Formation Mechanism of Eutectic Microstructure for $CaHfO_3/HfO_2$

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Abstract: The mechanism of fine eutectic structure formation for $CaHfO_3/HfO_2$ was investigated. $CaHfO_3/HfO_2$ eutectic solidification film was prepared using a high-power laser with 1400W. The film preparation was conducted in a furnace at 1300°C. The scanning speed of laser was set to 500 to 2000 mm/s. The scanning speed of the laser was greatly varied to create a solidified film and the intermediate steps of micro-structure formation were observed. The micro-structure morphology immediately after solidification was a structure in which an intermediate phase was surrounded by an HfO_2 phase. $CaHfO_3$ phase deposited in dot-like form from the intermediate phase. It was confirmed that the dot-like deposit phase connected through atomic diffusion at high temperatures, ultimately forming a fine lamellar structure. It was confirmed that the fine eutectic microstructure of $CaHfO_3/HfO_2$ is not formed by competitive growth at the melting point during conventional eutectic solidification, but rather is ultimately formed through repeated phase separation after the solidification.

Keywords: $CaHfO_3/HfO_2$ Eutectic Film, Lamellar Structure, Laser irradiation, Diffusion.

1. INTRODUCTION

The binary phase diagram of CaO and HfO_2 has been studied in detail by Senft and Stubican [1]. A stable complex oxide $CaHfO_3$ exist in this system. The eutectic temperature for $CaHfO_3/HfO_2$ is 2500°C which is 300°C higher than that of $CaZrO_3/ZrO_2$ [2]. It is known that $CaHfO_3$ phase shows strong luminescence property under exposing UV light [3]. $CaHfO_3$ phase is promising as an optical material, and therefore, much research has been conducted on it. On the other hand, there is little research on its application as a high-temperature material. Hf is a rare and expensive element. Therefore, research into high-temperature materials has focused on the more affordable $CaZrO_3$. The $CaZrO_3$ and the CaO-stabilized ZrO_2 phases have high corrosion resistance at high temperatures and excellent heat insulating property [4,5]. The complex oxide of $CaZrO_3$ is used as a nozzle material in blast furnaces due to its excellent heat resistance, corrosion resistance, and wear resistance. From this, it can be inferred that both the $CaHfO_3$ phase and the HfO_2 phase have excellent corrosion resistance.

It has been suggested that a $CaHfO_3/HfO_2$ eutectic exists in the CaO-HfO_2 system. However, this has not been investigated in detail experimentally, and the liquidus line is shown as a dashed line [1]. In our previous study, where Zr sites in $CaZrO_3/ZrO_2$ eutectic were replaced with Hf and solidified, a eutectic structure was obtained even when partially replaced with Hf [6]. Therefore, it is expected that $CaHfO_3/HfO_2$ eutectic exists.

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The phase diagram proposed by Senft and Stubican [1] predicts that the final eutectic structure is formed by several phase transitions and phase decompositions during the cooling process after solidification. In this study, we investigated structural changes in samples with varying solidification rates, with the aim of capturing the intermediate stage in which a stable structure is formed through phase separation after solidification.

2. EXPERIMENTAND METHODS

$CaCO_3$ of 99.9% purity and HfO_2 of 98% purity powders with 2 μm particle size (Kojundo Chemical Laboratory Co., Ltd.) were used as starting materials. The starting powders were weighed to be $CaHfO_3/HfO_2$ eutectic compositions. Pellets of the mixed powder were sintered at 1500°C. Eutectic composition slurry was coated on a porous zirconia substrate of 10 mm x 10 mm x 5 mm, dried, and sintered at 1200°C for 2 hours to obtain high adhesion between the substrate and the applied oxides layer.

The solidified film with the eutectic compositions were prepared by laser irradiation method using the high-power fiber laser apparatus MF-C2000A-MC at AMADA WELD TECH CO., LTD. The spot size of the laser was fixed to 0.5 mm. Laser wavelength and power were fixed to 1070 nm and 1400 W, respectively. As in our previous report on the preparation of $CaZrO_3/ZrO_2$ eutectic films [6], the sample was heated to 1300°C using a pot furnace and irradiated with the laser while heated. Only applied oxide layer with eutectic composition was melted by the laser irradiation. The scanning speed of laser was set to 500–2000 mm/s.

An electron microscope (TM4000Plus, Hitachi High Tech., Co., Ltd.) was used to observe the surface of the

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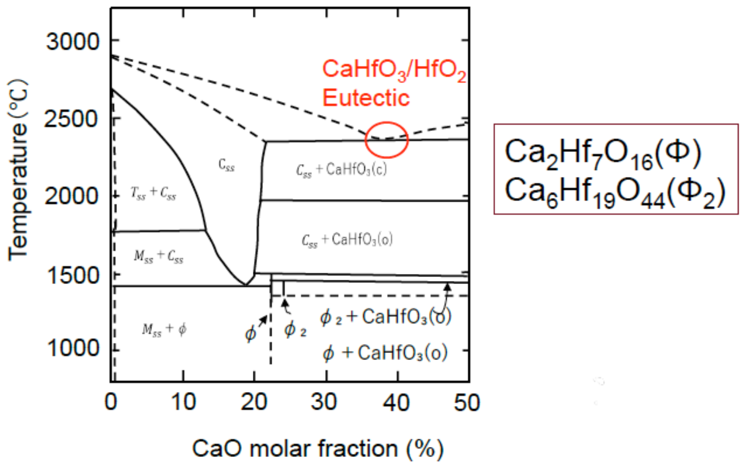


Figure 1: CaO-HfO_2 phase diagram proposed by Senft and Stubican [1].

solidified film samples. Phase identification was performed using an X-ray diffractometer (Bruker, D2 Phaser).

3. RESULTSAND DISCUSSION

The phase diagram proposed by Senft and Stubican is shown in Figure **1** [1]. According to the phase diagram, the stable phase is formed through the following steps.

1st Stabilized cubic HfO_2 phase and cubic $CaHfO_3$ phase formed at melting point.

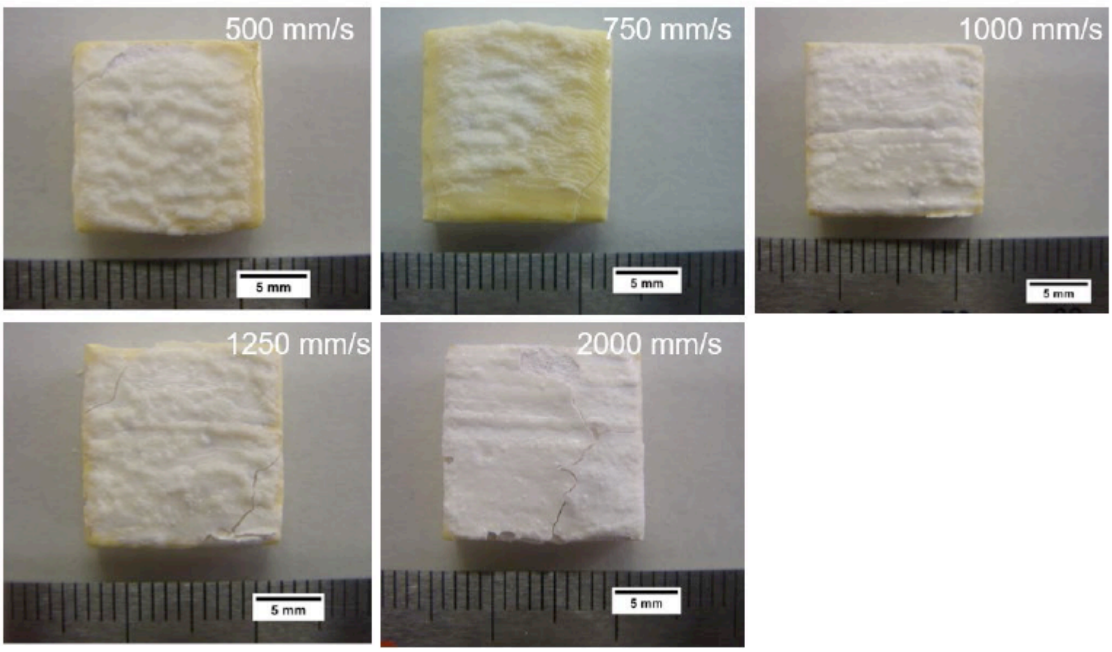
2nd The cubic $CaHfO_3$ phase transformed into orthorhombic $CaHfO_3$ phase at 2000°C.

3rd The Stabilized cubic HfO_2 phase decomposed into $Ca_6Hf_{19}O_{44}$ phase at 1500°C.

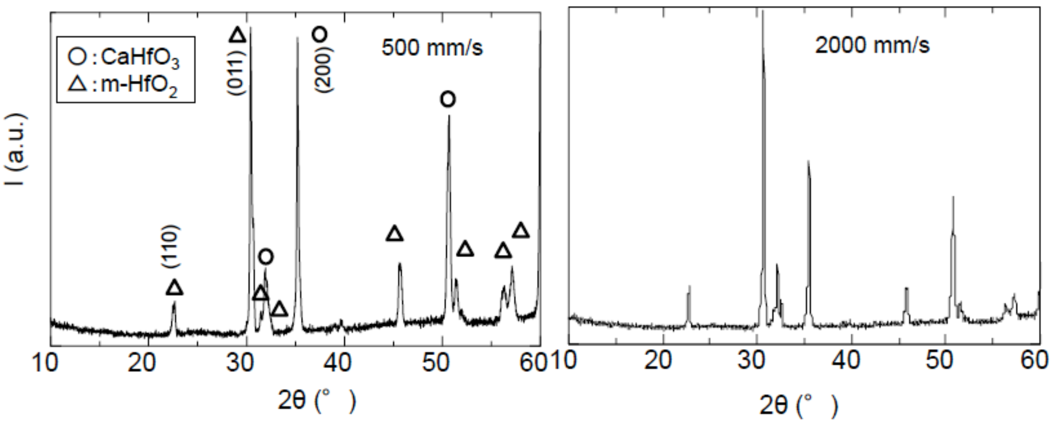
4th The $Ca_6Hf_{19}O_{44}$ phase decomposed into $Ca_2Hf_7O_{16}$ phase below 1400°C.

Ultimately, a stable eutectic $CaZrO_3$/partially stabilized monoclinic HfO_2 is formed. Namely, two step phase decompositions of intermediate phases occur to form a stable eutectic micro-structure.

Figures **2** show the external views of the solidified film. Only the eutectic oxide applied to the substrate surface could be melted and solidified. Figures **3** show the X-ray diffraction patterns from the surface of the solidified film. Here, X-ray patterns of 500 and 2000 mm/s samples are shown as examples. In all cases, peaks for only monoclinic HfO_2 phase and orthorhombic $CaHfO_3$ phase were observed. Intermediate phases $Ca_6Hf_{19}O_{44}$ and $Ca_2Hf_7O_{16}$ are also thought to exist. Many peaks for the intermediate



Figures 2: The external views of the solidified film.



Figures 3: X-ray diffraction patterns from the surface of the solidified film.

phases are hidden by the peaks of monoclinic HfO_2 phase and orthorhombic $CaHfO_3$ phase, so no clear peaks for the intermediate phases were observed. As the scanning speed increased, the intensity ratio for the 011 peak of the HfO_2 phase became strong. The intensity ratios of the other peaks of the HfO_2 phase and the peak intensity ratio of the $CaHfO_3$ phase were constant. As the scanning speed increases, the supercooling degree of the melt increases. It is thought that the intermediate phase generated at high temperatures will freeze at 1300°C. In this case, the growth of the surface where the atomic density of the intermediate phase becomes small is prioritized. When changing from the intermediate phase to monoclinic HfO_2, it is predicted that excess CaO components will be discharged from the intermediate phase and a stable structure will be formed. Since the orientation of the intermediate phase is directly reflected, it is thought that the faster the scanning speed, the more it is reflected in the orientation of the HfO_2 phase that is ultimately produced.

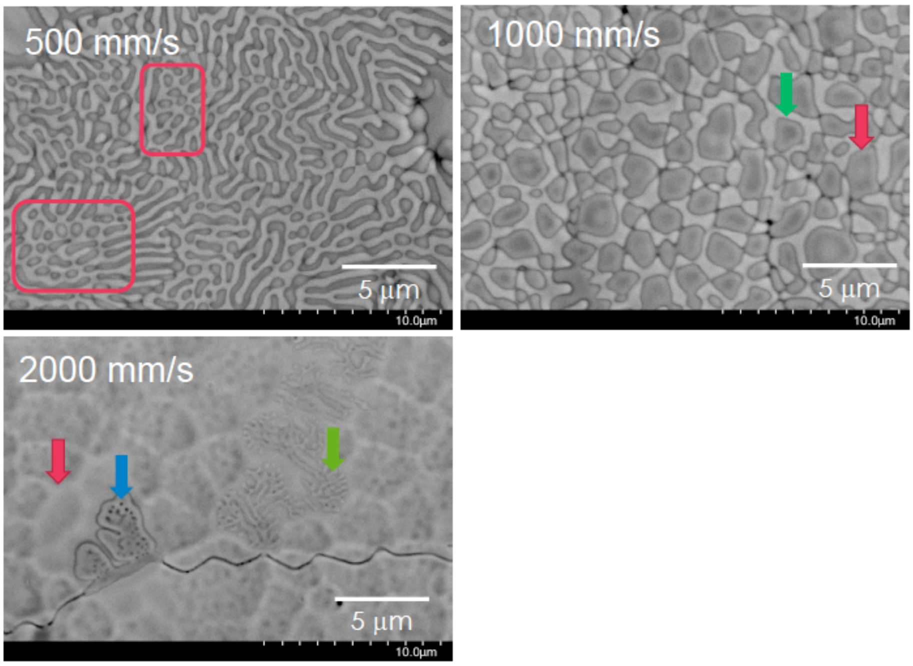
Figures **4** show electron microscope images of the film surface. A fine lamellar structure of less than 1 μm was formed in the 500 mm/s sample. The white phase represents the HfO_2 phase, and the gray phase represents the $CaHfO_3$ phase. A similar lamellar structure has also been observed in solidified $CaZrO_3/ZrO_2$ eutectics [6]. No lamellar structure was formed in samples at 1000 mm/s and 2000 mm/s.

As the scanning speed increases, the intermediate phase becomes more likely to freeze. When considering the formation process of eutectic lamellar structures, it is easier to understand by examining samples with fast scanning speeds of 2000 mm/s in order. No eutectic lamellar structure was observed in the 2000 mm/s sample. In this case, the white phase indicated by the red arrow surrounded the gray phase. As indicated by the blue arrow, a darker gray phase in the form of dots was deposited within the gray phase. The light gray phase corresponds to the intermediate phase. In addition, in some areas, as indicated by the green arrows, dot-like deposit phases were connected to form lamellar structures. A clear image was observed in the 1000 mm/s sample. No lamellar structure was obtained. Micro-structures surrounded by white phases were observed. As indicated by the green arrow, a darker gray phase is depositing in the gray phase. In addition, as indicated by the red arrow, a light gray phase was observed to deposit within the gray phase. In the 500 mm/s sample, lamellar structures appear to have formed at first glance. Structures in which white phases appear to have deposited within gray dot-like phases, as indicated by the red frame, were also observed. The microstructure formation mechanism can be considered as shown in Figure **5**.

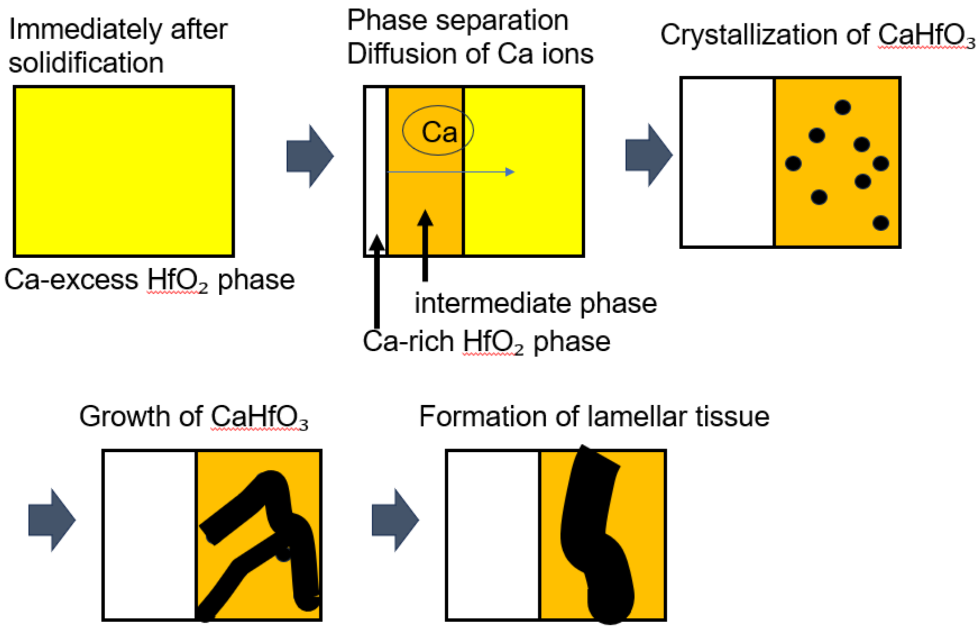
These results indicate that phase separation of the intermediate phase occurs during the cooling process after the eutectic solidification, ultimately forming a stable fine lamellar structure monoclinic HfO_2 phase and $CaHfO_3$ phase. In normal eutectic solidification, two phases crystallize during solidification and eutectic structure is formed through competitive growth. However, the lamellar structure shown in Figure **4** can be said to be formed by phase separation accompanied by atomic diffusion after solidification. It can be said that the final fine lamellar structure is formed by the phase separations shown in the phase diagram.

This structure formation mechanism is thought to be applicable to $CaZrO_3/ZrO_2$ eutectic structures as well. Our previous report has confirmed that when amorphous phase with $CaZrO_3/ZrO_2$ eutectic compositions are heat treated, phase separation occurs repeatedly and ultimately resulting in the formation of a stable phase [7].

The formation of lamellar structures is thought to occur due to the diffusion of Ca ions after solidification.



Figures 4: Electron microscope images of the film surface.



Figures 5: Schematic lamella structure formation process.

Results from this study show that lamellar structures were obtained in samples of 500 mm/s, while an intermediate state was confirmed in samples of 2000 mm/s. Regarding the balance between Ca diffusion rate at 1300°C and the heat input from laser irradiation, the scanning speed of 500 mm/s approaches sufficient equilibrium. On the other hand, whereas scanning speed of the 2000 mm/s results in a supercooled state, leading to a non-equilibrium microstructure.

Therefore, it is considered that the final microstructure of $CaZrO_3/ZrO_2$ eutectic is formed by the same mechanism as in this study. The ionic radii of Zr ions and Hf ions are nearly identical. However, since the atomic mass of Hf is greater than that of Zr, in the case of Hf system, Ca ion diffusion is thought to be suppressed. Therefore, it is considered that non-equilibrium frozen structures are readily obtained in the $CaHfO_3/HfO_2$ system.

4. CONCLUSION

Solidified films were prepared by melting a $CaHfO_3/HfO_2$ eutectic composition with a high-power laser. When the scanning speed was increased, the intermediate phase was frozen. The final solidified film formed a fine lamellar structure. It was considered that the final lamellar structure was not eutectic structure formed by competitive growth of two phases during solidification. The lamellar structure was formed by phase separation accompanied by atomic diffusion after solidification.

The $CaHfO_3/HfO_2$ eutectic has a melting point 300°C higher than the $CaZrO_3/ZrO_2$ eutectic. It is expected to exhibit superior corrosion resistance compared to $CaZrO_3/ZrO_2$ eutectic. It shows promise as EBC film for next-generation gas turbines exposed to corrosive species at ultra-high temperatures. The $CaHfO_3/HfO_2$ eutectic is expected to exhibit superior corrosion resistance compared to other existing materials. Going forward, detailed data will be required to verify whether the coating can withstand high pressures and to assess its erosion resistance.

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CONFLICTS OF INTEREST

The author declared no conflicts of interest.

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