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-