

This issue of *MRS Bulletin* introduces a new department, TECHNOLOGY ADVANCES.

This department provides up-to-date reports of materials developments that begin to bridge the gap between research innovation and application of advanced materials technologies. Coordinated by *MRS Bulletin's* 2000 Visiting Scientist, Renée G. Ford of Renford Communications, Ltd., the articles present new developments and their progress toward appli-

cations. Opportunities for outside interaction, such as collaborations or technology licensing, are listed at the end of each article to facilitate further advancement of the technology. While it may not be possible to predict which technologies will be successful in the commercial market, the examples cited here present some paths to consider.

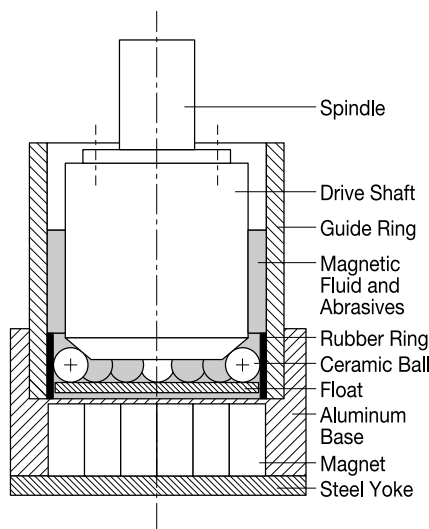
Magnetic Float Polishing Provides Improved Method for Finishing Advanced Ceramic Balls for Bearings

At Oklahoma State University (OSU), magnetic float polishing (MFP), a technique that was initially investigated in Japan, has been further developed and combined with chemical-mechanical polishing (CMP) to polish ceramic balls. The Si_3N_4 balls produced by the OSU finishing technology are reported to be of sufficient quality for bearing applications, and the process has also been found to be successful for finishing balls of other advanced ceramics and glasses.

Among various advanced ceramics, Si_3N_4 , because of its high toughness, is the material of choice for ceramic bearings. A critical factor affecting the performance and reliability of advanced ceramics for hybrid bearing applications is the quality of the surface produced by polishing. Furthermore, because of their high hardness and inherent brittleness, ceramics are extremely sensitive to surface defects caused by grinding and polishing. Since fatigue failure is directly related to surface imperfections, defects must be minimized in order to achieve the required performance reliability in service.

The conventional finishing of Si_3N_4 balls is essentially similar to the method used (V-groove lapping) for the finishing of steel balls, which involves low polishing speeds (~50 rpm), high loads (~10 N per ball), and use of a costly diamond abrasive. With MFP, the material removal rate can be high (~1 $\mu\text{m}/\text{min}$). The abrasives used are closer to the hardness of the work material, which minimizes the damage in the initial stages, and are considerably less costly than diamond abrasive. Ceria (CeO_2) has been found to be the most effective abrasive for finishing Si_3N_4 balls, producing a damage-free surface with a surface roughness R_a of <4 nm, a total roughness (peak to valley), R_t , of <4 nm, and sphericity 0.15–0.25 μm .

The MFP technique is based on the magneto-hydrodynamic behavior of a



Schematic of the magnetic float polishing (MFP) apparatus for finishing Si_3N_4 balls.

magnetic fluid that levitates nonmagnetic objects dispersed in it. Either permanent or electromagnets can be used. The figure above shows a schematic of the apparatus used with permanent magnets. A bank of Nd-Fe-B magnets, arranged so that the direction of their north and south poles is alternated, are positioned below an aluminum chamber filled with the required amount of magnetic fluid and an appro-

propriate abrasive (5–10 vol%). When a magnetic field is applied, the magnetic particles in the fluid are attracted downward to the region of the higher magnetic field, and an upward buoyant force is exerted on all nonmagnetic materials to push them to the area of lower magnetic field. The abrasive grains and the acrylic float (flexible support) are inside the chamber. Since these are diamagnetic materials, they are levitated by the magnetic buoyant force. The forces applied by the abrasive on the ceramic balls are extremely low (<1 N/ball) and controllable.

The ceramic balls are carried by an acrylic float, which produces uniform polishing pressure. The drive shaft is fed down to contact the balls (three-point contact) and press them down to reach the desired force or height. The balls are polished by the abrasive grains under the action of the magnetic levitational force as the spindle rotates. The higher polishing speeds (1000–10,000 rpm) considerably reduce the overall finishing time. These higher speeds are achievable because the polishing shaft is driven by a high-speed, high-precision air-bearing spindle with a stepless speed regulation up to 10,000 rpm. A batch of balls can be finished in 16–20 h (actual polishing time). The potential damage at and near the surface of the polished ceramic balls is minimized by the very low polishing load plus the use of a flexible support.

Chemical-mechanical polishing (CMP) depends on both the chemical and mechanical effectiveness of the abrasive in relation to the material being polished and the environment under the polishing conditions. Because material removal from Si_3N_4 by CMP does not depend on the hardness of the abrasive but on the chemical potential and the removal of the reaction layer, abrasives considerably softer than Si_3N_4 can be used. The abrasive reacts chemically (oxidation-reduction) with the Si_3N_4 to form a thin layer of silicon dioxide (SiO_2) on the surface that can be removed by water plus the abrasive. The chemical reaction can continue only when this layer is removed continuously.

Technology Advances provides up-to-date reports of materials developments that show potential to bridge the gap between research innovation and application of advanced materials technologies. If you encounter or are involved with materials research that shows potential for commercialization and would like to present these developments, contact Renée G. Ford, Renford Communications, Ltd., P.O. Box 72, Harrison, NY 10528-0072; tel. 914-967-0955; fax 914-967-7927; or e-mail renford@compuserve.com.

The surface of a uniaxially hot-pressed Si_3N_4 ball, finished using the MFP technique from an initial diameter of 13.4 mm to a final diameter of 12.7 mm, shows an essentially smooth surface with minimal surface defects. Application of the MFP technique obtains a very high finish and accuracy with very little or no surface and near-surface damage, such as microcracks, because of the extremely low levels of controlled force used. This technique is considerably faster than conventional V-groove lapping; it can process small batches (10–20 balls), unlike conventional lapping where a large number is required to meet the alignment and accuracy requirements; and it requires fewer polishing steps because the balls can be processed from the as-received condition to the finished condition in one operation; therefore, the polishing equipment does not need to be changed for roughing, semi-finishing, and finishing. The financial benefit of MFP is that it can be incorporated readily into an existing manufacturing facility, keeping capital costs low, and it runs on relatively low costs largely because of the use of conventional abrasives and the less severe polishing conditions.

The finishing technology developed at OSU has also been demonstrated for finishing batches of balls of other advanced ceramics, such as alumina (Al_2O_3) and zirconia (ZrO_2), as well as glasses.

Opportunities

Oklahoma State University is interested in establishing strategic alliances for commercialization of this technology with both small and large manufacturers. A range of options are available, including joint ventures, technology licensing, and venture-capital investment.

Source: For technology, Dr. Ranga Komanduri, Professor and MOST Chair in Intelligent Manufacturing, Mechanical & Aerospace Engineering, Oklahoma State University, Stillwater, OK 74078; tel. 405-744-5900; fax 405-744-7873; e-mail ranga@ceat.okstate.edu. For commercialization: Dr. Guven Yalcintas, Director of Intellectual Property Rights, Oklahoma State University, Stillwater, OK 74078; tel. 405-744-8920; fax 405-744-8979; e-mail: yalcint@okstate.edu.

Technique Combines Fiber Bundling and Filler Removal to Form Tailored Multichannel Porous Materials

A technique for the fabrication of multichannel porous materials (MPM) and components with strictly controlled diameter, length, and distribution of hollow channels has been patented (U.S. Patent 5,774,779) by the Material and Electrochemical Research Corporation (MER). The process



Multichannel tubes produced by the multichannel porous materials (MPM) technique.

combines two types of existing technologies: (1) bundling fibers and drawing them down, and (2) removing a second phase to produce a porous material. The technique can be used to produce a variety of porous profiles, sheets, rods, tubes, and near-net-shape products with tailored properties.

The process for fabricating MPMs involves three key steps. In the first step, rods composed of two materials in the form of an outer shell and an inner core are made by coextruding, using two extruders, two different powders previously mixed with thermoplastic binders (similar to those used for injection molding). During the coextrusion, the mixture of the matrix powder consisting of a material such as steel, Ti, Cu, other metals, or a ceramic with a binder becomes the matrix for the multichannel structure, and forms the shell of the bimaterial rod. The second powder, an organic or inorganic filler material plus a binder, forms the core of the bimaterial rod. (The core material subsequently is removed through evaporation, melting, or dissolution to form channels or other pore shapes such as spiral or conic.) The core can occupy from 1% to 95% of the rod's cross section. The diameter of the bimaterial rods produced in this first step can range from 100 μm to 20,000 μm .

Depending on the desired shape and size of the final product, the second step presents two options. The first involves re-extruding the bundle of rods through a die to produce a green composite with a specified diameter, number of fibers, and cross section. The alternative is to compact the material in a die without further extrusion of the rods. The compacting process makes it possible to fabricate complex shapes.

Temperature and composition of the mixture affect the plasticity of the green bodies and can be adjusted to allow extensive plastic deformation during forming. Both re-extrusion and compaction of the shells of the bimaterial rods join to form a green body consisting of a continuous matrix (matrix powder + binder) "reinforced" with fiber cores (filler powder + binder).

In a third step, the binder is burned out and the green body is sintered, causing the fibers to burn out and leaving behind open channels.

The figure shows examples of the variety of MPM densities and anisotropies that can be produced with this technique. The size, shape (straight, spiral, or conical), distribution, and number of channels can be controlled via extrusion or compacting or both. The process is applicable to most materials, including metals, alloys, intermetallics, ceramics, and composites. Near-net-shape components with densities from 5% to 100% can be obtained. The walls between the channels can be either porous or nonporous, and single-layer or multilayer.

The mechanical properties and plasticity of MPMs are reported to be much higher than those of conventional porous materials. Traditional powder metallurgy methods often produce materials with irregularly shaped and distributed pores that can act as stress concentrators that degrade strength and ductility, particularly at high porosity. The expectation is that in certain structural applications, MPMs could even replace nonporous materials fabricated by powder metallurgy and other particulate processes, thereby realizing weight savings of 30–40%.

The developers suggest several potential applications, including biomedical im-

plants, highly efficient filters, “biporous” filters using the additional porosity of the walls between channels for a second level of filtering, heat exchangers (owing to the large surface area of MPMs), and self-lubricating composites.

For biomedical implants, tailoring diameter, orientation, and distribution of pore channels can help optimize the load-bearing properties of the implant.

Traditionally, pipe-type heat-exchanger development has been largely directed to increasing the outer surface area of pipes. The diameter of the ribs of the tubes in heat exchangers is generally about three to five times that of the pipe itself. Consequently, the tubes have to be placed at a considerable distance from each other, which increases the size of the heat exchanger. An appropriately designed MPM would reduce considerably the distance between tubes, thus enabling more compact designs. The developers further suggest that this could lead to the development of innovative concepts for high-temperature, structural load-bearing heat exchangers to provide controlled cooling in aerospace vehicles, and that MPMs with very small diameter channels could be used for fabricating micro heat exchangers for electronic devices and miniaturized energy systems.

Filling the channels with lubricants can create self-lubricating composites. In tribological tests of silicon nitride MPMs infiltrated with a lubricating polymer, a marked reduction in the friction coefficient was obtained, with minimal loss of mechanical strength. Lightweight, strong composites for load-bearing parts could be made by infiltrating with low melting temperature alloys or resins.

Opportunities

The MER Corp. is interested in working with companies on joint applications development.

Source: Lev Tuchinsky, Senior Research Manager, MER Corp., 7960 S. Kolb Rd., Tucson, AZ 85706; tel. 520-574-1980 ext. 31; fax 520-574-1983; e-mail ltuch@opus1.com.

Rigid Urethane Foams Produced from Soybean Oil Demonstrate More Thermal Stability than Petrochemical-Based Foams

A polyol with a good balance between hydroxyl content and viscosity has been synthesized at the Kansas Polymer Research Center from soybean oil, and rigid urethane foams have been created from a blend of this soy polyol and glycerin. These foams have comparable

mechanical and insulating properties to conventional foams of petrochemical origin, plus higher thermal and thermo-oxidative stabilities than conventional petrochemical foams.

Rigid polyurethane foams are widely used in thermal insulation and packaging because of their higher strength and weight-carrying capacity, compared with other commercial packaging foam materials, as well as their ease of processing and their ability to be formed into complex shapes. Most rigid urethane foams are based on polypropylene oxide (PPO) triols and MDI (diphenyl methane-4,4'-diisocyanate). PPO polyols (polyalcohols) are relatively inexpensive materials, but foams based on them tend to be sensitive to hydrolysis and to absorb moisture. Replacing PPO-based rigid urethane foams with vegetable oil-based polyurethane foams would overcome these limitations, provided that the mechanical and thermal insulating properties are comparable.

Although polyols of natural origin, such as castor oil and those derived from the chemical transformation of vegetable or fish oils, have been used as building blocks for polyurethane materials, the challenge has remained to find natural polyols that both perform well and can be produced economically. Performance relies on achieving a proper balance between hydroxyl content and viscosity. The economics of their production is tied to the price and the availability of the starting oils and their transformation processes. Since most vegetable oils are more expensive than petroleum-based raw materials, to transform them cost-effectively requires minimizing the number of steps and using cost-effective reagents.

The soy polyol is prepared in a two-stage process. First, soybean oil is chemically reacted to form epoxidized soybean oil (ESO). The raw (or commercially available) ESO is then directly reacted with methanol to yield the soy polyol. This process is applicable to a variety of vegetable oils. Soy polyols prepared in this way are comparable in price to commercial petroleum-based polyols. The density of soy polyol is 1.018 g/cm³, and the color is yellow or pale yellow. Hydroxyl numbers of 184, 196, and 215 mg KOH/g give a viscosity of 7200, 6000, and 10,400 mPa s at 30°C, respectively. Polyurethane cast resins, rigid foams, binders, sealants, adhesives, and coatings are among their potential uses.

Soy-based foams have a compressive strength that is about 50% higher than the PPO-based foams. Their thermal-insulating

properties are comparable, with *R* (thermal resistivity) values of about 53 mK/W for PPO foam and about 55 mK/W for soy-204. Soy-based rigid polyurethane foams using cyclopentane as the blowing agent are similar in strength to hydrochlorofluorocarbon (HCFC)-blown soy foams. Cyclopentane is believed to be more compatible with soy-based polyols than with PPO-based polyols, owing to a closer polarity to the former.

Glycerin works well as a cross-linker, having a high hydroxyl content and a suitable viscosity for blending with soy polyols. The compressive strength increases linearly with the amount of glycerin, but an excessive amount results in brittle foams. Water has traditionally been added to rigid-foam formulations because it reacts with isocyanate to form very rigid polyurea structures in the foam, increasing its strength. The researchers found that the compressive strength of soy foams increases exponentially with an increasing amount of water. Fully water-blown soy foams are also feasible, and work in this direction is in progress.

A comparison of the thermal and thermo-oxidative behaviors of soy-based and PPO-based foams indicates that the former are more stable toward both thermal degradation and thermal oxidation. The PPO-based polyol contains ether linkages in the molecule, which are less stable toward thermal degradation and thermal oxidation than the hydrocarbon and ester linkages present in the soy polyol. It is suggested by the developers that the absence of ether linkages is the reason the soy polyols are much more stable than PPO-based polyols with respect to thermal oxidation. Because of their greater stability when exposed to heat and humidity, soy-based rigid urethane foams are expected to find particular use for thermal insulation in refrigeration, for hot-pipe and underground pipeline wrappings, and for other application areas where a hydrophobic polyol is required.

Opportunities

The Kansas Polymer Research Center welcomes inquiries regarding collaborative and consultative applications research, pilot-plant production of soy polyols, and licensing of soy polyols and their rigid urethane-foam technologies.

Source: Dr. Andrew Guo, Research Scientist, and Dr. Zoran Petrovic, Research Director, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS 66762-7560; tel. 316-235-4928; fax 316-235-4919; e-mail zpetrovi@pittstate.edu. □