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RE_2O_3-SiO_2 ガラスへの熱処理による亀裂修復の観察
Observation of crack healing by heat treatment on RE_2O_3-SiO_2 glass

大川采久 [1], **Nguyen Thanh Son**[2], 長谷川拓哉 [1], 中山忠親 [3], 石川毅彦 [4], 下西里奈 [4], 小山千尋 [4], 織田裕久 [4], 増野敦信 [5], 殷澍 [1,6]

Ayahisa OKAWA[1], Nguyen Thanh SON[2], Takuya HASEGAWA[1], Tadachika NAKAYAMA[3], Takehiko ISHIKAWA[4], Rina Shimonishi[4], Chihiro KOYAMA[4], Hirohisa ODA[4], Atsunobu MASUNO[5], and Shu YIN[1,6]

[1] 東北大学 多元物質科学研究所, Institute of Multidisciplinary Research for Advanced Material (IMRAM), Tohoku University
[2] 釧路工業高等専門学校 創造工学科, Department of Creative Engineering, National Institute of Technology, Kushiro College
[3] 長岡技術科学大学 極限エネルギー密度工学研究センター, Extreme Energy-Density Research Institute, Nagaoka University of Technology
[4] 宇宙航空研究開発機構, Japan Aerospace Explanation Agency, Tsukuba
[5] 京都大学 大学院工学研究科, Graduate School of Engineering, Kyoto University
[6] 東北大学 材料科学高等研究所, Advanced Institute for Materials Research (WPI-AIMR), Tohoku University

1. Introduction

SiC fiber reinforced SiC matrix composites (SiC_f/SiC_m) show promise for future gas turbine blade applications. However, SiC suffers from recession in high-temperature, water vapor rich environments, necessitating an environmental barrier coating (EBC). Typical EBC systems comprise a Si bond coat for oxidation resistance and adhesion improvement, topped with rare earth (RE) silicates like $RE_2Si_2O_7$. High-entropy RE silicates, containing five or more equimolar RE elements, have recently gained interest for enhancing EBC performance. The β- $RE_2Si_2O_7$ structure (with RE 6-coordination under 0.885 Å) [1] is considered most promising due to its lack of polymorphism during operation temperature range.

To effectively protect SiC from water vapor recession, EBCs must be dense. However, conventional thermal spraying processes result in rapid cooling and amorphization of coatings due to temperature differences with the substrate. While subsequent annealing crystallizes the coating, it also leads to residual cracks and pores, compromising EBC effectiveness. On the other hand, the potential for crack healing through irreversible phase transitions during annealing (from metastable to stable phases with volume expansion)[2] is appealing, but the thermal evolution of coating microstructure and phases remains poorly understood. This analysis is further complicated by SiO volatilization during thermal spraying, localized element segregation in coatings[3], and the multi-element of REs[4]. Moreover, the crucial thermophysical properties[5] of RE silicates for thermal spraying processes have not been reported. This study aims to elucidate the thermal evolution of microstructure and phases in RE silicate glasses without local element segregation, demonstrating crack healing potential, and to determine their thermophysical properties.

2. Experimental Procedures

To form β-$RE_2Si_2O_7$, the rare earth elements Lu, Yb, Er, Y, and Ho were selected. The term "3RE" will be used to denote RE sites with equal molar ratios of Lu, Yb, and Er, while "5RE" will represent the inclusion of Ho and Y. Separate aqueous solutions of RE nitrate ($RE(NO_3)_3 \cdot nH_2O$) and sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) were prepared using 30 mL of distilled water each, maintaining a stoichiometric RE:Si ratio of 1.0. The Na_2SiO_3 solution was treated with 2M HCl, while dilute ammonia was added dropwise to the $RE(NO_3)_3$ solutions. These solutions were then combined and sealed in an autoclave, which was held at 220°C for 3 h. The resulting powder was washed via centrifugation and subsequently heat-treated at 1600°C for 10 h in air. The powder was then subjected to CO_2 laser irradiation using a gas-levitation furnace. X-ray diffraction was employed to analyze the crystallographic phases of the powders prior to CO_2 laser irradiation. Raman spectroscopy was used to examine the laser-irradiated samples. The density of the glass was determined using a pycnometer. Vickers-indented samples were heat-treated in air: 10 h at 1000°C, then 10 h at 1025°C.

3. Results and discussion

XRD analysis revealed that the main phases of the synthesized powders were β-$RE_2Si_2O_7$. A slight shift in diffraction peaks towards lower angles was observed as the average RE ionic radius increased beyond that of Yb, indicating lattice expansion with the incorporation of larger RE elements. These irradiated samples exhibited only broad bands in their spectra, suggesting an amorphous structure similar to as-sprayed $RE_2Si_2O_7$ reported in previous studies[6]. EDS analysis confirmed that the stoichiometric ratios in all irradiated samples generally aligned with the initial ratios, and rare earth elements were uniformly distributed throughout the samples. Glass densities were measured at 6.41 g/cm^3, 6.34 g/cm^3, and 5.80 g/cm^3 for Yb, 3RE, and 5RE samples, respectively. The theoretical density of β-$Yb_2Si_2O_7$ is 6.15 g/cm^3, this suggests the possibility of volume expansion during crystallization. Upon exposure to 1000°C, the Yb sample exhibited partial devitrification, while the 3RE and 5RE samples retained their transparency. Subsequent heat treatment at 1025°C induced complete devitrification in all samples, suggesting crystallization had occurred. New surface cracks were observed in all samples following heat treatment at 1000°C. The cracks formed by pre-Vickers indentation showed partial healing (Fig. 1). This microstructural evolution could be attributed to various factors such as viscous flow, crystallization, or volume expansion associated with phase transitions from metastable to stable phases. Further elucidation of these mechanisms warrants additional investigation in subsequent studies.

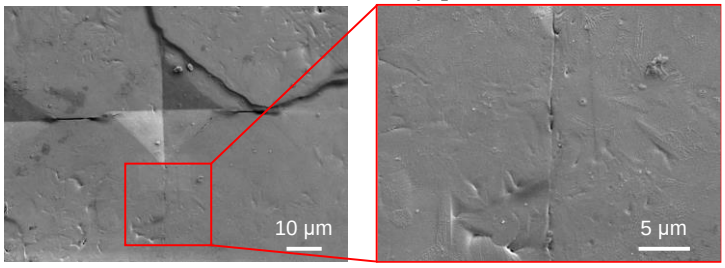

Figure 1. Surface images of the Yb sample after annealing at 1025 °C for 10 h in air.

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