

RFe₁₂基稀土永磁材料的研究进展

郭家瑞^{1,2}, 王亚娜^{1,2}, 宋文鹏^{1,2}, 郑立允^{1,2}, 黄光伟^{1,2*}

¹河北工程大学材料科学与工程学院, 河北 邯郸

²河北省稀土永磁材料与应用工程研究中心, 河北 邯郸

收稿日期: 2022年3月21日; 录用日期: 2022年4月8日; 发布日期: 2022年4月15日

摘要

为了实现社会的可持续发展, 响应“双碳”目标的号召, 助力“双碳”目标的达成, 迫切需要具有低CO₂或无CO₂排放的绿色技术。永磁材料作为绿色技术的关键材料被广泛应用于风力发电、轨道交通、人工智能等技术领域。为了提高这些技术在应用过程中的电力转换效率, 需要一种比NdFeB永磁材料性能更优异的永磁材料。具有ThMn₁₂晶体结构的RFe₁₂ (R为稀土元素, 一般为Sm)基化合物即是有潜力满足当前绿色技术发展的永磁材料。本文将RFe₁₂基稀土永磁材料的相稳定性、磁性能, RFe₁₂基薄膜、粉体及块体磁体的研究进展进行综述。最后, 结合目前RFe₁₂基稀土永磁材料的研究现状, 提出一种适合于块体RFe₁₂基稀土永磁材料制备的技术手段并对其进行探讨。

关键词

永磁材料, ThMn₁₂, 块体, 磁性能

Recent Advances in RFe₁₂-Based Permanent Magnets

Jiarui Guo^{1,2}, Yana Wang^{1,2}, Wenpeng Song^{1,2}, Liyun Zheng^{1,2}, Guangwei Huang^{1,2*}

¹College of Materials Science and Engineering, Hebei University of Engineering, Handan Hebei

²Hebei Engineering Research Centre for Rare Earth Permanent Magnetic Materials & Applications, Handan Hebei

Received: Mar. 21st, 2022; accepted: Apr. 8th, 2022; published: Apr. 15th, 2022

Abstract

In order to realize sustainable development of the society, respond to the call of the “dual carbon”

*通讯作者。

goal and help achieve the “dual carbon” goal, green technologies with low or no CO₂ emissions are urgently needed. As the key material of green technologies, permanent magnetic materials are widely used in wind power generation, rail transit, artificial intelligence and other technical fields. In order to enhance the power conversion efficiency of these technologies in the application process, a new type of permanent magnetic material with better performance than NdFeB permanent magnetic material is urgently needed. RFe₁₂ (R stands for rare earth elements, usually Sm) based compound with ThMn₁₂ crystal structure is a permanent magnetic material that has the potential to meet the development of current green technologies. In this review, the phase stability and magnetic properties of RFe₁₂-based rare earth permanent magnetic materials, as well as the research progress of RFe₁₂-based thin films, powders and bulk magnets are reviewed. Finally, according to the current research status of RFe₁₂-based rare earth permanent magnetic material, a novel technology suitable for the preparation of bulk RFe₁₂-based rare earth permanent magnet material is proposed and discussed.

Keywords

Permanent Magnets, ThMn₁₂, Bulk, Magnetic Properties

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1. 引言

随着全球温室效应的加剧, 社会需要绿色技术的发展以至于能够较少或避免 CO₂ 气体的排放, 实现“双碳”目标。因此, 需要开发出高效节能的发电机和电动机以实现绿色、节能环保的目的。为了实现发电机和电动机的高效节能, 高性能的永磁材料必不可少[1] [2] [3]。尽管目前已有性能优异的 NdFeB 稀土永磁材料作为绿色技术的核心材料支撑, 但由于 NdFeB 稀土永磁材料具有较低的居里温度, 使其很难满足发电机和电动机在工作温度 150℃左右的正常运行[4]。因此, 急需开发出一种性能优异的永磁材料, 特别是高温磁性能优于 NdFeB 磁体的永磁材料来满足各绿色科技的需求。ThMn₁₂ 晶体结构的 RFe₁₂ (R 为稀土元素, 一般为 Sm) 基化合物由于其含有最低的稀土元素且具有优异的内禀磁性能, 是一种有潜力满足当前绿色技术发展的永磁材料[5] [6] [7]。

ThMn₁₂ 四方结构的 RFe₁₂ 基稀土永磁材料由于其具有高的饱和磁化强度、高的磁晶各向异性场和高度居里温度, 早在上世纪 90 年代就被磁学研究者发掘[8]-[12]。但当时人们并没有认为它是新一代的永磁材料。原因之一是因为 RFe₁₂ 基化合物的结构不稳定。通常, 需采用 Ti、V、Cr、Mn、Al、W、Si、Mo 和 Zr 等合金元素的添加, 才能获得室温下稳定的 ThMn₁₂ 结构的 RFe₁₂ 基化合物[13]-[21]。而这些合金元素的添加将会降低所得到磁性合金的饱和磁化强度。第二个原因即是低的矫顽力, 因为 RFe₁₂ 基化合物不像 NdFeB 合金一样具有富稀土相甚至是非磁性相的多相结构, 能够在磁体受到反向磁场作用下有效地阻碍反向畴核的形成, 反向畴的运动甚至是反向磁矩的转动[22] [23]。因此 RFe₁₂ 基磁体很难获得高的矫顽力。而彼时的 NdFeB 合金由于其独特的组织结构, 易于通过液相烧结、热压热变形等技术获得高性能的块体磁体, 顺理成章成为了永磁材料应用领域的引领者[24] [25] [26] [27]。但是, 在社会的高速发展驱使下, 各高新技术领域对永磁材料的性能要求越来越高且对永磁材料的需求量也越来越大, 这将造成大量昂贵稀土战略元素的消耗[2] [28] [29]。因此, 永磁材料的研究又转向了贫稀土甚至是无稀土永磁材料领域。RFe₁₂ 基稀土永磁体本着其含有最低的稀土元素且具有优异的磁特性, 再次受到了全球磁性材料研

研究者的广泛关注和研究。

为了推广 RFe_{12} 基稀土永磁材料的开发研究, 促进 RFe_{12} 基稀土永磁材料的发展与实际应用, 本文先后对 RFe_{12} 基稀土永磁材料的相稳定性、磁性能, RFe_{12} 基薄膜、粉体及块体磁体的研究进展进行综述。最后, 结合目前 RFe_{12} 基稀土永磁材料的研究现状, 提出一种适合于块体 RFe_{12} 基稀土永磁材料制备的技术手段并对其进行探讨。磁学研究者可通过参考本综述, 增进对 RFe_{12} 基稀土永磁材料研究现状的把控, 明晰 RFe_{12} 基稀土永磁材料开发研究过程中存在的科学技术问题。

2. RT_{12} 相的晶体结构和相稳定性

RFe_{12} 型稀土永磁材料的晶体结构为 $ThMn_{12}$ 四方晶体结构, 空间点群为 $I4/m\bar{m}$, 稀土原子 R 占据空间结构的 2a 晶位, Fe 原子占据 8i、8j 和 8f 三种不同的晶位, 其晶体结构如图 1 所示[7]。

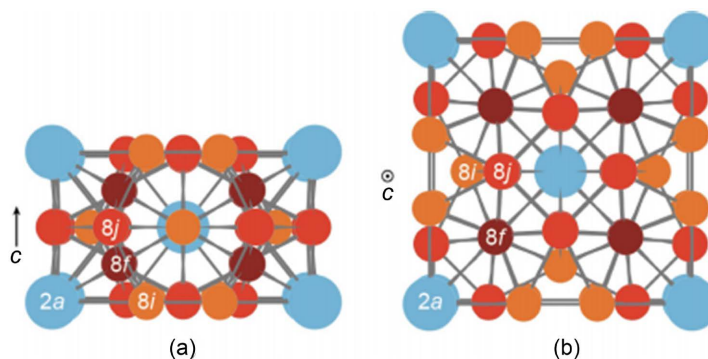


Figure 1. Schematic representation of a $ThMn_{12}$ unit cell along (a) the $[100]$ direction and (b) the $[001]$ direction c [7]

图 1. (a)沿 $[100]$ 方向和(b) $[001]$ 方向的 $ThMn_{12}$ 单胞示意图[7]

RFe_{12} 相的最大缺点即是室温不稳定。根据 Kobayashi 等人的研究, 导致 RFe_{12} 相室温不稳定的一个原因是占据 8i 晶位的 Fe-Fe 哑铃对中 Fe 原子间的距离过大[30]。据计算, 在 8i、8j 和 8f 晶位上, Fe 原子间距离分别为 0.271 nm、0.259 nm 和 0.251 nm。与 Fe 原子自身的原子半径相比(~ 0.252 nm), 8i 位点的原子间距离更大。8i 位点的原子间距离越大, 由于局域化导致的电子动能就会增加, 最终导致结构的不稳定。因此, 铁-铁哑铃中距离越大, 会使晶体结构越不稳定。而为了稳定结构, 很有必要采用非磁性元素进行添加实现元素的取代, 改变原子间距。大量的研究表明, 采用大原子半径的非磁性元素去稳定 RFe_{12} 相时, 这些元素倾向于取代 8i 位点。但是又有研究表明, 采用小原子半径的元素进行取代时, 这些小原子半径的元素在三个不同的铁位点上取代而得到的形成能是相似的。这意味着原子半径较小的相稳定元素可以等效地在 8i、8j 和 8f 三种不同的晶位进行取代。除了采用非磁性元素对 8i、8j 和 8f 三种不同的晶位进行取代来实现 RFe_{12} 相的稳定外, 还有研究报道, 一些元素如 Zr 是通过替代 R 位点来稳定 $ThMn_{12}$ 结构的, 即是 Zr 对 2a 位点的 R 元素进行取代。研究者认为, 这是由于 R 的原子半径非常大, 它给其周围的元素施加了大量的应力, 这可能是导致 Fe 原子在 8i 和 8j 位点上距离较大的原因之一。通过将 2a 位置的稀土元素用原子直径较小的元素取代, 总能量就会减少, 从而稳定 $ThMn_{12}$ 结构。表 1 为不同的相稳定元素、原子半径和取代位点的相关数据。

尽管大量的研究表明, 采用相稳定元素的取代能够实现 $ThMn_{12}$ 型晶体结构的稳定, 但是通过稳定元素的取代实现相稳定的深层次物理机理并没有得到普遍的理解。需要进一步的研究来充分了解添加其他元素致使相稳定的物理机制。这些基础研究可以为如何实现稳定 $ThMn_{12}$ 型晶体结构的前提下, 实现合金的饱和磁化强度降低最小和保持较大的磁晶各向异性场。这将有助于开发出高性能的 RFe_{12} 型稀土永磁材料。

Table 1. Phase stabilizing elements, their atomic radii, and substitution sites**表 1.** 相稳定元素, 它们的原子半径及取代晶位

相稳定元素	原子半径(nm)	取代位点	参考文献
Ti	0.147	8i	[4] [8] [9] [31] [32]
V	0.134	8i	[10] [11] [12] [13] [32] [33]
Cr	0.128	8i, 8j, 8f	[10] [32]
Mo	0.139	8i	[14] [15] [32]
Si	0.132	8j, 8f	[14] [32] [34]
Al	0.143	8j, 8f	[34]
Mn	0.127	8i, 8j, 8f	[19] [35]
Zr	0.160	2a	[30]
Co	0.125	8j, 8f	[19] [21]
Nb	0.146	8i	[16]
Ta	0.146	8i	[17]
Sm	0.180		
Fe	0.126		

3. RFe₁₂ 基稀土永磁材料的制备

3.1. RFe₁₂ 基薄膜磁体的制备与磁性能

尽管二元的 RFe₁₂ 磁体不能以块体的形式稳定存在, 但可以将其制备成薄膜形式。最近, Hirayama 等人和 Sato 等人通过在 W 或 V 缓冲的单晶 MgO 衬底上外延生长, 获得了 NdFe₁₂ (随后转化为 NdFe₁₂N_x)、SmFe₁₂ 和 Sm(Fe, Co)₁₂ 薄膜磁体, 且这些薄膜磁体呈现出极强的织构, 展示出明显的磁各向异性[36] [37]。图 2 为 Sm(Fe, Co)₁₂ 薄膜磁体的微结构表征。如图所示, 样品显示了 ThMn₁₂ 结构的外延生长。虽然图 2(c) 的透射电镜截面图显示了柱状结构, 但这些晶粒呈现出轻度的错位, 如图 2(d) 的纳米束衍射模式所示。

将所得到薄膜磁体的稀土元素含量(at%)、居里温度(T_c)、饱和磁化强度(M_s)、磁晶各向异性场(H_a)以及理论磁能积($(BH)_{\max}^{\text{Th}}$)与常用磁体的相关参数进行比较表明(表 2 所示), RFe₁₂ 基磁体确实具有利用最少含量的稀土元素, 储存更高的磁能积和显示优异的温度稳定性的优点, 如 SmFe_{9.6}Co_{2.4} 薄膜磁体的理论磁能积可高达 79 MGOe, 明显高于 NdFeB 的 64 MGOe。此外, 这些磁体由于具有更高的居里温度(400°C~610°C), 可满足 150°C~200°C 重要温度范围内设备的使用。但遗憾的是, 这些薄膜材料矫顽力不高, 而且薄膜不能作为永磁体装配到设备上使用。此外, 采用外延生长的技术, 由于存在大量的非磁性基底物, 很难实现高性能永磁材料的制备。

Table 2. The rare earth content (at%), T_c , M_s , H_a and theoretical magnetic energy product of RFe₁₂ based magnets were compared with those of common magnets**表 2.** RFe₁₂ 基磁体的稀土含量(at%), T_c , M_s , H_a 及理论磁能积与常用磁体的比较

化合物	T_c (°C)	M_s (T)	H_a (T)	R (at%)	$(BH)_{\max}^{\text{Th}}$ (MGOe)	参考文献
SmCo ₅	681	1.1	6.5	16.7	30.3	[38]
Sm ₂ Co ₁₇	920	1.25	44	10.5	39	[38]
Nd ₂ Fe ₁₄ B	313	1.6	7	11.8	64	[4]
NdFe ₁₂ N _x	~550	1.7	6~8	7.7	72.3	[39] [40]
SmFe _{9.6} Co _{2.4}	586	1.78	12	7.7	79	[36]
Sm _{0.74} Zr _{0.26} (Fe _{0.8} Co _{0.2}) ₁₂	402	1.9	8.9	5.7	90.3	[41]

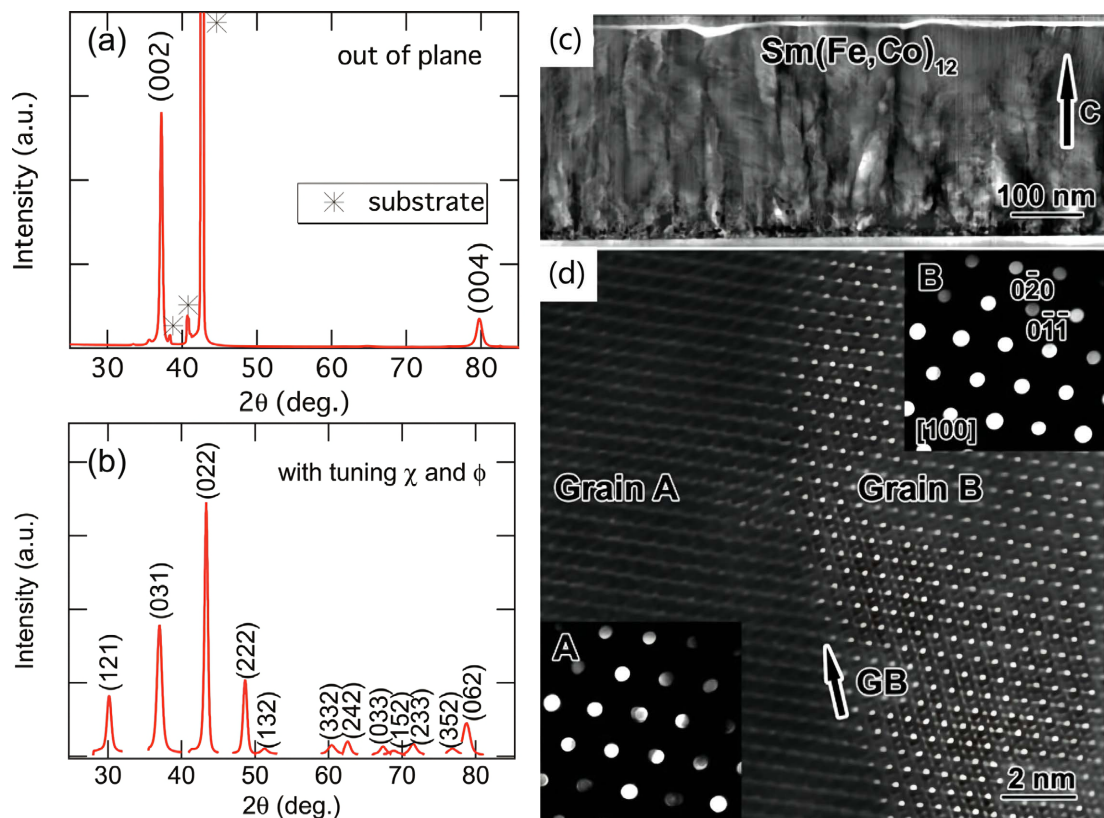


Figure 2. XRD patterns of (a) Out-of-plane; (b) Various planes with tuning the angle of the sample; (c) Cross-sectional bright-field TEM image; (d) Magnified view of HAADF-STEM image and nano-beam electron diffraction NBED patterns measured at the two regions. The arrow in (c) represents the direction of the c-axis, and the arrow in (d) shows the grain boundary [37]

图 2. 样品面外(a)及不同角度下的 XRD 谱图(b); (c) 横断面明场透射电镜图像; (d) 放大的 HAADF-STEM 图像和在两个区域测量的纳米束电子衍射 NBED 图。(c)中的箭头表示 c 轴的方向, (d)中的箭头表示晶界[37]

3.2. 非平衡技术制备 RFe_{12} 基条带和粉体的研究进展

通常采用非平衡技术如熔体快淬或机械合金化能够获得不稳定或亚稳材料[42]-[48]。针对 RFe_{12} 基磁体来说, 已有大量的研究采用熔体快淬或机械合金化实现了一系列 RFe_{12} 基磁体的制备。E. W. Singleton 等人通过熔体快淬获得软磁特性的合金, 并对获得的合金在 $700^{\circ}\text{C}\sim 1050^{\circ}\text{C}$ 进行退火, 获得了矫顽力约为 7.7 kOe , 具有 ThMn_{12} 型结构的 $\text{Sm}_{10}\text{Fe}_{80}\text{Ti}_{7.5}\text{B}_{2.5}$ 磁体[49]。Lizhong Zhao 等人通过熔体快淬加后续退火制备了 ThMn_{12} 型结构的 $\text{Sm}_x\text{Zr}_{0.2}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.5}\text{Ti}_{0.5}$ ($x = 0.8\sim 1.4$) 磁体, 并深入研究了 Sm 含量对所制备磁体的相结构、微结构和磁性能的影响[50]。得出在 $\text{Sm}_x\text{Zr}_{0.2}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.5}\text{Ti}_{0.5}$ 合金成分中, 当 $x = 1.2$ 时, 退火后合金结构中存在顺磁非晶晶界相。这项工作为 ThMn_{12} 型结构稀土永磁体的成分设计和结构优化提供了一条有用途径。L. Schultz 等人采用球磨工艺加后续退火获得了具有 ThMn_{12} 型结构的 Sm-Fe-V 纳米晶磁体, 所获得的 $\text{Sm}_{15}\text{Fe}_{70}\text{V}_{15}$ 纳米晶磁体具有高达 11.7 kOe 的矫顽力[51]。L. Bessais 等人通过高能球磨加后续退火对 $\text{Sm}(\text{Fe}_{12-x}\text{Co}_x)_{11}\text{Ti}$ ($x < 2$) 纳米晶磁体的结构演变与磁性能之间的关系进行研究。得出纳米晶的 $\text{SmFe}_9\text{Co}_2\text{Ti}$ 磁体可作为一种半硬磁材料用于磁记录领域[52]。A.M. Gabay 等人采用机械化学的方法制备出了以 ThMn_{12} 型结构为主相, 具有各向异性的 $RFe_{10}\text{Si}_2$ 磁粉(这里的 R 为 Sm, Ce 和 Zr 的组合), 所获得磁粉的 XRD 如图 3 所示[53]。这些磁粉有潜力成为具有贫稀土, 无 Nd、Co 等昂对元素且具有磁能积为 $12\sim 20\text{ MGOe}$ 的永磁材料。

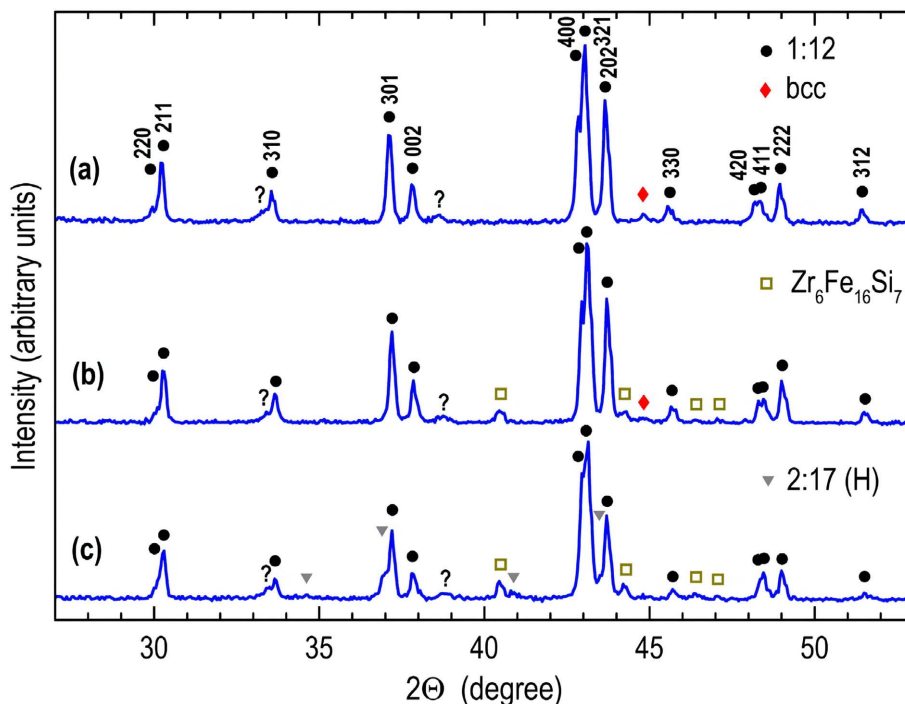


Figure 3. XRD spectra of (a) $\text{Sm}_{0.7}\text{Zr}_{0.3}\text{Fe}_{10}\text{Si}_2$; (b) $\text{Sm}_{0.3}\text{Ce}_{0.3}\text{Zr}_{0.4}\text{Fe}_{10}\text{Si}_2$; (c) $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{Fe}_{10}\text{Si}_2$ powders collected (washed) after processing at $T_a = 1150^\circ\text{C}$. “1:12” and “2:17 H” stand for the ThMn_{12} and $\text{Th}_2\text{Ni}_{17}$ structure types, respectively [53]

图 3. (a) $\text{Sm}_{0.7}\text{Zr}_{0.3}\text{Fe}_{10}\text{Si}_2$; (b) $\text{Sm}_{0.3}\text{Ce}_{0.3}\text{Zr}_{0.4}\text{Fe}_{10}\text{Si}_2$; (c) $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{Fe}_{10}\text{Si}_2$ 粉末在 $T_a = 1150^\circ\text{C}$ 处理后的 XRD 谱图。“1:12”和“2:17 H”分别代表 ThMn_{12} 和 $\text{Th}_2\text{Ni}_{17}$ 结构类型[53]

尽管人们通过熔体快淬、高能球磨以及机械化学合成方法实现了 RFe_{12} 基磁粉的制备，获得的磁粉如 $\text{Sm}_x\text{Zr}_{0.2}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.5}\text{Ti}_{0.5}$ ($x = 0.8\sim 1.4$, at%)、 $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{10.5}\text{Cu}_{0.5}\text{Ti}$ 、 $\text{Sm}_{15}\text{Fe}_{70}\text{V}_{15}$ 和 $\text{R}_x\text{Fe}_{10}\text{Si}_2$ ($\text{R} = \text{Sm}$, $\text{Sm}_{0.7}\text{Zr}_{0.3}$, $\text{Sm}_{0.3}\text{Ce}_{0.3}\text{Zr}_{0.4}$ 和 $\text{Ce}_{0.6}\text{Zr}_{0.4}$) 等均展现出优异的磁性能[49] [50] [51] [52] [53]。但与薄膜磁体一样，粉状磁体也很难作为永磁体进行设备的装配使用。但可喜的是，可以通过现有的这些非平衡制备技术，实现一系列 RFe_{12} 基磁粉的制备，这将为块体 RFe_{12} 基磁体的制备打下坚实的前驱粉体供给基础。有潜力使用如熔体快淬、高能球磨或者是机械化学方法所制备的粉体前驱物，后期采用恰当的块体成型技术，实现大块 RFe_{12} 基磁体的制备。

3.3. RFe_{12} 基块体磁体的研究进展

在永磁材料的应用领域，使用量最大，使用形式最普遍的是块体磁体，图 4 为商用形状各异的块体磁体以及块体磁体在永磁电机中的装配图。

基于永磁材料的发展和市场对块体永磁材料的需求，块体永磁材料的制备技术得到了不同程度的发展。目前制备块体磁体的制备技术主要有粉末冶金加后续的高温烧结成型技术，该技术的工艺流程图如图 5 所示[54]。采用该技术所制备的块体磁体主要有市场应用占有率最高的烧结 NdFeB 磁体以及高温技术领域应用的烧结 SmCo 磁体。此外就是热压热变形技术，工艺流程图如图 6 所示，此技术主要是应用于块体 NdFeB 纳米晶永磁体、永磁环的制备[55]。除了粉末冶金加高温烧结成型技术、热压热变形技术能够实现块体磁体的制备外，粘接成型技术也被广泛地应用于低中等磁性能块体磁体的制备，其技术核心就是采用粘接剂与磁粉进行混合，然后通过模压、挤压以及注塑等方式实现块体柔性磁体的制备，工艺流程如图 7 所示[56]。



Figure 4. Bulk permanent magnets and permanent magnet motor

图 4. 块体永磁体及永磁电机

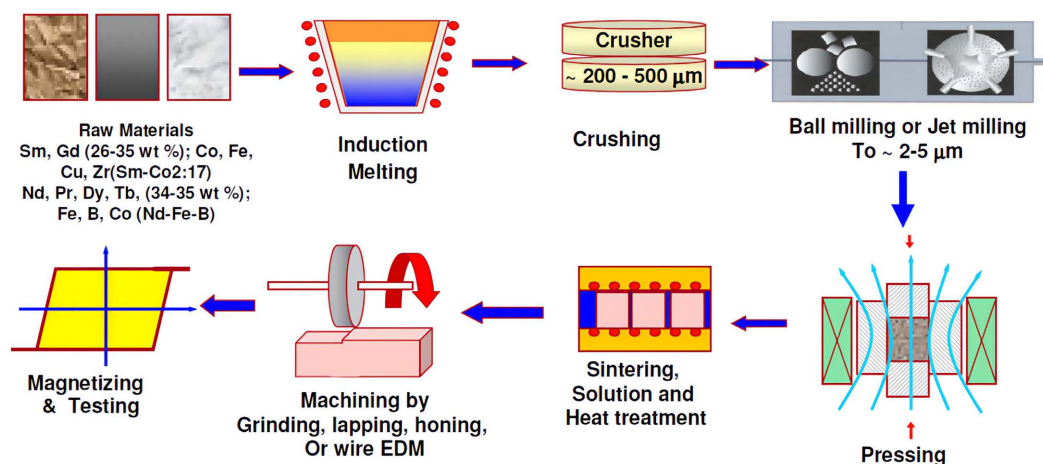


Figure 5. Sintering process flow chart of bulk magnet [54]

图 5. 块体磁体的烧结工艺流程图[54]

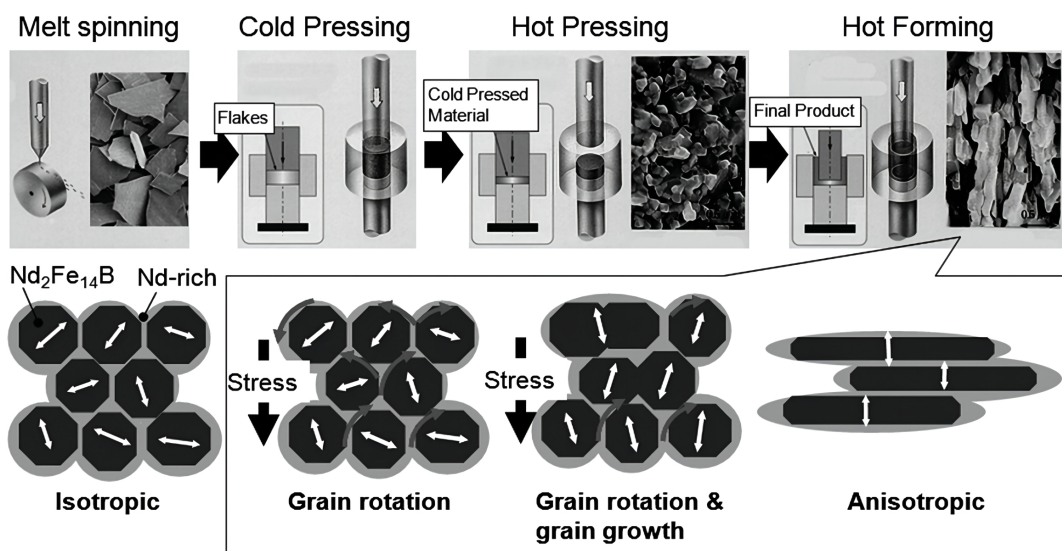


Figure 6. Process flow chart of preparing bulk NdFeB nanocrystalline magnets by hot pressing and hot deformation [55]

图 6. 热压热变形制备块体 NdFeB 纳米晶磁体的工艺流程图[55]

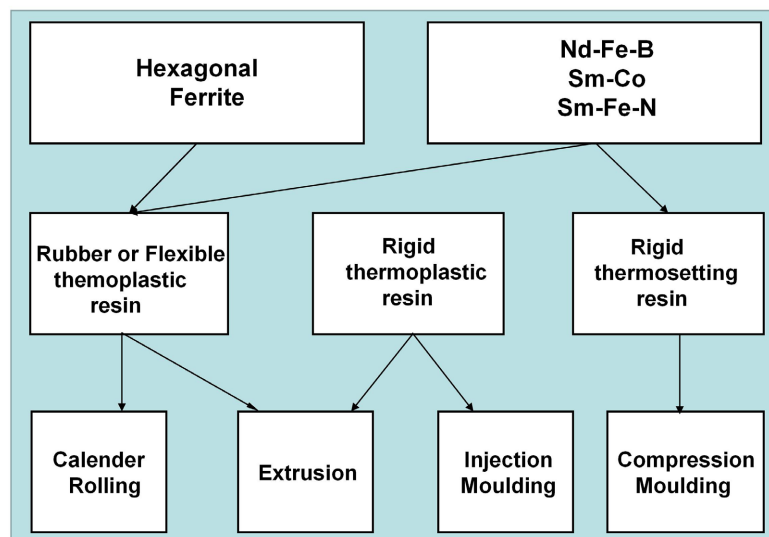


Figure 7. Summary of materials and processes involved in bonded magnet manufacture [56]

图 7. 粘接磁体涉及的材料及工艺流程总结[56]

尽管目前已存在发展较为成熟的块体磁体制备技术。但是对于 RFe_{12} 基块体磁体的制备仍然是一个巨大的挑战。首先, 采用传统的粉末冶金加高温烧结技术很难实现高性能 RFe_{12} 基块体磁体的制备, 因为 RFe_{12} 基合金不像 NdFeB 合金一样在组织结构中存在有低熔点的富稀土相, 因此很难实现烧结下 RFe_{12} 基磁体的致密化[4]。此外, RFe_{12} 基合金在较高的温度下容易发生分解, 这种结构的高温不稳定性很难适用于高温烧结工艺[57]。Dirba 等人为了克服采用烧结技术实现块体 RFe_{12} 基磁体制备的难点, 采用添加低熔点合金来降低烧结温度的思路[58]。然而, 由于所制备的磁体存在大量的界面缺陷, 使所制备的块体磁体的矫顽力仅为 3 kOe。最近, Otsuka 等人基于 Sm-Fe-M (M 为 Ti 和 V) 合金成分, 采用烧结技术, 通过对磁体的成分、结构和性能进行系统研究, 成功制备出矫顽力为 8.2 kOe, 最大磁能积约为 12.5 MGOe 的块体各向异性 Sm-Fe-V 磁体[59]。该工作指出, 诱导富 Sm 的非化学计量比成分形成晶界相和通过相稳定元素的选取形成低熔点晶界相对提高 RFe_{12} 基磁体的矫顽力是很重要的, 同时可以通过诱导出现的这些低熔点晶界相来实现块体 RFe_{12} 基磁体的烧结制备。尽管采用烧结技术一定程度上实现了块体 RFe_{12} 基磁体的制备, 但是磁体的性能仍然较低。

基于热压热变形工艺能够实现高性能块体各向异性纳米晶 NdFeB 永磁体的制备, 除烧结技术被采用进行块体 RFe_{12} 基磁体的制备外, 热压热变形技术也被研究者们应用于块体 RFe_{12} 基磁体的制备研究[60]。然而, 诸多研究表明, 采用热压热变形工艺很难实现高性能块体 RFe_{12} 基磁体的制备。如 A.M. Schönhöbel 等人采用热压热变形所获得的 RFe_{12} 基块体磁体显示各相同性或较弱的各向异性, 导致尽管块体磁体的矫顽力高达 9.6 kOe, 但是其剩磁仅为 4.9 kG, 从而使变形后块体磁体的磁能积仅为 5.3 MGOe, 难以推广应用[60]。根据传统热压热变形的工业特点(变形温度高, 变形过程时间长, 采用的变形先驱体为纳米晶)以及目前采用此技术进行研究的相关结果表明, 采用传统的热压热变形技术很难实现块体 RFe_{12} 基纳米晶磁体具有晶粒细小的硬磁纳米晶沿其易磁化轴方向形成织构的组织结构, 从而很难保证块体磁体同时具有高的矫顽力和高的剩磁以及良好的方形度, 以致于难以获得高磁能积的块体磁体。

采用粘接技术能够很好地将 RFe_{12} 基粉体与粘接剂相结合, 得到块体的 RFe_{12} 基磁体, 如 Y.C. Yang 等人成功制备出 $\text{Nd(Fe, M)}_{12}\text{N}$ (M 为各种过渡元素) 各向异性磁粉, 磁粉有潜力用于高性能粘接磁体的制备[61]。但是对粘接磁体来说, 由于含有一定的有机剂, 这将会稀释磁体的磁性能, 同时会影响磁体在

高温下的使用。目前来说,粘接磁体的发展一方面需要开发出性能优异的各向异性磁粉,同时需要开发出具有抵抗高温环境的粘接剂,这才能拓展粘接磁体的应用领域。

在采用传统的成型技术很难实现高性能块体 RFe_{12} 基磁体制备的背景下,研究者们不断地探索一些新的途径来对块体 RFe_{12} 基磁体进行制备研究。Saito 等人采用放电等离子烧结技术(SPS)成功地制备出块体的 $\text{SmFe}_{11}\text{Ti}$ 纳米晶磁体[62]。尽管在短时低温的变形条件下,能够有效地控制硬磁纳米晶粒尺寸(20~50 nm)和稳定硬磁相,但是制备过程中的变形应力较低,获得的磁体为各向同性。Hui-Dong Qian 等人采用高压压实加后续退火技术通过前期十几个 GPa 的压力实现粉体的全致密,并通过后续的退火工艺控制高压后块体的纳米化,最终实现细小晶粒尺寸和稳定硬磁相 $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11}\text{Ti}$ 纳米晶磁体的制备,但获得的磁体仍为各向同性,得到磁体的磁能积为 12.2 MGOe,未实现磁体性能的大幅度提高[63]。

综合目前块体 RFe_{12} 基磁体制备研究的现状,现有的制备技术很难实现高性能块体 RFe_{12} 基磁体的制备。主要的原因概括起来就是目前所采用的制备技术仅能实现一个或两个结构因子的控制。而对于高性能块体永磁材料的制备除了需要是块体这样的基本前提外,还需要所制备的磁体具有良好的微观组织形态如硬磁相具有沿其易磁化轴方向的织构,良好的界面结构,均匀细小的晶粒尺寸等[1] [64] [65]。这样苛刻的结构特征要求,需要新颖的制备技术和研究思路的引入,才有希望实现高性能块体 RFe_{12} 基磁体的制备,从而促进 RFe_{12} 基磁体的开发与拓展应用。

4. 制备 RFe_{12} 基块体磁体的潜在技术及思路探讨

随着社会对低碳环保、高效节能以及高速可持续发展的要求,各产业对永磁材料的需求量目前已经达到以 80~100 千吨每年逐年递增的趋势攀升,这将会造成大量昂贵稀土战略元素的消耗[66] [67]。因此,开发低稀土甚至是无稀土高性能永磁材料,势不可挡。 RFe_{12} 基稀土永磁材料凭借能够利用最少的稀土元素来实现优异磁性能磁体制备潜力,如今已成为全球磁性材料开发研究的焦点之一[5] [6] [7]。

从目前的发展现状来看,阻碍 RFe_{12} 基稀土永磁体开发应用的关键即是很难制备出块体各向异性高性能的 RFe_{12} 基稀土永磁体。在前文 3.3 的阐述与讨论中,也指明现有的制备技术和研究思路很难实现块体各向异性高性能 RFe_{12} 基稀土永磁体的制备。因此,急需引入一些新颖的制备技术和研究思路,方可实现块体各向异性高性能 RFe_{12} 基稀土永磁体的制备及实际应用。

近年来,为突破块体纳米复合永磁材料中实现硬磁相织构和软磁相形态同步控制的瓶颈,高压热压缩变形技术被 Zhang 等人所开发,并利用该技术能够将温度场、应力场和应变场协调耦合的特点,通过对非晶状态或部分非晶的前驱粉体压坯进行高压热压缩变形,刻意地在前驱物非晶化过程中施加高应力、大应变,利用晶体应变能各向异性诱导纳米晶的取向生长,成功地在高软磁含量(28 wt%)和细小的晶粒尺寸(~10 nm)下诱导出 SmCo 硬磁纳米晶沿其易磁化轴方向的织构,获得了高达 28 MGOe 的磁能积,制备流程如图 8 所示[68] [69] [70]。随后,此技术相继被拓展应用于单相以及复杂多相块体纳米晶永磁材料的制备研究中,实现了块体纳米晶磁体中硬磁纳米晶织构的形成和磁性能的提高[71] [72] [73] [74]。图 9 展示了采用高压热压缩变形技术制备出了高性能块体各向异性的 $\text{SmCo/FeCo} + \text{NdFeB}$ 纳米晶磁体[73]。这充分说明在这样一个多场耦合的变形条件下,能够通过控制温度场、应力场等能量给予,基于晶体各晶面的应变能各向异性理论,实现对纳米晶材料中纳米晶粒的取向调控和纳米晶材料微观组织的优化[70] [73] [75]。

由于高压热压缩变形技术具有变形温度低(500℃~650℃),应变速率快(0.1~0.01 s^{-1})以及高的单轴应力(≥ 1 GPa),如果采用高压热压缩变形技术对具有单轴各向异性的块体 RFe_{12} 基纳米晶磁体进行制备研究,将能够对硬磁纳米晶的晶体学取向(织构)进行调控,有潜力实现硬磁纳米晶沿其易磁化轴方向择优取向的块体各向异性 RFe_{12} 基纳米晶磁体的制备。此外,通过高压热压缩变形工艺参数以及用于变形的粉体前

驱物结构形态的调控, 可实现 RFe_{12} 基纳米晶磁体硬磁相的结构稳定控制、晶粒尺寸的控制, 界面结构的优化等, 有潜力实现高性能块体各向异性 RFe_{12} 基纳米晶永磁材料的制备。

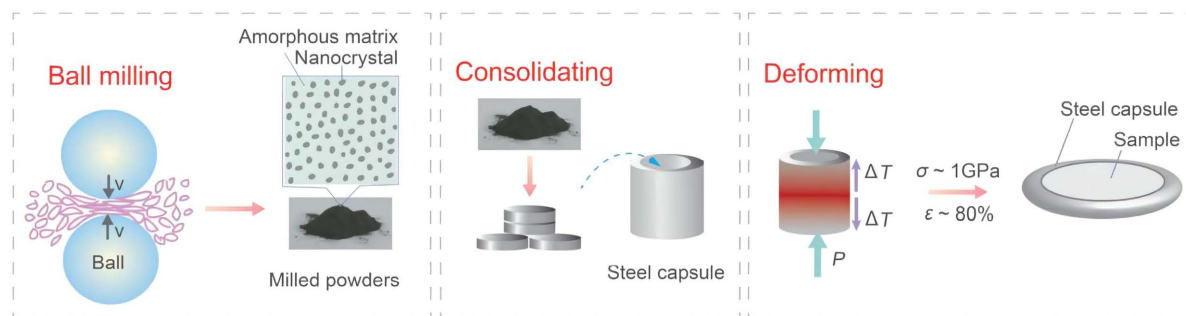


Figure 8. Process flow chart of bulk anisotropic SmCo/Fe(Co) nanocomposite permanent magnets prepared by high-pressure thermal compression deformation technology [70]

图 8. 采用高压热压缩变形技术制备块体各向异性 SmCo/Fe(Co) 纳米复合永磁体的工艺流程图 [70]

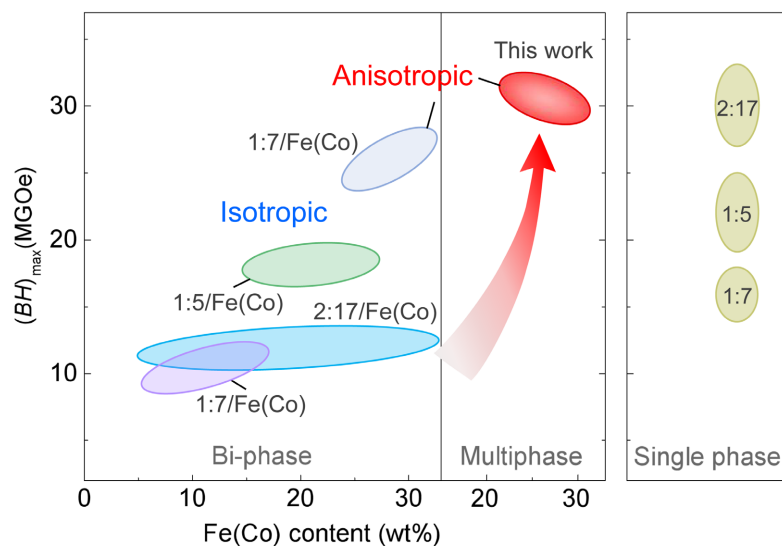


Figure 9. Comparison of magnetic energy product between anisotropic bulk SmCo/FeCo + NdFeB multiphase layered heterogeneous nanocomposite permanent magnetic materials and other SmCo bulk permanent magnetic materials [73]

图 9. 各向异性块体 SmCo/FeCo + NdFeB 多相层状异质纳米复合永磁材料与其它 SmCo 系块体磁体磁能积的比较 [73]

5. 总结

本文对 RFe_{12} 基稀土永磁材料的相稳定性、磁性能, RFe_{12} 基薄膜、粉体及块体磁体的研究进展进行了综述。总结了目前 RFe_{12} 基稀土永磁材料的发展现状及存在的关键科学技术问题。结合目前 RFe_{12} 基稀土永磁材料的研究现状, 提出一种适合于制备块体各向异性高性能 RFe_{12} 基稀土永磁材料的技术手段和研究思路并对其进行了探讨。文中所涉及的观点, 有助于推进 RFe_{12} 基稀土永磁材料研发与实际应用, 进而助力“中国制造 2025”、“节能环保”、“人工智能”、“5G”技术及“双碳”目标的达成。

基金项目

河北省自然科学基金(No. E2021402001); 邯郸市科学技术研究与发展计划项目(No. 21422111275)。

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