The Current Status of Environmental Barrier Coatings and Future Direction of Thermal Spray Process*1

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In the next-generation of turbine engines, improving the heat resistance and reducing the weight are the essential solutions to increasing the thermal efficiency and reducing fuel consumption and CO2 emissions. Silicon-based ceramics (e.g., SiCf/SiC ceramics matrix composites (CMCs) and monolithic Si3N4) are the leading candidates for these applications because of their extreme light weight and superior heat resistance compared to the current Ni-based alloys. The main challenge of the Si-based ceramics is oxidation and volatilization of the silica in the high-temperature combustion gas environment with the water vapor and thereby its rapid recession. The most promising approach is protecting the surface of the ceramic matrix composites from the water vapor attack by an external environmental barrier coating (EBC) layer. Since the early 1990s, a lot of efforts have been made to develop suitable EBCs; however, no single material can satisfy all the EBC requirements. Thereby, the current EBC trends are directed to the development of multilayered EBCs, with different functions as a significant solution to prevent CMC recession and to maximize its performance for next engine generation. This paper discusses the history, current status, and future trends of EBC development not only in the world but also in Japan. Furthermore, it introduces future prospects of fine particle spraying in EBC developments.

[doi:10.2320/matertrans.MT-T2021003]

(Received November 29, 2021; Accepted April 14, 2022; Published June 3, 2022)

Keywords: turbine engine, environmental barrier coating (EBC), ceramic matrix composite (CMC), mullite, barium strontium aluminosilicate (BSAS), rare-earth (RE) silicate, multilayer, thermal expansion coefficient, recession, fine particle spray

1. Outline of Applications of Turbine Engines and EBCs

A gas turbine engine, such as a diesel engine or gasoline engine, is an internal combustion engine that obtains rotational kinetic energy through rotation of a turbine by a high-temperature gas flow generated by fuel combustion. Gas turbine engines are relatively lightweight, they are used in aircraft as a jet engine that gains thrust from a jet flow and also in power generation systems of various sizes from a large one to a small one used as emergency power generation equipment. They are also used for high efficiency combined cycle power generation in combination with a steam turbine to improve efficiency. Gas turbine engines are thus indispensable for maintaining the quality of life in modern society.

Gas turbine engines include a compressor that compresses the intake air, a combustor that mixes and combusts the atomized fuel and compressed air, a turbine that obtains rotational motion from the high-temperature, high-speed combustion gas jet flow, and an exhaust port where gas is discharged. The technological development of high-temperature components for the combustors and turbines exposed to high-temperature combustion gas is one of the most important challenges for improving the performance of turbine engines. At present, these high-temperature parts are mainly fabricated by applying ceramic thermal barrier coatings (TBCs) consisting mainly of yttria-stabilized zirconia (YSZ) onto Ni-based heat-resistant alloys. The surface temperatures of TBC, heat-resistant alloy, and the combustion gas temperature, which depend on the system, are typically 1100°C–1200°C, 1000°C, and 1400°C–1500°C, respectively; in the newest gas turbines for power generation, the gas temperatures exceed 1600°C.1–3 This high combustion gas temperature has been achieved through advances in the cooling technology for the turbine blade surface. However, increasing the efficiency and output of gas turbine engines requires further increases in the combustion gas temperature (in practice, the turbine inlet temperature (TIT)). However, as previously mentioned, the combustion gas temperature exceeds the durable temperature of the high-temperature materials used in turbine blades and combustors, revealing an urgent need for the development of materials that can be used at the higher temperatures in next-generation gas turbines.

As will be described later, further increases in the TIT will be required in response to various technical, social, and economic demands; likewise, further developments in material technology will be required to realize higher TITs. In addition to the development of various new TBC processing technologies, the use of ceramic matrix composites (CMCs), mainly SiCf/SiC composites, for high-temperature components of turbine engines is being widely investigated. SiCf/SiC composites exhibit a high durability of 1000–1400°C and strong potential for use as high-temperature heat-resistant materials. However, their main shortcomings are poor oxidation resistance of the interface layers (C and BN) between the reinforced fibers and the matrix in actual high-temperature environments and poor water vapor recession resistance of the SiC matrix. These shortcomings let the development of environmental barrier coatings (EBCs) as an active research area for realization of CMCs. This article reviews the technological developments related to EBC technology.

*1This Paper was Originally Published in Japanese in J. Jpn. Thermal Spray Soc. 57 (2020) 76–87.
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2. Transition from Thermal Barrier Coatings to Environmental Barrier Coatings and Thermal/Environmental Barrier Coatings

In gas turbine engines such as aircraft engines and gas turbines for power generation, the temperature of the combustion gas exceeds the durable temperature of the Ni-based superalloys used in the combustors and turbines; thus, thermal barrier coatings (TBCs) are widely used to protect these components from the high-temperature combustion gases.\(^\text{(4)}\) In general, a ceramic material with a low thermal conductivity (e.g., YSZ) is used for TBCs to ensure sufficient thermal insulation. Improving the power and efficiency of the system necessitates an increase in the TIT of the combustion gas, where improvements of the thermal barrier and component cooling technologies by application of TBCs play major roles. Large-scale cooling reduces the efficiency of the system because of the cooling of the components with gases, water, and steam in their interior and on their surface.\(^\text{(5–7)}\) Therefore, achieving higher TIT temperatures to increase the power and efficiency of turbine engines requires Ni-based superalloys to be replaced with a lightweight ceramic-based composite (i.e., a CMC) material with good high-temperature durability.\(^\text{(8,9)}\)

Si-based ceramics (\(\text{SiC}/\text{SiC}\) and \(\text{Si}_3\text{N}_4\) composites) are the most promising candidate materials with respect to the heat resistance and mechanical properties required for the high-temperature components of turbine engines.\(^\text{(10–13)}\) These composites are extremely lightweight and exhibit excellent heat resistance and high-temperature mechanical properties compared with the Ni-based superalloys currently used in gas turbines. These features are important issues for improving the thermal efficiency of the system, improving fuel efficiency, and reducing \(\text{CO}_2\) emissions, and their applicability is being investigated. However, oxidation/volatilization and thickness reduction in high-temperature water vapor environments are major shortcomings of Si-based ceramic materials (Fig. 1).\(^\text{(14–18)}\) For example, SiC reacts with high-temperature water vapor at a temperature of \(1100\,^\circ\text{C}\) or higher and silicon hydroxide volatilizes as follows:

\[
\text{SiC} (s) + 2\text{O}_2 (g) = \text{SiO}_2 (s) + \text{CO}_2 (g)
\]
\[
\text{SiO}_2 (s) + 2\text{H}_2\text{O} (g) = \text{Si(OH)}_4 (g)
\]

For \(\text{SiC}/\text{SiC}\) to be used as a high-temperature material in turbine engines, the problem of oxidative thickness reduction must be overcome. Therefore, studies on environmental barrier coatings (EBCs) to protect \(\text{SiC}/\text{SiC}\) from degradation in high-temperature water vapor environments are underway.\(^\text{(19)}\)

3. Required Functions for Multilayer EBCs

The key characteristics of EBC systems that protect CMCs from rapid degradation by high-temperature water vapor are summarized as follows:\(^\text{(20–22)}\)

- Environmental stability (high-temperature steam resistance, calcium–magnesium–aluminosilicate (CMAS) resistance)
- Chemical compatibility of coating interfaces upon exposure to high temperatures
- High adhesion
- Low thermal conductivity (reduced cooling gas)
- Low residual stress (small thermal expansion coefficient difference, high phase stability, low elastic modulus, high sintering resistance)

However, no materials simultaneously satisfy/meet all of these requirements. Therefore, the current focus of EBC development aims at EBC systems consisting of multilayer coatings with different functions.\(^\text{(19)}\)

Multilayer EBCs are composed of a bond-coat (BC) layer and a topcoat (TC) layer (Fig. 2a). The main role of the BC layer is to ensure high adhesion between the CMC and the TC layer. In addition, as shown in Fig. 2b, the incorporation of additional layers to impart different functions depending on the application environment (e.g., chemical compatibility, matching of thermal expansion coefficient difference, stability against high-temperature steam, high-temperature mechanical properties, environmental resistance, and low thermal conductivity) is also being explored.\(^\text{(20,22,23)}\)

Since 1990, various advances have led to the development of several generations of EBCs.\(^\text{(19)}\) Currently, metallic Si is used as a BC material because it provides excellent adhesion between the CMC and TC; however, Si melts at \(1414\,^\circ\text{C}\), which limits its application at higher temperatures.

4. History of EBC Development

4.1 Early EBC materials: mullite and BSAS

In the early stages of EBC development, the application of \(\text{Al}_2\text{O}_3\), YSZ, mullite, and other coatings to the surface of...
SiC/SiC components was investigated. These coatings were intended to protect the BN layer used in the fiber/matrix interface against oxidative degradation. Among them, mullite was considered a promising protective coating material because its thermal expansion coefficient was similar to that of SiC/SiC. However, mullite coating can contain significant amount of amorphous phase when they are deposited by an atmospheric spraying method (i.e., atmospheric air plasma spray (APS)) upon rapid quenching. This amorphous component leads to cracking and delamination because of volume shrinkage during subsequent thermal exposure. Therefore, NASA developed a so-called in-situ crystallization coating method, where a SiC substrate was heated to the crystallization temperature of mullite (~1050°C) during coating formation, realizing a coating with a delamination resistance greater than 1200 h at 1300°C. In the mid-1990s, SiO2 was found to be vaporized as a hydroxide under high-temperature steam, and not only SiC/SiC and Si3N4 but also mullite exhibit insufficient resistant to thickness reduction in high-temperature steam environments. Researchers have, therefore, developed a two-layer EBC system by superimposing 8YSZ (ZrO2 with 8-mass% Y2O3), which has been used successfully in gas turbine/jet engines, onto mullite. Although this method combines materials with substantially different thermal expansion coefficients, adhesion, as evaluated by thermal cycle tests under atmospheric conditions, has been reported to be high. However, the large difference in thermal expansion coefficients among YSZ, mullite, and SiC (YSZ: 10 × 10⁻⁶, mullite: 5.3 × 10⁻⁶, SiC: 4.5 × 10⁻⁶K⁻¹, respectively) led to cracking in high-temperature water vapor environments. The formation of cracks allowed the high-temperature vapor reach to the base material, resulting in degradation of SiC/SiC by oxidation.

Barium strontium aluminosilicate (BSAS: BaO–SrO–Al₂O₃–SiO₂) has been developed to suppress the crack formation. This material system was designed to possess a thermal expansion coefficient similar to that of SiC and to reduce the vapor corrosion recession of SiO₂. Mullite/BSAS with BSAS topcoat instead of YSZ suppressed a propagation of cracks that appeared in the mullite bond coat, thereby providing enhanced protection of the SiC/SiC base material. Furthermore, the combination of a mullite bond coat and BSAS led to further improvements in crack resistance; a water vapor resistance test at 1200°C showed that the coating exhibited excellent environmental resistance. However, in a higher temperature water vapor environment at 1300°C–1400°C, BSAS reacted with SiO₂ (or Si(OH)₂), which were formed on the surface of SiC, to form a low-viscosity glass phase; then, CO(g) was generated during the oxidation of SiC, leading to the formation of large pores along the interface. Therefore, a structure of Si/mullite/BSAS or Si/mullite–BSAS/BSAS, in which a Si bond coat was applied as a diffusion barrier, improved an environmental barrier function. However, a perfect environmental protection was not achieved in long-term tests. In case when the intermediate layer was mullite, cracks were formed and the underlying layer was oxidized; meanwhile, in the case of a mullite–BSAS intermediate layer, a low-viscosity glassy phase and pores were formed at the interface with the underlying layer. The formation of cracks was attributed to the difference in thermal expansion coefficients among YSZ, mullite, BSAS, SiC, and Si and to the associated residual stress. Thus, compared with the TBC system, such as Ni-based superalloy/MCrAlY bond coat/8YSZ, a difference in thermal expansion coefficients among the layer materials was more prominent in the EBC system, as the EBC system was composed of brittle ceramic materials.

4.2 Silicates

Rare-earth (RE) silicates are currently considered the most promising candidate EBC materials. Among them, Yb-silicate is considered to exhibit the best properties because of which SiO₂ is less reactive than that of BSAS, exhibiting a high corrosion resistance to CMSAS and high-temperature steam. Yb-silicate also exhibits good stability, a high melting point, and a thermal expansion coefficient similar to those of CMC materials such as SiC and Si₃N₄. Two types of RE silicates are known: rare-earth monosilicates (RE₂SiO₅) and rare-earth disilicates (RE₂Si₂O₇). The monosilicates are more stable at high temperatures than the disilicates and also more stable in high-temperature steam environments. Meanwhile, the thermal expansion coefficient of the disilicates is smaller than those of the monosilicates and has values similar to those of the CMC base material. Regarding the oxidative evaporation rate in water vapor environments, the disilicates exhibit approximately the same value as BSAS and the monosilicates exhibit even lower values. In addition, RE silicates exhibit excellent chemical compatibilities with Si-based ceramic materials. Because of their various aforementioned features and characteristics, RE silicates are considered the most promising candidate EBC materials. Table 1 summarizes the thermal expansion coefficients and melting points for the main RE silicates and common oxide ceramic materials.

4.3 Other candidate materials

In the early 2000s, various oxide ceramics, such as Al₂O₃ and YSZ, and various complex oxide materials, such as Al₂TiO₅, Al₅Si₂O₁₃ (mullite), and RE silicates (RE = Er, Lu, Sc, Yb, Y), were evaluated as EBC materials. In collaboration with the Oak Ridge National Laboratory in the United States, several works were reported on the water vapor recession behavior of these materials. Particular attention was being devoted to Lu-based silicates as their thermal expansion coefficients were similar to those of SiC and Si₃N₄ and as they exhibited superior resistances to steam oxidation recession. Generally, RE silicates are oxidized under high-temperature steam atmospheres and Si is released at the initial stage to produce an RE monosilicate and Si(OH)₄. However, in the case of Y₂SiO₅ and Lu₂SiO₅, the regeneration of the disilicate has been reported to occur through a reaction with SiC and H₂O:

\[2Y_2SiO_3(s) + 2SiC(s) + 3O_2(g)\]
\[\rightarrow 2Y_2Si_2O_7(s) + 2CO(g)\]
\[2Lu_2SiO_5(s) + H_2O(g)\]
\[\rightarrow Lu_2Si_2O_7(s) + Lu_2O_3(s) + nH_2O(l)\]
Table 1 Thermal expansion coefficient (CTE) and melting point of typical rare-earth silicates and oxide ceramic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Average CTE ($\times 10^{-6} \text{K}^{-1}$)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC, SiC/SiC</td>
<td>4.5-5.5 (2)</td>
<td>2545 (90)</td>
</tr>
<tr>
<td>Si$_2$N$_2$</td>
<td>3.4-4 (20)</td>
<td>1875 (71)</td>
</tr>
<tr>
<td>Si</td>
<td>3.5-4.5 (2)</td>
<td>1416 (70)</td>
</tr>
<tr>
<td>Mullite</td>
<td>5.6-6 (20)</td>
<td>1800 (90)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>6.8-8.4 (6), 9.6 (6)-(7)</td>
<td>2072 (61)</td>
</tr>
<tr>
<td>Y$_2$SiO$_3$</td>
<td>5.6 (3)</td>
<td>1900 (65)</td>
</tr>
<tr>
<td>Er$_2$SiO$_3$</td>
<td>5.7 (3), 7.8 (4)</td>
<td>1980 (50)</td>
</tr>
<tr>
<td>Yb$_2$SiO$_3$</td>
<td>3.5-4.5 (2), 7.8 (3)-(4)</td>
<td>1950 (62)</td>
</tr>
<tr>
<td>Y$_2$Si$_2$O$_7$</td>
<td>4.4-6</td>
<td>1850 (6)</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>6.8-8.4 (6)</td>
<td>2415 (90)</td>
</tr>
<tr>
<td>La$_2$Si$_2$O$_7$</td>
<td>3.8-4.2 (3)-(7)</td>
<td></td>
</tr>
<tr>
<td>Sc$_2$Si$_2$O$_7$ + SiO$_2$</td>
<td>5.6 (7)</td>
<td>1860 (90)</td>
</tr>
<tr>
<td>BSAS (monoclinic celsian)</td>
<td>4.4 (2)</td>
<td>1500 (52)</td>
</tr>
<tr>
<td>BSAS (hexagonal celsian)</td>
<td>7-8 (7)</td>
<td>1500 (71)</td>
</tr>
<tr>
<td>Y$_2$Si$_2$O$_7$</td>
<td>3.9 (9)</td>
<td>1775 (50)</td>
</tr>
<tr>
<td>Lu$_2$Si$_2$O$_7$</td>
<td>6.7 (4)-(8)</td>
<td></td>
</tr>
<tr>
<td>Sc$_2$Si$_2$O$_7$</td>
<td>5.4 (11)</td>
<td>1850 (90)</td>
</tr>
<tr>
<td>Garnet (Y$_3$Al$_2$O$_12$)</td>
<td>9.1 (11)</td>
<td></td>
</tr>
</tbody>
</table>

Ueno et al. also conducted a basic study on a zircon (ZrSiO$_4$) sintered body as an EBC material.\(^{62}\) We also investigated zircon deposited by plasma spray and found that, because of the rapid cooling and solidification rates, zircon split into a composite coating of amorphous SiO$_2$ and nonequilibrium tetragonal ZrO$_2$ and was subsequently regenerated during the subsequent thermal exposures. The porosity was found to increase because of a large volume contraction upon regeneration. In addition, the addition of Y$_2$O$_3$ was found to suppress the large volume contraction at high temperatures and to improve the adhesion to the SiC base material.\(^{63}\)

A detailed comparative study has been reported regarding the behavior of monosilicates and disilicates during the reaction with high-temperature steam.\(^{34}\) Each RE monosilicate of Y, Gd, Er, Yb, and Lu was subjected to a thermal exposure test at 1350°C in an environment of 90% water vapor and 10% air, and the behavior of each oxidation reaction was investigated. All of the monosilicates except Gd produced the corresponding disilicate by the reaction with high-temperature steam.\(^{34}\) Each RE monosilicate and disilicate was produced. This is called splats. During the thermal spray coating process, these splats are deposited to form a highly aniso-

A new trend is the development of T/EBCs, which have both environment-barrier (EBC) and thermal barrier (TBC) functions.\(^{50}\) Materials that could simultaneously achieve excellent water vapor oxidation resistance and thermal barrier performance have been investigated in this regard. It has explored materials that exhibited high water vapor oxidation resistance and low thermal conductivity by doping two appropriately selected RE elements into RE silicates. The development of new materials by adding multiple RE elements is an active research area, where China is in the lead.\(^{64,65}\)

In addition to the steam oxidation recession, corrosion deterioration caused by complex oxides, CMAS, originated from volcanic ash and dust has become a major problem, particularly in aircraft jet engines. Protective coating materials are being developed, including RE silicates and other complex oxides (e.g., YAlO$_3$ and Y$_3$Al$_5$O$_{12}$).\(^{35,38,66}\) As previously described, further advances in EBC technology require optimization of the coating process as well as the development of new materials.

5. EBC Deposition Methods

5.1 EBCs and thermal spraying

Electron Beam-Physical Vapor Deposition (EB-PVD) has been widely adopted to produce TBCs for aircraft jet engines, while APS mainly for EBCs. In general, APS utilizes Ar as the working gas to generate the plasma by discharging using a water-cooled nozzle-shaped copper (Cu) anode and a tungsten (W) cathode. When a secondary gas such as H$_2$ or N$_2$ is added, the plasma becomes a high-temperature and high-speed plasma jet and is ejected from the nozzle. The spraying material powder is injected into the plasma, then it is heated, melted, and accelerated toward the substrate material to form a coating. Thermal spray processes are classified according to the deposition atmosphere and the form of the spraying material, and each process has excellent features.\(^{22}\) Powder materials as large as 20–60 µm for ceramics and ~100 µm for metals are usually used as the thermal spray materials. These particle size ranges have been determined empirically from the viewpoint of operability during deposition process, such as ensuring excellent fluidity and relatively-easy injection into the plasma jet. The powder which is injected into the plasma jet is heated, melted, accelerated, impinged on a substrate, then flattened and solidified rapidly.\(^{67}\) The flattened particles obtained in this manner are called splats. During the thermal spray coating process, these splats are deposited to form a highly aniso-
tropic and unique structure called a lamellar structure.\textsuperscript{68-71} The anisotropy greatly contributes to the thermal barrier characteristics, and APS has played a central role because of the need to form large turbine blades with complex shapes for use in gas turbines for power generation. On the other hand, EB-PVD is mainly used in aircraft applications because of its high thermal cycling characteristics. The current shift of EBC from EB-PVD to APS implies a coming important market for the thermal spray industry and is also interesting from an academic perspective as well.

### 5.2 Atmospheric plasma spraying method

Lee et al. have prepared Si bond coats, mullite, and mullite–BSAS on SiC/SiC by APS, and have used BSAS, RE disilicates (RE = Yb, Sc), Sc$_2$Si$_2$O$_7$/Sc$_2$O$_3$, RE monosilicates (RE = Lu, Yb, Er, Y), and YSHF as EBC topcoats.\textsuperscript{22} Cojocaru et al. used thermal exposure tests to investigate the high-temperature stability of EBC deposited by APS of Si/mullite/Y$_2$SiO$_5$ based on the thermal stress of each layer.\textsuperscript{75} The volatilization of Si during APS causes the Yb$_2$SiO$_5$ powder to decompose into two phases: Yb$_2$SiO$_5$ and Yb$_2$O$_3$ and the decomposition of the 3:2 mullite powder (3Al$_2$O$_3$/2SiO$_2$) to the 2:1 mullite phase (2Al$_2$O$_3$/SiO$_2$) has also been reported. Bakan reported a comparative study on the structure of Yb$_2$SiO$_5$ formed by each process of APS, suspension plasma spraying (SPS), VLPPS, and high velocity oxy-fuel (HVOF) spraying.\textsuperscript{70} When Yb$_2$SiO$_5$ powder was sprayed, X-ray diffraction analysis showed that almost entire APS coating was amorphized and Yb$_2$O$_3$ crystals were partly present. By contrast, in HVOF, although the deposition temperature was \(\sim\)125°C–150°C, the proportions of amorphous phase, Yb$_2$Si$_2$O$_7$ crystal phase, and Yb$_2$SiO$_5$ crystal phase were 48% (smaller than that in APS), 49%, and 3%, respectively. Bakan et al. considered that the crystalline phase and the amorphous phase correspond to the unmolten phase and the molten phase, respectively.\textsuperscript{74} This interpretation suggests that HVOF suppresses the overheating of particles to a greater extent than APS. Vassen et al. compared these processes with actual CMC substrates and reported the results.\textsuperscript{75} Figure 3 shows a cross-sectional view of the coating obtained using each process. In APS coating with a high amorphous content, large vertical cracks are introduced; by contrast, in the material with half the amorphous content sprayed by HVOF, the crack morphology shifts to micro-cracks. Fan et al. also investigated LaMgAl$_{11}$O$_{19}$ (LMA) and reported on the high-temperature stability of Yb$_2$Si$_2$O$_7$/LMA and Si/Yb$_2$SiO$_5$/LMA EBCs on C$_3$/SiC.\textsuperscript{75} In Japan, Kuroda et al. at NIMS have investigated plasma spraying of LMA.\textsuperscript{76}

### 5.3 Low-pressure plasma spraying

Low-pressure plasma spraying (LPS) is a method of plasma spraying in an inert reduced-pressure atmosphere. Compared with the APS method, the length and the velocity of the plasma jet is longer, and higher in LPS respectively, which results in a higher in-flight particle velocity with a lower heating capability.\textsuperscript{77} LPS is therefore mainly used for high-quality thermal spray coating of metal-based materials.

Although ceramic deposition by LPS has also been reported,\textsuperscript{78} the utilization of LPS as an EBC deposition process is scarce. The aforementioned lower heating capability was considered to limit the applicability of LPS for ceramic spraying. One of the authors has investigated the high-temperature stability and delamination resistance of EBCs on sintered SiC while maintaining a high substrate temperature by preheating the plasma jet.\textsuperscript{65} A coating was deposited in an Ar atmosphere at 0.05 MPa, which was mainly intended to provide efficient substrate pre-heating by plasma-jet elongation\textsuperscript{77} in a reduced-pressure atmosphere rather than the formation of the LPS coating. Bakan and Vassen et al. have reported the formation of Yb$_2$Si$_2$O$_7$ via very low-pressure plasma spraying (VLPS) at the pressure further reduced to 200 Pa.\textsuperscript{53,74} The crystal phase of Yb$_2$Si$_2$O$_7$ was obtained at a ratio of 93% when the substrate was heated to 980°C. Figure 3(d) shows the cross-sectional structure of the coating deposited by VLPS, revealing that a uniform coating was fabricated without large cracks.

### 5.4 Suspension plasma spraying method

The SPS method is a spraying technique, in which a fine powder (1 µm or less) dispersed in a liquid such as alcohol is injected directly into a plasma jet as an initial spraying material, where the suspension is atomized, evaporated, agglomerated, melted, then impacted and deposited. Although SPS can deposit dense coatings with small pore diameters and few microcracks compared with conventional thermal spray coatings, SPS is mainly intended to be used as a fabrication method of porous coatings, such as TBCs and SOFCs, as it can deposit porous coatings with unique structures.\textsuperscript{79,80} The use of SPS for EBC development is also being considered.\textsuperscript{81} Bakan et al. reported that the deposition of Yb$_2$Si$_2$O$_7$ powder by SPS revealed that most part of coatings were amorphous, even though the fraction of amorphous phase was slightly lower than that by APS.\textsuperscript{74} The crystalline phase was also transformed into Yb$_2$SiO$_5$ and Yb$_2$O$_3$ phases.
because of the volatilization of Si. The Yb$_2$SiO$_5$ phase contained a monoclinic variant, which was not observed in APS. Ogawa et al. have reported an attempt to add SiO$_2$ to suppress the formation of Yb$_2$SiO$_5$ due to the selective evaporation of SiO$_2$ during SPS of Yb$_2$Si$_2$O$_7$.82)

5.5 Plasma spray-PVD (PS-PVD) method

Plasma spray-physical vapor deposition (PS-PVD) method generates a plasma jet under high vacuum of 100 Pa, which considerably valued higher for thermal spray, evaporates an injected powder material, and deposits the vaporized material onto the material surface to form a coating. Under this reduced pressure, plasma jets exhibit substantially different properties than those used in APS and LPS; the length of the jet extends to ~2 m or more, and the diameter is ~30 cm.83) Selecting appropriate values for deposition parameters such as the spray distance enables the formation of various structures such as dense, porous columnar, and splat-layered ones. Studies using the PS-PVD method have mainly examined its applicability for depositing TBCs as splat-layered ones. Studies using the PS-PVD method have of various structures such as dense, porous columnar, and parameters such as the spray distance enables the formation of coating. Under this reduced pressure, plasma jets exhibit substantially different properties than those used in APS and LPS; the length of the jet extends to ~2 m or more, and the diameter is ~30 cm.83)

5.6 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) method is a coating technique, in which a precursor gas is chemically reacted on the surface of a base material to fabricate a target compound material. It is generally utilized to process functional thin films which are used in semiconductor industry. While CVD enables the fabrication of dense and high-quality coatings, there was a report on an EBC system, which consisted of CVD-SiC coatings on the surface of SiC/SiC substrates with a bond coat and topcoat.20,89,90)

5.7 Slurry coating method

In slurry coating process, a suspension, made by mixing a fine ceramic powder whose diameter is ~1 µm or less with an organic solvent, is coated onto the material surface and then calcined to form a coating. Although it is not a new coating method, only a few examples of slurry coatings for high-temperature applications such as TBC have been reported. The ceramic must be calcined after the coating process, making the method impractical on metal substrates. However, when the substrate is CMC and a high-temperature treatment is possible, the slurry coating method is advantageous because of its simplicity and low cost compared with other coating methods. If such coatings can be developed to provide the requisite environmental resistance (e.g., delamination resistance and water vapor recession resistance), the impact of this method on the industry would be large.81-96)

6. SiC/SiC Composite and Coatings on SiC Fiber

High density, high-temperature stability, and crack-healing ability are required for CMC matrices. Fiber stability at high temperatures is also required to ensure adequate defect tolerance as a CMC. Oxidation and corrosion stability under exposure to high-temperature gases and hence the development of EBCs are also significant requirements.97)

Methods for fabricating CMCs are roughly classified into the chemical vapor infiltration (CVI) method, solid-phase infiltration (SPI) method, polymer impregnation (infiltration) and pyrolysis (PIP) method and melt infiltration (MI) (also known as the liquid-silicon infiltration (LSI) method).98-100) The MI method leads to residual Si in the CMC matrix.101) Therefore, it is difficult to use in an environment with 1400°C (melting point of Si) or higher. The MI method has reportedly been adopted by NASA and General Electric,97,101,102) whereas the CVI method is promoted by IHI.99)

The main advantage of CMC is that the interface between the fiber and the matrix is covered with an interface coating (or called fiber coating); the presence of this interface layer with weak adhesion separates the fiber from the matrix, resulting in an improved defect tolerance.97,99) Because the defect tolerance of CMCs is influenced by the material and properties of this fiber coating, fiber coatings are currently actively researched. Generally, C and BN are used; however, because C is oxidized and disappears at 600°C or higher, BN is considered more suitable for aircraft engine applications.99)

It is generally used in a temperature/stress region where the matrix does not crack, since the SiC fiber itself can deteriorate rapidly at high temperatures in the absence of a matrix. At temperatures higher than 900°C–1200°C, fiber degradation can occur because of matrix cracking. On the contrary, the fibers can be protected by oxidation in the further higher temperature range.103) AFRL has tested a fiber coating of Y$_2$Si$_3$O$_7$ instead of BN and confirmed an improvement in steam resistance at 1000°C.104,105)

Ito et al. at Yokohama National University have proposed an integrated manufacturing method for CMC EBCs, matrices, and fiber EBCs using the CVD method.106) A deposition rate of 430 µm h$^{-1}$ has been achieved with Y monosilicate by the laser-heated CVD method.107)

7. Market Forecasts and Current Situation of Domestic EBC System Development

The demand for higher efficiency of jet engines and gas turbines is gradually increasing year by year in response to increasing crude oil prices and increasing interest in environmental protection. To satisfy these demands, improving engine cycle efficiency by operating each element of the engine at higher temperatures and pressures is important. Therefore, the TIT has been increasing year by year; currently, 1600°C class systems with a thermal efficiency higher than 60% have been installed for large gas turbines. These improvements are attributed to the technological development of Ni-based superalloys with a higher temperature capability, TBCs, and cooling of turbine blades. However, further improvements in the operating temperature require the introduction of ceramic materials with higher
durable temperatures. The features, performance, and technical issues have already been introduced in the previous sections. We here explain some of the background information related to the introduction of ceramic materials.

7.1 Environmental conservation issues

An international agreement about reducing greenhouse gas emissions was discussed at the United Nations Framework Convention on Climate Change (commonly known as the COP), which was held in Paris in 2015. The so-called “Paris Agreement”, which incorporates numerical targets for controlling greenhouse gas emissions in various countries, took effect in 2016.\textsuperscript{108,109}

The Paris Agreement is the successor to the “Kyoto Protocol”, established in 1997, and features the following objectives:

- Keep the average global temperature rise well below 2°C compared to before the Industrial Revolution and make efforts to maintain it by 1.5°C.
- Peak out greenhouse gas emissions as soon as possible, and balance greenhouse gas emissions (through reforestation, etc.) in the second half of the twenty-first century. Two global long-term goals and medium-term goals have been set. For example, the goals for Japan, USA, and Europe are as follows:
  - Japan: Reduce CO\textsubscript{2} emissions by 26% by 2030 (compared to fiscal year 2013 emissions)
  - USA: Reduce CO\textsubscript{2} emissions by 26%–28% by 2025 (compared to fiscal year 2005 emissions)
  - EU: Reduce CO\textsubscript{2} emissions by 40% by 2025 (compared to fiscal year 1990 emissions)

To achieve its numerical target, Japan has begun to examine research programs such as “reconstruction of energy mix for low emission”, “active introduction of renewable energy”, and “promotion of energy saving policy”.

In response to the aforementioned extremely strong demands for controlling greenhouse gas emissions from the viewpoint of environmental conservation, advancing gas turbines and jet engines toward “higher efficiency”, “lighter weight”, and the “introduction of low emission fuels such as hydrogen” is important. Against this background, the active introduction of ceramic materials into the high-temperature operating sections of gas turbines and jet engines is regarded as important.

7.2 Future forecast of aircraft engine demand

According to the “Market Forecast for Commercial Aircraft 2019–2038” (Japan Aircraft Development Association),\textsuperscript{110} global air passenger transportation is increasing by 4.4% every year. The number of aircraft is expected to increase substantially in response to this increasing demand. In 2038, it will be necessary to operate \~40,000 aircraft, which is almost 1.7 times the number of aircraft operating in 2018. Here not only the replacement of the old engines but also a drastic increase in the number of new engines will be required. Therefore, the number of passenger jet aircraft forecasted to be delivered in 2019–2038 (20 years) is 35,312. The breakdown is as follows: replacement of 18,915 current aircraft (54% of the number of delivered aircraft), with the addition of 16,397 new aircraft to meet future demand.

As for a type of operation to meet the ever-increasing demand for private passenger transport, hub airports in each major region of the world are connected by large aircraft, where passengers are distributed to small and medium-sized aircraft and are transported from there to each city. Therefore, narrow-body aircraft with 120–160 seats will represent the largest increase in new type of operation. Demand in the air transportation field is expected to steadily increase in the future.

Therefore, in addition to reducing CO\textsubscript{2} emissions as a measure one against global warming, strong global demand exists for technology to control increasing airfares due to increasing crude oil prices.

7.3 Japan’s energy supply after the Great East Japan Earthquake

In Japan, nuclear power generation has been temporarily suspended nationwide following the Great East Japan Earthquake that occurred on March 11, 2011. Approximately 90% of the electric power demand is covered by thermal power generation at present, by which we can see Japanese energy power supply relies on thermal power generation. The development of new gas turbine technologies such as more efficient systems and hydrogen combustion systems to reduce CO\textsubscript{2} emissions is therefore important.

In Japan, the development of hydrogen combustion gas turbine technology is being achieved with the goal of comprehensively developing technology for using hydrogen as a low emission energy medium from upstream (hydrogen production technology) to downstream (effective utilization technology) in the “International Clean Energy System Technology for Hydrogen (WE-NET)” (Phase I: 1993–1998, and Phase II: 1999–2003). The development of hydrogen combustion turbine technology was implemented as part of Sub-Task 8 in Phase I. It included (1) evaluating optimum systems for hydrogen combustion turbines, (2) developing combustion control technologies, (3) developing main components such as turbine blades and rotors, (4) developing main components, and (5) developing ultra-high-temperature materials.\textsuperscript{111} An evaluation of the durability of ceramic materials at combustion gas temperatures of 1700°C was also conducted. The behavior of YSZ TBCs fabricated by EB-PVD in a hydrogen combustion environment was investigated, and mostly good results were achieved.\textsuperscript{112,113} Although the tests were conducted in a high-temperature and high-pressure environment, the test duration was short (30 min); further investigations are required to assess the long-term durability of these TBCs.

The development of EBC technology to protect the ceramic components from corrosion and recession by high-temperature steam is the most important issue for both improving the TIT and increasing the efficiency of hydrogen combustion turbines. More active approaches are needed in Japan to advance these technologies.

7.4 Development of EBC system technology in Japan

In Japan, in addition to the development of EBC technology in the WE-NET (International Clean Energy System Technology for Hydrogen Utilization, 1993–2002) mentioned in the preceding section, EBC technology has also
been developed as one of the elemental technologies in various national projects, including Synergy Ceramics (1994–2003) and ESPR (Environment-friendly Next-generation Supersonic Propulsion System, 1999–2004). Some of the main items will be introduced as follows:

For the technological development of ceramic gas turbines, the Central Research Institute of Electric Power Industry’s group investigated the effects of \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) impurities on the recession characteristics of 13.7 mass\% \(\text{Y}_2\text{O}_3\)-\(\text{ZrO}_2\) in a combustible environment containing steam.\(^{114}\) Based on this result, a multilayered coating of RE-silicate/YSZ—the so-called T/EBC coating—has been developed and was supplied to a combustion-environment-exposure test.\(^{115}\)

We have reported the development of YSZ/\(\text{Y}_2\text{Si}_2\text{O}_7\) composite coatings using zircon as a starting material and the improvement of its high-temperature stability and adhesion to \(\text{SiC}\).\(^{63,116}\)

As previously mentioned, Ohji \textit{et al.} conducted joint research with the United States focusing on the Lu-silicate as an EBC material for \(\text{Si}_3\text{N}_4\) and reported numerous findings.\(^{56,57,62}\)

Kitaoka \textit{et al.} developed an EBC system as part of the Cross-Ministerial Strategic Innovation Promotion Program (SIP, 2014–2018).\(^{117-119}\) The research focused on oxygen diffusion within the EBC layers, which had significantly different oxygen partial pressures at their front and back surfaces, to develop an ideal EBC system for \(\text{SiC}/\text{SiC}\). A proposed multilayer laminated structure of \(\text{SiAlON}\) layers (adhesion), dense mullite layers (oxygen barrier), \(\text{Yb}_2\text{Si}_3\text{O}_7\) graded layers (water vapor barrier), and porous \(\text{Yb}_2\text{Si}_3\text{O}_7\) layers (thermal shock relaxation) has been proposed for \(\text{SiC}/\text{SiC}\). In addition, Hasegawa \textit{et al.} investigated the deposition of EBC elements such as mullite via the aerosol deposition (AD) method.\(^{120,121}\)

8. Summary and Future Expectations for Thermal Spray Processes

EBCs are required to be more multifunctional. Although the integrated structure of T/EBC coatings has begun to be investigated from the viewpoint of thermodynamic stability, a multilayering structure is becoming a critical requirement for further solution as each layer is responsible for one function. Figure 4 shows a comparison between the TBC and EBC systems.\(^{122}\) The T/EBC system based on \(\text{Ni}\)-based superalloys has a five-layer multilayer coating system that includes the metallic BC layer and the TGO-layer formed at the interface, and these layers have different coating structures. Therefore, coating processes also need to be improved to satisfy these demands. This multilayering is one of the basic design approaches for \(\text{SiC}/\text{SiC}\).\(^{2,123}\) Furthermore, in the T/EBC system, where TBCs and EBCs are combined, a Si coating was sprayed onto a \(\text{SiC}/\text{SiC}\) substrate, followed by a layer with a graded structure from mullite to BSAS to deposit a BSAS coating. A single layer of BSAS has been used to address the problem of water vapor corrosion, and a graded-composition YSZ or a new ceramic material was applied as a thermal barrier layer.\(^{124}\) A multilayer structure with approximately five layers is also required here, and therefore highly developed coating technologies are required for both TBC and EBC systems. In high-temperature applications, the key is how to suppress the thermal stresses caused by the difference in thermal expansion coefficients between the substrate material and the coating layers.\(^{122}\) However, the design concepts are fundamentally different: TBCs are based on a \(\text{Ni}\)-based superalloy with a large thermal expansion coefficient, whereas EBCs are a ceramic coating system based on a \(\text{SiC}\)-based CMC with a small thermal expansion coefficient.

Figure 5 shows the steam corrosion rates and thermal expansion coefficients for water vapor-corrosion-resistant EBC candidate materials.\(^{125}\) The construction of an EBC with an appropriate thermal expansion coefficient based on the thermal expansion coefficient of the base material is important. In particular, a dense coating is required as an environmental barrier, and cracks in the coatings are not permissible unless the coating exhibits self-healing ability. Thermal stress relaxation can be achieved by the structure
control, such as gradient composition structure and proper coating thickness. Thus, the role of coating processes gets more significant. Consequently, the functions and characteristics required for EBCs are diverse. Even with conventional coating deposition methods, greater optimization is required, including optimization of the base material, coating material, and coating structure to be formed. Therefore, benchmark comparative investigations between these coating processes are important. Efforts to incorporate not only thermal spraying technology but also various new processes and further optimizations of EBC film formation process will be strongly required in the future. In fact, as described in a recent T/EBCh development report from NASA, recently developed techniques include varying the coating fabrication techniques for each layer.126

In Chapter 5, various coating methods were introduced. A survey of the thermal-spraying-related methods, which contain a particularly large number of parameters, reveals that most of them were prepared under the conditions recommended for the conventional equipment; only a few reports have discussed controlling the coating structure at most by substrate heating. For example, if the preferential volatilization of Si occurs, substantially increasing the temperature above the melting point is unsuitable. Therefore, LPS under mild conditions could be more appropriate process than the conventional APS, which tends to cause evaporation of the particle surface through rapid heating. Thus, the properties of the coating could be dramatically changed by the selection of an appropriate particle heating mode.

In addition, the deposition of dense coatings requires a reduction of the deposition elements in size, so that the spraying of fine particles is considered a promising solution for EBC deposition. The spraying methods include processes such as AD, which can be used to fabricate a dense coating without particle melting, which is in contrast to SPS using the same fine particles. Some works using AD for developing EBCs have been reported.120,121,127 In addition, a recently developed hybrid aerosol deposition method has partly overcome the problems contained in a particularly large number of parameters, revealing that the function and characteristics required for the conventional equipment; only a few reports have discussed controlling the coating structure at most by substrate heating. For example, if the preferential volatilization of Si occurs, substantially increasing the temperature above the melting point is unsuitable. Therefore, LPS under mild conditions could be more appropriate process than the conventional APS, which tends to cause evaporation of the particle surface through rapid heating. Thus, the properties of the coating could be dramatically changed by the selection of an appropriate particle heating mode.

Recent estimates indicate that reducing CO2 emissions by 80% in 2050 compared to 2013 levels will require reducing the emissions from power generation facilities to nearly zero; to this end, hydrogen energy is considered a key energy source.133 From this perspective, an energy system that uses hydrogen as an energy medium is important in all aspects. The partial pressure of water vapor will be even higher in power generation systems that use hydrogen combustion, leading a further demand for EBCs. Under these circumstances, the demand for coating methods will naturally increase, and the demand for the fine particle spray coating technology is expected to increase in the near future.

REFERENCES