

构型熵对稀土锆酸盐陶瓷抗 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ 侵蚀性能的影响王晓波^{1,2}, 贺智勇², 杨 潇³, 王 峰², 李江涛³, 张启富^{1,2}

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摘 要: 随着航空涡轮发动机性能的提升, 涡轮进口温度持续升高, 传统的 YSZ 热障涂层已不能满足使用要求, 稀土锆酸盐陶瓷材料以其优异的特性, 被认为是最有潜力成为下一代热障涂层的候选材料。通过无压固相烧结工艺在 1650 °C 保温 10 h 条件下制备了 $\text{Y}_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.5}\text{Gd}_{0.5})_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.33}\text{Gd}_{0.33}\text{Er}_{0.33})_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.25}\text{Gd}_{0.25}\text{Er}_{0.25}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$ 5 种稀土锆酸盐陶瓷, 旨在研究构型熵对稀土锆酸盐陶瓷抗 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) 侵蚀性能的影响。研究结果表明: $(\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$ 抗 CMAS 侵蚀性能最好, 1300 °C 保温 5 h 侵蚀条件下, 侵蚀深度仅为 22 μm 。利用 5 种稀土锆酸盐陶瓷的组离子半径和光学碱度对其抗 CMAS 侵蚀性能进行了综合分析, 结果显示: 离子半径和光学碱度对稀土锆酸盐陶瓷抗 CMAS 侵蚀性能均有一定影响。将 5 种稀土锆酸盐陶瓷粉体与 CMAS 混合烧结, 利用 XRD、SEM、EDS 对反应产物进行了表征, 稀土锆酸盐陶瓷与 CMAS 主要反应产物为近球形的 RE-ZrO₂ 和针柱状晶体 RE-apatite (RE: Y, Gd, Er, Yb, Lu), 其中 RE-apatite 有利于减缓 CMAS 的侵蚀程度, 提高稀土锆酸盐陶瓷抗 CMAS 侵蚀性能。此外, 对稀土锆酸盐陶瓷抗 CMAS 侵蚀机理进行了分析, 当稀土锆酸盐陶瓷与 CMAS 反应时, 通过“溶解-再沉淀”机制结晶生成 RE-ZrO₂ 和 RE-apatite 形成致密层, 阻止 CMAS 进一步侵蚀的作用。

关键词: 稀土锆酸盐陶瓷; 构型熵; 高熵陶瓷; 热障涂层

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热障涂层(TBCs)能有效隔离高温气体, 保护涡轮叶片基体, 降低叶片表面温度, 可以进一步提高航空发动机推力^[1]。厚度为 100~500 μm 的热障涂层, 配合涡轮叶片内部冷却, 可以将高温合金表面温度降低 100~300 °C^[2]。因此, 热障涂层与先进高温结构材料技术、高效冷却技术成为提高燃气涡轮发动机效率的三大核心技术^[3-5]。

作为热障涂层材料需具有导热系数低、耐高温、膨胀系数与基体匹配、热耐久性高、热循环寿命长等特性^[6-8]。近几十年, 综合性能优异的 7%~8%(质量分数)钇稳定氧化锆(YSZ)常用做 TBCs 材料^[9-11]。随着人们对航空涡轮发动机推重比、轻量化、稳定性的要求不断提高, 涡轮叶片表面工作温度将超过 1300 °C^[4, 12]。服役温度高于 1200 °C 时, YSZ 涂层会发生相变及烧结, 冷却过程中 YSZ 由四方相转变

为单斜相发生体积膨胀, 导致涂层脱落^[13-14]。此外, 来自灰尘、沙土、火山灰等的 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ 化合物(CMAS)会在 TBCs 表面熔融并对 TBCs 造成严重侵蚀损伤而导致涂层失效^[15-17], 目前 CMAS 侵蚀已成为 TBCs 不得不解决的问题。为满足未来涡轮发动机发展的需求, 新型热障涂层材料急需研制。近年新型 TBCs 材料得到广泛研究, 如稀土锆酸盐、磷酸盐、钨酸盐等, 均表现出优于 YSZ 的抗 CMAS 侵蚀性能^[18-23], 其中: 稀土锆酸盐的抗 CMAS 侵蚀性能研究最为引人注目。许多学者对单组分、双组分和五组分稀土锆酸盐陶瓷的抗 CMAS 侵蚀性能做了大量研究^[24-28], 但三组分、四组分稀土锆酸盐陶瓷抗 CMAS 侵蚀性能相关报道较少。

“高熵”的概念由学者 Yeh 和 Cantor 分别在合金领域提出^[29-30], 高熵材料是由 5 种或以上元素形

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成的固溶体, 具有巨大的组合空间, 能够实现改进和定制化组合^[31]。2015 年, Rost 等将“高熵”的概念引入到陶瓷领域^[32], 自此高熵陶瓷成为了各国科研人员的研究热点。陶瓷的晶格由阴离子和阳离子 2 种不同的亚晶格组成, 阴离子和一些空位倾向占据阴离子亚晶, 而阳离子亚晶格则会被不同的阳离子随机占据, 陶瓷的摩尔构型熵 (S_{conf}) 可以表示为:

$$S_{\text{conf}} = -R \sum_i^N x_i \ln x_i \quad (1)$$

式中: R 为摩尔气体常数 ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); x_i 为元素的摩尔分数; N 为元素种类数。

根据式(1)的计算结果, 可将陶瓷分为以下几种: $S_{\text{conf}} \geq 1.5R$ 为高熵陶瓷, $1.0R \leq S_{\text{conf}} < 1.5R$ 为中熵陶瓷, $S_{\text{conf}} < 1.0R$ 为低熵陶瓷^[33-35]。根据上述分类及表 2 所列构型熵可知: 单组分、双组份稀土锆酸盐陶瓷属于低熵陶瓷, 三组分、四组份稀土锆酸盐陶瓷属于中熵陶瓷, 五组分稀土锆酸盐陶瓷属于高熵陶瓷。

根据 Clark^[36]和 Che 等^[37]的研究可知: 具有大分子量、无序萤石结构的化合物易获得低热导率。Y、Gd、Er、Yb、Lu 5 种元素在稀土元素中属于离子半径小、相对原子质量高的元素, 其合成的锆酸盐陶瓷晶型通常为无序的萤石结构, 并且具有大分子量。此外, 前期研究工作表明采用电等离子烧结工艺 (SPS) 工艺制备的 ($\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}$)₂Zr₂O₇ 陶瓷具有低热导率、高热膨胀系数和优异的抗 CMAS 侵蚀性能。另根据 Tian 等^[38]的研究发现: 相对于烧绿石结构, 缺陷萤石结构更有利于提高材料体系的抗 CMAS 侵蚀性能。低热导率、与高温镍基合金相近的高热膨胀系数、优异的抗 CMAS 侵蚀性能是未来 TBCs 材料必须具备的性能。因此, 以 Y、Gd、Er、Yb、Lu 5 种稀土元素为基础, 制备了从低熵到高熵的 5 种稀土锆酸盐陶瓷, 重点研究了构型熵增长对稀土锆酸盐陶瓷抗 CMAS 侵蚀性能的影响。

1 实验

1.1 陶瓷试样制备

5 种稀土锆酸盐陶瓷 $\text{Y}_2\text{Zr}_2\text{O}_7$ 、($\text{Y}_{0.5}\text{Gd}_{0.5}$)₂Zr₂O₇、($\text{Y}_{0.33}\text{Gd}_{0.33}\text{Er}_{0.33}$)₂Zr₂O₇、($\text{Y}_{0.25}\text{Gd}_{0.25}\text{Er}_{0.25}\text{Yb}_{0.25}$)₂Zr₂O₇、($\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}$)₂Zr₂O₇ 均以 Y_2O_3 、 Gd_2O_3 、 Er_2O_3 、 Yb_2O_3 、 Lu_2O_3 粉体(虔东稀土集团, 质量分

数 $\geq 99.99\%$)以及 ZrO_2 粉体(山东国瓷, 纯度 $\geq 99.95\%$)为原料, 按照各陶瓷试样化学计量比进行称量, 以氧化锆球为磨介, 酒精为溶剂球磨 10 h 进行原料混合, 料浆经 80 °C、24 h 干燥处理后研磨、过筛得到混合粉体。将混合粉体压制成 $\phi 20 \text{ mm} \times 3 \text{ mm}$ 圆片后经 200 MPa 冷等静压保压 3 min 得到陶瓷素坯, 利用高温烧结炉在 1650 °C 保温 10 h 制得陶瓷样品。

1.2 抗 CMAS 侵蚀实验

根据文献[39]报道的 CMAS 经典配比 33CaO-9MgO-13AlO_{1.5}-45SiO₂ 进行玻璃相制备。按照 CMAS 化学计量比称量, 以氧化锆球为磨介、酒精为溶剂, 球磨 10 h 进行原料混合, 料浆经 80 °C、24 h 干燥处理后研磨、过筛得到混合粉体。将混合粉体放进坩埚, 经 1400 °C 保温 4 h 后取出放进去离子水中得到 CMAS 玻璃, 将其研磨过 200 目筛得到 CMAS 粉体备用。抗 CMAS 侵蚀实验中, 按照 20 mg/cm² 的规格在陶瓷圆片上均匀布 CMAS 粉, 将完成布粉的圆片放置于坩埚中, 在 1300 °C 空气气氛中保温 5 h 进行侵蚀实验。之后试样沿中心线切开, 横截面进行研磨抛光至表面粗糙度 1 μm, 用于观察侵蚀层形貌及厚度。将 CMAS 粉分别与 5 种锆酸盐陶瓷粉体按 1 : 1 的质量比混合并在 1300 °C 空气气氛中保温 5 h, 用以研究不同锆酸盐陶瓷在 CMAS 侵蚀过程中的反应产物。

1.3 样品表征

X 射线衍射(XRD, D8-focus, Bruker, Germany)主要用于样品物相和晶体结构分析。测试条件: Cu 靶, K_α 射线, 管电压 60 kV, 管电流 100 mA, 扫描范围 20°~80°, 步长 0.02°。样品微观形貌以及侵蚀后样品横截面形貌通过扫描电子显微镜(SEM, S4300, Hitachi, Japan)进行分析, 同时利用 X 射线能谱(EDS)对锆酸盐陶瓷及其与 CMAS 反应产物进行元素分析。

2 结果与讨论

2.1 物相与微观形貌分析

5 种稀土锆酸盐陶瓷 $\text{Y}_2\text{Zr}_2\text{O}_7$ 、($\text{Y}_{0.5}\text{Gd}_{0.5}$)₂Zr₂O₇、($\text{Y}_{0.33}\text{Gd}_{0.33}\text{Er}_{0.33}$)₂Zr₂O₇、($\text{Y}_{0.25}\text{Gd}_{0.25}\text{Er}_{0.25}\text{Yb}_{0.25}$)₂Zr₂O₇、($\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}$)₂Zr₂O₇ (分别标记为 H1、H2、H3、H4、H5)均在 1650 °C 保温 10 h 条件下烧结, 其 XRD 分析结果如图 1a 所示。从 XRD 谱中可以看出, 衍射峰(111)、(200)、(220)、(311)、(222)、(400)均为缺陷萤石结构的特征峰^[40-41], 没有出现第 2 相

衍射峰,表明5种稀土锆酸盐陶瓷都形成了单一的缺陷萤石结构。

缺陷萤石结构属于 No.225, $Fm\bar{3}m$ 空间群,可以用 $A_2B_2O_7$ 来表示, A、B 随机占据 4a (0, 0, 0) 空间点位, O 原子占据 7/8 的 8c (0.125, 0.125, 0.125) 空间点位,有 1/8 的氧空位^[42]。本工作所研究的 5 种稀土锆酸盐陶瓷中 Y、Gd、Er、Yb、Lu 占 A 点位, Zr 占 B 点位,各元素的离子半径如表 1 所示。 $A_2B_2O_7$ 型氧化物晶体结构主要受 A、B 点位阳离子半径比 r_A/r_B 的影响, r_A 、 r_B 分别表示 A 点位和 B 点位离子的平均半径,当 $r_A/r_B < 1.46$ 时,倾向形成缺陷萤石结构;当 $1.46 < r_A/r_B < 1.78$ 时,倾向形成烧绿石结构;当 $r_A/r_B > 1.78$ 时倾向形成单斜晶体结构^[42]。由表 2 可知,5 种稀土锆酸盐陶瓷的 r_A/r_B 均小于 1.46,易形成缺陷萤石结构,这与 XRD 分析结果一致。

分别对 5 种稀土锆酸盐陶瓷的 XRD 分析结果进行了 Rietveld 精修,见图 1b~图 1f。通过 Rietveld 精修获得各稀土锆酸盐陶瓷的晶胞参数 a_0 ,由表 2 可知,5 种稀土锆酸盐陶瓷的晶胞参

数由大到小顺序为 H2、H3、H4、H1、H5,这与图 1a 中 5 种稀土锆酸盐陶瓷衍射峰向高角度的偏移规律一致。根据 Bragg 定律 $\lambda = 2d\cos\theta$ 可知(λ 为入射光的波长, d 为晶面间距, θ 为入射光与晶面法线的夹角),入射光 λ 确定的情况下,晶面间距 d 越小,入射角 θ 就越大,相应的衍射峰就会向高角度偏移。此外,立方晶系的晶面间距 d 与晶胞参数 a_0 有如下函数关系:

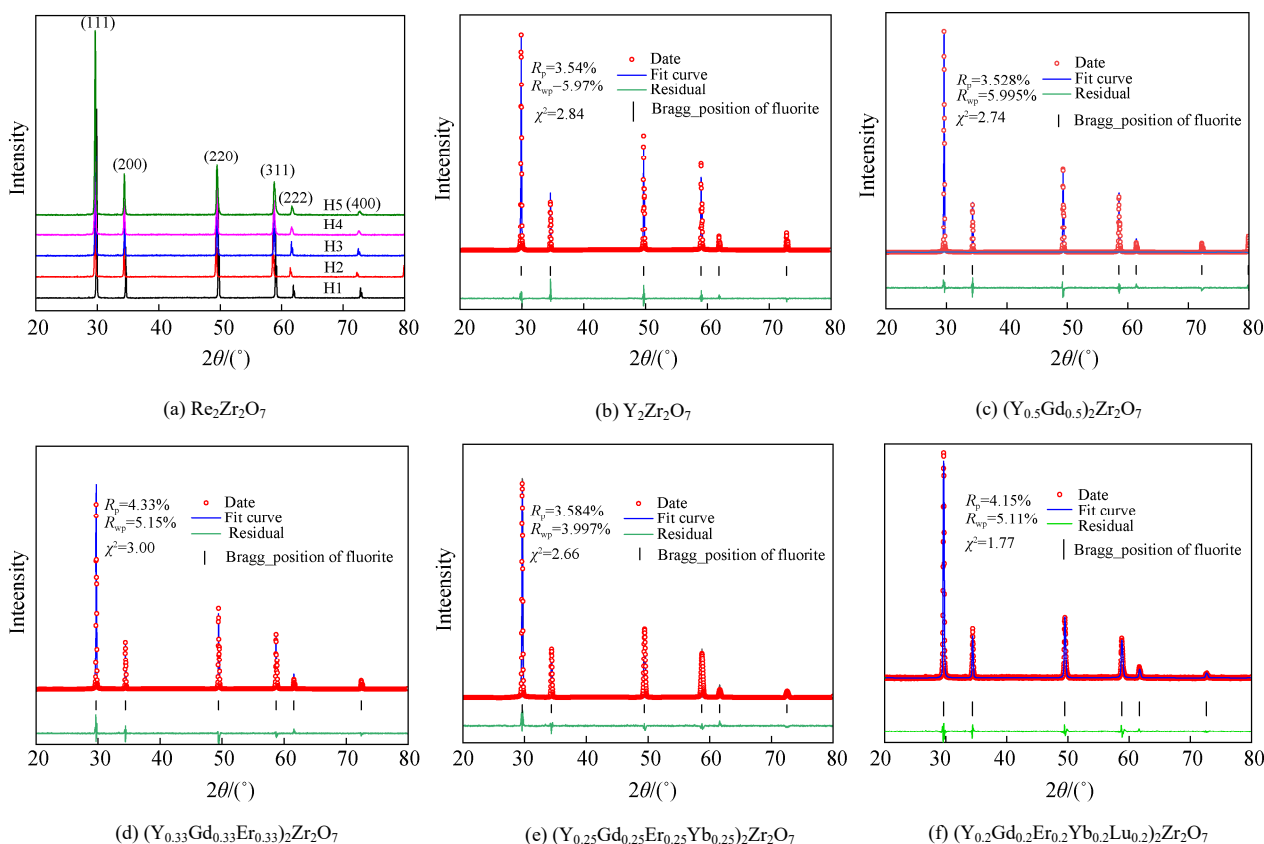
$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

式中: h 、 k 、 l 为晶面指数。通过式(2)可以看出晶面间距 d 与晶胞参数 a_0 正相关,由此得出结论:晶胞参数 a_0 越小,衍射峰就会越向高角度偏移。

表 1 各元素离子半径(稀土元素配位数为 8, Zr 配位数为 6)^[43]

	Y^{3+}	Gd^{3+}	Er^{3+}	Yb^{3+}	Lu^{3+}	Zr^{4+}
$r/\text{\AA}$	1.019	1.053	1.004	0.985	0.977	0.720

r is elemental ion radius.



R_p is unweighted residual factor; R_{wp} is weighted residual factor; χ^2 is goodness of fit

图 1 稀土锆酸盐陶瓷的 XRD 谱以及 Rietveld 精修谱

Fig. 1 XRD patterns and Rietveld fit of $RE_2Zr_2O_7$

表 2 5 种稀土锆酸盐陶瓷的构型熵、原子半径比、晶胞参数、光学碱度

Table 2 Configurational entropy, cation radius ratios, cell parameters and optical basicity of $\text{RE}_2\text{Zr}_2\text{O}_7$

Samples	S_{conf}	$r_{\text{A}}/r_{\text{B}}$	$a_0/\text{\AA}$	A
H1	0	1.415	5.201	0.920
H2	0.693R	1.439	5.232	0.958
H3	1.099R	1.424	5.217	0.936
H4	1.386R	1.410	5.206	0.920
H5	1.609R	1.399	5.194	0.910

A is optical basicity; S_{conf} is configurational entropy; r_{A} is mean ionic radius of rare-earth elements; r_{B} is ionic radius of Zr^{4+} ; a_0 is cell parameter.

为了进一步研究 5 种稀土锆酸盐陶瓷的微观结构和元素分布, 采用放大 100 00 倍的 SEM 照片以及通过 EDS 面扫获得的组成元素分布图对热腐蚀后陶瓷表面进行了分析, 如图 2 所示。5 种稀土锆酸盐陶瓷均由不同大小的多边形晶粒组成, 其中 H1、H2、H3 开气孔较多, 主要分布于晶界处, 部分存在于晶内; H4、H5 相对开气孔较少, 晶界明显, 致密度较高。EDS 元素分布图显示组成 5 种稀土锆酸盐陶瓷的稀土元素和锆元素分布均匀, 均未出现元素偏析现象, 表明稀土锆酸盐陶瓷的整个制备工艺参数及流程设计较为合理。

2.2 抗 CMAS 侵蚀性能分析

5 种稀土锆酸盐陶瓷在 $1300\text{ }^{\circ}\text{C}$ 经历 5h CMAS 侵蚀后的 SEM 照片以及相应的元素分布图如图 3 所示。可以看出 5 种稀土锆酸盐陶瓷 CMAS 侵蚀区域均存在明显的 2 层, 上层较为疏松, 称为“渗透层”, 下层较为致密, 称为“再沉淀层”。渗透层中近球形颗粒排列疏松, 中间穿插着较大尺寸针柱状晶体, 周围有 CMAS 玻璃相环绕; 再沉淀层由微纳米级细小颗粒和针柱状晶体组成, 针柱状晶体沿颗粒生长。结合 SEM 照片以及元素 Si 和 Zr 分布图可知: CMAS 侵蚀深度 $\text{H2} > \text{H3} > \text{H1} > \text{H4} > \text{H5}$ 。尽管稀土锆酸盐陶瓷抗 CMAS 侵蚀性能并没有随熵值增加而提高, 但高熵稀土锆酸盐陶瓷抗 CMAS 侵蚀性能要优于低熵和中熵陶瓷。在 $1300\text{ }^{\circ}\text{C}$ 保温 5 h 的侵蚀条件下, H5 的侵蚀深度仅为 $22\text{ }\mu\text{m}$ 。这一现象的原因在于稀土锆酸盐陶瓷的化学组成对其抗 CMAS 侵蚀能力有显著影响。为验证这一假设, 下面将从离子半径、光学碱度 2 个方面进行探讨。

图 4 展示了 5 种稀土锆酸盐陶瓷的高倍显微照片, 选取相应的针柱状晶体和近球形颗粒进行了 EDS 元素点分析, 具体结果如表 3 所示。5 种稀土锆酸盐陶瓷与 CMAS 在 $1300\text{ }^{\circ}\text{C}$ 反应 5 h 后的

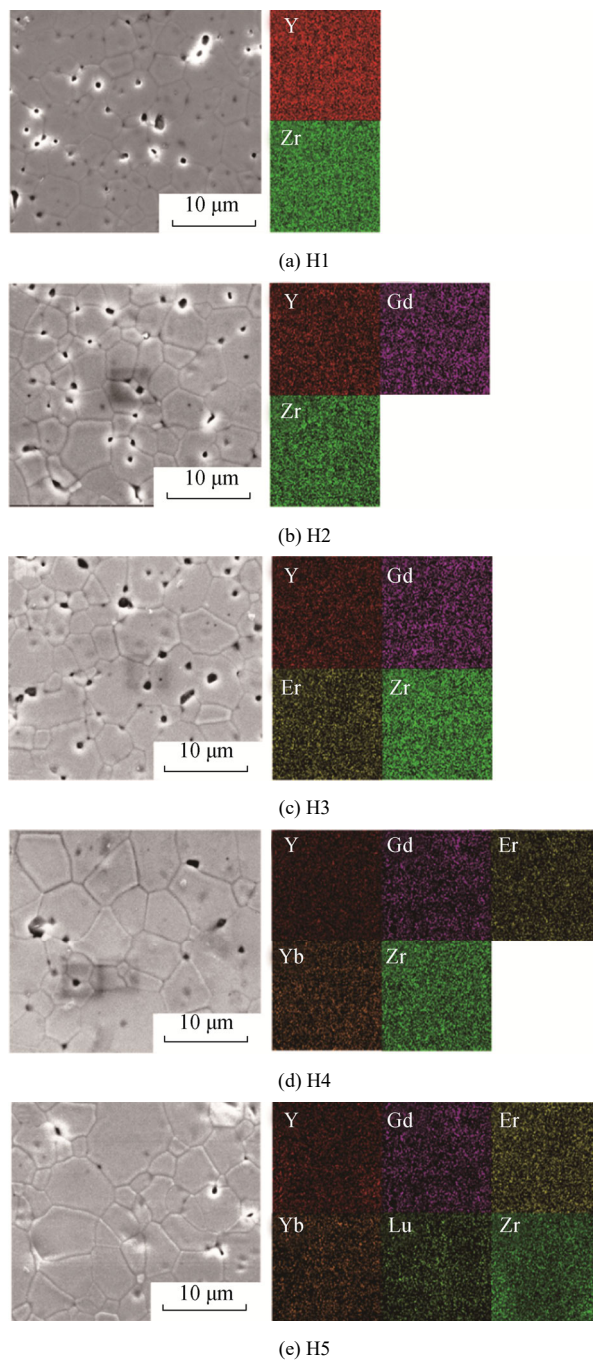


图 2 热腐蚀后 5 种稀土锆酸盐陶瓷的 SEM 照片和 EDS 元素分布图

Fig. 2 SEM images and corresponding elemental mappings of $\text{RE}_2\text{Zr}_2\text{O}_7$ after thermal corrosion

XRD 谱图如图 5 所示。通过 XRD 分析可以确定, 反应产物中包含萤石结构相、磷灰石结构相和铝方柱石, 这与之前的文献报道相一致^[44]。铝方柱石应该是由稀土锆酸盐陶瓷和 CMAS 反应过程中诱导熔融 CMAS 结晶析出产物。结合表 3 中的 EDS 分析结果可知: 图 4 中近球形颗粒为 RE-ZrO_2 (RE: Y, Gd, Er, Yb, Lu), 针柱状晶体为 RE-apatite, RE-apatite 的生成有助于减缓 CMAS 对陶瓷基体侵

蚀^[24]。关于稀土陶瓷抗 CMAS 侵蚀机理可以用“溶解–再沉淀”机制解释,如图 6 所示。当稀土锆酸盐陶瓷与 CMAS 反应时, RE^{3+} 和 Zr^{4+} 由陶瓷块体溶解到 CMAS 熔体中,大离子半径的 RE^{3+} (Gd、Y) 优先与 CMAS 中的 Ca^{2+} 、 Si^{4+} 反应生成 RE-apatite,小离子半径 RE^{3+} (Er、Yb、Lu) 优先固溶到 ZrO_2 晶格内,生成萤石结构的 RE- ZrO_2 ,并沿陶瓷晶粒表面开始生长,这与 EDS 测试结果相一致。这一过程

受 RE^{3+} 和 Zr^{4+} 溶解速率控制,当 RE-apatite 和 RE- ZrO_2 的沉淀速度大于 CMAS 侵蚀速度时形成致密层,阻止 CMAS 的进一步侵蚀;随着侵蚀时间的推移,RE-apatite 和 RE- ZrO_2 晶体长大到一定程度,RE- ZrO_2 开始向再沉淀层生长,RE-apatite 沿径向生长成针柱状晶体并远离再沉淀层到渗透层和剩余 CMAS 熔体中(图 4),这一过程的反应速度主要受阳离子扩散的控制^[45]。

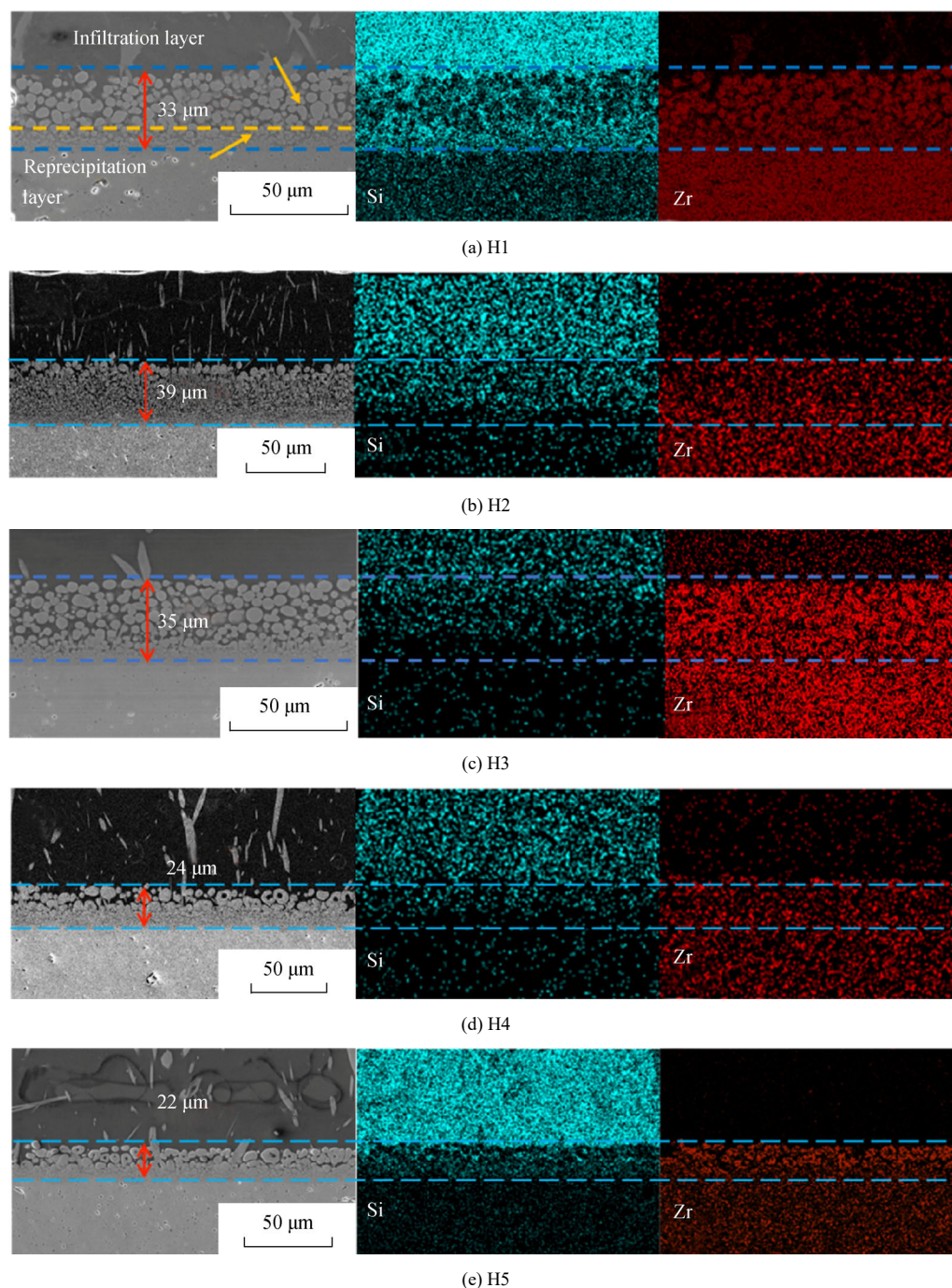


图 3 CMAS 侵蚀后(1300 °C, 5 h) 5 种稀土锆酸盐陶瓷剖面 SEM 照片和 EDS 元素 Si、Zr 分布图

Fig. 3 Cross-sectional SEM micrographs of $\text{RE}_2\text{Zr}_2\text{O}_7$ pellets infiltrated with molten CMAS (1300 °C, 5 h) and corresponding EDS elemental Si and Zr maps

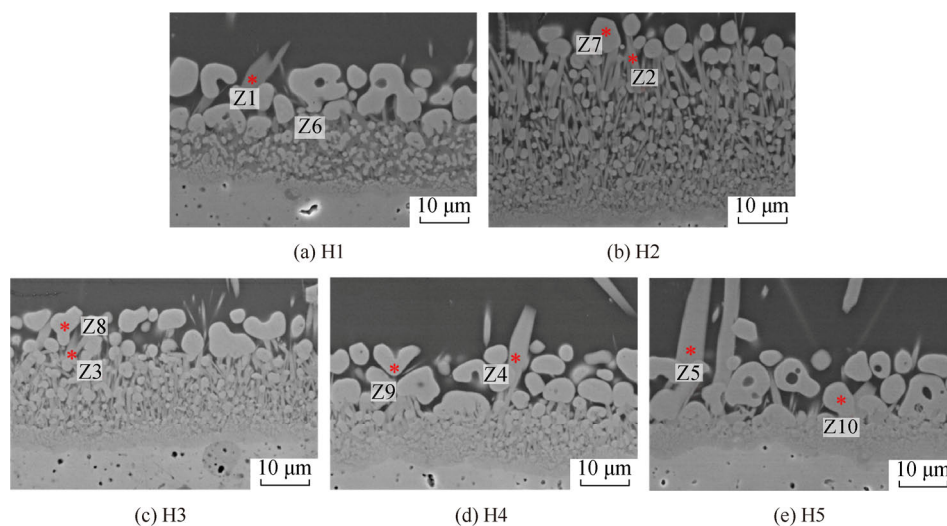


图 4 CMAS 侵蚀后(1300 °C, 5 h) 5 种稀土锆酸盐陶瓷高倍剖面 SEM 照片

Fig. 4 High magnification cross-sectional SEM micrographs of $\text{RE}_2\text{Zr}_2\text{O}_7$ pellets infiltrated with molten CMAS (1300 °C, 5 h)

表 3 CMAS 侵蚀后(1300 °C, 5 h) 5 种稀土锆酸盐陶瓷 EDS 成分分析

Table 3 EDS compositions of $\text{RE}_2\text{Zr}_2\text{O}_7$ pellets infiltrated with molten CMAS (1300 °C, 5 h) $x/\%$

Position	Zr	Y	Gd	Er	Yb	Lu	Si	Ca
Z1		51.66					28.49	19.85
Z2		10.74	13.08				40.81	35.37
Z3		12.47	14.89	13.42			30.17	29.04
Z4		9.97	11.59	10.20	9.49		31.05	27.70
Z5		7.27	10.00	7.61	7.50	7.10	32.36	28.16
Z6	80.77	19.23						
Z7	82.05	8.26	9.69					
Z8	80.63	6.02	4.28	9.07				
Z9	78.13	5.77	2.36	6.52	7.23			
Z10	76.69	4.15	1.71	5.27	6.20	5.98		

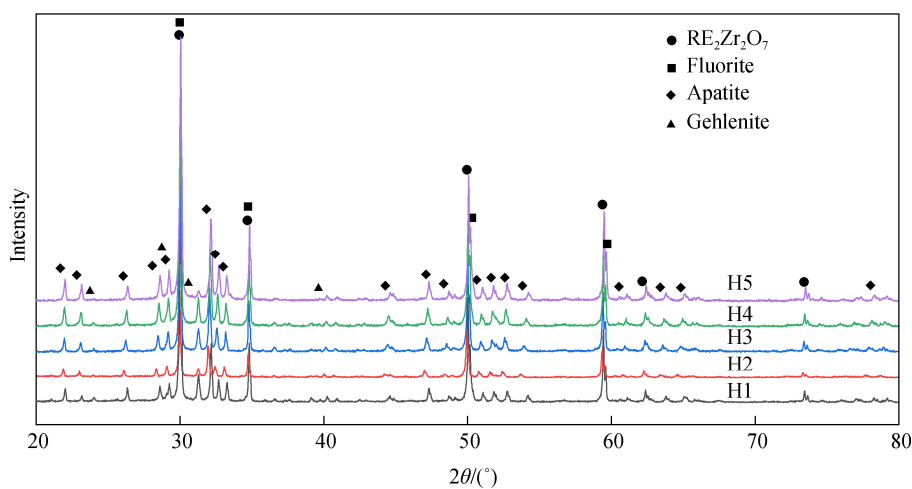
 x is mole fraction; Z1–Z10 are the points in Fig. 4.

图 5 5 种稀土锆酸盐陶瓷和 CMAS 在 1300 °C、5 h 反应后的 XRD 谱

Fig. 5 XRD patterns of $\text{RE}_2\text{Zr}_2\text{O}_7$ and CMAS mixture reacted at 1300 °C for 5 h

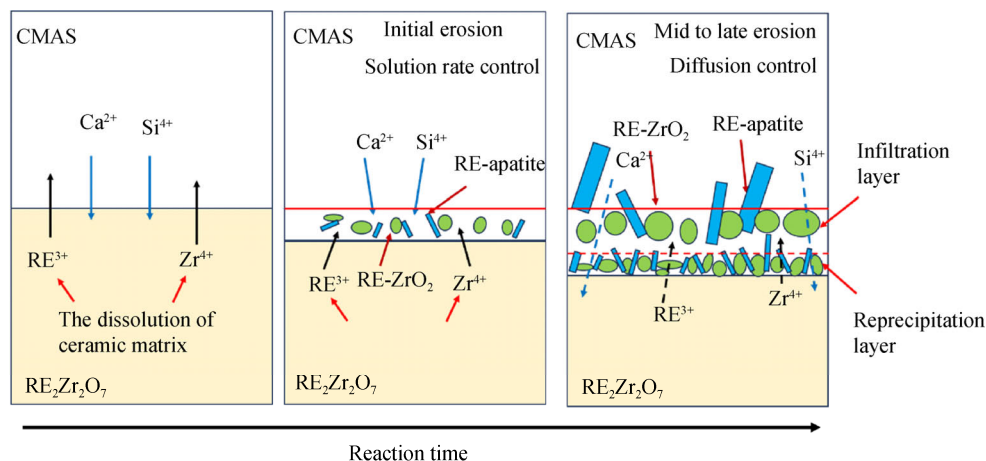


图6 稀土锆酸盐陶瓷抗CMAS侵蚀机理示意图

Fig. 6 Schematic diagram showing for the mechanism of rare earth zirconate ceramics resistance to CMAS erosion

由表2可知, 5种稀土锆酸盐陶瓷中 r_A/r_B 值由大到小的顺序为H2、H3、H1、H4、H5, 同CMAS侵蚀深度顺序一致, 实验结果表明: CMAS侵蚀深度随组分平均离子半径的减小而减小。稀土锆酸盐陶瓷抗CMAS侵蚀过程中, 反应产物RE-apatite的化学式一般可以表达为: $(Ca_{2-y}RE_y)RE_6(SiO_4)_6O_n$, n 值是由阳离子化学价决定的, y 值跟 RE^{3+} 半径有关, 其半径越接近 Ca^{2+} 半径(1.18 Å), y 值就越大^[24, 44]。因此, 随着 RE^{3+} 半径越接近 Ca^{2+} 半径, 生成RE-apatite就需要侵蚀更深的陶瓷基体以获得更多的稀土元素, 这与实验结果相符。但Drexler等^[24]对比了 $Y_2Zr_2O_7$ 和 $Yb_2Zr_2O_7$ 的抗CMAS侵蚀性能发现: 尽管 Yb^{3+} 半径小于 Y^{3+} , 在1200℃保温4h的侵蚀条件下, $Yb_2Zr_2O_7$ 的侵蚀深度(40 μm)是 $Y_2Zr_2O_7$ 侵蚀深度(20 μm)的2倍; 这是由于RE-apatite在CMAS熔体中的结晶倾向随 RE^{3+} 半径减小而减小^[46], $Yb_2Zr_2O_7$ 在CMAS侵蚀过程中形成Yb-apatite效率低于 $Y_2Zr_2O_7$, 没有能够快速形成致密层, 由此产生了较大的侵蚀深度。综合上述分析, 稀土锆酸盐陶瓷抗CMAS侵蚀性能的优劣不能单以组分平均离子半径大小确定, 材料构型熵也起到一定的作用。

光学碱度的概念最早是由Duffy等^[47]提出, 用来进行玻璃中氧化物的化学活性分类。光学碱度概念是基于路易斯酸碱理论提出的, 该理论认为酸碱反应导致酸从碱中获得电子形成配位键。光学碱度用来表示金属氧化物配位键中氧离子提供电子的程度。具有极高化率的阳离子吸引电子远离氧, 导致这种氧化物变弱碱性(低光学碱度); 而拥有低极化率阳离子的氧化物具有高光学碱度^[48]。根据文献

[49]报道, 多种氧化物组成的物质光学碱度计算公式如下:

$$A = X_A \times A_A + X_B \times A_B + X_C \times A_C \cdots \quad (3)$$

式中: X_A 、 X_B 、 $X_C \cdots$ 表示各氧化物贡献氧离子的比例; A_A 、 A_B 、 $A_C \cdots$ 表示各氧化物的光学碱度。

组成稀土锆酸盐陶瓷的各氧化物光学碱度如表4所示, 根据式(3)可计算出CMAS(33CaO–9MgO–13AlO_{1.5}–45SiO₂)的光学碱度为0.626, 5种稀土锆酸盐陶瓷的光学碱度如表2所示。H1~H5与CMAS的光学碱度差 ΔA 分别是: 0.294、0.332、0.310、0.294、0.284, 按照 ΔA 大小顺序排列: H2>H3>H1=H4>H5, 这与CMAS侵蚀深度顺序基本一致。可以看出: 同等条件下, 稀土锆酸盐陶瓷与CMAS之间光学碱度差 ΔA 越大, 两者反应速度越快, CMAS侵蚀深度越大, 这与相关文献报道的研究结论相一致^[50–51]。由此说明, 光学碱度对于选择热障涂层材料有一定参考作用。

表4 各氧化物的光学碱度
Table 4 Optical basicity of oxides

Oxides	A	Ref.
Y ₂ O ₃	1.00	[52]
Gd ₂ O ₃	1.18	[53]
Er ₂ O ₃	0.929	[54]
Yb ₂ O ₃	0.893	[54]
Lu ₂ O ₃	0.886	[54]
ZrO ₂	0.86	[55]
CaO	1.00	[49]
MgO	0.78	[49]
Al ₂ O ₃	0.60	[49]
SiO ₂	0.48	[49]

3 结论

利用高温固相法合成了 $\text{Y}_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.5}\text{Gd}_{0.5})_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.33}\text{Gd}_{0.33}\text{Er}_{0.33})_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.25}\text{Gd}_{0.25}\text{Er}_{0.25}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7$ 、 $(\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$ 5 种稀土锆酸盐陶瓷, 晶型均为缺陷萤石结构。稀土锆酸盐陶瓷抗 CMAS 侵蚀机理分析发现: 侵蚀层分为明显的 2 层, 分别是渗透层和再沉淀层; 其中, 再沉淀层主要由近球形的萤石结构 RE-ZrO_2 和针柱状的 RE-apatite 晶体组成, 形成致密层阻碍 CMAS 进一步侵蚀基体。重点开展了构型熵的增加对 5 种稀土锆酸盐陶瓷抗 CMAS 侵蚀性能的影响研究, CMAS 侵蚀深度 $\text{H}_2 > \text{H}_3 > \text{H}_1 > \text{H}_4 > \text{H}_5$, 其中 H_5 的抗 CMAS 侵蚀性能最好, $1300\text{ }^\circ\text{C}$ 保温 5 h 侵蚀条件下, 侵蚀深度仅为 $22\text{ }\mu\text{m}$ 。结果表明: 稀土锆酸盐陶瓷抗 CMAS 侵蚀性能的优劣不随构型熵的增加而增加, 但高熵稀土锆酸盐陶瓷抗 CMAS 侵蚀性能优于低熵和中熵稀土锆酸盐陶瓷。此外, 稀土锆酸盐陶瓷抗 CMAS 侵蚀性能会受构型熵、稀土离子半径的共同影响。引入了光学碱度的概念对 5 种稀土锆酸盐陶瓷抗 CMAS 侵蚀性能进行了分析。同等条件下, 稀土锆酸盐陶瓷与 CMAS 之间光学碱度差 ΔA 越大, 两者反应速度越快, CMAS 侵蚀深度越大。光学碱度可以作为新型热障涂层材料选择的一个参考指标。

今后稀土锆酸盐热障涂层材料的开发应关注如下几点:

1) 选择高熵稀土锆酸盐陶瓷做热障涂层材料, 其抗 CMAS 侵蚀性能要优于低熵和中熵材料; 2) 可以将光学碱度作为材料初步选择的参考, 在理论上筛选出抗 CMAS 侵蚀性能较好的材料; 3) 稀土离子半径需大小搭配, 保证制备的陶瓷材料晶型为缺陷萤石结构; 另外, 陶瓷材料应在消耗较少基体的前提下, 能够快速与 CMAS 反应生成针柱状 RE-apatite 晶体与近球形 RE-ZrO_2 , 并迅速形成致密层减缓 CMAS 的进一步侵蚀。

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Effect of Configuration Entropy on Resistance of Rare-earth Zirconate Ceramics to CaO-MgO-Al₂O₃-SiO₂

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Extended Abstract

Introduction Thermal barrier coatings (TBCs) are capable of effectively isolating high-temperature gases, protecting the turbine blade matrix, reducing blade surface temperatures, and consequently enhancing aero engine thrust. TBCs with a thickness ranging from 100 to 500 μm in conjunction with internal turbine blade cooling can decrease the surface temperature of the superalloy by 100–300 $^{\circ}\text{C}$. In recent decades, yttrium-stabilized zirconia (YSZ) containing 7%–8% (by mass) is widely utilized as a material for thermal barrier coatings (TBCs) due to its superior properties. With the increasing demands for thrust-to-weight ratio, weight reduction, and stability in aviation turbine engines, the surface temperature of blade is expected to surpass 1300 $^{\circ}\text{C}$. When the operating temperature exceeds 1200 $^{\circ}\text{C}$, the YSZ coating undergoes the phase transformation and sintering. For cooling, it transitions from the tetragonal phase to the monoclinic phase, leading to coating volume expansion. Moreover, calcium-magnesium-alumino-silicate (CMAS) compounds derived from dust, sand, and volcanic ash can melt on the TBC surface, causing a severe erosion and ultimately leading to coating failure. The existing CMAS erosion becomes a challenge for TBCs. It is thus necessary for the evolving requirements of future turbine engine development to develop novel thermal barrier coating materials. Recent studies focus on new TBCs materials, including rare-earth zirconates, phosphates, and hafnates, which exhibit an enhanced CMAS erosion resistance, compared to YSZ. In this paper, the CMAS erosion resistance of rare-earth zirconates was investigated.

Methods $\text{Y}_2\text{Zr}_2\text{O}_7$ (H1), $(\text{Y}_{0.5}\text{Gd}_{0.5})_2\text{Zr}_2\text{O}_7$ (H2), $(\text{Y}_{0.33}\text{Gd}_{0.33}\text{Er}_{0.33})_2\text{Zr}_2\text{O}_7$ (H3), $(\text{Y}_{0.25}\text{Gd}_{0.25}\text{Er}_{0.25}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7$ (H4), $(\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$ (H5) were synthesized by a solid-state synthesis method at 1650 $^{\circ}\text{C}$ for 10 h. The glass phase was prepared according to the classical composition of 33CaO–9MgO–13Al₂O₃–45SiO₂. In the CMAS erosion resistance test, CMAS powder was uniformly applied to ceramic discs at a density of 20 mg/cm². The discs were then placed in a crucible and maintained in an air atmosphere at 1300 $^{\circ}\text{C}$ for 5 h to conduct the erosion experiment. Subsequently, the samples were sectioned along the centerline, and the cross-sections were ground and polished to achieve a surface roughness of 1 μm , facilitating the observation of the morphology and thickness of the eroded layer. To analyze the reaction products of different zirconate ceramics during CMAS erosion, CMAS powder was mixed with five types of zirconate ceramic powders at a mass ratio of 1:1 and heated in an air atmosphere at 1300 $^{\circ}\text{C}$ for 5 h.

Results and discussion All the five rare-earth zirconate ceramics exhibit a single, defective fluorite structure. After five rare-earth zirconate ceramics are eroded at 1300 $^{\circ}\text{C}$ for 5 h, the CMAS erosion depths are ranked as H2 > H3 > H1 > H4 > H5. Despite the fact that the CMAS corrosion resistance of rare-earth zirconate ceramics does not improve with increasing entropy, the CMAS corrosion resistance of high-entropy rare-earth zirconate ceramics is superior to that of low- and medium-entropy ceramics. After heating at 1300 $^{\circ}\text{C}$ for 5 h, the erosion depth of H5 is only 22 μm . The mechanism of resistance to CMAS erosion in rare-earth ceramics can be elucidated through the "dissolution-reprecipitation" mechanism. Upon interaction between rare-earth zirconate ceramics and CMAS, RE³⁺ and Zr⁴⁺ dissolve from the ceramic matrix into the CMAS melt. RE³⁺ ions with larger ionic radii (such as Gd³⁺ and Y³⁺) react with Ca²⁺ and Si⁴⁺ in the CMAS to form RE-apatite. Conversely, RE³⁺ ions with smaller ionic radii (such as Er³⁺, Yb³⁺, and Lu³⁺) preferentially incorporate into ZrO₂ lattice, forming a fluorite-structured RE-ZrO. When the precipitation rates of RE-apatite and RE-ZrO₂ exceed the erosion rate of CMAS, a dense protective layer forms, effectively preventing further CMAS erosion. The average rare-earth ion radius and optical basicity both affect the corrosion resistance of five rare-earth zirconate ceramics to CMAS.

Conclusions $\text{Y}_2\text{Zr}_2\text{O}_7$, $(\text{Y}_{0.5}\text{Gd}_{0.5})_2\text{Zr}_2\text{O}_7$, $(\text{Y}_{0.33}\text{Gd}_{0.33}\text{Er}_{0.33})_2\text{Zr}_2\text{O}_7$, $(\text{Y}_{0.25}\text{Gd}_{0.25}\text{Er}_{0.25}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7$, and $(\text{Y}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$ were synthesized by a high-temperature solid-state reaction method. These five rare-earth zirconate ceramics exhibited a defective fluorite crystal structure. The analysis of the mechanism of resistance to CMAS erosion in these ceramics revealed that the erosion layer consisted of two distinct layers, i.e., an infiltration layer and a reprecipitation layer. The reprecipitated layer primarily comprised near-spherical fluorite-structured RE-ZrO₂ and RE-apatite crystalline pillars, forming a dense barrier that prevented further CMAS penetration into the substrate. The impact of configurational entropy on the CMAS corrosion resistance of these five rare-earth zirconate ceramics was investigated. The CMAS corrosion depths were found to be H2 > H3 > H1 > H4 > H5, and H5 exhibited the optimum CMAS corrosion resistance, showing a corrosion depth of only 22 μm after heating at 1300 $^{\circ}\text{C}$ for 5 h. The findings indicated that while the resistance to CMAS erosion in rare-earth zirconate ceramics did not strictly increase with increasing configurational entropy, high-entropy rare-earth zirconate ceramics demonstrated a superior resistance, compared to low- and medium-entropy counterparts. In addition, the CMAS corrosion resistance of rare-earth zirconate ceramics was influenced by both configurational entropy and the radius of rare earth ions. A concept of optical basicity was introduced to evaluate the corrosion resistance of five rare-earth zirconate ceramics against CMAS. Under identical conditions, a larger optical basicity difference (ΔI) between the rare earth zirconate ceramics and CMAS resulted in a higher reaction rate and deeper erosion by CMAS. The optical basicity could serve as a valuable reference for selecting new thermal barrier coating materials.

Keywords rare-earth zirconate ceramics; configurational entropy; high entropy ceramics; thermal barrier coating