Fundamental Study of Suspension Plasma Sprayed Silicate Coatings*

Ryotaro Yanaoka¹, Yuji Ichikawa¹, Kazuhiro Ogawa¹, Takaya Masuda² and Kazuto Sato²

¹Fracture and Reliability Institute, Tohoku University, Sendai 980-8579, Japan
²Fujimi Incorporated, Kakamigahara 509-0103, Japan

It is predicted that the operating temperatures of next-generation aircraft engines will exceed the present critical temperatures of any of the conventional metallic materials (<1400°C). As a result, it is likely that the application of SiC/SiC ceramic matrix composites (CMC) as primary materials. When exposed to an oxidative environment, SiC forms a protective silica scale. This layer provides additional protection from problems that may occur upon oxidation. It will, however, react with the water vapor formed during the combustion process, creating gaseous silicon hydroxides that will reduce its thickness. This problem has hindered the practical realization of CMC engines in aircrafts. Consequently, environmental barrier coatings (EBCs) are required to protect CMC components from oxidative degradation and thus ensure the reliability of CMC engines. In this study, a new deposition process, namely, the suspension plasma spray (SPS) process, is proposed to form the EBC. It produces much denser coatings by feeding a suspension of particles that are a single micron in size. It was confirmed that the coating structure and composition resulting from the SPS process were largely influenced by the residence time of the suspensions in the plasma flame. Subsequently, the optimum spray conditions were examined and discussed.

(Received January 27, 2020; Accepted April 20, 2020; Published June 25, 2020)

Keywords: suspension plasma spray, silicate coatings, environmental barrier coatings, ceramic matrix composite, silicon carbide

1. Introduction

Due to the global increase in aviation demand, there is a significant incentive to lessen the fuel consumption of aircraft engines, achieving energy savings, and reducing their environmental load. In this respect, the reduction of the weight of the aircraft fuselage the weight of the high-temperature engines, is a key objective. Ni-base superalloys are commonly used materials for turbine blades, which are high-temperature components within these engines. Highly efficient next-generation aircraft engines, however, comprise blades with densities approximately three times higher than the traditionally used metal materials. SiC ceramic matrix composites (CMCs) are one such promising next-generation material with high heat resistance.1) Practical application of these CMCs, however, is challenged by the reduction in thickness that occurs due to oxidation under a high-temperature steam environment. To protect these components from this deterioration and damage, and ensure their reliability, it is necessary to apply environmental barrier coatings (EBCs). These EBCs are generally composed of multiple layers of ceramic coatings.2)–4) They must be stable and dense in a high-temperature steam environment and provide improved environmental shielding. Furthermore, electron beam physical vapor deposition (EB-PVD) methods, which may be used to apply these coatings, experience problems in terms of both their coating formation speed and their coating density.

In this study, suspension plasma spraying (SPS)5,6) has been proposed as a new EBC-deposition method. Using this method, the powder material is applied as a suspension, making it possible to apply particles of the order of a single µm, unattainable by conventional plasma spraying due to its rheology.7) Because fine particles are supplied by the SPS method, the powder material can be melted easily, reducing both the pore size and microcracks, and forming a dense coating.8) Additionally, this method allows for the formation of a columnar structure, which presents the potential to reduce thermal stress resulting from the usage environment by tuning the coating-formation conditions.9) As CMCs are expected to be used at a higher temperature in future applications, it is likely that the EBC layer will require a thermal barrier.10) Therefore, it is beneficial that the SPS method can form both dense EBC layers and columnar TBC layers. It is also desirable that it can form such coatings with varying functions in one single process. While there have been many studies on the application of the SPS method to obtain TBCs, there are limited research results regarding the SPS method in the formation of EBCs. In this study, the applicability of Yb₂Si₂O₇,11) which has been proposed as a topcoat material in EBCs in recent years, has been examined. Both APS and SPS methods have been used to form coatings and the variations in structure and composition have been evaluated. Furthermore, for the SPS method, the impact of the spraying parameters on the coating structure and composition has been evaluated. Finally, based on the results obtained in this study, a pathway for future improvement of the SPS EBC method has been proposed.

2. Experimental

2.1 Preparation of specimen materials

In this study, a 2 mm thick Aluminum plate and SiC sintered body were prepared as the substrate materials. The Aluminum plate was used in as-sprayed coating observations, while the SiC sintered body was used in high-temperature oxidation testing. In this high-temperature oxidation test, a Silicon bond coat, applied by the APS method, was introduced to improve adhesion. Yb₂Si₂O₇ powder, prepared via granulation sintering, was used as the feed-stock material. The average powder particle size was 3.40 µm for the SPS method and 35.2 µm in the case of the APS method. Figure 1 presents an SEM image of the powder used in the study. When using the SPS method, the suspension concentration was 10 wt.%, with ethanol used as the suspension dispersion.
medium. The coating was applied to the substrate, fixed to the jig, using the Praxair (SG-100) and Progressive Surface (100HE) spray guns for the APS and SPS methods, respectively. The APS and SPS construction conditions are detailed in Tables 1 and 2, respectively. The output of the APS-method spray gun was controlled by the current, and Ar and He gases were used. Conversely, Ar, N2, and H2 gases were used in the SPS process.

2.2 High-temperature oxidation test

Each deposited specimen was subjected to a high-temperature oxidation test, under atmospheric pressure, using a high-temperature electric furnace (Nitto Kagaku Co. Ltd., NHK-170AF). The testing temperature was 1300°C, and the test time was varied from 0 to 100 h. After the test, the furnace was left to cool to room temperature, at which point the specimen was removed.

2.3 Measurement of in-flight particle velocity and temperature

The velocity and temperature of the in-flight particles were measured to clarify their relationship with various SPS method spray parameters. To obtain these measurements, a thermal spray process measuring system (TECNAR, Accuraspray-G3C) was used. This system involves detection of light emissions, caused by powder passing through the measurement area, by an optical sensor comprising two optical fibers in the center head and a CCD camera. The average particle temperature was calculated using a two-color thermometer by quantifying the phase shift of the detected light emission waveform.

2.4 Coating evaluation

2.4.1 X-ray fluorescence (XRF) analysis

As depicted in Fig. 2, SPS spraying was performed over a two-minute period in a water-filled stainless container, with the subsequent precipitated particles collected. X-ray fluorescence (XRF) analysis was carried out to evaluate the material composition before and after thermal spraying by means of Shimadzu XRF-1700.

The effect of the different spray parameters and influencing factors on the degree of SiO2 volatilization was discussed. Due to operational limitations, the distance from the spray gun to the water surface, for the purpose of particle recovery, was 700 mm. The actual spray distances for coating sample preparation were 80–120 mm and 76 mm for the SPS and APS methods, respectively. This resulted in a minor discrepancy and a subsequent variation in the degree of volatilization.

2.4.2 X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) was performed on the feed-stock powder and on each coating using Shimadzu Maxima XRD-7000. The material composition and the crystallinity before and after thermal spraying were evaluated, and the impact of the key spray parameters and influencing factors on these characteristics was discussed.

2.5 Cross-sectional evaluation of the coatings

Each coating was cut and embedded with resin. The cross-sectional area was mirror-finished by wet polishing using a diamond disk, followed by buffing with a single crystal diamond suspension (9 µm and 3 µm), and an alumina liquid abrasive. SEM images were then captured and EDX analysis performed on the finished cross-section.

3. Results and Discussion

3.1 Coating evaluation

3.1.1 XRF analysis and in-flight particle measurement

The XRF measurement results for each specimen are presented in Fig. 3. It was confirmed that the proportion of the SiO2 component within the collected powder was smaller in all of the prepared coatings than in that of the as-supplied powder. This decrease in SiO2 content was also noted to be significantly greater in the SPS coatings when compared to the APS coatings. It has been reported previously that in the case of Rare earth Element (RE) silicates containing 20 μm 20 μm

Fig. 1 SEM images of the feedstock Yb2Si2O7 powder: (a) APS and (b) SPS.

Table 1 Spraying conditions of APS coatings.

<table>
<thead>
<tr>
<th>Material</th>
<th>Gas Ar/He [psi]</th>
<th>Current [A]</th>
<th>Traverse speed [mm/s]</th>
<th>Distance [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb2Si2O7</td>
<td>50/50</td>
<td>900</td>
<td>400</td>
<td>120</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td>100</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 2 Spraying conditions of SPS coatings.

<table>
<thead>
<tr>
<th>Gas Ar/N2/H2 [slm]</th>
<th>Plasma power [kW]</th>
<th>Suspension Concentration [wt.%]</th>
<th>Traverse speed [mm/s]</th>
<th>Distance [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>85/57/57</td>
<td>105</td>
<td>10</td>
<td>1500</td>
<td>76</td>
</tr>
<tr>
<td>133/63.5/63.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180/70/70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 Technique for collection of flying particles.

20 μm

Fig. 1 SEM images of the feedstock Yb2Si2O7 powder: (a) APS and (b) SPS.
Yb$_2$Si$_2$O$_7$, the partial pressures of SiO and SiO$_2$ in the material are significantly higher than those of the other components at 2000°C or higher than these silicate melting point of each material. This decrease in the SiO$_2$ component ratio suggests that the SiO$_2$ component in Yb$_2$Si$_2$O$_7$ will volatilize when the flying particles are exposed to a high-temperature plasma flame that exceeds the melting point of the material. A volatilization phenomenon such as this may occur remarkably near the powder surface, where the temperature is higher. The average particle size of the powder used in this study was approximately 30 µm for APS and 3 µm for SPS. This phenomenon was noticeable in the SPS coatings with a larger specific surface area than that of the supplied powder. In the case of the SPS coatings, there was a correlation between the gas flow rate and the ratio of the contained SiO$_2$ components. It was observed that a lower gas flow rate led to a greater degree of SiO$_2$ volatilization.

The relationship between the gas flow rate and the particle velocity, measured during coating formation, is presented in Fig. 4, while the relationship between the gas flow rate and the particle temperature is shown in Fig. 5.

Through examination of Figs. 4 and 5, it was estimated that the gas flow rate and the in-flight particle velocity/temperature were proportional to one another. Regarding the in-flight particle temperature, when the gas flow rate was increased from 200 to 320 SLM (Volume flow rate L/min in 0°C, 101.325 kPa), the temperature rose from 3600 to 4000°C, which is approximately twice the melting point of Yb$_2$Si$_2$O$_7$ (1850°C). This suggests that a change in temperature in this high-temperature environment does not significantly impact the volatility of SiO$_2$. On the other hand, the particle velocity was observed to increase from 700 to 900 m/s with the previously described change in gas flow rate. In this instance, the distance from the gun to the substrate was set at approximately 80 mm, implying that, when the particle velocity rose from 700 to 900 m/s, the particle residence time in the gas flow decreased by approximately 30%. For this reason, the change in particle velocity, caused by altering the gas flow rate, has a significant effect on the volatilization degree of SiO$_2$. With a lower gas flow rate, the residence time of the flying particles in the high-temperature plasma flame was extended. The resulting in-flight particle velocity was then reduced and an increased amount of SiO$_2$ was volatilized. Based on these findings, it is assumed that a larger extent of SiO$_2$ volatilization occurs close to the central location of the plasma generation, where the temperature gradually decreases as the particles move further away.

3.1.2 X-ray diffraction

Figure 6 presents the XRD results from the as-sprayed coating. It was observed that this coating has a broader peak on the low-angle side when compared to the supplied powder for both the SPS and APS coatings. Furthermore, almost no Yb$_2$Si$_2$O$_7$ peak was observed. It was concluded that the as-sprayed coating was primarily amorphous material. The SPS coating was found to be slightly more crystalline than the APS coating, with this variation in crystallinity thought to
be largely due to the difference in particle size. The smaller particle size in the SPS coating allows for easier heat transmission, which causes the crystallization of these particles to progress further than those in the APS method.

Figure 7 depicts the XRD results obtained after the high-temperature oxidation test. It was confirmed that, after this test, the broad amorphous peak on the low-angle side disappeared and crystallization progressed in both the SPS and APS coatings. It was also confirmed that the coating contained Yb$_2$Si$_2$O$_7$ and Yb$_2$SiO$_5$, suggesting that, due to SiO$_2$ volatilization, an amount of Yb$_2$Si$_2$O$_7$ became Yb$_2$SiO$_5$. When contrasting the peak intensities of two coatings, the composition ratio was higher of Yb$_2$SiO$_5$ in the SPS coating and of Yb$_2$Si$_2$O in the APS coating. This may be due to the difference in the SiO$_2$ component volatilization between the two processes, as confirmed by the XRF analysis results described earlier. By varying gas flow rates in the SPS method, the Yb$_2$Si$_2$O$_7$ peaks disappeared under a flow rate of 200 SLM, with Yb$_2$O$_3$ peaks confirmed around 29°, 34°, 49° and 58° of Fig. 7.

Therefore, the coating composition after the high-temperature oxidation test depends on the volatilization amount of the SiO$_2$ component during the coating formation. This is considered to correlate with the residence time of the particles within the plasma flame.

It is predicted that a coating with a high ratio of Yb$_2$Si$_2$O$_7$ can be achieved when the coating is formed under a proportionately higher gas flow rate.

3.2 Cross-sectional SEM observation and EDX analysis

Figure 8 shows the cross-sectional backscattered electron image of the as-sprayed coating. It was observed that the SPS coating has a significantly smaller pore size, a denser structure, and a smaller number of microcracks than the APS coating. In terms of the uniformity of the coating structure, it was observed that both coatings exhibited multiple regions with different contrasts. The results of the EDX analysis on the coating cross-section are presented in Fig. 9. The increase and decrease of the signal intensity of Si and Yb elements in both coatings were confirmed by the contrast brightness. It is considered that the dark region, with the high signal intensity of Si, is a region close to Yb$_2$Si$_2$O$_7$, and the bright region is a region with components close to Yb$_2$SiO$_5$.

Figure 10 shows the cross-sectional backscattered electron image of the coating after the high-temperature oxidation test. It was confirmed that, after this test, the coating structure changed substantially when compared to the as-sprayed coating. In the APS coating, a lamellar structure consisting of bright and dark areas was confirmed. From EDX analysis, shown in Fig. 11, it is considered that the lamellar structure is composed of Yb$_2$SiO$_5$ and Yb$_2$Si$_2$O$_7$, since bright and dark regions of the contrast are composed of components close to Yb$_2$SiO$_3$ and Yb$_2$Si$_2$O$_7$, respectively. This phase is produced under equilibrium cooling conditions. Due to the rapid solidification of the droplets, the metastable phase was observed in the as-sprayed coating. However, it is assumed that such microstructural changes occurred after the high-temperature oxidation test, because the equilibrium cooling condition was achieved by furnace cooling.

Figure 12 displays the Yb$_2$O$_3$–SiO$_2$ binary system phase diagram. When the content of SiO$_2$ is 50 mol% or less, the phase is Yb$_2$O$_3$ + Yb$_2$SiO$_5$. However, XRD results (Figs. 6
and 7) showed that Yb$_2$SiO$_5$ + Yb$_2$Si$_2$O$_7$ phase is main component in coatings with gas flow rates of 320 SLM and 260 SLM. In these cases, the SiO$_2$ component ratio is higher than it is at 200 SLM. Even though the same feedstock powder was used, different phases were obtained by changing the gas flow rate. It can be observed from the phase diagram that the SiO$_2$ component ratio increased after the high-temperature oxidation test. The reason for this is unclear; however, it is possible that Si, used as a bond coat, has diffused into the coating by heat treatment. This is a topic for further study.

In addition, the SPS coating presented regions with different contrasts, and the lamellar structure seen in the APS coating was not observed. The disparities in structure are thought to be due to the varying particle size. Further investigation is required to confirm this hypothesis. Under different gas flow rates, the SPS coating exhibited structural changes that were different to those in the APS coating. This was observed under all conditions, and it can be seen that the spray conditions differ. Based on the EDX analysis and XRD results, as depicted in Figs. 6, 7, and 11, it was inferred that the bright region is Yb$_2$O$_3$, the middle region is Yb$_2$SiO$_5$, and the dark region is Yb$_2$Si$_2$O$_7$. Image processing was used to calculate the area ratios of the three contrasted regions. These results are presented in Fig. 13. It was noted that the ratio of each region varies with the gas flow rate. Yb$_2$O$_3$ + Yb$_2$SiO$_5$ were identified at a gas flow rate of 200 SLM, Yb$_2$O$_3$, Yb$_2$SiO$_5$ + Yb$_2$Si$_2$O$_7$ at 260 SLM, and Yb$_2$SiO$_5$ + Yb$_2$Si$_2$O$_7$ at 320 SLM. This agrees with the XRF and XRD results, and is presumed to be due to the variation in SiO$_2$ volatilization. At a gas flow rate of 200 SLM, a significant amount of SiO$_2$ has volatilized, with only Yb$_2$O$_3$ + Yb$_2$SiO$_5$ remaining. Analyzing the results described above, a gas flow rate of 320 SLM appears to be the most appropriate to suppress the volatilization of SiO$_2$ and form the most dense coating possible. Previous research has suggested that this should comprise the composite structure of Yb$_2$SiO$_5$ + Yb$_2$Si$_2$O$_7$. While several oxidation examples do exist, it was found to be difficult to form a coating solely composed of Yb$_2$Si$_2$O$_7$ by controlling the gas flow rate, as was done in this study.

However, in the case of the Yb$_2$Si$_2$O$_7$ coating sprayed at a gas flow rate of 260 SLM, the area ratio of Yb$_2$SiO$_5$ calculated after the high-temperature oxidation test is approximately 85%; almost single-phase Yb$_2$SiO$_5$. This is highest proportion of Yb$_2$SiO$_5$ within any coating, deposited...
was observed between the in-

composition analysis, using XRF and XRD, a correlation
2. E

volatilization volume of SiO2. The degree of volatilization
using Yb2SiO5 powder, in any study that we have conducted
the SiO2 and Yb2SiO5 components within this coating were
4.87 and 13.03 wt.%, respectively. It is therefore predicted
that it is possible to compensate for the volatilized SiO2 lost
during construction, by using Yb2Si2O7 powder with a more
significant proportion of SiO2 component than Yb2SiO5. In
doing so, the effectiveness of the SiO2-rich suspension can
be increased. It is predicted that this suspension could be
applied to other silicate materials, and that utilizing the SPS
method to deposit it can form a dense coating with a uniform

composition.

4. Conclusions

The purpose of this study was to examine the applicability
of EBCs deposited via the SPS process. Using Yb2Si2O7,
a common EBC topcoat material in recent years, coatings
were prepared by the SPS and APS methods. The variations
in coating structure and composition as a result of different
thermal spraying processes were evaluated. The SPS process
was then examined further, and the effect of the spray
parameters on the coating structure and composition was
evaluated. The control factors were estimated and the ideal
deposition conditions for EBC coatings were investigated.
The key findings are as follows:

1. Comparison with APS coatings

The XRF and XRD analysis of the coating composition
confirmed that the SiO2 component was significantly
volatilized in the case of the SPS coating. This was due
to the small feed-stock powder size and the large total surface
area.

From the cross-sectional SEM images and EDX analysis,
it was confirmed that the SPS coating was dense, and the
structure change behavior, upon high-temperature oxidation,
varied between the different processes.

2. Effect of spray parameters

By means of in-flight particle velocity measurement and
composition analysis, using XRF and XRD, a correlation
was observed between the in-flight particle velocity and the
volatilization volume of SiO2. The degree of volatilization
increased with slower in-flight velocity and longer exposure
time in the plasma flame.

Through examination of the cross-sectional SEM images
and EDX analysis, a correlation was found between the
coating density and the gas flow rate. When a Yb2Si2O7
suspension was used to deposit a coating under appropriate
conditions, the coating comprised a single phase of Yb2SiO5.
The results suggest that the volatilized SiO2 component has
been supplemented through incorporation of a powder with a
more significant proportion of the SiO2 component.

Acknowledgments

This work was supported by the Japan Society for the
Promotion of Science (JSPS) Core-to-Core Program A.
Advanced Research Networks “International Research
Center for Intelligent Layer Materials and Layer Structures
for Energy Saving.” JSPS KAKENHI Grant Numbers
JP16K14109, and the EBC working group of the Japan
Thermal Spray Society.

REFERENCES

301.
1033.
1791–1797.
Japanese).
Japanese).
9) A. Ganvir, N. Curry, S. Bjorklund, N. Markocsan and P. Nylen:
1705–1715.
3069–3083.
14) S. Oki and K. Ueno: Thermal Spray Technology Handbook, (Japan
15) N.A. Toropov, I.A. Bondar and F.Y. Galakhov: Trans Int Ceram
pp. 85–103.