

热循环处理对 $(\text{Gd}_{0.9}\text{Yb}_{0.1})_2\text{Zr}_2\text{O}_7/\text{Yb}_2\text{O}_3$ 稳定 ZrO_2 热障涂层力学性能的影响

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摘 要: 新型掺杂改性的锆酸钪涂层材料有望成为下一代航空发动机热端部件的关键防热材料。采用大气等离子喷涂工艺, 在 Inconel 600 基底上制备了 $(\text{Gd}_{0.9}\text{Yb}_{0.1})_2\text{Zr}_2\text{O}_7/\text{Y}_2\text{O}_3$ 稳定 ZrO_2 (GYbZ/8YSZ)热障涂层, 在 1 100 °C 完成了 100 次热循环处理, 系统分析了涂层成分、微观结构和力学性能的演变。结果表明, 在喷涂前后和后期的热循环处理过程中, GYbZ 材料结构稳定; 在涂层界面产生了热生长氧化层, 其逐渐增厚至 20 μm ; 在 50 次热循环后, 涂层弹性模量与硬度分别达到最大值 182.01 GPa 和 9.13 GPa; 高温原位压痕测试表明, 在 700 °C 后, GYbZ 涂层表面高温硬度基本趋于稳定。经过不同次数热循环处理后, 涂层残余应力变化范围为-41.02~-123.67 MPa, 断裂韧性范围为 0.93~2.02 $\text{MPa}\cdot\text{m}^{1/2}$ 。系统地讨论了高温长时间热处理过程中 GYbZ/8YSZ 体系微观结构演变与力学性能的关联, 为后续可靠性预测提供了重要的实验依据。

关键词: 热障涂层; 氧化钪掺杂锆酸钪; 高温硬度; 断裂韧性; 残余应力

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随着航空航天技术的不断发展, 要求发动机具有更长的使用寿命、更高的使用效率以及更优异的高温稳定性, 这些性能的提升将会增加发动机的表面温度以及工作负荷^[1-2], 使得高温构件的服役环境愈加严苛复杂。陶瓷层热障涂层作为一种表面防护技术, 具有低热导率、高稳定性、高热膨胀系数等特点, 被广泛应用于飞机发动机的涡轮叶片、导向叶片和涡轮桨等热端部件表面, 降低镍基高温合金表面温度, 使发动机能够在高温下长期稳定服役^[3-6]。

20 世纪 80 年代, 8% (质量分数) Y_2O_3 稳定 ZrO_2 (8YSZ)材料被成功应用到飞机发动机的高温部件表面, 并一直沿用至今。然而, 传统的 8YSZ 热障涂层只能在 1 200 °C 以下保持性能稳定, 在 1 200 °C 以上会出现严重烧结以及相变等不利因素, 破坏热障涂层结构, 从而导致其失效^[7-9], 已无法满足未来发动机的高温服役要求。为了胜任航空发动

机更高性能的提升要求, 发展可以在超高温下服役的新型热障涂层陶瓷材料成为了研究重点^[7, 10]。

在众多新型热障涂层材料中, 稀土锆酸盐($\text{RE}_2\text{Zr}_2\text{O}_7$, RE 为稀土元素)脱颖而出。同时, $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZO)受到广泛关注和研究^[11-15]。GZO 的熔点约 2 570 °C, 相变温度约为 1 530 °C, 远高于 8YSZ 的相变温度(1 170 °C), 在 1 000 °C GZO 的热导率约为 $1.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, 比 8YSZ 的热导率 $2.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 降低了 30%左右^[3, 16]。Doleker 等^[16]研究了在 1 100 °C 8YSZ 涂层和 GZO 涂层的抗氧化性能, 结果表明: 8YSZ 涂层的氧化速率更快, 氧化层更厚, GZO 涂层具有更优异的抗氧化性能。GZO 的烧绿石结构与萤石结构均为立方晶型, 相转变过程不会产生体积效应, 对涂层体系无危害^[17]。然而, GZO 涂层的热膨胀系数和断裂韧性偏小, 导致在高温冷却时, GZO 涂层容易从基底上发生剥离脱落或产生较多的裂纹而失效^[18-20]。

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研究表明, 8YSZ 作为过渡涂层, 用于制备双陶瓷层热障涂层(GZO/8YSZ 涂层), 可使 GZO 涂层性能扬长避短, 延长其使用寿命^[3, 21–22]。另外, 稀土元素掺杂可以在一定程度上影响 GZO 的热力学性能^[14, 23]。Li、Guo 和 Wang 等^[8, 24–25]分别发现 Sc 掺杂 GZO 后, 涂层的热膨胀系数、硬度和断裂韧性提高, 且在涂层表面形成连续、致密的反应层, 以阻止熔盐侵蚀。研究发现在超过 1 000 °C 后, Dy 掺杂 GZO 的涂层热膨胀系数有所增加^[26]。Zhao 等^[27]利用密度泛函理论, 计算得到 Th 掺杂 GZO 后, 涂层具有更小的热导率和弹性模量, 且热膨胀系数增加。Jiang 等^[28]研究发现 Nb 和 Cu 共掺杂 GZO 后, 涂层热膨胀系数降低, 在高温下热扩散系数增加。Guo 等^[29]提出 Yb 掺杂 GZO 形成 $(\text{Gd}_{0.9}\text{Yb}_{0.1})_2\text{Zr}_2\text{O}_7$ (GYbZ) 后, 涂层性能可得到显著提升: GYbZ 比 GZO 具有更低的导热系数; 在 1 400 °C GYbZ 的导热系数比 GZO 降低约 20%; 在 1 200 °C GYbZ 涂层的热膨胀系数可与 8YSZ 相当。进一步研究表明, 通过电子束物理气相沉积(EB-PVD)制备的 GYbZ/8YSZ 涂层具有超过 3 700 个热循环寿命和热冲击寿命^[30]。Zhen 等^[31]研究发现 GYbZ 比 8YSZ 导热率低约 27%, 且 GYbZ 具有更优异的抗烧结能力。由于掺杂与 Gd 离子半径、原子质量差异较大的 Yb 元素, GYbZ 晶格无序化程度增加、晶格发生畸变, 使断裂能增加, 断裂韧性增强^[32–33]。然而, 目前主要侧重研究 GYbZ/8YSZ 涂层的热导率、热膨胀系数、抗烧蚀等性能, 对高温力学性能演变特性及失效机理研究仍旧不够充分。

本工作采用大气等离子喷涂技术制备了 GYbZ/8YSZ 热障涂层, 模拟服役环境, 探究在 1 100 °C 经过不同次数热循环处理后涂层的成分和微观结构变化; 采用压痕技术, 表征了涂层的弹性

模量、硬度、断裂韧性和残余应力, 完善了涂层热物理参数、力学参数数据库, 有助于进一步掌握 GYbZ/8YSZ 涂层宏微观高温失效机理。

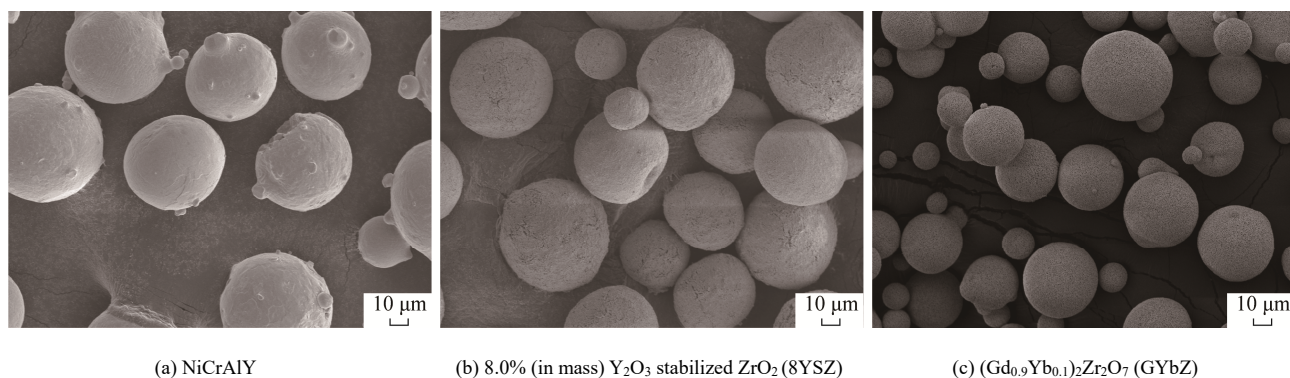
1 实验

1.1 涂层制备及热处理

采用大气等离子喷涂工艺(APS, ZB80X, 北京航天振邦公司), 在厚度 2 mm 的 Inconel 600 镍基高温合金表面制备了 GYbZ/8YSZ 涂层。粘结层为 NiCrAlY 粉末(天津德天助非晶纳米科技有限公司, $D_{50}=45\text{ }\mu\text{m}$), 陶瓷层粉末分别为 8YSZ(天津德天助非晶纳米科技有限公司, $D_{50}=45\text{ }\mu\text{m}$)和 GYbZ(内蒙古工业大学, $D_{50}=35\text{ }\mu\text{m}$), 如图 1 所示。制备流程为: 首先对镍基高温合金基底使用无水乙醇去污除油, 40 目(0.425 mm)碳化硅颗粒喷砂处理后, 依次喷涂约 100 μm 的 NiCrAlY 粘结层、250 μm 的 8YSZ 层和 100 μm 的 GYbZ 层。大气等离子喷涂参数如表 1 所示。原始涂层样品宏观形貌如图 2 所示。对 $\phi 20\text{ mm}$ 的 GYbZ/8YSZ 涂层样品进行热循环处理, 在 1 100 °C 马弗炉(SX3-14-14, 湖南湘潭市仪器仪表有限公司)中, 保温 1 h, 取出自然冷却至室温。热循环次数为 10 次、50 次和 100 次, 样品数量为 12 个。压痕测试前, 使用 1 000 目(13 μm)、2 000 目(6.5 μm)和 3 000 目(4.3 μm)的砂纸, 对 GYbZ/8YSZ 涂层表面打磨、抛光, 有利于提高测试精度。

1.2 物相与微观结构测试

采用 X 射线衍射(XRD, D8 ADVANCE, Bruker, 德国, $\text{Cu K}\alpha\text{ }\lambda=1.541\text{ }\text{\AA}$)和扫描电子显微镜(SEM, JSM-7900F, 日本), 分析涂层的物相和微观形貌变化。XRD 测试的 2θ 范围为 $10^\circ\sim 90^\circ$, 扫描速率约 $8^\circ/\text{min}$, 电压 40 kV, 电流 40 mA; SEM 测试的电压范围为 5~12 kV。



(a) NiCrAlY

(b) 8.0% (in mass) Y_2O_3 stabilized ZrO_2 (8YSZ)(c) $(\text{Gd}_{0.9}\text{Yb}_{0.1})_2\text{Zr}_2\text{O}_7$ (GYbZ)

图 1 喷涂粉末微观形貌

Fig. 1 Micromorphologies of spray powders

表 1 大气等离子喷涂工艺参数

Table 1 Preparation parameters of air plasma spraying (APS)

Material	Voltage/V	Current/A	Ar flow rate/(L·min ⁻¹)	H ₂ flow rate/(L·min ⁻¹)	Powder feed rate/(g·min ⁻¹)	Spray distance/mm
NiCrAlY	69	550	46	9.9	20–24	120
8YSZ	68	560	35	11.9	20–24	100
GYbZ	68	560	35	11.9	20–24	100



图 2 APS 制备的 GYbZ/8YSZ 涂层样品

Fig. 2 GYbZ/8YSZ coatings prepared by APS

1.3 维氏压痕测试

采用课题组自主研制的超高温压痕仪, 表征 700~1 100 °C 范围内 GYbZ/8YSZ 涂层的原位硬度, 如图 3 所示。采用维氏压痕仪(上海研润光机科技有限公司, HMAS-130MV), 在常温下表征热循环前后 GYbZ/8YSZ 涂层的硬度、断裂韧性和残余应力。选用不同的载荷完成不同目的的测试, 保载时间为 15 s。

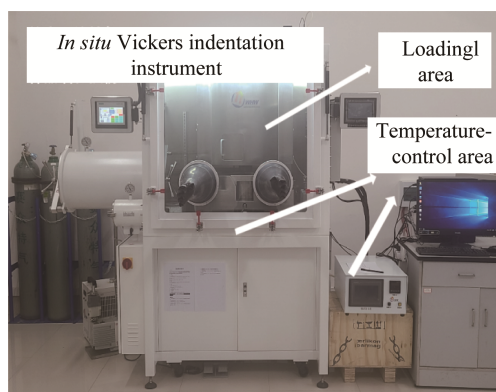


图 3 超高温维氏压痕仪

Fig. 3 Ultra high temperature Vickers indentation instrument

对于涂层显微硬度 H 测试, 需要选择合适的载荷 P , 谨防载荷过大导致涂层开裂。通过观测残余压痕对角线 d_1 和 d_2 值, 根据式(1)计算得到硬度^[34-35]:

$$H = 1.8544 \frac{P}{d^2} \quad (1)$$

式中: d 为残余压痕对角线平均值。压痕载荷为 100 g。

对于涂层断裂韧性 K_{IC} 和残余应力 σ_r 的测试,

需要选用较大的载荷, 既能产生合适的裂纹, 又不至于压崩脆性的陶瓷涂层。压痕载荷卸载后, 原位观测涂层表面的残余印记, 测量涂层表面裂纹 c_1 、 c_2 和压痕对角线 d_1 、 d_2 后, 采用公式(2), 分别估算被测涂层位置的断裂韧性和残余应力^[34, 36-37]:

$$K_{IC} = K_P + K_r = \chi \frac{P}{c^{3/2}} + \left(\frac{4\sigma_r t^{1/2}}{\sqrt{\pi}} - \frac{2t\sigma_r c^{-1/2}}{\sqrt{\pi}} \right) \quad (2)$$

式中: K_P 和 K_r 分别为载荷和残余应力对 K_{IC} 的贡献; t 为压痕深度; $\chi = \delta(E/H)^{1/2}$, 其中 E 为涂层弹性模量, δ 为与压针形状相关的参数, $\delta = 0.016 \pm 0.004$; c 为 2 条径向裂纹 c_1 和 c_2 的平均值。

对公式(2)进行变换, 得到

$$\frac{P}{c^{3/2}} = \frac{\left(K_{IC} - \frac{4\sigma_r t^{1/2}}{\sqrt{\pi}} \right)}{\chi} + \frac{2t\sigma_r c^{-1/2}}{\chi\sqrt{\pi}} \quad (3)$$

将 $P/c^{3/2}$ 定义为 y 轴, $c^{-1/2}$ 定义为 x 轴。选用不同的载荷 P_i , 得到对应的裂纹长度 c_i 。以线性函数的方式, 拟合不同的试验测试点, 获得直线的斜率 $2t\sigma_r/\chi\sqrt{\pi}$ 和截距 $(K_{IC} - 4\sigma_r t^{1/2}/\sqrt{\pi})/\chi$, 从而得到被测涂层位置的断裂韧性和残余应力。

1.4 弹性模量测试

采用纳米压痕法(Hysitron Ti Premier, Bruker, 德国)测定 GYbZ/8YSZ 涂层热循环前后的弹性模量。压头为 Berkovich 压头。载荷为 10 mN, 保载时间为 10 s。在同一载荷下, 每个试样进行 6 次测试。由公式(4)和公式(5)计算得到弹性模量^[38]:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (4)$$

$$E_r = \frac{1}{2\beta h_c} \sqrt{\frac{\pi}{10.5}} \frac{dP}{dh} \quad (5)$$

式中: E 和 ν 为被测材料的弹性模量和 Poisson 比; h_c 为压针接触深度; $E_i = 1\,141.00$ GPa; $\nu_i = 0.07$; $\beta = 1.03$ 。

2 结果与讨论

2.1 GYbZ 涂层物相分析

图 4 为 GYbZ 粉末和涂层的 XRD 测试结果。

由图 4 可见, 原始粉末和涂层均为纯相, 在喷涂过程中 GYbZ 粉末不发生分解与转化。涂层中 GYbZ 相的衍射峰强度增加, 这是由于在 APS 过程中 GYbZ 发生熔融、铺展、固化后, 形成了结晶良好的 GYbZ 相。在 $2\theta \approx 37^\circ$ 和 45° 处, GYbZ 粉末和 GYbZ 涂层的 XRD 谱均没有显示衍射峰, 表明 GYbZ 粉末和涂层为亚稳态的缺陷萤石结构, 与 Guo 等^[30] 和 Zhen 等^[31] 研究结果一致。与烧绿石结构相比, 缺陷萤石结构有序性降低, 其原因可能是半径较小的 Yb^{3+} 掺杂后, 降低了 $r(\text{RE}^{3+})/r(\text{Zr}^{4+})$ 比值, 使材料结构无序化增加^[29–31]。

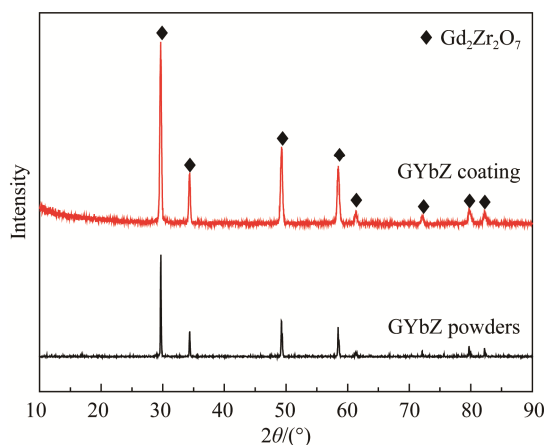


图 4 GYbZ 粉末与涂层的 XRD 谱

Fig. 4 XRD patterns of GYbZ powders and coating

图 5 为经过不同次数热循环处理后 GYbZ 涂层的 XRD 谱。由图 5 可见, 在 $1\,100\,^\circ\text{C}$ 经过 10 次、50 次和 100 次热循环处理后, GYbZ 涂层仍显示为缺陷萤石结构, 与原始涂层保持一致的相结构, 高温相稳定性好。所有 GYbZ 涂层的 XRD 测试中没有显示新物质的生成, 表明 GYbZ 涂层性质稳定, 未发生化学反应。经过热循环处理后, GYbZ 涂层的 XRD 衍射峰半峰宽变窄, 这是由于在热处理过程中涂层吸收能量促进了 GYbZ 晶粒生长^[24]。

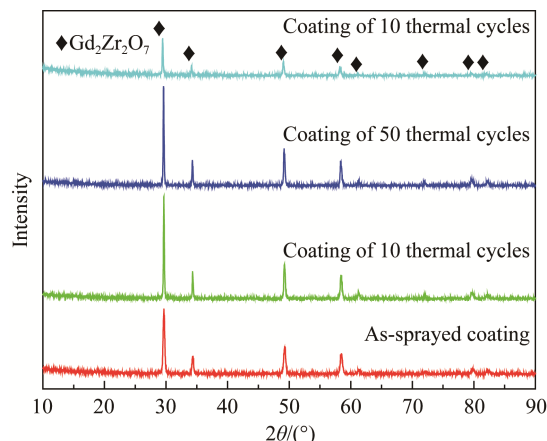


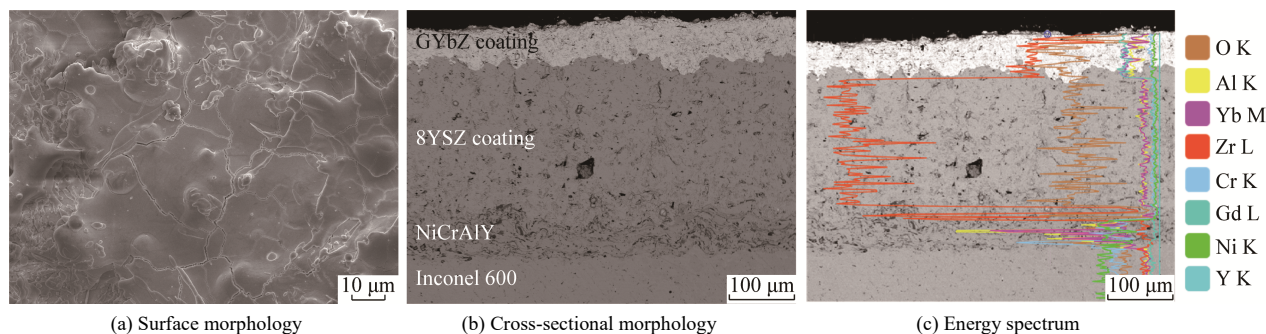
图 5 经过不同次数热循环处理后 GYbZ 涂层的 XRD 谱

Fig. 5 XRD patterns of GYbZ coatings after different cycles of heat treatment

2.2 GYbZ/8YSZ 涂层微观结构分析

图 6 为原始 GYbZ/8YSZ 涂层的微观形貌和元素分布图。在热喷涂过程中, 涂层熔融铺展状态较好。在撞击、铺展、冷却、固化过程中, 熔融的喷涂粒子产生淬火应力, 且各层之间由于热膨胀系数不匹配产生热应力, 使得涂层中分布较多微裂纹, 如图 6a 所示。GYbZ/8YSZ 涂层各层之间结合良好, 结合界面清晰无裂纹; 内部存在较多微小孔隙, 如图 6b 所示。均匀分布的孔隙使涂层具有较好的隔热性能。考虑各层热膨胀系数的差异, 该涂层结构有利于缓解残余应力。能谱分析表明, 最顶层由 Gd、Yb、Zr 以及 O 元素组成, 第 2 层主要由 Zr、O 和 Y 元素组成, 第 3 层主要由 Ni、Cr、Al 和 Y 元素组成, 基底主要由 Ni 元素组成, 分别对应 GYbZ 层、8YSZ 层、粘结层和 Ni 高温合金基底, 如图 6c 所示。

图 7 为在 $1\,100\,^\circ\text{C}$ 经不同次数热循环处理后 GYbZ/8YSZ 涂层的微观形貌照片。随热循环次数增加, 涂层表面粗糙程度加重、裂纹宽度增加。经过 50 次和 100 次热循环处理后涂层表层发生部分剥落现象。经过 10 次热循环后, 涂层发生轻微烧结; 陶瓷层内产生较多微小裂纹; 粘结层与 8YSZ 层间产



(a) Surface morphology

(b) Cross-sectional morphology

(c) Energy spectrum

图 6 原始 GYbZ/8YSZ 涂层微观结构分析

Fig. 6 Microstructure analysis of as-sprayed GYbZ/8YSZ coatings

生宽度较小、非连续的横向裂纹, 同时在该界面处产生了热生长氧化物, 如图 7a 所示。经过 50 次热循环后, 8YSZ 层内产生垂直裂纹; 粘结层与 8YSZ 层界面处的横向裂纹宽度增加、具有连续性, 如图 7b 所示。经过 100 次热循环后, 涂层烧结严重, 产生大孔洞; 陶瓷层内的垂直裂纹继续生长, 贯穿 GYbZ 层和 8YSZ 层; 涂层结构完整性受到破坏, 如图 7c 所示。破坏性的裂纹首先出现在涂层与粘结层界面处, 与涂层中初始裂纹的产生规律相符^[36]。通过观察发现, 垂直裂纹主要存在于陶瓷层, 陶瓷

层间未产生明显的横向裂纹, 具有较好的结合性能, Zhen 等^[31]和 Chen 等^[39]在研究热障涂层的氧化失效行为时, 观察到了类似的现象。粘结层易发生氧化, 生成热生长氧化物^[30, 40]。在热循环过程中, 热生长氧化物逐渐生长, 呈现连续层状结构。热循环至 100 次后, 热生长氧化物层增厚至 20 μm 左右。热生长氧化物层的热膨胀系数与粘结层和 8YSZ 层相差较大, 在热循环过程中氧化物层附近存在较大的应力奇异性, 使粘结层与 8YSZ 层间产生横向裂纹, 导致涂层与基底分离^[41-43]。

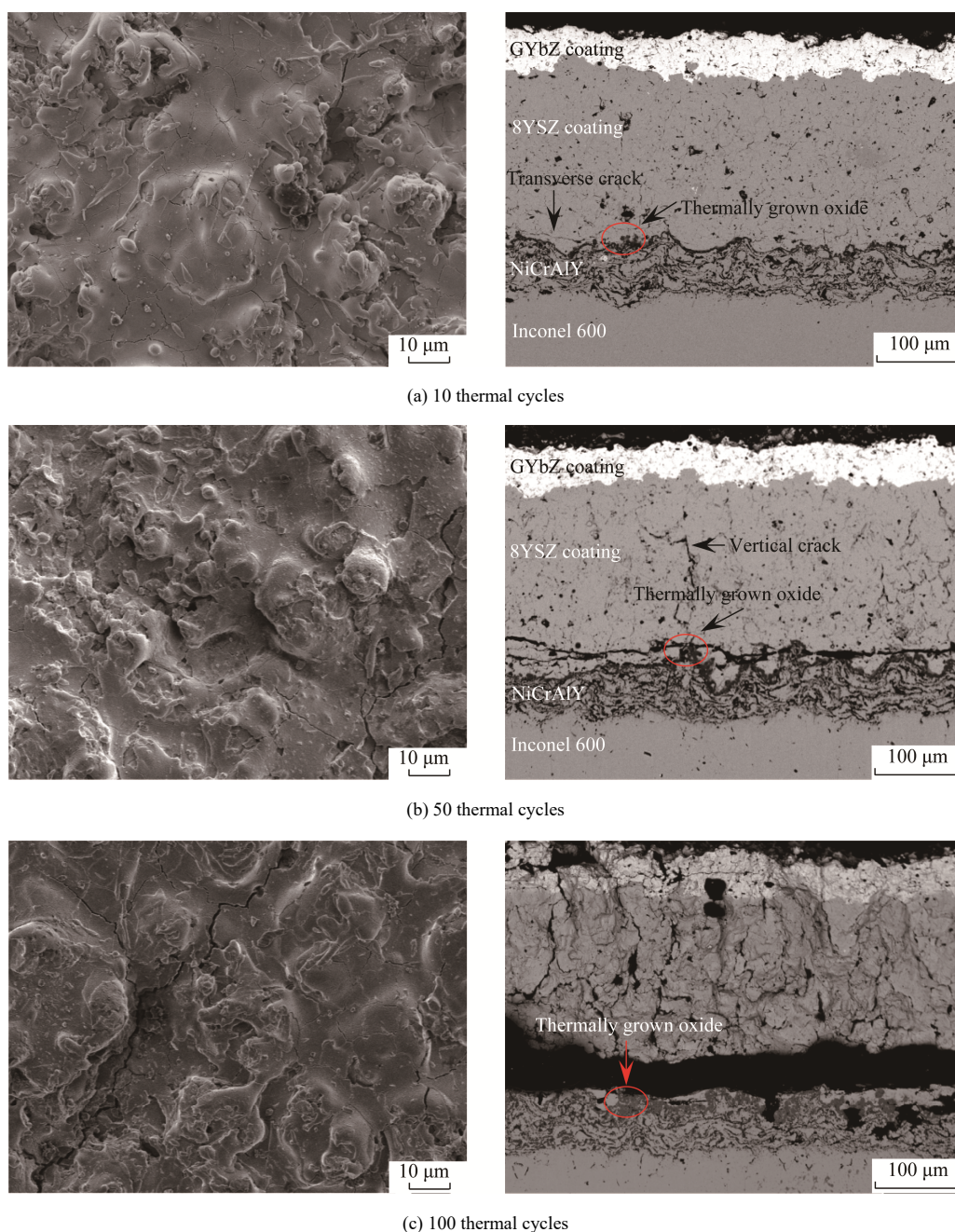


图 7 热循环后 GYbZ/8YSZ 涂层的表面和截面微观形貌

Fig. 7 Surface and cross-sectional micromorphology of GYbZ/8YSZ coatings after thermal cycling

图 8 为原始涂层和热循环后涂层表层的孔隙率。原始涂层中分布的孔隙较多, 孔径范围较宽, 孔隙率为 14.61%。随热循环次数增加, 涂层孔隙逐渐减少。经过 10 次热循环后, 涂层孔隙率为 10.47%。热循环次数达到 100 次后, 涂层发生较大程度烧结, 孔隙率降低至 5.01%。经过 1 100 °C 热循环处理后, 涂层中的大孔径孔隙逐渐收缩, 小孔径孔隙逐渐闭合, 孔径分布趋于均匀。

为进一步探究热循环后 GYbZ/8YSZ 涂层的微观变化, 对 GYbZ/8YSZ 涂层进行线性元素分布分析, 如图 9 所示。结果表明, 经过 100 次热循环后, Gd、Zr 和 Y 元素仍主要存在于顶层和 8YSZ 陶瓷层中。在 100 次热循环后, 粘结层区域的氧含量明显增加, 如图 9c 所示。这使得粘结层中的 Al、Cr、Ni、Y 元素发生氧化的程度增加。对 100 次热循环后涂层热生长氧化物进行元素分析, 发现 O、Al、Cr、Ni、Y 元素的质量分数大约为 37.26%、5.60%、56.35%、0.55%和 0.24%。说明热生长氧化物成分主要由 Cr_2O_3 和 Al_2O_3 组成。氧化物的生成会使涂层

体系发生一定的体积变化, 也会导致涂层界面之间的结合逐渐发生失稳, 对涂层产生不利影响^[40]。热循环过程中, 陶瓷层产生的垂直裂纹促进了氧气在涂层内部的扩散^[44], 加速了热生长氧化物的生长, 导致热生长氧化物层逐渐增厚。

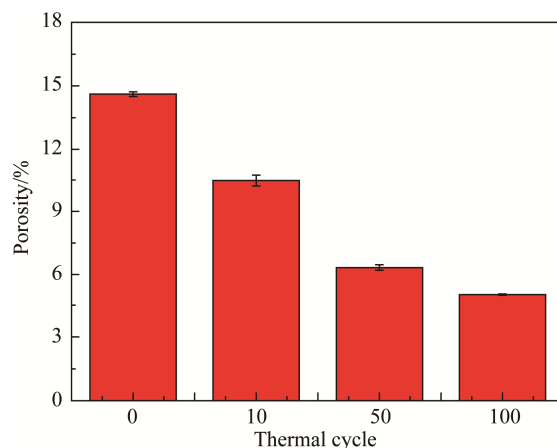


图 8 热循环过程涂层孔隙率变化

Fig. 8 Variation of coating porosity during thermal cycling

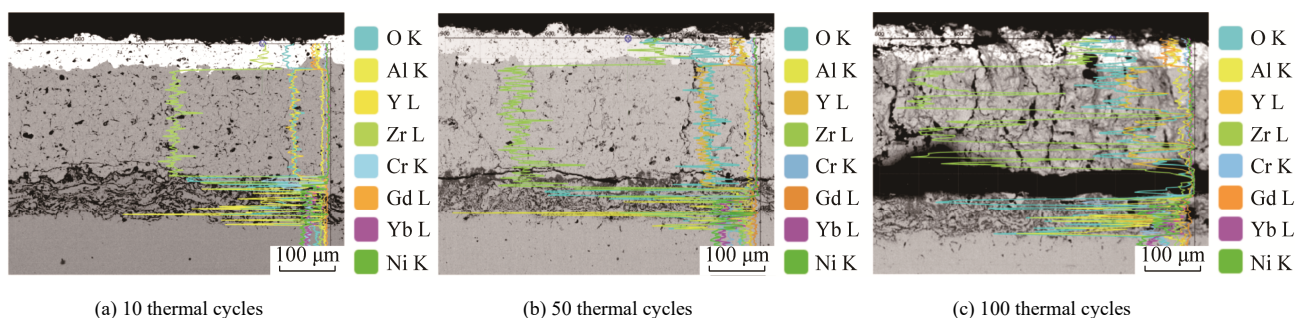


图 9 热循环后的 GYbZ/8YSZ 涂层能谱

Fig. 9 Energy spectra of GYbZ/8YSZ coatings after thermal cycling

2.3 GYbZ/8YSZ 涂层弹性模量表征

图 10 为采用纳米压痕法获得经不同次数热循环处理后 GYbZ/8YSZ 涂层表层的弹性模量。如图 10a 所示, 经过热处理后的涂层载荷–位移曲线比原始涂层更光滑, 这可能是原始涂层中孔隙较多导致的结果^[45]。在相同载荷作用下, 热循环 10 次和 50 次后, 涂层压痕位移更小, 体现了这 2 种涂层的弹性模量较原始涂层和 100 次热循环后的涂层更大, 抵抗外力侵入的能力更强。等离子喷涂制备的原始涂层弹性模量为 106.53 GPa, 比 EB-PVD 制备的 GZO 涂层 (149.70~167.90 GPa) 和烧结制备的 GYb_{0.06}Z (210.00 GPa) 陶瓷低^[29, 46–47]。随热循环处理次数增加, 涂层弹性模量先增加后减小。在 50 次热循环处理后, 涂层弹性模量达到最大值 182.01 GPa, 如图 10b 所示。经热循环处理后, 涂层发生烧结,

致密性提升, 弹性模量增加, 可能会加剧涂层体系的应力差异性, 诱使裂纹萌生、扩展^[11, 30, 40]。在热循环达 100 次后, 涂层氧化加重, 层间结合力减弱, 陶瓷层内部产生大量贯穿性的垂直裂纹, 致使涂层结构发生破坏, 弹性模量降低^[48]。

2.4 GYbZ/8YSZ 涂层硬度表征

图 11 为经不同次数热循环处理后 GYbZ/8YSZ 涂层表层的硬度。为减小脆性涂层的数据离散性, 先对硬度数据进行 Webb 模数分析, 如图 11a 所示。由图 11a 可见, 所选取的数据基本分布在拟合直线两侧, 偏离较小, 说明数据误差小, 可靠性强。原始 GYbZ 涂层硬度为 5.09 GPa, 略小于 EB-PVD 制备的 GZO 涂层 (6.20~7.70 GPa) 和烧结制备的 GZO (6.00~9.50 GPa)、GYbZ 陶瓷块体 (努氏硬度为 8.80 GPa)^[29, 30, 46–47, 49]。与弹性模量的结果类似, 大

气等离子喷涂制备的涂层存在较高的孔隙率,进而影响了涂层热力学参数。在 50 次热循环后,涂层具有最大硬度 9.13 GPa,主要归结于在热循环过程中晶粒长大和硬化的结果。而在 100 次热循环后涂层硬度减小为 8.64 GPa,主要原因是涂层产生大量横向和垂直裂纹,抗变形能力减弱,硬度降低^[32]。在

本工作中,随热循环次数增加,涂层硬度呈现先增加后减小规律,与已报道的 8YSZ 涂层^[36]和 GZO/8YSZ 涂层^[44]表层硬度变化规律相似。涂层硬度适当增加,可增强涂层的耐磨性,提升涂层抵抗外力破坏的能力,但硬度过大会使涂层脆性增加,加大涂层发生开裂的风险。

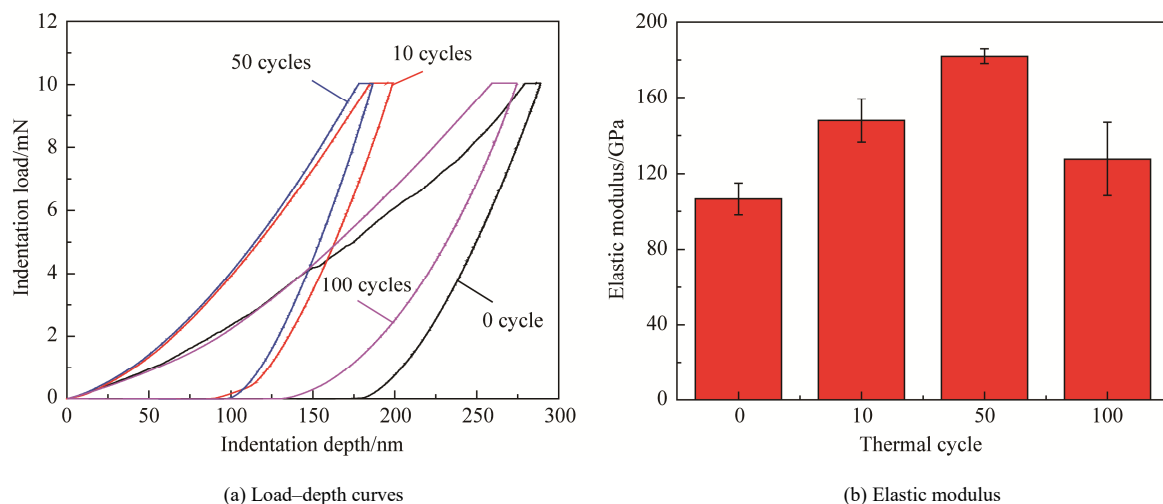


图 10 热循环过程 GYbZ/8YSZ 涂层弹性模量演变

Fig. 10 Evolution of elastic modulus of GYbZ/8YSZ coatings during thermal cycling

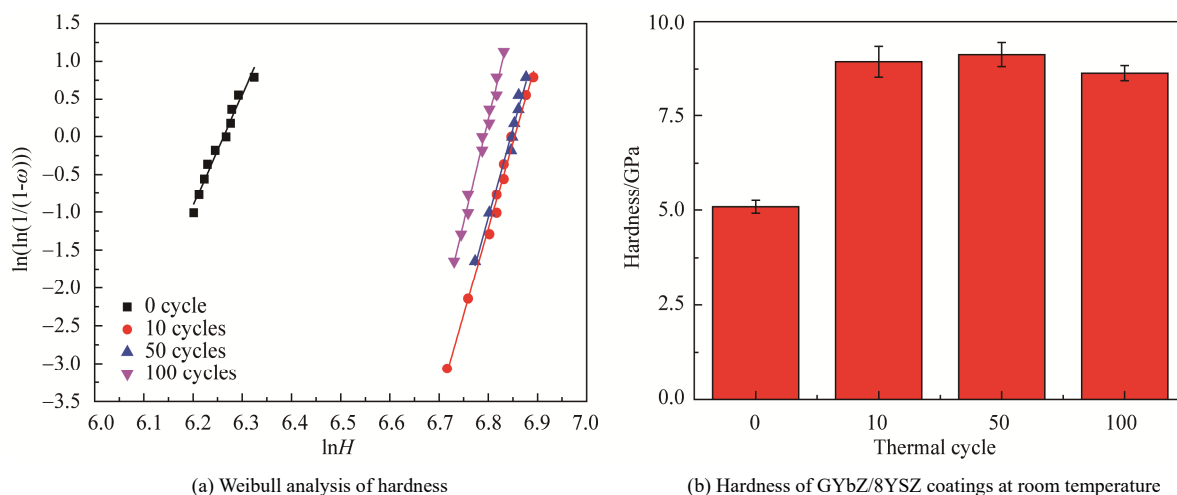


图 11 热循环过程 GYbZ/8YSZ 涂层硬度演变

Fig. 11 Evolution of hardness of GYbZ/8YSZ coatings during thermal cycling

图 12 为在常温和 700~1 100 °C 范围内 GYbZ/8YSZ 涂层表层原位硬度。从室温升温至 700 °C,涂层的硬度由 5.09 GPa 降低到 2.20 GPa。在 700~1 100 °C 范围内,涂层的硬度变化较小,在 2.00 GPa 左右波动。当温度达到 1 100 °C 时,涂层硬度为 1.81 GPa。温度升高,晶格无序化程度增加会减弱涂层的抗变形能力,导致硬度降低^[32]。然而,随测试温度不断增加,虽然涂层的硬度整体呈下降趋势,但在 700 °C 之后,温度对涂层硬度的影响似

乎不是特别明显。

2.5 GYbZ/8YSZ 涂层残余应力和断裂韧性表征

图 13 为不同次数热循环处理后 GYbZ/8YSZ 涂层表层的残余应力与断裂韧性。根据式(2)和式(3),将 3 组不同压痕载荷和对应的裂纹长度进行线性拟合处理,获得斜率和截距,从而计算得到涂层残余应力与断裂韧性,如图 13a 所示。热循环前后 GYbZ/8YSZ 涂层表层的 σ_r 如图 13b 所示。在 APS 过程中,高温下喷涂粉末熔融快速撞击并沉积

到基体, 导致原始涂层中产生 σ_r 。原始涂层的 σ_r 为 -41.02 MPa, 略小于已报道的 GYbZ/8YSZ 涂层表面 σ_r (-51.40 MPa)^[38]。热循环过程中, 涂层体系的热膨胀失配使得残余应力不断累积。10 次热循环后, 涂层 σ_r 累积至 -147.30 MPa。50 次热循环后, 受微裂

纹的影响, σ_r 减小为 -123.67 MPa。100 次热循环后, 较大的裂纹导致应力松弛, 使涂层 σ_r 不断减小。当 σ_r 为负值时, 表示其为压缩应力。现有结果表明, 冷却后涂层 σ_r 均表现为压缩应力, 有利于涂层结构的稳定性。

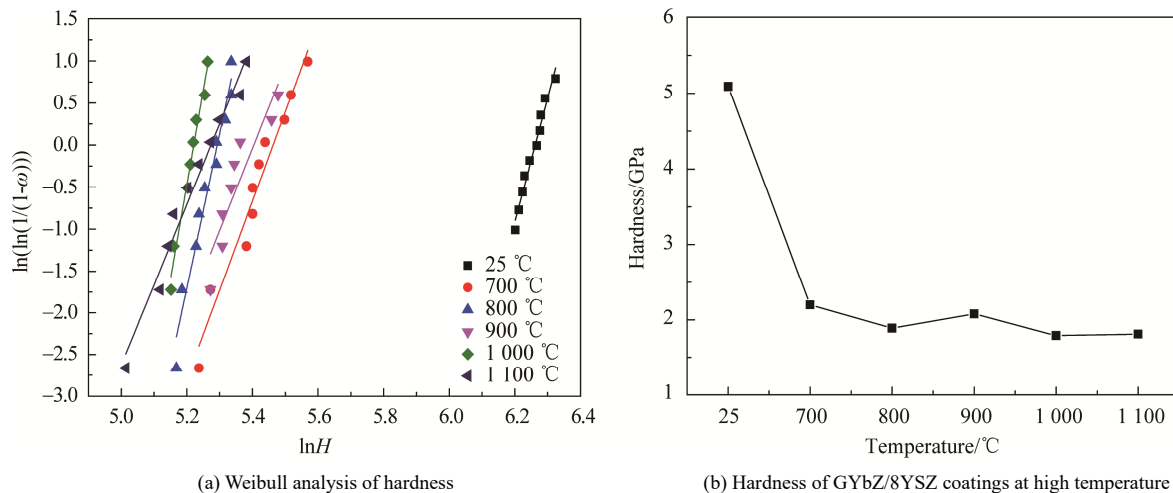


图 12 高温下 GYbZ/8YSZ 涂层的硬度演变

Fig. 12 Evolution of hardness of GYbZ/8YSZ coatings at high temperature

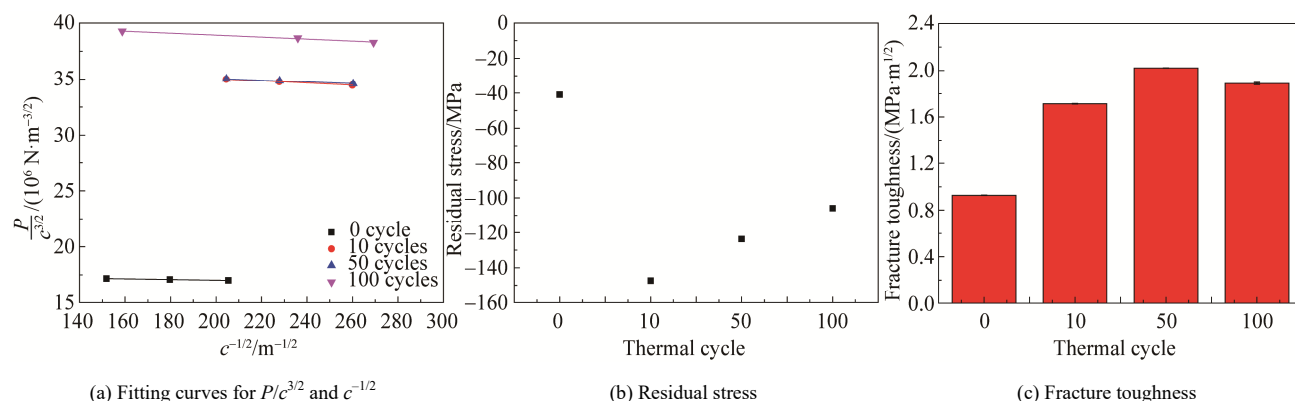


图 13 热循环过程 GYbZ/8YSZ 涂层残余应力和断裂韧性演变

Fig. 13 Evolution of residual stress and fracture toughness of GYbZ/8YSZ coatings during thermal cycling

图 13c 为热循环前后 GYbZ/8YSZ 涂层表层的 K_{IC} 。原始 GYbZ 涂层的 K_{IC} 为 $0.93 \text{ MPa}\cdot\text{m}^{1/2}$, 略大于已知的 GZO($0.82 \text{ MPa}\cdot\text{m}^{1/2}$)、GYb_{0.06}Z 块体 ($0.77 \text{ MPa}\cdot\text{m}^{1/2}$)^[29, 50]和 GYbZ 涂层($0.80 \text{ MPa}\cdot\text{m}^{1/2}$)^[51]的 K_{IC} 。通过 Yb 掺杂取代部分 Gd 位, 增强了 GYbZ 涂层材料无序化程度, 造成晶格畸变, 使断裂能增加, 从而提升了材料的 K_{IC} 。随热循环次数增加, 涂层 K_{IC} 先增大后减小, 在 50 次热循环后达最大值 $2.02 \text{ MPa}\cdot\text{m}^{1/2}$, 在 100 次热循环后下降为 $1.89 \text{ MPa}\cdot\text{m}^{1/2}$ 。原始涂层内部存在较多孔隙, 受外力作用后易萌生裂纹, 裂纹沿孔隙边缘快速扩展。经 10 次和 50 次热处理后, 涂层孔隙减少, 致密区域起到阻挡裂纹扩展的作用; 另外, 微裂纹可在一定程度上提升涂

层的应变容限^[32]; 同时, 涂层中存在残余压缩应力, 可在一定程度上抑制裂纹的萌生扩展, 增强涂层的 K_{IC} ^[34, 52]。在热循环后期, 氧化和大量裂纹的产生使涂层结构稳定性下降, 缺陷增多, 力学性能下降。

3 结论

采用 APS 制备了 GYbZ/8YSZ 热障涂层, 系统分析了热处理前后涂层成分、微观结构、力学参数的演变规律, 主要结论为:

1) 喷涂前后 GYbZ 材料结构稳定, 没有产生新相, 结晶度高, 材料性质稳定。原始 GYbZ/8YSZ 涂层中孔隙分布均匀, 各层结合界面清晰。

2) 在 1100°C 经 100 次热循环后, GYbZ 涂层

仍为缺陷萤石结构, 具有优异的高温相稳定性。随热循环次数增加, 在粘结层与 8YSZ 界面形成约 20 μm 厚的热生长氧化物层。

3) 随热循环次数增加, 涂层发生烧结, 致密性提升。在 50 次热循环后弹性模量与硬度均达到最大值, 分别为 182.01 GPa 和 9.13 GPa。从室温至 700 $^{\circ}\text{C}$, 涂层硬度降低至 2.20 GPa。在 700~1100 $^{\circ}\text{C}$, 涂层硬度变化幅度较小, 保持在 2.00 GPa 左右。

4) 原始涂层残余应力为 -41.02 MPa, 在热循环过程中变化至 -123.67 MPa。残余压缩应力有助于提升涂层的断裂韧性, 使其由 0.93 $\text{MPa}\cdot\text{m}^{1/2}$ 增加至 2.02 $\text{MPa}\cdot\text{m}^{1/2}$ 。

本工作系统分析了高温热处理过程中 GYbZ/8YSZ 涂层力学性能的演变特性, 进一步揭示了涂层力学性能与宏微观失效的关系, 对后续提升涂层可靠性和寿命预测提供重要的参考。

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Effect of Heat-Treatment on Mechanical Properties of (Gd_{0.9}Yb_{0.1})₂Zr₂O₇/Yb₂O₃ Stabilized ZrO₂ Coatings During Thermal Cycling

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Extended Abstract

Introduction Thermal barrier coatings can be used for the stable operation of aircraft engines under high-temperature environments due to their excellent oxidation resistance, corrosion resistance and heat insulation properties. However, the high-temperature phase transition of conventional 8.0% (in mass fraction) Y₂O₃ stabilized ZrO₂ ceramic (8YSZ) materials exists when the service temperature exceeds 1 200 °C. Developing thermal barrier coatings, such as rare-earth zirconates and rare-earth silicate, becomes popular. (Gd_{0.9}Yb_{0.1})₂Zr₂O₇ (GYbZ)/8YSZ coatings with a low thermal conductivity and a high temperature phase stabilization are regarded as potential thermal protective materials. At present, some work focus on the preparation properties optimization of air plasma spraying, electron beam physical vapor deposition and plasma spray physical vapor deposition techniques, respectively. It is important to *in-situ* investigate the mechanical properties and failure mechanisms of GYbZ/8YSZ coatings at > 1 200 °C.

Methods GYbZ/8YSZ thermal barrier coatings were prepared with NiCrAlY, 8YSZ and GYbZ powders on an Inconel 600 nickel-based superalloy with the thickness of 2 mm *via* air plasma spraying. GYbZ/8YSZ thermal barrier coatings were subjected to thermal cycle treatments in a Muffle furnace at 1 100 °C for 1 h, and then cooled to room temperature for 1 thermal cycle. The times of thermal cycles were 10, 50 and 100, respectively. The phase and microstructure of the coatings were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) before and after heat-treatments. The elastic modulus, hardness, fracture toughness and residual stress were measured by an indentation method at different temperatures.

Results and discussion The XRD patterns show that GYbZ powder and the as-sprayed coating are a defective fluorite structure, and the doping of Yb³⁺ with small ionic radius makes the material change from a pyrochlore structure to a defective fluorite structure. In addition, the samples treated for different thermal cycles all maintain a defective fluorite structure, indicating that GYbZ has an excellent high-temperature phase stability. The SEM images show that the surface of the as-sprayed GYbZ coating has a good melting state, and massive micro-cracks are distributed on the surface, which is caused due to the quenching stress generated by the molten spray particles during the preparation process and the thermal stress generated by the mismatch between the thermal expansion coefficients between the layers. The bonding between the layers of GYbZ/8YSZ coatings is good, and the bonding interface is clear without any cracks. There are tiny pores in the interior. The distribution of elements in each layer is consistent with the design. After thermal cycling, the crack width of the coating surface gradually widens and the porosity gradually decreases. The thermal growth oxide (TGO) produced between the bond layer and the 8YSZ layer gradually increases, and the TGO grows to 20 μm after 100 thermal cycles. The generation of TGO leads to a large amount of stress concentration, leading to the initiation and rapid expansion of transverse cracks in the bonding layer and 8YSZ, and damages the structural stability of the GYbZ/8YSZ coatings. Also, some vertical cracks occur in GYbZ layer and 8YSZ layer. The results of element distribution test show that the oxygen content in the bond layer increases gradually with the increase of the number of thermal cycles. The creation of vertical cracks in the coating promotes the diffusion of oxygen, thus accelerating the growth of heat-grown oxides.

The results of mechanical properties test show that the elastic modulus and hardness of GYbZ/8YSZ coatings surface firstly increase and then decrease with the increase of thermal cycle, and have the maximum values at 50 thermal cycles. After thermal cycling, the coating is sintered and its densification is improved, resulting in an increase in the elastic modulus and hardness. After 100 thermal cycles, the coating oxidation is serious, the binding force between coatings is weakened, massive vertical cracks occur in the coating, the coating structure is damaged, the deformation resistance is weakened, and the elastic modulus and hardness are reduced. The hardness of the coating decreases from 5.09 GPa to 2.20 GPa from room temperature to 700 °C. At 700–1 100 °C, the hardness of the coating is 2.00 GPa. The residual stress of the as-sprayed coating is –41.02 MPa. The residual stress accumulates due to thermal expansion mismatch of coating system during thermal cycling. After 10 thermal cycles, the residual stress accumulates to –147.30 MPa. After 50 thermal cycles, the stress relaxation caused by cracks gradually reduces the residual stress. After 100 thermal cycles, the residual stress decreases to –105.92 MPa. The results show that the residual stress of the coating before and after thermal cycling is a compressive stress. The fracture toughness of the as-sprayed GYbZ coating is 0.93 MPa·m^{1/2}. The fracture toughness of the coating firstly increases and then decreases with the increase of the number of thermal cycles, and has a maximum value of 2.02 MPa·m^{1/2} after 50 thermal cycles. After heat-treatment, the pores of the coating reduce, and the dense area and the compressive stress

can prevent the crack propagation. Some microcracks can increase the strain tolerance of the coating to a certain extent, and enhance the fracture toughness of the coating. After 100 thermal cycles, oxidation and massive destructive cracks lead to the instability of the coating structure, the increase of defects and the decline of performance.

Conclusions The pore distribution in the as-sprayed GYbZ/8YSZ coatings was uniform, and the bonding interface of each layer was clear. Before and after thermal cycling, GYbZ coating was a defective fluorite structure and had an excellent high-temperature stability. The density of the coating increased with the increase of the number of thermal cycle, occurring some transverse and vertical cracks, and the TGO thickness grew to 20 μm . After 50 thermal cycles, the elastic modulus and hardness reached the maximum values, which were 182.01 GPa and 9.13 GPa, respectively. From room temperature to 700 $^{\circ}\text{C}$, the coating hardness reduced to 2.20 GPa. At 700–1 100 $^{\circ}\text{C}$, the coating hardness was 2.00 GPa. During the thermal cycle, the residual stress of the coating varied from -41.02 MPa to -123.67 MPa , and the fracture toughness varied from $0.93\text{ MPa}\cdot\text{m}^{1/2}$ to $2.02\text{ MPa}\cdot\text{m}^{1/2}$.

Keywords thermal barrier coatings; ytterbium oxide doped gadolinium zirconate; high-temperature hardness; fracture toughness; residual stress