Thermal Properties of Oxides With Magnetoplumbite Structure for Advanced Thermal Barrier Coatings

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Abstract

Oxides having magnetoplumbite structure are promising candidate materials for applications as high-temperature thermal barrier coatings because of their high thermal stability, high thermal expansion, and low thermal conductivity. In this study, powders of LaMgAl$_{11}$O$_{19}$, GdMgAl$_{11}$O$_{19}$, SmMgAl$_{11}$O$_{19}$, and Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ magnetoplumbite oxides were synthesized by citric acid sol-gel method and hot pressed into disk specimens. The thermal expansion coefficients (CTE) of these oxide materials were measured from room temperature to 1500 °C. The average CTE value was found to be ~9.6×10$^{-6}$/C. Thermal conductivity of these magnetoplumbite-based oxide materials was also evaluated using steady-state laser heat flux test method. The effects of doping on thermal properties were also examined. Thermal conductivity of the doped Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ composition was found to be lower than that of the undoped GdMgAl$_{11}$O$_{19}$. In contrast, thermal expansion coefficient was found to be independent of the oxide composition and appears to be controlled by the magnetoplumbite crystal structure. Thermal conductivity testing of LaMgAl$_{11}$O$_{19}$ and LaMnAl$_{11}$O$_{19}$ magnetoplumbite oxide coatings plasma sprayed on NiCrAlY/Rene N5 superalloy substrates indicated resistance of these coatings to sintering even at temperatures as high as 1600 °C.

Introduction

Thermal and environmental barrier coatings (T/EBCs) (refs. 1 to 4) will play a crucial role in advanced gas turbine engine systems because of their ability to significantly increase engine operating temperature and reduce cooling, thus greatly help to achieve low emission and high efficiency goals. Under the NASA Ultra Efficient Engine Technology (UEET) program, advanced T/EBC systems are being developed to provide vital thermal and environmental protection for Si-based ceramic components such as combustor liner and vanes at gas temperatures exceeding 1760 °C (3200 °F) in the harsh oxidizing and water-vapor containing combustion environments of the turbine engines. The T/EBC system is required to have significantly increased phase stability, lower lattice and radiation thermal conductivity, and improved sintering and thermal stress resistance under the engine high-heat-flux and severe thermal cycling conditions.

Higher operating temperatures of turbine engines result in significant improvements in fuel consumption, efficiency, and emissions. The base materials (super-alloys, Si-based ceramics and composites, etc.) of the hot-section components have certain upper use temperature limits depending
upon their physical, mechanical and corrosion characteristics. To improve their performance, surfaces of these materials are coated with thermal/environmental barrier coatings. Zirconia partially stabilized with 7 wt% yttria (7YSZ) is the current state-of-the-art thermal barrier coating (TBC) material. However, use of 7YSZ is limited to 1200 °C. At higher temperatures, the relatively porous 7YSZ coating sinters resulting in higher thermal conductivity and making it less effective as TBC. The sintered and densified coatings can also reduce thermal stress/strain tolerance, which will have significant adverse effects on the durability of the TBC. To further increase the operating temperature of turbine engines, alternate TBC materials with lower thermal conductivity, higher operating temperatures and better sintering resistance are required.

Oxides with magnetoplumbite structure of the general composition , LnMAl11O19 (Ln = La to Gd; M = Mg, Mn to Zn), have high melting point, high thermal expansion, and low thermal conductivity which make them suitable for applications as high-temperature thermal barrier coatings. Also, sintering in these oxides is suppressed due to low ionic diffusion in magnetoplumbites. Lanthanum magnetoplumbites such as LaMAl11O19 (M = Mg, Mn to Zn, Cr, . . . .) have been earlier proposed (refs. 5 to 8) for TBC applications. However, the La-containing magnetoplumbites are not highly stable at elevated temperatures in water containing atmosphere, such as in the combustion environment of turbine engines, and show significant continuous weight loss (ref. 9). During water vapor stability testing of LaMAl11O19 magnetoplumbite at 1500 °C, significant weight loss of 0.037 mg/cm².h was observed (ref. 9) indicating poor stability in water-containing atmosphere. Magnetoplumbites of composition LnMAl11O19 (Ln = Ce to Gd; M = Mg, Mn to Zn, or a mixture of monovalent and trivalent ions) probably should have higher stability in water-containing combustion environment than the earlier proposed La-magnetoplumbites. Mechanical properties including flexure strength, fracture toughness and flexural creep of some of these magnetoplumbite oxides have been recently investigated (ref. 10).

It has been reported (refs. 11 and 12) that co-doping of YSZ (4.6 mol% Y2O3) with one or more oxides (Yb2O3, Gd2O3, Nd2O3, Sm2O3, Er2O3, Sc2O3, NiO) results in lower thermal conductivity due to defect cluster formation. Similar reduction in thermal conductivity has also been demonstrated (refs. 13 and 14) for La2Zr2O7 pyrochlore oxides by doping and co-doping with Gd and Yb at the La-site. The primary objective of the present study was to evaluate the thermal properties of various magnetoplumbite oxides. The thermal conductivity of a number of magnetoplumbite oxides has been measured at temperatures up to 1150 °C using a steady-state laser heat-flux technique. Coefficients of thermal expansion have also been determined from room temperature to 1500 °C. The effects of doping with other metal oxides in the magnetoplumbite structure on thermal conductivity have also been investigated. Preliminary results for LaMgAl11O19 and LaMnAl11O19 magnetoplumbite oxide coatings plasma sprayed on NiCrAlY/Rene N5 superalloy substrates are also presented.

**Experimental Methods**

**Powder Synthesis**

Sol-gel citric acid method was used for the powder synthesis of LnMgAl11O19 magnetoplumbite oxides where Ln = Gd, La, or Sm and the doped compound Gd0.7Yb0.3MgAl11O19. Details of powder processing approach used in the present study are described elsewhere (ref. 15). To describe the process briefly, stoichiometric amounts of Mg, Al, La, Sm, Gd, and Yb nitrates were dissolved in water. Calculated amount of citric acid (COOH CH2C(OH)COOHCH2COOH), about 1.2 moles per mole of metals in the nitrate solution, was separately dissolved in water. The metal nitrate solutions were gradually added to the boiling citric acid solution. A clear yellowish solution resulted depending on the composition of the metal nitrate mixtures. The solutions were heated at ~115 °C for about 48 hr to evaporate water and resulting in the formation of clear orange gels. On further heat treatment, the gels turned into yellowish foams. The foams were slowly heated (1 °C/min) to 350 °C and held for 5 to 8 hr to remove volatile organic compounds. The resulting brown porous materials were amorphous magnetoplumbite oxides and some charred organic material. The foams were grinded to powder and
further calcined at 800 °C for 5 to 8 hr to burn off residual carbon. From x-ray diffraction, the resulting white powders were found to be partially crystalline magnetoplumbites oxide. Small amounts of powders were also heat treated in ambient air at various temperatures.

**Hot Pressing**

For thermal conductivity and thermal expansion measurements, 10 g each of the above sol-gel derived powders were unidirectionally hot-pressed at 1600 °C and 27.6 MPa (4 KSI) pressure for 4 hr in vacuum using a 25.4 mm. diameter graphite die. Translucent beige colored disks of ~4.5 mm thickness were obtained. The hot pressed discs were heat treated at 800 °C for 8 hr in air for oxidation of the carbon in the samples.

**Plasma Spraying**

Spray-dried LaMgAl11O19 and LaMnAl11O19 magnetoplumbite oxide powders obtained from commercial source were used for plasma spraying. Rene N5 (General Electric Company, Fairfield, CT) nickel-base superalloy substrates (25.4 mm in diameter and 3.2 mm in thickness) were used. NiCrAlY bond coat was applied on Rene N5 by low-pressure plasma-spraying. For thermal conductivity measurements, LaMgAl11O19 and LaMnAl11O19 magnetoplumbite oxide coatings were plasma sprayed on to NiCrAlY/Rene N5 substrates.

**X-ray Diffraction**

X-ray diffraction (XRD) patterns were recorded at room temperature using a step scan procedure (0.02°/2θ step, count time 0.5 or 1 s). A Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing Copper Kα radiation was used.

**Thermal Expansion Measurements**

Thermal expansion measurements were carried out in air in a Unitherm (Unitherm Cemcon) high temperature dilatometer system (Anter Corporation, Pittsburgh, PA) from room temperature to 1500 °C with the heating and cooling rates of 5 °C/min, and 10 min dwell time at 1500 °C. The specimens used were 98 to 99 percent dense hot pressed disks 25.4 mm in diameter and ~2.8 mm in thickness. The average value of linear coefficient of thermal expansion was determined for each specimen using two heating and cooling cycles.

**Thermal Conductivity Measurements**

One inch diameter (25.4 mm) hot pressed discs were used for thermal conductivity measurements. Thermal conductivity testing of the ceramic discs or plasma sprayed coatings was carried out using a 3.5 kW CO2 laser (wavelength 10.6 μm) high-heat flux rig. A schematic diagram of the test rig is shown in figure 1. Photos of the actual test facilities and the general test approach have been described elsewhere (refs. 13, 16, and 17). In this steady-state laser heat flux test method, the specimen surface was heated by a laser beam, and backside air-cooling was used to maintain the desired temperature. A uniform laser heat flux was obtained over the 23.9 mm diameter aperture region of the specimen surface by using an integrating ZnSe lens combined with the specimen rotation. Platinum wire flat coils (wire diameter 0.38 mm) were used to form thin air gaps between the top aluminum aperture plate and stainless-steel back plate to minimize the specimen heat losses through the fixture.
Thermal conductivity of ceramic materials, $k$, can be determined from the pass-through heat flux $q_{\text{thru}}$ and measured temperature difference $\Delta T$ across the ceramic specimen thickness $l$ under the steady-state laser heating conditions

$$k = \frac{q_{\text{thru}} \cdot l}{\Delta T}$$

(1)

The actual pass-through heat flux $q_{\text{thru}}$ for a given ceramic specimen was obtained by subtracting the laser reflection loss (measured by a 10.6 μm reflectometer) and the calculated radiation heat loss (total emissivity was taken as 0.50 for the oxides) at the ceramic surface from the laser delivered heat flux, i.e.,

$$q_{\text{thru}} = q_{\text{delivered}} - q_{\text{reflected}} - q_{\text{radiated}}$$

(2)

Note that the non-reflected laser energy (approximately 97 percent of the total delivered laser energy) is absorbed at or near the specimen surfaces because of the quite high emissivity at the 10.6 μm laser wavelength region for the oxides. For the hot pressed bulk specimens, the temperature difference $\Delta T$ in the ceramic was directly measured by using two 8 μm pyrometers at both specimen front heating and back side air cooling surfaces.

**Results and Discussion**

X-ray diffraction patterns for the sol-gel derived powders of various magnetoplumbite compositions heat treated at 1400 °C are shown in figure 2. The XRD patterns match with the magnetoplumbite crystal structure (JCPDS card no. 26–873). Even after high temperature heat treatments, the powders do not appear to be completely crystalline and some amorphous phase is still present. This indicates that the crystallization of sol-gel prepared amorphous powder into magnetoplumbite structure proceeds slowly.
Figure 2.—X-ray diffraction patterns of sol-gel derived of LaMgAl$_{11}$O$_{19}$, SmMgAl$_{11}$O$_{19}$, and GdMgAl$_{11}$O$_{19}$ magnetoplumbite oxides compositions after 1400 °C heat treatments in air.
Results for thermal expansion measurements of LaMgAl$_{11}$O$_{19}$, SmMgAl$_{11}$O$_{19}$, and GdMgAl$_{11}$O$_{19}$ magnetoplumbite oxides from room temperature to 1500 °C are shown in figure 3. Data for the doped Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ magnetoplumbite composition are also included. The value of average thermal expansion coefficient of these materials, from room temperature to 1500 °C, is found to be ~9.5 to 9.7×10^{-6}/°C. Thermal expansion behavior of all these oxides appears to be independent of the composition. It appears that the thermal expansion of these oxides is controlled by their basic magnetoplumbite crystal structure rather than their composition based on the individual rare earth elements present. Thermal expansion of these magnetoplumbite materials is comparable to that of 7YSZ and also is a good match for the superalloys.

Thermal conductivity of LaMgAl$_{11}$O$_{19}$, SmMgAl$_{11}$O$_{19}$, and GdMgAl$_{11}$O$_{19}$ magnetoplumbite oxide specimens hot-pressed from sol-gel derived powders, as a function of surface test temperature from room temperature to 1150 °C, is shown in figure 4. The material thermal conductivity exhibited little temperature dependence. It is also apparent from figure 4 that the GdMgAl$_{11}$O$_{19}$ and SmMgAl$_{11}$O$_{19}$ compositions have lower thermal conductivity than LaMgAl$_{11}$O$_{19}$. Effect of doping with Yb at the Ln site in GdMgAl$_{11}$O$_{19}$ on the thermal conductivity is shown in figure 5. Results of figures 4 and 5 clearly show that the doped composition Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ has lower thermal conductivity than the undoped GdMgAl$_{11}$O$_{19}$ magnetoplumbite. In earlier studies (refs. 13 and 16) it has been reported that doping with one or more trivalent rare-earth elements Nd, Eu, Dy, Gd, and Yb cations at the A sites in A$_2$B$_2$O$_7$ pyrochlores, such as La$_2$Zr$_2$O$_7$, resulted in lower thermal conductivity. It has also been demonstrated (refs. 9, 11, and 12) that co-doping of HfO$_2$ and YSZ (4.6 mol% Y$_2$O$_3$) with one or more oxides (Yb$_2$O$_3$, Gd$_2$O$_3$, Nd$_2$O$_3$, Sm$_2$O$_3$, Er$_2$O$_3$, Sc$_2$O$_3$, NiO) resulted in lower thermal conductivity due to defect cluster formation.
Figure 4.—Thermal conductivity, as a function of surface test temperature, of LaMgAl$_{11}$O$_{19}$, SmMgAl$_{11}$O$_{19}$ and GdMgAl$_{11}$O$_{19}$ magnetoplumbite oxides hot-pressed from sol-gel derived powders.

Figure 5.—Thermal conductivity, as a function of surface test temperature, of GdMgAl$_{11}$O$_{19}$ and Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ magnetoplumbites oxide specimens hot-pressed from sol-gel derived powders. The rare earth doped specimen showed lower thermal conductivity than the undoped material.
From X-ray diffraction analysis, the crystalline magnetoplumbite oxide as well as amorphous phases were found to be present in the as plasma-sprayed coatings. Figure 6 shows preliminary results for the thermal conductivity measurements of LaMgAl$_{11}$O$_{19}$ and LaMnAl$_{11}$O$_{19}$ magnetoplumbite coatings plasma sprayed on to NiCrAlY/Rene N5 substrates, tested at 1600 to 1620 °C with pass-through heat flux of 100 W/cm$^2$, as a function of time. Thermal conductivity of the coating did not change with time indicating resistance of the plasma-sprayed porous coating against densification even at temperatures as high as 1600 °C. Sintering of these oxide coatings is suppressed due to low ionic diffusion in the magnetoplumbite structure. The layered magnetoplumbite structure (ref. 5) contains fully occupied mirror planes due to the presence of highly charged La$^{3+}$ cation in an oxygen position in the hexagonal close-packed structure of oxygen ions. This results in suppression of the diffusion of oxide ion vertical to the crystallographic c-axis and resistance towards densification of the porous coating by sintering. The oxide coatings maintain their porosity and microstructure even after 20 hr exposure at temperatures up to 1600 °C. Further work is in progress to optimize the plasma spraying parameters of magnetoplumbite coatings on superalloys, monolithic ceramics and ceramic matrix composite substrates. The effects of long term annealing at elevated temperatures as well as thermal cycling on the characteristics and stability of these coatings are also being investigated. The results of these studies will be reported in the future.

**Summary**

LaMgAl$_{11}$O$_{19}$, GdMgAl$_{11}$O$_{19}$, SmMgAl$_{11}$O$_{19}$, and Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ oxide powders having magnetoplumbite structure were synthesized by sol-gel process and hot pressed into 2.54 cm diameter discs. Thermal conductivity was measured up to ~1150 °C using a steady-state laser heat flux test method. The average thermal expansion coefficient of these materials from room temperature to 1500 °C and was found to be ~9.6×10$^{-6}$/°C. The effects of doping on thermal properties were also examined. Thermal conductivity of the doped Gd$_{0.5}$Yb$_{0.5}$MgAl$_{11}$O$_{19}$ composition was found to be lower than that of the undoped GdMgAl$_{11}$O$_{19}$. On the other hand, thermal expansion coefficient was found to be independent of the composition and appears to be controlled mainly by the magnetoplumbite crystal structure.
Preliminary results of thermal conductivity testing at 1600 °C for LaMgAl_{11}O_{19} and LaMnAl_{11}O_{19} magnetoplumbite oxide coatings plasma-sprayed on NiCrAlY/Rene N5 superalloy substrates are also presented. The plasma-sprayed coatings did not sinter even at temperatures as high as 1600 °C.

References

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## Abstract

Oxides having magnetoplumbite structure are promising candidate materials for applications as high-temperature thermal barrier coatings because of their high thermal stability, high thermal expansion, and low thermal conductivity. In this study, powders of \( \text{LaMgAl}_{11}O_{19} \), \( \text{GdMgAl}_{11}O_{19} \), \( \text{SmMgAl}_{11}O_{19} \), and \( \text{Gd}_{0.7}\text{Yb}_{0.3}\text{MgAl}_{11}O_{19} \) magnetoplumbite oxides were synthesized by citric acid sol-gel method and hot pressed into disk specimens. The thermal expansion coefficients (CTE) of these oxide materials were measured from room temperature to 1500 °C. The average CTE value was found to be \( \sim 9.6 \times 10^{-6}/\text{C} \). Thermal conductivity of these magnetoplumbite-based oxide materials was also evaluated using steady-state laser heat flux test method. The effects of doping on thermal properties were also examined. Thermal conductivity of the doped \( \text{Gd}_{0.7}\text{Yb}_{0.3}\text{MgAl}_{11}O_{19} \) composition was found to be lower than that of the undoped \( \text{GdMgAl}_{11}O_{19} \). In contrast, thermal expansion coefficient was found to be independent of the oxide composition and appears to be controlled by the magnetoplumbite crystal structure. Thermal conductivity testing of \( \text{LaMgAl}_{11}O_{19} \) and \( \text{LaMnAl}_{11}O_{19} \) magnetoplumbite oxide coatings plasma sprayed on \( \text{NiCrAlY/Rene N5 superalloy substrates indicated resistance of these coatings to sintering even at temperatures as high as 1600 °C.} \n
## Subject Terms

Thermal barrier coatings; Thermal conductivity; Thermal expansion; Magnetoplumbites; Oxide ceramics