



非晶合金的磁热效应

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摘要 随着全球变暖与温室效应等问题日益突出, 人类迫切需求环保且高效的新型制冷技术, 基于磁热效应的磁制冷技术具有满足以上要求巨大前景, 然而该技术目前主要受限于寻找适合磁制冷循环且具有大磁热性能的材料, 非晶合金是一种在磁制冷领域极具发展前景的材料, 近年来受到许多关注. 本文整理和总结磁热非晶合金相关性能以及应用前景, 磁热非晶合金包括稀土基非晶合金、多主元稀土非晶合金、过渡族元素体系非晶合金、非晶复合材料.

关键词 非晶合金, 稀土元素, 过渡族元素, 磁热性能

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1 引言

目前制冷耗电约占全球总耗电量的20%, 制冷所产生的CO₂占世界总CO₂排放量的10%^[1], 并且到2050年全球对制冷需求将增加3倍以上(<https://www.iea.org/reports/the-future-of-cooling>), 因此亟需对环境友好并且工作效率较高的制冷技术. 基于磁热效应(Magnetocaloric effect)的磁制冷(Magnetic refrigeration)技术工作时不产生温室气体, 并且其工作效率可达理想卡诺循环的30%–60%^[2], 因此, 该技术得到广泛关注^[3].

磁热效应是磁性材料在施加和撤除外加磁场条件下发生的一种物理现象, 其性能通常由等温磁熵变和绝热温变来表示^[4]. 磁材料总熵由各子系统熵组成, 若

仅考虑晶格系统和自旋系统, 则材料总熵表达式如下所示:

$$S = S_L + S_M, \quad (1)$$

其中, S 为总熵, S_L 为晶格熵, S_M 为磁熵.

磁性材料的晶格和自旋系统间存在着密切的能量交换. 在绝热条件下, 磁性材料总熵值不变, 由此, 上式可改写为

$$\Delta S_L(\Delta H) + \Delta S_M(\Delta H) = 0, \quad (2)$$

其中, $\Delta S_L(\Delta H)$ 为绝热磁熵变, $\Delta S_M(\Delta H)$ 为绝热晶格熵变, ΔH 为磁场变化. 传统磁性材料通常具有铁磁-顺磁相变, 磁相变过程中材料结构不发生改变, 在施加外磁场的条件下, 材料内未成对自旋电子趋向于向外加磁

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场方向转动, 磁熵值降低, $\Delta S_M(\Delta H) < 0$, 并导致 $\Delta S_L(\Delta H) > 0$, 即材料绝热温度上升, $\Delta T_{ad} > 0$. 等温条件下, 材料 $\Delta S_L(\Delta H) = 0$, 因此, 材料总熵变值等于磁熵变值, 磁热效应可由磁熵变值衡量, 磁熵变最大值通常在磁性材料磁相变温度附近.

磁热材料的开发是制约磁制冷技术发展的主要因素. 根据材料相变类型, 磁热材料通常可分为一级相变和二级相变材料, 一级相变材料通常具有较高的磁熵变值, 如在 5 T 变化磁场条件下, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ 合金最大磁熵变值为 $19.6 \text{ J kg}^{-1} \text{ K}^{-1}$ ^[5], $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$ 合金最大磁熵变值为 $20.3 \text{ J kg}^{-1} \text{ K}^{-1}$ ^[6], $\text{MnFeP}_{0.45}\text{As}_{0.55}$ 最大磁熵变值为 $18 \text{ J kg}^{-1} \text{ K}^{-1}$ ^[7], 但此类材料由于其自身所具有的结构相变导致不可避免的磁滞与热滞, 并且此类材料制冷温区较窄, 部分材料使用有毒元素, 从而导致此类材料在实际磁制冷工况中存在不可长时间使用以及安全等问题, 限制其在实际制冷工况中的应用.

二级相变材料通常具有较宽的制冷温区, 不具有磁滞与热滞, 因此二级相变材料适用于磁制冷循环. Gd 金属为典型二级相变材料, 并已在众多磁制冷样机进行应用, 但 Gd 金属价格昂贵且易氧化, 并具有二级相变材料中普遍存在的磁熵变值较低问题.

非晶合金具有不同于晶体合金的结构, 如非晶合金具有短程有序但长程无序的原子结构, 使得该类合金具有拓扑无序以及化学无序特征^[8,9], 以及合金不具有位错、晶界等缺陷结构, 这导致非晶合金普遍具有较高的强度、硬度和抗腐蚀性能^[10,11]. 非晶合金作为结构和功能材料具有广阔的应用前景, 磁性非晶合金是非晶合金研究领域的一个重要分支, 此类非晶合金可分为含稀土非晶合金过渡族元素体系非晶合金. 磁性非晶合金在软磁材料与磁热材料领域有着良好应用前景^[9]. 磁性非晶合金普遍为二级相变材料, 并且非晶合金磁相变温度可在较大范围内调节^[12,13], 综合上述非晶合金结构和性能特点, 其在用作磁热材料方面展现出显著优势. 因此, 磁热非晶合金是非晶合金领域的研究热点.

值得注意的是, 近年来, 多主元合金设计理念被引入到磁热材料设计中, 多主元合金通常指合金由 5 种或 5 种以上主要元素组成, 混合熵 ($\Delta S_{\text{mix}} \geq 1.5R$ (R 为摩尔气体常数, $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$)), 或合金含有 5 种或 5 种以上主要元素, 所有元素含量在 5 at.%–35 at.% 之间^[14–16]. 多主元合金目前已展现出优异的性能, 如力

学性能^[17]和磁热性能^[18,19]. 例如具有二级相变特征的 $\text{Gd}_{20}\text{Tb}_{20}\text{Dy}_{20}\text{Ho}_{20}\text{Er}_{20}$ 合金在 5 T 变化磁场条件下的最大磁熵变值为 $8.6 \text{ J kg}^{-1} \text{ K}^{-1}$ ^[19]. 多主元合金具有特殊的成分(原子在晶格中随机分布使得合金化学无序)和结构特征^[20], 有学者将多主元合金设计理念引入到非晶合金体系中, 从而得到多主元非晶合金, 此类合金兼具以上两种合金的一些特点, 如拓扑无序与化学无序, 这使得此类合金相比非晶合金和多主元合金具有一些较优异的性能, 其中包括磁热性能^[21].

埃里克森制冷循环是一种高效制冷循环, 理想埃里克森循环要求磁热材料需具有在宽温区的恒定磁熵变值(平台状磁热曲线)^[22]. 单一磁性材料难以满足这一要求, 而具有多个磁转变温度的非晶复合材料具有获得平台状磁热曲线的巨大可能性. 但对材料进行机械叠加后, 合金虽具有类平台状磁热曲线, 但复合材料磁热性能为各组分磁热性能的平均结果, 表明各组分间无相互作用. 而非晶复合材料非晶与晶体两相间交互作用可有效提升材料的磁热性能^[13].

含稀土非晶合金又可分为稀土基非晶合金、多主元稀土非晶合金. 本文将综述磁热非晶合金所涉及的稀土基非晶合金、多主元稀土非晶合金、过渡族元素体系非晶合金和非晶复合材料相关研究进展.

2 非晶合金磁热性能

2.1 稀土基非晶合金磁热性能

重稀土元素普遍具有较大的等效磁矩, 这有利于合金具有优异的磁热性能. 稀土基非晶合金磁热性能已得到广泛报道.

2013 年, Huo 等人^[23]研究一系列 Tm 基非晶合金—— $\text{Tm}_{39}\text{RE}_{16}\text{Co}_{20}\text{Al}_{25}$ ($\text{RE} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$), 所有合金均具有完全非晶结构, 合金居里温度在 2–12 K 范围内, 5 T 变化磁场条件下, $\text{Tm}_{39}\text{Ho}_{16}\text{Co}_{20}\text{Al}_{25}$ 最大磁熵变值最高, 为 $18.3 \text{ J kg}^{-1} \text{ K}^{-1}$ (图 1), 这一数值高于二级相变典型材料 Gd 金属的最大磁熵变值 $10.6 \text{ J kg}^{-1} \text{ K}^{-1}$ (5 T)^[5], 并与其他二级相变典型材料性能数值接近, 如 GdCoC 合金(最大磁熵变值 $20 \text{ J kg}^{-1} \text{ K}^{-1}$ (2 T)^[24])、 $\text{Gd}_2\text{CuTiO}_6$ 双钙钛矿氧化物(最大磁熵变值 $21.2 \text{ J kg}^{-1} \text{ K}^{-1}$ (3 T)^[25]), PrZnSi 和 NdZnSi 合金(最大磁熵变值分别为 16.27 和 $15.42 \text{ J kg}^{-1} \text{ K}^{-1}$ (7 T)^[26]), 非常接近于一级相变典型材料

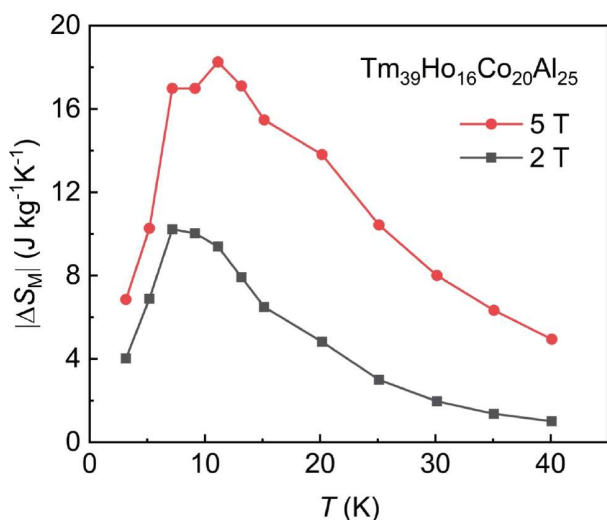


图 1 (网络版彩图) $\text{Tm}_{39}\text{Ho}_{16}\text{Co}_{20}\text{Al}_{25}$ 非晶合金在 2 和 5 T 变化磁场下的磁熵变曲线. 图片来自文献[23]

Figure 1 (Color online) Magnetic entropy changes as a function of temperature under the magnetic field changes of 2 and 5 T for $\text{Tm}_{39}\text{Ho}_{16}\text{Co}_{20}\text{Al}_{25}$ amorphous alloy. Figure is taken from ref. [23].

$\text{Gd}_5\text{Si}_2\text{Ge}_2$, $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$, $\text{MnFeP}_{0.45}\text{As}_{0.55}$ 的最大磁熵变值 18–20.3 $\text{J kg}^{-1} \text{K}^{-1}$ (5 T)^[5–7].

磁性过渡族元素通常与合金中稀土元素形成反铁磁作用, 从而降低合金磁热性能, 对此, Ma 等人^[27]利用无磁性的 Cu 进行成分设计, 并利用有利于非晶形成能力的二元深共晶成分设计并得到 $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ 薄带, 薄带具有完全非晶结构(图 2(a)), 由于合金中 Cu 与 Al 无磁性, 从而导致合金中仅存在 RKKY 磁交互作用, 这导致合金具有极低的居里温度 4.4 K (图 2(b)), 合金

在 5 T 变化磁场下最大磁熵变值为 13.4 $\text{J kg}^{-1} \text{K}^{-1}$ (图 2(c)), 合金具有在极低温制冷领域的应用前景.

2.2 多主元稀土非晶合金磁热性能

Huo 等人^[28]于 2013 年最早开发出多主元稀土非晶合金成分—— $\text{Ho}_{20}\text{Er}_{20}\text{RE}_{20}\text{Co}_{20}\text{Al}_{20}$ (RE = Gd, Dy, Tm), 所有合金均具有完全非晶结构, $\text{Ho}_{20}\text{Er}_{20}\text{TM}_{20}\text{Co}_{20}\text{Al}_{20}$ 合金的最大磁熵变值在 5 T 变化磁场下达 15 $\text{J kg}^{-1} \text{K}^{-1}$ (图 3(a)), 并且所有合金均具有二级相变特征. 该团队还对 $\text{Gd}_{20}\text{Tb}_{20}\text{Dy}_{20}\text{TM}_{20}\text{Al}_{20}$ (TM = Fe, Co, Ni)^[21]以及 $\text{Gd}_{20}\text{Ho}_{20}\text{Er}_{20}\text{TM}_{20}\text{Al}_{20}$ (TM = Fe, Co, Ni)^[29]进行研究, 合金磁性能与磁热性能结果表明, 合金居里温度可在 25–112 K 这一大温度区间范围内调节(图 3(b)和(c)), $\text{Gd}_{20}\text{Ho}_{20}\text{Er}_{20}\text{Co}_{20}\text{Al}_{20}$ 合金的最大磁熵变值最高, 为 10.2 $\text{J kg}^{-1} \text{K}^{-1}$ (5 T)(图 3(c)和(d)), 并且拓扑无序与化学无序作用使得这些多主元稀土非晶合金具有较宽的制冷温区, 最宽为 116 K.

此外, 该团队^[30]将多主元非晶合金主要元素数量增加至 10, 获得 $\text{Gd}_{10}\text{Tb}_{10}\text{Dy}_{10}\text{Ho}_{10}\text{Er}_{10}\text{Y}_{10}\text{Ni}_{10}\text{Co}_{10}\text{Ag}_{10}\text{Al}_{10}$ 合金, 并且合金具有完全非晶结构, 居里温度为 24 K, 5 T 变化磁场条件下最大磁熵变值为 10.64 $\text{J kg}^{-1} \text{K}^{-1}$ (图 4(a)), 最大绝热温变达 6.66 K (图 4(b)).

以上多主元磁热合金元素比例均为等比例, 这些合金通常被称为第一代多主元磁热合金, 目前多主元磁热合金已发展至第二代, 即合金元素比例为非等比, 这为合金成分设计开启广阔的发展空间, 第二代多主

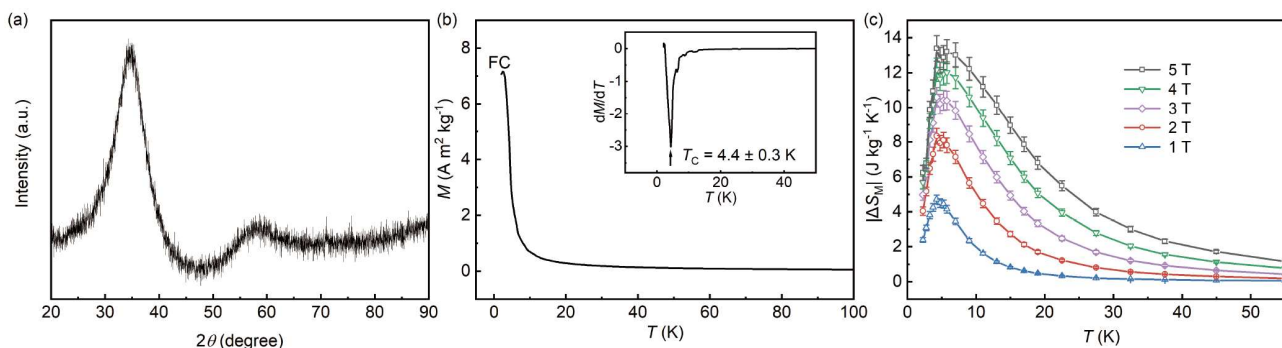


图 2 (网络版彩图) (a) $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ 薄带 X 射线衍射谱. (b) $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ 薄带磁化强度 (M) 随温度 (T) 变化曲线, 插图显示 dM/dT 随温度变化曲线. (c) $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ 薄带磁熵变随温度变化曲线(变化磁场条件为 1, 2, 3, 4 和 5 T). 图片来自文献[27]

Figure 2 (Color online) (a) X-ray diffraction pattern for the $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ ribbon. (b) Magnetization (M) as a function of temperature (T) of $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ ribbon with the inset showing the dM/dT - T curve. (c) The temperature dependence of magnetic entropy changes for $(\text{Tm}_{67}\text{Cu}_{33})_{80}\text{Al}_{20}$ ribbon under the magnetic field changes of 1, 2, 3, 4, and 5 T. Figures are taken from ref. [27].

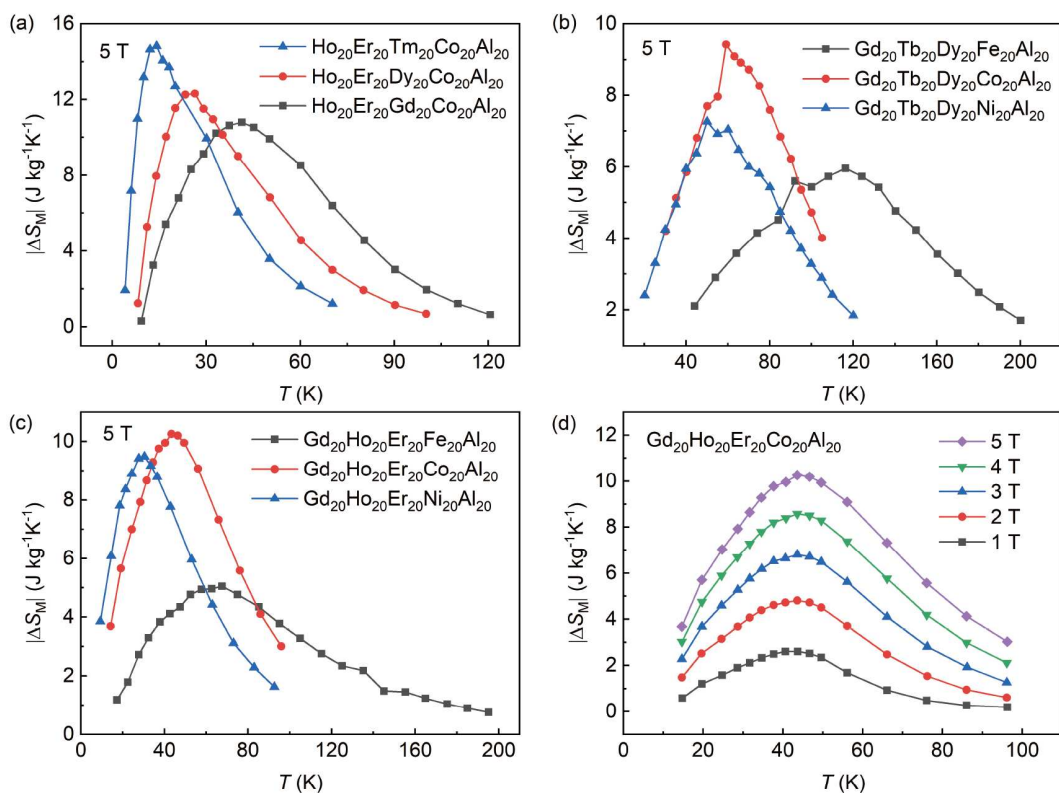


图 3 (网络版彩图) (a) $\text{Ho}_{20}\text{Er}_{20}\text{RE}_{20}\text{Co}_{20}\text{Al}_{20}$ ($\text{RE} = \text{Gd}, \text{Dy}, \text{Tm}$)合金在5 T变换磁场条件下磁熵变随温度变化曲线. (b) $\text{Gd}_{20}\text{Tb}_{20}\text{Dy}_{20}\text{TM}_{20}\text{Al}_{20}$ ($\text{TM} = \text{Fe}, \text{Co}, \text{Ni}$)合金在5 T变换磁场条件下磁熵变随温度变化曲线. (c) $\text{Gd}_{20}\text{Ho}_{20}\text{Er}_{20}\text{TM}_{20}\text{Al}_{20}$ ($\text{TM} = \text{Fe}, \text{Co}, \text{Ni}$)合金在5 T变换磁场条件下磁熵变随温度变化曲线. (d) $\text{Gd}_{20}\text{Ho}_{20}\text{Er}_{20}\text{Co}_{20}\text{Al}_{20}$ 合金磁熵变随温度变化曲线(变化磁场条件为1, 2, 3, 4和5 T). 图片来自文献[21,28,29]

Figure 3 (Color online) (a) The temperature dependence of magnetic entropy changes for $\text{Ho}_{20}\text{Er}_{20}\text{RE}_{20}\text{Co}_{20}\text{Al}_{20}$ ($\text{RE} = \text{Gd}, \text{Dy}, \text{and Tm}$) alloys under a magnetic field change of 5 T. (b) Magnetic entropy changes as a function of temperature under a magnetic field change of 5 T for $\text{Gd}_{20}\text{Tb}_{20}\text{Dy}_{20}\text{TM}_{20}\text{Al}_{20}$ ($\text{TM} = \text{Fe}, \text{Co}, \text{and Ni}$) alloys. (c) The temperature dependence of magnetic entropy changes for $\text{Gd}_{20}\text{Ho}_{20}\text{Er}_{20}\text{TM}_{20}\text{Al}_{20}$ ($\text{TM} = \text{Fe}, \text{Co}, \text{and Ni}$) alloys under a magnetic field change of 5 T. (d) Magnetic entropy changes as a function of temperature under the magnetic field changes of 1, 2, 3, 4 and 5 T for $\text{Gd}_{20}\text{Ho}_{20}\text{Er}_{20}\text{Co}_{20}\text{Al}_{20}$ alloys. Figures are taken from refs. [21,28,29].

元磁热合金突破第一代多主元磁热合金的性能限制^[31].

Yin等人^[32]利用共晶比例混合法设计并制备 $\text{RE}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24}$ ($\text{RE} = \text{Gd}, \text{Dy}, \text{Ho}$)多主元合金, 合金均具有完全非晶结构, 相比于具有非晶纳米晶结构的 $\text{Gd}_{25}\text{Tb}_{25}\text{Co}_{25}\text{Al}_{25}$ 合金, 共晶比例混合法所利用的二元深共晶成分有利于提升合金的玻璃形成能力(图5(a)–(d)), $\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24}$ 合金具有三种设计的合金中最宽的制冷温区(图5(e)), 这源于此合金具有在112–205 K温区内最大的团簇种类分散度(最为无序的结构, 图5(f))以及其临界指数 β 最接近于0.5.

2.3 过渡族元素体系非晶合金磁热性能

Li等人^[33]获得具有完全非晶结构的 $(\text{Fe}_{11.4}\text{Si}_{1.6}-$

$\text{La})_{(96-x)/14}\text{B}_x\text{Nb}_4$ ($x = 14.8, 19, 23.2$)合金, 合金居里温度位于491–504 K范围内, 即使在较大外磁场下, 合金具有极小的磁滞回线, 合金5 T变化磁场下最大磁熵变值位于2.03–2.67 $\text{J kg}^{-1} \text{K}^{-1}$ 区间内(图6), 设计的 $(\text{Fe}_{11.4}-\text{Si}_{1.6}\text{La})_{(96-x)/14}\text{B}_x\text{Nb}_4$ ($x = 14.8, 19, 23.2$)具有极宽的制冷温区, 最宽可达182 K.

Li等人^[34]设计Fe基非晶合金 $(\text{Fe}_{0.71}\text{RE}_{0.05}-\text{B}_{0.24})_{96}\text{Nb}_4$ ($\text{RE} = \text{Tb}, \text{Ho}, \text{Tm}$), 所有合金居里温度均高于400 K, Tm掺杂合金的最大磁熵变值最高, 在1.5 T变化磁场条件下为1.21 $\text{J kg}^{-1} \text{K}^{-1}$ (图7), 这与大多数Nanoperm型合金磁熵变值接近.

该团队^[35]选择 $(\text{Fe}_{0.71}\text{Tm}_{0.05}\text{B}_{0.24})_{96}\text{Nb}_4$ 进行进一步的成分调整, 从而得到 $(\text{Fe}_{0.76-x}\text{Tm}_x\text{B}_{0.24})_{96}\text{Nb}_4$ ($x = 0, 0.01, 0.05, 0.1, 0.17, 0.18$)合金, 当 $x < 0.18$ 时, 合金具有

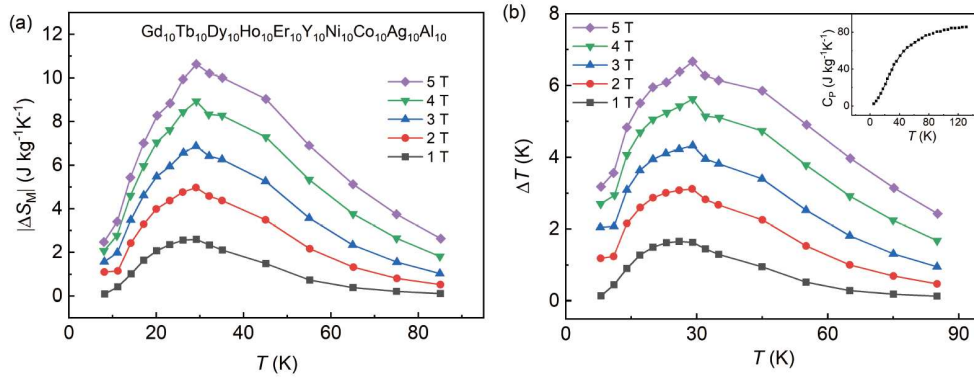


图 4 (网络版彩图) Gd₁₀Tb₁₀Dy₁₀Ho₁₀Er₁₀Y₁₀Ni₁₀Co₁₀Ag₁₀Al₁₀合金(a) 磁熵变值随温度变化曲线(变化磁场条件为1, 2, 3, 4和5 T)和(b) 绝热温变随温度变化曲线. 插图为无磁场条件下合金热容随温度变化曲线. 图片来自文献[30]

Figure 4 (Color online) (a) Magnetic entropy changes and (b) adiabatic temperature changes as a function of temperature under the magnetic field changes of 1, 2, 3, 4, and 5 T for the Gd₁₀Tb₁₀Dy₁₀Ho₁₀Er₁₀Y₁₀Ni₁₀Co₁₀Ag₁₀Al₁₀ alloy. The inset shows the temperature dependence of heat capacity under 0 T. Figures are taken from ref. [30].

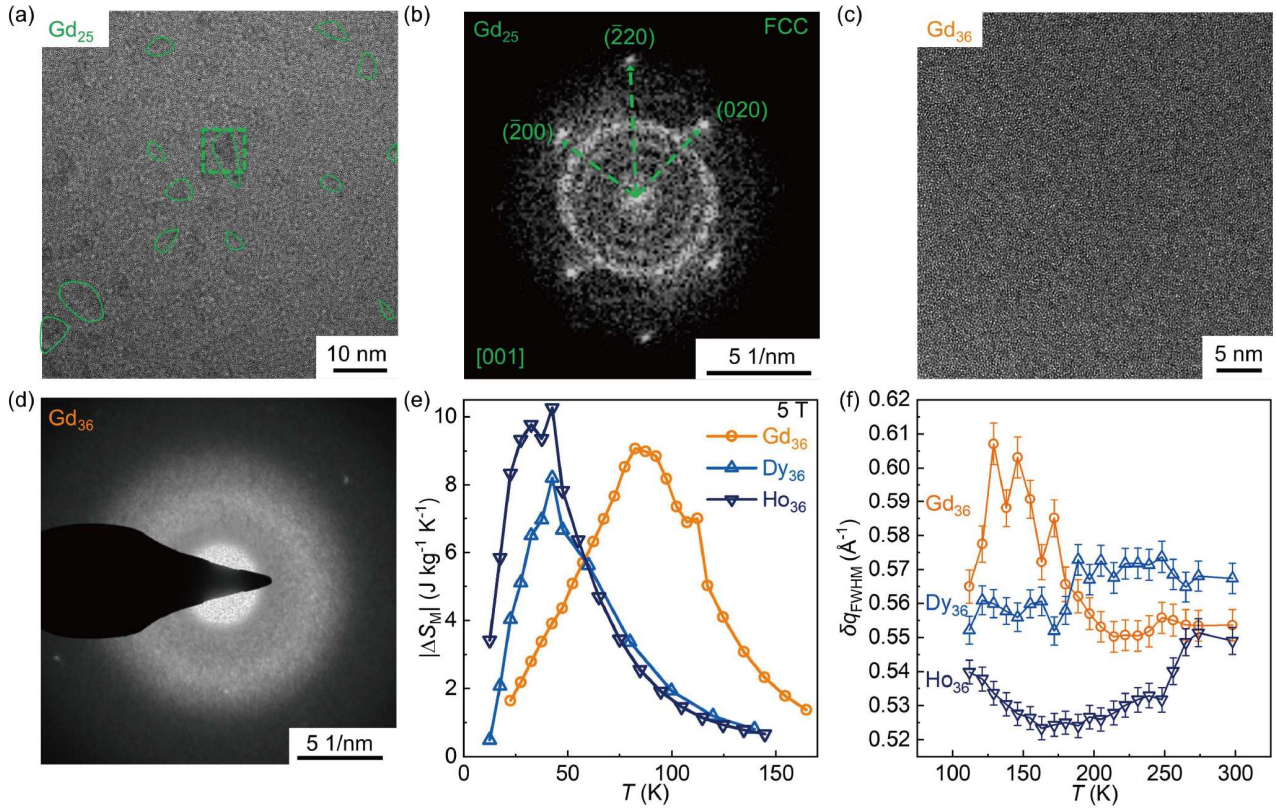


图 5 (网络版彩图) Gd₂₅Tb₂₅Co₂₅Al₂₅合金(a) 高分辨透射电镜显微图和(b) 选区电子衍射花样结果. Gd₃₆Tb₂₀Co₂₀Al₂₄合金(c) 高分辨透射电镜显微图和(d)选区电子衍射花样结果. (e) 5 T变化磁场条件下, RE₃₆Tb₂₀Co₂₀Al₂₄ (RE = Gd, Dy, Ho)合金磁熵变随温度变化曲线. (f) RE₃₆Tb₂₀Co₂₀Al₂₄ (RE = Gd, Dy, Ho)合金同步辐射曲线第一衍射峰半高宽随温度变化曲线. 图片来自文献[32]

Figure 5 (Color online) (a) The high-resolution transmission electron microscope image and (b) selected area electron diffraction result of Gd₂₅Tb₂₅Co₂₅Al₂₅. (c) The high-resolution transmission electron microscope image and (d) selected area electron diffraction result of Gd₃₆Tb₂₀Co₂₀Al₂₄ alloys. (e) The temperature dependence of magnetic entropy changes for RE₃₆Tb₂₀Co₂₀Al₂₄ (RE = Gd, Dy, and Ho) alloys under a magnetic field change of 5 T. (f) The temperature dependence of the full width at half maximum (FWHM) of the first diffraction peak in the synchrotron radiation curves of RE₃₆Tb₂₀Co₂₀Al₂₄ alloys (RE = Gd, Dy, and Ho) alloys. Figures are taken from ref. [32].

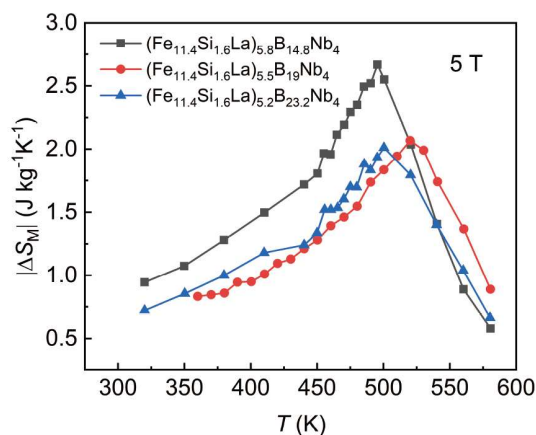


图 6 (网络版彩图) $(\text{Fe}_{11.4}\text{Si}_{1.6}\text{La})_{96-x/14}\text{B}_x\text{Nb}_4$ ($x = 14.8, 19, 23.2$)合金在5 T变化磁场条件下磁熵变随温度变化曲线. 数据来自文献[33]

Figure 6 (Color online) The temperature dependence of magnetic entropy changes for $(\text{Fe}_{11.4}\text{Si}_{1.6}\text{La})_{96-x/14}\text{B}_x\text{Nb}_4$ ($x = 14.8, 19$, and 23.2) alloys under a magnetic field change of 5 T. Data are taken from ref. [33].

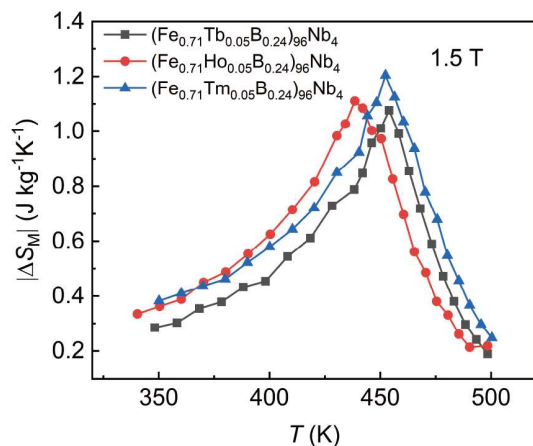


图 7 (网络版彩图) $(\text{Fe}_{0.71}\text{RE}_{0.05}\text{B}_{0.24})_{96}\text{Nb}_4$ (RE = Tb, Ho, Tm)合金在1.5 T变化磁场条件下磁熵变随温度变化曲线. 图片来自文献[34]

Figure 7 (Color online) The temperature dependence of magnetic entropy changes for $(\text{Fe}_{0.71}\text{RE}_{0.05}\text{B}_{0.24})_{96}\text{Nb}_4$ (RE = Tb, Ho, and Tm) alloys under a magnetic field change of 1.5 T. Figure is taken from ref. [34].

完全非晶结构, 随着Tm含量增加, 合金居里温度持续降低至室温附近(图8(a)), 并且合金饱和磁化强度持续降低, 而最大磁熵变值与饱和磁化强度之间存在线性关系(图8(b)).

Zhang等人^[36]设计Co基非晶合金 $\text{Co}_{75-x}\text{Mo}_{10-x}\text{Si}_{10}\text{B}_{5+x}$ ($x = 5, 6.5, 10$), 随着Co含量的增加, 合金居里温度由104 K升高至343 K, 根据以上结果, 该团队设计居里温度位于室温附近(310 K)的合金—— $\text{Co}_{68.5}\text{Mo}_{10-x}$

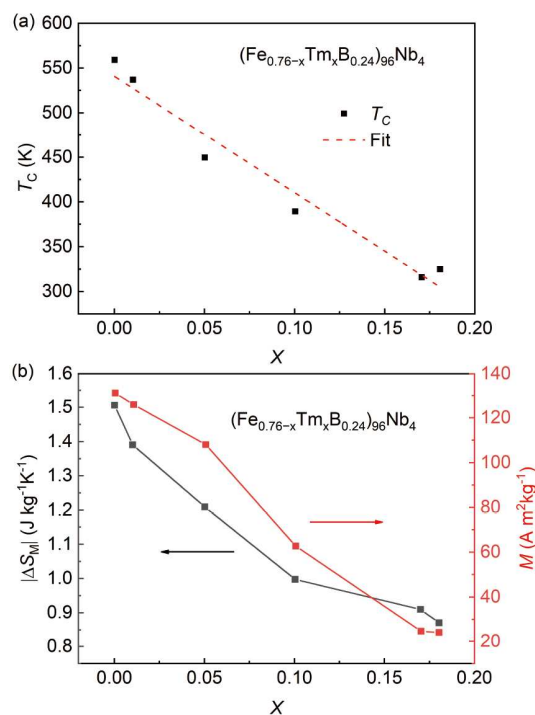


图 8 (网络版彩图) $(\text{Fe}_{0.76-x}\text{Tm}_x\text{B}_{0.24})_{96}\text{Nb}_4$ ($x = 0, 0.01, 0.05, 0.1, 0.17, 0.18$)合金(a) 居里温度随成分变化图和(b) 最大磁熵变值与饱和磁化强度随成分变化图. 图片来自文献[35]

Figure 8 (Color online) Compositional dependence of (a) Curie temperature, (b) maximum magnetic entropy change and saturation magnetization of the $(\text{Fe}_{0.76-x}\text{Tm}_x\text{B}_{0.24})_{96}\text{Nb}_4$ ($x = 0, 0.01, 0.05, 0.1, 0.17$, and 0.18) alloy. Figures are taken from ref. [35].

$\text{Si}_{10}\text{B}_{11.5}$, 该合金在5 T变化磁场条件下最大磁熵变值为 $0.86 \text{ J kg}^{-1} \text{ K}^{-1}$ (图9).

2.4 稀土基非晶复合材料磁热性能

稀土基非晶合金中稀土元素间磁交互作用为强度较弱的RKKY交互作用, 并且为提升合金非晶形成能力, 稀土基非晶合金成分设计中通常添加与稀土元素间混合热为负值且绝对值较大的无磁性元素, 如Al, 这种无磁性元素倾向于隔离磁性过渡族原子^[37], 降低体系的磁交互作用, 从而导致稀土基非晶合金居里温度较低. 相比于稀土基非晶合金, 稀土基晶体合金通常具有较高的磁转变温度, 如二级相变典型材料Gd金属居里温度为292.2 K. 因此, 非晶晶体复合材料极有可能具有近室温平台状磁热曲线.

Feng等人^[38]利用偏离深共晶成分设计并获得 $\text{Er}_{45}\text{Cu}_{45}\text{Al}_{10}$ 合金, 合金具有非晶纳米晶双相结构, 纳米晶结构为 ErCuAl 和 Cu_9Al_4 , 合金居里温度与最大磁

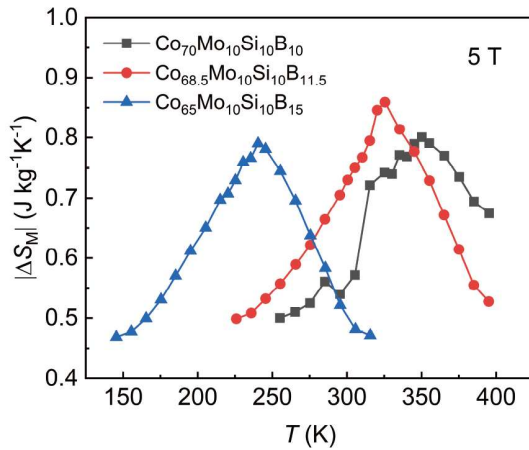


图 9 (网络版彩图) $\text{Co}_{75-x}\text{Mo}_{10}\text{Si}_{10}\text{B}_{5+x}$ ($x = 5, 6.5, 10$) 合金在 5 T 变化磁场条件下磁熵变随温度变化曲线. 数据来自文献[36]

Figure 9 (Color online) The temperature dependence of magnetic entropy changes for $\text{Co}_{75-x}\text{Mo}_{10}\text{Si}_{10}\text{B}_{5+x}$ ($x = 5, 6.5$ and 10) alloys under a magnetic field change of 5 T. Data are taken from ref. [36].

熵变值分别为 6.6 K 与 $14.6 \text{ J kg}^{-1} \text{ K}^{-1}$ (图 10), 在较高变化磁场条件下, 合金磁热曲线除在居里温度附近出现的最大磁熵变峰以外, 还在较高温区 (10–20 K) 存在一

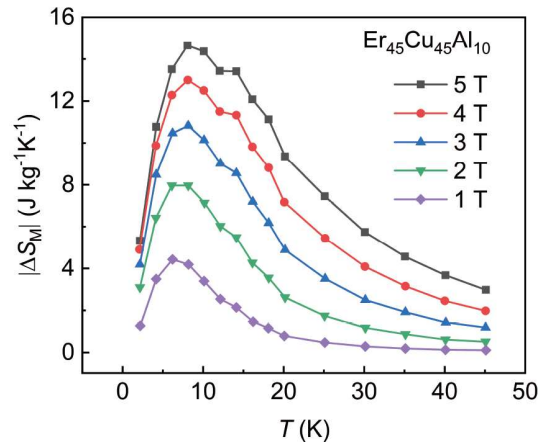


图 10 (网络版彩图) $\text{Er}_{45}\text{Cu}_{45}\text{Al}_{10}$ 合金磁熵变随温度变化曲线 (变化磁场条件为 1, 2, 3, 4 和 5 T). 图片来自文献[38]

Figure 10 (Color online) The temperature dependence of magnetic entropy changes for $\text{Er}_{45}\text{Cu}_{45}\text{Al}_{10}$ alloys under the magnetic field changes of 1, 2, 3, 4, and 5 T. Figure is taken from ref. [38].

较小磁熵变峰.

Feng 等人^[39]还通过设计具有高 Gd 含量 $\text{Gd}_{90-x}\text{Ni}_x\text{Al}_{10}$ ($x = 5, 10, 15$) 合金, 获得非晶纳米晶双相结构, 纳米晶结构为 Gd 和 GdNi 相 (如图 11(a)), 纳米晶含量随着

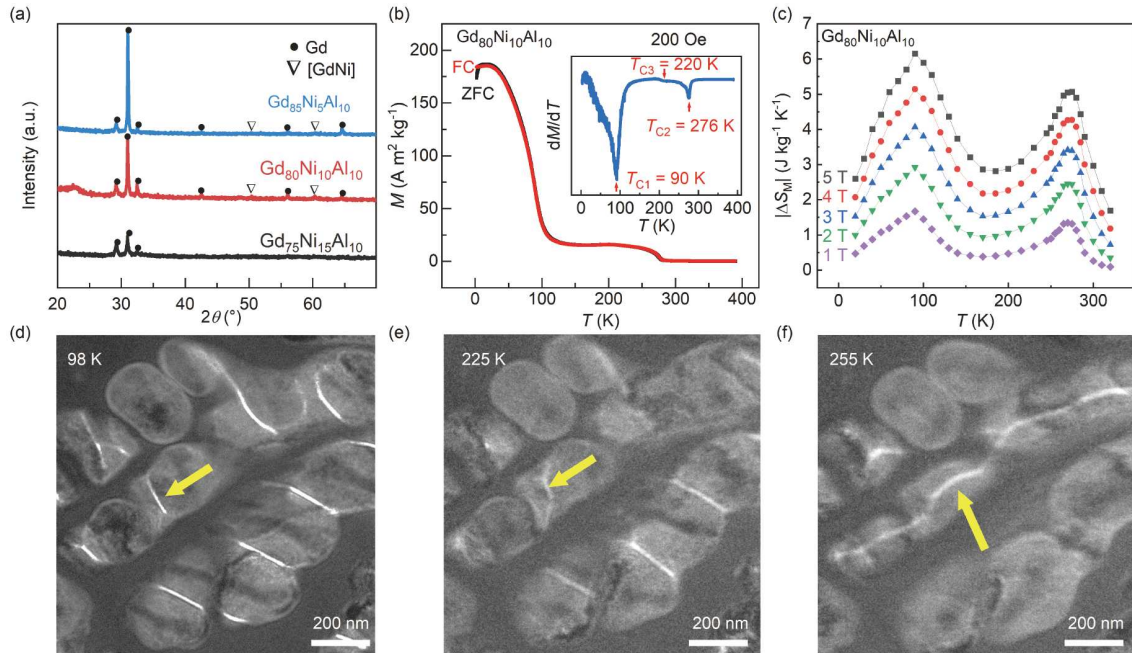


图 11 (网络版彩图) (a) $\text{Gd}_{90-x}\text{Ni}_x\text{Al}_{10}$ ($x = 5, 10, 15$) 合金 X 射线衍射谱. (b) $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ 合金磁化强度 (M) 随温度 (T) 变化曲线, 插图为 dM/dT 随温度变化曲线. (c) $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ 合金磁熵变随温度变化曲线 (变化磁场条件为 1, 2, 3, 4 和 5 T). $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ 合金在 (d) 98 K, (e) 225 K 和 (f) 255 K 洛伦兹透射电镜显微图. 图片来自文献[39]

Figure 11 (Color online) (a) X-ray diffraction patterns for the $\text{Gd}_{90-x}\text{Ni}_x\text{Al}_{10}$ ($x = 5, 10$, and 15) alloys. (b) Magnetization (M) as a function of temperature (T) of $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ alloy with the inset showing the dM/dT - T curve. (c) The temperature dependence of magnetic entropy changes for $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ alloy under the magnetic field changes of 1, 2, 3, 4, and 5 T. The magnetic domains characterized by Lorentz transmission electron microscope in overfocus model for $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ microwire at (d) 98 K, (e) 225 K, and (f) 255 K. Figures are taken from ref. [39].

Gd含量增多而升高, $x = 5$ 与 $x = 10$ 合金均具有三个居里温度, 分别为87, 273和220 K ($x = 5$)和90, 276和220 K ($x = 10$) (图11(b)), $x = 15$ 合金具有两个居里温度, 分别为93和263 K, 所有合金的磁熵变曲线均具有明显的双峰特征, 纳米晶对非晶相磁热性能的稀释作用以及非晶相与纳米晶居里温度差过大, 导致合金最大磁熵变峰值较低($5.72\text{--}6.15 \text{ J kg}^{-1} \text{ K}^{-1}$ (5 T)), $\text{Gd}_{80}\text{Ni}_{10}\text{Al}_{10}$ 合金具有极宽的制冷温区——70–270 K (图11(c)), 对该合金使用洛伦兹透射电子显微镜进行低温到室温的原位磁畴结构表征, 结果表明磁畴壁随着温度升高由垂直于纳米枝晶变为平行于纳米枝晶(图11(d)–(f)), 从而证明变磁性阻止复合材料中非晶相与晶体Gd巨大的居里温度差导致的磁热性能下降。

Chen等人^[40]利用高Gd含量设计合金成分 $\text{Gd}_{70}\text{Co}_{10}\text{Al}_{20}$, $\text{Gd}_{80}\text{Co}_{10}\text{Al}_{10}$, $\text{Gd}_{85}\text{Co}_5\text{Al}_{10}$ 和 $\text{Gd}_{80}\text{Co}_5\text{Al}_{15}$, 当Gd含量大于80 at.% (包含80 at.%)时, 合金具有非晶晶体双相结构, 晶体结构为Gd, $\text{Gd}_{80}\text{Co}_{10}\text{Al}_{10}$, $\text{Gd}_{85}\text{Co}_5\text{Al}_{10}$ 和 $\text{Gd}_{80}\text{Co}_5\text{Al}_{15}$ 合金居里温度分别为116和271 K, 98和264 K以及98和264 K, 这些双相合金磁熵变曲线均存在双峰特征, 磁熵变峰值分别为4.06和

$2.64 \text{ J kg}^{-1} \text{ K}^{-1}$, 4.31 和 $3.29 \text{ J kg}^{-1} \text{ K}^{-1}$ 以及 4.24 和 $5.07 \text{ J kg}^{-1} \text{ K}^{-1}$, 此外, 双相合金制冷温区极宽, 均大于200 K (图12)。

Chen等人^[41]后续在GdFeAl非晶晶体双相合金基础上, 利用Mn添加设计成分 $\text{Gd}_x(\text{MnFeAl}_2)_{100-x}$ ($x = 75, 80, 85$), 如图13(a)所示, 所设计的合金均具有非晶晶体双相结构, 晶体结构为Gd, 且晶体相随Gd含量增加而升高, Mn元素的添加降低了晶体相居里温度的同时使得非晶相具有较高居里温度, 合金居里温度分别为165和260 K ($x = 75$), 171和245 K ($x = 80$)以及165和246 K ($x = 85$), 所设计的合金磁熵变峰值最大值为 $5.4 \text{ J kg}^{-1} \text{ K}^{-1}$ (图13(b)–(d)), 特别地, 如图13(c)所示, $\text{Gd}_{80}(\text{MnFeAl}_2)_{20}$ 合金具有平台状磁热曲线。

Yin等人^[42]利用Fe掺杂设计并获得 $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{100-x}\text{Fe}_x$ ($x = 0, 1, 2, 3$)多主元合金纤维, $x = 2$ 与 $x = 3$ 合金具有非晶纳米晶双相结构(图14(a)), 纳米晶结构为Face-Centered Cubic (FCC), Fe与稀土元素间接近于0的混合热造成合金非晶形成能力降低, 并且结合纤维制备所使用的熔体抽拉方法黏附层中自由表面区较低的冷却速率导致双相结构的产生, 合金居里温

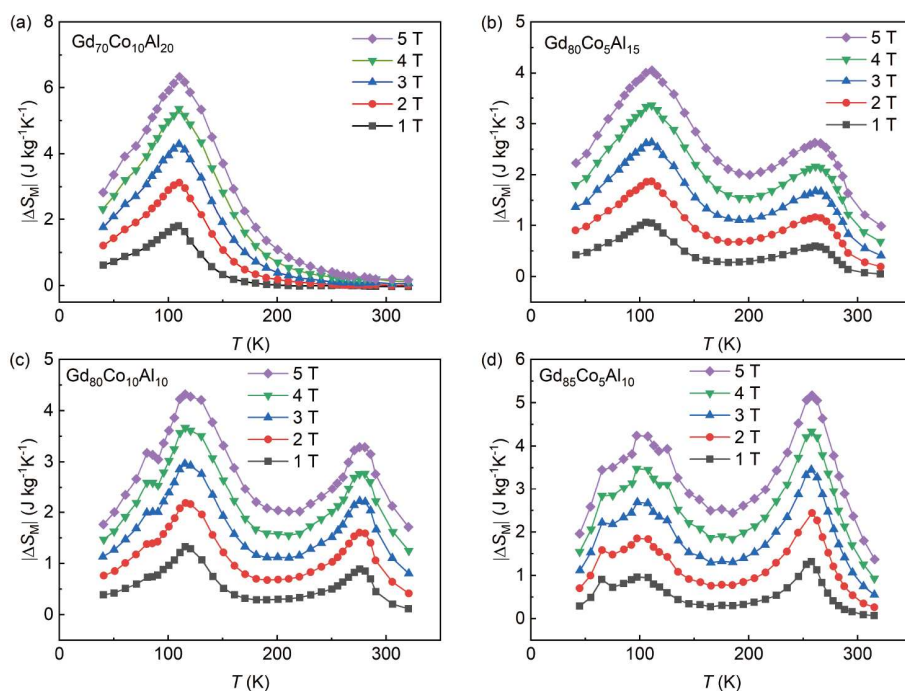


图 12 (网络版彩图) (a) $\text{Gd}_{70}\text{Co}_{10}\text{Al}_{20}$, (b) $\text{Gd}_{80}\text{Co}_5\text{Al}_{15}$, (c) $\text{Gd}_{80}\text{Co}_{10}\text{Al}_{10}$ 和(d) $\text{Gd}_{85}\text{Co}_5\text{Al}_{10}$ 合金磁熵变随温度变化曲线(变化磁场条件为1, 2, 3, 4和5 T)。图片来自文献[40]

Figure 12 (Color online) Magnetic entropy changes as a function of temperature for (a) $\text{Gd}_{70}\text{Co}_{10}\text{Al}_{20}$, (b) $\text{Gd}_{80}\text{Co}_5\text{Al}_{15}$, (c) $\text{Gd}_{80}\text{Co}_{10}\text{Al}_{10}$, and (d) $\text{Gd}_{85}\text{Co}_5\text{Al}_{10}$ alloys under the magnetic field changes of 1, 2, 3, 4, and 5 T. Figures are taken from ref. [40]

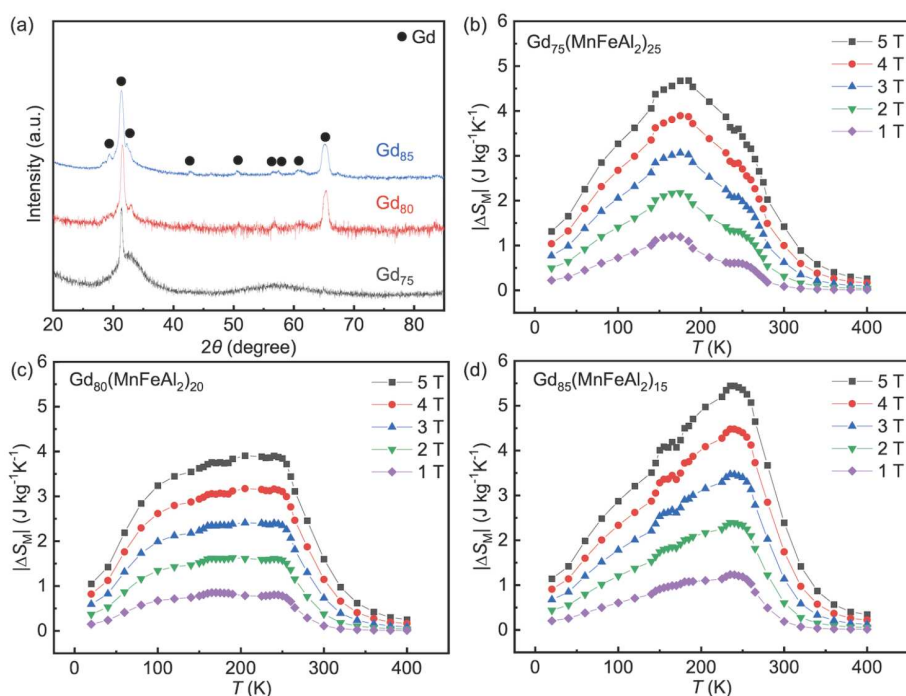


图 13 (网络版彩图) (a) $Gd_x(MnFeAl_2)_{100-x}$ ($x = 75, 80, 85$)合金X射线衍射谱. (b) $Gd_{75}(MnFeAl_2)_{25}$, (c) $Gd_{80}(MnFeAl_2)_{20}$ 和(d) $Gd_{85}(MnFeAl_2)_{15}$ 合金磁熵变随温度变化曲线(变化磁场条件为1, 2, 3, 4和5 T). 图片来自文献[41]

Figure 13 (Color online) (a) X-ray diffraction patterns for the $Gd_x(MnFeAl_2)_{100-x}$ ($x = 75, 80, 85$) alloys. Magnetic entropy changes as a function of temperature for (b) $Gd_{75}(MnFeAl_2)_{25}$, (c) $Gd_{80}(MnFeAl_2)_{20}$, and (d) $Gd_{85}(MnFeAl_2)_{15}$ alloys under the magnetic field changes of 1, 2, 3, 4, and 5 T. Figures are taken from ref. [41].

度随Fe含量增加由81 K ($x = 0$)升高至108 K ($x = 3$)(图14(b)), Fe掺杂合金克服多主元非晶合金居里温度普遍小于60 K的限制, 如图14(b)所示, 磁熵变峰值由8.9降低至 $7.6 \text{ J kg}^{-1} \text{ K}^{-1}$ (5 T).

非晶合金为亚稳材料, 通过退火与施加应力等方法可以促进合金发生弛豫与晶化行为[43,44], 这有助于利用结构调控提升非晶合金磁热性能[39,42]. 基于此, Yin等人[45]对 $(Gd_{36}Tb_{20}Co_{20}Al_{24})_{97}Fe_3$ 纤维进行电流退火处理, 结果表明合金纳米晶含量随着电流密度的增大而升高(图14(c)), 相比于未退火合金, 退火合金居里温度变化极小(如图14(d)插图所示), 这导致非晶基体与纳米晶之间的成分存在差异, 在一定电流密度范围内, 以上成分差异未影响合金临界指数(图14(d)), 故这些电流密度处理的合金获得拓宽的制冷温区, 但磁熵变峰值并未受影响(图14(d)).

3 总结和展望

综上, 磁热非晶合金作为磁制冷工质具有以下特点.

(1) 将上述非晶合金磁热性能数据进行整理, 如图15所示, 稀土基非晶合金与多主元稀土非晶合金的磁熵变峰值明显呈现随着磁转变温度的降低而升高的趋势, 稀土合金磁热性能变化规律可由平均场理论进行解释[46].

(2) 非晶合金居里温度对成分敏感, 稀土基非晶合金与多主元稀土非晶合金工作温区基本在低温区, 这些合金在氦气和氢气低温液化领域具有较大的应用前景, 即77–4和77–20 K (前期利用液氮进行制冷)温区制冷. 过渡族元素体系非晶合金与稀土基非晶复合材料的制冷温区可以达到近室温. 并且, 随着非晶合金中稀土元素与过渡族元素替换或相关元素成分改变, 非晶合金磁转变温度可在较大温度范围内连续调节, 这为设计连续降温磁制冷机提供巨大便利.

(3) 磁热非晶合金普遍为二级相变材料, 适合磁制冷循环.

(4) 纳米晶化可实现非晶合金平台状磁热曲线, 适当的成分设计和退火处理获得的稀土基非晶复合材料, 具有获得平台状磁热曲线的巨大潜力.

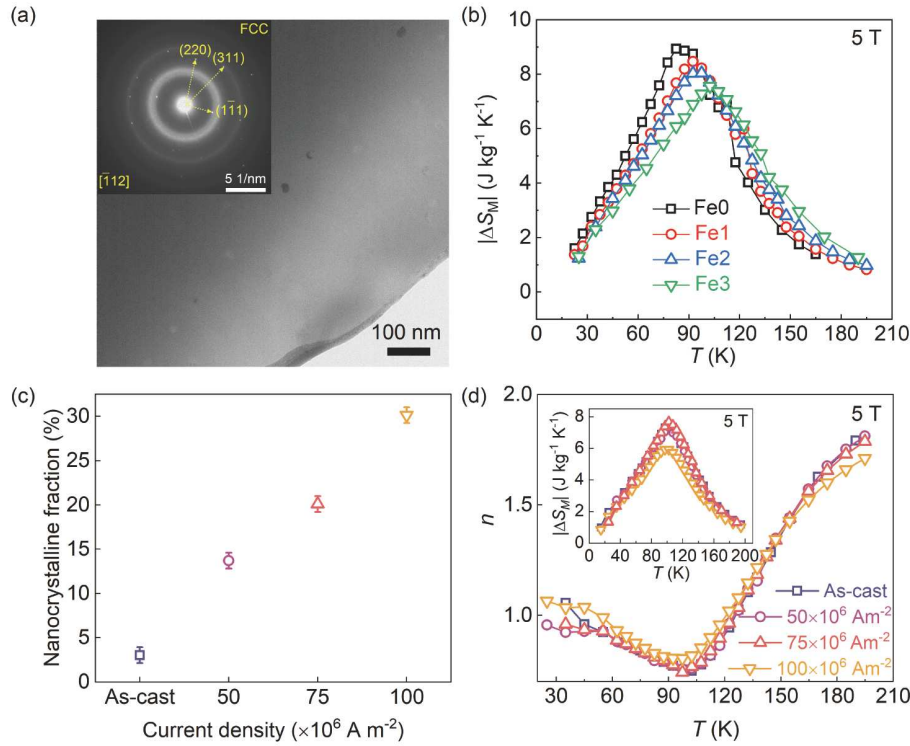


图 14 (网络版彩图) (a) $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{97}\text{Fe}_3$ 透射电镜显微图, 插图为选区电子衍射花样结果. (b) $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{100-x}\text{Fe}_x$ ($x = 0, 1, 2, 3$) 多元合金纤维磁熵变随温度变化曲线. (c) $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{97}\text{Fe}_3$ 纤维纳米晶含量随电流密度变化结果. (d) 在 5 T 变化磁场下, $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{97}\text{Fe}_3$ 退火纤维指数 n 随温度变化曲线(插图为磁熵变随温度变化曲线). 图片来自文献 [42,45]

Figure 14 (Color online) (a) Transmission electron microscope image of $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{97}\text{Fe}_3$ microwire with the inset showing the selected area electron diffraction result. (b) The temperature dependence of magnetic entropy change for $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{100-x}\text{Fe}_x$ ($x = 0, 1, 2, 3$) microwires under a magnetic field change of 5 T. (c) The nanocrystalline fraction of $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{97}\text{Fe}_3$ microwire as a function of current density. (d) The temperature dependence of exponent n for annealed $(\text{Gd}_{36}\text{Tb}_{20}\text{Co}_{20}\text{Al}_{24})_{97}\text{Fe}_3$ microwires under a magnetic field change of 5 T with the inset showing the magnetic entropy change as a function of temperature. Figures are taken from refs. [42,45].

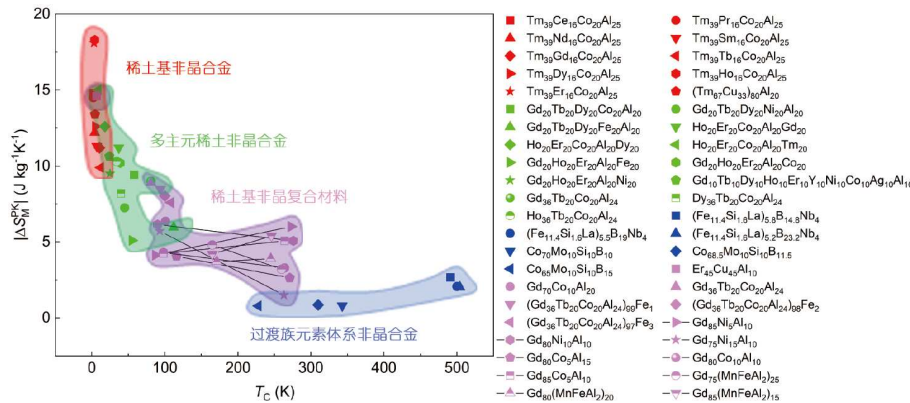


图 15 (网络版彩图) 总结的非晶合金磁熵变峰值(5 T 变化磁场)与磁转变温度关系, 图片中稀土基非晶复合材料连线表示材料磁熵变曲线具有双峰特征, 并且材料可在两峰位间工作. 数据来自文献[21,23,27-30,32,33,36,38-42]

Figure 15 (Color online) Summary of the relationship between the peak values of magnetocaloric entropy changes of amorphous alloys, under a magnetic field change of 5 T, and their magnetic transition temperatures. In the image, the lines connecting the rare earth-based amorphous composites indicate that the magnetic entropy change curves exhibit a dual-peak feature and the materials can work within the range between the two peaks. Data are taken from refs. [21,23,27-30,32,33,36,38-42].

(5) 由于非晶合金无序结构, 使得非晶合金普遍具有较宽的制冷温区.

磁热非晶合金研究难点:

(1) 过渡族元素体系非晶合金与稀土基非晶复合材料磁熵变峰值较低, 对于满足实际磁制冷循环的性能要求, 仍存在较大差距, 因而限制了其实际应用. 需探究如何提升这些合金的磁热性能.

(2) 非晶合金为亚稳材料, 在长时间使用过程中, 非晶合金是否会发生结构弛豫, 进而影响其制冷能力尚未可知, 如何确保其在长期使用中的稳定性是研究中的一大难题.

(3) 使用非晶合金制冷机的制冷效率可能较高, 但此种制冷机制冷量(制冷能力)是否满足实际使用需求, 还需进一步探究.

(4) 非晶材料制备通常面临一些挑战, 尤其是确保大规模稳定生产比表面较大的磁热非晶合金. 例如, 快

速冷却中合金微观结构和成分分布等稳定性情况.

磁热非晶合金未来研究方向:

(1) 非晶合金是一种亚稳材料, 在玻璃转变温度以下退火可发生结构弛豫, 弛豫对于非晶合金性能与晶化行为均可产生影响, 因此, 通过调控弛豫行为来精确控制非晶合金结构并提升合金磁热性能具有巨大潜力.

(2) 前期磁热非晶合金成分探索大多停留在试错法阶段, 基于高通量表征技术和大数据分析等材料研发新手段开发有潜力的磁热非晶合金, 实现磁热非晶合金高效探索, 未来也将是该领域的研究趋势.

(3) 结合密度泛函理论计算和第一性原理计算可对非晶合金结构、热力学特征及磁性演变进行模拟分析, 从而实现材料设计和性能预测的优化.

(4) 研究新的制备方法, 如喷涂、增材制造等, 有助于制备更大规模、更高效的磁热非晶合金, 提高合金的稳定性和性能.

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The magnetocaloric effect of amorphous alloys

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As global warming and greenhouse effects become increasingly prominent, there is an urgent need for new refrigeration technologies that are environmentally friendly and highly efficient. Magnetic refrigeration technology based on the magnetocaloric effect has great potential to meet the above requirements. However, this technology is currently limited by the challenge of finding materials that are suitable for the magnetic refrigeration cycle and exhibit high magnetocaloric performance. Amorphous alloys are highly promising materials in the field of magnetic refrigeration and have attracted significant attention in recent years. This paper reviews the properties and application prospects of magnetocaloric amorphous alloys, including rare earth-based amorphous alloys, multi-principal rare earth-element alloys, transition metal-based amorphous alloys and amorphous composites.

amorphous alloys, rare earth elements, transition metal elements, magnetocaloric properties

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