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Inquiries concerning rights for the commercial use of this invention should be addressed to the Patent Counsel, Ames Research Center, (650) 604-5104. Refer to ARC-15092.

Scandia-and-Yttria-Stabilized Zirconia for Thermal Barriers

These compositions offer thermal stability greater than that of yttria-stabilized zirconia.

John H. Glenn Research Center, Cleveland, Ohio

Zirconia stabilized with both scandia and yttria in suitable proportions has shown promise of being a superior thermal-barrier coating (TBC) material, relative to zirconia stabilized with yttria only. More specifically, a range of compositions in the zirconia/scandia/yttria material system has been found to afford increased resistance to deleterious phase transformations at temperatures high enough to cause deterioration of yttria-stabilized zirconia.

Yttria-stabilized zirconia TBCs have been applied to metallic substrates in gas turbine and jet engines to protect the substrates against high operating temperatures. These coatings have porous and microcracked structures, which can accommodate strains induced by thermal-expansion mismatch and thermal shock. The longevity of such a coating depends upon yttria as a stabilizing additive that helps to maintain the zirconia in an yttria-rich, so-called “non-transformable” tetragonal crystallographic phase, thus preventing transformation to the monoclinic phase with an associated deleterious volume

change. However, at a temperature greater than about 1,200 °C, there is sufficient atomic mobility that the equilibrium, transformable zirconia phase is formed. Upon subsequent cooling, this phase transforms to the monoclinic phase, with an associated volume change that adversely affects the integrity of the coating.

Recently, scandia was identified as a stabilizer that could be used instead of, or in addition to, yttria. Of particular interest are scandia-and-yttria-stabilized zirconia (SYSZ) compositions of about 6 mole percent scandia and 1 mole percent yttria, which have been found to exhibit remarkable phase stability at a temperature of 1,400 °C in simple aging tests. Unfortunately, scandia is expensive, so that the problem becomes one of determining whether there are compositions with smaller proportions of scandia that afford the required high-temperature stability. In an attempt to solve this problem, experiments were performed on specimens made with reduced proportions of scandia. The criterion used to judge

these specimens was whether they retained the “non-transformable” tetragonal phase after a severe heat treatment of 140 hours at 1,400 °C. On the basis of this criterion and limited data, the locus of favored compositions is specified as follows: mole percent of yttria = $8.55 - 1.5 \times$ (mole percent of scandia) between and near the compositional end points of

- 4.9 mole percent scandia and 1.2 mole percent yttria and
- 3.7 mole percent scandia and 3.0 mole percent yttria.

In addition, it appears that a composition of ≈ 3 mole percent scandia and ≈ 2.5 mole percent yttria may confer the desired phase stability at 1,400 °C.

This work was done by Derek Mess of Cambridge Microtech, Inc., for Glenn Research Center. Further information is contained in a TSP (see page 1).

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Commercial Technology Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-16789.

Environmentally Safer, Less Toxic Fire-Extinguishing Agents

Water droplets would be microencapsulated in flame-retardant polymers.

John F. Kennedy Space Center, Florida

Fire-extinguishing agents comprising microscopic drops of water microencapsulated in flame-retardant polymers have been proposed as effective, less toxic, non-ozone-depleting, non-global-warming alternatives to prior fire-extinguishing agents. Among the prior fire-extinguishing agents are halons (various halocarbon fluids), which are toxic and contribute both to depletion of upper-atmospheric ozone and to global warming. Other prior fire-extinguishing agents are less toxic and less environmentally harmful but, in comparison

with halons, are significantly less effective in extinguishing fires.

The proposal to formulate new water-based agents is based on recent success in the use of water mist as a fire-suppression agent. Water suppresses a flame by reducing the flame temperature and the concentration of oxygen available for the combustion process. The temperature is reduced because the water droplets in the mist absorb latent heat of vaporization as they evaporate. The concentration of oxygen is reduced because the newly generated

water vapor displaces air.

Unfortunately, water mists are difficult to produce in confined spaces and can evaporate before they reach the bases of flames. The proposal addresses both of these issues: The proposed fire-extinguishing agents would be manufactured in microencapsulated form in advance, eliminating the problem of generating mists in confined spaces. Because of the microencapsulation, the droplets would not evaporate until exposed directly to the heat of flames. In addition, the proposal calls for the in-

production of free radicals that would inhibit the propagation of the chemical reactions of the combustion reactions.

Manufacturing of a fire-extinguishing agent according to the proposal would begin with the formulation of a suitable polymer (e.g., a polybromostyrene) that would contribute free radicals to the combustion process. The polymer would be dissolved in a suitable hydrocarbon

liquid (e.g., toluene). Water would be dispersed in the polymer/toluene solution, then another hydrocarbon liquid (e.g., hexane) that is not a solvent for the polymer would be added to the mixture to make the dissolved polymer precipitate onto the water droplets. The resulting polymer-coated droplets would be removed from the coating mixture by filtration, dried, and stored for use.

This work was done by Clyde F. Parrish of Kennedy Space Center.

This invention is owned by NASA, and a patent application has been filed. Inquiries concerning nonexclusive or exclusive license for its commercial development should be addressed to the Technology Programs and Commercialization Office, Kennedy Space Center, (321) 867-8130. Refer to KSC-12236.

Multiaxial Temperature- and Time-Dependent Failure Model

This model should be applicable to a variety of materials.

Marshall Space Flight Center, Alabama

A temperature- and time-dependent mathematical model predicts the conditions for failure of a material subjected to multiaxial stress. The model was initially applied to a filled epoxy below its glass-transition temperature, and is expected to be applicable to other materials, at least below their glass-transition temperatures. The model is justified simply by the fact that it closely approximates the experimentally observed failure behavior of this material: The multiaxiality of the model has been confirmed (see figure) and the model has been shown to be applicable at temperatures from -20 to 115 °F (-29 to 46 °C) and to predict tensile failures of constant-load and constant-load-rate specimens with failure times ranging from minutes to months.

The model is embodied in the following equation for the failure condition:

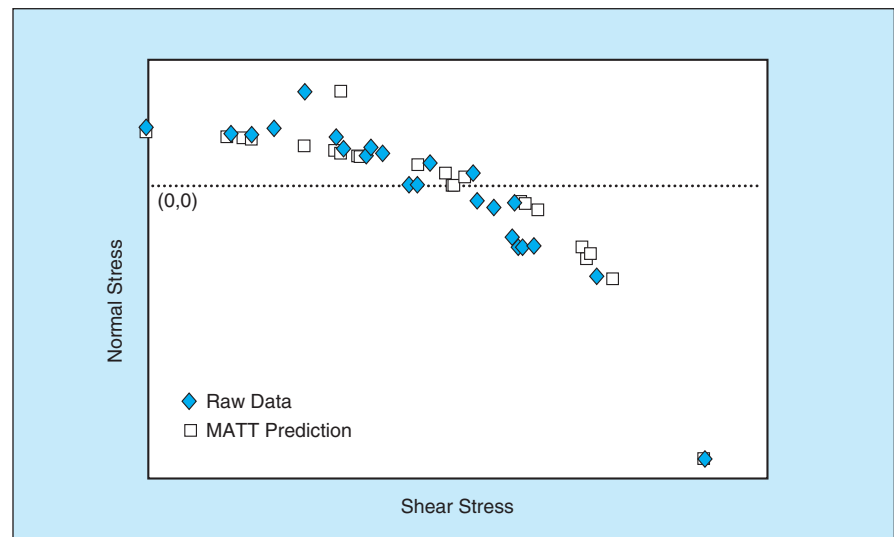
$$AP^2J_2 + BP I_1 = 1$$

where

- A and B are parameters that define the shape of an ellipsoidal failure surface in multiaxial stress space;
- P is a scaling factor that accounts for the temperature and time dependences of the material;
- J_2 is the second deviatoric stress invariant, given by

$$\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2 - \sigma_{11}\sigma_{22} - \sigma_{11}\sigma_{33} - \sigma_{22}\sigma_{33} + 3(\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{23}^2)$$

- I_1 is the first stress invariant, given by $\sigma_{11} + \sigma_{22} + \sigma_{33}$;
- the numerical subscripts denote Cartesian coordinate axes; and
- σ_{ij} denotes the stress.



Experimental and Predicted Failure Points are plotted here for "napkin-ring" specimens of a filled epoxy that were loaded with both normal and shear stresses at a temperature of 70 °F (21 °C).

In the special case of constant P , this model is equivalent to a modified Drucker-Pager model, and to the Tsai-Wu failure model that is traditionally used in evaluating composite materials.

The model is calibrated by use of data from tensile and shear failure experiments. Data from tensile-adhesion and shear-adhesion failure tests of the material to which the model was initially applied show that the ratio between shear and tensile failure loads has a value of ≈ 0.8 , independent of time and temperature. This constant ratio, in combination with one sensor data point, can be used to calculate the values of A (1.0 for this material) and B (0.31754 for this material).

The value of the scale factor P is simply whatever value is needed to

make a given failure surface pass through a known failure point for a given temperature and failure time. Hence, for example, once A and B are known, P as a function of time and temperature can be determined simply by solving the basic model equation for P and then inserting stress values from tensile or shear tests that involve known failure times and temperatures.

This work was done by David Richardson, Michael McLennan, Gregory Anderson, David Macon, and Alicia Batista-Rodriguez of Thiokol Propulsion Corp. for Marshall Space Flight Center. For further information, please contact the company at (435) 863-3511. MFS-31750