Multicomponent, Rare-Earth-Doped Thermal-Barrier Coatings

Thermal conductivities are reduced while maximum use temperatures are increased.

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Multicomponent, rare-earth-doped, perovskite-type thermal-barrier coating materials have been developed in an effort to obtain lower thermal conductivity, greater phase stability, and greater high-temperature capability, relative to those of the prior thermal-barrier coating material of choice, which is yttria-partially stabilized zirconia. As used here, "thermal-barrier coatings" (TBCs) denotes thin ceramic layers used to insulate air-cooled metallic components of heat engines (e.g., gas turbines) from hot gases. These layers are generally fabricated by plasma spraying or physical vapor deposition of the TBC materials onto the metal components.

A TBC as deposited has some porosity, which is desirable in that it reduces the thermal conductivity below the intrinsic thermal conductivity of the fully dense form of the material. Undesirably, the thermal conductivity gradually increases because the porosity gradually decreases as a consequence of sintering during high-temperature service. Because of these and other considerations such as phase transformations, the maximum allowable service temperature for yttria-partially stabilized zirconia TBCs lies in the range of about 1,200 to 1,300 °C. In contrast, the present multicomponent, rare-earth-doped, perovskite-type TBCs can withstand higher temperatures.

A material of this type comprises the following ingredients:

- The base material is a high-melting-temperature perovskite oxide — a compound having the chemical formula ABO_3, where A is a metal cation having a valence of +2 and B is a metal cation having a valence of +4. Examples of A include Sr, Ba, Ca, and variable valence rare-earth and transition metals; examples of B include Zr and Hf.
- The base material is doped with a pair or multiple pairs of highly stable oxides of general chemical formula M_2O_3, where M is a metal cation of valence +3. The pairing of the oxides is such that they are related as electron donor and acceptor, respectively. The paired oxides can be divided into two groups, denoted I and II. Group I comprises scandia and ytterbia. The radii of their trivalent cations are smaller than those of zirconia and hafnia. The group-I cations are believed to typically become incorporated into B sites, where they are further believed to act as electron acceptors. Group II comprises neodymia, samaria, gadolinia, and lanthania. The radii of their trivalent cations are larger than that of yttria. The group-II cations are believed to typically become incorporated into A sites, where they are further believed to act as electron donors. The incorporation of the dopant trivalent cations into A and B sites enhances the stability of the base material phase and promotes the formation of significantly higher concentrations of immobile extended defects and clusters of defects, thereby greatly reducing the intrinsic thermal conductivity and the rate of sintering.
- Yttria can be included as a phase stabilizer in addition to, or instead of, the aforementioned dopant oxides.

In a preferred composition, the total concentration of yttria and/or the other phase-stabilizing oxides lies between 4 and 30 mole percent. Ytterbia is favored over scandia as the group-I oxide because of the high cost of scandia. Alternatively, scandia in a concentration of as much as 20 percent of that of yttria can be employed to overdope the group-I oxide. Other alternative formulations are also possible.

Compositions tested to date include $SrZrO_3$ + yttria (up to 6 mole percent) + group-I oxide (ytterbia) up to 2 mole percent + group-II oxide (gadolinia) up to 2 mole percent. Pre-sintering thermal conductivities, as determined by a laser heat-flux test at an initial surface temperature of about 3,000 °F (about 1,650 °C), have ranged between 0.6 and 0.8 W/m·K. Test data have also indicated that sintering essentially ceases after 20 hours. The thermal conductivities in the cases of compositions that include the paired doping oxides have been found to range from about a third to half of the thermal conductivities of undoped $SrZrO_3$ and of $SrZrO_3$ doped with yttria only. Excellent durability has also been demonstrated in the sintering and thermal-cycling tests at temperatures up to about 3,000 °F (about 1,650 °C).

This work was done by Robert A. Miller of **Glenn Research Center** *and Dongming Zhu of the U.S. Army Research Laboratory. 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, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17432-1.

Reactive Additives for Phenylethynyl-Containing Resins

Processability is improved.

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Phenylethynyl-containing reactive additive (PERA) compounds and mixtures have been found to be useful for improving the processability of oligomers, polymers, co-oligomers, and copolymers that contain phenylethynyl groups. The additives can be incorporated in different forms:

- A solution of an amide acid or an imide of a PERA can be added to a solution of phenylethynyl-containing oligomer, polymer, co-oligomer, or copolymer; or
- An imide powder of a PERA can be mixed with a dry powder of a phenyl-

ethynyl-containing oligomer, polymer, co-oligomer, or copolymer.

The effect of a given PERA on the processability and other properties of the resin system depends on whether the PERA is used in the amide acid or an imide form. With proper formulation, the PERA reduces the melt viscosity of the resin and thereby reduces the processing pressures needed to form the adhesive bonds, consolidate filled or unfilled moldings, or fabricate fiber-reinforced composite laminates. During thermal cure, a PERA reacts with itself as well as with the phenylethynyl-containing host resin and thereby becomes chemically incorporated into the resin system.

The effects of the PERA on mechanical properties, relative to those of the host resin, depend on the amount of PERA used. Typically, the incorporation of the PERA results in (1) increases in the glass-transition temperature (T_g), modulus of elasticity, and parameters that characterize behavior under compression, and (2) greater retention of the aforementioned mechanical properties at elevated temperatures without (3) significant reduction of toughness or damage tolerance.

Of the formulations tested thus far, the ones found to yield the best overall results were those for which the host resin was the amide acid form of a phenylethynyl-terminated imide (PETI) co-oligomer having a molecular weight of 5,000 g/mole [hence, designated PETI-5] and a PERA denoted as PERA-1. PETI-5 was made from 3,3′,4′4′-biphenyl-tetracarboxylic dianhydride, 3,4′-oxydianiline (3,4′-ODA), 1,3-bis(3-aminophenoxy) benzene (1,3-APB), and 4-phenylethynylphthalic anhydride (PEPA). PERA-1 was made from 3,5-diamino-4′-phenylethynylbenzophenon and equimolar amounts of phthalic anhydride and PEPA. To make PERA-1 in the imide form, the aforementioned ingredients were processed by refluxing in glacial acetic acid. To make the amide form of PERA-1, the ingredients were reacted in N-methyl-2-pyrrolidinone (NMP) under nitrogen at a temperature of 23 °C (see figure).

On the basis of the processability and other properties, a blend comprising 20 weight percent of PERA-1 and 80 weight percent PETI-5 was selected for further evaluation. Relative to neat PETI-5, the blend exhibited an increase in T_g; improved processability; and comparable values of shear strength in adhesion to titanium panels, open-hole compressive properties, compression properties after impact, and resistance to microcracking.
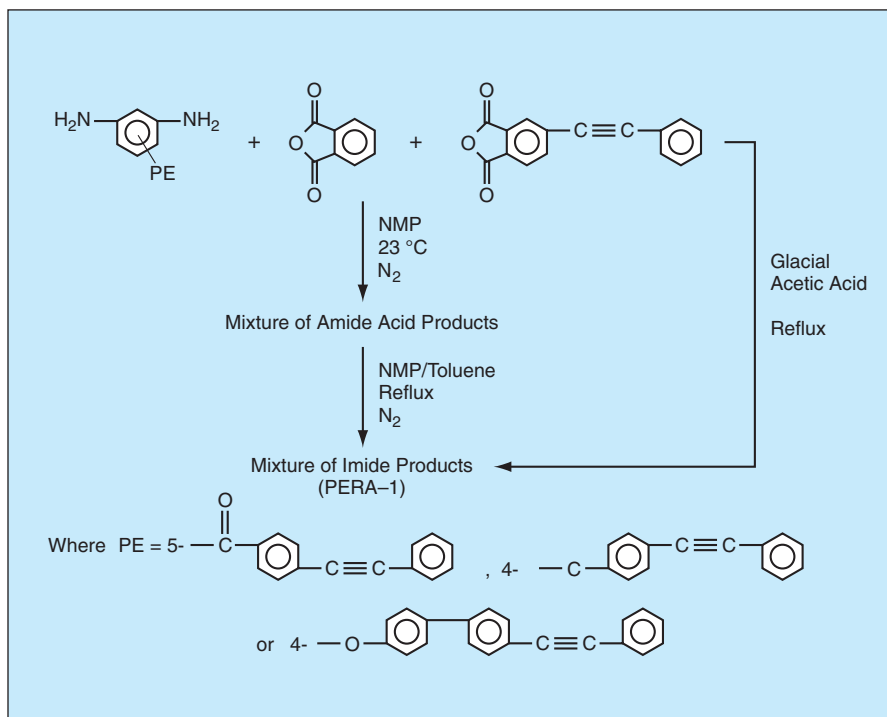
PERA-1 Is a Mixture of either amide acids or imides, depending upon which synthesis route is followed.