Microstructure formation of $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic

Kyosuke SEYA, Byung-Koog JANG* and Shunkichi UENO†

College of Engineering, Nihon University, Koriyama, Fukushima 963–8642, Japan
*National Institute for Materials Science, Tsukuba, Ibaraki 305–0047, Japan

The microstructure formation of $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic prepared by unidirectional solidification and rapid solidification was examined. The microstructure of the $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic samples showed lamellar structure and the relationship between the inter-lamellar spacing $\lambda$ and solidification rate $R$ can be expressed by $\lambda R=constant$. A small amount of tetragonal $\text{HfO}_2$ phase exists in the sample prepared by rapid solidification. Only monoclinic $\text{HfO}_2$ phase can be found in the eutectic samples prepared by unidirectional solidification. A tensile stress was induced in $\text{Al}_2\text{O}_3$ phase during the cooling step due to the transformation of $\text{HfO}_2$ from tetragonal to monoclinic phase. The tensile stress of the $\text{Al}_2\text{O}_3$ phase in the eutectic structure was estimated to be 420 MPa.

Key-words: $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic, Unidirectional solidification, Rapid solidification

1. Introduction

On the application of Si-based non-oxides ceramics for gas turbine hot section component, an oxidation-corrosion resistance environmental barrier coating (EBC) layer is required. Some oxides, such as zirconia, hafnia and rare earth silicates show excellent water vapor corrosion resistance under high speed steam jet environment or gas turbine conditions at high temperatures. Over the last development of EBC for non-oxides ceramics, oxides EBC layers were prepared by plasma spraying, dipping, laser ablation, spattering, reaction sintering method etc. on the non-oxides ceramics substrate. Since the EBC layer is composed of polycrystalline solid, a small amount of glassy phase exist at the grain boundary and the boundary glassy phase easily corroded by water vapor in steam jet or gas turbine condition then, a porous structure is formed in the EBC layer, even if the crystalline of oxide EBC material shows an excellent water vapor corrosion resistance. The corrosive gases easily pass through the porous channel of EBC layer and the non-oxides ceramics substrate oxidized. Hence, an EBC layer without boundary glassy phase or a control for the corrosion of boundary glassy phase is required on the development EBC for non-oxides ceramics in future.

On the solidification of oxides eutectic, the excess impurities is removed from the solidified bulk by a segregation and an eutectic structure without boundary glassy phase is formed. Hence, the oxides eutectic, especially the eutectic with zirconia, hafnia or rare earth silicates phase is hopeful material for EBC layer. In our previous report, a steam jet test for the silicon nitride ceramics with $\text{Lu}_2\text{Si}_2\text{O}_7$–mullite eutectic EBC layer which was prepared by plasma spraying method was examined at 1473 K. Since the glassy phase was formed on the surface of each grain during the plasma spraying process, the glassy phase was removed by water vapor and a porous structure was formed in the EBC layer during the steam jet test. Hence, EBC layer which consist of an eutectic structure without the boundary glassy phase is desired on the development of new EBC for non-oxides ceramics.

Further, fine microstructure is required to the eutectic EBC to distribute the residual stress in each crystal. The microstructure formation of oxides eutectic closely depends on the solidification rate. For example, cellar structure are formed in the $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ eutectic that prepared by rapid solidification process. Commonly, the microstructure is formed by diffusion limited of each component during the solidification. Hence, a eutectic system which consisted of a cation with large ionic radii is hopeful for EBC material. Since the $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic is included $\text{HfO}_2$ which shows an excellent corrosion resistance and Hf ion which has a large ionic radius, $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic is hopeful material of EBC for non-oxides ceramics. However, no information for the microstructure formation of $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic is obtained. In this report, the microstructure of $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic was examined.

2. Experiments

The $\text{Al}_2\text{O}_3$–$\text{HfO}_2$ eutectic samples were prepared by rapid solidification and unidirectional solidification using the optical floating zone apparatus. $\text{Al}_2\text{O}_3$ powder (99.9% purity, Kojyundo Chemical Laboratory Co., Ltd.) and $\text{HfO}_2$ powder (98% purity, Kojyundo Chemical Laboratory Co., Ltd.) were used as starting materials. The powders were mixed in molar ratio of $\text{Al}_2\text{O}_3$: $\text{HfO}_2 = 67:33$ according to the reference in ethanol. After drying at 353 K in air, the mixed powder was pressed into rod shape with 5 mm diameter and 100 mm in length. The calcination was performed at 1473 K for 3.6 ks in air and the feed rod was prepared.

The unidirectional solidification and rapid solidification were performed using optical floating zone apparatus in Ar atmosphere. 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. 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 environmental gas was introduced into the quartz tube. The solidification rate was controlled between 1.4 and 28 $\mu$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 thermal cycling test for the rapid solidified samples was performed between room temperature and 1673 K.

The sample which prepared by rapid solidification was crushed into powder by tungsten mortar. The powder X-ray diffraction measurement was performed using X-ray diffraction apparatus of D2-PHASE (Bruker AXS K.K.). The residual stress for the corundum phase in the eutectic structure was measured by Raman sifts. The Ramman shift for the solidified sample was measured using laser Ramman spectrophotometer NRS-1000 (JASCO Co. Ltd. at The University of Tokyo). The laser with 532 nm in wave length was used for the measurement. The exposure integration was 3 times and the exposure time was fixed to 1 s.

The transversal and longitudinal cross-sections of the solidified samples were observed by SEM.

3. Results and discussion

Figures 1 show the longitudinal cross section of SEM images with backscattered electron for the samples prepared by unidirectional solidification in solidification rate (a) 1.4 µm/s, (b) 2.8 µm/s, (c) 5.5 µm/s, (d) 13.9 µm/s and (e) 28 µm/s, respectively. The white phase is HfO₂ phase and dark phase is Al₂O₃ phase. The primary Al₂O₃ phase periodically appeared along the solidification direction. The distance of Al₂O₃ primary phase along the solidification direction linearly increased with increasing solidification rate as shown in Fig. 2. A colony structure appears in Figs. 1(d) and 1(e). On the other hand, Fig. 3 show the magnified longitudinal cross section images of the coupled growth zone. The inter-lamellar spacing decreased with increasing solidification rate and the relationship between the inter-lamellar spacing and solidification rate R can be expressed by \( \lambda \propto R^{-0.437} \). The solidification rate for above reference is later than that of our present experiment. Zheng et al. prepared the Al₂O₃–HfO₂ eutectic sample by Bridgmann method with the solidification rate between 3.6 and 43 µm/s and the microstructure of the sample showed rod structure. The solidification rate for above reference is within the solidification rate range of our present experiment. On the other hand, Bourbon et al. prepared the Al₂O₃–ZrO₂ eutectic sample by unidirectional solidification using CO₂ laser with the solidification rate between 0.08 and 2.2 µm/s. The microstructure of the sample for the reference 11) showed lamellar structure and the relation between the inter-lamellar spacing \( \lambda \) and solidification rate R can be expressed by \( \lambda R = \text{constant} \). The solidification rate for above reference is later than that of our present experiment. Lopato et al. suggested that the microstructure formation for Al₂O₃–HfO₂ eutectic is very similar to that for Al₂O₃–ZrO₂ eutectic. Schmid and Viechnicki prepared the Al₂O₃–ZrO₂ eutectic sample by Bridgmann method with the solidification rate between 3.6 and 43 µm/s and the microstructure of the sample showed rod structure. The solidification rate for above reference is within the solidification rate range of our present experiment. On the other hand, Bourbon et al. prepared the Al₂O₃–ZrO₂ eutectic sample by unidirectional solidification using CO₂ laser with the solidification rate between 0.08 and 2.2 µm/s. The microstructure of the sample for the reference 11) showed lamellar structure and the relation between the inter-lamellar spacing \( \lambda \) and solidification rate R can be expressed by \( \lambda R = \text{constant} \).
the Al₂O₃–ZrO₂ eutectic sample by rapid solidification in high pressure and the microstructure of the sample showed rod structure. The previous reports for the preparation of Al₂O₃–ZrO₂ eutectic sample suggest that the microstructure of this eutectic change from a lamellar structure to rod structure with increasing the solidification rate. For the Al₂O₃–ZrO₂ eutectic, a lamellar structure is obtained below 3 μm/s in the solidification rate and rod structure is formed above 3 μm/s in the solidification rate. However, in the case of Al₂O₃–HfO₂ eutectic, only lamellar structure is formed even if the sample was prepared by rapid solidification process.

Since the relation between inter-lamellar spacing \( \lambda \) and solidification rate \( R \) for Al₂O₃–ZrO₂ eutectic and Al₂O₃–HfO₂ eutectic according to Jacson-Hunt theory, diffusion of component atoms are the rate limited on the formation of the microstructure. Hence, it is considered that the differences in the microstructure formation between Al₂O₃–ZrO₂ eutectic and Al₂O₃–HfO₂ eutectic caused by the differences of diffusion coefficient of Zr and Hf ion in molten state of Al₂O₃–ZrO₂ and Al₂O₃–HfO₂ eutectic composition. Since the distance of Al₂O₃ primary phase along solidification direction linearly increased with increasing solidification rate as shown in Fig. 2, the appearance of Al₂O₃ primary phase caused by periodic deviation from the coupled growth zone due to concentration fluctuation behind the solid–liquid interface during the steady state of unidirectional solidification.

The thermal cycling test for the rapid solidified samples was performed between room temperature and 1673 K for 3 times. Figure 6 shows the external view of the sample after the test. No cracks were induced by the thermal test.

Figure 7 shows the powder X-ray diffraction pattern of the sample prepared by rapid solidification. The bulk sample was crushed into powder by tungsten mortar. Almost peaks can be indexed as monoclinic HfO₂ phase and corundum phase. However, a weak peak at 20° = 30.37° can be indexed as (101) of the tetragonal HfO₂ phase. Hence a small amount of tetragonal phase exists in the sample prepared by rapid solidification. Since the tetragonal HfO₂ shows stress-induced martensitic transformation, it is concerns that the monoclinic HfO₂ phase found in Fig. 7 generated by the crushing the bulk sample. To wipe out the fear of this matter, the X-ray diffraction measurement for the bulk sample prepared by rapid solidification was conducted. Where, the sample was embedded in a resin mold and polished by diamond disk. The X-ray diffraction data was obtained from the polished longitudinal cross section of the sample. The X-ray diffraction pattern for the bulk sample was same to that of Fig. 7, namely, a weak peak for tetragonal HfO₂ phase was detected. In the Al₂O₃–HfO₂ binary phase diagram, tetragonal HfO₂ phase exist above 2063 K. In the case of Al₂O₃–HfO₂ eutectic prepared by rapid solidification, a small amount of tetragonal phase quenched from high temperature to room temperature. Figure 8 shows the X-ray diffraction pattern of the bulk sample of Fig. 1(e) which was prepared by unidirectional solidification. No peaks for the tetragonal HfO₂ phase were detected. Since the cooling rate for unidirectional solidification is later than that for the rapid solidification, all of the tetragonal phase was transformed into monoclinic phase during the cooling step of the unidirectional solidification process.

Figure 9 shows the Raman shift for Al₂O₃ phase in the eutectic sample and ruby single crystal as a reference. The Raman shift data was collected from the area of 40 μm square of the
sample of Fig. 1(e) which was prepared by unidirectional solidification process. In this area, eutectic structure and Al₂O₃ primary phase are included. The peaks for R1 and R2 for Al₂O₃ phase in eutectic sample slightly shifted from peaks of the ruby single crystal. In this eutectic sample, all of tetragonal HfO₂ phase transformed into monoclinic phase during the cooling step of the unidirectional solidification as shown in Fig. 8. Since the transformation of HfO₂ phase from tetragonal phase to monoclinic phase involved a large volume expansion, a tensile stress will be induced in Al₂O₃ phase. The tensile stresses for Al₂O₃ phase can be calculated from the Raman shift according to the reference. A tensile stress for Al₂O₃ phase in Al₂O₃–HfO₂ eutectic prepared by unidirectional solidification process can be estimated to 420 MPa. The tensile stress of Al₂O₃ phase in Al₂O₃–ZrO₂ eutectic sample prepared by laser floating zone method was 460 MPa which is good agreement with the result of our experiment. Even though a large stress is induced on the Al₂O₃–HfO₂ or Al₂O₃–ZrO₂ interface in the eutectic structure during the cooling step due to the transformation form tetragonal to monoclinic phase, the stress is distributed to the long Al₂O₃–HfO₂ or Al₂O₃–ZrO₂ interface and no cracks were induced by the transformation.

4. Conclusion

In this paper, the microstructure formation of Al₂O₃–HfO₂ eutectic was investigated. The microstructure for the Al₂O₃–HfO₂ eutectic samples prepared by unidirectional solidification and rapid solidification showed lamellar structure and the relationship between the inter-lamellar spacing $\lambda$ and solidification rate R can be expressed by $\lambda^2 R = \text{constant}$. No structure transformation from rod structure to lamellar structure was observed in Al₂O₃–HfO₂ eutectic. A small amount of tetragonal HfO₂ phase quenched from high temperature to room temperature by rapid solidification. A tensile stress was induced in Al₂O₃ phase during the cooling step due to the transformation of HfO₂ from tetragonal to monoclinic phase. The tensile stress in Al₂O₃ phase was estimated to 420 MPa.

References