Vapor–Deposited Functionally Gradient Materials

Toshio HIRAI** and Makoto SASAKI**

Various methods are used in inhomogeneous functional graded technology to control the constituent elements of a composite material. Functional graded technology includes chemical and physical processes for such control. The vapor deposition method can be used to fabricate a film or a platelike material directly without need of melting or sintering. Furthermore, composition control of dispersion is comparatively easy in the direction perpendicular to the deposition surface. Fabrication of compositional graded materials (so called functionally gradient materials, FGMs) has been attempted using the vapor deposition method. For instance, Ti–TiC and Ti–TiN FGMs have been fabricated using physical vapor deposition (PVD), and SiC–TiC multilayer film and SiC/C FGM has been fabricated using chemical vapor deposition (CVD). In this paper, functional graded technology employing the vapor deposition method is reviewed.

Key Words: Ceramics, Thermal Stress, Residual Stress, Thermal Shock, Silicon Carbide, Carbon, Titanium Carbide, Titanium Nitride, Titanium, Vapor Deposition, Functionally Gradient Material

1. Introduction

In recent years, various highly functional ceramic materials have been developed paralleling the progress in the control of material characteristics made possible by the ability to control the fine structures of materials.

Furthermore, various methods have been attempted in the development of ceramic base composites for the purpose of improving the essential characteristics of monolithic ceramics. Interest in ceramic base composites (nanocomposites) has been focussed on control of the size of the dispersion phase, having from a few to 10 nm or more\(^{(1)}\)\(^{(2)}\). With a decrease in the size of the dispersion phase in the composite, it expected that material with characteristics not seen in conventional composites can be developed. Furthermore, a "finecomposite" has recently been conceived which takes pores, defects, crystal structure, crystal orientation, dispersion conditions and other factors involved in the "dispersion phase"\(^{(3)}\) into consideration.

In the traditional research regarding composites, homogeneous distribution of dispersion has been considered to be indispensable. Uniformity of composite characteristics was achieved as a result. The design and tailoring of nanocomposites and finecomposites have been further developed in recent years. A certain function can be given to one material that has an inhomogenous characteristic by changing the density or composition of composites. In recent years, equipment for aerospace applications has required materials resistant to extreme conditions, e.g., high temperatures and an oxidizing atmosphere of > 2 000 K on one side and a temperature of around 1 000 K on the other\(^{(4)}\)\(^{(5)}\).

Various methods are used in inhomogeneous functional graded technology to control the constituent elements of a composite. Functionally gradient material (FGM) is obtained by physical or chemical treatment of starting materials such as vapor, liquids, and solids. These processing technologies are shown in Table 1.

The vapor deposition method can be used to fabricate a film or a platelike material directly with-
out melting or sintering. Furthermore, composition control of the dispersion perpendicular to the deposition surface. In this paper, the functional graded technology involved in the vapor deposition method is reviewed.

2. Fabrication Methods

Figure 1 illustrates the CVD setup which is composed of a gas controlling system, a reaction chamber, an exhaust system, an exhaust gas treatment system, a heating system, and a system of temperature measurement and control. Formation of various ceramic nanocomposites and finecomposites on a substrate is possible by controlling the composition of the input gas.

Figure 2 shows the PVD setup (ion plating) which is composed of a reaction chamber, an exhaust system, and devices for metal evaporation control, plasma generation, and gas input. This PVD setup can achieve a functional graded coating at relatively low temperatures by a reaction with the metal vapor and plasma-enhanced gas.

3. Inhomogeneous Materials Prepared by Vapor Deposition

3.1. Ti/TiC compositional graded film

Ti-TiC-Ti multilayer film and compositional graded film were prepared on carbon steel (carbon, 0.44 mass %) and Ti substrates by the use of a hollow-cathode electric discharge of Ar and C_2H_2 gases. The Ti/C ratio is a film is controlled by changing the C_2H_2 gas flow rate during deposition. The multilayer film changes into the desired composition by heat treatment in a vacuum at 1123 K for 35 hrs. Figure 3 shows the compositional change of the multilayer film on a Ti substrate after heat treatment. The TiC exists throughout a film as coated. On the other hand, the C component of TiC is diffused throughout the film and thus shows a gradient of C concentration. The compositional change of C content is achieved, while, in the case of a carbon steel substrate, the C content of a film is greater. This is because C in carbon steel

Table 1 Methods for the preparation of the inhomogeneous materials

<table>
<thead>
<tr>
<th>Phase</th>
<th>Process</th>
<th>Method</th>
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<tbody>
<tr>
<td>gas</td>
<td>chemical</td>
<td>chemical vapor deposition (CVD)</td>
</tr>
<tr>
<td>physical</td>
<td>ion plating</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sputtering</td>
<td></td>
</tr>
<tr>
<td></td>
<td>molecular beam epitaxy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ion implantation</td>
<td></td>
</tr>
<tr>
<td>liquid (melt)</td>
<td>chemical</td>
<td>electrodeposition</td>
</tr>
<tr>
<td>physical</td>
<td>spray</td>
<td>eutectic reaction</td>
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<tr>
<td></td>
<td>solidification</td>
<td></td>
</tr>
<tr>
<td>solid</td>
<td>chemical</td>
<td>thermal decomposition</td>
</tr>
<tr>
<td></td>
<td>sintering</td>
<td>smearing</td>
</tr>
<tr>
<td></td>
<td>physical</td>
<td>partial crystallizing</td>
</tr>
<tr>
<td></td>
<td>diffusion</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 Schematic diagram of the CVD setup
(1) H_2 gas, (2) CH_4 gas, (3) mass flow meter, (4) program controller, (5) SiCl_4 reservoir, (6) constant temperature bath, (7) ribbon heater, (8) pressure regulator, (9) water-cooled reaction chamber, (10) work coil, (11) pressure gauge, (12) optical pyrometer, (13) substrate, (14) graphite heater, (15) pump

Fig. 2 Schematic diagram of the ion plating setup
(1) gas, (2) electron beam, (3) metal source, (4) reaction chamber, (5) substrate, (6) r.f. power supply, (7) d.c. power supply, (8) pressure gauge, (9) pressure regulator, (10) pump
diffuses into the film.

Figure 4 illustrates the compositional change of the multilayer film on a carbon steel substrate after heat treatment. The C content becomes even due to the diffusion of C from carbon steel into the film at high temperature. The composition of Ti-TiC film is comparatively stable when the Ti substrate is used. However, it becomes unstable when a carbon steel substrate is used. These results show the influence of the substrate on the compositional stability at high temperatures.

3.2. Ti/TiN compositional graded film

Ti/TiN multilayer film is prepared on Ti and Cu substrates by the hollow-cathode ion plating method employing Ti vapor and plasma-enhanced N₂ gas. Compositional graded film is subsequently obtained by heat treatment. The TiN phase is observed in this film. The composition distribution and Knoop hardness of this film are shown in Fig. 5.

3.3. SiC-TiC multilayer film

Although the fabrication of SiC-TiC compositional graded film has not been achieved, related SiC-TiC multilayer film is herein introduced.

Coating on the C/C composite with SiC for the purpose of attaining oxidation resistance is achieved; however, thermal fatigue of the SiC film occurs under cyclic heating. Therefore, TiC film is introduced between the SiC film and the C/C composite using PVD or CVD.

The PVD TiC film is prepared in an ion plating chamber with the reaction of Ti vapor and CH₄ gas taking place at 1173 K. The CVD TiC or SiC film is prepared in a hot-wall-type reactor. The CVD conditions used are as follows: a TiCl₄-C₄H₁₀ or SiCl₄-C₂H₆ system, deposition temperatures of 1273 to 1673 K, and total gas pressures of 6.5 to 13 kPa. The evaluation of oxidation resistance is carried out by measuring the weight change of a specimen in atmosphere at 1573 K for 1 hr. An oxidation resistance test of SiC(CVD)/Ti or Ti-TiC(PVD)-coated C/C composite was conducted, and the results are shown in Table 2. Oxidation resistance of this specimen improved drastically with the introduction of TiC between the SiC film and the C/C composite.

Table 2 Oxidation resistance of the SiC-TiC multilayer-coated C/C composite

<table>
<thead>
<tr>
<th>Composition-thickness</th>
<th>Method</th>
<th>Composition-thickness</th>
<th>Weight loss (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC 6 mm</td>
<td>CVD</td>
<td>SiC 140 mm</td>
<td>17.78</td>
</tr>
<tr>
<td>TiC 10 mm</td>
<td>CVD</td>
<td>SiC 77 mm</td>
<td>5.10</td>
</tr>
<tr>
<td>TiC 18 mm</td>
<td>CVD</td>
<td>SiC 89 mm</td>
<td>0.70</td>
</tr>
<tr>
<td>Ti-TiC 21 mm</td>
<td>PVD</td>
<td>SiC 85 mm</td>
<td>5.10</td>
</tr>
<tr>
<td>Ti-TiC 21 mm</td>
<td>PVD</td>
<td>SiC 87 mm</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Oxidation condition (1573 K for 1 hr in atmosphere)

Fig. 3 Compositional distributions of the Ti-TiC-Ti multi-layer film on the Ti substrate after heat treatment.

Fig. 4 Compositional distributions of the Ti/TiC functionally gradient film on the carbon steel substrate after heat treatment.

Fig. 5 Compositional distribution and Knoop hardness of the Ti/TiN functionally gradient film.
SiC-coated C/C composite suffered cracking under the same conditions. On the other hand, cracking of SiC-TiC-coated C/C composite drastically decreased. SiC-coated C/C composite has a low residual stress. However, the residual stress of SiC/TiC-coated C/C composite is compressive. For this reason, tensile stress occurs in SiC film at the time of cooling due to the difference of the thermal expansion coefficient between the C/C composite and the SiC film (C/C: 0; SiC: 4.6 × 10^-6 K^-1). Cracking in SiC film released the stress. On the other hand, compressive stress occurs in the SiC/TiC-coated C/C composite and cracking is restrained by compressive stress. Figure 6 shows the relationship between oxidation resistance and the thickness ratio of TiC to SiC. Oxidation resistance increases with increasing TiC/SiC thickness ratio because the compressive stress of the film increases with increasing TiC/SiC thickness ratio. It is conceivable that excess compressive stress in a film causes the detachment of the film at the TiC/SiC ratio of 0.5. The functional graded TiC/SiC coating on the C/C composite is examined to minimize the film thickness as much as possible.

SiC/TiC functional graded materials on stainless steel are examined by the use of a thermochemical dissolution cycle (UT-3) of water. The UT-3 cycle has materials resistant to extreme conditions, e.g., a temperature of 1273 K and above, and a corrosion atmosphere of Br2-O2. Ceramic coating of the stainless steel (SUS 304) is attempted. TiC-coated SUS 304 has a superior corrosion resistance. However, if microcracks develop in the TiC film, the corrosion resistance decreases. The corrosion resistance of TiC/SiC-coated SUS 304 was greater than that of TiC-coated SUS 304. The corrosion resistance of SiC film is superior to that of TiC film. It is expected that functional graded ceramic material will be characterized by thermal stress relaxation and superior corrosion resistance.

3.4. SiC/TiC functional graded film

Recently, equipment for aerospace applications has required materials resistant to extreme conditions, e.g., a high temperature difference exceeding 1000 K, with a high-temperature oxidizing atmosphere of >2000 K on one side and a temperature of around 1000 K on the other side. SiC is desirable for use as a surface material because of its excellent characteristics of oxidation resistance. Carbon is suitable in terms of its affinity with a C/C composite base material. SiC/TiC functional graded material characterized by composition change from SiC to C is thought to be suitable as a thermal barrier material.

Figure 7 shows the radial distributions of stress, temperature and Young’s modulus of the SiC/C FGM cylinder for the case where the strength/stress ratio is unity or less. These distributions are calculated on the assumption that the cylinder consists of an SiC monolith with a thickness of 1 mm and that the SiC/C ratio changes gradually in the region from 1 mm to 10 mm of thickness where the SiC/C composition is uniform in the direction of the c-axis. Figure 8 shows the compositional distribution under the above conditions. As shown in Fig. 7, there is essentially no temperature distribution in the region from the internal face to the median thickness for several reasons as follows: the thermal conductivity of SiC is about twice that of carbon and the internal face is the higher-temperature side. The volume fraction of carbon is not high (about 20%) in this region. The SiC side, having a lower thermal expansion coefficient at the same temperature, is subjected to tensile stress, while the median thickness section containing carbon is subjected to...
compressive stress. The stress becomes tensile again in the region from the median thickness to the external face due to the rapid temperature decrease which is accompanied by a reduced thermal expansion coefficient.

An SiC/C FGM cylinder having a composition similar to that shown in Fig. 8 was produced using CVD. The SiCl$_4$-C$_3$H$_6$-H$_2$ system was used as a source gas. The [Si]/([Si] + [C]) ratio was changed stepwise as shown in Table 3, where the flow rate of H$_2$ acting as a carrier for SiCl$_4$ was controlled while that of C$_3$H$_6$ was kept constant. The stepwise change in the [Si]/([Si] + [C]) ratio in the feed mixture enabled production of an SiC/C FGM film, with a continuous gradient composition, consisting of SiC, SiC-C, C-SiC and C phases on the substrate in this order. They were deposited on the substrate to a thickness of 1.0 mm, the deposition time being 100 min.

The broken line in Fig. 9 represents the controlled profile of [Si]/([Si] + [C]) in the feed gas mixture, and the solid line represents the profile calculated on the assumption that the gases diffuse uniformly in the CVD chamber. The abscissa in Fig. 9 represents the film thickness estimated by multiplying the deposition time (min) for each step by the film growth rate (nm min$^{-1}$).

Figure 10 shows the microstructure observed by a scanning electron microscope, of the cross-sectional surface of the SiC/C FGM film. A 150-µm-thick, dense SiC phase and an 800-µm-thick SiC/C phase were formed on the graphite substrate in this order. The SiC/C ratio changed gradually in the composite phase, on which a 50-µm-thick C phase was formed. The portion where the concentration of the dispersed C accounted for 40 to 60 mol% of the total was especially porous$^{[14]}$.

Thermal shock resistance of the materials was investigated by the laser heating method$^{[15]}$. Figure 11 illustrates the relationship between laser power density and calculated temperature difference under the conditions.

Table 3 CVD condition for the preparation of SiC/C functionally gradient material using a SiCl$_4$-H$_2$-C$_3$H$_6$ system

<table>
<thead>
<tr>
<th>Deposition temperature, K</th>
<th>1773</th>
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</thead>
<tbody>
<tr>
<td>Total gas pressure, kPa</td>
<td>6.7</td>
</tr>
<tr>
<td>Si/(Si+C) in input gas</td>
<td>0.66 0.62 0.58 0.52 0.23 0</td>
</tr>
<tr>
<td>Deposition time, min</td>
<td>10 15 15 10 20 30</td>
</tr>
</tbody>
</table>

Fig. 9 Relationship between the Si content of SiC/C FGM and Si/(Si+C) in gas phase

Fig. 8 Suitable compositional distribution of SiC/C FGM predicted by calculations

Fig. 10 SEM photograph of the cross-sectional surface of SiC/C FGM

(a) graphite substrate; (b) SiC; (c) SiC-C; (d) C
Fig. 11 Relationship between laser power density and calculated temperature difference under thermal shock resistance test\(^{(13)}\) in the film thickness of ▲0.3, ◇0.8 and ◊1.8 in mm (open circle, no cracking; closed circle, cracking)

thermal shock resistance test. The laser power density by which SiC NFGM suffered cracking was 5.8 MWM\(^{-2}\); however, that by which SiC/C FGM (film thickness, 1.8 mm) suffered cracking was 7.4 MWM\(^{-2}\). Increasing the thickness of the SiC/C FGM layer from 0.8 mm to 1.8 mm, the temperature difference within the layer increased from 390 K to 560 K. The laser power density which induced cracking was 7.4 MWM\(^{-2}\) in the thickness of not only 0.8 mm but 1.8 mm. To define the criterion of cracking, thermal stresses under local heating were calculated using a two-dimensional nonsteady model. Figure 12 shows the calculated hoop stress of the surface of SiC NFGM and SiC/C FGM at a heat flux of 3.6 MWM\(^{-2}\). Tensile stress was generated in the part which was not irradiated by laser. The tensile stress is close to the fracture strength of SiC (650 MPa); thus, it can by considered that SiC NFGM suffered cracking by this hoop tensile stress. In the case of SiC/C FGM, it can be considered that cracking occurred at a relatively high heat flux of 7.3 MWM\(^{-2}\) by the same hoop tensile stress.

SiC/C FGM is a good candidate for use as film on C/C composite\(^{(12,13)}\). Figure 13 shows a schematic diagram of the cross-sectional surface of thermal barrier material composed of C/C composite and SiC/C FGM film. With the use of SiC/C FGM coating, improvement of the oxidation resistance of C/C composite is expected.

4. Conclusions

The preparation techniques of inhomogeneous material by control of phase distribution by CVD or PVD have been reviewed. The functionally gradient material (FGM) is an excellent example of an inhomogeneous material similar to materials which can be seen in the natural world.

New developments of inhomogeneous materials by following natural materials such as trees, shells and bones are anticipated in the near future.

References


(5) Niino, M., Hirai, T. and Watanabe, R., Function-


Microstructure of CVD SiC-C Nanocomposites, J. Mat. Sci., in press.


Toshio Hirai

Date of birth: Oct 7, 1937. Toshio Hirai is a professor at Institute for Materials Research, Tohoku University. He obtained a B. Eng. in 1960 and M. Eng. in 1962 from University of Osaka Prefecture, and D. Eng. in 1968 from Osaka University. His main field of research is synthesis, structure and properties of ceramics and ceramic composites including nanocomposites, finecomposites and functionally gradient composites materials.

Makoto Sasaki

Date of birth: May 6, 1953. Makoto Sasaki is a research associate at Institute for Materials Research, Tohoku University. A chemical engineer, he obtained a B. Eng. in 1977 from Utsuminoi University, and M. Eng. in 1979 from Tokyo Metropolitan University. His current research work concerns the development of new heatresistant ceramic composite materials.