

(TiZrNbTaMe)C (Me=V, Cr, Mo, W)高熵陶瓷的显微结构 演变及元素分布

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摘 要: 随着航空航天、核能和特种冶炼行业的快速发展, 对新型超高温、抗辐照、耐腐蚀等极端环境使役性能需求不断提升, 亟需新材料创制和性能调控。过渡金属碳化物具有高熔点、抗辐照、耐腐蚀和理化性能稳定等优异性能, 是极端环境用特种陶瓷重要的组成部分。现今, 碳化物陶瓷更是逐渐从单一组元发展到多组元碳化物固溶体体系, 乃至高熵陶瓷体系。本工作采用热压烧结, 制备 4 种高熵碳化物陶瓷(TiZrNbTaMe)C (Me=V, Cr, Mo, W), 比较 Me 元素对陶瓷组织结构和力学性能的影响。结果表明: 4 种高熵碳化物陶瓷均呈现面心立方结构, 其中 V、Cr 和 Mo 元素有助于烧结促进致密化, 致密度均超过 98%。除(TiZrNbTaCr)C 外, 其他高熵陶瓷体系的金属元素分布均匀, 而 Cr 元素在(TiZrNbTaCr)C 陶瓷中出现晶界偏聚现象, 导致碳化物晶粒中的 Cr 含量较低。Cr 元素在碳化物高熵陶瓷中的固溶度与金属元素的种类和含量密切相关。(TiZrNbTaCr)C 陶瓷具有最佳的综合力学性能, 其维氏硬度为 29.8 GPa, 断裂韧性为 3.71 MPa·m^{1/2}。

关键词: 过渡金属碳化物; 高熵陶瓷; 组织演变; 力学性能

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超高温陶瓷包括一系列高熔点的材料, 如过渡金属碳化物、氮化物及硼化物^[1-2], 特别是过渡金属碳化物以优良高温力学性能、稳定理化性能、耐腐蚀和抗辐照性能, 在高超声速飞机、火箭发动机以及第四代核反应堆等极端环境中展现出广阔的应用前景^[3-5]。然而, 传统单组元过渡金属碳化物陶瓷已经无法满足新兴极端环境对材料使役性能需求, 亟需开发出新型高性能超高温材料^[6-9]。

近年来, 多组元“高熵”概念极大地扩展了材料成分设计和性能优化的范围。通过多种组元引入, 增加材料“高熵效应”, 不仅增强材料的热力学稳定性, 还引入晶格畸变和动力学迟滞扩散效应, 有效改善材料的理化性能^[10-11]。单相碳化物高熵陶瓷一经报道便引起研究人员广泛关注^[6, 12]。Sarker 等^[13]首次引入熵形成能力(EFA)来评价高熵碳化物陶瓷的单相稳定性, 并成功合成了(HfNbTaTiZr)C 等高

熵碳化物陶瓷。与单一组元碳化物相比, 多组元陶瓷在综合性能上表现更佳, 包括硬度、抗蠕变、抗氧化和抗辐照性能, 这些改进主要源于其复杂的组元成分、电子结构和晶格畸变^[6, 14-16]。Harrington 等^[17]对 5 组元过渡金属碳化物高熵陶瓷进行系统的硬度测试。结果表明, 高熵陶瓷硬度普遍高于基于混合定律计算预测值, 其中(TiZrHfNbTa)C 的硬度更是高达 32 GPa (300 mN)。Liu 等^[18]通过 DFT 原理计算和实验验证, 提出晶格畸变是影响碳化物高熵陶瓷硬度的决定性因素, 解释了碳化物高熵陶瓷的硬化机制。Wang 等^[19]报道了(ZrTaNbTi)C 高熵陶瓷的抗辐照性能, 其在 3 MeV Zr²⁺辐照后保持了较高的相稳定性, 没有发生相变, 也没有形成空洞或元素的偏析, 表现出了优异的抗离子辐照性能。对碳化物高熵陶瓷的抗氧化性能研究结果表明, 由于碳化物高熵陶瓷中的成分复杂性,

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使得其在氧化过程中形成多种成分复杂的氧化物保护层,有效地抑制氧的向内扩散,因此表现出卓越的抗氧化性^[15, 20]。此外,在抗蠕变性能上高熵陶瓷也优于单一碳化物,例如(TiZrNbTaMo)C高熵陶瓷抗蠕变性能明显优于单组元 TaC 陶瓷,在 1400~1600 °C 温度条件和 200~300 MPa 应力下,(TiZrNbTaMo)C 高熵陶瓷的稳态蠕变速率范围为 $2.1 \times 10^{-8} \sim 2.7 \times 10^{-6} \text{ s}^{-1}$ ^[21]。

然而,目前关于碳化物高熵陶瓷的研究主要集中于单相形成能力判定、制备工艺优化以及服役性能的开发。针对高熵陶瓷体系筛选和成分设计理论的研究仍显不足,尤其是元素种类对碳化物高熵陶瓷的物相组成、显微组织以及力学性能影响。本工作采用热压烧结制备(TiZrNbTaMe)C (Me=V, Cr, Mo, W)高熵陶瓷,并探讨 Me 元素种类对(TiZrNbTaMe)高熵陶瓷的物相、组织结构及力学性能的影响。

1 实验

1.1 材料制备

原材料包括 ZrO₂ (纯度>99.9%, 1~3 μm, 上海超威纳米技术有限公司)、TiO₂ (纯度>99.5%, 1~2 μm, 宁波新福钛白粉有限公司)、Ta₂O₅ 和 Nb₂O₅ (纯度>99.9%, 1~2 μm, 北京兴荣源科技有限公司)、V₂O₅ (纯度>99.9%, 1~4 μm, 湖南三丰钒业有限公司)、MoO₃ 和 WO₃ (纯度>99.9%, 1~4 μm, 上海在邦化工有限公司)、Cr₂O₃ (纯度>99.9%, 1~3 μm, 上海乃欧纳米科技有限公司)和炭黑(纯度>99%, 1~2 μm, 新疆雅克拉有限公司)。高熵陶瓷(TiZrNbTaV)C、(TiZrNbTaCr)C、(TiZrNbTaMo)C 和 (TiZrNbTaW)C 中,金属元素含量预设计为等摩尔比。称量炭黑和氧化物粉体。将粉末混合物放入硬质合金罐中,以硬质合金球为研磨介质,使用行星球磨机(Fritsch, model P4, Germany)进行球磨,球料比为 20:1,转速为 250 r/min,球磨 20 h。将球磨后的混合粉体过 100 目筛,放入石墨坩埚中。使用真空无压烧结炉(WS0404, Ningxia Sincere Co. Ltd., China),在真空条件下,1500 °C 碳热还原 1 h 合成碳化物粉体。将合成的碳化物粉末装入石墨模具中,采用两步法热压烧结(AVS, model 1540, USA),在 1850 °C 保温 1 h,然后在 2100 °C 保温 0.5 h,压力为 30 MPa,真空度约为 10 Pa,升降温速率为 20 °C/min。

1.2 样品表征与测试

采用 X 射线衍射仪(XRD; D/max-B, Rigaku,

Japan)测定碳化物陶瓷的物相,使用 Cu-K_α 系射线,工作电压为 40 kV,电流为 50 mA,扫描速度为 0.1 (°)/min,扫描范围为 10°~90°,进行相组成分析和 Le-Bail 精修。采用 FullProf 软件包计算所有固溶体相的晶格参数。采用扫描电子显微镜(SEM; Quanta 200FEG, USA)对材料微观组织结构和元素含量及分布进行分析表征。采用透射电子显微镜(TEM; Talos F200X, USA)对材料的微观组织结构、元素含量及分布、晶界特征进行分析。根据材料显微照片中存在孔隙,利用图像分析软件(Photoshop, Adobe, USA)测量样品中孔隙占比率,并计算相对密度。利用 ImageJ 软件采用线截距法从显微照片中测量平均晶粒尺寸,计数超过 300 个晶粒。使用维氏硬度计(HVS-30),在 9.8 N 载荷下进行维氏硬度测量,保压时间为 15 s。采用压痕法测量断裂韧性。维氏硬度和断裂韧性的计算公式如下^[22]:

$$H_v = 1.8544 \times 10^{-3} \times \frac{F}{d^2} \quad (1)$$

式中: F 为载荷(N); d 为压痕对角线长度的平均值(mm)。

$$K_{IC} = P \left(\pi \left(\frac{C_1 + C_2}{4} \right) \right)^{-\frac{3}{2}} (\tan^{-1} \beta) \quad (2)$$

式中: P 为施加荷载(N); C_1 和 C_2 为斜裂纹长度(m); β 为常数, 68°。

为分析原子尺寸差异的影响考虑晶格畸变 δ , 可以通过以下公式计算:

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\sum_{j=1}^n c_j r_j} \right)} \quad (3)$$

式中: c_i 、 c_j 和 r_i 、 r_j 分别代表第 i 、 j 种单组元碳化物的摩尔分数和晶格常数。

采用 Ω_{A-B} 描述为 A-A、B-B 和 A-B 相互作用的函数,最近邻相互作用表示为:

$$\Omega_{A-B} = zL \left[u_{A-B} - \frac{1}{2}(u_{A-A} + u_{B-B}) \right] \quad (4)$$

式中: z 为配位数; L 为阿伏伽德罗常数; u_{A-A} 、 u_{B-B} 和 u_{A-B} 分别为 A-A、B-B 和 A-B 相互作用的能量。

2 结果与讨论

2.1 物相与显微结构

(TiZrNbTaMe)C (Me=V, Cr, Mo, W)高熵陶瓷的 XRD 谱如图 1 所示。由图 1 可见,所有样品均展现出单相面心立方晶体结构的特征。对高熵陶瓷的晶格常数深入分析,结果表明,不同体系的衍射峰的

相对位置从左到右依次对应为(TiZrNbTaCr)C、(TiZrNbTaW)C、(TiZrNbTaMo)C 和(TiZrNbTaV)C, 晶格常数逐渐减小。为更加精确地比较不同体系晶格常数的变化, 对(TiZrNbTaMe)C 4 种陶瓷的 XRD 衍射峰进行 Le-Bail 精修, 计算得到的晶格常数由表 1 列出, 与 XRD 衍射峰峰位变化规律吻

合。除(TiZrNbTaCr)C 体系外, 其它 3 种陶瓷的晶格常数变化规律与相对应的单组元碳化物陶瓷的晶格常数的混合平均值的变化规律一致, 也与相应的 Me 原子半径的变化规律相符($r_W > r_{Mo} > r_V$)。然而(TiZrNbTaCr)C 晶格常数表现出异常增大的现象。

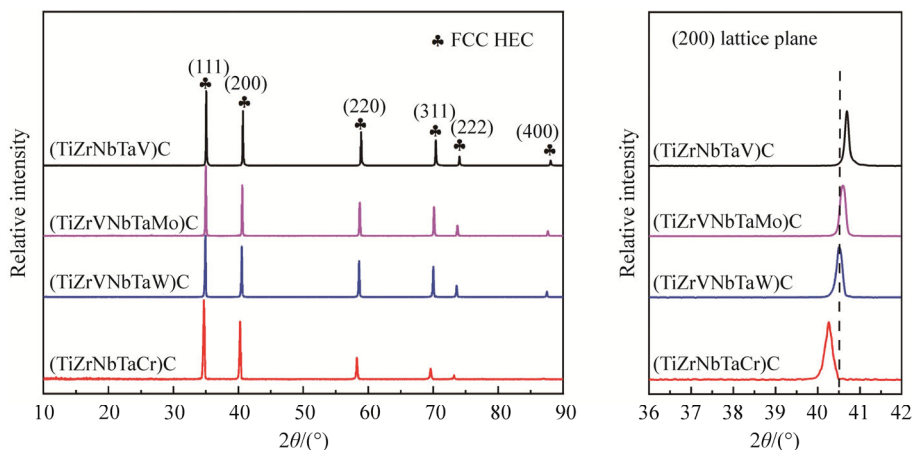


图 1 热压烧结制备的(TiZrNbTaMe)C(Me=V, Cr, Mo, W)高熵陶瓷的 XRD 谱

Fig. 1 XRD patterns of (TiZrNbTaMe)C (Me=V, Cr, Mo, W) high-entropy ceramics prepared by hot pressing

表 1 (TiZrNbTaMe)C 高熵陶瓷晶格常数和对应单组元碳化物陶瓷的晶格常数

Table 1 Lattice parameters of (TiZrNbTaMe)C high-entropy ceramics and corresponding single-component carbide ceramics

System	Lattice parameter/Å	System	Lattice parameter/Å	System	Lattice parameter/Å
(TiZrNbTaV)C	4.437	TiC	4.335	VC	4.161
(TiZrNbTaCr)C	4.471	ZrC	4.723	CrC	4.071
(TiZrNbTaMo)C	4.455	NbC	4.506	MoC	4.383
(TiZrNbTaW)C	4.454	TaC	4.481	WC	4.390

Note: The lattice constant of (TiZrNbTaMe)C high-entropy ceramics is obtained by XRD refinement, and the lattice constant of single-component carbide ceramics is from the materials project website and is calculated by first principles.

(TiZrNbTaMe)C 高熵陶瓷的 SEM 照片和元素面分布谱如图 2 所示。由图 2 可见, 除(TiZrNbTaW)C 体系外, 其余 3 种高熵陶瓷的孔隙率较低, 其致密度均超过 98% (见表 2), 且元素分布相对均匀。(TiZrNbTaCr)C 体系的能谱结果显示, 晶粒内 Ti、Zr、Nb 和 Ta 元素含量较高, 而 Cr 元素含量相对较低。对(TiZrNbTaCr)C 的元素含量进行进一步分析 (见图 3), 除 Cr 元素外, 其余 3 种金属元素在晶界和晶粒内部含量接近等摩尔比。然而, 在三叉晶界处, Cr 元素的含量约为晶粒内部的 6 倍, 同时其他 4 种元素在晶界处的含量低于晶粒内部的含量, 表明 Cr 元素在晶界处发生了显著的偏聚现象。这也再次印证由于(TiZrNbTaCr)C 陶瓷中的 Cr 元素含量较低, 其晶格常数表现出异常增大、偏离理论等摩尔比条件所计算晶格常数数值的现象。

透射电子显微镜(TEM)分析结果如图 4 所示。碳化物晶粒的晶体结构为面心立方结构(FCC)。晶界元素分布结果表明, 晶界处 Cr 元素偏聚现象明显, 而其他 4 种金属元素分布较为均匀, 这与 SEM-EDS 分析结果一致。高分辨率原子像可以观察到 Cr 元素偏聚的晶界处存在部分位错等缺陷。Cr 元素在晶界的偏聚可能与具有低熔点的铬碳化物有关。例如, Cr_3C_2 的熔点约为 1810 °C, 而烧结温度高达 2100 °C, 在烧结过程中铬碳化物可能形成液相并聚集在晶界处。此外, Cr 元素在高熵陶瓷的固溶度可能还受到成分的影响, 在所选的金属元素中, Cr 元素的原子直径最小, 因此, Cr 元素在(TiZrNbTaCr)C 体系的固溶度较低, 更倾向于偏聚到局部受压的晶界位置或形成第二相^[23-24]。对于(TiZrNbTaW)C 体系, 致密度较低的主要原因为碳热还原合成粉体中存

在局部团聚, 粉体烧结活性降低。与(TiZrNbTaMo)C 体系相比, (TiZrNbTaV)C 和(TiZrNbTaCr)C 体系的晶粒尺寸明显降低, 分别为 2.69 μm 和 5.39 μm 。表

明 V 与 Cr 元素添加有助于改善(TiZrNbTaMe)C 体系烧结性能, 同时抑制晶粒异常长大, 从而提高陶瓷的致密度并降低晶粒尺寸^[25]。

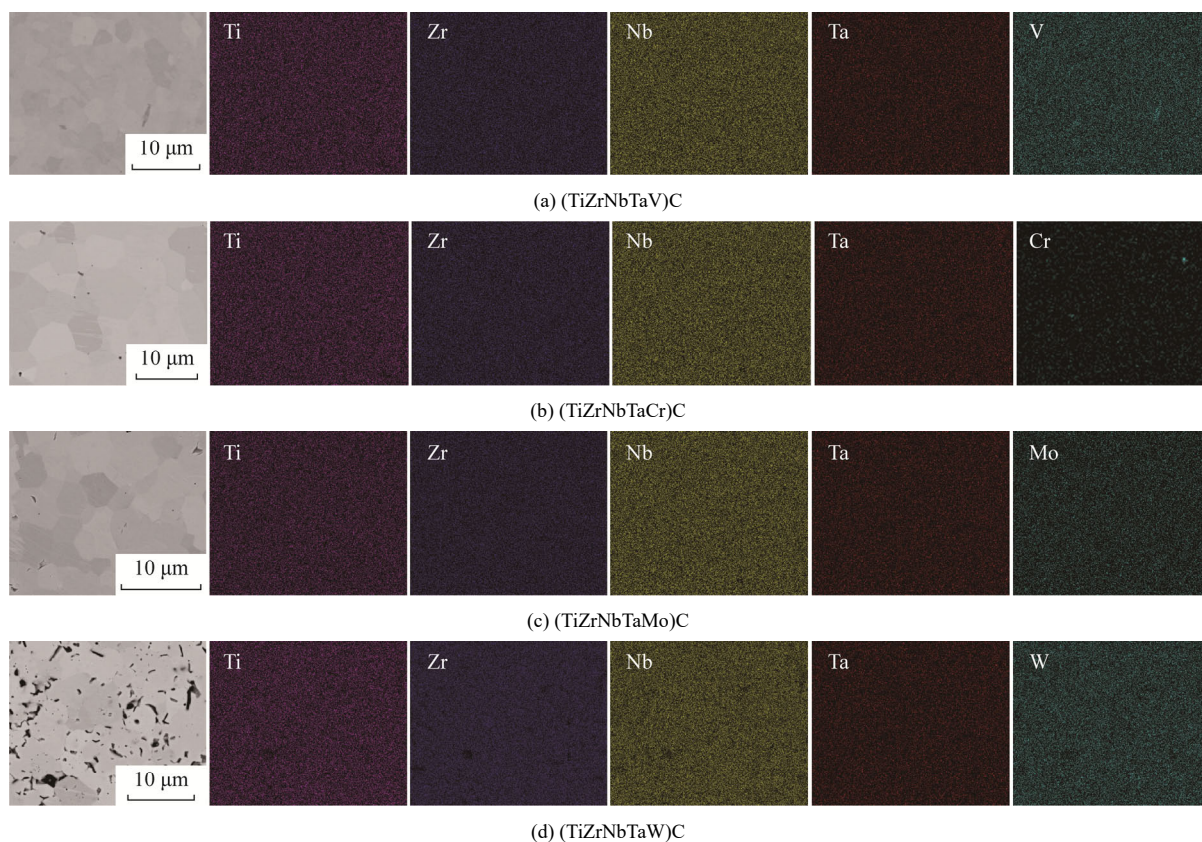


图 2 热压烧结制备的(TiZrNbTaMe)C 高熵陶瓷的 SEM 照片及元素面分布图

Fig. 2 SEM images and element distribution of (TiZrNbTaMe)C high-entropy ceramics prepared by hot pressing sintering

表 2 (TiZrNbTaMe)C 高熵陶瓷的致密度、平均晶粒尺寸和力学性能

Table 2 Relative density, average grain size and mechanical properties of (TiZrNbTaMe)C high-entropy ceramics

Samples	Relative density/%	Average grain size/ μm	Vicker's Hardness/GPa	Fracture Toughness/($\text{MPa}\cdot\text{m}^{1/2}$)	Lattice distortion/%
(TiZrNbTaV)C	98.4	2.69±0.82	21.3±0.7	3.68±0.12	4.21
(TiZrNbTaCr)C	99.1	5.39±2.41	29.8±1.1	3.71±0.17	4.87
(TiZrNbTaMo)C	98.6	8.80±3.00	25.3±0.3	3.28±0.12	2.99
(TiZrNbTaW)C	94.8		16.7±0.3	3.10±0.40	2.97

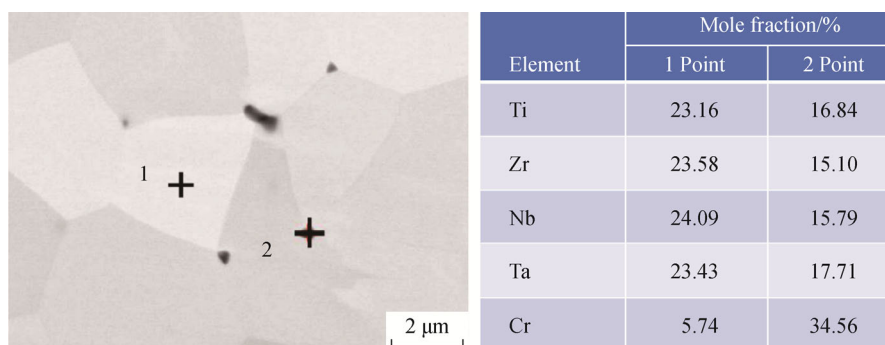


图 3 (TiZrNbTaCr)C 高熵陶瓷高倍 SEM 照片及元素点分析

Fig. 3 High magnification SEM images and elemental analysis of (TiZrNbTaCr)C high-entropy ceramics

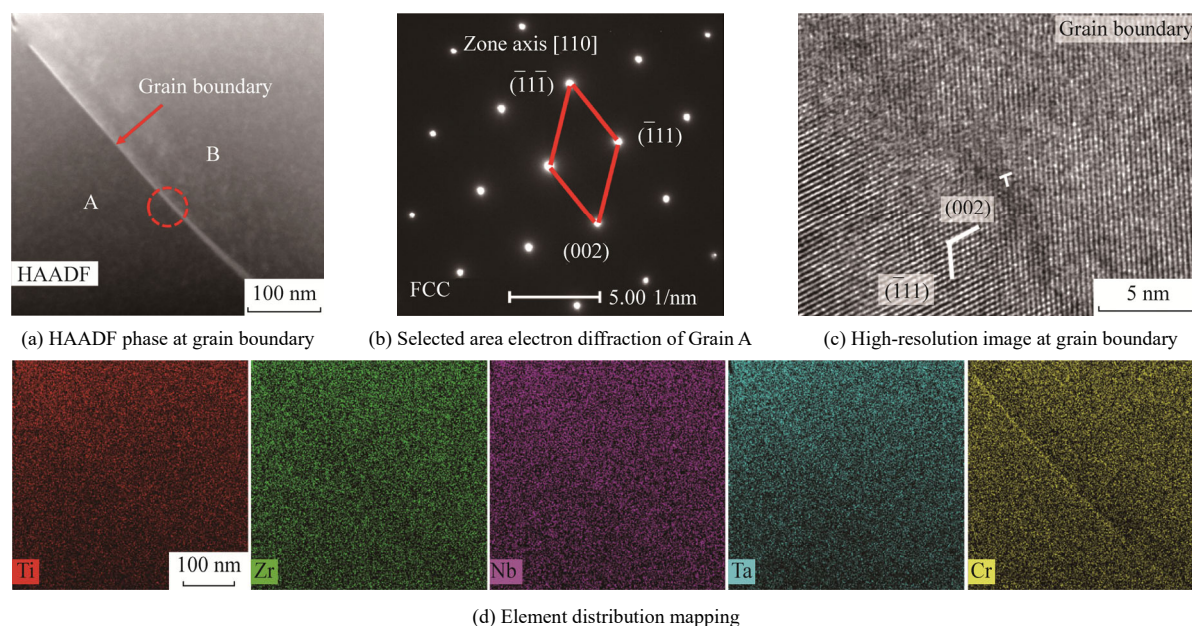


图 4 (TiZrNbTaCr)C 高熵陶瓷的 TEM 分析

Fig. 4 TEM analysis of (TiZrNbTaCr)C high-entropy ceramics

2.2 力学性能

(TiZrNbTaMe)C 高熵陶瓷的维氏硬度和断裂韧性汇总于表 2。由于(TiZrNbTaW)C 体系较低的致密度导致其维氏硬度较低; (TiZrNbTaCr)C 体系晶格畸变达到 4.87%, 远高于其他 3 种体系。由于 CrC 的晶格常数远低于其他单组元碳化物陶瓷, 因此尽管 Cr 元素并未完全固溶进碳化物晶粒中, 该体系仍具有较大的晶格畸变, 高晶格畸变使固溶强化效果显著增强, 使晶粒内的硬度得以提升。此外, 晶界处 Cr 元素偏聚形成的晶界相具有第二相增强效果, 并促进了碳化物高熵陶瓷的致密化。晶粒内固溶强化、晶界第二相增强以及该体系的高致密度均有利于材料硬度提高。

对于(TiZrNbTaV)C 和(TiZrNbTaMo)C 体系, 其致密度相近且元素分布均匀。根据 Hall-Petch 关系式^[26], 晶粒尺寸更小的(TiZrNbTaV)C 应具有更高的硬度。然而, (TiZrNbTaV)C 陶瓷的硬度却低于(TiZrNbTaMo)C 陶瓷。此外, (TiZrNbTaV)C 陶瓷的晶格畸变量也低于(TiZrNbTaMo)C 陶瓷。这表明陶瓷的硬度不仅取决于晶粒尺寸和晶格畸变, 还受到元素种类和弹性模量等本征因素的制约, 如元素种类和弹性模量。维氏硬度本征关系式如式 4 所示^[27]:

$$H_v = 0.92(G/B)^{1.137} G^{0.708} \quad (4)$$

式中: B 为体积模量(GPa); G 为剪切模量(GPa)。为更准确地评估陶瓷的硬度, 进一步通过理论计算比较高熵陶瓷的模量, 这将为探索高硬度高熵陶瓷体系提供有价值的参考。此外, (TiZrNbTaMe)C

高熵陶瓷的断裂韧性相近, 其原因为 4 种碳化物高熵陶瓷均缺乏有效的增韧机制, 均为单相材料, 因此其断裂韧性无明显变化。

2.3 Ti 与 Zr 元素含量对(TiZrNbTaCr)C 陶瓷中 Cr 元素分布的影响

之前的研究表明, 碳化物高熵陶瓷中 Cr 元素的晶内固溶度和晶界处的富集对于材料的力学性能、抗氧化性能以及抗水蒸气腐蚀性能等具有显著影响^[28-30]。在本工作中, 含 Cr 体系也表现出了最佳的综合性能, 因此, 探究 Cr 元素在碳化物高熵陶瓷中分布的影响因素是含 Cr 碳化物高熵陶瓷成分设计和性能优化的重要科学问题。目前关于碳化物高熵陶瓷晶内和晶界 Cr 元素含量的调控及可控制备的研究尚不深入。Cr 元素在晶界偏聚, 难以固溶进入碳化物晶粒中除了可能与低熔点铬碳化物相在晶界处聚集有关外, 还可能与金属元素之间的相互作用相关。为进一步揭示 Cr 元素在(TiZrNbTaMe)C 体系中固溶度较低的原因, 利用 DFT 计算得到过渡金属碳化物中 Cr 元素与各金属元素之间的相互作用系数(Ω)。 Ω_{Cr-Ti} 、 Ω_{Cr-Zr} 、 Ω_{Cr-Nb} 、 Ω_{Cr-Ta} 的数值分别为 24.677、143.363、63.299、49.878 kJ/mol, 数值越低, 形成固溶体的能力越强。其它 4 种元素之间的相互作用参数 Ω_{Ti-Zr} 、 Ω_{Ti-Nb} 、 Ω_{Ti-Ta} 、 Ω_{Zr-Nb} 、 Ω_{Zr-Ta} 、 Ω_{Nb-Ta} 分别为 55.178、-9.708、-39.739、3.927、3.427、-4.691 kJ/mol。由计算结果可知, Cr 元素与其他金属元素的相互作用参数数值较高, 表明 Cr 元素难以与其他金属元素形成固溶体, 从而偏向于在晶界处

富集。此外在前期的研究中发现,在 $\text{TiC-ZrC-Cr}_3\text{C}_2$ 体系中 Cr 元素更易富集在富 Ti 的区域,与 Zr 元素难以相互固溶^[31],该结果与 Cr 元素与 Ti 和 Zr 元素的相互作用参数的大小相吻合。根据此理论,碳化物高熵陶瓷中 Cr 元素的固溶度与其他金属元素的种类和含量密切相关。由于 Ti 元素和 Zr 元素与 Cr 元素之间的相互作用参数分别为最小和最大,可以推测 Ti 元素和 Zr 元素含量对 Cr 元素在碳化物高熵陶瓷中的固溶度具有更为明显的影响。因此,为调控 $(\text{TiZrNbTaCr})\text{C}$ 体系中的 Cr 元素含量及分布,设计制备不同 Ti 和 Zr 含量的 $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ 陶瓷($x=0, 0.2, 0.3$ 和 0.4)。在相同制备工艺下所制备的 $(\text{TiZrNbTaCr})\text{C}$ 体系的 XRD 分析结果表明(见图 5),4 种碳化物高熵陶瓷均为单相面心立方结构的碳化物固溶体。随着 x 值增加(即 Ti 元素含量增加),高熵陶瓷晶格常数逐渐减小,衍射峰峰位向右偏移。SEM 显微结构照片表明(见图 6),4 种高熵陶瓷中无明显气孔存在,较为致密,但在三叉晶界处可见不同衬度的第二相。Cr 元素在 4 种碳化物陶瓷中的固溶度分析结果表明(见图 7)。当 $x=0$ 时, $(\text{Zr}_{0.4}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ 陶瓷中 Cr 元素的固溶度仅为 3.18% (摩尔分数)。随着 x 值的增加, Cr 元素固溶度逐渐提高, $x=0.4$ 时,由于体系中不含 Zr 元素, Cr 元素在晶粒内的固溶度达到最大值,约为 8.68%。以上结果充分表明, Ti 元素含量增加和 Zr 元素含量减少有利于提高 Cr 元素在碳化物高熵陶瓷中的固溶度。

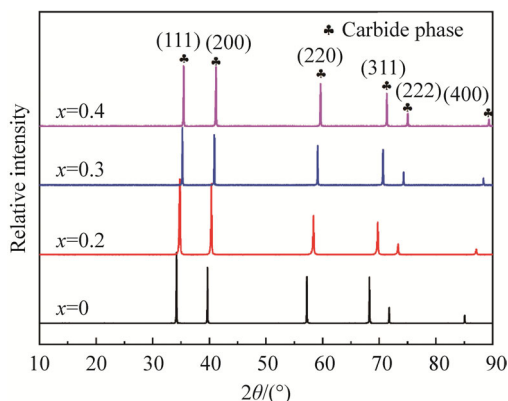


图 5 $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ 陶瓷的 XRD 谱
Fig. 5 XRD patterns of $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ ceramics

3 结论

采用热压烧结方法制备 $(\text{TiZrNbTaMe})\text{C}$ ($\text{Me}=\text{V}, \text{Cr}, \text{Mo}, \text{W}$) 4 种碳化物高熵陶瓷,详细探究了碳化物高熵陶瓷中 Me 元素对微结构演变和元素分布的

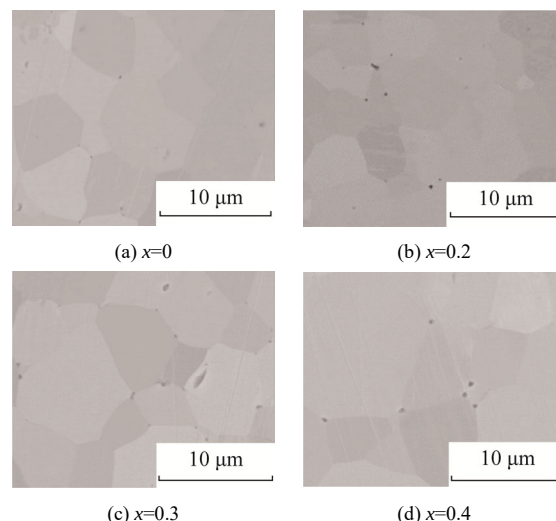


图 6 $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ 陶瓷 SEM 照片
Fig. 6 SEM images of $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ ceramics

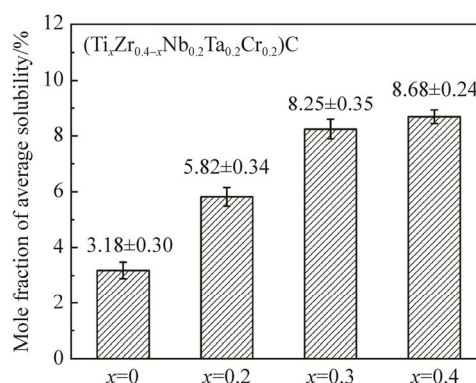


图 7 Cr 元素在 $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ 陶瓷中的固溶度
Fig. 7 Solid solubility of Cr in $(\text{Ti}_x\text{Zr}_{0.4-x}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ ceramics

影响。4 种碳化物高熵陶瓷均为面心立方结构,其中 V、Cr 和 Mo 元素有利于促进烧结致密化,致密度均超过 98%。除 $(\text{TiZrNbTaCr})\text{C}$ 外,其他高熵陶瓷体系中元素分布均匀。 $(\text{TiZrNbTaCr})\text{C}$ 陶瓷中 Cr 元素在晶界处存在明显偏聚现象,导致晶粒内部的 Cr 含量较低。Cr 元素在碳化物高熵陶瓷中的固溶度与金属元素种类和含量密切相关。提升 Ti 元素含量有助于提升 Cr 元素在碳化物高熵陶瓷中的固溶度,其中 $(\text{Ti}_{0.4}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Cr}_{0.2})\text{C}$ 体系的 Cr 元素在晶粒内的固溶度达到最大值,约为 8.68%。 $(\text{TiZrNbTaCr})\text{C}$ 陶瓷具有最佳的综合力学性能,其维氏硬度和断裂韧性分别达到 29.8 GPa 和 $3.71 \text{ MPa} \cdot \text{m}^{1/2}$ 。

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Microstructural Evolution and Elemental Distribution of (TiZrNbTaMe)C (Me=V, Cr, Mo, W) High-Entropy Ceramics

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Extended Abstract

Introduction Ultra-high temperature ceramics include a series of high melting point materials, such as transition metal carbides,

nitrides and borides, especially transition metal carbides with excellent high-temperature mechanical properties, stable physico-chemical properties, corrosion resistance and radiation resistance, showing broad prospects for application in the hypersonic aircraft, rocket engines, fourth-generation nuclear reactor, and other extreme environments. However, the traditional single-component transition metal carbide ceramics have been unable to meet the emerging requirements under extreme environments, there is an urgent need to develop a new high-performance material under ultra-high temperature. In recent years, the concept of multi-component “high entropy” has greatly expanded the scope of material composition design and property optimization. Compared with single-component carbides, multi-component ceramics perform better in terms of overall properties, including hardness, creep resistance, oxidation resistance and radiation resistance. These improvements mainly result from their complex component composition, electronic structure and lattice distortion. At present, the influence of elemental species on the microstructure evolution and mechanical properties of carbide high-entropy ceramics is not reported. In this paper, (TiZrNbTaMe)C (Me=V, Cr, Mo, W) high-entropy ceramics are prepared by hot press sintering, and the effects of Me elemental species on the physical phase, microstructure evolution, and mechanical properties of (TiZrNbTaMe) high-entropy ceramics are investigated.

Methods In this work, (TiZrNbTaMe)C (Me=V, Cr, Mo, W) high-entropy ceramics with equimolar ratio were prepared by carbothermal reduction-assisted hot pressing using transition metal oxides and carbon black as raw materials. The oxides and carbon black were mixed using a planetary ball mill (Fritsch, model P4, Germany). Carbide powders were obtained by carbothermal reduction under vacuum using a pressureless sintering furnace (WS0404, Ningxia Sincere Co. Ltd., China) with a process of 1500 °C /1 h. The synthesized carbide powders were loaded into graphite molds, and the ceramic samples were prepared by a two-step hot pressing method (AVS, model 1540, USA). The samples were held at 1850 °C for 1 h, and then at 2100 °C for 0.5 h under pressure of 30 MPa or 10 Pa. Phase analysis was carried out by X-ray diffractometry (XRD; D/max-B, Rigaku, Japan) using Cu-K α rays. Scanning electron microscopy (SEM; Quanta 200FEG, USA) was used to analyze the microstructure and elemental content and distribution. Transmission electron microscopy (TEM; Talos F200X, USA) was used to analyze the microstructure, elemental content and distribution, and grain boundary characteristics of the materials. The relative densities of the samples were measured using image analysis software (Photoshop, Adobe, USA) based on the pores in the SEM photographs. Vickers hardness was measured using a Vickers hardness tester (HVS-30) at a load of 9.8 N with a holding time of 15 s. Fracture toughness was also measured using the indentation method. The interaction parameters between the metal elements were also calculated using DFT calculation.

Results and discussion The high-entropy ceramics are all characterized by an FCC crystal structure. Except for the (TiZrNbTaW)C sample, the porosity of the other three high entropy ceramics is low, and their density exceeds 98% and the element distribution is relatively uniform. Compared with the (TiZrNbTaMo)C sample, the grain sizes of the (TiZrNbTaV)C and (TiZrNbTaCr)C samples are significantly reduced, which are 2.69 μm and 5.39 μm , respectively. This shows that the addition of V and Cr elements helps to improve the sintering properties of the (TiZrNbTaMe)C system and inhibit grain growth. The element content analysis results of (TiZrNbTaCr)C show that the Cr element segregates significantly at the grain boundaries, while the other four metal elements are distributed more evenly. The segregation of Cr at the grain boundaries may be related to chromium carbides with low melting points. For example, the melting point of Cr $_3$ C $_2$ is about 1810 °C, while the sintering temperature is as high as 2100 °C, suggesting that chromium carbides may form a liquid phase and aggregate at the grain boundaries during sintering. In addition, the complex composition of high-entropy ceramics may also affect the solid solubility of Cr. The interaction coefficients between Cr and each metal element in transition metal carbides show that the interaction parameter values of Cr and other metal elements are high. It is difficult for Cr to form a solid solution with other metal elements, thus tending to be enriched at the grain boundaries. Therefore, (Ti $_x$ Zr $_{0.4-x}$ Nb $_{0.2}$ Ta $_{0.2}$ Cr $_{0.2}$)C ceramics with different Ti and Zr contents ($x=0, 0.2, 0.3$ and 0.4) were designed and prepared. The effect of Ti content on the solid solubility of Cr in the (TiZrNbTaCr)C sample was investigated. As the x value increases from 0 to 0.4, the solid solubility of Cr in the grains increases from 3.18% to 8.68%. It shows that the increase of Ti content is beneficial to improve the solid solubility of Cr. In addition, for the (TiZrNbTaCr)C sample, the high lattice distortion leads to solid solution strengthening in the grains and the high density of the system increases its hardness, which has the best mechanical properties. Its Vickers hardness and fracture toughness reach 29.8 GPa and 3.71 MPa·m $^{1/2}$, respectively.

Conclusions The four (TiZrNbTaMe)C (Me=V, Cr, Mo, W) high-entropy ceramics are all face-centered cubic structures, and the elements are uniformly distributed in the high-entropy ceramic systems except for the (TiZrNbTaCr)C sample. The (TiZrNbTaCr)C sample is also characterized by the presence of a significant Cr segregation at grain boundaries, resulting in a low Cr content inside the grains. The (TiZrNbTaCr)C sample has the best overall mechanical properties, with the Vickers hardness and fracture toughness reaching 29.8 GPa and 3.71 MPa·m $^{1/2}$, respectively. In-depth studies show that the solid solubility of Cr element in high-entropy carbide ceramics is closely related to the species and content of metal elements. Enhancing the content of Ti element helps to improve the solid solubility of Cr element in high-entropy carbide ceramics, in which the solid solubility of Cr element in the grain of (Ti $_{0.4}$ Nb $_{0.2}$ Ta $_{0.2}$ Cr $_{0.2}$)C system reaches the maximum value of about 8.68%.

Keywords transition metal carbides; high-entropy ceramics; microstructure evolution; mechanical properties