Nanomaterials: Reality Versus Hype

Dr. Lawrence T. Kabacoff
Office of Naval Research
875 North Randolph Street
Arlington, VA 22203-1995
USA

kabacol@onr.navy.mil

ABSTRACT

For most people, the term "structural nanomaterial" would appear to be a contradiction. In fact, bulk materials and coatings can be fabricated with microstructures which incorporate nanoscale features, often in combination with features on other scales, and which exhibit remarkable properties. While many claims made about these materials are ill founded (i.e. hype), extraordinary progress has been made on nanostructured ceramics and metals. The hype arises from a failure to take into account all of the properties required for the intended application (for example, increasing strength while destroying ductility). Nevertheless, it is possible to develop nanomaterials with revolutionary (as opposed to evolutionary) properties which are not deficient in some other characteristic. To do this, it is necessary to think of "nano" not as a goal, but as a degree of freedom which permits the design of novel microstructures which result in unprecedented properties. Cleverness and hard work are still required.

1.0   INTRODUCTION

Nanotechnology is commonly defined as a "the creation of useful/functional materials, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale."[1] The term "control of matter on the nanometer length scale" can mean, for example, creation of multilayers with nanometer scale layer thicknesses, nanoscale structures such as quantum dots, memory elements or MEMS, or nanoscale particles. This is certainly the most commonly held mental image of a nanomaterial. The concept of "nanoscale structural materials" does not seem to fit at all into this picture. The problem is with the meaning of the word "control". In fact, control can also mean "statistical control", which means that bulk materials with a random distribution of nanoscale features (such as a material with nanoscale grains) also fit within the definition of a nanomaterial. Such materials, in fact, exhibit profoundly novel properties.

Historically, there have been two separate communities pursuing "nanotechnology". The first community has its roots in the famous lecture by Richard Feynman in which he speculated on the advances which could be achieved by building materials "from the bottom up" and controlling structure at the atomic level. This community has included researchers in such areas as integrated circuits, data storage, optical devices, sensors, and catalysis. However, there is another community which developed out of the pioneering work of Herb Gleiter in the 1980's in which he fabricated nanoscale particles by gas condensation and consolidated these particles into bulk ceramics with intriguing properties [2]. This community was initially interested the

economical synthesis of large quantities of high quality nanoparticles, and in the processing and characterization of "bulk" materials with very fine grain size. These interests lead to the organization of a "working group" which has organized an ongoing series of international conferences which convenes every two years. It was this working group which coined the phrase "nanostructured materials" at a meeting in Atlantic City, New Jersey in 1988. The two communities developed independently of each other, expanding their interests to overlap each other, but remained separate. Many (if not most) of those involved in each community were originally only vaguely aware of the other. In recent years, there has been wide publicity attending research on "nanostructures", but much less on research on bulk "nanostructured materials". Surprisingly (and for those in the field, frustratingly) a large segment of the nanotechnology world remains unaware of the enormous progress that has been made in the processing and understanding of such materials, particularly structural materials. It is common to attend lectures on nanotechnology which either do not mention bulk materials and coatings or deny the possibility of near term success in their creation. One of the major purposes of this Specialists Meeting is to bridge that gap.

2.0   CHANGING (BUT NOT NECESSARILY IMPROVING) PROPERTIES

The basic premise underlying nanotechnology is the fact that, as microstructural scale is reduces below a certain threshold, various properties begin to change radically. This threshold depends on the property of interest but is commonly somewhere around 100 nanometers. There are several reasons for this change. The first is that as the size of an object shrinks the surface-to-volume ratio increases. Below 100 nanometers, this change becomes very rapid. At about ten nanometers, the percentage of atoms in the object lying at the surface approaches fifty percent. This object could be a nanoscale structure with an external surface, or it could be a grain in a polycrystalline material, in which case the surface is a grain boundary. Nanostructured materials are frequently referred to as "grain boundary materials." Another very important factor has to do with the fact that most phenomena underlying the properties of a material exhibit a characteristic length. For example, in a magnetic material the characteristic length is the exchange correlation length, which arises from quantum mechanical effects and is a measure of the distance over which one atom can magnetically influence another atom. In optical phenomena the characteristic length is just the wave length of the radiation. When the physical scale of a material, whether it is an external dimension or a microstructural feature, becomes smaller than the characteristic length, the corresponding property *must* change radically.

As an example, consider the deformation of a pure nickel surface under the action of a diamond indenter [3]. In conventional nickel, surface deformation occurs via the creation of slip steps within the interiors of grains which have a spacing of approximately 30 nm. This is illustrated on the left in Figure 1. If, however, the grain size is less than 30 nm, these slip steps cannot possibly form since the grain is smaller than the step spacing. This can be seen on the right, which shows a similar indentation in a nanostructured nickel surface. Whatever the deformation mechanism, it must be different, and the deformation behavior must also be very different.

There is a great deal of "hype" surrounding nanotechnology, and nanoscale structural materials suffer from their share. In this case the hype usually stems from two misconceptions. The first is a belief that all one need do is reduce the average grain size to well below 100 nm to achieve greatly improved properties. This is overly simplistic and only occasionally correct. The microstructures of modern structural materials can be quite complex, as are structure/property relationships. It matters how one includes nanoscale features and how these interact with other features with different length scales. The second mistake is to focus on a large improvement of some particular property without regard to the effect on other important factors. While strength is often the focus of development efforts, one cannot ignore other properties such as ductility,

toughness, creep resistance, corrosion, modulus, manufacturability, and operating environment (e.g. temperature). Cost is also an extremely important factor which must be judged relative to the value of the component or system. A miraculous material which no one can afford to buy is of only academic interest. The hype surrounding nanotechnology has distracted from what are, in reality, extraordinary advances. The problems facing development of nanoscale structural materials have been challenging, but significant progress is being made and some nanomaterials have actually reached commercialization.
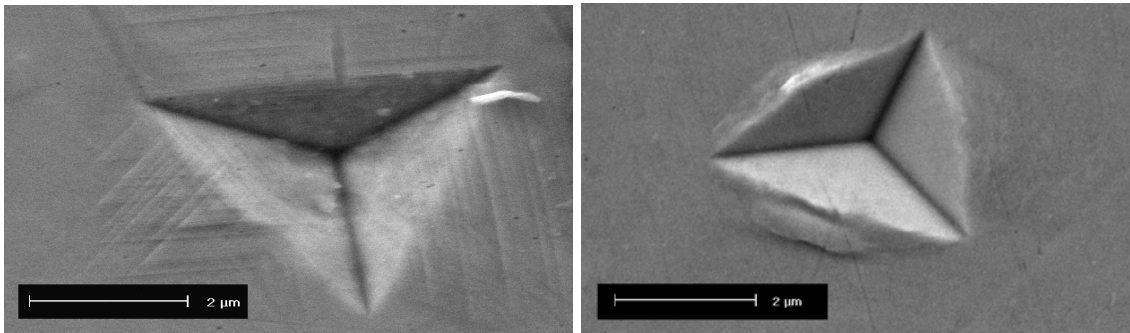

Figure 1: Indentation made on a conventional (left) and nanostructured (right) Ni surface.

The problem of improving one property at the expense of another can be illustrated by looking at strength, ductility and fatigue crack growth versus grain size. It is well known that the strength (and hardness) of a metal increases as the average grain size decreases. This dependence, known as the Hall-Petch relationship, is given by $\sigma \sim Kd^{-1/2}$ and persists down to grain sizes as low as 10 nm, even though the mechanism which is assumed to give rise to it cannot possibly operate in such small grains. As the strength increases, the ductility decreases. In addition, new mechanisms begin to operate which lead to a ductility much lower in tension than in compression. We begin to get properties more like a ceramic but with none of its advantages. There are also major changes in the fatigue properties. It is observed in pure nanocrystalline metals that while the initiation of fatigue cracks is inhibited, the propagation of a crack once formed is greatly enhanced as the grain size is reduced. This is illustrated in Figure 2, which shows fatigue cracks in a notched pure nickel with three different average grain sizes [4]. It is clear that the rapid propagation of fatigue cracks in the nanocrystalline material is due to the relatively small area exposed by the advancing crack. We are left with fatigue properties which are both better and worse depending on the application and nature of the applied stress.
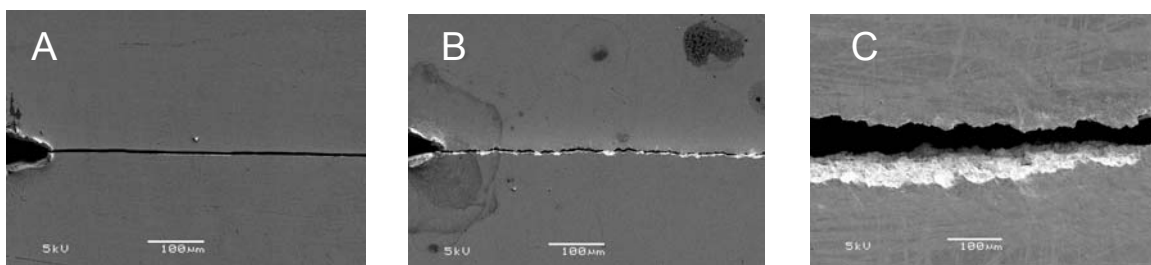

Figure 2: Notched fatigue cracks in nanostructured (A), sub-micron (B), and conventional Ni.

3.0 CHALLENGES FOR THE DEVELOPMENT OF BULK NANOMATERIALS

Although the field of nanomaterials for structures and coatings is really only a small part of the wider field of "Nanotechnology", it is, nevertheless, a very large and diverse field encompassing the work of hundreds of laboratories and research groups. It is difficult to organize the topic in a coherent manner. One may begin by dividing the topic into coatings and structures. These can be further divided by type of material: metals, ceramic, polymers, or combinations of these. Finally, we can divide processing methods into two broad categories. The first is a "bottom up" approach, in which atoms, molecules, or nanoscale particles are assembled to form a bulk material or coating. This might include vapor deposition, electrodeposition, or sintering of a compact formed of nanoparticles. The second is a "top down" approach, in which a conventional material is modified in such a way as to introduce nanoscale features into the microstructure. An example of his would be reduction of the average grain size of a metal by subjecting it to severe plastic deformation. With such a wide variety of materials and approaches it is difficult to generalize about the issues facing the nanomaterials community, but it is possible to outline, in a broad manner, the challenges that have needed (and in many cases, still needs) to be overcome in order to successfully exploit these materials for military and commercial applications.

The first challenge to be faced was the obvious one of how to make the materials in the first place. The original (and most straightforward) approach for bulk metals and ceramics was to consolidate compacts of nanoparticles by some form of application of heat. This has turned out to be quite difficult. There are two reasons for this. The first is that nanoparticles have very large surface area so that any surface coating or contaminant (such as an oxide scale) will comprise a large volume fraction of the product. This is more a serious problem for metals than ceramics, but is a factor for both. A second problem is that the thermodynamic driving force for grain growth during sintering is very large and it is difficult to retain a nanoscale grain size at the temperatures normally employed for consolidation. The first problem can only be addressed by very careful materials selection and process control. It is also necessary to insure that there is enough deformation of the particles to break up any oxide coating in order for good consolidation to take place. The second problem has been approached by finding alternatives to simple thermal methods of consolidation such as pressureless sintering or hot isostatic pressing. For example, one can make use of microwaves to selectively heat particle surfaces rather than the entire volume. Densification can be achieved very rapidly and grain growth can be minimized. There are many other strategies as well, some of them "top down" and some "bottom up". Severe plastic deformation applied to a bulk metal can refine the microstructure down to somewhere of the neighborhood of 150 nm. While this is a little outside the "nanomaterial" definition, such materials nevertheless show very interesting properties. Plastic deformation can also be applied to a conventional powder which is then consolidated using conventional powder metallurgy techniques. Recently, deformation has been used instead of heat to consolidate a compact of copper at room temperature [5].   This is illustrated in Figure 3. Other metals have been consolidated at somewhat elevated temperatures, but well below the temperatures normally used for thermally based methods. Yet another approach has been to use a very rapid electrodeposition technique to fabricate continuous sheets of material with thicknesses as high as one or two millimeters, thick enough for structural applications. Each of these methods will be discussed in detail in later presentation.
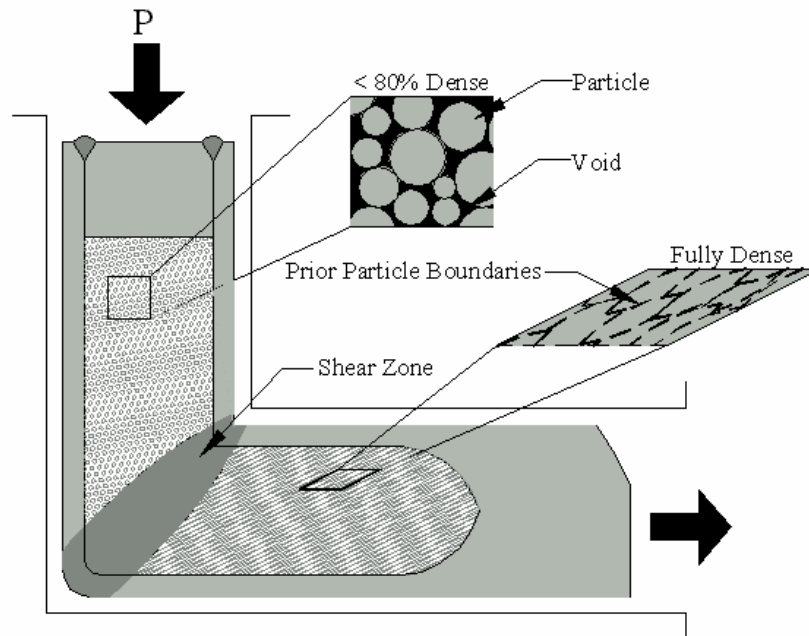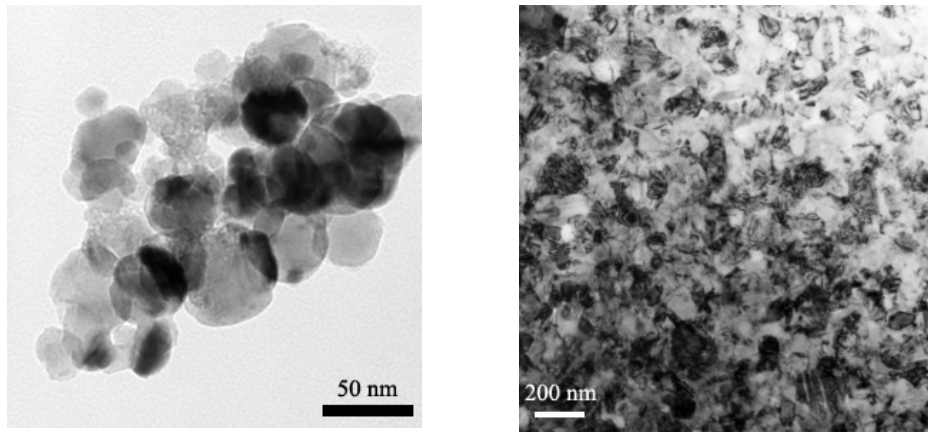
Figure 3: Consolidation of Cu nanoparticles using ECAP.

The processing of nanoceramics has been even more difficult than metals. Plastic deformation is not appropriate, and very high temperatures are required for sintering. Moreover, because the mechanical properties are controlled by "weak link statistics", it is necessary to achieve a very high degree of densification. Doing this without grain growth is quite difficult. Microwave sintering has been used effectively, as has a process call "Spark Plasma Sintering", in which a pulsed electrical discharge activates the particle surfaces (presumably by formation of a plasma). In recent years, a totally new paradigm has been developed which avoids the use of nanoparticles. This technique derives from the observation that when a liquid or vapor combining two or more immiscible phases is rapidly quenched, it can form a homogeneous, metastable (often amorphous) powder. A device for producing such a powder is illustrated in Figure 4 [6]. Here, a conventional APS (air plasma spray) gun has been adapted by the addition of a water-cooled shroud which confines the plasma. An aqueous solution of precursors is introduced as an aerosol, which is pyrolized

to form an oxide vapour. A converging-diverging nozzle at the bottom produces rapid quenching and subsequent formation of a homogeneous powder. This powder can be formed into a compact and sintered, during which the homogeneous material decomposes *in situ* to form a nanocomposite. Grain growth is limited by the geometric constraint provided by the immiscibility of the phases. Grains of one phase cannot grow past grains of another phase. The sintering can be carried out at lower temperature because the decomposition promotes the sintering process. The microstructure obtained for a composite of alumina and zirconia is illustrated in Figure 5 [6]. This method only works for composites and only for combinations of phases the have no mutual solubility in the solid state. Thus far, only oxide composites have been attempted. This method was first exploited in the fabrication of ceramic nanocomposite coatings fabricated by plasma spray.
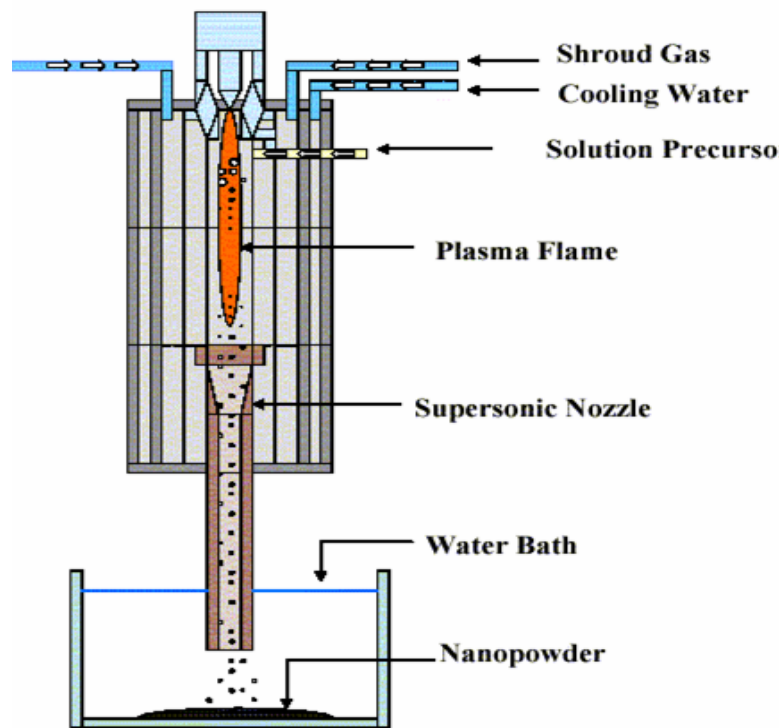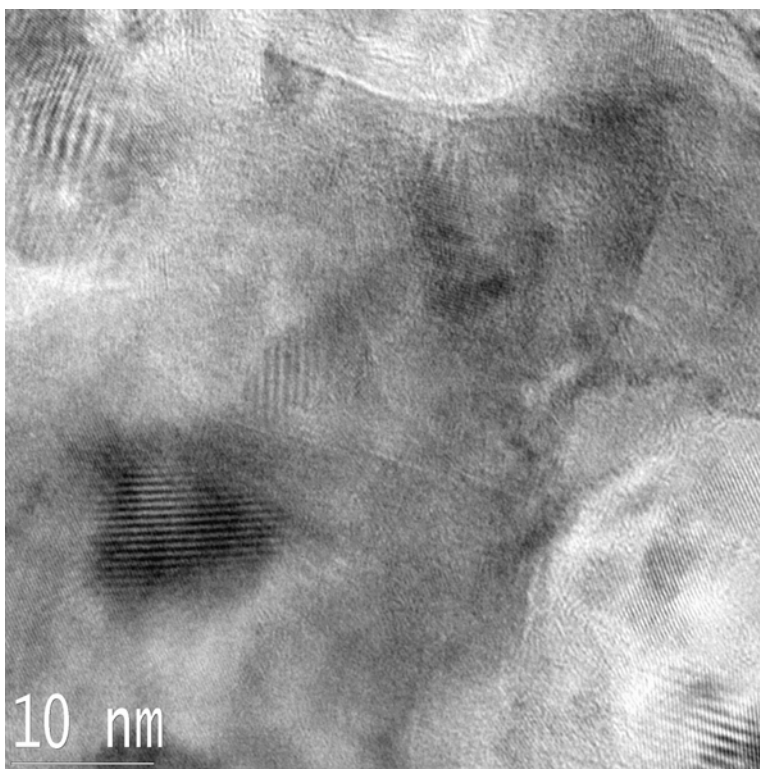
Figure 4: A device for the synthesis of homogeneous mixed oxide powders.

Figure 5: HRTEM image of a fully dense Al_2O_3-20vol.% $MgAl_2O_4$ nanocomposite.

The next challenge has been trying to understand the behavior of these materials. This effort was initially complicated by the lack of high quality, reproducible material on which to carry out experiments. The early literature was full of contradictions, and it was later found that much of the data were artefacts of the processing rather than intrinsic properties. For metals, the first good studies were carried out on electrodeposited materials [7]. Test specimens large enough for valid mechanical measurements were made available to a number of laboratories, and progress in understanding their properties has been very rapid. Theoretical work such as molecular dynamic simulation has also been very useful and cooperation between the experimentalists and theorists has been excellent. More recently, material fabricated by severe plastic deformation of either bulk or powder has been carried out with some success. While there is a great deal of work still to do, we believe we have made a fairly good beginning at understanding of the processes of deformation and failure in these materials.

The next challenge, one closer to the concerns of designers and manufacturers, has been how to exploit these materials, i.e. how to make a material which was not just different, but sufficiently better to justify its use. Here, a summary is practically impossible, not only because of the enormous variety of materials under discussion, but also because of the fact that different applications depend on different aspects of the materials. Moreover, most of these materials and applications will be discussed extensively in the presentations at this meeting. It is useful, however, to site a few examples by way of illustration.

4.0   EXAMPLES

One of the most important examples is the problem of obtaining very high strength in a metal without sacrificing other properties such as toughness. The degree of toughness required depends on the application. For example, Rocketdyne, the manufacturer of engines for the space shuttle, was faced with the problem of finding an alternative to titanium for the impellers in the liquid hydrogen fuel pumps (Figure 4), which were suffering from hydrogen embrittlement. The requirement here was to match the specific strength of titanium. Toughness was not a significant issue.   Since there was no existing alloy with the required properties, Rocketdyne investigated nanostructured aluminum alloys as a possible solution. This led to the development of an Al-Ti-Cu alloy with yield strength of over 700 MPa and a specific strength much better than the titanium alloy previously used [8]. Space shuttle engines with nano-aluminum impellers are now being tested. For applications requiring good toughness, a very fruitful approach has been to process alloys in such a way as to obtain, not a uniformly nanoscale material, but a material with a microstructure encompassing more than one length scale.   Large grains can be combined with regions comprised of nanoscale grains (a bi-modal microstructure) to obtain greatly enhanced strength while maintaining a reasonable level of ductility. This has been carried out for a number of aluminum alloys with great success. For example, a 5083 Al alloy with about double the strength of the conventional off the shelf alloy but with comparable ductility and toughness has been achieved [9].
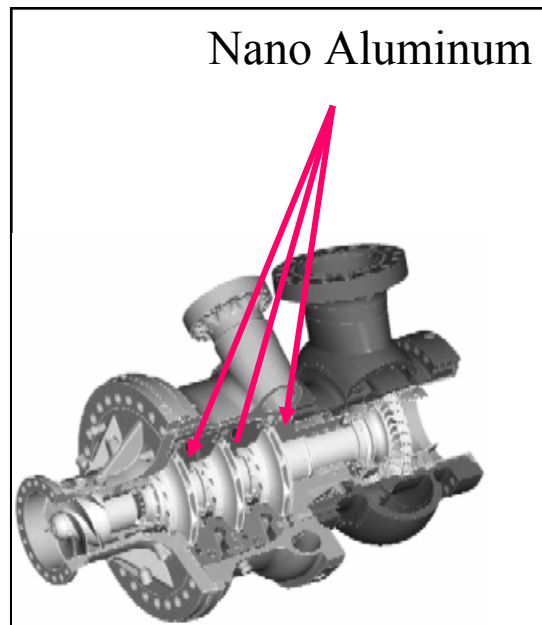

Figure 6: Liquid hydrogen cryopump for Space Shuttle Main Engine.

Another aspect of nanomaterials which has motivated materials developers has been the phenomenon of the superplastic deformation of ceramics. Superplastic forming of net shapes is routine in industry for certain alloys, i.e. titanium alloys used for aerospace applications. At sufficiently high temperature, these alloys deform easily and rapidly enabling the fabrication of inexpensive complex shapes.   This has never been possible for ceramics. However, it has been observed that superplastic deformation does indeed occur in

ceramics provided that the average grain size is in the nanoscale region. While this has been observed in many nanoceramics, getting this deformation at high enough strain rates and at low enough temperatures to be commercially viable has proven to be difficult. The required temperatures have tended to be in the range of 1400 to 1800 ^{o}C which is somewhat too high to be cost effective. Strain rates have tended to be low. Even if good strain rates are achieved, there is a tendency to get rapid grain growth at those temperatures causing the superplasticity to disappear. A recent breakthrough has been achieved by a research group at the University of California, Davis. Using a proprietary process, they have succeeded in deforming a disc of an alumina-zirconia-spinel nanocomposite into a complex shape at a temperature of 1130 ^{o}C and a strain rate of 10^{-2} (i.e. About 1% per second) [10]. This is shown in Figure 7. The total deformation took about twenty minutes. This would be economically viable provided the process proves to be reproducible and can be applied to other compositions.
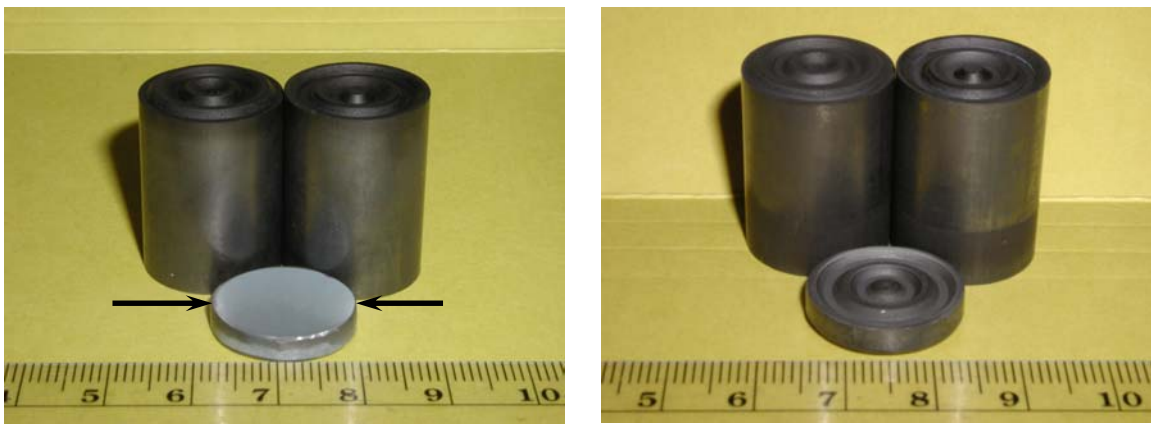
Figure 7: Superplastic deformation of an alumina-magnesia-spinel disc.

As a final example, we consider a problem which the US Navy had been dealing with for several years. Mine countermeasures ships (minesweepers) are constructed entirely of non-ferrous materials. Thus, the propeller shafts are made out of a bronze alloy rather than steel. This bonze is soft enough that debris trapped in the staves and seal areas was actually grinding the shafts leading to catastrophic failure in about 18 months (Figure 6a). Finding a suitable coating to protect the shafts proved to be very difficult. Polymers were too soft, and metal coatings would produce galvanic currents which could be detected by a mine. No ceramic coatings worked because the shafts undergo significant torsional strain and vibration during operation. Ceramics are notoriously brittle and lack any strain tolerance. Ultimately a bi-modal ceramic nanocomposite of alumina and titania was selected for testing. This coating, applied by conventional plasma spray, had exhibited remarkable strain tolerance and adhesion to the substrate. After four years of regular ship operations, the coatings are still intact and show no signs of scoring or spalling (Figure 6b). The coatings have now being applied to three more ships of the class.
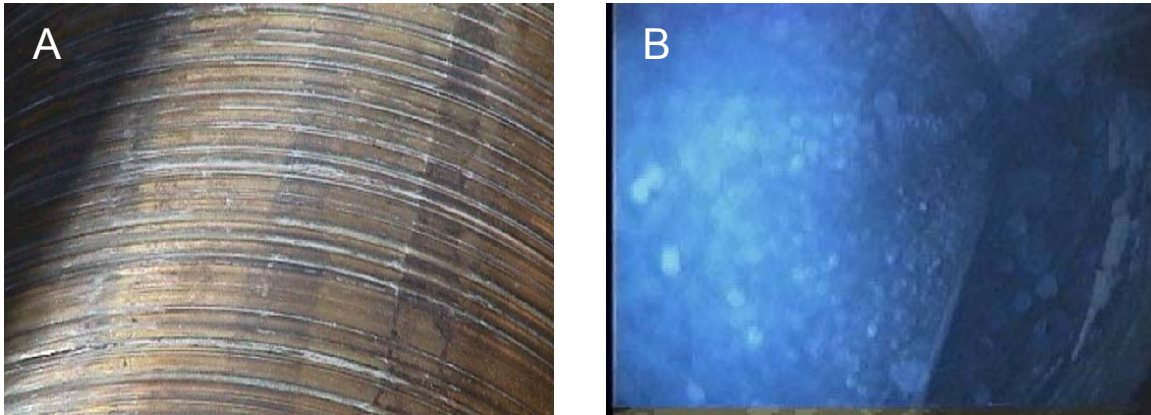
Figure 8: Coated and uncoated bronze shaft. The coated shaft is seen after four years of service.

5.0   CONCLUSION

As these presentations unfold, two things should become apparent. The first is that development of nanomaterials is much more than the reduction of grain size. "Nano" is not an end in itself, but is, rather, a tool which enables development of new microstructures with some remarkable properties. Each material has some degree of uniqueness and carries its own degree of difficulty and benefit. One size definitely does not fit all! The second is that most nanomaterials are not exotic or something to be ready decades from now. Some materials are commercially available or will be soon. Others should emerge in the five to ten year timeframe. Still others, such polymers reinforced with single wall nanotubes, will need major new breakthroughs before they can be successfully manufactured at an affordable cost. It is important to look at each new nanomaterial by itself rather than relying on sweeping generalizations. Many will be truly revolutionary in their impact on military vehicles.

6.0   REFERENCES

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