

无压两步烧结法制备超细晶 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵陶瓷

耿 畅, 李 玉, 李琳琳, 张 帅, 娄程广, 李汶金, 苏兴华

(长安大学材料科学与工程学院, 西安 710061)

摘 要: 超细晶高熵陶瓷具有优异的机械及物理化学性能。然而, 由于烧结后期晶粒的快速长大, 使得超细晶高熵陶瓷的常规无压烧结制备非常困难。采用两步烧结法, 克服了无压烧结致密化过程中晶粒的快速长大, 成功制备了理论密度为 99.0%、晶粒尺寸为 162 nm 的 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵陶瓷。与常规无压烧结方法相比, 两步烧结所制备的样品不仅具有更细小的晶粒尺寸, 还具有更均匀的微观结构, 这使其具有优良的力学性能, 其硬度达到 12.5 GPa, 断裂韧性达到 $2.4 \text{ MPa}\cdot\text{m}^{1/2}$ 。无压两步烧结法解决了传统无压烧结方法难以制备超细晶高熵陶瓷的困难, 将有助于探索超细晶高熵陶瓷的物理化学性能, 并有助于推动超细晶高熵陶瓷的广泛应用。

关键词: 高熵陶瓷; 锆酸盐; 超细晶; 两步烧结; 力学性能

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高熵陶瓷是指由 4 种或 4 种以上的主元素共享 1 个或多个 Wyckoff 位的多组分离子化合物。由于它具有多样的成分和微观空间结构以及独特的性能, 这类化合物越来越受到人们的关注^[1-3]。迄今为止, 已经开发出多种高熵陶瓷, 例如氧化物^[4-8]、硼化物^[9-10]、碳化物^[11-13]、氮化物^[14-15]、硫化物^[16-17]和硅化物等^[18-19], 在热防护、极端环境、储能、环保、催化、固体氧化物燃料电池和超导等方面均具有广阔的应用前景。其中, 具有烧绿石/缺陷—萤石结构的高熵锆酸盐陶瓷作为高熵氧化物中的一员, 因其具有超低的热导率、高温环境下的热稳定性、优异的化学耐久性以及抗辐照稳定性^[20-24], 得到了研究者的广泛关注^[25-28]。然而, 高熵锆酸盐陶瓷的韧性普遍较差, 这严重束缚了其在工业领域的应用。

研究表明, 减小晶粒尺寸可以有效提升高熵陶瓷的韧性^[29-32]。Ma 等研究发现, 平均晶粒尺寸为 $(98\pm35) \text{ nm}$ 的 $(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ta}_{0.25}\text{Ti}_{0.25})\text{C}$ 高熵纳米陶瓷显示了高的断裂韧性, 可达 $(4.3\pm0.4) \text{ MPa}\cdot\text{m}^{1/2}$ ^[29]。此外, 晶粒尺寸为 220 nm 的 $(\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 超细晶高熵陶瓷也

显示了高的断裂韧性, 达到 $3.4 \text{ MPa}\cdot\text{m}^{1/2}$ ^[32]。然而, 超细晶或纳米晶高熵陶瓷的常规烧结制备非常困难。由于迟滞扩散效应的存在, 高熵陶瓷的烧结制备通常需要在高温(通常高于 1500°C)进行长时间保温(几到几十小时)。在此过程中, 晶粒不可避免地会发生长大^[33]。此外, 高熵陶瓷中高浓度的氧空位会增加阳离子扩散和迁移速率, 从而加快晶粒的长大速率^[34]。在实际制备过程中, 高熵陶瓷的晶粒生长还受到迟滞扩散效应、施加压力和烧结环境等因素的影响。Cheng 等研究发现, 由于离子半径不同、键长不同, 导致在高熵陶瓷的烧结过程中产生了迟滞扩散效应, 使得阳离子的扩散速率减缓, 晶粒长大被抑制^[35]。研究者还采用高压烧结技术来制备超细晶或纳米晶高熵锆酸盐陶瓷^[31-32, 36]。

Deng 等采用 5 GPa 的高压烧结技术制备了平均晶粒尺寸为 8.28 nm 的 $(\text{Eu}_{0.2}\text{Dy}_{0.2}\text{Nd}_{0.2}\text{La}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵纳米陶瓷^[31]。Wu 等开发了一种超高压(压力高达 10 GPa)的烧结技术, 成功制备出了超细晶 $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Eu}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵陶瓷, 其平均晶粒尺寸为 151 nm ^[36]。然而, 采用这些高压烧结技术难以制备复杂形状的陶瓷制品。此外, 高压烧

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第一作者: 耿 畅(1998—), 男, 硕士研究生。

通信作者: 苏兴华(1981—), 男, 博士, 教授。

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First author: GENG Chang (1998—), male, Master candidate.

E-mail: gengchang@chd.edu.cn

Correspondent author: SU Xinghua (1981—), male, Ph.D., Professor.

E-mail: suxinghua@chd.edu.cn

结技术需要复杂且昂贵的设备。因此,开发超细晶高熵陶瓷的常规烧结(大气环境下的无压烧结)方法,对于高熵陶瓷在工业领域的广泛应用具有重要的研究意义。

2000 年,Chen 等提出了两步烧结法,利用陶瓷材料晶界扩散和晶界迁移的动力学差异来控制晶粒的快速长大,从而制备出纳米晶陶瓷^[37–39]。两步烧结法首先将样品加热到较高温度,保温较短时间(几秒或几分钟)或不保温,以达到相对较高的致密度,然后将温度迅速降低,并将样品在较低温度下持续保温,在维持晶界扩散的同时抑制晶界的迁移,直到样品达到完全致密化。两步烧结法工艺设备简单,已被应用于制备具有超细晶粒尺寸的各类材料^[40–41]。然而,关于两步烧结法制备超细晶或纳米晶高熵锆酸盐陶瓷的报道很少。

本工作以 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 陶瓷为研究对象,系统研究了无压烧结过程中的烧结动力学特征和微观结构的变化规律,发现平均粒径为 25 nm 的 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 生坯,通过常规无压烧结方法,可得到平均晶粒尺寸为 540 nm 的致密块体,而采用两步烧结法,可制备出平均晶粒尺寸为 162 nm 的致密块体,晶粒尺寸减小了约 3 倍,并且晶粒尺寸分布更窄,微观结构更均匀。本研究有助于理解高熵锆酸盐陶瓷的烧结动力学,并为无压烧结制备超细晶或纳米晶高熵锆酸盐陶瓷提供了一个新的途径。

1 实验

1.1 高熵陶瓷粉体制备

$(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵陶瓷粉体采用聚丙烯酰胺凝胶法制备^[33]。使用纯度(质量分数)为 99.9% 的稀土硝酸盐六水合物 $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE}=\text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Y}$)、氯化锆($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.9%)、丙烯酰胺(AM, $\text{C}_3\text{H}_5\text{NO}$, 99.0%)、N-N'-亚甲基双丙烯酰胺(MBAM, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$, 99.0%)和过硫酸铵 $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, 99.0%作为起始原料。首先,将 $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 和 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 在去离子水中按 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 的化学计量比混合均匀并剧烈搅拌 30 min 后,得到透明澄清的溶液,其中 Zr^{4+} 的浓度为 0.02 mol/L。然后将摩尔比为 24:2:1 的 AM、MBAM 和 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 依次加入上述溶液中,并剧烈搅拌使其完全溶解。其中 AM/Zr^{4+} 在混合溶液中的摩尔比为 80:1。之后,将混合溶液在 80 °C 水浴加热直到凝胶化现象发生。随后,将湿

凝胶在 80 °C 的烘箱中干燥 3 d 得到干凝胶。最后,将干凝胶在 1 000 °C 的空气气氛中煅烧 2 h,即制备得到 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 陶瓷粉体。

1.2 烧结制备

将制得的高熵陶瓷粉体在 300 MPa 单轴压力下压制成直径为 8 mm、厚度为 (2.0 ± 0.1) mm 的陶瓷生坯,然后分别采用常规烧结和两步烧结在空气气氛中烧结。对于常规烧结,将生坯加热至 1 200~1 500 °C 并保温 2 h。对于两步烧结,首先将生坯加热至高温 T_1 并保温一定时间 t_1 ,然后将温度快速降低(-20 °C/min)至温度 T_2 并保温一定时间 t_2 ,此后,样品随炉冷却至室温。需要说明的是,在加热过程中,炉温达到 1 000 °C 之前的加热速率为 10 °C/min;炉温达到 1 000 °C 之后的加热速率为 5 °C/min。

1.3 样品表征

采用 Bruker D8 Davinci 型 X 射线衍射仪(XRD, 德国)对样品的晶体结构进行表征。通过 JEOL-2100 F 型透射电子显微镜(TEM, 日本)及配备的能量色散 X 射线光谱仪(EDS)表征高熵陶瓷粉体的形貌和元素分布。对烧结实验后所得的样品,利用 Hitachi S-4800 型场发射扫描电子显微镜(SEM, 日本)观察其微观结构,并用 Nano Measurer 软件对样品的平均晶粒尺寸(随机选取 200 个以上晶粒)进行测定。

采用 Archimedes 排水法测量烧结后样品的密度,采用 GSAS-II 软件对 XRD 数据进行 Rietveld 精修以获得样品的晶胞参数及理论密度。通过 HV-1000 A 型显微 Vickers 硬度计(莱州华银试验仪器有限公司,中国)在 9.8 N 载荷及 15 s 的保压时间下测试样品的 Vickers 硬度,并利用压痕法表征样品的断裂韧性。利用安捷伦 U9820A 纳米压痕仪 G200 (美国)测试样品的杨氏模量。

2 结果与讨论

图 1 为高熵陶瓷粉体的 XRD 谱、TEM 照片及 EDS 谱。由图 1a 可见,所有衍射峰与缺陷萤石相匹配良好,表明起始高熵陶瓷粉体具有缺陷萤石型晶体结构。由图 1b 可见,粉体分散性良好,平均粒径为 25 nm。此外,图 1c 结果表明,起始粉体中元素分布均匀,无偏析现象。

为了研究高熵陶瓷粉体的致密化和晶粒生长行为,首先进行了常规烧结(CS)实验,不同烧结条件下所得结果见表 1。

图 2 为常规烧结 2 h 所制备样品的 SEM 照片。由图 2 可以看出,在 1 200 °C 和 1 300 °C 所得样品显

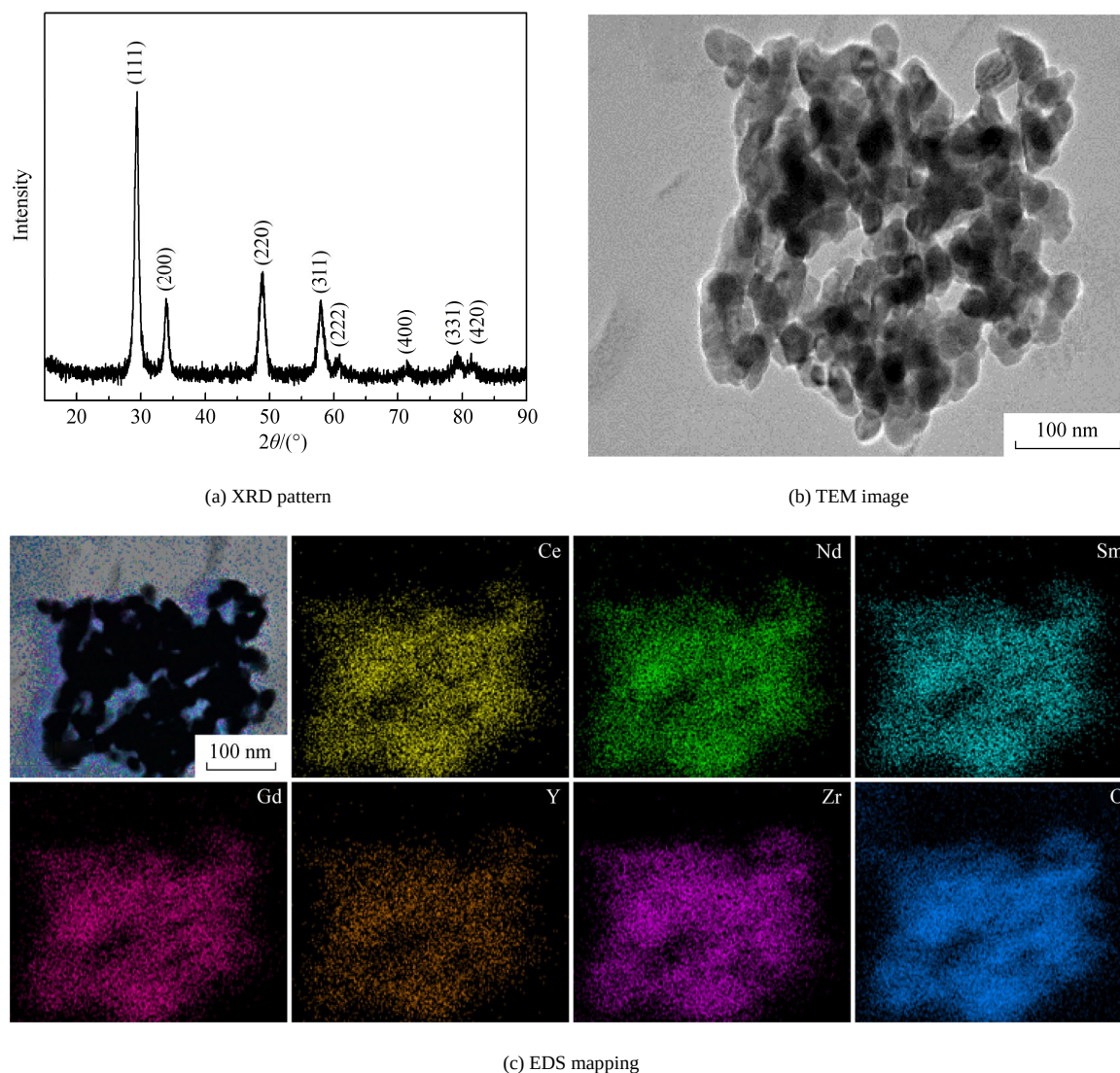


图 1 高熵陶瓷粉体的 XRD 谱、TEM 照片及 EDS 谱

Fig. 1 XRD pattern, TEM image, and EDS mapping of high-entropy ceramic powders

表 1 常规烧结样品的相对密度和晶粒尺寸

Table 1 Relative density and grain size data for conventional sintering (CS)

Sintering condition	$T/^{\circ}\text{C}$	t/min	Relative density/%	Grain size/nm
CS1	1 200	120	75.8	146
CS2	1 300	120	79.5	184
CS3	1 400	120	89.6	306
CS4	1 500	120	99.4	540

示出疏松多孔的微观结构,表明致密度较低,这和密度测试的结果相一致(表 1)。随着烧结温度的增加,样品中气孔逐渐减少。经过 1 500 $^{\circ}\text{C}$ 烧结后,样品显示出致密的微观结构。

图 3 为常规烧结样品温度和晶粒尺寸及相对密度的相互关系曲线。由图 3a 可以看出,当烧结温度高于 1 300 $^{\circ}\text{C}$ 时,相对密度和晶粒尺寸均增加迅速。

在 1 500 $^{\circ}\text{C}$ 烧结 2 h 后,可以制备得到相对密度为 99.4% 的致密高熵陶瓷。在已经报道的研究工作中,由于多离子共存引起的迟滞扩散效应,高熵铈酸盐陶瓷的烧结制备往往需要在 1 500 $^{\circ}\text{C}$ 以上的高温下进行长时间(几十小时)保温才能达到完全致密^[42-43]。本工作中,高熵陶瓷粉体在 1 500 $^{\circ}\text{C}$ 烧结 2 h 后即可实现完全致密化,表明通过聚丙烯酰胺凝胶法所制备的高熵纳米陶瓷粉体具有优异的烧结活性。

为进一步了解高熵陶瓷粉体的烧结动力学过程,绘制了晶粒尺寸和相对密度的相互关系曲线,如图 3b 所示。由图 3b 可以看出,当相对密度大于 89.6% 以后,晶粒长大速率明显加快,这与传统的固相烧结理论是一致的。传统烧结理论认为,在烧结初期和烧结中期,坯体中的开气孔对晶界迁移有“钉扎”作用,使得晶粒长大缓慢;烧结后期(坯体的

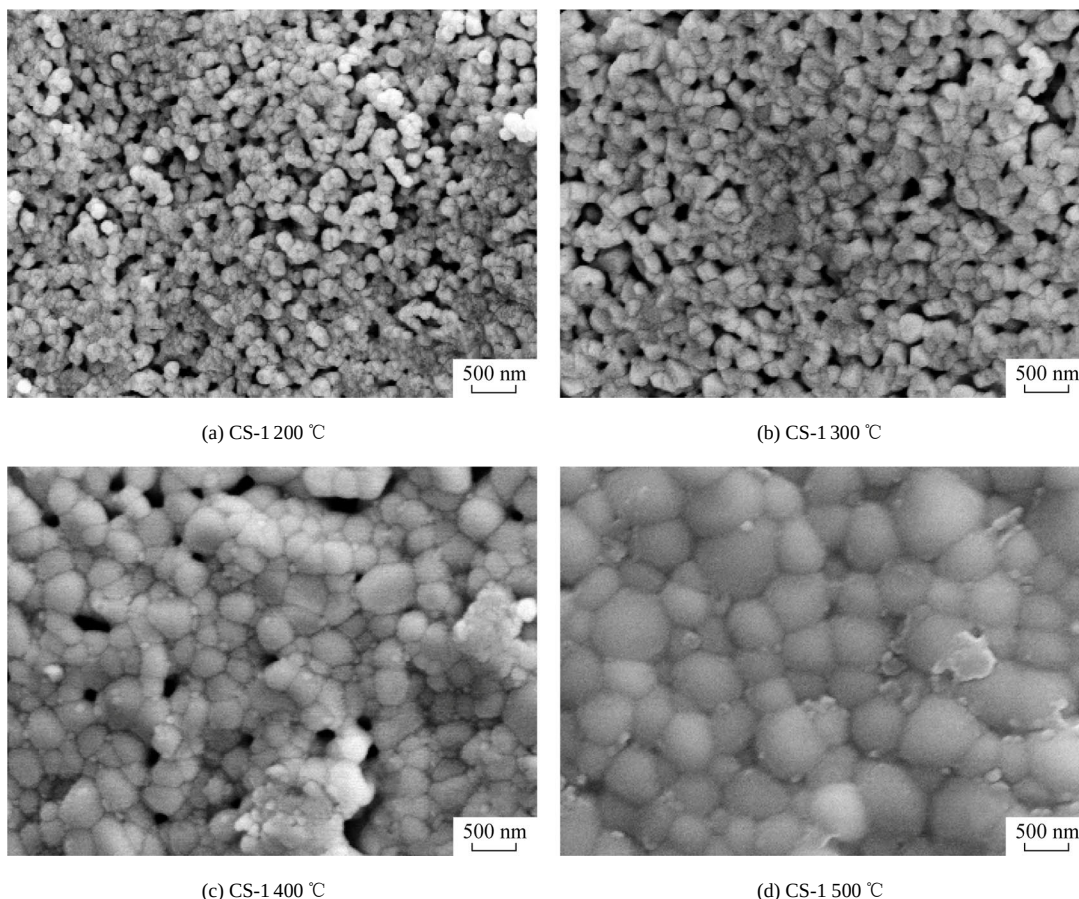


图 2 常规烧结 2 h 所制备样品的 SEM 照片

Fig. 2 SEM images of samples prepared by conventional sintering for 2 h

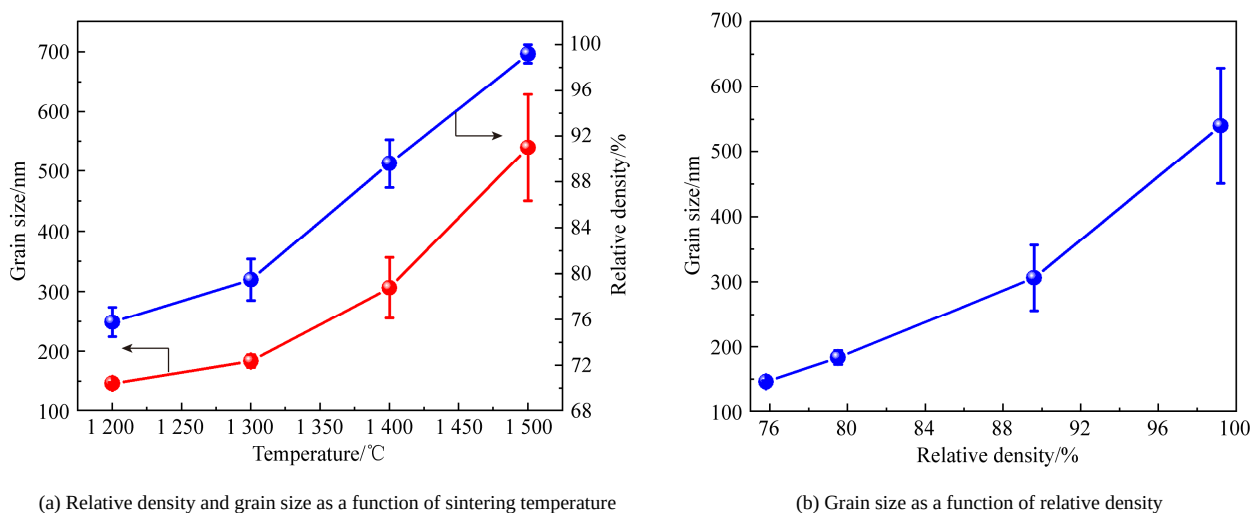


图 3 常规烧结样品温度和晶粒尺寸及相对密度的相互关系曲线

Fig. 3 Relationship between temperature, grain size and relative density of sample prepared by conventional sintering

相对密度约大于 86%), 开气孔转变为闭气孔, 气孔的“钉扎”效应减弱, 晶粒发生快速长大。在 1 200 °C 和 1 300 °C 温度下烧结的样品中, 气孔为联通的开放孔道(图 2a 和图 2b), 可有效“钉扎”晶界, 阻碍晶界运动, 使得晶粒生长缓慢。经过 1 400 °C 烧结后,

开放的孔道破裂进而形成封闭的气孔(对应于 89.6% 的相对密度), 如图 2c 所示。此后, 随着气孔“钉扎”效应的减弱, 晶粒长大速率加快。因此, 采用传统无压烧结技术来制备超细晶高熵陶瓷时, 必须要利用开气孔对晶界迁移的“钉扎”效应。

图 4 为常规烧结样品及其 Rietveld 精修 XRD 谱, 由图 4a 和图 4b 可以看出, 1 200~1 400 °C 烧结的样品展示了典型的缺陷萤石型晶体结构。1 500 °C 烧结的样品中出现了烧绿石型晶体结构所特有的超晶格(311)、(331)、(511)和(531)衍射峰, 表明样品晶体类型为烧绿石型。可以看出, 当烧结温度超过 1 400 °C 时, 样品发生了从缺陷萤石结构到烧绿石结构的相变。进一步对 1 400 °C 和 1 500 °C 烧结样品的

XRD 谱进行了 Rietveld 精修, 如图 4c 和图 4d 所示。可以看出, Rietveld 精修结果和实验结果吻合良好。根据精修结果, 确定了缺陷萤石型样品的晶格常数为 5.275 Å, 烧绿石型样品的晶格常数为 10.549 Å, 这与根据 Vegard 定律获得的晶格常数(分别为 5.270 Å 和 10.577 Å)非常吻合。此外, 基于 Rietveld 精修, 可计算出缺陷萤石相样品的理论密度为 6.424 g/cm³, 烧绿石相样品的理论密度为 6.359 g/cm³。

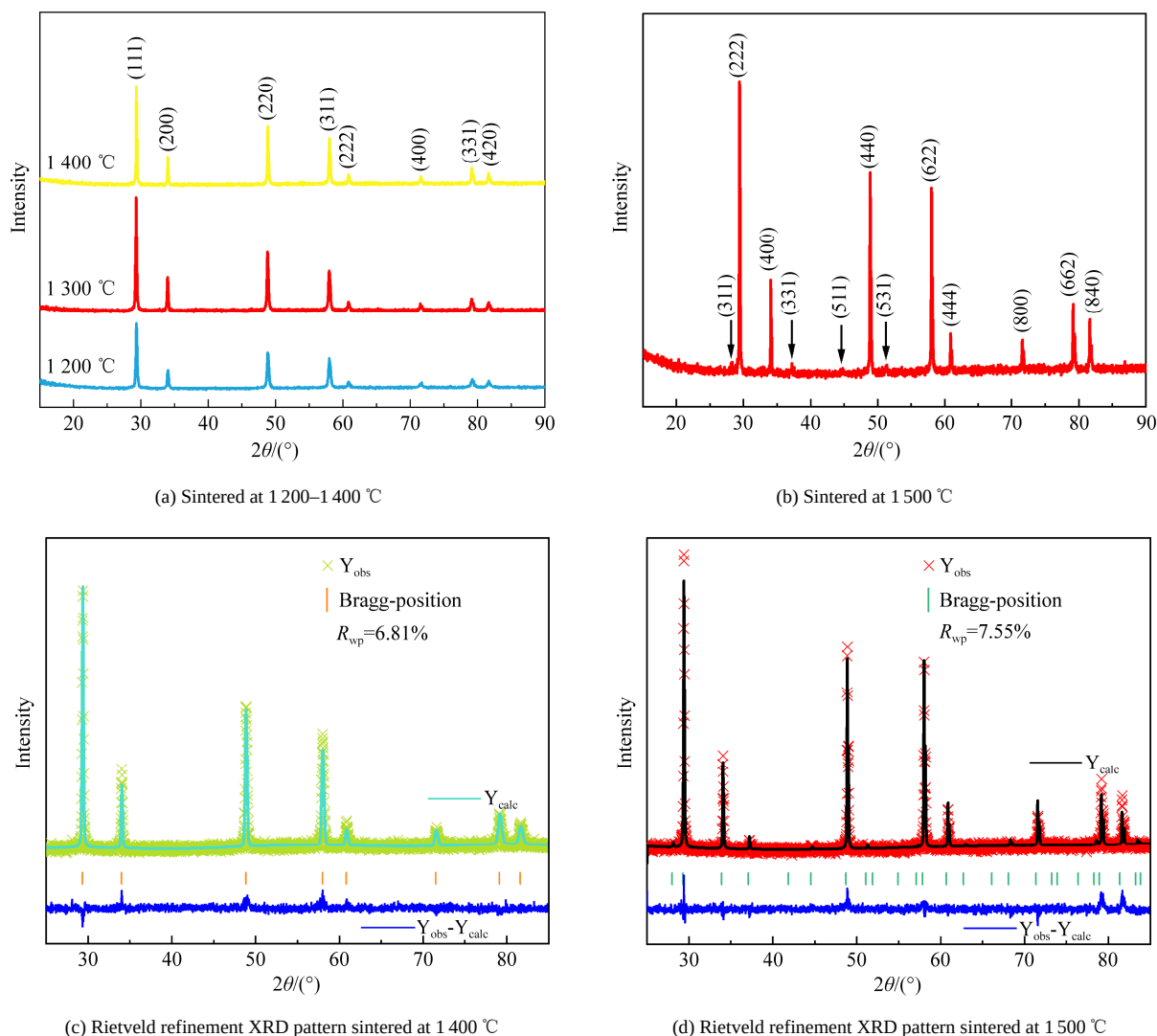


图 4 常规烧结样品及其 Rietveld 精修 XRD 谱
Fig. 4 XRD patterns and Rietveld refinement XRD pattern of samples

一般情况下, 高熵稀土(RE)锆酸盐陶瓷在高温下的晶体结构主要取决于阳离子的平均半径比 $r_{\text{RE}}/r_{\text{Zr}}$ ^[44]。当 $r_{\text{RE}}/r_{\text{Zr}}$ 小于 1.46 时, 倾向于形成缺陷萤石型晶体结构(空间群 $Fm\bar{3}m$); 当 $r_{\text{RE}}/r_{\text{Zr}}$ 为 1.46~1.78 时, 倾向于形成烧绿石结构(空间群 $Fd\bar{3}m$)。此外, 高熵稀土锆酸盐陶瓷的晶体结构也受到温度的影响, 缺陷萤石结构在较高的温度下将转变为烧绿石

结构^[33]。 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 的平均离子半径比 $r_{\text{RE}}/r_{\text{Zr}}$ 为 1.501 (表 2), 根据平均离子半径比的经验定律, 其物相结构在高温下倾向于形成烧绿石型晶体结构, 这和 XRD 结果相一致(图 4)。

依据 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵陶瓷致密化和晶粒长大的烧结特性, 本工作进行了两步烧结(TSS)实验, 其烧结制度的示意图如图 5 所示。

首先将生坯加热到温度 T_1 ，保持一定时间 t_1 后迅速降低至温度 T_2 ，然后保持时间 t_2 ，直到样品实现完全致密化。两步烧结实验的具体烧结参数和实验结果如表 3 所示。由表 3 可知，TSS1 和 TSS2 烧结条件下所得样品晶粒尺寸较小(91 nm 和 94 nm)，但是致密度较低(相对密度仅为 85.0%和 87.2%)。这表明经过第一步的烧结(1 400 °C，10 min)之后，样品未能达到临界密度，使得第二步的烧结难以实现致密化^[37]。当 T_1 增加到 1 500 °C 时，可以获得较高的致密度，但样品的晶粒尺寸也随之增加(如表 3 中 TSS3、TSS4、TSS5 和 TSS6 所示)。此外， T_2 和 t_2 对致密度和晶粒尺寸也有一定影响。

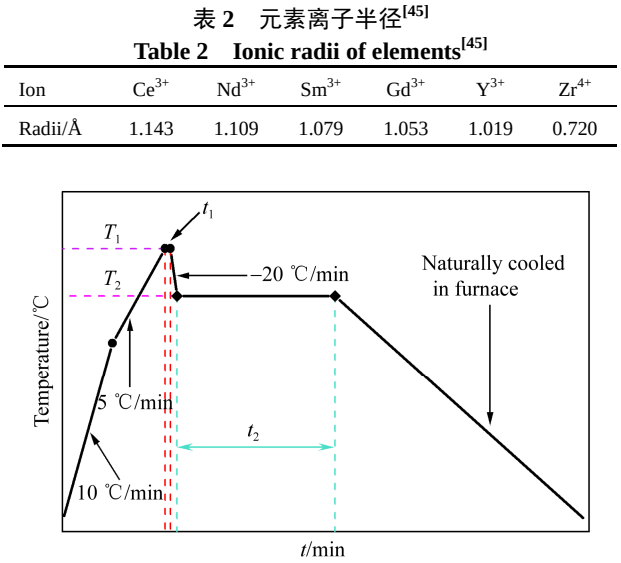


图 5 两步烧结的加热曲线示意图

Fig. 5 Schematic heating profile for two-step sintering

表 3 两步烧结实验参数及所得样品的相对密度和晶粒尺寸

Table 3 Relative density and grain size data for two-step sintering (TSS)

Sintering condition	T_1 /°C	t_1 /min	T_2 /°C	t_2 /h	Density/%	Grain size/nm
TSS1	1 400	10	1 250	5	85.0	91
TSS2	1 400	10	1 300	5	87.2	94
TSS3	1 500	10	1 250	5	97.4	129
TSS4	1 500	10	1 200	8	99.0	162
TSS5	1 500	10	1 300	5	99.2	188
TSS6	1 500	10	1 350	5	99.2	189

图 6 为两步烧结法所制备样品的 SEM 照片。由表 3 和图 6 可以看出，在相同的 T_1 和 t_1 下，随着 T_2 和 t_2 的增加，样品的致密度和晶粒尺寸也发生了缓慢增加。这些结果表明，在第二步烧结中还没有完全实现晶界迁移的“冻结”。尽管在第二步烧结中

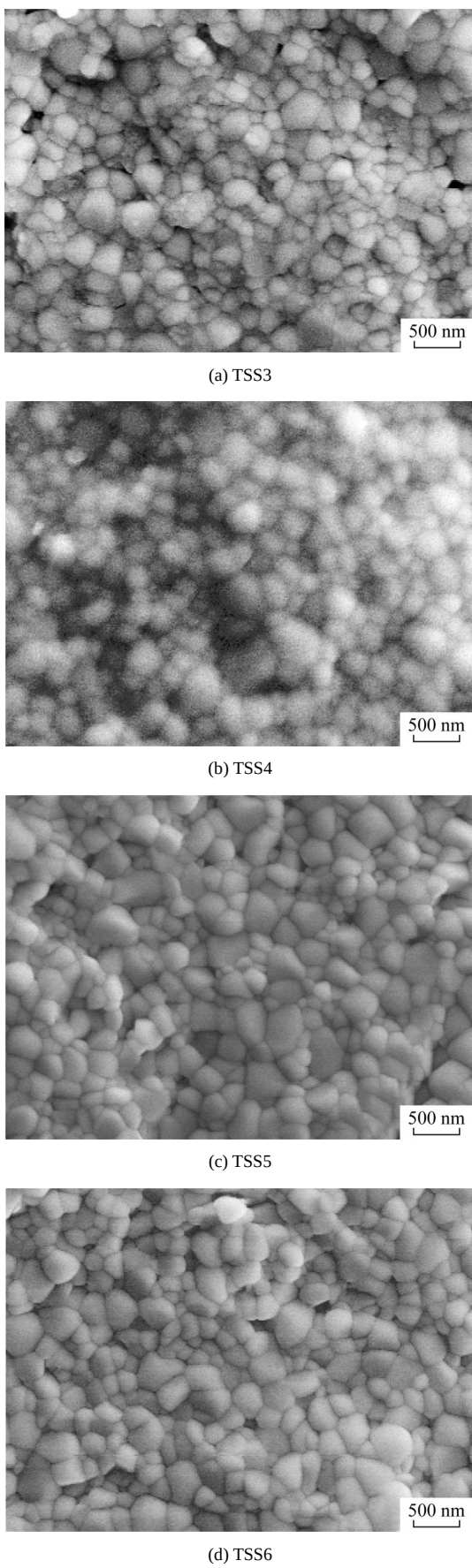


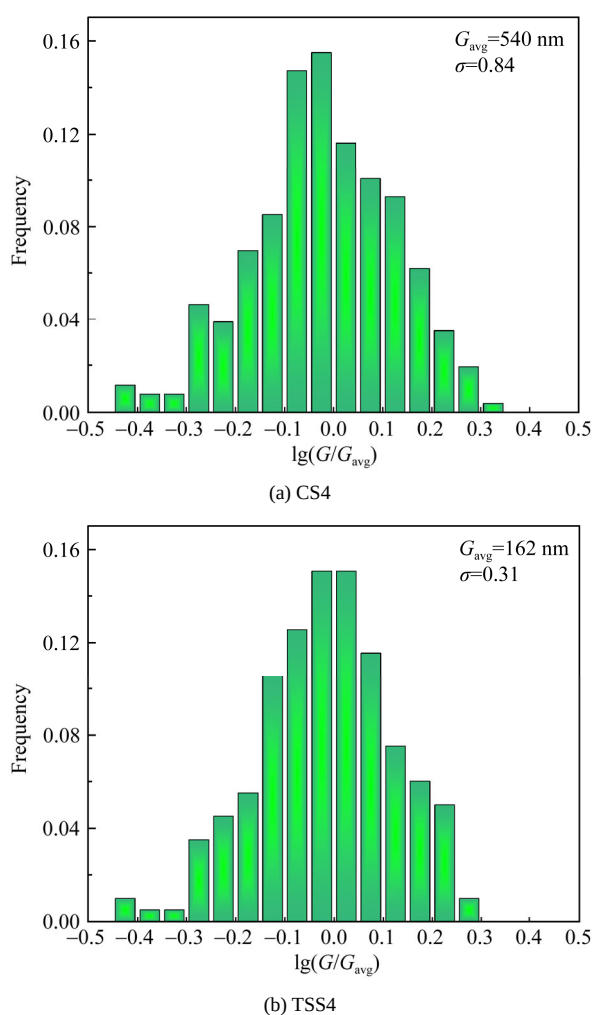
图 6 两步烧结法所制备样品的 SEM 照片

Fig. 6 SEM images of samples prepared by TSS

发生了晶粒的缓慢生长, 但是采用两步烧结法仍然成功制备了平均晶粒尺寸为 162 nm 的超细晶高熵陶瓷(TSS4)。

与传统烧结方法相比, 两步烧结法不仅可以有效抑制晶粒的快速长大从而获得超细晶粒, 还可以获得更窄晶粒尺寸分布的均匀微观结构。

图 7 为常规烧结样品(CS4)和两步烧结样品(TSS4)的归一化晶粒尺寸分布图以及 σ 数据。由图 7 可以看出, 两步烧结样品的归一化晶粒尺寸分布标准差 σ 为 0.31, 远低于常规烧结的样品($\sigma=0.84$), 表明两步烧结样品的晶粒尺寸分布均匀性远高于常规烧结的样品^[37-38]。



G_{avg} is the average grain size; σ is standard deviation of normalized grain size, which is ratio of standard deviation Σ of grain-size distribution to average grain size G_{avg} .

图 7 样品的归一化粒度分布图以及 σ 数据

Fig. 7 Normalized grain size distribution and σ value of sample

通过显微硬度计和压痕法对常规烧结(CS4)和两步烧结(TSS4)所制备样品的 Vickers 硬度(H_V)及断

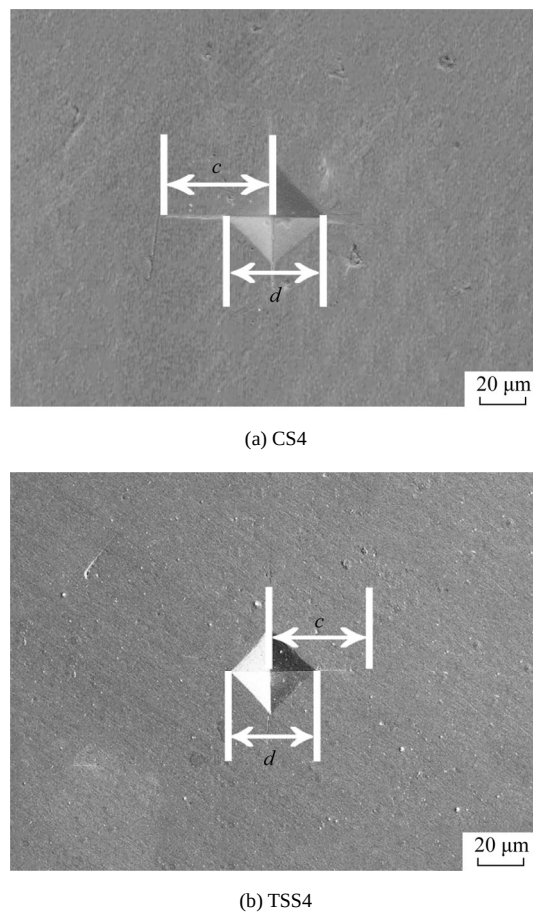
裂韧性(K_{IC})进行了计算, 计算公式如下所示^[46]:

$$H_V = 0.1891 \frac{F}{d^2} \quad (1)$$

$$K_{\text{IC}} = 0.016 \left(\frac{E}{H_V} \right)^{1/2} \frac{F}{c^{3/2}} \quad (2)$$

其中: F 为施加在样品上的载荷(9.8 N); d 为压痕对角线的平均长度; E 为杨氏模量; c 为从压痕中心到裂纹尖端的平均半裂纹长度。利用纳米压痕测试技术得到了样品 CS4 和样品 TSS4 的杨氏模量, 分别为 220 GPa 和 245 GPa。

图 8 为样品的压痕形貌。由图 8 可以看出, 常规烧结(CS4)所得样品的 Vickers 硬度为 11.0 GPa, 断裂韧性为 $2.0 \text{ MPa} \cdot \text{m}^{1/2}$, 两步烧结(TSS4)所得样品的 Vickers 硬度为 12.5 GPa, 断裂韧性为 $2.4 \text{ MPa} \cdot \text{m}^{1/2}$ 。明显可以看出, 两步烧结法所制备样品的硬度和断裂韧性优于常规烧结的样品, Vickers 硬度与断裂韧性分别增加了 13.6%和 20.0%, 这可能是来自于细晶粒的强化效应及均匀的微观结构。



d is indent diagonal length; c is half-crack length measured from center of indentation to tip of crack.

图 8 样品的压痕形貌

Fig. 8 Indented scar morphologies of samples

3 结论

采用无压两步烧结法成功制备了相对密度为 99.0%，平均晶粒尺寸为 162 nm 超细晶 $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ 高熵陶瓷。当温度高于 1400 °C 时，发生了缺陷萤石结构向烧绿石结构的相变。与常规烧结相比，两步烧结法可制备出具有更细小晶粒和更均匀粒径分布的高熵陶瓷，这使其具有良好的力学性能，其 Vickers 硬度可达 12.5 GPa，断裂韧性可达 $2.4 \text{ MPa}\cdot\text{m}^{1/2}$ 。无压两步烧结法也可用于制备其他体系的超细晶甚至纳米晶高熵陶瓷。本工作为常规无压条件下制备超细晶高熵陶瓷提供了一个新的途径，有助于促进高熵陶瓷在工业领域的广泛应用。

参考文献:

- [1] ROST C M, RAK Z, BRENNER D W, et al. Local structure of the $\text{Mg}_x\text{Ni}_x\text{Co}_x\text{Cu}_x\text{Zn}_x\text{O}$ ($x=0.2$) entropy-stabilized oxide: An EXAFS study[J]. J Am Ceram Soc, 2017, 100(6): 2732–2738.
- [2] OSES C, TOHER C, CURTAROLO S. High-entropy ceramics[J]. Nat Rev Mater, 2020, 5: 295–309.
- [3] AAMLID S S, OUDAH M, ROTTLE J, et al. Understanding the role of entropy in high entropy oxides[J]. J Am Chem Soc, 2023, 145(11): 5991–6006.
- [4] SARKAR A, VELASCO L, WANG D, et al. High entropy oxides for reversible energy storage[J]. Nat Commun, 2018, 9(1): 3400.
- [5] AKRAMI S, EDALATI P, FUJI M, et al. High-entropy ceramics: Review of principles, production and applications[J]. Mater Sci Eng R Rep, 2021, 146: 100644.
- [6] LI L L, JI P C, GENG C, et al. Facile synthesis of high-entropy $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ nanopowders and their electrochemical properties as supercapacitor electrode[J]. J Energy Storage, 2023, 73: 109182.
- [7] LI S, PENG Z J, FU X L. $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Al}_{0.5}\text{Mg}_{0.5}\text{O}_4$ high-entropy oxide with high capacity and ultra-long life for Li-ion battery anodes[J]. J Adv Ceram, 2023, 12(1): 59–71.
- [8] FRACCHIA M, CODURI M, GHIGNA P, et al. Phase stability of high entropy oxides: A critical review[J]. J Eur Ceram Soc, 2024, 44(2): 585–594.
- [9] YANG W Z, ZHU Q Q, XIAO G R, et al. Metal deficient AlB_2 -type $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})_{1-\delta}\text{B}_2$ high-entropy diborides with high hardness[J]. Ceram Int, 2023, 49(3): 5522–5526.
- [10] SMITH S M II, FAHRENHOLTZ W G, HILMAS G E. Pressureless sintering of high-entropy boride ceramics[J]. J Eur Ceram Soc, 2023, 43(12): 5168–5173.
- [11] HAN L, CHEN Y, ZHANG H, et al. Low-temperature synthesis of six-principal-component high-entropy transition-metal carbide aerogel thermal insulator[J]. J Am Ceram Soc, 106(2): 841–847.
- [12] ZENG L Y, WANG Z Q, SONG J, et al. Discovery of the high-entropy carbide ceramic topological superconductor candidate $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Nb}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2})\text{C}$ [J]. Adv Funct Materials, 2023, 33(40): 2301929.
- [13] HU J J, YANG Q K, ZHU S Y, et al. Superhard bulk high-entropy carbides with enhanced toughness via metastable *in situ* particles[J]. Nat Commun, 2023, 14(1): 5717.
- [14] KUMAR N G, ANDREAS K, MAYRHOFFER PAUL H, et al. On correlations between local chemistry, distortions and kinetics in high entropy nitrides: An *ab initio* study[J]. Acta Mater, 2023, 255: 118951.
- [15] YUAN M Y, GAO X X, GU X L, et al. Simultaneous enhancement of hardness and wear and corrosion resistance of high-entropy transition-metal nitride[J]. J Am Ceram Soc, 2023, 106(2): 1356–1368.
- [16] HEWAGE N W, VISWANATHAN G, YOX P, et al. Synthesis of chiral high-entropy sulfides for non-linear optical applications[J]. Inorg Chem Front, 2023, 10(22): 6613–6621.
- [17] LIN L, WANG K, SARKAR A, et al. High-entropy sulfides as electrode materials for Li-ion batteries[J]. Adv Energy Mater, 2022, 12(8): 2103090.
- [18] SHARMA P, BALASUBRAMANIAN G. High configurational entropy driven increased heat capacity of refractory multicomponent di-silicides[J]. Materialia, 2023, 30: 101861.
- [19] LIU B, YANG W Z, XIAO G R, et al. High-entropy silicide superconductors with W_5Si_3 -type structure[J]. Phys Rev Materials, 2023, 7: 014805.
- [20] XU L, NIU M, WANG H J, et al. Response of structure and mechanical properties of high entropy pyrochlore to heavy ion irradiation[J]. J Eur Ceram Soc, 2022, 42(14): 6624–6632.
- [21] LIU D B, SHI B L, GENG L Y, et al. High-entropy rare-earth zirconate ceramics with low thermal conductivity for advanced thermal-barrier coatings[J]. J Adv Ceram, 2022, 11(6): 961–973.
- [22] WANG Z Z, ZHU C Z, WANG H, et al. Preparation and irradiation stability of $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore high-entropy ceramic for immobilization of high-level nuclear waste[J]. J Nucl Mater, 2023, 574: 154212.
- [23] LUO X W, LUO L R, ZHAO X F, et al. Single-phase rare-earth high-entropy zirconates with superior thermal and mechanical properties[J]. J Eur Ceram Soc, 2022, 42(5): 2391–2399.
- [24] ZHOU L, LI F, LIU J X, et al. High-entropy $\text{A}_2\text{B}_2\text{O}_7$ -type oxide ceramics: A potential immobilising matrix for high-level radioactive waste[J]. J Hazard Mater, 2021, 415: 125596.
- [25] ZHAO G L, CAI S K, ZHANG Y, et al. Reactive flash sintering of high-entropy oxide $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$: Microstructural evolution and aqueous durability[J]. J Eur Ceram Soc, 2023, 43(6): 2593–2600.
- [26] LIU D B, WANG Y G, ZHOU F F, et al. A novel high-entropy $(\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$ ceramic aerogel with ultralow thermal conductivity[J]. Ceram Int, 2021, 47(21): 29960–29968.
- [27] WANG Y H, JIN Y J, DING Z Y, et al. Microstructure and electrical properties of new high-entropy rare-earth zirconates[J]. J Alloys Compd, 2022, 906: 164331.
- [28] ZHU J T, MENG X Y, ZHANG P, et al. Dual-phase rare-earth-zirconate high-entropy ceramics with glass-like thermal conductivity[J]. J Eur Ceram Soc, 2021, 41(4): 2861–2869.
- [29] MA M D, SUN Y N, WU Y J, et al. Nanocrystalline high-entropy carbide ceramics with improved mechanical properties[J]. J Am Ceram Soc, 2022, 105(1): 606–613.
- [30] LUO S C, GUO W M, PLUCKNETT K, et al. Fine-grained dual-phase high-entropy ceramics derived from boro/carbothermal reduction[J]. J Eur Ceram Soc, 2021, 41(6): 3189–3195.
- [31] DENG M, HUANG Z Y, GUO W Y, et al. An inverse Hall-Petch behavior and improving toughness in translucent nanocrystalline

- high-entropy zirconate ceramic[J]. *J Eur Ceram Soc*, 2023, 43(4): 1746–1750.
- [32] MA M D, HAN Y J, ZHAO Z S, et al. Ultrafine-grained high-entropy zirconates with superior mechanical and thermal properties[J]. *J Materiomics*, 2023, 9(2): 370–377.
- [33] TAN L, SU X, YANG J, et al. Facile synthesis of high-entropy zirconate nanopowders and their sintering behaviors[J]. *J Adv Ceram*, 2023, 12: 498–509.
- [34] ZHOU L, LIU J X, TU T Z, et al. Fast grain growth phenomenon in high-entropy ceramics: A case study in rare-earth hexaaluminates[J]. *J Adv Ceram*, 2023, 12(1): 111–121.
- [35] CHENG Y Y, ZHOU L, LIU J X, et al. Grain growth inhibition by sluggish diffusion and Zener pinning in high-entropy diboride ceramics[J]. *J Am Ceram Soc*, 2023, 106(8): 4997–5004.
- [36] WU Z T, JI W, ZHANG J Y, et al. Grain-refining fabrication of nanocrystalline $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Eu}_{0.2})_2\text{Zr}_2\text{O}_7$ high-entropy ceramics by ultra-high pressure sintering[J]. *J Mater Sci Technol*, 2023, 167: 205–212.
- [37] LI X Y, ZHANG L, DONG Y H, et al. Pressureless two-step sintering of ultrafine-grained tungsten[J]. *Acta Mater*, 2020, 186: 116–123.
- [38] DONG Y H, YANG H B, ZHANG L, et al. Ultra-uniform nanocrystalline materials *via* two-step sintering[J]. *Adv Funct Materials*, 2021, 31(1): 2007750.
- [39] CHEN I W, WANG X H. Sintering dense nanocrystalline ceramics without final-stage grain growth[J]. *Nature*, 2000, 404(6774): 168–171.
- [40] QUE Z Y, LI X Y, ZHANG L, et al. Resolving the sintering conundrum of high-rhenium tungsten alloys[J]. *J Mater Sci Technol*, 2023, 166: 78–85.
- [41] KANG W S, GUO X J, GAO B T, et al. Enhanced resistivity and piezoelectric response in $\text{BiFeO}_3\text{-BaTiO}_3$ *via* two-step sintering[J]. *J Eur Ceram Soc*, 2023, 43(14): 6041–6049.
- [42] TENG Z, ZHU L N, TAN Y Q, et al. Synthesis and structures of high-entropy pyrochlore oxides[J]. *J Eur Ceram Soc*, 2020, 40(4): 1639–1643.
- [43] LI X J, YU H D, GAO S, et al. Preparation of high entropy ceramics with ultra-low lattice thermal conductivity using the high-pressure and high-temperature method[J]. *Mater Charact*, 2023, 199: 112792.
- [44] TENG Z, TAN Y Q, ZENG S F, et al. Preparation and phase evolution of high-entropy oxides $\text{A}_2\text{B}_2\text{O}_7$ with multiple elements at A and B sites[J]. *J Eur Ceram Soc*, 2021, 41(6): 3614–3620.
- [45] SHANNON R D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides[J]. *Acta Cryst Sect A*, 1976, 32(5): 751–767.
- [46] REN K, WANG Q K, SHAO G, et al. Multicomponent high-entropy zirconates with comprehensive properties for advanced thermal barrier coating[J]. *Scr Mater*, 2020, 178: 382–386.

Preparation of Ultrafine-Grained $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ High-Entropy Ceramics *via* Pressureless Two-Step Sintering

GENG Chang, LI Yu, LI Linlin, ZHANG Shuai, LOU Chengguang, LI Wenjing, SU Xinghua
(School of Materials Science and Engineering, Chang'an University, Xi'an 710061, China)

Extended Abstract

Introduction High-entropy zirconate ceramics (HEZCs) have been studied extensively in recent years for the potential applications in thermal barrier coatings and high-level nuclear waste immobilization. While these HEZCs have the issue of poor toughness, which impedes their applications. The toughness of HEZCs can be improved by decreasing its grain size. While preparation of ultrafine-grained or nanocrystalline HEZCs is a challenge because the rapid grain growth inevitably occurred at high temperature densification process (typically above 1500 °C).

In this work, the challenge of preparing dense ultrafine-grained high-entropy ceramics through conventional pressureless sintering process was addressed *via* a simple two-step sintering method. Ultrafine-grained $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ high-entropy zirconate with 99.0% theoretical density and 162 nm grain size was fabricated. Compared to the conventional method, two-step sintering provided the high-entropy zirconate with finer grain size and better microstructural uniformity, and excellent comprehensive mechanical properties including high hardness of 12.5 GPa and high fracture toughness of 2.4 MPa·m^{1/2}. This work could help to understand the sintering kinetics of HEZCs, and also supplied a guidance to prepare the ultrafine-grained or nanocrystalline HEZCs by pressureless sintering method.

Methods The starting high-entropy $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ ceramic powders were prepared *via* a polyacrylamide gel method. Analytical grade rare earth nitrate hexahydrates $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (RE=Ce, Nd, Sm, Gd, Y) with a purity of 99.9%, zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.0% purity), acrylamide (AM, $\text{C}_3\text{H}_5\text{NO}$, 99.0% purity), N-N'-methylene-bis-acrylamide (MBAM, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$, 99.0% purity) and ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 99.0% purity) were used as starting materials, which were purchased from Macklin Chemical (Shanghai, China). First, $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were mixed in distilled water according to the stoichiometric ratio of $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$. After a vigorous stirring for 30 min, a clear solution was obtained and the concentration of Zr^{4+} was 0.02 mol/L. Then the AM, MBAM and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with a mole ratio of 24/2/1 were added in the above solution and dissolved completely by vigorous stirring. The mole ratio of AM/ Zr^{4+} (abbreviated as A/Zr) in mixed solution was 80/1. After that, the mixed solution was heated in a water bath at 80 °C until it converted into wet gel. Subsequently, the wet gel was dried in an oven at 80 °C for 72 h to obtain the xerogel. Finally, $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ powders were prepared

after a calcination of the xerogel at 1 000 °C for 2 h in air.

These $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ powders were uniaxially pressed into green pellets with a diameter of 8 mm and a thickness of (2 ± 0.1) mm under 300 MPa, then it was sintered in air through conventional sintering and two-step sintering. For the conventional sintering, the green pellets were heated to 1 200–1 500 °C and held for 2 h directly; For the two-step sintering, the green pellets were firstly heated to a higher temperature of T_1 and held for time of t_1 , then immediately cooled down to a lower temperature of T_2 and held for time of t_2 . After that, the samples were naturally cooled down to room temperature in the furnace. It should be noted that in the heating process, the heating rate was 10 °C/min before 1 000 °C. After the furnace temperature reached to 1 000 °C, the heating rate was down to 5 °C/min.

The crystalline phases of samples were detected by X-ray diffractometer (XRD, Bruker D8 Davinci with Cu K α radiation, Germany). The microstructure and element distribution of HEZC powders were characterized by transmission electron microscopy (TEM, JEOL-2100 F, Japan) equipped with energy dispersive X-ray spectroscopy (EDS). The morphology of sintered sample was observed by field emission scanning electron microscopy (SEM, Hitachi S-4800, Japan). The average grain size of sintered sample was determined by Nano Measurer software. At least 200 grains were randomly selected in measurement. The density of sintered sample was measured by Archimedes method. The relative density was calculated according to the theoretical density derived from the Rietveld refinement. The Vickers hardness and fracture toughness were evaluated by a micro-Vickers hardness tester (HV-1000A, Laizhou Huayin, China) under a load of 9.8 N with dwelling time of 15 s. The nanoindentation tests were carried on a Nano Indenter G200 (U9820A, Agilent Technologies), using a constant strain rate of 0.05/s. The Young's modulus was calculated according to the Oliver-Pharr method from the loading-unloading curve.

Results and discussion All diffraction peaks of the starting powders $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ prepared via polyacrylamide gel method matched well to that of the defective fluorite phase, indicating that the starting powder was single-phased HEZC with defective fluorite structure. The TEM image of HEZC powders presented that the average particle size was about 25 nm. The EDS mapping of HEZC revealed the homogeneous distribution of elements without segregation.

Samples sintered at 1 200 °C and 1 300 °C exhibited a porous structure; When sintered at 1 400 °C, it exhibited a relatively dense structure, and some closed pores were still remained in the sample; When sintered at 1 500 °C, a dense and pore-free microstructure can be observed. It should be noted that the dense HEZC bulks with relative density of 99.4% can be prepared when sintered at 1 500 °C for 2 h, implying a high sintering activity. The grain size increased slowly as the sintered temperatures increased from 1 200 °C to 1 400 °C, whereas grain size increased rapidly beyond 1 400 °C. Therefore, the rapid grain growth could be avoided if sintering temperatures below 1 400 °C in the conventional sintering. However, the densification process could not be accomplished under such sintering conditions. The pore pinning effect was of great significance for preparing the ultrafine-grained or nanocrystalline HEZCs via pressureless sintering method. And based on the XRD analysis, it can be concluded that the structure of $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ evolved from the defective fluorite toward to the pyrochlore at temperatures above 1 400 °C.

With the understanding of the sintering behavior of HEZC, two-step sintering (TSS) could be provided to achieve the high densification and fine grain size by suppressing the rapid grain growth in the final sintering stage. the ultrafine-grained HEZC with an average grain size of 162 nm was prepared by TSS4, the sample showed that the compact microstructure with homogeneous ultrafine grains was obtained. In addition to retarding the rapid grain growth and obtaining the finer grain size, two-step sintering also could help to achieve a uniform microstructure with a narrower grain-size distribution compared to the conventional sintering. Two-step sintered sample (TSS4) has a lower σ (0.31, the ratio of the standard deviation Σ of grain-size distribution to the average grain size G_{avg}) than that of the conventionally sintered sample (CS4, $\sigma=0.84$). The Vickers hardness and fracture toughness of the HEZC sample prepared by CS4 were 11.0 GPa and $2.0 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. Meanwhile, these values of sample prepared by TSS4 were 12.5 GPa and $2.4 \text{ MPa}\cdot\text{m}^{1/2}$, increased by 13.6% and 20.0%, respectively. The hardness and fracture toughness of samples prepared by two-step sintering were much better than those of conventional sintering, owing to the ultra-fined and homogeneous microstructure.

Conclusions Pressureless two-step sintering process is successfully used to prepare the dense and ultrafine-grained high-entropy $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ ceramics with a relative density of 99.0% and an average grain size of 162 nm, as the phase transformation from defective fluorite to pyrochlore occurred over 1 400 °C. In addition, this process could achieve the higher grain-size uniformity and finer grain size, as compared to that of the conventional sintering. Owing to the ultrafine grain size and high microstructural uniformity, the high-entropy $(\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$ ceramics possessed the excellent mechanical properties with higher Vickers hardness of 12.5 GPa and fracture toughness of $2.4 \text{ MPa}\cdot\text{m}^{1/2}$. It was believed that pressureless two-step sintering method could be used to prepare other high-entropy ceramics with fine grain size and high quality.

Keywords high-entropy ceramics; zirconate; ultrafine-grained; two-step sintering; mechanical properties