Review Article

Formation of Al_2O_3 - HfO_2 Eutectic EBC Film on Silicon Carbide Substrate

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The formation mechanism of Al_2O_3 - HfO_2 eutectic structure, the preparation method, and the formation mechanism of the eutectic EBC layer on the silicon carbide substrate are summarized. Al_2O_3 - HfO_2 eutectic EBC film is prepared by optical zone melting method on the silicon carbide substrate. At high temperature, a small amount of silicon carbide decomposed into silicon and carbon. The components of Al_2O_3 and HfO_2 in molten phase also react with the free carbon. The Al_2O_3 phase reacts with free carbon and vapor species of AlO phase is formed. The composition of the molten phase becomes HfO_2 rich from the eutectic composition. HfO_2 phase also reacts with the free carbon and HfC phase is formed on the silicon carbide substrate; then a high density intermediate layer is formed. The adhesion between the intermediate layer and the substrate is excellent by an anchor effect. When the solidification process finished before all of HfO_2 phase is reduced to HfC phase, HfC- HfO_2 functionally graded layer is formed on the silicon carbide substrate and the Al_2O_3 - HfO_2 eutectic structure grows from the top of the intermediate layer.

1. Introduction

Since silicon carbide ceramic and its composites show high specific strength and high oxidation resistance at elevated temperatures, these materials are promised to be used as gas turbine hot section components [1]. However, under high speed exhaust gas and high temperature normally present in these applications, the surface of silicon carbide ceramics is oxidized and the formed silica layer is easily corroded by water vapor promoting the recession of the ceramic component. For example, Yuri and Hisamatsu suggested that silicon carbide ceramics will be recessed about 3 mm under gas turbine conditions at 1523 K for 10,000 hours [2]. Hence on the application of silicon carbide and its composites for gas turbine hot sections component, an oxidation-corrosion resistance environmental barrier coating (EBC) layer is required. Some oxides, such as ZrO_2 , HfO_2 , and $\text{Lu}_2\text{Si}_2\text{O}_7$, show excellent water vapor corrosion resistance under gas turbine conditions at elevated temperatures [3, 4]. On the development of EBC for nonoxides ceramics, oxides EBC layers were prepared by plasma spraying [3]. Since the EBC layer is composed of polycrystalline solid,

a small amount of glassy phase exists at the grain boundary and it can be easily corroded by water vapor under gas turbine condition; then, a porous structure is formed through the EBC layer, even if the crystalline phase of oxide EBC material shows an excellent water vapor corrosion resistance. The corrosive gases easily pass through the porous channel of the EBC layer and the silicon carbide substrate will be oxidized. Hence, an EBC layer without boundary glassy phase is required for the development of future EBC.

On the solidification of oxides eutectic, the excess impurities will be removed from the bulk by segregation [5]. Hence, the eutectic composites, especially the eutectic with ZrO_2 , HfO_2 , or $\text{Ln}_2\text{Si}_2\text{O}_7$ (Ln = rare earth) phase, are promising materials for EBC.

In our previous report, an oxides eutectic EBC without boundary glassy phase and its preparation method are proposed [6]. In this review, we focused on the Al_2O_3 - HfO_2 eutectic EBC and its preparation method and the formation mechanism of the Al_2O_3 - HfO_2 eutectic EBC layer will be summarized.

FIGURE 1: Longitudinal cross section of back scattering electron SEM images for the samples prepared by unidirectional solidification in solidification rate (a) $1.4 \mu\text{m/s}$, (b) $14 \mu\text{m/s}$, and (c) $28 \mu\text{m/s}$, respectively [7].

2. Structure Formation of Al_2O_3 - HfO_2 Eutectic

The microstructure formation of oxide eutectic composites closely depends on the solidification rate. Commonly, the microstructure of the eutectic is formed by limited diffusion of each component during the solidification. Hence, it can be predicted that a fine microstructure will be formed when the eutectic system includes a large cation such as hafnium ion and/or rare earth ion. Since the Al_2O_3 - HfO_2 eutectic includes HfO_2 which shows an excellent corrosion resistance, Al_2O_3 - HfO_2 eutectic is a promising material for EBC system. The microstructure formation of Al_2O_3 - HfO_2 eutectic is reported in a previous work of the authors [7].

The experimental procedures are described in detail in [7]. The eutectic samples were prepared by rapid solidification and unidirectional solidification using an optical floating zone apparatus. The powders of Al_2O_3 and HfO_2 were mixed in molar ratio of $\text{Al}_2\text{O}_3 : \text{HfO}_2 = 67 : 33$ according to [8]. The mixed powder was pressed into rod shape samples of 5 mm in diameter. The calcination was performed at 1473 K for 3.6 ks in air and the feed rod was prepared. The thermal cycling test for the rapid solidified samples was performed between room temperature and 1673 K. The solidification was performed in Ar atmosphere using floating zone apparatus. The pressure was controlled to 0.2 MPa for all solidification process. Xenon lamp was used as an optical source. The Xenon lamp and sample put on the focus in the elliptical mirror which has two focuses. The feed rod was hooked on upper shaft.

For the experiment of unidirectional solidification, another feed rod was fixed with lower shaft. This melting system was set up in a quartz tube. The solidification rate was controlled between 1.4 and $28 \mu\text{m/s}$. For the experiment of rapid solidification, the molten phase drops on a copper plate. The distance between the melting position and the copper plate was fixed to 0.23 m. The residual stress for the corundum phase in the eutectic structure was measured by Raman shifts. The transversal and longitudinal cross sections of the solidified samples were observed by SEM.

Figure 1 shows the longitudinal cross section SEM images obtained for the samples prepared by unidirectional solidification, using solidification rates of (a) $1.4 \mu\text{m/s}$, (b) $14 \mu\text{m/s}$, and (c) $28 \mu\text{m/s}$, respectively [7]. The white phase denotes HfO_2 phase and dark phase denotes Al_2O_3 phase. The interlamellar spacing decreased with increasing solidification rate and the relationship between the interlamellar spacing λ and solidification rate R can be expressed by $\lambda \propto R^{-0.437}$ as shown in Figure 2 [7]. The sample prepared by rapid solidification process also showed a lamella structure [7].

Lopato and Shevchenko suggested that the microstructure formation for Al_2O_3 - HfO_2 eutectic is very similar to that for Al_2O_3 - ZrO_2 eutectic [8]. The formation mechanism of Al_2O_3 - ZrO_2 eutectic was examined by several researchers [9–11]. The relationship between the interlamellar spacing λ and solidification rate R can be expressed by $\lambda^2 R = \text{constant}$ for Al_2O_3 - ZrO_2 eutectic [10]. For the Al_2O_3 - ZrO_2 eutectic, a lamellar structure is obtained below $3 \mu\text{m/s}$ in

FIGURE 2: The relationship between the interlamellar spacing and solidification rate [7].

FIGURE 3: The powder X-ray diffraction pattern of the sample prepared by rapid solidification [7].

the solidification rate and rod structure is formed above $3 \mu\text{m/s}$ in the solidification rate [9–11]. However, in the case of $\text{Al}_2\text{O}_3\text{-HfO}_2$ eutectic, only lamellar structure is formed even if the sample was prepared by rapid solidification process. Since the relation between interlamellar spacing λ and solidification rate R for $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and $\text{Al}_2\text{O}_3\text{-HfO}_2$ is eutectic according to Jackson-Hunt theory, the diffusion of component atoms are the limiting parameter at an established solidification rate for the formation of the microstructure. The differences in the microstructure formation between $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and $\text{Al}_2\text{O}_3\text{-HfO}_2$ are eutectic caused by the differences between diffusion coefficients of zirconium and hafnium ions during the solidification.

Figure 3 shows the powder X-ray diffraction pattern of the sample prepared by rapid solidification process [7]. Almost all peaks can be indexed as monoclinic HfO_2 and corundum phases. However, a weak peak at $2\theta = 30.37^\circ$ can

FIGURE 4: The Raman shift for Al_2O_3 phase in the eutectic sample [7].

be indexed as $(101)_t$ of the tetragonal HfO_2 phase [12]. In the $\text{Al}_2\text{O}_3\text{-HfO}_2$ binary phase diagram, tetragonal HfO_2 phase exists above 2063 K [8]. On the other hand, no peaks for the tetragonal HfO_2 phase were detected for the sample prepared by unidirectional solidification. Since the cooling rate for unidirectional solidification is lower than that for the rapid solidification, all of the tetragonal phase is transformed into monoclinic phase during the cooling step of the solidification process.

Figure 4 shows the Raman shift for Al_2O_3 phase in the eutectic sample prepared by unidirectional solidification and ruby single crystal as a reference [7]. The peaks of R1 and R2 for Al_2O_3 phase in eutectic sample slightly shifted from peaks of the ruby reference. Since the transformation of HfO_2 phase from tetragonal to monoclinic phase involved a large volume expansion, a tensile stress will be induced in Al_2O_3 phase. The tensile stresses for Al_2O_3 phase can be estimated to 420 MPa from the Raman shift [6]. Even though a large stress is induced on the $\text{Al}_2\text{O}_3\text{-HfO}_2$ interface in the eutectic structure due to the transformation from tetragonal to monoclinic phase, the stress is distributed to the long $\text{Al}_2\text{O}_3\text{-HfO}_2$ interface and no cracks are induced by the transformation.

3. Reactivity of $\text{Al}_2\text{O}_3\text{-HfO}_2$ Component with Silicon Carbide Substrate at High Temperatures

First we tried to prepare the $\text{Al}_2\text{O}_3\text{-HfO}_2$ eutectic film on silicon carbide substrate by heat treatment using electric furnace. Silicon carbide bulk (JAPAN FINE CERAMICS CO., LTD.) was used as substrate. In this silicon carbide bulk, carbon and boron were included as sintering agents. The slurry of Al_2O_3 and HfO_2 with the eutectic composition was applied to the surface of the substrate by a brush. The heat treatment was performed at 2573 K under Ar flow. The heating rate was controlled to 0.33 K/s. When the target temperature was reached, the power source of the furnace was shut down.

FIGURE 5: The external view of the samples after the heat treatment at 2573 K.

Figure 5 shows the external view of the sample after the heat treatment at 2573 K. From the phase diagram of Al_2O_3 - HfO_2 system, the melting temperature of Al_2O_3 - HfO_2 eutectic is 2163 K [8]. However, the mixed powder was not melted down during the heat treatment. From the X-ray diffraction patterns from the surface of the sample, HfC phase was detected, where all of Al_2O_3 phase was vaporized from the surface of the substrate and all of HfO_2 phase reduced to HfC phase. It is known that the vapor pressure of aluminium oxide is higher than that of hafnium oxide. The vapor species for aluminium oxide is Al , AlO , and Al_2O at high temperatures [13]. The vapor pressure for the AlO species is higher than that of the others above 2200 K and the vapor pressure of this species is 10^{-9} kg/cm^2 at 2200 K [13]. Hence, it is considered that the Al_2O_3 component reacts with free carbon and the formed AlO species vaporized from the surface of the substrate during the heating step. The film as shown in Figure 5 is easily peeled off from the substrate. These results suggest that if a rapid heating process is applied for the preparation of the eutectic Al_2O_3 - HfO_2 film, a multilayered EBC film with HfC as intermediated layer and Al_2O_3 - HfO_2 eutectic structure as the top coat can be prepared by controlling the reduction reaction between the film components and the substrate.

4. Preparation of Al_2O_3 - HfO_2 Eutectic Film Using Optical Zone Melting Method

Since the optical zone melting method is one of the rapid heating processes, the preparation of Al_2O_3 - HfO_2 eutectic film on silicon carbide substrate was performed using optical floating zone apparatus. The experimental procedures can be found in detail in a previous paper of the same author [6]. The slurry of the mixed powders with eutectic composition was dipped onto the silicon carbide substrate. The sample was calcined at 1200°C for 2 hours. A part of the dip coat layer was heated by light focusing.

First the damage of silicon carbide substrate by light focusing was examined. Figures 6(a) and 6(b) show the X-ray diffraction patterns of the silicon carbide substrate

before and after the light focusing. A peak for free carbon can be recognized in Figure 6(b). A small amount of the silicon carbide substrate decomposed to silicon and carbon according to the following:

The silicon carbide substrate used in this experiment possesses a small amount of carbon as sintering agent. In addition to this carbon, a small amount of free carbon will be generated by light focusing at high temperature. Hence, the preparation process of eutectic EBC film by the light focusing must be performed quickly to avoid the extensive generation of carbon. Figure 7 shows the schematic illustration for the preparation process of eutectic EBC film. The light is focused on the mixed powder with eutectic composition and a part of the mixed powder melts down. The melting zone is moved in one direction by moving the substrate as shown in the figure. The transference velocity is controlled to $111 \mu\text{m/s}$.

After the experiment it was found that fine powders were deposited on inner wall of the quartz tube during the solidification process. Figure 8 shows the powder X-ray diffraction pattern of the deposited powder [6]. A halo pattern was observed at $2\theta = 20\text{--}40^\circ$. The peaks can be identified by Si , Al , Al_2O_3 , and SiO_2 phases. Hence a small amount of Al_2O_3 component vaporized during the preparation of eutectic EBC film as predicted in the above section. Since the eutectic temperature of Al_2O_3 - HfO_2 is 2163 K [8], the temperature of the molten eutectic is higher than 2163 K. At temperatures above 2200 K, Al_2O_3 phase reacts with carbon and Al , AlO , or Al_2O species are formed [13]. Since the vapor pressure of AlO is higher than that of the others above 2200 K, it is considered that almost Al_2O_3 component will be vaporized as AlO according to the following:

Since the vapor pressure of HfO_2 is very low, no peaks for Hf or HfO_2 were detected in Figure 8. This result suggests that HfO_2 primary phase will be solidified on the substrate first and the Al_2O_3 - HfO_2 eutectic structure is formed on the HfO_2 primary phase. Furthermore, it is easy to predict that the primary HfO_2 phase reduced to HfC phase by a reaction with free carbon near the surface of the substrate.

Figures 9(a) and 9(b) show the X-ray diffraction pattern and SEM image from the surface of solidified EBC film [6]. Only corundum phase and monoclinic HfO_2 phases were identified. From the phase diagram of Al_2O_3 - HfO_2 , a tetragonal HfO_2 will be formed by the solidification. However, when the solidification rate is low, all of the tetragonal phase will transform to monoclinic phase as mentioned above. A lamella structure is formed on the surface of solidified EBC film as shown in Figure 9(b), where white phase denotes HfO_2 phase and black phase denotes Al_2O_3 phase.

Figure 10 shows the cross section SEM image of the EBC film, where the image was obtained by [6]. A high density white layer is formed as intermediate layer on the silicon carbide substrate. Since the Al_2O_3 - HfO_2 eutectic structure is formed from top of the intermediate layer, it is predicted that the top of the intermediate layer is HfO_2 phase. From the

FIGURE 6: The X-ray diffraction patterns (a) before and (b) after the light focusing [6].

FIGURE 7: The schematic illustration for preparation process of eutectic EBC film.

FIGURE 8: The powder X-ray diffraction pattern of the powder deposited inner wall of quartz tube [6].

experimental results using electrical furnace as mentioned above, it is easy to consider that HfC phase is formed on the silicon carbide substrate.

To examine the composition of the intermediate layer, a line analysis for the intermediate layer was performed as indicated in Figure 11(a). The concentration of carbon gradually decreases from the bottom of the intermediate layer to the top of the layer as shown in Figure 11(b). On the other hand, the concentration of oxygen gradually increases from the bottom of the intermediate layer to the top of the layer. This result suggests that the intermediate layer is a functionally graded layer. The primary HfO_2 phase reduced to HfC on the surface of the silicon carbide substrate.

The adhesion between the intermediate layer and silicon carbide substrate is excellent by an anchor effect as shown

in Figure 10 and no crack is induced in the layer. The coefficient of thermal expansion of HfC phase is smaller than that of HfO_2 phase and very similar to that of silicon carbide substrate. Hence, the excellent adhesion between the intermediate layer and substrate is obtained.

From the above experimental results, the formation mechanism of Al_2O_3 - HfO_2 eutectic film by the optical zone melting method can be explained as follows: (1) a small amount of Al_2O_3 component is reduced by the free carbon and vaporized from the melting zone; (2) since the composition of the molten phase becomes HfO_2 rich, HfO_2 primary phase is formed; (3) the primary HfO_2 phase is reduced to HfC phase on the solidification process and high density intermediate layer is formed; (4) when the solidification

FIGURE 9: The X-ray diffraction pattern (a) and SEM image (b) from the surface of solidified EBC film [6].

FIGURE 10: Cross section SEM image of the EBC film [6].

FIGURE 11: Line analysis for the first layer [6].

process finished, before all of HfO_2 phase is reduced to HfC phase, HfC-HfO_2 functionally graded layer is formed on the silicon carbide substrate and the $\text{Al}_2\text{O}_3\text{-HfO}_2$ eutectic structure grows from the top of the intermediate layer.

This process can be applied to different oxide eutectic systems that included HfO_2 and/or ZrO_2 phase such as $\text{CaZrO}_3\text{-ZrO}_2$ and $\text{Ln}_2\text{Zr}_2\text{O}_7\text{-ZrO}_2$ eutectic systems.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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