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Fundamental Considerations on Plasma Sprayed Ceramic Coating (Report IV)†

—Effects of Mullite Addition on Alumina—

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Abstract

The effects of mullite addition to commercial alumina on lowering porosity and suppression of the transformation of metastable alumina were investigated. Apparent porosity of sprayed alumina coat with some mullite decreases from 8.5% to 6.0% with increasing mullite content up to 20 wt%. Glassy phases in sprayed-mullite and alumina containing some mullite were identified as mullite glass from the results of DTA and X-ray diffraction analysis. Further, it was detected that the mullite glass exothermally recrystallized at about 950°C. From the results of X-ray diffraction analysis on specimens heat-treated at various temperature, it was indicated that the transformation of γ*-*Al_2O_3 *formed after plasma spraying was inclined to be retarded. The results of X-ray diffraction analysis also suggested that silica dissolved in* γ*-*Al_2O_3*, which was produced by the decomposition of mullite in plasma-spraying, gave suppressive effect on the transformation of* γ*-*Al_2O_3 *to* α*-*Al_2O_3*.*

1. Introduction

As described in the previous papers[1-3], the essential requirements for plasma sprayed ceramics are to avoid the porous property of these coatings and the formation of thermally unstable phases in order to apply them to heat- and corrosion-resistance coatings. In the case of plasma sprayed alumina, one of most significant problems is to depress the transformation of metastable phases to corundum because the transformation of γ- or δ-Al_2O_3 to corundum produces the thermal constraction of about 10%. According to Iler[4], the transformation of these metastable phases can be depressed by the addition of several percentage silica. Recently, it was reported that the addition of metallic chromium can depress the transformation of γ-Al_2O_3 to α-Al_2O_3 whereas it can be enhanced by the addition of metallic iron[5]. In previous paper[3], it was reported that the addition of zircon sand to zirconia is effective to lowering the porosity of plasma sprayed zirconia. Further, it was suggested that the effectiveness originates in the formation of vitreous silica. Therefore, in this study, the effects of mullite addition to alumina were investigated under the expectation that glassy phase from mullite may be effective to depression of γ-α transition and lowering of porosity in plasma sprayed alumina.

2. Experimental Procedures

Materials used were commercial alumina (METCO 105) and mullite (Nippon Kagaku Togyo Co. Ltd.) in which the existence of a few amount of alumina was detected from X-ray diffraction analysis. The chemical analyses of these materials are shown in **Table 1.** Powder mixtures of alumina and mullite were produced in alumina mortar using acetone as immersion liquid and these mixtures were used for plasma spraying

Table 1 Chemical analyses and particle size ranges of commercial alumina and mullite

Composition (wt%)	Raw materials	
	commercial Al_2O_3 (METCO 105)	mullite
Al_2O_3	98.5	69.58
SiO_2	1.	28.54
Fe_2O_3		.40
CaO		.60
MgO		.09
Na_2O		.05
K_2O		.03
Other oxides	Balance	.71
Typical size range	15~53 μ	<44 μ

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after drying fully. The apparatus used was a plasma spray gun of METCO 3MB type. Plasma spraying was conducted according to following spraying parameter set No. 5 for METCO 105 in technical bulletin;

current and voltage: 500A×60–75V,
gas flow: primary Ar, secondary H_2,
particle size: 15 μ–53 μ.

Steel rods used as substrate and the experimental condition of apparent porosity were the same conditions described in the previous papers[1),2)]. Drying of specimen in porosity measurement was performed at 500°C for 1 hr. DTA and X-ray diffraction analysis were also conducted with the same conditions described in the previous paper[2)]. Heat treatment of sprayed specimens was conducted as following conditions;

temperature: 930°C,
atmosphere: air,
time: 1 hr–100 hr.

The apparent transformation ratio of metastable phases to α-Al_2O_3 was calculated from the intensity of X-ray diffraction with following equation;

$$R_{as}=\frac{I_\alpha}{I_m-I_\alpha}\times 100\ (\%)\ \text{[as spraying]},$$

$$R_{an}=\frac{I_\alpha}{I_m-I_\alpha}\times 100\ (\%)\ \text{[after each annealing]},$$

$$\text{apparent transformation ratio}=\frac{R_{an}-R_{as}}{100-R_{as}}\ (\%),$$

where I_α is the intensity of (113) plane of α-Al_2O_3 and I_m is the intensity of (400) plane of γ-Al_2O_3 or (406) plane of δ-Al_2O_3.

3. Experimental Results

(1) The effect of mullite addition on lowering porosity

The effect of mullite addition on lowering porosity of plasma sprayed alumina is shown in **Fig. 1.** The result of zircon sand addition to zirconia which reported in the previous paper[3)] is shown together in this figure. It was detected that the addition of 20 wt% mullite or less was effective to lowering apparent porosity and it was lowered from 8.5% to 6.0%. Ineffectiveness of mullite addition over 20 wt% seems to be reliable even if scattering of each plot must be reconsidered. Mullite addition up to 20 wt% showed similar effect to the case of zircon sand addition. When the additive was over 20 wt%, the effectiveness of mullite addition to alumina was saturated whereas the addition of zircon sand to zirconia was inclined to have bad influence as reported in the previous paper.

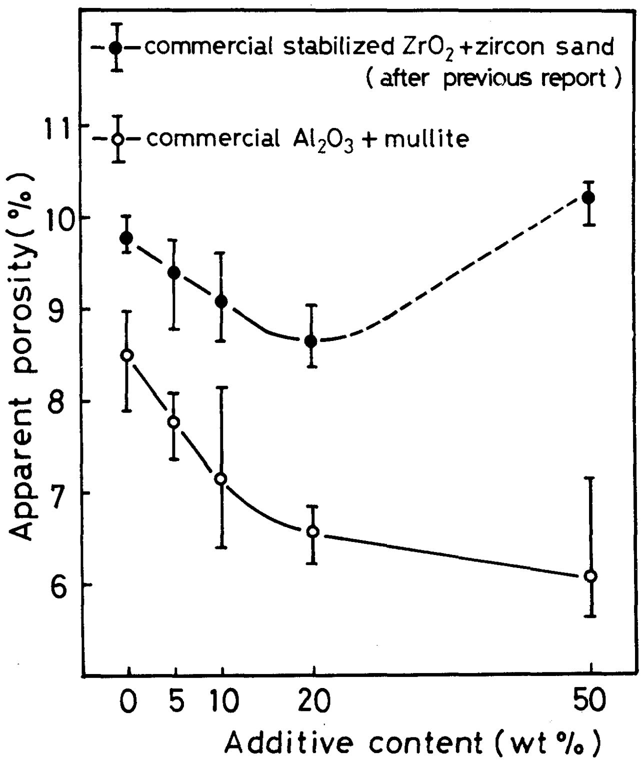

Fig. 1 The effect of mullite addition on lowering apparent porosity of sprayed alumina coating (The effect of zircon sand addition to zirconia is shown together.)

(2) Structure of sprayed mullite and its structural change after heat treatment

After plasma spraying, mullite with a few amount of α-Al_2O_3 changed into the mixture of mullite, γ-Al_2O_3 and glassy phases as shown in **Fig. 2.** From the results of DTA and X-ray diffraction analysis of heat-treated specimens, it was indicated that the glassy phases began to crystallize at about 900°C. After DTA from room temperature to 1200°C at the rate of 5°C/min, plasma sprayed mullite changed into well-crystallized mullite, δ-Al_2O_3 and small quantity of α-Al_2O_3. The X-ray diffraction pattern of the specimen which was annealed at 1200°C for 1 hr after DTA is also shown in Fig. 2. The pattern shows that peak heights of α-Al_2O_3 increase whereas those of δ-Al_2O_3 decrease and that the height of each peak due to mullite seems to be unchangeable as compared with their peaks in the pattern after annealing at 900°C. Furthermore, complete disappearance of δ-Al_2O_3 and development of α-Al_2O_3 was observed after annealing at 1300°C for 1 hr.

(3) Thermal properties of sprayed alumina containing mullite

As shown in **Fig. 3**, it was indicated from DTA results that the glassy phases exothermally crystallized

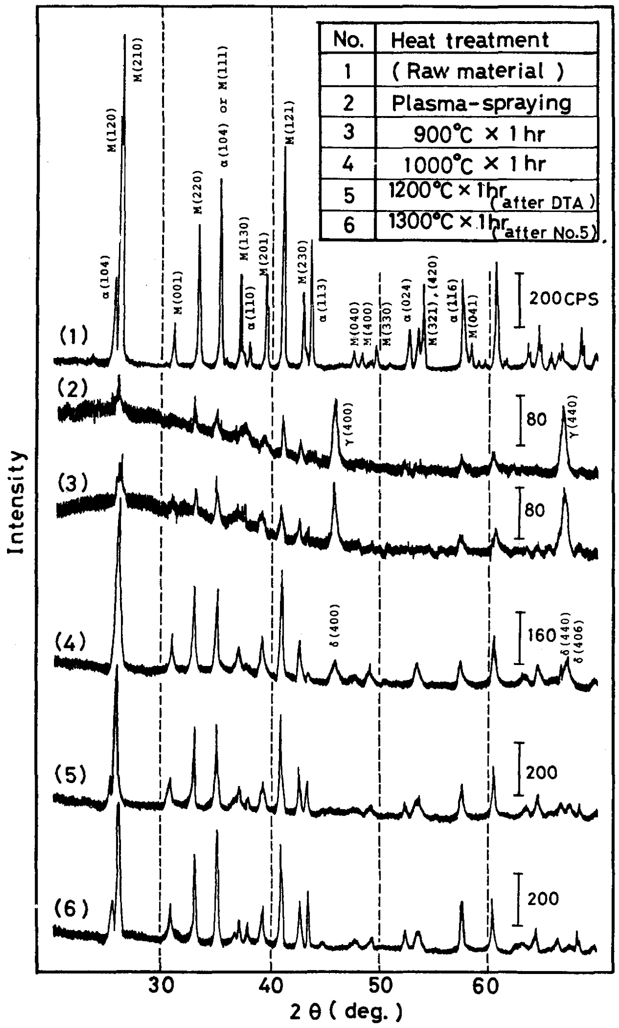

Fig. 2 Stepwise changes in X-ray diffraction patterns on heat treatment
(M: mullite, α: α-Al_2O_3, γ: γ-Al_2O_3, δ: δ-Al_2O_3)

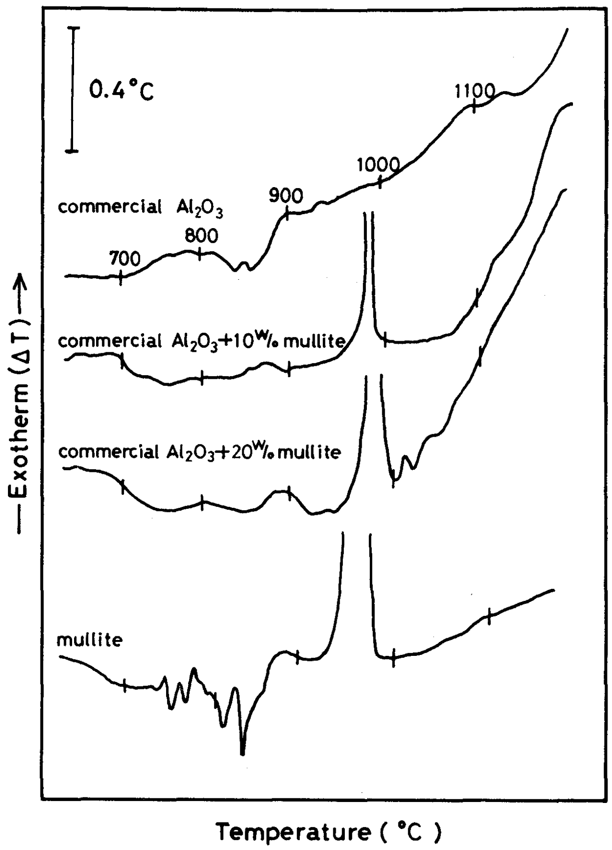

Fig. 3 DTA curves of sprayed alumina, alumina containing various content of mullite and mullite

at about 950 °C. According to the result of Takamori and Roy[6], it is supported that a large amount of the glassy phases is identified as mullite glass. In the result of DTA, however, it must be considered that the crystallization temperature is inclined to be higher than true temperature of crystallization. On the basis of DTA results, heat treatments were performed at 930 °C in order to observe phase transformation and estimate the apparent increment of α-Al_2O_3 which was transformed from metastable aluminas. **Figs. 4** and **5** show the results in which annealing time was taken as parameter. The crystallization of mullite glass in sprayed aluminas with 20 wt% and 50 wt% mullite rapidly developed during heat treatment for 1 hr and was nearly saturated afterwards. Likewise, transformation into α-Al_2O_3 rapidly developed during 4 hr annealing and gradual transformation was observed after that. The transformation of metastable aluminas to α-Al_2O_3 has an inclination to be more retarded when several weight percentage mullite was added. The inclination was also detected even in the case of 100 hr annealing. Further, Fig. 4 shows that the recrystallization of mullite nearly finished after annealing at 930 °C for 1 hr. However, the result of 5 wt% mullite addition in the curve of transformation ratio of mullite is likely to have to be reconsidered on account of the large experimental error.

4. Discussions

The appearance of saturation in Fig. 1 is noteworthy phenomenon but the phenomenon is likely to originate in the different cause from that in the case of zircon sand addition. It can be considered that the decrease of the porosity in sprayed alumina is attributable to the lower melting point of mullite than that of mullite and the similar viscosity of liquid mullite to liquid alumina[7]. Further, possibility of the formation of mullite glass seems to be responsible for lowering

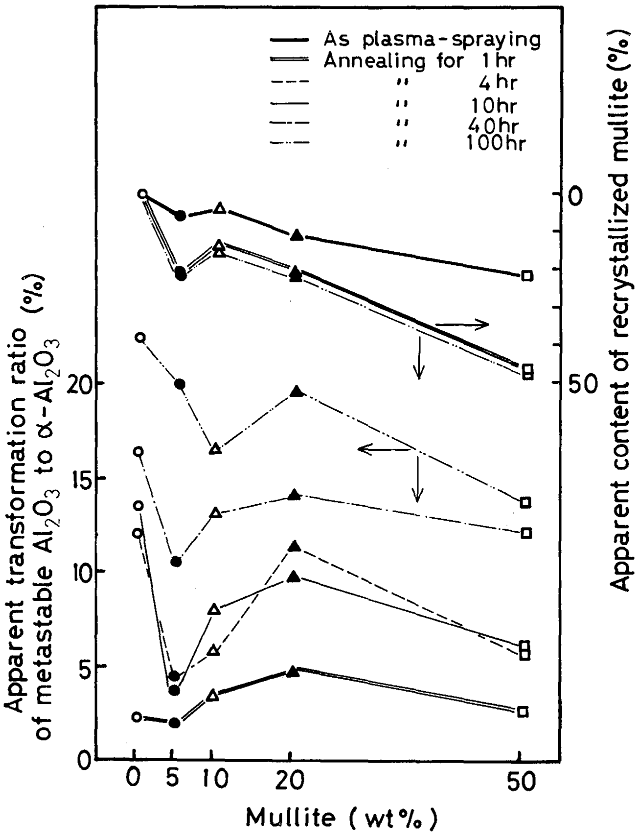

Fig. 4 Stepwise changes of apparent transformation ratio of metastable alumina to α-Al_2O_3 and apparent content of recrystallized mullite after annealing at 930°C for 1 hr to 100 hr

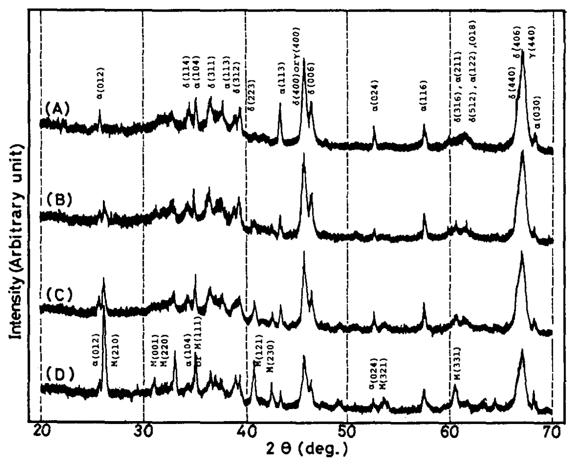

Fig. 5 Typical X-ray diffraction patterns of sprayed alumina with various content of mullite after annealing at 930°C for 10 hr ((A) commercial Al_2O_3, (B) commercial Al_2O_3 +10 wt% mullite, (C) commercial Al_2O_3+20 wt% mullite, (D) commercial Al_2O_3+50 wt% mullite)

porosity. Then, the saturation of lowering porosity is likely to attribute the fact that the properties of sprayed coat gradually approach to those of mullite itself though the porosity of sprayed mullite could not be measured in this study.

On the contrary, zircon sand decomposes into easily crystallizing zirconia and high viscous silica glass in a sprayed mixture of zirconia and zircon sand. Therefore, it is expected that the addition of zircon sand is less effective to lowering porosity of sprayed coat than that of mullite to alumina.

Such consideration can qualitatively explain the result shown in Fig. 1. That is, mullite addition could produce 2% reduction in porosity whereas zircon sand addition only about 1% reduction. The larger difference in porosity between sprayed alumina and zirconia would be attributable to the differences of easiness for vitrification and melting point between these materials. However, further investigation is desired to certify the inherent difference.

Subsequently, it would be reasonable to interpret that the existence of γ-Al_2O_3 in plasma sprayed mullite originates in the decomposition of mullite as well as the existence of a few amount of α-Al_2O_3 premixed in starting material. Takamori and Roy reported that flame sprayed mullite can completely be vitrified when it is quenched into water[6]. However, quenching velocity in this study would be fairly lower than that in their report because mullite was deposited on a steel rod. Therefore, the formation of crystalline as well as glassy mullite is reasonable result. Further, Davies et al. reported from thermodynamical consideration that mullite can decompose with evolution of SiO and O_2 under high temperature and low oxygen pressure[8]. In this study, it can be considered that such conditions are satisfied because plasma flame can raise the temperature of specimen particles to 3000°C or so and low oxygen pressure may be attained by Ar-H_2 atmosphere though for a very short time. Therefore, the decomposition of mullite is possible but most amount of glass phases in plasma sprayed mullite would be mullite glass because it is expected that silicious compounds due to mullite decomposition, in most cases, escape in the form of SiO and, therefore, SiO_2 glass is likely to be rare in plasma sprayed mullite. The identification of glassy phase as mullite glass can also be supported from the fact that only a large exothermic peak was observed in DTA measurements and this results show good agreement to the result reported by Takamori and Roy.

The fact that minima were detected at the mullite addition of 5 wt% to 10 wt% in Fig. 4 seems to be

Table 2 2θ of the peak due to (400) plane of γ-Al_2O_3 in sprayed coats

Raw material	γ (400) in 2θ (scann speed 0.125°/min)	γ (400) in 2θ (fixed time method 40 sec × 2)
Pure Al_2O_3	——	45.87_5
Commercial Al_2O_3	45.80	——
Commercial Al_2O_3 +10 wt% mullite	45.78	45.84_0
Commercial Al_2O_3 +20 wt% mullite	45.76	——
Commercial Al_2O_3 +50 wt% mullite	45.79	——
mullite	45.82	45.88_0

attributable to the dissolved SiO_2 into γ-Al_2O_3 which decomposed from mullite. The result shown in **Table 2** was only supported from the fact that slight shift of the peak due to (400) plane of γ-Al_2O_3 showed similar inclination to the curves shown in Fig. 5. However, it is necessary to reinvestigate the shifting behaviours of these peaks more precisely and to certify the dissolution of SiO_2 to γ-Al_2O_3.

5. Summary

The effect of mullite addition to commercial alumina on lowering porosity was investigated. Apparent porosity of sprayed alumina coat containing various content of mullite decreased from 8.5% to 6.0% with increasing mullite content up to 20 wt%. Phase transformation of sprayed alumina or alumina with some mullite was also investigated with DTA and X-ray diffraction analysis. Glassy phase in sprayed mullite and sprayed alumina containing some mullite was identified as mullite glass from these analysis. Further, it was detected that the mullite glass exothermally recrystallised into crystalline mullite at about 950°C. From the results of X-ray diffraction analysis on specimens heat-treated at various temperature, especially at 930°C, it was observed that the transformation of metastable alumina, especially γ-Al_2O_3, trends to be more suppressed with increasing mullite content. Further, it was suggested that silica dissolved in γ-Al_2O_3, which was produced by the decomposition of mullite, gave suppressive effect on transformation of γ-Al_2O_3 to α-Al_2O_3.

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