Formation Mechanism of Eutectic Microstructure for $Ca(Zr,Hf)O_3/(Zr,Hf)O_2$ by Rapid Solidification Process at High Temperature

Shunkichi Ueno[1,*], Haruka Ohta[1], Kanami Izawa[1], Cho Sunghun[2] and Tohru Sekino[2]

[1]*College of Engineering, Nihon University, Koriyama, Fukushima 963-8642, Japan*

[2]*SANKEN, Osaka University, Ibaraki 567-0047, Japan*

Abstract: $Ca(Zr_{1-x},Hf_x)O_3/(Zr_{1-x}Hf_x)O_2$ (x=0, 1/3, 0.5) eutectic film was prepared by rapid solidification process using high power laser irradiation method. The coating process was performed in an electric furnace at 1300°C. Solidified film with fine lamellar structure were obtained. When the Zr site was substituted with Hf, the lamellar spacing increased with the amount of the substitution. Separate from the solidification film prepared by laser irradiation, rapidly solidifying sample with x=0.1 composition was prepared using optical floating zone apparatus. The melt of the sample was free-fallen onto a copper dish. No film-like rapidly solidified sample was obtained. Hf ion was homogeneously solid-soluble in both phases of $CaZrO_3$ and phase ZrO_2.

Keywords: Eutectic film, Lamellar Structure, Laser irradiation, Rapid solidification, Diffusion.

1. INTRODUCTION

The binary phase diagram of ZrO_2-CaO includes eutectic of the $CaZrO_3$ phase and the CaO-stabilized ZrO_2 phase [1]. The eutectic temperature is 2200°C. Both phases have high corrosion resistance at high temperatures and excellent heat insulating property [2, 3]. The coefficient of thermal expansion (CTE) of the $CaZrO_3$ phase is 10×10^{-6}/K [4] and the CTE of ZrO_2 phase shows almost the same [5]. Thus, it is expected that the stress at the interface in solidified $CaZrO_3/ZrO_2$ eutectic sample will reduced. Based on these results of previous studies, it is expected that solidified $CaZrO_3/ZrO_2$ eutectic film can be excellent environmental barrier coating (EBC) material for gas turbine component. It has been reported that $CaZrO_3/ZrO_2$ eutectic microstructure obtained by laser-assisted floating zone melting exhibit a fine lamellar microstructure [6]. According to the CaO-ZrO_2 phase diagram, solidification of the melt with composition of $CaZrO_3/ZrO_2$ eutectic yields $CaZrO_3$ and CaO-stabilized ZrO_2 phases. During the cooling step, the stabilized ZrO_2 phases decomposed into tetragonal ZrO_2 and zirconia rich $Ca_6Zr_{19}O_{44}$ stoichiometric compound. At even lower temperatures, $Ca_6Zr_{19}O_{44}$ phase decomposed into monoclinic ZrO_2 and $CaZr_4O_9$ phase. At 1300°C, $CaZr_4O_9$ phase decomposed into $CaZrO_3$ and monoclinic ZrO_2 phases. It can be seen the microstructure is formed through a three-step phase separation after the solidification. We have experimentally shown that stable phases form through these phase separations by crystallization of amorphous phase with the eutectic composition [7]. The fine $CaZrO_3/ZrO_2$ eutectic structure shown in Ref. 6 is also inferred to be formed by repeated phase separation after solidification.

High-power laser can give a large amount of heat to a material instantaneously, making it possible to melt even oxides with ultra-high melting points. The $CaZrO_3/ZrO_2$ eutectic film can be prepared by laser irradiation [8]. However, when the solidified film was prepared by laser irradiation without preheating, the degree of undercooling of the melt increased, resulting in rapid crystallization from the melt and the formation of a columnar macrostructure. Phase separation during the cooling step after solidification was suppressed and a high-temperature type cubic zirconia phase crystallized.

In this study, we experimentally investigated whether it is possible to suppress the formation of columnar microstructure by rapid crystallization and effectively cause phase separation after solidification to form fine microstructure by heating the sample to 1300°C and irradiating it with laser while it is heated. In addition, we attempted to fabricate solidified film on a system substituted with hafnia, which has better corrosion resistance and a lower coefficient of thermal expansion than zirconia, and investigated the effect of the substitution of Hf.

*Address correspondence to this author at the College of Engineering, Nihon University, Koriyama, Fukushima 963-8642, Japan;
E-mail: ueno.shunkichi@nihon-u.ac.jp

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2. EXPERIMENT AND METHODS

$CaCO_3$ of 99.9% purity, ZrO_2 and HfO_2 of 98% purity powders (Kojundo Chemical Laboratory Co., Ltd.) were used as starting materials. The starting powders were weighed to be $Ca(Zr_{1-x}Hf_x)O_3/(Zr_{1-x}Hf_x)O_2$ (x=0, 1/3, 0.5) 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 fiber laser apparatus at TOCALO Co., Ltd. Laser wavelength, power, spot diameter, pitch spacing, and scanning speed were fixed to 1070 nm, 1000 W, 380 μm, 100 μm, and 2000 mm/s, respectively. The sample was heated to 1300°C using a pot furnace and irradiated with the laser while heated as shown in Figure **1**. Only applied oxide layer with eutectic composition was melted by the laser irradiation.

An electron microscope (TM4000Plus, Hitachi High Tech., Co., Ltd.) was used to observe the surface of the solidified film samples. Cross-sectional observation and elemental analysis of rapidly solidified sample was performed using a field emission electron microscope (Osaka University, JEOL Co., Ltd.). Phase identification was performed using an X-ray diffractometer (Bruker, D2 Phaser).

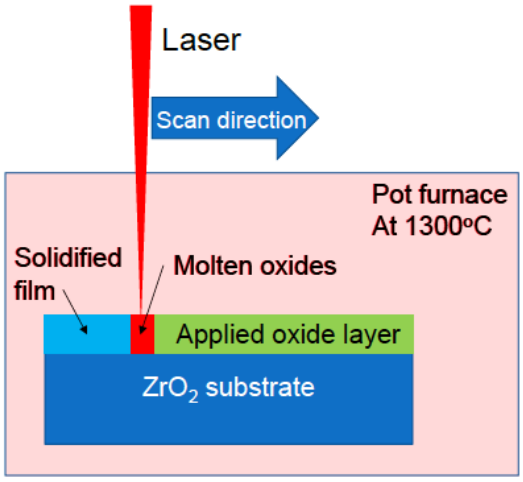

Figure 1: Schematic diagram for coating of eutectic film by laser irradiation method.

3. RESULTS AND DISCUSSION

For the purpose of studying the effect of substitution the Zr site of $CaZrO_3/ZrO_2$ eutectic structure with Hf, sintered sample with x=0.1 composition was melted using an optical floating zone furnace, and the droplets were free-fallen onto a copper dish to obtain rapidly solidified sample. The external view of the rapidly solidified sample is shown in Figure **2**. Translucent solidified sample was obtained. For the composition of x=0, when the solidified sample was prepared under the same conditions, it became film-like [8]. It is suggested that the partial substitution of Zr sites with Hf may have increased the tension of the melt. Powder X-ray diffraction pattern of the sample is shown in Figure **3**. Only $Ca(Zr,Hf)O_3$ phase and $(Zr,Hf)O_2$ phase can be indexed. The peak intensity ratio of each phase was the same as that of the $CaZrO_3/ZrO_2$ (x=0) eutectic sample we previously reported, which was prepared under the same rapid solidification process. Elemental analysis was performed on the fracture surface of the obtained sample. The results are shown in Figure **4**. In the elemental mapping of Ca, the bright areas are Ca-rich $CaZrO_3$ phase and the dark areas are Ca-stabilized ZrO_2 phase. Hf ions are found to be uniformly dissolved throughout the sample. Namely, when the Zr site was substituted by Hf in $CaZrO_3/ZrO_2$ eutectic, it was found that a eutectic microstructure was constituted with the $Ca(Zr,Hf)O_3$ and $(Zr,Hf)O_2$ solid solution phases.

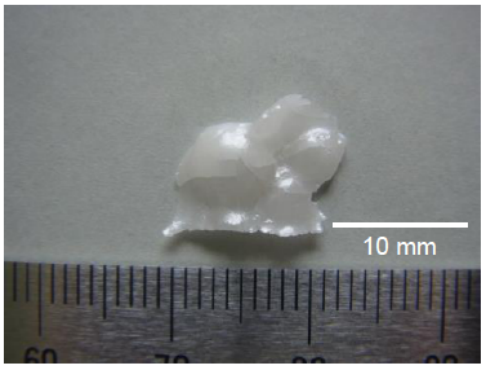

Figure 2: The external view of the rapidly solidified sample.

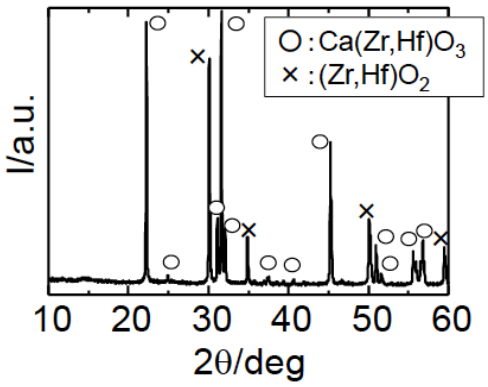

Figure 3: Powder X-ray diffraction pattern of the sample.

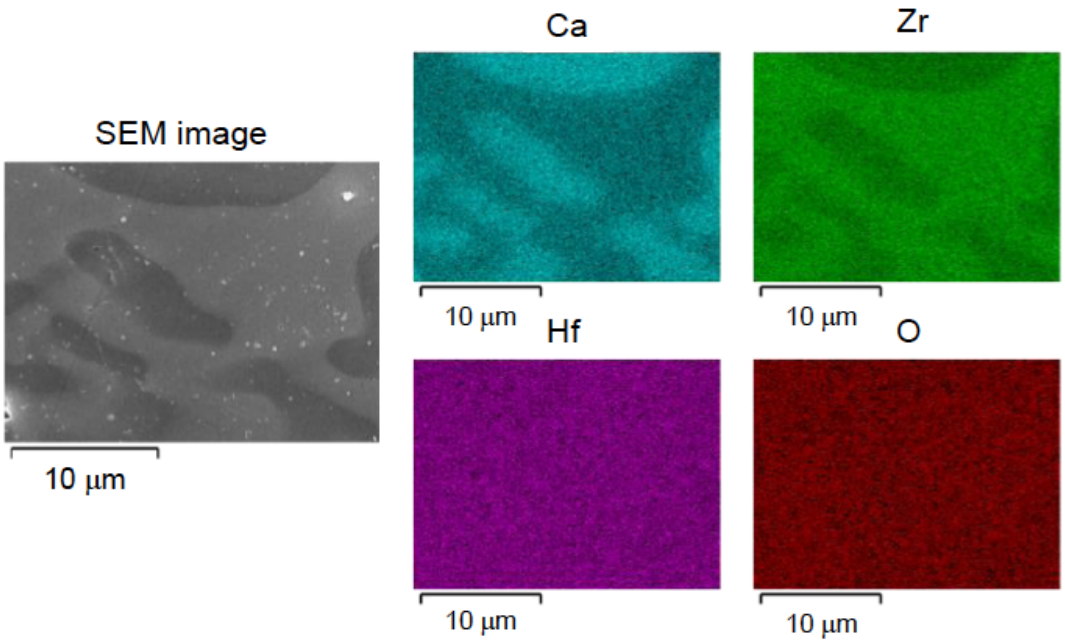

Figure 4: Elemental analysis for the sample.

Figure **5** shows a low-magnification SEM image of the solidified film surface for x=0 sample. A smooth surface structure was obtained. The surface for solidified $CaZrO_3/ZrO_2$ eutectic film, which was prepared under the same laser irradiation conditions without preheating, showed numerous macro cracks and a film composed of columnar crystals as shown in our previous report [8]. Solidification the eutectic composition while heated to 1300°C have prevented cracking because it relieved the tensile stress caused by the shrinkage of the film on cooling step after the solidification. At the same time, the degree of undercooling of the melt at the onset of solidification becomes small, resulting in a slower crystal growth rate and restrained of columnar crystal formation.

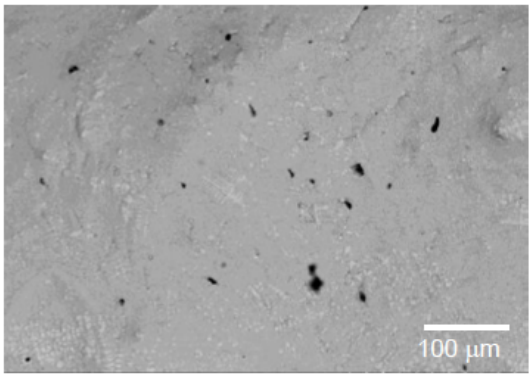

Figure 5: Low-magnification SEM image of the film surface.

Figure **6** shows the microstructure of the solidified film surface for x=0, 1/3, 0.5 samples. Fine lamellar structure was formed. The lamellar spacing of the x=0 sample is below 1/10 of that reported by Pena *et al* [6]. According to Jackson-Hunt theory, the product of the lamellar spacing and the solidification velocity to the -1/2 power is constant. [9]. Estimating the solidification rate at the surface of the sample in this study based on Pena *et al*.'s report, we find that it is about 100 mm/h or more, which is a condition for rapid solidification. Figure **7** shows the lamellar spacing for the x=0, 1/3, 0.5 samples. The lamellar spacing increases slightly with the amount of Hf substitutions.

The reason for the larger lamellar spacing when Zr is substituted by Hf is thought to be that the differences between the diffusion rate of oxygen ion in Zr and Hf. The diffusion coefficient of oxygen ion in zirconium metal strongly depends on the orientation of the crystals. The activation energy for the diffusion of oxygen ion in zirconium metal was determined to be 216.6 kJ/mol [10]. On the other hand, the activation energy for the diffusion of oxygen ion in hafnium metal was determined to be 137.2 kJ/mol [11]. Although Hf atoms is heavier element than Zr atom, they have a greater shielding effect than Zr, and the diffusion of oxygen ion is less dependent on crystallographic orientation and with less activation energy for the diffusion of oxygen ion in Hf metal, so the lamellar spacing is expected to increase with increasing Hf substitution.

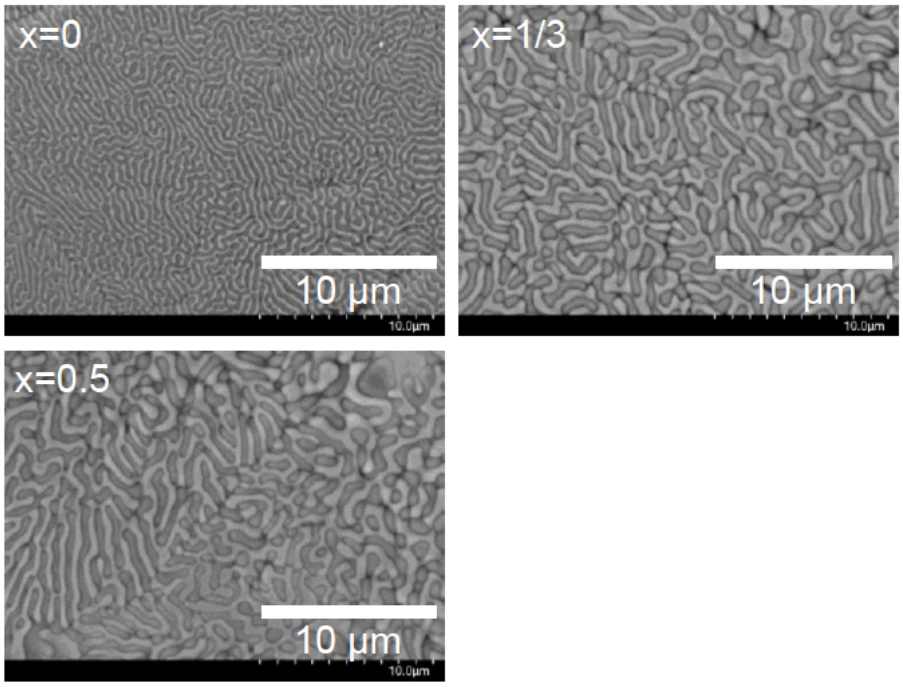

Figure 6: The microstructure of the surface for x=0, 1/3, 0.5 samples.

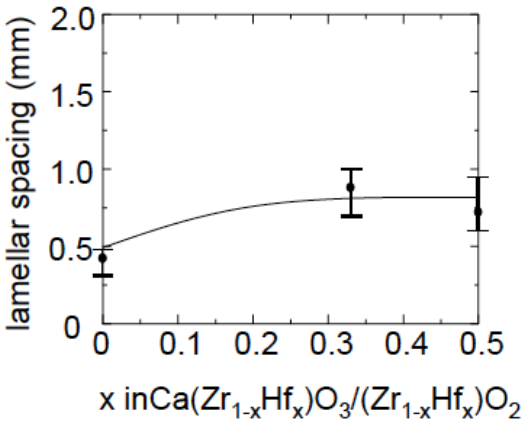

Figure 7: Lamellar spacing for the x=0, 1/3, 0.5 samples.

According to the CaO-ZrO_2 phase diagram as shown in Figure **8** [1], in the solidification of $CaZrO_3/ZrO_2$ eutectic composition, the $CaZrO_3$ phase and stabilized zirconia phases crystallize first. During the cooling process, the stabilized zirconia phase changes to a stoichiometric compound $Ca_6Zr_{19}O_{44}$ phase, and upon further cooling, this phase separates into $CaZr_4O_9$ phase and $CaZrO_3$ phase. At even lower temperatures, the $CaZr_4O_9$ phase separates into the $CaZrO_3$ phase and partially stabilized zirconia phase. In the crystallization of $CaZrO_3/ZrO_2$ eutectic composition amorphous prepared by the sol-gel method, it was confirmed that from the initial crystallized phases stepwise phase separation was followed by a transformation to a stable eutectic constitutive phase [7]. Since phase separation is repeated during the cooling process after the eutectic microstructure formation by the solidification, further microstructure refinement was expected. However, no positive experimental results were obtained in this experiment showing microstructure refinement due to phase separation.

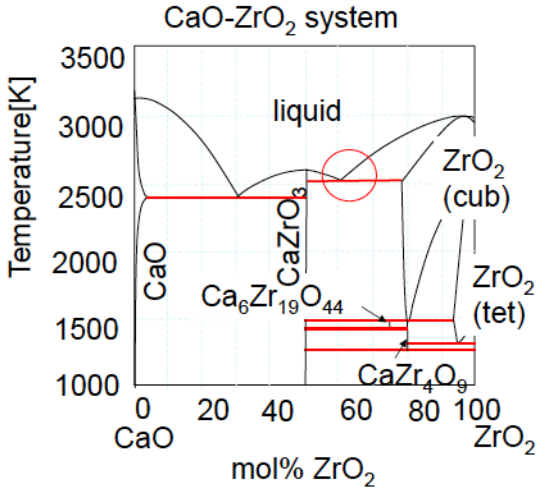

Figure 8: CaO-ZrO_2 binary phase diagram [1].

4. CONCLUSION

$Ca(Zr,Hf)O_3/(Zr,Hf)O_2$ eutectic solidification film was formed by laser irradiation method. By solidification in

an electric furnace at 1300°C, the formation of columnar crystals was restrained and a fine eutectic microstructure was formed. In each of the $CaZrO_3$ and ZrO_2 phases, Zr site were substituted by Hf ion. The lamellar spacing increased with the amount of Hf substitution. It is suggested that the diffusion rate of oxygen ions plays a significant role in the formation of this eutectic microstructure.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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