that the addition of fumed silica stiffens the aerogel network and reduces shrinkage during the supercritical-drying stage. Minimization of shrinkage enables establishment of intimate contact between thermoelectric legs and the composite material, thereby maximizing the effectiveness of the material for thermal insulation and suppression of sublimation.

To some extent, the properties of the composite can be tailored via the proportions of titania and other ingredients. In particular (see figure), the addition of a suitably large proportion of titania (e.g., 0.6 g/cm^3) along with a 10-percent increase in the amount of tetraethylorthosilicate [TEOS (an ingredient of the sol)] to an aerogel component having a density 40 mg/cm^3 makes it possible to cast a high-average-density (>0.1 g/cm^3) aerogel/particle composite having low shrinkage (2.3 percent).

This work was done by Jong-Ah Paik, Jeffrey Sakamoto, and Steven Jones of Caltech for **NASA's Jet Propulsion Laboratory**. *Further information is contained in a TSP (see page 1).*

In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

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Refer to NPO-42031, volume and number of this NASA Tech Briefs *issue, and the page number.*

Patches for Repairing Ceramics and Ceramic-Matrix Composites

Patches are simply pressed in place, then heated.

Lyndon B. Johnson Space Center, Houston, Texas

Patches consisting mostly of ceramic fabrics impregnated with partially cured polymers and ceramic particles are being developed as means of repairing ceramics and ceramic-matrix composites (CMCs) that must withstand temperatures above the melting points of refractory metal alloys. These patches were conceived for use by space-suited, space-walking astronauts in repairing damaged space-shuttle leading edges: as such, these patches could be applied in the field, in relatively simple procedures, and with minimal requirements for specialized tools. These design characteristics also make the patches useful for repairing ceramics and CMCs in terrestrial settings.

In a typical patch as supplied to an astronaut or repair technician, the polymer would be in a tacky condition, denoted as an "A" stage, produced by partial polymerization of a monomeric liquid. The patch would be pressed against the ceramic or CMC object to be repaired, relying on the tackiness for temporary adhesion. The patch would then be bonded to the workpiece and cured by using a portable device to heat the polymer to a curing temperature above ambient temperature but well below the maximum operating temperature to which the workpiece is expected to be exposed. The patch would subsequently become pyrolized to a ceramic/glass condition upon initial exposure to the high operating temperature. In the original space-shuttle application, this exposure would be Earth-atmosphere-reentry heating to about 3,000 °F (about 1,600 °C).

Patch formulations for space-shuttle applications include SiC and ZrO_2 fabrics, a commercial SiC-based pre-ceramic polymer, and suitable proportions of both SiC and ZrO_2 particles having sizes of the order of 1 µm. These formulations have been tailored for the space-shuttle leading-edge material, atmospheric composition, and reentry temperature profile so as to enable repairs to survive re-entry heating with expected margin. Other formulations could be tailored for specific terrestrial applications.

This work was done by Peter A. Hogenson, Gordon R. Toombs, Steven Adam, and James V. Tompkins of The Boeing Co. for **Johnson Space Center**.

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act {42 U.S.C. 2457(f)}, to The Boeing Company. Inquiries concerning licenses for its commercial development should be addressed to:

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Refer to MSC-24018, volume and number of this NASA Tech Briefs *issue, and the page number.*

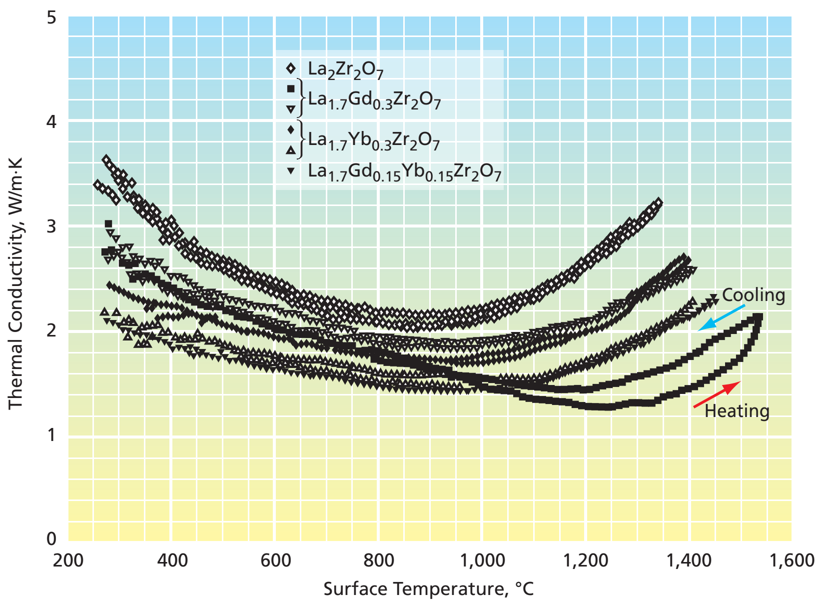
Lower-Conductivity Ceramic Materials for Thermal-Barrier Coatings

Thermal conductivities of certain pyrochlore oxides can be reduced by doping.

John H. Glenn Research Center, Cleveland, Ohio

Doped pyrochlore oxides of a type described below are under consideration as alternative materials for high-temperature thermal-barrier coatings (TBCs). In comparison with partially-yttria-stabilized zirconia (YSZ), which is the state-of-the-art TBC material now in commercial use, these doped pyrochlore oxides exhibit lower thermal conductivities, which could be exploited to obtain the following advantages:

- For a given difference in temperature between an outer coating surface and the coating/substrate interface, the coating could be thinner. Reductions in coating thicknesses could translate to reductions in weight of hot-section components of turbine engines (e.g., combustor liners, blades, and vanes) to



Measured Thermal Conductivities of hot-pressed disks of several related pyrochlore oxide compositions illustrate the benefit afforded by doping.

which TBCs are typically applied.

- For a given coating thickness, the difference in temperature between the outer coating surface and the coating/substrate interface could be greater. For turbine engines, this could translate to higher operating temperatures, with consequent increases in efficiency and reductions in polluting emissions.

TBCs are needed because the temperatures in some turbine-engine hot sections exceed the maximum temperatures that the substrate materials (superalloys, Si-based ceramics, and others) can withstand. YSZ TBCs are applied to engine components as thin layers by plasma spraying or electron-beam physical vapor deposition. During operation at higher temperatures, YSZ layers undergo sintering, which increases their thermal conductivities and thereby renders them less effective as TBCs. Moreover, the sintered YSZ TBCs are less tolerant of stress and strain and, hence, are less durable.

The materials that are sought as alternatives to YSZ are required to have and retain lower thermal conductivities and to be better able to withstand temperatures that degrade TBCs made of YSZ. The undoped versions of the doped pyrochlore oxides of the type now under consideration as alternatives to YSZ are of general composition $Ma_2Mb_2O_7$, where *Ma* denotes a 3+ cation (for example, La to Lu) and *Mb* a 4+ cation (for example, Zr, Hf, Ti). Doping has been investigated as a means of reducing thermal conductivities even further below those of YSZ coatings. In the doping approach investigated thus far, another cation is substituted for part of *Ma*, yielding a general composition of $Ma_{2-x}M_xMb_2O_7$, where x lies between 0 and 0.5 and *M* denotes a rare-earth or other suitable element.

In experiments, powders of various compositions were synthesized by a modified sol-gel method and calcined at appropriate temperatures to convert them into compounds of pyrochlore structure as confirmed by x-ray diffraction. These powders were hot pressed into dense disks of 1-in. (2.54-cm) diameter. The thermal conductivities of the disks were measured at various temperatures up to 1,550 °C by use of a steady-state laser heat-flux technique. The figure presents results of such measurements performed on several materials of general composition $La_{2-x}(Gd\ \text{and/or}\ Yb)_xZr_2O_7$, where $x = 0$ or 0.3. The thermal conductivities of all doped samples ($x = 0.3$) were less than those of the undoped ($x = 0$) sample [$La_2Zr_2O_7$]. The lowest conductivity — ranging from 40 to 50 percent below that of undoped sample — was exhibited by the sample co-doped with both Gd and Yb.

This work was done by Narottam P. Bansal of **Glenn Research Center** *and Dongming Zhu of the U. S. Army Research Laboratory. Further information is contained in a TSP (see page 1).*

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