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耐環境コーティングにおける相転移による微細構造進化の観察

Microstructure evolution during phase transitions in environmental barrier coating

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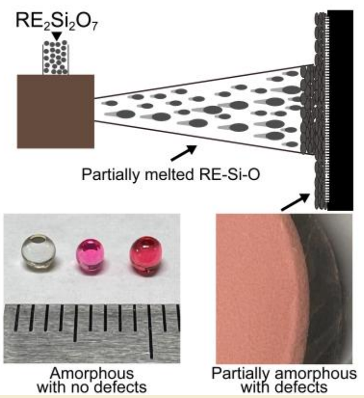

Abstract: Rare earth (RE) silicate environmental barrier coatings (EBCs) for silicon carbide (SiC) composites face challenges in achieving dense microstructures through thermal spray processing. The porous and fractured nature of as-sprayed coatings necessitates optimization of both spraying parameters and post-deposition heat treatment protocols. A critical knowledge gap exists in understanding the relationship between melt thermophysical properties and coating formation behavior. Due to the high melting temperatures of RE silicates (>1800°C), comprehensive thermophysical data for molten states remain largely unavailable. Establishing composition-dependent property databases and correlating them with microstructural evolution would enable systematic densification strategies. Thermal spray experiments revealed that compositionally complex systems exhibit enhanced crystallization retention for multi-component RE silicate under low plasma power conditions, likely attributed to elevated melting points in multi-component RE silicate systems. Post-spray heat treatment demonstrated potential for crack healing; however, the presence of pre-existing defects and compositional inhomogeneities within coatings complicates mechanistic understanding. To isolate fundamental phase transformation behavior from processing-induced complexities, dense RE silicate glasses were fabricated via containerless processing. Heat treatment studies of these defect-free glasses revealed crack healing during heat tretment. These findings contribute to the fundamental understanding of composition-microstructure relationships in high-entropy RE silicate EBCs, supporting the development of materials design strategies for next-generation gas turbine applications.

Keywords: environmental barrier coatings, rare earth silicate, atmospheric plasma spray

1. Introduction

Silicon carbide (SiC) fiber-reinforced composites are promising candidates for next-generation gas turbine blades due to their high-temperature stability. However, their long-term durability in steam-rich environments is compromised by active oxidation and corrosion, necessitating the application of environmental barrier coatings (EBCs). To address this, current EBC systems typically consist of a Si bond coat and an outer layer of rare-earth (RE) silicates such as $RE_2Si_2O_7$, which serve as the primary thermal and environmental barrier. Among these, β-$RE_2Si_2O_7$ (RE ionic radius ≤ 0.885 Å) is particularly promising due to its structural stability without polymorphic transitions under service conditions[1)]. Recently, equimolar multicomponent rare-earth (RE) silicates termed high entropy RE silicates have gained attention for their potential to enhance EBC performance through improved phase stability and thermal properties[2)]. Effective protection of SiC from steam degradation requires high-density EBCs. However, conventional thermal spray processes face two fundamental challenges. First, rapid cooling and amorphization of coatings occur due to temperature differences with the substrate, resulting in residual porosity and cracking. While molten state thermophysical properties critically influence spray coating behavior[3)], their measurement remains challenging for oxide ceramics due to extremely high melting points. This lack of data impedes the development of composition-based design strategies for optimizing coating quality. The thermophysical properties (viscosity, surface tension, etc.) of molten RE silicates are particularly unknown due to their extremely high melting points (>1800°C), severely hindering understanding of densification mechanisms. Second, although post-spray heat treatment enables crystallization of amorphous phases with potential crack healing through irreversible phase transitions[4)], SiO volatilization during spraying and initial defects complicate understanding of microstructural evolution. This study employs aerodynamic levitation to fabricate RE silicate glasses while avoiding crucible contamination and will be utilized the microgravity environment for precise measurement of thermophysical properties. This approach aims to elucidate the influence of RE element species on coating formation and establish composition-based design guidelines for thermal spray coating optimization. Furthermore, detailed thermal phase evolution analysis of defect-free RE silicate glasses will be conducted to demonstrate crack healing mechanisms.

2. Experimental Procedures

To form β-$RE_2Si_2O_7$ structures, rare earth elements with ionic radii ≤0.885 Å were selected based on structural stability criteria. Three representative compositions were selected: monolithic Yb, a ternary "3RE" system (equimolar Lu-Yb-Er), and a high-entropy "5RE" system (equimolar Lu-Yb-Er-Y-Ho). This compositional gradient allows for systematic evaluation of how increasing chemical complexity influences the thermophysical behavior and coating performance. For thermal spray coating preparation, powder mixtures maintaining RE_2O_3:SiO_2 = 1:2 stoichiometry was calcined at 1500°C, followed by granulation processing. Atmospheric plasma spraying was conducted at three power levels (22, 28, 33 kW) to investigate the effect of thermal input on coating microstructure and phase formation. Stoichiometric powder mixtures with RE_2O_3:SiO_2 molar ratio of 1:2 were processed using an aerodynamic levitation furnace with CO_2 laser heating. Vickers-indented samples were heat treated at 1000°C or higher. Microstructural characterization was performed using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy to evaluate phase composition, crystallinity, and structural evolution.

3. Results and discussion

3.1 Thermal Spray coating

XRD analysis of heat-treated powders at 1500°C revealed β-$RE_2Si_2O_7$ as the primary phase with residual RE_2SiO_5 as the secondary phase across all compositions. After spray process, no γ/δ-$RE_2Si_2O_7$ phases were detected, indicating that phase separation did not occur during the heat treatment process. Thermal spray coatings exhibited similar phase with powder, with increasing amorphous content correlating with higher plasma power ranging from 22 kW to 33 kW, indicating enhanced particle melting during deposition[5] (Fig.1). Under 22 kW conditions, the crystalline phase fraction increased significantly with increasing rare earth element complexity. This trend is consistent with reported melting point elevation of approximately 250°C in multi-component RE silicate systems[6], potentially contributing to reduced particle melting efficiency.

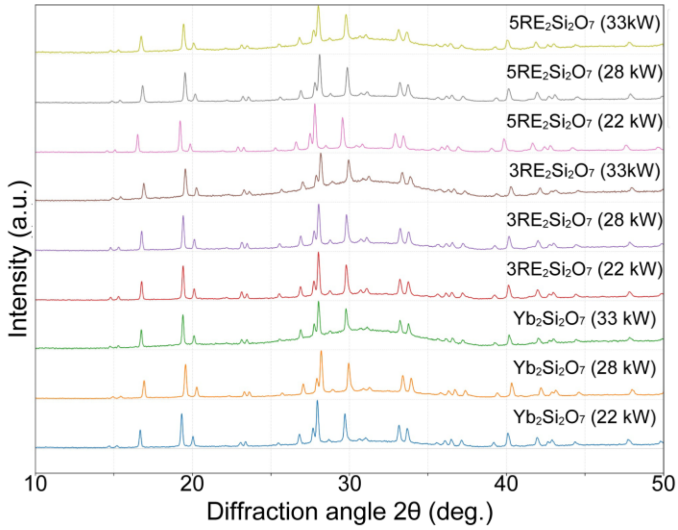

Fig.1 XRD patterns of as-sprayed samples

3.2 Glass Formation and microstructure evolution

Aerodynamic levitation successfully fabricated glasses with stoichiometric compositions confirmed by EDS analysis. The measured glass densities were 6.41 g/cm^3 for Yb, 6.34 g/cm^3 for 3RE, and 5.80 g/cm^3 for 5RE compositions. The density evolution during heat treatment followed a sequential transformation: from amorphous glass (6.41 g/cm^3) to metastable α-$Yb_2Si_2O_7$ (6.73 g/cm^3), and ultimately to stable β- $Yb_2Si_2O_7$ (6.15 g/cm^3)[7]. The initially formed metastable α phase exhibited higher density than the glass, while the final transformation to the β-phase demonstrated volumetric expansion effects, suggesting potential for defect healing mechanisms. Thermal treatment above 1000°C resulted in partial closure of Vickers indentation-induced cracks, suggesting that the α to β phase transformation may have contributed to crack healing through volume expansion-induced compressive stresses.

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Conflicts of Interest

The authors declare no conflict of interest.

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