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OFFICE OF NAVAL RESEARCH INITIATIVE ON WEAR RESISTANT NANOSTRUCTURED MATERIALS

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1. Introduction

Every year, the U. S. Navy spends many billions of dollars in the repair and maintenance of ships, aircraft and land-based vehicles. A significant portion of this money goes to the repair or replacement of worn or eroded components such as shafts, seals, hydraulic cylinders and bearings. Because of continuing budget cuts over the last several years, it has become imperative for the Navy to find ways to reduce this maintenance burden. This need is complicated by the fact that many of the wear surfaces in question are chrome plated, which, due to increasingly stringent environmental regulations, must now be replaced by some other coating technology. As a result, the Office of Naval Research has instituted an initiative to develop and implement new coating technology that takes advantage of the outstanding properties of newly emerging nanostructured materials. Moreover, the coatings are fabricated by thermal spray processing, a mature and widely available technique, and one that is already used for refurbishing worn or otherwise damaged ship and aircraft components. The objective of the program is to establish a coatings capability which can reduce life cycle cost of navy assets either by extending the service life of components or making possible the repair, rather than replacement, of the component. The extraordinary properties of these materials make both strategies possible.

2. Thermal Spray Processing

Generally speaking, thermal spray consists of the heating and accelerating of solid particles by injecting them into a hot gas stream, then impacting them onto a substrate to form a coating. There are a wide variety of techniques for carrying this out. The heated gas stream can be produced by a DC arc (plasma arc spraying), by combustion of a fuel such as kerosene (high velocity oxygen fuel, or HVOF), or even simple heating of compressed air (cold dynamic gas spray, or CDGS). Each method has a characteristic range of gas velocities and temperatures. For example, plasma arc spray can produce extremely high temperature (in excess of 10,000 °C) but velocities below 1,000 ft/sec. On the other hand, HVOF produces much higher velocities, but temperatures in the 2,000 –

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3,000 °C range. CDGS can produce up to Mach 4 gas velocities, but at a temperature of only about 300 °C. The choice of method depends on the material to be sprayed, the substrate, and the required quality of the coating (adhesion, porosity, etc.).

Thermal spray of nanostructured materials presents challenges not usually present when spraying conventional materials. For example, the ideal size and morphology of a particle for thermal spray is a 15 –30 μm dense spherical particle. Nanostructured ceramic powder is most frequently produced in the form of individual nanoscale particles. Such particles cannot easily be fed into an thermal spray system. Moreover, it is very difficult to entrain such particles or to bring about impact on a substrate. Such particles must be agglomerated into larger, "snowball" like structures, which can be injected into and carried by the gas stream. Another important class of nanostructured materials, cemented carbides (or cermets), is produced in the form of fragile, hollow shells. Beside the low density, such shells break apart in storage and handling, resulting in fine particles that clog the powder feeders. For these materials, it is necessary to either modify the production process to create dense spheres, or to re-agglomerate the material into a more favorable structure. Another issue when spraying nanostructured materials is the degree to which the particles melt. There are two ways to form a nanoscale microstructure in a thermal sprayed coating. Either the individual particles (or one or more phases within the particle) remain solid during the spray process (since melting destroys the nanoscale nature of the material), or a nanoscale structure is recovered during solidification at the substrate. In thermal spray of conventional materials, particles are almost always allowed to melt. Finally, the extremely high surface area of nanostructured materials can lead to excessive surface reactivity which, in turn, can degrade coating quality.

3. Program Summary

Studies have been carried out in three general areas: cermets, ceramics, and metals.

3.1 CERMETS

Two classes of cermets were investigated, WC-Co and Cr_4C_3-NiCr. WC-Co was manufactured in the form of hollow shells by Nanodyne with nominal compositions of 8, 12, and 15% Co. Initially, the shells were too fragile for use as thermal spray feed stock due to the presence of very fine particles (which clogged powder feeders). Three approaches were taken to solve this problem. The first involved the milling of the Nanodyne material to form micron sized particles followed by dispersal in a binder and spray drying. Further processing by a heat treatment can also be applied. Several companies are capable of this kind of processing. Under the ONR program, this work was carried out by Inframat. A second approach was to modify the parameters of the spray conversion process used by Nanodyne to manufacture the original hollow shells in order to produce shells with much thicker walls. This has been done successfully by Nanodyne, which can now produce nearly solid spheres. The third approach was to fabricate a cored wire consisting of a WC-Co core wrapped in a thin metal sheath. Thermal spray was carried out by twin wire arc spray. Sprayable nanostructured Cr_4C_3-NiCr powder was fabricated by attritor milling of conventional powder followed by dispersal in a binder. In this case, rather than spray drying, the binder was allowed to harden. The resulting material was then ground to form a sprayable powder.

A very large number of cermet coatings were fabricated by several thermal spray techniques. Most were done by HVOF, with some coatings produced by plasma spray and twin wire arc. In all cases, the adhesion was outstanding, typically a factor of two better than conventional coatings of similar composition. It was also found that residual stress was very low, resulting in a capability for producing very thick coatings. In a conventional coating, stress buildup limits coating thickness to typically 500 – 800μm. Nanostructured coatings were made up to 0.65 cm thick and could probably be made with arbitrary thickness. It was also found that the WC-15%Co coatings were remarkably tough and could be struck hard with a hammer without cracking or spalling. The hardness and wear resistance of the coatings varied widely depending on spray techniques and parameters used. Moreover, wear resistance did not correlate to hardness. Studies show that, while bulk sintered nanostructured WC-Co is much more wear resistant than the conventional analogue, the wear resistance of the nanostructured coatings is limited by the quality of the splat boundaries and that coating quality is not yet high enough to allow the nanostructured nature of the material come into play. Development efforts are continuing. Wear data on Cr_4C_3-NiCr is not yet available. However, the hardness of the nanostructured coatings is somewhat higher that that of the conventional coating.

3.2 CERAMICS

Two types of ceramic coatings were considered: hard coatings and thermal barrier coatings. The composition for the hard coatings was Al_2O_3 – 18%TiO_2 while that of the thermal barrier coating was 7YSZ (7% yttria stabilized zirconia). Sprayable powder was produced by reagglomerating individual nanoscale particles which were dispersed in a binder and spray dried, followed either by calcining or plasma densification. The resulting powders consisted of round dense particles of a size and flowability ideal for thermal spray powder feeders. Coatings were fabricated by plasma spray. Examination of the microstructure showed that partial melting had occurred and that the coatings consisted of a mixed nano/micro-scale structure. The nanoscale component varied from zero to over 60%. In the case of the hard coatings, adding proprietary dopants could increase the percentage of retained nanostructured material. The wear resistance of the hard coatings was found to be superior to that of the conventional material, being four times better in the best samples. The wear resistance correlated strongly with retained nanostructure. Adhesion was found to be much higher for the nanostructured coatings (more than twice the conventional value). It was observed that toughness was much higher, but quantitative measure of this has not yet been accomplished. It was also observed that post deposition grinding and polishing of the nanostructured coatings could be accomplished in about half the usual time and a much better final surface smoothness could be achieved.

In a recent effort, Inframat has succeeded in fabricating oxide ceramic coatings by injecting an aqueous solution of salts directly into a plasma flame, thus carrying out particle synthesis and deposition in the same operation. The resulting coatings were remarkably smooth, and porosity could be controlled by controlling process parameters. The mechanical and thermal properties of the coatings are now being characterized at Inframat and at UCONN. NEI and A&A company have also succeeded in producing coatings using a liquid, in this case using metal-organic precursors.

3.3 METALS

Sprayable powders of reasonably ductile alloys and metal matrix composites can most easily be obtained by attritor milling of conventional metal powders, which produces relatively large metal particles which exhibit a grain size typically 20 – 40 nm. However, these powders will almost certainly melt during deposition using most thermal spray techniques (an exception is CDGS). The nanoscale structure can be recovered upon solidification provided the material is rich in nucleation sites and solidification is rapid. These nucleation sites can be obtained by performing the milling under liquid nitrogen. This results in the creation of a fine dispersion of oxide/nitride particles which tend to collect at grain boundaries. Studies have been carried out on thermal spray of aluminum (with and without addition of micron scale SiC particles) and on a Ni-based alloy, 718. In each case, nanostructured coatings were successfully fabricated either by plasma spray in an inert atmosphere (Al, Al/SiC) or HVOF (718). These coatings have not yet been characterized. However, preliminary data indicate that the hardness of such coatings is significantly higher than that found in conventional coatings with the same composition.

4. Recent Publications

Much of the work described above has not been published, partly because of insufficient time, and partly because some of it is being carried out in industrial laboratories where the details are considered to be proprietary. Some of the work is presented elsewhere in these proceedings. A list of recent publications is presented below. It is suggested that interested persons contact the performers directly to obtain information.

1. Cheng, J., Jordan, E.H., Barber, B., and Gell, M. (1998) Thermal/residual stress in a thermal barrier coating system, *Acta Meterialia* **46**, 5839-5842.
2. Xiao, T.D., Jiang, S., Wang, D.M., Wang, Y., Zatorski, R., Strock, C.W. and Strutt, P.R. (1998) Thermal spray of nanostructured ceramic coatings for improved mechanical properties, in T.S. Sudarshan, K.A. Khor and M. Jeandin (eds.), *Surface Modification Technologies XII*, ASM International, Metals Park, pp. 489-493.
3. Cetegen, B.M. and Yu, W. (1999) Simultaneous particle temperature, velocity and size measurement in HVOF thermal sprays, *J. Thermal Spray Technology* **8**, 57-62.
4. Ahmed, I. And Bergman, T.L. (in press) Thermal modeling of plasma spray deposition of nanostructured ceramics, *J. Thermal Spray Technology*.
5. Wang, Y., Whang, S.H., Wang, T.D. and Strutt, P.R. (in press) Abrasive wear

characteristics of plasma sprayed nanostructured Al_2O_3/TiO_2 Coatings, *Wear.*

6. Skandan, G., Glumac, N., Chen, Y.-J., Cosandey, F., Heims, E. and Kear, B.H. (1998) Low-pressure flame deposition of nanostructured oxide films, *J. Am. Ceram. Soc.* **81**, 2753-2756.
7. Usmani, S., Sampath, S., and Herman, H. (1998) HVOF processing of nanostructured WC-Co coatings and their properties, *J. Thermal Spray Technol.* 7, 429-431.
8. He, J., Ice, M. and Lavernia, E.J. (1998) Synthesis and characterization of nanostructured Cr_3C_2-NiCr, *Nanostructured Materials* **10**, 1271-1283.
9. Lau, M.L., Gupta, V.V. and Lavernia, E.J. (1998) Mathematical modeling of particle behavior of nanocrystalline Ni during high velocity oxy-fuel thermal spray, *Nanostructured Materials* **10**, 715-722.

5. Performers

The initiative is being carried out by a large group of performers representing industry, universities, and Navy R&D centers and repair facilities. A list is given in Table 1, along with point of contact (sometimes arbitrarily chosen) and e-mail address.

TABLE 1. Performers, points of contact and e-mail addresses of participants.

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