

放电等离子体烧结制备纳米非晶 $\text{Al}_2\text{O}_3\text{--La}_2\text{O}_3\text{--ZrO}_2$ 三元共晶氧化物

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摘 要: 纳米非晶材料是由纳米非晶颗粒以及颗粒间非晶界面构成的新型材料, 表现出很多独特性能, 但其制备往往需要 >1 GPa 的高压来完成致密化。本工作采用溶胶凝胶法制备了较宽过冷液相区(844~914 °C)、平均粒径为 11.6 nm 的 $\text{Al}_2\text{O}_3\text{--La}_2\text{O}_3\text{--ZrO}_2$ (ALZ)纳米非晶粉末, 并通过放电等离子体烧结在 875~1 000 °C 条件下制备 ALZ 材料。结果表明, 在 875、900、927 °C 和 1 000 °C 烧结体相对密度分别达 87.6%、98.3%、96.6%和 91.5%, 其中, 在 900 °C、50 MPa 条件下烧结样品具有最大的相对密度和均匀的显微组织, 在 STEM-BF 和 HRTEM 下观察到了纳米晶相从非晶相基质中析出现象, 纳米压痕测试样品的平均纳米硬度和杨氏模量分别为 12.0 GPa 和 159.9 GPa。上述各烧结体相对密度大小主要与 ALZ 纳米非晶粉末在各温度下结晶度变化, 引起粉末黏性流动改变, 从而影响致密化进程有关。875 °C 烧结中 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 结晶度较大阻碍了非晶粉末的黏性流动; 而在 875~900 °C 会发生 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向结晶度较小 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 的相变, 这有利于黏性流动; 927 °C 和 1 000 °C 烧结的样品结晶度进一步增大不利于黏性流动。

关键词: 纳米非晶材料; 放电等离子体烧结; 过冷液相区; 氧化铝-氧化镧-氧化锆; 纳米压痕测试

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纳米非晶材料是由纳米级的非晶颗粒以及颗粒/颗粒之间的非晶界面构成的一类新型材料^[1]。因其兼具纳米尺度、非晶无序特征以及可控的原子和电子结构, 表现出很多不同于现有材料的独特性能。例如, $\text{Fe}_{90}\text{Sc}_{10}$ 纳米非晶材料(在 300 K 时)是强铁磁体, 而相应的熔融淬火玻璃是顺磁性的^[2]; 传统 SiO_2 玻璃为脆性材料, 而颗粒尺寸为 1.5 nm 的 SiO_2 纳米非晶材料可表现出 100% 的拉伸塑性变形^[3]。近期学者们发现以纳米非晶材料为基体并析出一定纳米晶粒的复合材料具有更优异的力学性能。Ming 等^[4]制备了一种由三维双连续晶态-非晶态纳米结构组成 Ti-Zr 基合金。由于无定形相对结晶域施加额外的应变硬化, 而结晶域防止了无定形相中的过早剪切局部化, 这种独特微结构以及协同变形机制使晶态-非晶态纳米复合材料具有超高屈服强度(1.80 GPa)、极限抗拉强度(2.3 GPa)和大均匀度 Ti-Zr 基

合金的延展性(7.0%)。Wu 等^[5]制备的非晶/纳米晶双相结构的镁基双相复合材料具有接近理想的 3.3 GPa 强度和 65 GPa 的低杨氏模量。然而上述纳米晶/纳米非晶复合材料的报道均为合金领域, 陶瓷领域鲜有学者研究。

无论是纳米非晶材料还是纳米晶/纳米非晶复合材料大都采用超高压成型来实现致密化, Nandam 在常温、6 GPa 的压力下制备了 Cu-Zr^[6]和 Pd-Si^[7]纳米非晶材料。Xu 等利用两步热压成型, 在 200~350 °C、1 GPa 压力下制备了相对密度为 98% 的 $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--Y}_2\text{O}_3$ 非晶陶瓷^[8]。超高压成型是利用纳米非晶粉体在高压下的塑性变形, 使非晶颗粒互相接触、挤压将气孔排出并在颗粒接触面通过界面扩散形成新的界面, 但这些研究均需要高压成型设备, 制备成本制约了该材料的进一步发展。

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不同于上述超高压成型, Rosenflanz 等^[9]采用黏性烧结将非晶粉体在过冷液相区进行固化, 利用非晶粉体在玻璃转化温度(T_g)以上具有较低黏度, 在外加压力下发生黏性流动来填充颗粒间的孔隙, 从而达到致密化^[10-13], 压力仅需 34 MPa, 有效避免了以往制备非晶材料所需要的不切实际的高压力。但是黏性烧结中的结晶会阻碍非晶粉末的黏性流动, 因此, 要求玻璃转化温度(T_g)与析晶温度(T_x)间需要足够宽的动力学窗口才能完成致密化。针对这一难题, Rosenflanz 等利用氧化铝-稀土氧化物体系($\text{Al}_2\text{O}_3\text{-RE}_2\text{O}_3$)调节 Al—O 多面体结构, 控制体系的玻璃形成能力, 显著增大了氧化物体系的动力学窗口, 制备出一系列致密的非晶陶瓷。然而, 黏性烧结在纳米非晶材料领域从未报道。

基于上述分析, 以 $\text{Al}_2\text{O}_3\text{-La}_2\text{O}_3\text{-ZrO}_2$ (ALZ)三元共晶氧化物为研究对象, 采用溶胶凝胶法制备具有较宽动力学窗口的 ALZ 纳米非晶粉末, 通过放电等离子烧结(SPS)在过冷液相区进行黏性烧结, 探究烧结温度对样品的物相组成和显微结构的影响, 并通过纳米压痕对纳米非晶复合材料进行力学性能测试

1 实验

1.1 样品制备

采用溶胶凝胶法合成了 57.3%(摩尔分数) $\text{Al}_2\text{O}_3\text{-19.7%La}_2\text{O}_3\text{-23%ZrO}_2$ 的非晶态粉末, 并在 800 °C 煅烧 1 h, 合成过程见文献[14]。使用 SPS 系统(Chenhua SPS-3T-3H-MIN)在真空下对 ALZ 非晶粉末进行烧结致密化。采用顶部和底部的石墨冲头进行单轴加压, 加载压力为 50 MPa。从室温到烧结温度(T_s)的升温速度为 100 K/min。烧结温度 T_s 为 875~1 000 °C, 保温时间为 5 min。致密样品呈圆柱形, 直径 15 mm, 厚度约 1 mm。

1.2 样品表征

用 Bruker D8 Davinci 型 X 射线粉末衍射仪分析产物物相组成, 测试条件: Cu 靶, 管电压 40 kV, 管电流 60 mA。用 STA 449F 型热重分析仪在空气气氛下研究前驱体的热失重过程, 升温速率为 10 °C/min。用 Hitachi S-4800 型扫描电子显微镜观察样品的显微形貌。用 FEI Tecnai G2 F20 型透射电子显微镜观察样品的显微组织和物相组成。用 KLA G200X 型纳米压痕仪测量样品的纳米硬度和杨氏模量, 工作模式为连续刚度法(CSM)。通过阿基米德法测定样品的体积密度。将样品研磨成粉末过 300 目筛, 采用比重瓶法测定粉体的真密度。根据体积

密度与真密度的比值, 可得到样品的相对密度。

2 结果与讨论

2.1 粉末表征

图 1 为在 800 °C 和 1 000 °C 煅烧 1 h ALZ 粉末的 X 射线衍射谱和 ALZ 前驱体的 TG-DSC 曲线。由图 1a 可见, 800 °C 煅烧的粉末只有较宽的衍射峰, 没有发现明显的晶化峰, 表明为非晶态。1 000 °C 煅烧的粉末结晶为 LaAlO_3 (PDF 97-017-0772)和 $\text{La}_2(\text{Zr}_2\text{O}_7)$ (PDF 97-015-3814)。由图 1b 可见, 从室温到 226 °C 的吸热峰伴随着 19.03% 的质量损失, 可以归因为物理和化学吸附水的蒸发。DSC 曲线中 546 °C 的放热峰伴随着 52.71% 的质量损失, 可以归因于有机物的氧化分解和燃烧。超过 600 °C 质量损失率可以忽略不计, 表明 600 °C 煅烧可以排除有机物。局部放大的 DSC 曲线表明, 非晶粉体的玻璃化转变温度(T_g)约为 844 °C, 结晶起始温度(T_x)约为 914 °C。纳米非晶粉体具有相当大的过冷液体区域($\Delta T_x = T_x - T_g = 70$ °C), 这将有利于黏性烧结获得致密样品。

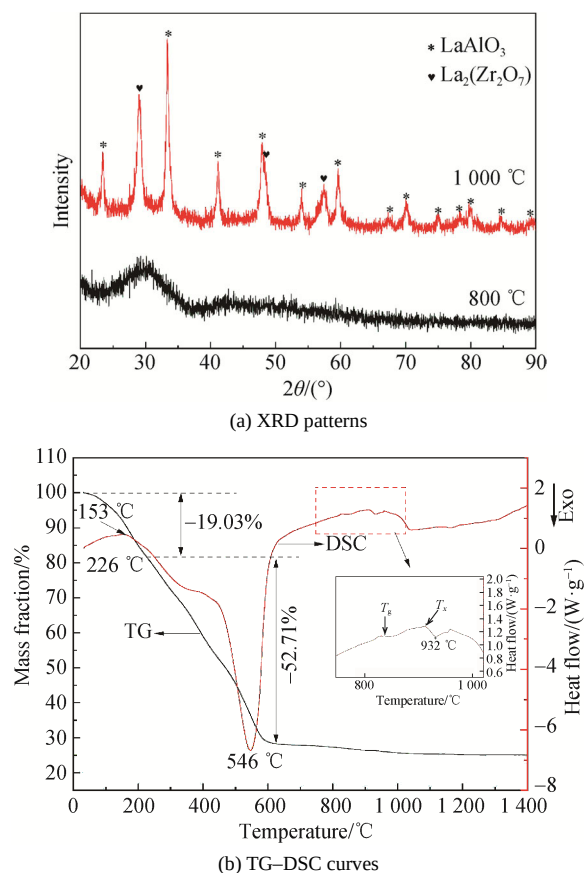
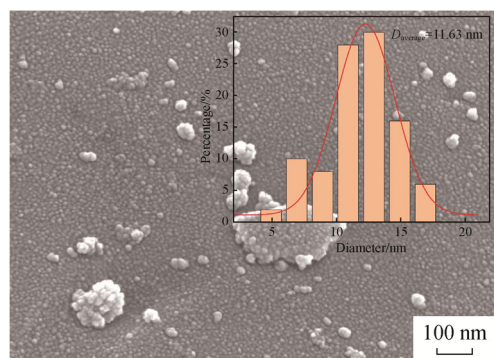


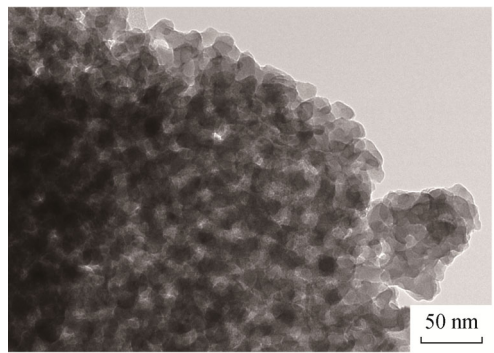
图 1 在 800 °C 和 1 000 °C 条件下煅烧 1 h ALZ 粉末的 X 射线衍射谱和 ALZ 前驱体的 TG-DSC 曲线

Fig. 1 XRD patterns of ALZ powders calcined at 800 °C and 1 000 °C for 1 h and TG-DSC curves of as-synthesized ALZ precursor

图 2 为在 800 °C 煅烧 1 h ALZ 粉末的 SEM 和 TEM 照片。由图 2a 与图 2b 可见, 非晶粉末为类球形的颗粒, 图 2a 插图表明, 非晶粉体粒度分布较窄, 平均颗粒尺寸约为 11.6 nm。



(a) SEM image



(b) TEM image

图 2 800 °C 煅烧 1 h ALZ 粉末的 SEM 和 TEM 照片

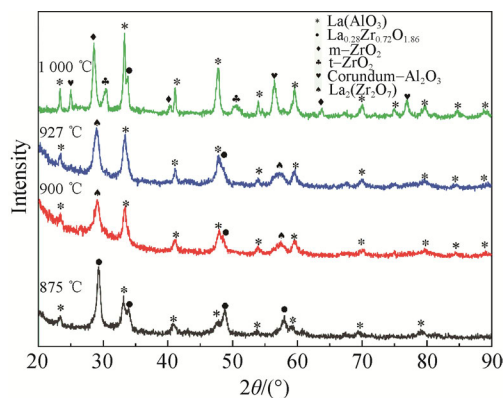
Fig. 2 SEM and TEM images of ALZ powder calcined at 800 °C for 1 h

2.2 烧结行为

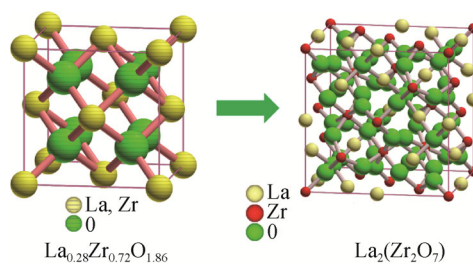
烧结温度直接影响烧结体的致密度、晶化程度和硬度等性质^[10]。由于黏度随温度急剧下降, 特别是在玻璃转变温度附近, 同样结晶程度太高也会影响样品的黏性流动。因此选择接近过冷液相区的烧结温度。

图 3 为在不同烧结温度下样品的 XRD 谱以及 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 相变的原子结构示意图。由图 3a 可见, 在 875 °C 烧结生成了 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ (PDF 04-002-7939) 和 $\text{La}(\text{AlO}_3)$ (PDF 97-019-1420), 由 jade 9 软件计算两相的含量分别为 68.4%(质量分数)和 31.6%。在 900 °C 和 927 °C 烧结生成了 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$, $\text{La}(\text{AlO}_3)$ 和 $\text{La}_2(\text{Zr}_2\text{O}_7)$ (PDF97-015-3814), 900 °C 下烧结三者的相含量分别为 28.1%, 31.4%和 40.4%; 927 °C 烧结三者的相含量分别为 16.5%、31.5%和 52.0%。在 875~927 °C, $\text{La}(\text{AlO}_3)$ 的含量(质量分数)比基本不变, 主要发生了 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 的相

变, 图 3b 为 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 相变的原子结构示意图且两相均为立方晶系。1 000 °C 条件下烧结样品几乎完全结晶, 由 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$, $\text{La}(\text{AlO}_3)$, m-ZrO₂(PDF 97-001-8190), t-ZrO₂(PDF 97-009-7004)和 Corundum- Al_2O_3 (PDF 97-001-0426) 5 种晶相组成。



(a) XRD patterns

(b) $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ phase transition to $\text{La}_2(\text{Zr}_2\text{O}_7)$ 图 3 在不同温度烧结样品的 XRD 谱和 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 相变的原子结构示意图Fig. 3 XRD patterns of specimens sintered at various temperatures and atomic structure diagram of $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ phase transition to $\text{La}_2(\text{Zr}_2\text{O}_7)$

与 DSC 结果相比, 样品在过冷液相区就发生了结晶。原因如下: 1)SPS 烧结过程中 Joule 热直接从烧结系统内部产生, 即使测温孔处与样品的距离很近, 都可能引起模具内外的温度值之间的差异, 导致样品的实际温度高于红外有效测量的温度^[15]; 2)晶化现象是 1 个与时间和温度有关的动力学现象^[16-17], DSC 是连续加热的模式, 而烧结是 5 min 内的等温过程。由于 T_s 等温退火的影响, 结晶可能在低于 T_x 的温度下发生; 3)烧结压力会影响非晶材料的晶化程度。Maurya 等^[18]报道称, 较高的烧结压力会导致原子的长程扩散受限, 仅促进原子的短程扩散, 从而更好地保持非晶相。也有学者报道增加外加压力可以抑制原子的迁移率, 从而显著提高 Zr 基和 Fe 基非晶合金的晶化温度^[19]。此外, 当烧结温度在过冷液相区时, 非晶陶瓷粉末黏度极剧下

降, 粉末在外加压力的作用下发生黏性流动来促进致密化, 较高的固结压力有助于增强非晶态粉末中的黏性流动。因此, 通过提高烧结压力, 有望得到致密的非晶态陶瓷样品。

图 4 为不同烧结温度下样品表面的 SEM 照片。由图 4 可见, 在 875 °C 烧结的样品中观察到大量气孔, 表明在该温度下没有实现完全致密化; 而在 900 °C 烧结的样品没有发现气孔, 实现了完全致密化; 在 875、900、927 °C 和 1000 °C 烧结样品的相对密度分别为 87.6%、98.3%、96.6% 和 91.5%。

表 1 计算了 875 °C 和 900 °C 烧结样品在 29° 附近 XRD 主衍射峰的晶粒尺寸。由表 1 可知,

875 °C 样品 XRD 主衍射峰为晶粒尺寸 14.2 nm 的 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.8}$, 而 900 °C 样品 XRD 谱主衍射峰为晶粒尺寸 9.9 nm 的 $\text{La}_2(\text{Zr}_2\text{O}_7)$, 这表明在 875 °C 烧结 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 结晶程度较大, 从而阻碍了非晶粉末的黏性流动, 出现大量气孔; 而在 900 °C 烧结 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 相结晶度相对较小有利于非晶粉末黏性流动, 仅在 50 MPa 的压力下通过黏性流动就实现致密化。因此, 结晶度较大的 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向结晶度较差的 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 的相变有利于非晶粉末通过黏性流动实现致密化。在 927 °C 和 1000 °C 烧结结晶度进一步增高不利于非晶粉末黏性流动, 出现了大量气孔。

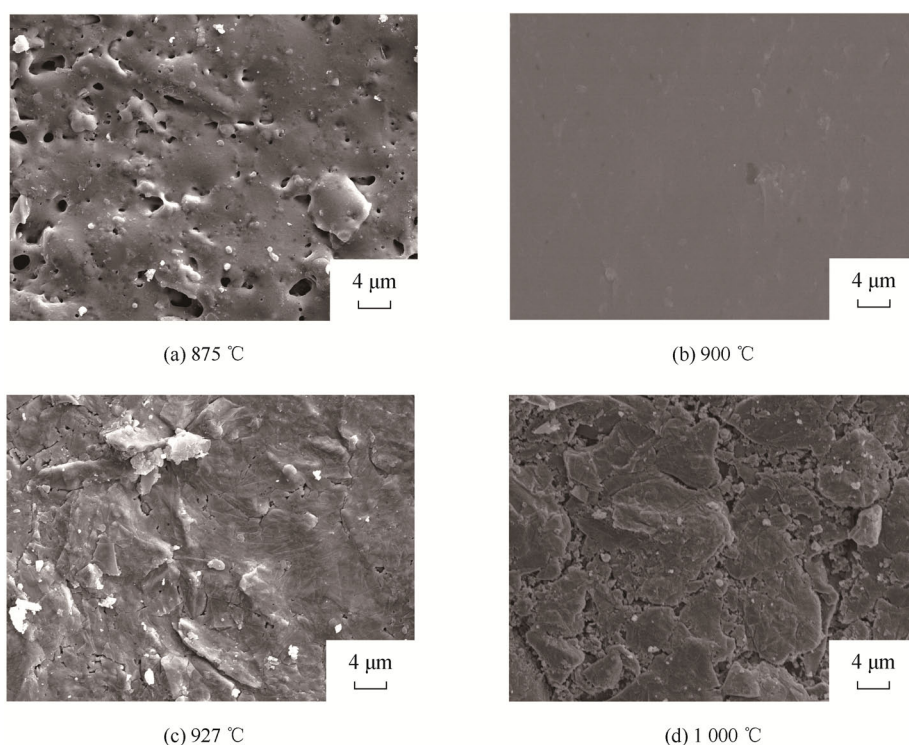


图 4 875、900、927 °C 和 1000 °C 条件下烧结样品的 SEM 照片
Fig.4 SEM microstructure of samples sintered at 875, 900, 927 °C and 1000 °C

表 1 875 °C 和 900 °C 烧结样品 XRD 主衍射峰的晶粒尺寸

Table 1 Grain size of XRD main diffraction peak of samples sintered at 875 °C and 900 °C

Sintering temperatures/°C	Centroid(2θ)/(°)	Left Angle(2θ)/(°)	Right Angle(2θ)/(°)	Peak FWHM(2θ)/(°)	Grain size/nm
875	29.219	28.001	30.574	0.625	14.2
900	29.026	27.409	30.573	0.867	9.9

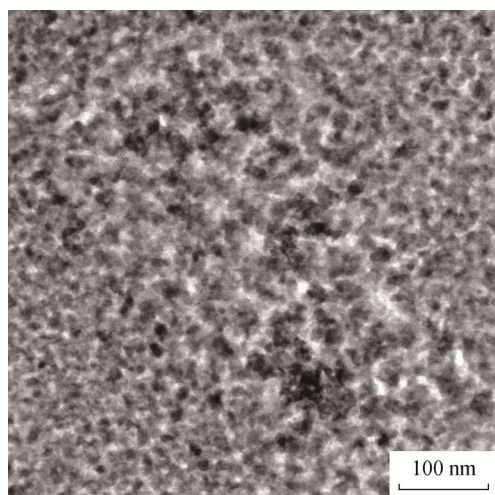
图 5 为在 900 °C 烧结样品的 STEM-BF 图和其 EDS 线扫和面扫图。由图 5a 可见, 900 °C 烧结样品的 STEM-BF 照片存在较暗区域和较亮区域, 通过进一步放大观察(图 5b)发现在暗区和暗区亮区交界处存在明显的晶格条纹, 而在亮区没有发现晶格条纹。析出的晶体为 $\text{La}(\text{AlO}_3)$,

$\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 和 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 相, 这与前面 XRD 谱的结果一致。EDS 线扫和面扫均表明亮区富含 Al 元素, 而暗区和暗区亮区交界处富含 Zr 和 La 元素。

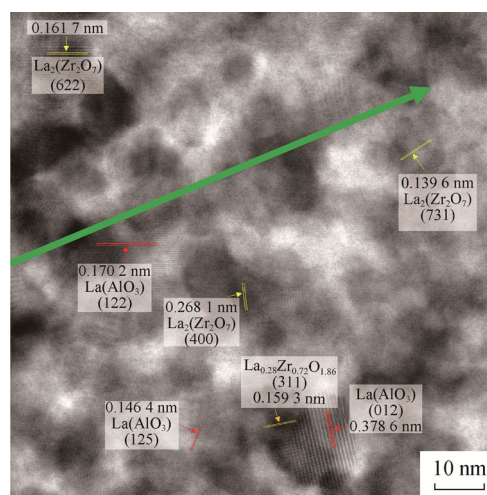
图 6 为在 900 °C 烧结样品的 HRTEM 照片。图 6 进一步说明了纳米晶相从非晶相基质中析出。圆

圈内部存在明显的晶格条纹, 其余部分表现为典型迷宫状的非晶结构。相应的快速 Fourier 变换图案呈

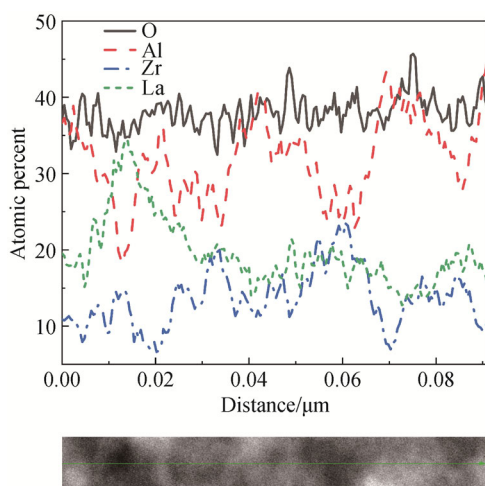
现出带有亮点的模糊背景, 证实了短程(非晶结构)和长程(晶体结构)有序排列的存在。



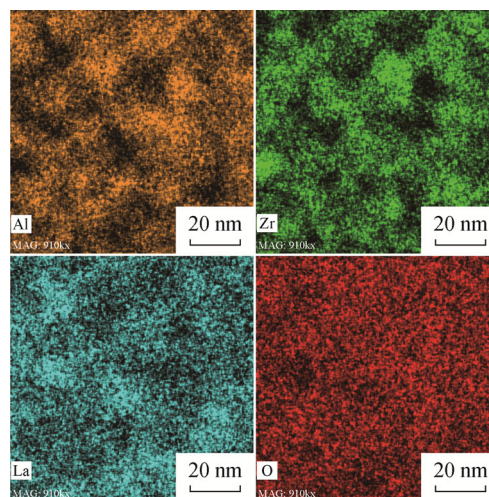
(a) STEM-BF image



(b) High resolution STEM-BF image



(c) EDS line scan of area indicated by green arrow in Fig. 5(b)



(d) EDS mapping of whole area in Fig. 5(b)

图 5 在 900 °C 烧结样品的 STEM-BF 照片、EDS 线扫图和 EDS 面扫图

Fig. 5 STEM-BF images, EDS line scan and EDS Mapping of the sample sintered at 900 °C

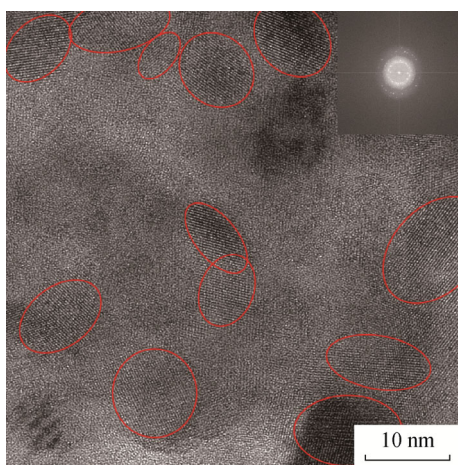


图 6 在 900 °C 烧结样品的 HRTEM 照片

Fig. 6 HRTEM image of samples sintered at 900 °C

2.3 力学性能

为了测定烧结样品的纳米硬度和杨氏模量, 进行了纳米压痕试验, 并采用了连续刚度模式(CSM)。图 7 为在 900 °C 和 927 °C 烧结样品的载荷-位移、硬度-位移、杨氏模量-位移曲线和压痕的 BSE-SEM 照片。由图 7a 可见, 压痕深度与载荷成正比, 本研究的最大载荷为 50 mN。图 7b 和图 7c 表明, 在较小的压痕深度下, 样品的纳米硬度和弹性模量的变化是不规律的。压痕尺寸效应会影响样品的硬度值^[20]。此外在纳米压痕的连续刚度测试中, 随着压痕深度和载荷的增加, 晶界、气孔、杂质、表面粗糙度等各种因素都会影响硬度和杨氏模量^[21]。除了微尺度的缺陷外, 原子尺度的缺陷, 包括空位、位

错和外来原子, 也会导致硬度和杨氏模量随位置的变化^[22-23]。由于微缺陷的复杂性和多变性, 使得其定量表征在实际测试中具有挑战性。选择变化相对平稳处作为样品的硬度和杨氏模量的值。900 °C 烧结样品的平均纳米硬度和杨氏模量分别为 12.0 GPa

和 159.9 GPa。927 °C 烧结样品的平均纳米硬度和杨氏模量分别为 11.8 GPa 和 166.0 GPa。在压痕的 BSE-SEM 照片中观察到剪切带(图 7d)。而在非晶态合金的纳米压痕实验中, 观察到剪切带是一种常见现象^[6]。

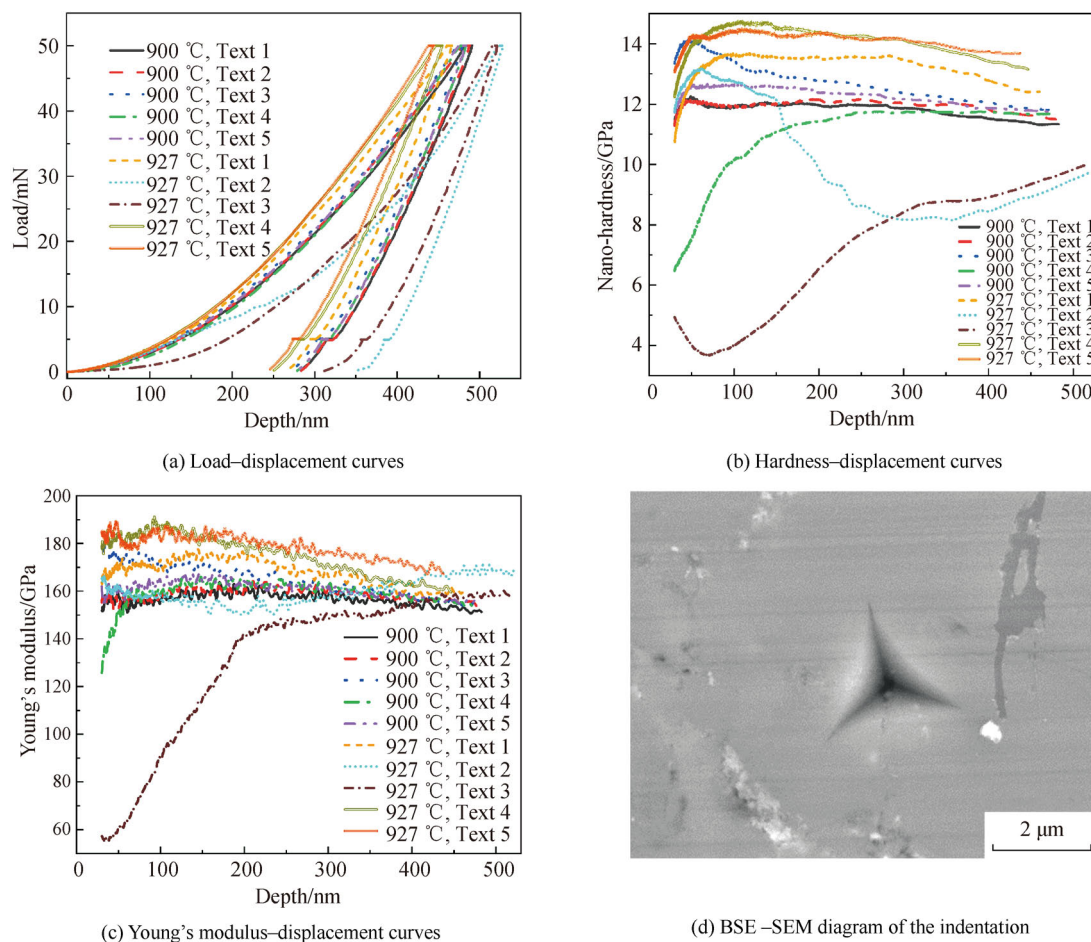


图 7 900 °C 和 927 °C 烧结样品的载荷-位移、硬度-位移、杨氏模量-位移曲线以及 900 °C 烧结样品压痕的 BSE-SEM 照片
Fig. 7 Load-displacement, hardness-displacement, Young's modulus-displacement curves for sintered samples at 900 and 927 °C, along with a BSE-SEM image illustrating the indentation of sintered sample at 900 °C

3 结论

1) 采用放电等离子烧结工艺可以在 900 °C 制备相对密度为 98.3% 的 ALZ 纳米非晶材料, 在 STEM-BF 和 HRTEM 下观察到纳米晶相从非晶相基质中析出, 析出的晶相为 $\text{La}(\text{AlO}_3)$, $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 和 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 相。纳米压痕测试该样品的平均纳米硬度和杨氏模量分别为 12.0 GPa 和 159.9 GPa。

2) 烧结体相对密度大小主要与不同烧结温度下纳米非晶粉末结晶度变化, 引起粉末黏性流动改变, 从而影响致密化进程有关。875 °C 烧结 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 结晶度较大阻碍了非晶粉末的黏性流动; 而在 875~900 °C 会发生 $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ 向结

晶度较小 $\text{La}_2(\text{Zr}_2\text{O}_7)$ 的相变, 较小的结晶度利于非晶粉末的黏性流动。当烧结温度为 927 °C 和 1000 °C 时结晶度进一步增大不利于非晶粉末的黏性流动。

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Preparation of Nanostructured–Amorphous $\text{Al}_2\text{O}_3\text{--La}_2\text{O}_3\text{--ZrO}_2$ Ternary Eutectic Oxides by Spark Plasma Sintering

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Extended Abstract

Introduction Nanostructured amorphous materials represent a novel class of materials characterized by nanostructured amorphous particles and amorphous interfaces between particles. Due to the nanometer scales, amorphous disorder, controllable atomic and electronic structure, this kind of material exhibits numerous unique properties distinct from conventional materials. Recently, scholars discovered that composites composed of nanostructured amorphous materials as the matrix with precipitated nanocrystals exhibited excellent mechanical properties. However, densification of both nanostructured amorphous materials and nanostructured amorphous composites was primarily achieved through ultra-high-pressure forming. During ultra-high-pressure forming, the plastic deformation of nanostructured amorphous powder under high pressure enabled amorphous particles to contact each other, extrude pores, and diffused through interfaces to form new interfaces. However, these studies required high-pressure forming equipment, and the associated costs constrained further applications.

In contrast to the ultra-high-pressure molding mentioned earlier, Rosenflanz et al. employed viscous sintering to consolidate

amorphous powder within the supercooled liquid region. This method utilized amorphous powder with low viscosity above the glass transition temperature (T_g) and its viscous flowed under external pressure to fill the pores between particles, thereby achieving densification. This approach only required 34 MPa pressure, effectively circumventing the unrealistically high pressures previously required for amorphous material preparation. However, crystallization during viscous sintering may impede the viscous flow of amorphous powder, necessitating a sufficiently wide kinetic window between the glass transition temperature (T_g) and crystallization temperature (T_x) to achieve densification. To address this issue, Rosenflanz et al. again employed an alumina–rare earth oxide system ($\text{Al}_2\text{O}_3\text{--RE}_2\text{O}_3$) to modulate the polyhedral structure of Al–O, regulated the glass formation ability of the system, substantially widen the kinetic window of the oxide system, and fabricated a range of dense amorphous ceramics. Nonetheless, viscous sintering process has never been reported in the realm of nanostructured amorphous materials.

Methods Amorphous powder of 57.3% $\text{Al}_2\text{O}_3\text{--}19.7\%\text{La}_2\text{O}_3\text{--}23\%\text{ZrO}_2$ (ALZ) was synthesized *via* sol-gel method and subsequently calcined at 800 °C for 1 h. The ALZ amorphous powder was then densified using the SPS system under vacuum conditions. Uniaxial compression was applied using graphite punches at the top and bottom, with a loading pressure of 50 MPa. The heating rate from room temperature to sintered temperatures (T_s) was set at 100 °C/min. The sintered temperatures ranged between 875 °C and 1 000 °C, with a holding time of 5 min. The obtained sample was cylindrical with a diameter of 15 mm and a thickness of 1 mm.

Results and discussion The powders calcined at 800 °C for 1 h was amorphous with an average particle size of 11.6 nm. The glass transition temperature (T_g) and crystallization onset temperature (T_x) of the obtained powders are 844 °C and 914 °C, respectively. Numerous pores can be observed in samples sintered at 875 °C, indicating an incomplete densification at this temperature, whereas no pores were detected in samples sintered at 900 °C. The relative densities of samples sintered at 875, 900, 927 °C and 1 000 °C were 87.6%, 98.3%, 96.6% and 91.5%, respectively. The main diffraction peaks in XRD pattern for the sample sintered at 875 °C corresponds to $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.8}$ with a grain size of 14.2 nm, when sintered at 900 °C, diffraction peaks of samples corresponded to $\text{La}_2(\text{Zr}_2\text{O}_7)$ with a grain size of 9.9 nm, which suggested that high degrees of crystallization of $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ sintered at 875 °C impeded the viscous flow of the amorphous powder, resulting in a formation of numerous pores. However, the relatively low crystallinity of $\text{La}_2(\text{Zr}_2\text{O}_7)$ phase sintered at 900 °C facilitated the viscous flow of the amorphous powder, and densification was achieved only under a pressure of 50 MPa. Thus, the phase transition formed $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$, which owned a higher crystallinity, to $\text{La}_2(\text{Zr}_2\text{O}_7)$ with lower crystallinity was advantageous for the densification of the amorphous powder *via* viscous flow. A further increase of crystallinity of samples sintered at 927 °C and 1 000 °C was not conducive to the viscous flow of the amorphous powder, resulted in the formation of numerous pores. STEM–BF images of sample sintered at 900 °C exhibited noticeable light–dark contrast. Upon further magnification, distinct lattice fringes can be observed at the interfaces of dark regions, while no lattice fringes were observed in the bright regions. The precipitated crystals were composed of $\text{La}(\text{AlO}_3)$, $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$, and $\text{La}_2(\text{Zr}_2\text{O}_7)$ phases, being consistent with that of XRD results. Both EDS line scanning and mapping revealed that the bright areas were composed of Al-enriched materials, whereas the interfaces between dark areas were Zr and La-enriched materials. Furthermore, the HRTEM image revealed that the nanocrystalline phase precipitates from the amorphous phase matrix.

Conclusions Nanostructured amorphous ALZ materials with a relative density of 98.3% can be prepared through spark plasma sintering at 900 °C. Nanocrystalline phases precipitated from the amorphous matrix were observed *via* STEM–BF and HRTEM, revealing the presence of $\text{La}(\text{AlO}_3)$, $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$, and $\text{La}_2(\text{Zr}_2\text{O}_7)$ phases. The average hardness and Young's modulus of samples were 12.0 GPa and 159.9 GPa, respectively. Meanwhile, samples sintered at 875, 927 °C and 1 000 °C existed notable pores, being originated from the changes in crystallinity of ALZ under different temperatures. The significant crystallization of $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ sintered at 875 °C impeded the viscous flow of amorphous powder. Concurrently, the phase transition from $\text{La}_{0.28}\text{Zr}_{0.72}\text{O}_{1.86}$ to $\text{La}_2(\text{Zr}_2\text{O}_7)$ with lower crystallinity occurred at 875–900 °C, which facilitated the viscous flow of amorphous powder. However, a further increase in crystallinity at 927 °C and 1 000 °C was not conducive to the viscous flow of amorphous powder.

Keywords nanostructured-amorphous materials; spark plasma sintering; supercooled liquid region; alumina–lanthania–zirconia; nano-indentation test