Synthesis of Nanostructured Films for Friction and Wear Resistance
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When the grain size of a material is reduced to the nanoscale, its mechanical properties become strongly influenced by the fact that a large fraction of the atoms in the material lie in grain boundaries. Evidence from a number of studies suggests that it should be possible to produce nanocrystalline composites that are superhard—possessing hardness rivalling diamond—and that also possess combinations of other properties that make them superior to diamond for applications requiring friction- and wear-resistance. Such superhard nanostructured films promise revolutionary improvements for wear protection for applications such as high-speed machining as well as in the emerging field of miniaturized moving parts in microelectromechanical systems (MEMS).

We have developed a process for depositing nanostructured films known as hypersonic plasma particle deposition (HPPD) [1-4]. HPPD is an extremely high-rate process, which is crucially important for commercial viability in areas such as machine tools and automotive parts. For example, we have deposited nanostructured silicon carbide films, with grain sizes around 20 nm, at rates exceeding 1 µm/s over a 2-cm-diameter area, and have achieved a hardness better than the top of the range for standard silicon carbide. That deposition rate is over three orders of magnitude higher than the typical deposition rate of SiC by chemical vapor deposition, and is comparable to the deposition rates obtained in thermal spray of course-grained coatings.

HPPD involves a one-step process in which nanoparticles are both synthesized and deposited. Vapor-phase reactants are injected into a thermal plasma, which is then expanded to low pressure through a nozzle. Rapid cooling in the nozzle drives the nucleation of nanoparticles, which are accelerated in the hypersonic free jet issuing from the nozzle. A substrate is positioned normal to the flow, and particles as small as a few nanometers in diameter impact the substrate at high velocity to form a dense, nanostructured coating. For example, for our typical conditions, numerical modeling indicates that 20-nm SiC particles impact the substrate at about 1700 m/s. Comparisons of high resolution scanning electron microscope (HRSEM) images of the films with measurements by scanning electrical mobility spectrometry of the aerosol sampled in-flight at the same location as the deposition substrate demonstrate that the grain size in the film corresponds closely to the size of the impacting particles.

In addition to developing HPPD for deposition of continuous films, we have also developed a modification of the process, known as focused particle beam deposition [5]. In this process the first-stage substrate is replaced by an aerodynamic lens assembly, which focuses the particles to a narrow beam, with beam widths on the order of tens of microns. By translating the substrate one can use the particle beam to deposit lines and patterns. The particle beam could be used in conjunction with standard microfabrication techniques, such as free-forming, insert-molding and masking, to fabricate MEMS parts. Because these deposits would be inherently nanostructured, they may offer superior friction- and wear-resistance, which are currently crucial limitations for MEMS parts such as miniature gears for micro-transmissions and electrodes for micro-electro-discharge machining.

We have used HPPD to deposit Si, SiC, Ti, TiC and multilayer Ti/TiC composites onto Mo and Si substrates. The reactants for these materials were SiCl₄ vapor, TiCl₄ vapor and methane. Fig. 1 shows HRSEM images taken at three depths in a typical SiC film. This film was 60 µm thick, deposited in a run time of 75 s. The grain size is about 20 nm in all three micrographs.
Rutherford backscattering spectrometry measurements of SiC films deposited at substrate temperatures around 700°C have found as-deposited densities around 95% of the theoretical density of SiC. The hardness of these films, measured by nanoindentation, has reached 37 GPa, above the top of the range for standard silicon carbide. Further improvements are possible by post-processing. We have explored post-processing by plasma sintering, hot-isostatic pressing and pressureless sintering. The results show that further densification without grain growth is possible; no grain growth is found for temperatures below approximately 950°C.

Figs. 2 and 3 show SEM images of deposits obtained using focused particle beams. Fig. 2 shows a typical needle-shaped “tower” deposited with SiC particles on a stationary substrate. Such towers were also deposited with titanium, for which high-resolution SEM images obtained from cross sections show grain sizes around 20 nm. Fig. 3 shows a pattern formed by SiC particles. The substrate was translated manually in a rapid zig-zag motion. The minimum line width is about 50 µm. As can be seen, towers began to grow at several points when the translation momentarily paused.
Future challenges

We see the main scientific and technical challenges for further development of friction- and wear-resistant nanostructured films as follows:

*Fundamental understanding of structure-property relations for nanostructured films*

While it has been demonstrated that nanostructured films can be extremely hard, it is not well understood how various deformation mechanisms contribute to the mechanical response of such films. Studies are needed that characterize the structure of these films over length scales ranging from atoms to nanosized grains, to the interfacial regions, to the entire film. Nanoindentation studies are needed to elucidate the deformation behavior over scales ranging from single nanoparticles to continuous nanostructured films. There is a need to develop atomistic and larger-scale numerical models to simulate nanoparticle deformation, in the contexts both of high-velocity particle impact on a surface and of the mechanical behavior of a nanostructured film.

*Superhardness: hardness rivalling diamond, wear-resistance superior to diamond*

Several recent studies have suggested that it should be possible to deposit nanocomposite coatings whose hardness rivals diamond, but which have other wear properties superior to diamond. Veprek and coworkers have suggested [6] that by appropriate choices of such composite materials one could avoid grain boundary sliding and thus obtain “superhardness” as the grain size drops below about 10 nm. This group recently reported a hardness of 80-105 GPa, comparable to diamond, for a nanocomposite consisting of mixed nanocrystalline grains of TiN and TiSi$_x$ ($x \approx 2$). As such nanocomposite material combinations are virtually unexplored, there is excellent reason to believe that combinations can be found that exhibit superhardness while also possessing other excellent wear properties (e.g. high hot hardness, fracture toughness, resistance to oxidation and chemical attack, low coefficient of friction).

*Friction- and wear-resistant MEMS*

Researchers in Japan have used narrow beams of nanoparticles together with microfabrication techniques to fabricate miniature piezoelectric actuators [7], but otherwise the use of nanoparticles in microfabrication, especially for MEMS, is largely unexplored. Tremendous opportunities exist, particularly as friction and wear are presently serious limitations in MEMS development. However, practical methods must be developed, that both deliver nanoparticles to a surface with sufficient precision and integrate that capability into MEMS fabrication systems.

References


