JASMAC Conference of the Japan Society of Microgravity Application

OS3-10

希土類珪酸塩ガラスの作製と相転移挙動の観察

Fabrication of rare earth silicate glasses and observation of phase transition behavior

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1. Introduction

SiC fiber reinforced SiC matrix composites (SiC_f/SiC_m) demonstrate potential as the next generation of gas turbine blades. However, SiC exhibits recession at high temperatures in an atmosphere with high water vapor. Therefore, an environmental barrier coating (EBC) is required. A general EBC system includes a Si bond coat, which obstructs oxidation and enhances adhesion, and a top coat of rare earth (RE) silicates such as RE_2SiO_5 and $RE_2Si_2O_7$. Recently, high entropy RE silicates with five or more equivalent molar RE have garnered attention to improve the properties for EBC. The most promising structure is the polymorphism-free β-$RE_2Si_2O_7$ structure (with 6-coordination of RE less than 0.885 Å)[1)].

To prevent water vapor recession of SiC, the EBC must be dense. However, coatings fabricated by typical thermal spraying processes are rapidly cooled and amorphized by the temperature difference with the substrate. Subsequent annealing crystallizes the coating, but eventually cracks and pores remain, compromising the effectiveness of the EBC. Although an irreversible phase transition from a metastable phase to a stable phase with volume expansion during annealing is attractive to cause crack healing in coatings[2)], an understanding of the thermal evolution of the coating microstructure and phases has not been established. The analysis is complicated by the volatilization of SiO in thermal spraying, the local element segregation of the coatings[3)], and the multi-element composition of RE[4)]. In addition, the thermophysical properties which are important parameters in thermal spraying[5)], have not been reported for RE silicate. The purpose of this study is to reveal the thermal evolution of microstructure and phases in RE silicate glasses without local element segregation, thereby demonstrating crack healing, and to measure the thermophysical properties.

2. Experimental Procedures

The RE elements Lu, Yb, Er, Y, and Ho were chosen to form β-$RE_2Si_2O_7$. Henceforth, RE sites with equal molar ratios of Lu, Yb, and Er will be denoted as 3RE, and when Ho and Y are included, it will be represented as 5RE. RE nitrate ($RE(NO_3)_3 \cdot nH_2O$) and sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) were dissolved in 30 mL of distilled water, respectively. The solutions were prepared to have stoichiometric ratios of RE:Si = 0.5 and 1.0. 2M HCl was added to the Na_2SiO_3 solution, while diluted ammonia was added dropwise to the $RE(NO_3)_3$ solutions. The two solvents were mixed, followed by sealing the mixed solution in a 100-mL autoclave with a 70% fill rate and holding at 220°C for 3 h. After washing by centrifugation, the obtained powder was exposed at 1600°C for 10 h in air. The powder was irradiated with a CO_2 laser using a gas-levitation furnace. The crystallographic phases of the powders before irradiated with a CO_2 laser were analyzed using X-ray diffraction. The CO_2 laser-irradiated samples were measured by Raman spectroscopy.

3. Results and discussion

From the XRD patterns, the main phases of the synthesized $RE_2Si_2O_7$ and RE_2SiO_5 powders were identified as β-$RE_2Si_2O_7$and X2-RE_2SiO_5, respectively. The diffraction peaks are slightly shifted toward the lower diffraction angles as the average RE ionic radius becomes larger than that of Yb as the RE element increases, causing lattice expansion. Figure 1 shows the photograph of CO_2 laser irradiated samples. RE_2SiO_5 showed recalescence after melting and quenching. In addition, RE_2SiO_5 was non-transparent, which suggests crystallization. Whereas $RE_2Si_2O_7$, with a SiO_2-rich composition, was transparent and vitrified, and pores were observed in the appearance of $RE_2Si_2O_7$. The Raman spectrum of RE_2SiO_5, the increase in the RE elements causes a marked broadening of the peak widths, indicating the presence of disordered atomic bonding. In addition, the Raman peaks corresponding to the Si-O bonds also become broader, which is attributed to the lattice distortion of the Si- and O- sublattices[6]. On the other hand, glassy $RE_2Si_2O_7$ shows only broad bands, suggesting that it was amorphous, similar to the as-sprayed $RE_2Si_2O_7$[7].

Figure 1. Photograph of the appearance of RE silicate after irradiation with a CO_2 laser

References

1) Luo, Y., Sun, L., Wang, J., Du, T., Zhou, C., Zhang, J., Wang, J.: Phase formation capability and compositional design of β-phase multiple rare-earth principal component disilicates. *Nat. Commun.*, **14** (2023) 1275, https://doi.org/10.1038/s41467-023-36947-6
2) Bakan, E., & Vaßen, R.: Crack healing mechanisms in atmospheric plasma sprayed Yb-silicate coatings during post-process heat treatment, *J Euro. Ceram. Soc.*, **43** (2023) 3684-3693, https://doi.org/10.1016/j.jeurceramsoc.2023.02.005
3) Vaßen, R., Bakan, E., Gatzen, C., Kim, S., Mack, D. E., Guillon, O.: Environmental barrier coatings made by different thermal spray technologies, *Coatings*, **9** (2019) 784, https://doi.org/10.3390/coatings9120784
4) Peng, Y., Luo, Z., Wang, H., Du, T., Zhang, J., Sun, L., Wang, J.: Crystallization and phase evolution in novel $(Gd_{1/6}Tb_{1/6}Dy_{1/6}Tm_{1/6}Yb_{1/6}Lu_{1/6})_2Si_2O_7$ environmental barrier coating. *Int. J. Appl. Ceram.*, ***20*** (2023) 896, https://doi.org/10.1111/ijac.14210
5) Nasiri, M. M., Dolatabadi, A., & Moreau, C.: Modeling of liquid detachment and fragmentation during the impact of plasma spray particles on a cold substrate, *Int. J. Heat Mass Transf.*, **189** (2022) 122718, https://doi.org/10.1016/j.ijheatmasstransfer.2022.122718
6) Liu, X., Zhang, P., Huang, M., Han, Y., Xu, N., Li, Y., Zhang, Z., Pan, W., Wan, C.: Effect of lattice distortion

in high-entropy $RE_2Si_2O_7$ and RE_2SiO_5 (RE= Ho, Er, Y, Yb, and Sc) on their thermal conductivity: Experimental and molecular dynamic simulation study. *J. Euro. Ceram. Soc.*, **43** (2023) 6407, https://doi.org/10.1016/j.jeurceramsoc.2023.06.052

7) Garcia, E., Sotelo-Mazon, O., Poblano-Salas, C. A., Trapaga, G., & Sampath, S.: Characterization of $Yb_2Si_2O_7$–Yb_2SiO_5 composite environmental barrier coatings resultant from in situ plasma spray processing. *Ceram. Int.*, **46** (2020) 21328, https://doi.org/10.1016/j.ceramint.2020.05.228