear set from an 80-ton air conditioning unit used on surface ships. The coated areas of these gears are indicated by the arrows. Currently gears are replaced on average at six year intervals. Eventually, abrasives form on the shaft, excess heat is generated and it welds to the aluminum sleeve in which it rotates, thus causing it to seize up. With application of the new coatings, these gears can be repaired instead of replaced. The damaged surface is ground down and replaced with a nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$. The savings fleet-wide from this one application is about \$500,000 per year, or about \$13,000,000 over the projected thirty-year life of these ships. When one considers the large number of other applications, such as pumps, valves, electric motors, diesel engines, bearings, journals and actuators, the magnitude of the cost savings becomes apparent. Moreover, most of these components are not military-specific. Coatings are now being applied to commercial hardware as well.

While nanostructured ceramic particles and thin films have been available for some time, nanostructured $\text{Al}_2\text{O}_3 - 13\text{TiO}_2$ represents the first bulk ceramic material to be commercialized. Other nanostructured coating materials are under development and are expected to become available in the near future. These include cemented carbides, such as Tungsten Carbide-Cobalt (WC-Co) and other ceramics, such as chrome oxide and yttria-stabilized zirconia. All of these coatings are expected to find a wide range of application and should greatly benefit both military and commercial operating and maintenance costs.

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Dr. Lawrence T. Kabacoff is a Program Officer in the Materials Science and Technology Division, at the Office of Naval Research, where he directs programs in synthesis and processing of nanostructured materials, electronic packaging, and IR transparent materials. He obtained a Ph.D. in Solid State Physics from the University of Connecticut in 1978. He then served as a Post Doctoral Research Fellow at Northeastern University until 1979, where he conducted research into the origins of glass formation and stability in metallic glasses. Subsequently, he joined the Naval Surface Warfare Center, White Oak, as a research Physicist in the Materials Division, where he conducted research on magnetoelastic metallic glasses and shape memory alloys. Since 1991, he has served as a program officer in the Materials Division of the Office of Naval Research. He has managed programs in the areas of acoustical damping in structural materials, fabrication of optical quality diamond, multi-chip module packaging, improvement of high temperature mechanical properties of sapphire (for IR domes), and synthesis and processing of nanostructured alloys and ceramics.