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HDDR 各向异性钕铁硼磁粉研究及应用进展

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摘　要:吸氢-歧化-脱氢-再复合工艺(HDDR)是生产各向异性钕铁硼磁粉的有效方法,其制备的各向异性粘结磁体性能高,重量轻,在提高微特电机功效、减轻重量等方面发挥着重要作用,目前在汽车、无人机等领域已产业化应用。为了提高磁粉性能,科研人员仍不断探究 HDDR 工艺与各向异性机理,采用晶界扩散法优化磁粉晶界结构,提高磁粉矫顽力与温度稳定性,同时将上述成果应用到废旧烧结钕铁硼回收中,节约稀土资源。HDDR 各向异性磁粉性能显著高于各向同性磁粉的,但形变塑性次之,研究者试图将其作为热变形磁体前驱原材料,进一步提升热变形磁体性能。HDDR 工艺细化晶粒的效果为提高烧结钕铁硼矫顽力提供了一条新的研究途径,但目前还未获得理想的成果。本研究主要介绍近年来 HDDR 工艺与机理的发展以及其在稀土磁体回收、热变形磁体、烧结磁体等方面的应用情况。

关键词:钕铁硼;HDDR 工艺;磁粉;磁各向异性

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Research and Application Progress on Production of Anisotropic NdFeB Magnetic Powder by HDDR Process

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Abstract: Hydrogenation-disproportionation-desorption-recombination (HDDR) process is an effective method to produce anisotropic NdFeB magnetic powders. The anisotropic bonded magnets prepared by HDDR process have excellent performance and light weight, which play an important role in improving the efficiency and reducing weight of micro-special motor. It has been industrialized and applied in automotive, drone and other fields. In order to improve the magnetic powder properties, the researchers are keeping investigating the HDDR process and the anisotropy mechanism. They optimize the grain boundary structure of the magnetic powders by using the grain boundary diffusion method to improve the coercivity and temperature stability of the magnetic powder, and apply the above achievements into the recycling of the waste sintered NdFeB to save rare earth resources. The magnetic property of the HDDR anisotropic magnetic powders is better than that of the isotropic magnetic powders, but the deformation plasticity comes after. The researchers attempt to take the HDDR magnetic powders as precursor material to fabricate hot deformation magnets to improve their performances. The effect of grain refinement of the HDDR process provides a new research approach for improving the coercivity of the sintered NdFeB magnets, however, until now, no ideal result has been obtained. In this paper, the development of HDDR process and its mechanism over the years are introduced, as well as its application in hot deformation magnets, sintered magnets and rare earth magnet recycling.

Keywords: NdFeB; HDDR process; magnetic powder; magnetic anisotropy

钕铁硼 NdFeB 材料因其优异的磁性能而被广泛应用于新能源汽车、风电、工业机器人等高

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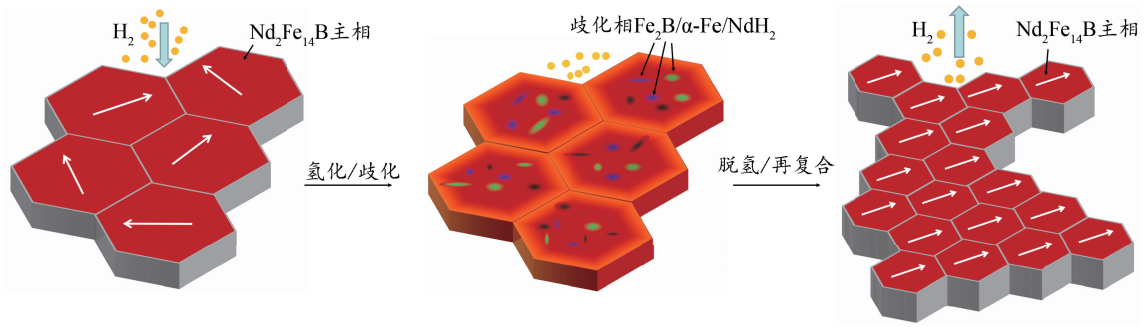
新技术领域，伴随着低碳环保产业的发展，智能制造的持续深化，对钕铁硼材料的需求正在逐年上升。2021 年，中国烧结钕铁硼产量 20.71 万吨，同比增长 16.0%，粘结钕铁硼产量 0.94 t，同比增长27.2%。磁粉是制造钕铁硼产品的关键材料，工艺吸氢-歧化-脱氢-再复合（HDDR）是一种高效、经济的制备各向异性钕铁硼磁粉的方法。自 1989 年 Takeshita T[1] 开发出 HDDR 工艺以来，研究者对 HDDR 工艺不断进行改进，磁粉性能也不断提高。目前，HDDR 钕铁硼磁粉主要用于制备各向异性粘结磁体，研究者在提高 HDDR 磁粉性能的同时，也在尝试 HDDR 工艺在稀土磁体回收、热变形磁体、烧结磁体等方向的应用。本研究将主要介绍近年来 HDDR 工艺与机理的发展，以及其在热变形磁铁、烧结磁体、稀土磁体回收等方面的应用情况。

1　HDDR 工艺与各向异性机理研究

HDDR 工艺是在一定温度和氢气压力下，晶粒粗大的 $Nd_2Fe_{14}B$ 母合金吸氢破碎并歧化成 Fe_2B、α-Fe 和 NdH_2。然后降低氢压，歧化产物脱氢并再复合成 $Nd_2Fe_{14}B$ 相，如式（1）所示。通过添加合金元素或调整合适的氢压、温度，$Nd_2Fe_{14}B$晶粒细化并产生了一定晶体取向（如图 1 所示），从而制备出具有磁各向异性的磁粉（如图 2、图 3 所示）。

$$Nd_2Fe_{14}B+H_2 \xrightarrow[HD]{\text{氢化/歧化}} NdH_2+\alpha\text{-}Fe+Fe_2B \xrightarrow[DR]{\text{脱氢/再复合}} Nd_2Fe_{14}B+H_2\uparrow \quad (1)$$



（a）母合金微观组织　（b）歧化物微观组织　（c）磁粉微观组织

图 1　HDDR 微观组织示意图

Fig. 1　Schematic diagram of HDDR microstructure

1.1　HDDR 工艺研究

Kwon H W 等[2] 多次采用 HDDR 工艺处理 $Nd_{15}Fe_{77}B_8$合金，发现第二次磁粉矫顽力最高，且与 DR 时间息息相关。Nishiuchi T 等[3] 研究了 DR 时间对 $Nd_{12.5}Fe_{73}Co_8B_{6.5}$磁粉矫顽力的影响，发现矫顽力随着 DR 时间的延长缓慢增加，约在 15 min 时突升，20 min 时最大，接近 1 000 kA/m。作者认为，在晶界处形成的富 Nd 相使矫顽力升高。Vintaikin B E 等[4] 发现，FeCoNdBZr 软磁相材料 DR 阶段氢压低于 3.2 kPa 时，磁粉未发现软磁相α-Fe，高于 3.2 kPa 时不同程度地存在 α-Fe。Sugimoto S 与 Horikawa T 等[5-9] 通过研究 HD 处理温度、氢压、时间与磁粉晶粒形态的关系，发现磁粉各向异性的产生强烈依赖于歧化物板条状织构。为了获得性能均衡的磁粉，作者认为 NdFeBGaNb 合金 HD 阶段温度 820 ℃、氢压 30 kPa、时间 3 h 最适宜，500 ℃氢破碎前处理可提高磁粉性能，从而获得利磁 B_r = 1.34 T、内禀矫顽力 H_{cj} = 1 230 kA/m、最大磁能积 (BH) max = 330 kJ/m^{3}的磁粉以及 B_r = 0.95 T、H_{cj} = 1 160 kA/m、(BH) max = 147 kJ/m^{3}的粘结磁体。

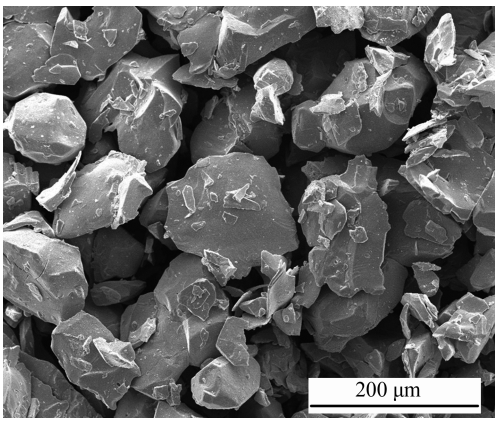


图 2　HDDR 钕铁硼磁粉形貌

Fig. 2　Morphology of HDDR NdFeB magnetic powders

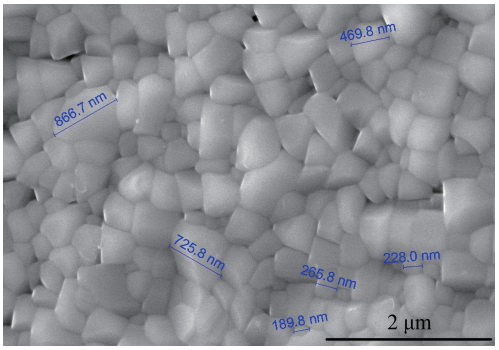


图 3　HDDR 钕铁硼晶粒形貌

Fig. 3　Morphology of HDDR NdFeB magnetic grains

1.2　HDDR 各向异性机理研究

HDDR NdFeB 磁粉的磁各向异性源于晶体织构,但目前对磁粉晶体织构形成的机理还未有统一的认识,主要有残余核解释、中间相理论和定向形核解释。其中残余核解释、中间相理论基本观点都认可存在传递介质,即合金 $Nd_2Fe_{14}B$ 母相的晶体学取向传递给再复合后的 $Nd_2Fe_{14}B$ 相。残余核解释认为添加 Co、Zr 等合金元素能提高 NdFeB 母相热力学稳定性,抑制歧化反应,歧化反应结束时还残留着 $Nd_2Fe_{14}B$ 的细小晶核,作为 $Nd_2Fe_{14}B$ 再复合相的形核点诱发各向异性[10-11]。中间相理论认为,NdFeB 合金在 HDDR 相变过程中,某些特定歧化物或中间相与 $Nd_2Fe_{14}B$ 母相、$Nd_2Fe_{14}B$ 再复合相都存在一定的取向关系,是各向异性的可能成因。目前提出的几种歧化物或中间相包括:歧化相 α-Fe/NdH_2[6-7,12]、Fe_2B[13-16]、中间相 Fe_3B[17-18]、α-Fe[19] 以及添加 Zr 形成的新相[20-21]。

Honkura Y 和 Gutfleisch O 等[14]研究歧化产物时发现,后期产物中只有 Fe_2B 具有各向异性晶体结构,进而可能影响 $Nd_2Fe_{14}B$ 各向异性的形成。Tomida T[22]和 Gutfleisch O[18,23]等在研究歧化过程中发现存在中间相 Fe_3B,且该相与母相 $Nd_2Fe_{14}B$ 存在一定的晶体学位向关系,当歧化时间延长时,Fe_3B 会进一步分解成 α-Fe 和 Fe_2B。根据短的歧化时间促进材料各向异性形成,而长的歧化时间导致各向同性形成这一实验现象,他们认为中间相 Fe_3B 的存在与材料的各向异性相关。

Sepehri-Amin H 等[15]研究表明,Fe_2B 与初始 $Nd_2Fe_{14}B$ 相、再复合 $Nd_2Fe_{14}B$ 相存在 $[420]_{Fe_2B}$ // $[211]_{Nd_2Fe_{14}B(initial)}$、$[00\bar{2}]_{Fe_2B}$ // $[\bar{1}11]_{Nd_2Fe_{14}B(initial)}$、$[042]_{Fe_2B}$ // $[223]_{Nd_2Fe_{14}B(recombined)}$、$[\bar{1}\bar{1}2]_{Fe_2B}$ // $[2\bar{2}0]_{Nd_2Fe_{14}B(recombined)}$ 等位向关系,高度取向的 Fe_2B 相遗传了原始 $Nd_2Fe_{14}B$ 相取向,并在 DR 阶段传递给再复合的 $Nd_2Fe_{14}B$ 相形成各向异性织构。但歧化物中并未发现 Fe_3B 相,同时 NdH_2 和 α-Fe 相与初始 NdFeB 晶相不存在明显的特定位向关系。再复合 $Nd_2Fe_{14}B$ 相在 Fe_2B/NdH_2 界面优先形核,并沿着 NdH_2/α-Fe 界面生长。3DAP 显示 B 元素在 NdH_2/α-Fe 界面处富集,为 $Nd_2Fe_{14}B$ 相的形成提供必要的 B 元素。

TaKizawa R 等[19]通过 TEM-PED、SEM-EBSD 等分析发现,初始 $Nd_2Fe_{14}B$ 相经过 HD 处理后未残留 $Nd_2Fe_{14}B$ 相及 Fe_3B 相。Fe_2B 相在 HD 处理的后期才会形成,并且分布不均匀,取向差较大。故而否定了残留 $Nd_2Fe_{14}B$、Fe_3B 和 Fe_2B作为“记忆介质”的论点。在 DR 处理初期,再复合 $Nd_2Fe_{14}B$ 相在 NdH_2/α-Fe 界面处形成,这与 Sepehri-Amin H 等[15]实验结论不同。在 HD 阶段前期,α-Fe 和 NdH_2 晶粒呈织构形态,但 NdH_2 相的晶粒取向在长大的过程中遭到破坏,因此作者认为 α-Fe 最有可能诱导 $Nd_2Fe_{14}B$ 相生成各向异性织构。

Kim T H 等[16]在研究歧化产物时,同样未发现残留的 $Nd_2Fe_{14}B$ 相及 Fe_3B 相。在 HD 阶段,板条状 α-Fe 和 NdH_2 相生长方向杂乱,并且随着 HD 时间的延长,板条形态逐渐球化。歧化产物

Fe_2B 相(001)晶面在初始 NdFeB 相(001)晶面上形成,并呈 45°面内取向,沿着[001]晶向长大。Fe_2B 相(001)晶面与 NdFeB 相(001)晶面具有高的原子堆积密度和低的界面能,形核畸变小。[001]晶向上 B 元素扩散速度快,利于晶粒长大。在 DR 阶段,再复合 $Nd_2Fe_{14}B$ 相反而行之,从而获得初始 NdFeB 相特定的取向,其中 Fe_2B 相起到取向传递的媒介作用。实验结果表明,低的歧化氢压可以减缓歧化反应速度,形成高度取向的 Fe_2B 相,有利于 NdFeB 材料获得更好的各向异性;高的歧化氢压导致 Fe_2B 相取向混乱,致使 NdFeB 材料各向异性劣化。

Horikawa T 等[6,8]研究表明,板状取向的 α-Fe/NdH_2对各向异性的诱导有很大的促进作用。日本东北大学 Nakamura H 等[24-25]根据低的脱氢温度导致各向同性,而高的脱氢温度却使材料产生各向异性的实验事实,提出了脱氢再复合过程中 $Nd_2Fe_{14}B$ 晶粒的择优生长是 HDDR NdFeB 各向异性的起因。

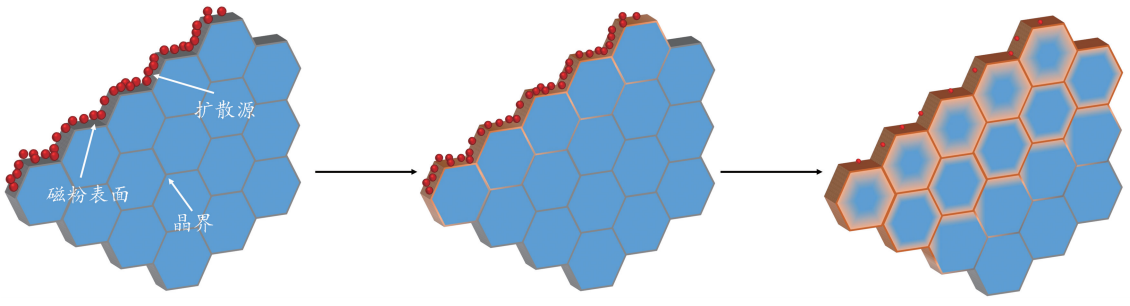
综上所述,HDDR 各向异性机理目前还处于探究阶段,机理研究的不明晰导致磁粉工艺的模糊性与不确定,从文献实验结果及实际生产中看,通过调整温度、氢压等参数获取高度取向的板条状歧化物对磁粉的各向异性形成至关重要。

2　HDDR 工艺应用研究

2.1　HDDR 钕铁硼磁粉晶界扩散技术研究

钕铁硼磁性材料由于居里温度点低,温度特性差,其在汽车驱动电机等新型领域的应用受到了限制。为了解决上述问题,人们通常会在 NdFeB 合金中直接添加重稀土(如 Dy、Tb)取代主相中的 Nd,形成各向异性场更高的 $(Nd,Dy)_2$-$Fe_{14}B$或$(Nd,Tb)_2Fe_{14}B$[26-27],从而提高矫顽力与温度稳定性。但重稀土原子与 Fe 原子亚铁磁性耦合,在原材料里直接添加 Dy、Tb 合金会造成磁体剩磁下降。为此 Park K T 等[28]开发出渗 Dy/Tb 晶界扩散技术。在烧结钕铁硼磁体表面溅射 Dy 和 Tb 重稀土层,热处理后磁体矫顽力明显提高而剩磁几乎不降。Dy 元素沿晶界渗入磁体并在主相 $Nd_2Fe_{14}B$ 周边形成$(Nd,Dy)_2$-$Fe_{14}B$ 薄壳,如图 4 所示。Gong Q H 等[29]的模拟计算显示,$(Nd,Dy)_2Fe_{14}B$ 薄壳 6~8 nm 厚即可获得足够的矫顽力与热稳定性。2003 年,Hamada N 等[30]受上述实验启发,将 $Dy_{70}Fe_{30}$ 粉末与(NdFeBNbGa)d-HDDR 磁粉混合热扩散处理,磁粉的矫顽力和热稳定性都有所提高,磁能积达到目前 HDDR 粘结体的最高值 213 kJ/m^3。

Dy、Tb 等重稀土资源稀缺,原材料成本昂贵,为此研究者探究其他非重稀土扩散物。APT 分析表明,HDDR 磁粉的晶界富钕相少且薄于烧结体[31-33],此结果说明 HDDR 磁粉晶界存在磁交换耦合,易在晶界附近形成反磁化畴相。孙爱芝、岳明等[34-35]对 HDDR 钕铁硼材料的磁化特性研究表明,富钕相对材料畴壁的钉扎是决定其矫顽力的关键因素。Sepehri-Amin H 等[36]将 $Nd_{70}Cu_{30}$粉末添加到 HDDR 钕铁硼磁粉中热扩散处理,磁粉的矫顽力 H_{cj}由 1 321 kA/m 提高到 1 552 kA/m。研究表明,扩散前后磁粉晶粒无明显长大,晶界变宽,富钕相在晶界分布更加均匀连续,这是提高 HDDR 钕铁硼磁粉矫顽力的微观



(a) 扩散前　　(b) 扩散中　　(c) 扩散后

图 4　钕铁硼磁粉晶界扩散示意图

Fig. 4　Schematic diagram of diffusion of NdFeB magnetic powder through grain boundary

组织要求。国内外诸多学者后续对磁粉晶界扩散技术开展了广泛研究,如表 1 所示。研究的扩散物主要是重稀土合金 Dy-Fe、低熔点共晶化合物 RE-Cu/RE-Al、稀土氢化物 REH_x 等。从这些研究成果来看,扩散处理后的磁粉矫顽力都有不同程度的提高,磁体温度稳定性得到改善。目前爱知制钢已将 NdCuAl[37] 晶界扩散技术运用到实际生产中,推出了高矫顽力、高热稳定性的 NdFeB 各向异性磁粉。

表 1　各向异性 NdFeB 磁粉晶界扩散处理性能变化情况

Table 1　Changes in properties of anisotropic NdFeB magnetic powder by grain boundary diffusion treatment

磁粉成分	扩散物	样品	材料性能（扩散处理前）			材料性能（扩散处理后）		
			B_r/T	H_{cj}/(kA·m^{-1})	(BH)max/(kJ·m^{-3})	B_r/T	H_{cj}/(kA·m^{-1})	(BH)max/(kJ·m^{-3})
NdFeBNbGa[30]	$Dy_{70}Fe_{30}$	磁粉	1.38	1 030.0	343	1.38	1 080.0	358
NdFeBNbGa[38]	DyFeH	粘结磁体	—	—	—	—	1 250.0	192
$Nd_{12.5}Fe_{72.8}Co_{8.0}B_{6.5}Ga_{0.2}$[36]	$Nd_{80}Cu_{20}$	磁粉	—	1 321.0	—	—	1 552.0	—
NdFeNbB[37]	$Nd_{80}Cu_{20}$/$Nd_{80}Al_{20}$	磁粉	—	—	—	1.28	1 433.0	—
$Pr_{13}Fe_{79.4}B_7Nb_{0.3}Ga_{0.3}$[39]	$Pr_{68}Cu_{32}$	磁粉	1.40	796.0	255	—	1 114.0	—
$Nd_{13}Fe_{79.4}B_7Nb_{0.3}Ga_{0.3}$[40]	$Pr_{68}Cu_{32}$	磁粉	1.40	1 035.0	326	—	1 433.0	—
$Ce_{13}Fe_{80}B_7$[41]	$Ce_{72}Cu_{28}$	磁粉	—	31.8	—	—	115.4	—
$Nd_{11.7}Fe_{82.1}B_{6.2}$[42]	$Pr_{68}Cu_{32}$	磁粉	—	208.6	—	—	980.1	—
Nd-Fe-B-Nb[43]	NdH_x	磁粉	0.91	756.0	—	1.04	955.0	—
$Nd_{12.5}Fe_{余}Ga_{0.3}Nb_{0.2}B_{6.4}$[44]	NdH_x	磁粉	—	1 072.0	—	—	1 216.0	—
	NdH_x/Cu	磁粉	—	1 072.0	—	—	1 320.0	—

2.2　钕铁硼 HDDR 回收研究

稀土是重要战略资源,也是不可再生资源。近年来持续的全球供给造成我国稀土矿储量急剧下降。钕铁硼材料中稀土含量约 30%,是稀土产业中最大的消费领域。随着磁性器件使用寿命的限制和磁体性能的衰减,会产生越来越多的废旧钕铁硼磁体。对废旧稀土磁体循环再利用不仅有利于节约稀土资源,保护生态环境,更能促进我国稀土产业的可持续发展。目前烧结钕铁硼磁体主要是湿法回收,回收率较高、稀土产品纯度好,但回收过程存在废气、废液二次污染。对于氧化程度不高的块状烧结钕铁硼材料,同理于 HDDR 制粉,可用氢气回收处理制备各向异性磁粉。Sheridan R S 等[45-46]、Yue M 等[47-48] 先后开展 HDDR 回收烧结钕铁硼工艺的研究,如表 2 所示。回收磁粉因为含氧量高、存在烧结晶粒长大等原因,致使矫顽力较回收前有所降低,Ikram A 等认为 HDDR 回收磁粉更适合制备粘结磁体[49] 或等离子放电烧结(SPS)磁体[50-51]。同时部分研究者采用扩散工艺提升回收磁粉或磁体的性能。

氢气回收烧结钕铁硼可以直接制备磁粉,用于制造粘结或烧结钕铁硼磁体,具有高效、环保、流程短的特点。德国克劳斯塔尔工业大学 Elwert T、英国伯明翰大学 Walton A 等开展新能源汽车驱动电机钕铁硼[60]、HDD 磁体[61] 氢处理回收研究,但不同成分的钕铁硼磁体 HDDR 处理工艺有差异[45]。若要形成产业,涉及磁性器件回收、拆卸、分类等环节,需要政策支持与产业链配套。

2.3　HDDR 磁粉制备热变形(热压)磁体研究

钕铁硼热变形磁体具有性能优异、温度稳定性好、耐腐蚀性强等优点,应用前景宽广,有望替代烧结钕铁硼磁体。目前制备热变形磁体的前驱磁粉有快淬磁粉和 HDDR 磁粉。快淬磁粉在贴辊面和自由面组织差异大,造成热变形磁体的

结构不均匀,粗晶区准周期性分布[62]。相比于快淬磁粉,HDDR 磁粉具有性能好、晶粒尺寸均匀等优点,适合用于制备热变形热压磁体。1992 年 McGuiness P J 等[63]首次采用 HDDR $Nd_{16}Fe_{76}B_8$磁粉制备出热变形磁体($B_r \approx 0.69$ T、$H_{cj} \approx 1\ 200$ kA/m、$(BH)\max \approx 90$ kJ/m^3)。Nozawa N 等[64]在热变形过程中发现,富钕相沿着晶界重新连续均匀分布有助于矫顽力的提高,从而制备出 $B_r = 0.92$ T、$H_{cj} = 1\ 031$ kA/m、$(BH)\max = 143$ kJ/m^{3}的 $Nd_{13.5}Fe_{72.0}Co_{8.0}B_{6.5}$热变形磁体,热变形后矫顽力提升 25%。2017 年 Cha H R 等[65]研究了形变温度与速率对磁体性能的影响,在温度 700 ℃、应变 1.4、应变率 0.001 S^{-1}形变条件下,800 ℃退火处理后获得磁体性能:$B_r = 1.24$ T、$H_{cj} = 827.6$ kA/m、$(BH)\max = 283.3$ kJ/m^3。Matin M A 等[66]发现,当热变形温度超过 650 ℃时,HDDR 磁粉中残留的氢气会使 NdFeB 氢化,形成 α-Fe 和 Fe_2B 相,劣化性能。

表 2 氢处理回收废旧块状烧结钕铁硼磁体情况

Table 2 The progress of recycling waste bulk sintered NdFeB magnets by hydrogen treatment

回收烧结钕铁硼成分	材料性能(磁体回收前)			材料性能(磁体回收后)			回收形式	回收工艺添加扩散物
	B_r/T	H_{cj}/(kA·m^{-1})	$(BH)\max$/(kJ·m^{-3})	B_r/T	H_{cj}/(kA·m^{-1})	$(BH)\max$/(kJ·m^{-3})		
$Nd_{14}Fe_{80}B_6$[52]	—	1 114.0	—	—	716.0	—	磁粉	$HD+DyF_3$
$Nd_{14}Dy_{0.6}B_6Al_{0.7}Fe_{78}$[53]	1.32	960.0	325.0	1.35	750.0	—	磁粉	HD
				1.24	830.0	290.0	烧结磁体	
$Nd_{13.78}Dy_{0.66}B_{6.30}Al_{0.76}-Fe_{75.51}C_{0.32}O_{1.84}$[54]	1.18	870.0	260.0	1.18	695.0	260.0	烧结磁体	HD
$Nd_{13.4}Dy_{0.8}Al_{0.7}Nb_{0.3}-Fe_{78.5}B_{6.3}$[55]	1.36	860.0	340.0	1.10	800.0	129.0	磁粉	HD+HDDR
$Nd_{13.4}Dy_{0.8}Al_{0.7}Nb_{0.3}-Fe_{78.5}B_{6.3}$[56-57]	1.36	860.0	340.0	1.08	840.0	175.0	磁粉	HDDR
	1.35	1 332.9	328.3	1.35	1 332.9	328.3	烧结磁体	DyH_3
NdCuFeCoBPrDy-GaTbCAlO[58]	1.32	1 230.0	—	0.90	841.4	111.6	粘结磁体	HDDR
$Nd_{10.1}Fe_{79.9}B_{5.9}-Pr_{3.0}Dy_{0.7}Co_{0.4}$[49]	1.42	1 131.0	—	1.26	1 226.0	255.0	磁粉	HDDR
$Nd_{10.6}Fe_{78.9}B_{5.7}-Dy_{3.7}Co_{1.1}$[49]	1.13	2 795.0	—	—	—	140.0	磁粉	HDDR
$Nd_{13.4}Dy_{0.6}Fe_{78.6}-B_{6.1}Nb_{0.4}Al_{0.7}$[51,59]	1.19	1 170.0	250.0	0.90	830.0	124.0	磁粉	HDDR+SPS
				0.79~0.80	1 120.0~1 160.0	100~110	SPS 磁体	

Yoo J G 等[67]研究均匀化退火对 $Nd_{12.5}Fe_{bal}-Ga_{0.3}Nb_{0.2}B_{6.4}$ HDDR 磁粉及热变形磁体的影响,发现退火处理甩带制备的磁粉矫顽力(1 035 kA/m)比未退火的(1 195 kA/m)低,但两者热变形后磁体矫顽力几乎相同,接近 717 kA/m,磁体剩磁分别为 1.26 T 和 1.22 T。在热变形过程中,晶粒从 250 nm 长大到 1~2 μm,小于烧结磁体但大于快淬热变形磁体。Kirchnery A 等[68]开展机械化合(高能球磨)、快淬、HDDR 等 3 种磁粉热变形实验,结果表明,球磨、快淬磁粉热变形应力指数为 3,HDDR 的仅为 2,HDDR 热变形抗力明显高于快淬磁粉的,这与 HDDR 磁粉晶粒(平均 300 nm)大于快淬磁粉(平均 50 nm)有关[69];同时磁粉热变形后晶粒长大,矫顽力降低[70]。研究者通过添加 $Nd_{70}Cu_{30}$[71]、Pr-Cu[72],涂覆 $Nd_{70}Cu_{30}$[73]、NdH_x/Cu[74]等热扩散方式提高热变形磁体矫顽力及形变能力。

目前热变形磁体主要前驱材料是快淬磁粉。在产业方面,日本大同电子热变形磁体产量达上千吨,主要应用于 EPS 电机及机器人伺服电机。

国内宁波金鸡、银河磁体等均实现批量生产,但热变形工艺存在组织不均匀、工艺稳定性差、成形效率低、成本高等不足,影响大规模推广使用。

2.4　HDDR 各向异性粘结钕铁硼磁体研究

粘结 NdFeB 永磁材料可直接加工成环状等复杂形状,尺寸精度高,且易于大批量自动化生产,近些年在电子产品器件、汽车等领域得到大量应用。粘结磁体是磁粉和粘结剂树脂构成的复合材料,按成形方式可分为模压、注射、挤出和压延 4 种。HDDR 磁粉经过十几年发展,主要用于模压各向异性粘结磁体的生产。MnBi、SmFeN、SmCo 材料温度特性好于 NdFeB 的,且磁粉粒径小于 NdFeB 磁粉的。研究者将 MnBi[75]、SmFeN[76-80]、SmCo[81-82] 磁粉与 NdFeB 磁粉搭配,能显著提高模压磁体密度与磁性能,改善温度特性,其中添加 SmFeN 磁粉的综合性能最好。

大批量 HDDR 制粉和高效成形技术是制约 HDDR 粘结磁体商业化的关键因素。HDDR 工艺条件要求苛刻,磁粉量大时,钕铁硼相变引起温度、氢压波动大,导致磁粉性能劣化。模压成形工艺是将磁粉与粘结剂树脂混合造粒,置于模腔内在磁场作用下温压成形。影响磁体性能的因素包括磁粉性能与粒度[83]、磁粉表面处理[84-85]、树脂改性[80,86-87]、模具结构设计等,同时必须精准控制压机压力、磁场强度与树脂融化/固化时间,才能获得高密度、高取向的粘结磁体。日本爱知制钢是全球唯一可大批量生产各向异性粘结钕铁硼磁体的企业,2002 年该公司推出了各向异性 MAGFINE 系列产品,最大磁能积可达 200 kJ/m^3。国内北京科技大学、中船集团七二五所等单位制备的磁粉性能与爱知制钢的几乎相当,其中中船集团七二五所通过自主设备开发,模具磁路设计、树脂粘结剂研究等,已突破模压取向成型技术,批产产品性能达 160 kJ/m^3。目前稀土粘结磁体市场几乎被钕铁硼各向同性粘结产品所垄断。理论上各向异性磁体的磁能积是各向同性磁体的 4 倍,为了满足器件高效节能、轻量小型化需求,开发更高性能的各向异性的粘结磁体势在必行。

2.5　HDDR 磁粉制备烧结钕铁硼磁体研究

微磁学[88-89]模拟表明,减小晶粒尺寸可以降低局部退磁因子和矫顽力温度系数,从而提升内禀矫顽力。韩景智等[90]通过优化 HDDR 工艺,将磁粉晶粒尺寸从 400 nm 细化到 250 nm,晶界富钕相均匀分布,矫顽力从 920 kA/m 提升到 1 440 kA/m。Nakamura M 等[91]通过 HDDR+氦气气流磨工艺,获得平均粒径 500 nm 左右的单晶磁粉。随后,研究人员开发出亚微米烧结钕铁硼磁体[92-93],但磁体的矫顽力并未获得预期的提升。丁广飞等[94]采用 HDDR+HD+气流磨工艺制备出粒度 1 μm 以下的磁粉,但烧结磁体(H_{cj}=1 172 kA/m)并没有获得理想的矫顽力,磁体晶界富钕相分布不连续[95],因此技术上仍待突破。

3　结语

HDDR 各向异性粘结钕铁硼磁体开发历史悠久,目前其磁能积是各向同性粘结磁体的两倍。该磁体能显著提升微特电机电能-机械能转化效率,满足电动器件节能和轻量化要求,在新能源汽车、无人机、智能家电等领域应用前景广阔。2003 年丰田旗下的爱知制钢向市场推出各向异性粘结磁体,并形成了一定产业化规模。我国在 HDDR 制粉设备上已完成 50 kg 级工业化验证,但在磁体成形技术方面仍不成熟,性能也与国外的有一定差距,这严重制约了 HDDR 磁体的市场发展。为此我们必须加强产学研、多学科结合,一方面,加强各向异性机理、晶界扩散机理协同研究,指导 HDDR 工艺调整,并与晶界扩散技术相结合,实现 HDDR-晶界扩散工艺相统一,在一个设备里完成HDDR-晶界扩散,提高磁粉性能与制备效率;另一方面,加强树脂粘结剂、成形设备开发,提高磁体性能与成形效率,随着生产自动化日益精进,各向异性粘结钕铁硼磁体性价比优势越来越明显。

近几年,英国伯明翰大学联合汽车制造商等使用“废磁性材料氢处理工艺”(HPMS)来实现稀土回收和稳定稀土供应链。我国是全球最大的钕铁硼生产国与消费国,在磁体回收利用技术领域接近世界先进水平,如何进一步提高回收磁体的性能和实现工业化生产是未来研究的重点。“十四五”国家重点研发计划已将可再生稀

土材料二次利用列为共性关键技术。我国在热变形(热压)、晶粒细化等制备技术方面,同美国、日本等发达国家仍存在一定的差距,HDDR 工艺为制备性能优异的热变形磁体、烧结磁体提供新的可能,具有潜在研究与使用价值。

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