Formation of Mullite Coating by Aerosol Deposition and Microstructural Change after Heat Exposure

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Optimal parameters for the aerosol deposition (AD) of a mullite coating and the microstructural change of the coating after heat exposure in air were investigated. Mullite, which is a component of environmental barrier coatings, was deposited on glass, Al2O3 and Si by the AD method. The angle of the gas flow direction from the nozzle to the substrate plane should be 60° to produce a homogeneous mullite coating. The deposition rate increased with the gas flow rate when the gas flow rate was in the range from 18 to 36 L/min. Further increase of the gas flow rate resulted in the formation of a heterogeneous coating. The mullite coating formed with the optimized parameters was almost fully dense and crystalline. The chemical composition of the mullite coating was almost the same as that of the raw mullite powder used for deposition. The coating was composed of a single mullite phase. No delamination was observed at the interface between the Si substrate and the mullite coating. The interface did have undulations; therefore, it was considered that the substrate and the coating were bonded due to the anchor effect. Heat treatment was performed at 1573 K for a mullite coating deposited on a Si substrate. When the specimen was exposed to heat for 10 h, the coating at the surface side and the coatings at the central part and near the interface between the substrate and the coating were composed of two phases, (Al2O3+Mullite) and (SiO2+Mullite), respectively. Further heat exposure results in the formation of a reacted layer of two phases (SiO2+Mullite) containing more than 80 mol% of SiO2 near the interface. The thickness of the layer increased with increasing heat exposure time. The formation of the reacted layer was due to the diffusion of Al present in the mullite coating to the coating surface and the diffusion of Si into the coating from the Si substrate. [doi:10.2320/matertrans.MT-M2019354]

Keywords: environmental barrier coating, aerosol deposition, mullite, heat exposure

1. Introduction

SiC fiber-reinforced SiC matrix composite materials (SiC/SiC) that are lightweight and have excellent heat resistance have been examined for use as high-temperature components in high-pressure turbines of next-generation aircraft engines. The environment of application is assumed to be a combustion environment that contains high temperature oxygen and water vapor. In such environment, it is known that the oxides and hydroxides formed at the SiC/SiC substrate volatilize, so that the substrate recedes. Therefore, the application of multilayered environmental barrier coatings (EBCs) composed of a material such as mullite with excellent oxygen-shielding properties has been investigated. A three-layer structure using Si as a bonding layer, mullite as an oxygen shielding layer, and rare earth (RE)-silicate as a water vapor shielding layer has been proposed recently.

Conventional EBCs have been formed by atmospheric plasma spraying. However, the coating becomes porous with this method, and depending on the deposition conditions, can become an amorphous coating. Therefore, in a high temperature environment, the coating shrinks by sintering, and tensile stress is generated in the interface direction, which causes vertical cracking in the coating. Damage to such coatings is a problem because it leads to a decrease in the environmental barrier performance and delamination of the coating.

The aerosol deposition (AD) method is known to produce dense and crystalline coatings at room temperature. The basic approach of the AD process was reported by Hayashi and then developed by Akedo. The ability to form a coating with a thickness of a few microns without heating is one advantage of the AD method. A coating produced by the AD method is considered to be formed by fracture or plastic deformation of the particles upon impact with the substrate. This principle of coating formation is referred to as room temperature impact consolidation. There has also been a principle proposed whereby the particles rub against the wall surface of the nozzle and are projected from the tip of the nozzle as positively charged particles to the substrate, while negative electrons fly from the substrate side immediately before the particles reach the substrate; the negative electrons collide with the deposition gas, which generates plasma to form the coating. In the past, various powders such as ZrO2, Al2O3, AlN have been used to form coatings. Therefore, it was considered that a coating can be formed by the AD method, even a mullite coating, which is a constituent material of EBCs, and a stable coating could be manufactured, even when the mullite is used in high temperature environments. However, the process technology and oxidation resistance of dense mullite coatings formed by the AD method have not yet been reported. Furthermore, understanding the influence of atmospheric heat exposure on the microstructure of mullite coatings produced by the AD method should lead to the establishment of the ideal conditions for the production of EBCs with excellent oxygen shielding properties.
In this study, the deposition conditions for the coating of mullite particles by the AD method were established, and the effect of atmospheric heat exposure on the structure of the mullite coating was experimentally examined.

2. Experimental Procedure

Figure 1 shows a schematic diagram of an AD device, which consists of two chambers, an aerosol chamber and a deposition chamber. The raw material powder is introduced to the aerosol chamber, and the substrate is placed on an XY stage in the deposition chamber. To form a coating, the aerosol chamber is first evacuated and a carrier gas is flowed into the aerosol chamber to generate an aerosol. The raw material powder used in this work was mullite (Al₆O₁₃Si₂; KM101, KCM Corporation Co., Ltd.), a common constituent material of EBCs, and the composition of the powder (Al₂O₃ 71.9 mass%; impurities: Fe₂O₃ 0.013, TiO₂ 0.004, CaO 0.008, MgO 0.012, Na₂O 0.012, K₂O 0.008, ZrO₂ 0.001 mass%) was almost the same as the stoichiometric composition (Al₂O₃ 71.8 mass%) of mullite. Figure 2 shows a scanning electron microscopy (SEM) micrograph of the raw material powder used for the deposition process. The median diameter (D₅₀) of the powder was 1.63 µm, and although the powder was angular, it had a substantially equiaxial particle shape. The powder was passed through a #60 sieve to remove large agglomerates of the powder, and then dried at 523 K. Helium was used as the carrier gas. Glass, Al₂O₃, and Si single crystal were used as substrates. Coating was performed using two types of nozzles; the dimensions (width × thickness) of the nozzle ports were 5 × 0.5 mm and 20 × 0.5 mm. During the AD process, the gas flow rate, angle between the substrate surface and the direction of gas flow from the nozzle (nozzle angle), nozzle-substrate distance, scanning speed, and the number of scans were 12 to 42 L/min, 60 or 90°, 3 mm, 150 mm/min, and 30 times, respectively. The conditions under which a coating was obtained were experimentally examined with a focus on the nozzle angle and the gas flow rate.

The thickness of the formed coating was measured using a contact type surface roughness meter. The crystal structure of the coating was identified using X-ray diffraction (XRD). The specimens were subjected to heat exposure in air at 1573 K for 10, 50, and 100 h. The surface and cross-sectional microstructures of the mullite coating before and after heat exposure were observed using optical microscopy and SEM. The composition of the coating was analyzed using energy dispersive X-ray spectroscopy (EDX).

3. Results and Discussion

3.1 Effect of nozzle angle on mullite coating formation

In the formation of mullite coating using a 5 mm wide nozzle, the effect of the nozzle angle on coating formation was investigated. Here, the gas flow rate was fixed at 14 L/min. Figure 3 shows the specimens when the mullite particles were deposited on an Al₂O₃ substrate at an angle of 60° or 90° and with the nozzle angle shown in Fig. 1. In the case of a nozzle angle of 90°, almost no coating remained on
The substrate after deposition. Therefore, no film was formed (Fig. 3(a)). On the other hand, in the case of a nozzle angle of 60°, although the coating was not homogeneous, the coating remained, even after ultrasonic cleaning in alcohol. Therefore, the formation of a coating was confirmed (Fig. 3(b)).

The relation between the nozzle angle and the condition of the coating after deposition by the AD method has been reported for PZT and Sm–Fe–N powder. When coating is performed under the same deposition conditions but changing the angle between the nozzle and the substrate, the deposition rate is almost constant when the angle is 90° to 70°, according to the definition of the nozzle angle in this experiment. However, when the angle is smaller, the deposition rate decreases. It has also been reported that at a certain critical angle, the condition changes from deposition to etching. A larger flow rate of the gas also causes the critical angle to become smaller. The same tendency was also observed in the coating of Sm–Fe–N powder. When the nozzle angle is in the range of 90° to 60°, there is no significant difference in the deposition rate; however, when the nozzle angle is smaller, the deposition rate decreases. Furthermore, the roughness of the coating tends to decrease with the nozzle angle. When the nozzle angle is 90°, the gas flow from the nozzle was reported to be disturbed by collision with the substrate, and the disturbed gas flow in the vicinity of the substrate suppressed the formation of a uniform coating. On the other hand, when the nozzle angle is small, the gas flow collision with the substrate flows in one direction in the vicinity of the substrate. Therefore, it is considered that formation of the coating is not disturbed and a uniform coating with a small surface roughness is obtained. In the present study, when the nozzle angle was 60°, mullite powder was formed, but when the nozzle angle was 90°, mullite powder was not formed. From these results, the characteristics of the mullite coating tend to be different from those of PZT or Sm–Fe–N powder coatings.

Similar to cold spray technology, it is considered that there is a critical particle velocity necessary for coating formation by the AD method. In the cold spray method, a coating is generally formed at atmospheric pressure, and the gas flow immediately after injection from the nozzle exceeds the speed of sound. Therefore, the velocity of the particles becomes sufficiently high. However, when the gas stream collides with the substrate, it is reflected and the velocity of the particles is largely disturbed. As a result, a shock wave is generated in the vicinity of the substrate, so that the gas flow is rapidly decelerated. This deceleration of the gas flow results in a significant decrease of the particle velocity. Coating is performed under reduced pressure in the AD method; therefore, it is considered that the effect of particle deceleration in the vicinity of the substrate is sufficiently smaller than that in the cold spray method. However, in a report on simulation of the velocity of the gas flow injected from the nozzle by the AD method, the velocity of the He gas injected at a nozzle angle of 90° became a maximum immediately after injection and exceeded the sonic velocity. The gas flow then rapidly decelerates when the gas approaches the substrate, and the velocity of the gas in the vicinity of the substrate that flowed from the center portion of the nozzle was almost zero. This is considered to be due to the influence of the gas flow collision with the substrate. Furthermore, the flow direction of the gas changes significantly when the gas leaves the center portion of the nozzle.

From these results, it is considered that the mullite coating was formed as follows. For coating at a nozzle angle of 90°, the aerosol gas stream that carries the particles collides with the substrate and is pushed back from the substrate in the vertical direction, which generates pressure. As a result, the speed of the particles to the substrate is reduced to equal or lower than the critical speed required for the formation of coating; therefore, the formation of a coating is prevented. On the other hand, when the nozzle angle is 60°, the gas flow collision with the substrate flows in one direction in the vicinity of the substrate, and the pressure pushed back from the substrate is reduced when compared with that at 90°. Therefore, the collision speed is not significantly lowered, and speed that is equal to or higher than the critical speed necessary for the formation of the coating is maintained; therefore, a coating is formed.

3.2 Effect of gas flow rate on formation of a mullite coating

The effect of the gas flow rate on the formation of a coating was examined using a glass substrate. Here, the nozzle width and nozzle angle used for the deposition were 20 mm and 60°, respectively. Figure 4 shows the deposition rate of mullite as a function of the He gas flow rate. When deposition was performed at gas flow rates of 18, 24, and 36 L/min, the deposition rates were 0.08, 0.3, and 0.5 μm/min·cm², respectively, which indicates that the deposition rate increases with the gas flow rate. However, when the gas flow rate was further increased to 42 L/min, the deposition rate became 9 μm/min·cm² because an inhomogeneous coating with scattered non-deposition regions was formed.

The relationship between the gas flow rate and the deposition rate at a nozzle angle of 90° in the AD method has been reported for the deposition of TiN or Al₂O₃ powder. In either case, the deposition rate increases with the gas flow rate, and then tends to decrease after reaching a maximum value. The formation of a coating by the AD method is considered to be caused by room temperature impact consolidation by the fracture and/or plastic deformation of particles at the time of particle collision. When the gas

![Fig. 4 Relationship between deposition rate and gas flow rate.](image-url)
flow rate is low, many particles cannot obtain the sufficient critical velocity to cause room temperature impact consolidation, and the particles are repelled from the substrate or fly without reaching the substrate, so that no coating is deposited on the substrate. When the gas flow rate reaches or exceeds the critical velocity necessary for the coating formation of a particle, then coating on the substrate begins, and as the gas flow rate increases, many particles exceed the critical velocity. Therefore, the deposition rate of mullite in this study is also considered to increase with the gas flow rate for the same reason. On the other hand, when the gas flow rate is too high, the deposition rate decreases due to abrasion of the coating caused by the collision of particles on the coating surface with an increase in the particle velocity.\(^{25}\) In addition, although the particle velocity increases immediately after injection from the nozzle, the gas reflected by the substrate increases, even if the nozzle angle is 60°, and the particle velocity tends to be reduced in the vicinity of the substrate. Therefore, there is a possibility that coating formation is hindered. Furthermore, while the increased gas flow increases the amount of powder that rolls up in the aerosol chamber, it is also considered that the rolled-up powder that is delivered to the deposition chamber with large particle size collides with the coating at high speed, and wears down the coating surface.\(^{10}\) As a result, the coating produced with a gas flow rate of 42 L/min was an inhomogeneous coating with undeposited regions that remained after cleaning. At present, it has not been confirmed whether a larger size of powder is discharged from the nozzle due to an increase in the gas flow rate. In future work, we intend to confirm this by collecting the powder from the nozzle to determine whether powder with a large particle diameter roll up with an increase in the gas flow rate and flies from the nozzle to the substrate. In addition, the contribution of large particles to abrasion of the coating surface will also be examined.

In this study, the gas flow rate that enables uniform coating of mullite with He gas is in the range from 30 to 36 L/min. Although the optimum flow rate is dependent on parameters such as the type of powder, chamber pressures, and nozzle shape, it is presumed that there is an optimum flow rate capable of providing a suitable coating by the AD method. It has generally been reported that the particle velocity of the raw material powder sent to the substrate is in the range of 150 to 400 m/s as a condition for coating formation by the AD method.\(^{6}\) A similar velocity range was obtained in this study.

### 3.3 Microstructure of deposited mullite coating

A coating in which mullite was deposited on a Si substrate by simulating the bond coating and oxygen shielding coating in EBCs was prepared using a 20 mm wide nozzle with a nozzle angle of 60° and a gas flow rate of 30 to 36 L/min. Figure 5 shows micrographs of the mullite coating, the entire specimen and the surface microstructure of the as-deposited condition. No macroscopic defects were observed on the coating. The entire substrate, except for its sides that were masked was covered by the coating (Fig. 5(a)). Microstructural SEM observations revealed no cracks or chips on the coating surface (Fig. 5(b)). Furthermore, a flat region where particles are crushed by collision was observed on a part of the coating surface. Therefore, the particles are considered to deform by collision with the substrate during deposition. Figure 6 shows XRD patterns obtained from the raw mullite powder and that from the mullite coating after deposition. Although a detailed explanation is given later in section 3.4, the results obtained from a mullite coating after atmospheric heat exposure at 1573 K for 100 h are also shown (Fig. 6(c)). Diffraction lines from the Si substrate can be observed from the deposited specimen. However, the other diffraction lines coincide with the diffraction lines from the mullite raw powder. Therefore, the deposited coating maintained the same crystal structure as the raw material powder. In addition, no broad patterns due to an amorphous phase or SiO\(_2\) diffraction lines that indicated oxidation at the substrate interface were observed. These results confirmed that there was no oxidation of the substrate, and it was possible to form a uniform and crystalline mullite coating.

Figure 7 shows EDX analysis results obtained by measuring a cross-section of a mullite coating deposited on a Si substrate. The thickness of the coating was 15 µm, and fine pores were observed in the cross-section of the coating, regardless of the direction of thickness of the coating (Fig. 7(a)). However, the coating generally had a dense structure. Elemental mapping of the cross-sectional structures revealed that Si, Al, and O are uniformly distributed throughout the coating (Fig. 7(b)). In addition, a quantitative compositional analysis was performed on the surface, center
and in the vicinity of the interface between the Si substrate and the mullite coating (shown by the yellow framed areas in Fig. 7(b). From the ratio of Al and Si, the molar fractions of Al₂O₃ and SiO₂ were determined and the phase dependence on the location of the mullite coating was confirmed. The mole fraction of Al₂O₃ at the surface, center, and in the vicinity of the interface of the coating were 59.3, 61.4, and 59.7 mol%, respectively, which was almost the same as the 60.1 mol% Al₂O₃ mole fraction for the raw mullite powder. These results indicate that the obtained coating was a crystalline single-phase mullite coating, regardless of the thickness direction. Figure 7(c) shows the microstructure in the vicinity of the interface between the Si substrate and the mullite coating. No delamination was observed at the interface, and the surface of the Si substrate, which was smooth prior to the deposition, formed an undulated region with a height of about 300 nm following deposition.

As shown in reports of the deposition principle of the AD method,⁶⁻¹⁰ it is considered that the mullite particles ejected from the nozzle are fixed by crushing and deformation while forming an anchor layer on the substrate surface. It is considered that the particles subsequently fly, one after another, to form a coating by repeated cracking and deformation while crushing the coating on the substrate. In this study, the formation of a flat-shaped region in which the particles on the surface structure of the deposited specimen were considered to have been deformed by collision and the formation of an undulated part with a height of about 300 nm in the cross-sectional structure which is considered to be the anchor layer were observed by microstructure observation. From these results, it is considered that the same phenomenon has occurred.

### 3.4 Microstructural change of mullite coating after atmospheric heat exposure

Specimens of mullite coating with a thickness of 15 µm formed on a Si substrate were subjected to atmospheric heat exposure at 1573 K for 10, 50 and 100 h. Deposition was performed under the same conditions as those used to produce the microstructure shown in Fig. 5. Figure 8 shows micrographs of the surface of the specimen exposed to atmospheric heat. The crystal grains of mullite grew as the heat exposure time increased. For heat exposure of 50 h or more, the surface exhibited rougher surface profile, and when exposed to heat after 100 h, cracks were observed on the surface of the coating. Figure 9 shows the results of the elemental distribution of the partial area of the cross-sectional microstructures for the specimens exposed to heat for various times. Although it is difficult to understand from the SEM results, EDX analysis indicated that the ratio of Al was decreased in the mullite coating in the vicinity of the Si substrate due to heat exposure. On the other hand, the ratio of Si increased. In the mullite coating, the area near the substrate where the Al ratio decreases and the Si ratio increases is called the reacted layer. The thickness of the reacted layer increased with the heat exposure time. On the other hand, the thickness of the mullite coating decreased, and the total thickness of the mullite coating and the reacted layer increased. Furthermore, the reacted layer obtained was a dense layer. The phase composition of the mullite coating after 100 h of atmospheric heat exposure at 1573 K was confirmed from the results in Fig. 6(c). Diffraction lines of SiO₂ and mullite were observed, which indicates that the entire coating, including the mullite coating and the reacted layer, is composed of two phases of SiO₂ and mullite. In
addition, to understand the phase change of the mullite coating with respect to the location in the coating thickness direction due to heat exposure, the composition of the coating, including the mullite coating and the reacted layer, was quantitatively analyzed on the surface, center, and vicinity of the Si substrate of the coating (Figs. 9(b), (d), and (f) in the yellow frames) to determine the ratio of Al$_2$O$_3$ for various heat exposure times. Figure 10 shows the ratio of the obtained Al$_2$O$_3$ as a molar fraction. Figure 11 is a part of the phase diagram of SiO$_2$ and Al$_2$O$_3$. The composition of the raw mullite powder used in this study is shown by the dashed line. Although there was a single phase of mullite prior to heat exposure, after heat exposure at 1573 K for 10 h, the molar fraction of Al$_2$O$_3$ was 71.8% near the surface of the coating, and from the phase diagram, this can be determined as a (Al$_2$O$_3$+mullite) two-phase region. The ratios of Al$_2$O$_3$ and mullite were 24.6 and 75.4 mol%, respectively. Al$_2$O$_3$ accounts for approximately 25% in addition to mullite. On the other hand, in the central part of the coating and in the vicinity of the Si substrate, the molar fractions of Al$_2$O$_3$ were 52.0 and 43.0 mol%, respectively, and both can be confirmed as (SiO$_2$+mullite) two-phase regions. From the phase diagram, the ratios of SiO$_2$ at the center of the coating and that in the vicinity of the substrate were 11.6 and 26.9 mol%, respectively. Therefore, even in the same (SiO$_2$+mullite) two-phase region, more SiO$_2$ is present in the vicinity of the substrate than in the central region of the coating. As heat exposure was further extended to 50 and 100 h, the mole fraction of Al$_2$O$_3$ decreased in the respective regions of the coating. The mole fraction of Al$_2$O$_3$ generally ranges from 45 to 55 mol% near the surface and center of the coating, and is about 10 mol% near the Si substrate. Therefore, any region is a (SiO$_2$+mullite) two-phase region; however, the ratio of SiO$_2$ and mullite varied depending on the location. The ratio of SiO$_2$ near the surface and the center of the coating was in the range of 6.5 to 23.5 mol%, and mullite more was present than SiO$_2$. On the other hand, in the vicinity of the Si substrate, the ratio of SiO$_2$ was 83.0 mol%, which was approximately four times as much as mullite. The ratio of SiO$_2$ is thus increased in any region of the coating with heat exposure, and the reacted layer shown in Fig. 9 is a (SiO$_2$+mullite) two-phase state that contains more than 80% SiO$_2$.

It has been reported that when an oxygen partial pressure gradient is applied to the upper and lower surfaces of mullite and Al$_2$O$_3$ wafers at high temperature, oxygen permeates from the side of high oxygen partial pressure to the side of low oxygen partial pressure, while Al diffuses from the side of low oxygen partial pressure to the side of high oxygen partial pressure. In this study, the atmosphere around the surface of the mullite coating on the Si substrate was under a high oxygen partial pressure and that in the vicinity of the interface between the Si substrate and the mullite coating was under a low oxygen partial pressure, which infers that the same phenomenon would occur, i.e., Al diffuses from the vicinity of the interface between the Si substrate and the mullite coating to the coating surface on the high oxygen partial pressure side. As a result, the concentration of Al increases near the surface of the coating and decreases near the interface. Therefore, when a specimen where the mullite was deposited on a Si substrate was heat exposed at 1573 K for 10 h, it was considered that the Al diffused toward the mullite coating surface, which resulted in a (Al$_2$O$_3$+mullite) two-phase region where the surface of the coating became Al$_2$O$_3$-rich and the (SiO$_2$+mullite) two-phase region in the center and in the vicinity of the Si substrate became SiO$_2$-
rich. With extended heat exposure, the ratio of SiO₂ increases in all regions, which indicates that the diffusion of Si from the substrate into the mullite coating occurs. Therefore, it is considered that the reacted layer was formed by the diffusion of Al in the mullite coating to the surface and the diffusion of Si from the Si substrate to the coating.
The SiO$_2$ contained in the reacted layers is known to lead to deterioration of the performance of the coating.

Therefore, to suppress the formation of a reacted layer, it will be necessary to prevent the decomposition of mullite using a material that contains Al and is capable of supplying Al instead of Si as a bonding layer. It is considered that the material system in which Si in the bonding layer is difficult to diffuse into the coating will also be required.

### 4. Conclusions

An experimental study was conducted on the conditions for the formation of mullite coatings using the AD method and the microstructural changes of the mullite coating by heat exposure in air were investigated. The following conclusions were made.

1. When the nozzle angle was 90°, no mullite coating was obtained. On the other hand, the formation of a coating on the substrate was confirmed by setting the nozzle angle to 60°.

2. The deposition rate increased with the gas flow rate in the range from 18 to 36 L/min. However, when the gas flow rate was increased to 42 L/min, an inhomogeneous coating with undeposited regions was formed.

3. The mullite coating formed on a Si substrate was a homogeneous, crystalline, single phase mullite coating that was generally dense and had little compositional deviation from the raw material powder. There was no delamination at the interface between the Si substrate and the mullite coating after deposition and the interface had undulations; therefore, it is considered that the formation of an anchor layer contributes to the successful bonding of the coating to the substrate.

4. When a mullite coating deposited on a Si substrate was heat exposed at 1573 K for 10 h, the vicinity of the coating surface became a (Al$_2$O$_3$ + mullite) two-phase region, and the center and the vicinity of the Si substrate became (SiO$_2$ + mullite) two-phase regions. Further heat exposure resulted in the formation of a (SiO$_2$ + mullite) two-phase reacted layer that contained 80% or more SiO$_2$ in the vicinity of the interface. The thickness of the layer increased with the heat exposure time. The formation of the reacted layer is considered to be caused by the diffusion of Al in the mullite coating to the surface, and the diffusion of Si from the Si substrate to the coating.

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