Thermal emissivity and high-temperature stability of thermal insulating materials produced by mixing powdered porous MgAl2O4 ceramics with commercial insulating castable

Shuko AKAMINE1,†

1Research and Development, CoorsTek KK, 30 Soya Hadano, Kanagawa 257–8566, Japan

Conventional industrial thermal insulating materials have a porous structure and provide resistance to thermal conduction. However, this structure permits heat transfer through radiation. Hence, they exhibit high thermal conductivity at temperatures higher than 1000 °C. To achieve high total-thermal-insulation efficiency, we recently developed new insulating materials, called THERMOSCATTTM, which greatly suppress radiation heat transfer. Their thermal conductivity was measured to be less than 0.3 W/(m·K) at 1500 °C. These insulating materials consist of porous MgAl2O4 ceramics having 1–5 μm pores which restrain heat transfer through radiation, which was consistent with the Mie scattering theory. From the thermal emissivity estimated from reflectance measurements, the porous MgAl2O4 ceramics had near-zero hemispherical spectral emissivity values in the wavelength range of 0.35–5 μm. Mixing these powdered porous MgAl2O4 ceramics with a conventional commercial insulating castable ceramics is shown to successfully reduce heat transfer through radiative Mie scattering. This report describes the experimental result of the powdered porous MgAl2O4 ceramics mixed into the commercial insulating castable.

Key-words: Aluminates, Porous materials, Thermal barrier coatings (TBC), Thermal conductivity, Optical properties

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1. Introduction

In recent years, as highlighted in the UN Climate Action Summit 2019, there has been significant growth in the awareness of the need for energy conservation and reducing the emission of greenhouse gases such as CO2. Within this, industries with high thermal energy consumption are striving to increase energy efficiency and savings. The steel, glass, and ceramics industries, in particular, must address this issue as an urgent task. As such, these industries require thermal insulating materials with low thermal conductivity and high heat resistance. As reported in former study,1) the thermal conductivity of porous materials can be represented by the sum of the thermal conductivity of the influence of conduction, the influence of convection and the thermal transport through radiation. However, it is well known that total thermal insulation efficiency of a material is more strongly affected by the high-temperature insulation efficiency than by the low-temperature insulation efficiency.2) and that radiation heat transfer becomes dominant in high-temperature regions above 1000 °C. From Radiation intensity calculated by Planck’s low,3) it can be derived that the main wavelength of black body radiation at 1000–1500 °C is 1–5 μm.

There are three methods to restrict radiation heat transfer. First method is absorbing the light in 1–5 μm range wavelength and converting into heat. Some insulating materials include micrometer-sized crystalline particles such as TiO2 or SiC absorb infrared radiation. However, this method needs nano-order sized structure to restrict conduction heat transfer and it is too difficult to maintain these structures over 1000 °C.4) Second method is reflecting the light in 1–5 μm range wavelength by regular reflection like a mirror.5) However, hundreds of nano-order sized layered structure is needed to occur regular reflectance and it is better than first method in terms of its size, however, it is still difficult to maintain the structure in heat-cool cycles. Finally, the third method is reflecting the light in 1–5 μm range wavelength by diffuse reflection like a cloud floating in the sky. According to the Mie theory,6) the scattering intensity increases rapidly as the size of the scatterer approaches that of the incident wavelength. Based on this theory, to reflect light by diffuse reflection 1–5 μm structure is needed. The scale of third method structure is larger than those of first and second nano-order sized structure.

† Corresponding author: S. Akamine; E-mail: Shuko.Akamine@coorstek.com
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Therefore, the third one is superior to use in high temperature circumstance. Based on this, we precisely synthesized magnesium aluminate spinel, MgAl₂O₄, as a restricting radiation insulating material with controlled pore size. From the mechanism of restricting heat radiation transfer, porous MgAl₂O₄ ceramics having 1–5 μm pores and grain clusters would have high reflectance and low emissivity at the wavelength range of 1–5 μm. Hence, we measured reflectance and estimated thermal emissivity of porous MgAl₂O₄ ceramics. The porous MgAl₂O₄ ceramics had near-zero hemispherical spectral emissivity values in the wavelength range of 0.35–5 μm.³

The porous MgAl₂O₄ ceramics restricts radiation transfer with diffused reflectance, so this effect also expected with powdered porous MgAl₂O₄ ceramics. Therefore, it can be added in commercial insulating materials, such as commercial conventional insulating castable ceramics or fiber bulks. Here we described the improvement of thermal insulation performance by mixing powdered porous MgAl₂O₄ ceramics with a commercial insulating castable.

2. Experimental procedure

2.1 Fabrication and characterization

Fabrication of porous MgAl₂O₄ ceramics (THERMOSCAT™) are shown in reference.¹³ Porous MgAl₂O₄ ceramics was crushed and sieved with screen mesh having 1 mm aperture. The powdered porous MgAl₂O₄ ceramics is called as “TSP”, and was mixed into the commercial insulating Al₂O₃ castable “TMT-1600” (AGC Plibrico Co., Ltd.) having heat resistance over 1500 °C. The main component of this Al₂O₃ castable is Al₂O₃ and subcomponent is ZrO₂. This Al₂O₃ castable contains hollow particles that reduce thermal conductivity and improve heat resistance. The microscopic structures of the TSP and Al₂O₃ castable were examined using a scanning electron microscope (S-4800, Hitachi High-Tech Corp.).

The proportions of this mixture were shown as xTSP·(100 – x) Al₂O₃ castable, x = 0, 25 and 50 wt %. These powders were mixed together using mixer (KENMIX760, AICOHSHIA MFG. CO., LTD.) for about 15 min. After then, 18, 36 and 55 wt % water was further added respectively to obtain liquidity and kneaded for 15 min and casted the mixture into molds (width × depth × thickness: 70 mm × 114 mm × 25 mm). The hardened slurry (green body) was dried at 40 °C and subsequently sintered at 1500 °C in air, for 3 h.

The pore-size distribution of sintered specimen TSP and the porous MgAl₂O₄ ceramics were measured using the mercury intrusion method (Auto Pore IV 9500, Micromeritics Instrument Corp.). The bulk density and open porosity of the sintered specimen and the porous MgAl₂O₄ ceramics were measured using Archimedes’ method. The compressive strength of sintered specimen and the porous MgAl₂O₄ ceramics were measured using the universal testing machine (Autograph AG-2000C Shimadzu Corp.). The thermal conductivity of sintered specimen and the porous MgAl₂O₄ ceramics were measured by the transient hot wire method (HWM–15, at SpeinLab. Co. Ltd.) at temperatures ranging from the ambient temperature to 1500 °C, with Pt-13%Rh wire and type R thermocouple. Both wire and thermocouple are single-use.

2.2 Estimation of radiation heat transfer using thermal conductivity

As reported in our former study,¹) the thermal conductivity of porous materials, λ can be represented by the sum of the thermal conductivity of the solid material (the influence of conduction, λs), the thermal conductivity of air (influence of convection, λg), and the thermal transport through radiation, λr as described by Eq. (1).

\[ \lambda = \lambda_s + \lambda_g + \lambda_r \]  

At higher than 1000 °C, thermal transport by radiation dominates that by conduction and/or convection in high porosity insulating materials.²) In addition, the plot of λ vs the third power of the absolute temperature is the slope of that line gives the radiation coefficient, “A” with units of W/(m·K³). This function can be described by the following equation: a linear function.⁷)

\[ \lambda = AT^3 + B \]  

The radiation coefficient, “A” was obtained from the linear three-point plots at high temperatures.

3. Results and discussion

Figure 1 shows the scanning electron microscope image of the microstructure of TSP and Al₂O₃ castable. As shown in Fig. 1, the particle size of TSP is smaller than that of Al₂O₃ castable. In addition, the particles of TSP are aggregated of sub-micrometer sized grains.

Figure 2 shows pore-size distribution of xTSP·(100 – x) Al₂O₃ castable, x = 0, 25 and 50 wt %, TSP and the porous MgAl₂O₄ ceramics. As shown in Fig. 2,
TSP and the porous MgAl₂O₄ ceramics have two range order structures, 0.05–1 and 1–5 μm, whereas Al₂O₃ castable is mainly consist of over 10 μm range order structure. The pore volume in the range of 1–5 μm of TSP is less than that of the porous MgAl₂O₄ ceramics. When TSP and Al₂O₃ castable were mixed and the ratio of TSP was increased, the peak of pore-size distribution in range of 0.05–1 and 1–5 μm appeared.

**Table 1.** Bulk density, open porosity and compression strength of xTSP-(100 – x) Al₂O₃ castable, x = 0, 25 and 50 wt % and the porous MgAl₂O₄ ceramics

| Ratio of TSP, x [wt %] | Bulk density [g/cm³] | Open porosity [%] | Compressive strength [MPa] |
|------------------------|----------------------|------------------|-----------------------------|
| 0                      | 1.0                  | 53               | 11                          |
| 25                     | 1.1                  | 55               | 6.8                         |
| 50                     | 1.0                  | 63               | 4.8                         |
| The porous MgAl₂O₄ ceramics | 0.78                | 78               | 1.4                         |

Fig. 2. Pore-size distribution of porous xTSP-(100 – x) Al₂O₃ castable, x = 0, 25 and 50 wt %, TSP and the porous MgAl₂O₄ ceramics.

Fig. 3. Thermal conductivity of xTSP-(100 – x) Al₂O₃ castable, x = 0, 25 and 50 wt % and the porous MgAl₂O₄ ceramics.

Fig. 4. The radiation coefficient, “A” of xTSP-(100 – x) Al₂O₃ castable, x = 0, 25 and 50 wt % and the porous MgAl₂O₄ ceramics.

The porous MgAl₂O₄ ceramics and Al₂O₃ castable are produced by mixing powdered porous MgAl₂O₄ ceramics with commercial insulating castable.

**4. Conclusions**

It is found that the porous MgAl₂O₄ ceramics can improve the thermal insulation of the castable host mate-
rial even when its powder is simply mixed, because it restricts the thermal transport through radiation with diffuse reflection.

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