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Calcium–magnesium–aluminosilicate corrosion behaviors of rare-earth disilicates at 1400 °C

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Abstract

Environmental barrier coatings (EBCs) are used to prevent oxidation of underlying ceramic matrix composite (CMC) structural components in gas turbines. When the siliceous minerals deposit on the surface of EBCs, a glassy melt of calcium–magnesium–aluminosilicate (CMAS) will be formed, leading to the EBCs degradation. In this study, seven rare-earth disilicates ($RE_2Si_2O_7$, RE = Yb, Lu, La, Gd, Eu, Sc, and Y) were fabricated to analyze their CMAS corrosion behaviors. The results indicated that the $RE_2Si_2O_7$ could react with the CMAS in the temperature range of 1250–1350 °C. Reaction zones formed at the interfaces. For the $Yb_2Si_2O_7$, $Lu_2Si_2O_7$, $La_2Si_2O_7$, $Eu_2Si_2O_7$ and $Gd_2Si_2O_7$, the reaction zones dissolved into the molten CMAS and separated from the $RE_2Si_2O_7$. As for the $Sc_2Si_2O_7$ and $Y_2Si_2O_7$, the reaction zones could stay at the interface. They could effectively block the molten CMAS to penetrate into the $RE_2Si_2O_7$ and protect them from CMAS corrosion.

Keywords: Environmental barrier coatings; CMAS; Rare-earth disilicates; Corrosion

1. Introduction

Environmental barrier coatings (EBCs) are the key issue to ensure the durability of silicon-based ceramic matrix composites (CMCs) as high-temperature structural components for gas turbines.[1–3] The primary function of the EBCs is to prevent the protective silica scale, which is formed by the oxidation of the silicon-based ceramics, from volatilization by the high temperature, pressure, and steam in the combustion environment.[4–10] As a successful EBC material, it must have the properties of corrosion resistance, thermochemical stability, low oxygen permeability, low evaporation rate, and close coefficient of thermal expansion (CTE) to that of the CMCs,[4,11,12] among of which the corrosion resistance of EBCs are highly concerned.[13–15]

In the past investigations, many researchers have focused on the water-vapor corrosion and hot corrosion behaviors of the EBC materials.[16–22] Recently, the calcium–magnesium–aluminosilicate (CMAS) corrosion has attracted more attention because CMAS was found to have great effect on the durability of EBC materials.[23,24] The CMAS comes from the siliceous minerals (dust, sand, volcanic ash, runway debris) that enter into the gas turbine with the intake air and deposit on the surface of EBCs. The formed glassy melt of CMAS will react with silicate EBC materials, leading to the degradation of EBCs.[23] The problem becomes more serious in aircraft engines when the aircrafts fly through the desert or the volcanic ash-containing environment. Kendra M. Grant et al.[24] investigated the CMAS corrosion behavior of barium strontium aluminosilicate (BSAS), the first generation EBC material. The result showed that BSAS were susceptible to thermochemical degradation by molten CMAS. The interaction between BSAS and CMAS involved the dissolution of BSAS in the CMAS melt, and its re-crystallization as a modified celsian phase and secondary crystalline phases. Such an interaction was further aggravated by preferential penetration along the BSAS grain boundaries. Although Caitlin Maureen Toohey[25] reported the CMAS corrosion behavior of ytterbium silicate, the studies on the CMAS corrosion behaviors of rare-earth silicates, the second generation EBC materials, are limited in general. The mechanism for their CMAS corrosion behaviors is unclear yet.

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Usually, the rare-earth silicates include monosilicates and disilicates (RE_2SiO_5 and $RE_2Si_2O_7$, RE: rare-earth elements). When the RE_2SiO_5 exposure to the CMAS, the silica in CMAS can react with RE_2SiO_5, leading to the transformation to $RE_2Si_2O_7$.[25] This unpredictable phase change would induce stress, resulting in the degradation to the EBCs. However, when CMAS comes to contact with $RE_2Si_2O_7$, the silica-saturated disilicates remain chemically stable with no phase changes. It could be deduced that the $RE_2Si_2O_7$ should have better chemical stability with CMAS than RE_2SiO_5. Therefore, we investigated the CMAS corrosion behaviors of rare-earth disilicates in the present study. Seven $RE_2Si_2O_7$ (RE = Yb, Lu, La, Gd, Eu, Sc, and Y) were fabricated by sol-gel method. The CMAS corrosion tests of these rare-earth disilicates were carried out at 1400 °C in a 50%H_2O–50%O_2 water-vapor environment. The mechanism for the CMAS corrosion of these materials was proposed based on the results of X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental procedure

Seven $RE_2Si_2O_7$ (RE = Yb, Lu, La, Gd, Eu, Sc, and Y) were fabricated using a sol-gel process. $RE(NO_3)_3 \cdot 6H_2O$ (99.99% purity, A&C Rare Earth Materials Center, Ganzhou, China) and tetraethoxysilane (TEOS, Tianjin Bodi Chemical, Tanjin, China) were used as the raw materials in this process. Firstly, the $RE(NO_3)_3 \cdot 6H_2O$ and TEOS (the molar rate of Re: Si = 1:1.1) were dissolved in a mixture of ethanol and distilled water, respectively. The solution was stirred at room temperature for 12 h until the TEOS was fully hydrolyzed. The obtained solution was then heated in an oven at 60 °C for 10 h and 120 °C for 5 h to evaporate all of the solvent, followed by heat-treatment at 1000 °C. The obtained powders were ball-milled in a shock-type high-energy ball-milling machine (QM-3A High Speed Vibrating Ball Mill, Nanjing T-Bota Scietech Instruments & Equipment Co. Ltd., Nanjing, China) for 1 h. Then the ball-milled powders were pressed into bars with the dimensions of 3 mm × 5 mm × 25 mm. Finally, the bars were sintered at 1500 °C for 10 h in air to obtain the $RE_2Si_2O_7$ samples. The densities and the porosities of the samples were measured by Archimedes Method.

CMAS with a composition of 33Ca-9 Mg-13Al-45Si (all compositions in mole percent of single cation oxide formula units) was chosen in this study. CMAS of this composition melt at about 1235 °C.[26] Calcium oxide, magnesium oxide, aluminum oxide, and silicon dioxide (analytical reagent, Tianli Chemical Reagent Co., Ltd., Tianjin, China) were used as the raw materials to synthesize such a CMAS. All of these raw materials were weighed according to the molar ratio and mixed by a planetary ball mill (ND7-4 L, Nanda Instrument Plant, Nanjing, China) with the media of de-ionized water. The mixture was then dried and heated in air at 100 °C and 1200 °C for 10 h and 24 h, respectively. The obtained material was re-ground into powders and pressed into bars with the dimensions of 2 mm × 5 mm × 25 mm. These bars were sintered at 1200 °C for 2 h in air. The density of the as-fabricated bar is about 1.57 g/cm^3.

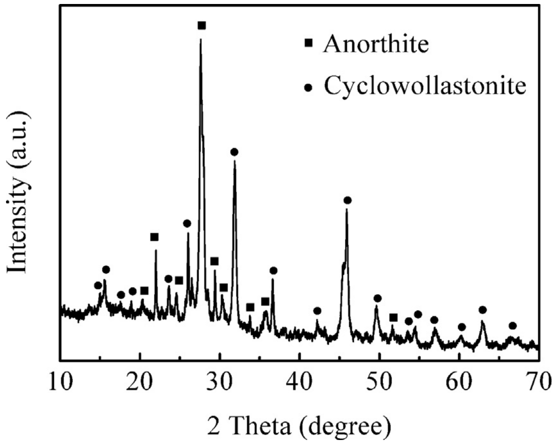

Fig. 1. XRD pattern of CMAS after heat-treated at 1200 °C for 5 h.

The CMAS corrosion behaviors of the $RE_2Si_2O_7$ were carried out at 1400 °C in a water-vapor environment for 10 h with the ramping rate of 5 °C/min. All the $RE_2Si_2O_7$ bars were polished to 1 μm. CMAS bars were uniformly put on the polished surface of each $RE_2Si_2O_7$ sample. The CMAS on $RE_2Si_2O_7$ surface is about 0.314 g/cm^2. The assemblages were then placed in a zirconia crucible. The water-vapor environment was 50% H_2O-50% O_2 with a total pressure of 1 atm flowing at a rate of 8.5×10^{-4} ms^{-1} (the flowing rate was estimated at room temperature). The water vapor was introduced into the alumina tube by means of oxygen carrier gas bubbling through the distilled water heated at 81.7 °C. Heating tape was used to keep the tube at a temperature of 120 °C on the water vapor entrance side of the furnace, which prevented condensation of the water vapor. The water vapor that condensed at the exit side of the tube was collected and used to verify our experimental conditions of 50% H_2O–50% O_2.

The phases of CMAS, as-fabricated $RE_2Si_2O_7$, and the reaction zone were analyzed by an X-ray diffractormeter (D/max-2400, Rigaku, Tokyo, Japan) with Cu $K\alpha$ radiation. Data were digitally recorded in a continuous scan in the range of angle (2θ) from 10° to 70° with a scanning rate of 0.08°/s. The differential scanning calorimetry (DSC) measurement was performed on a simultaneous thermal analyzer (NETZSCH STA 429 CD, Selb, Germany) with a ramping rate of 5 °C/min to investigate the reactions between CMAS and $RE_2Si_2O_7$. The cross-sections of the corroded samples were examined by scanning electron microscopy (SEM, JEOL-6700F, Tokyo, Japan). The elemental analysis was conducted by energy-dispersive spectroscopy (EDS, EDAX, USA).

3. Results and discussion

3.1. The DSC analysis of CMAS and $RE_2Si_2O_7$-CMAS system

The XRD pattern of the CMAS is shown in Fig. 1. The result indicates that the main phases of the CMAS are anorthite ($CaAl_2Si_2O_8$) and cyclowollastonite (β-$CaSiO_3$). The content of Mg is too low to be detected by X-ray diffractormeter.