钕铁硼废料中的铁回收利用现状

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摘　要: 首先对钕铁硼废料中稀土回收的各种湿法工艺进行了简要介绍, 然后着重对钕铁硼废料中铁资源回收利用的相关工艺如稀土与铁的共回收、回收稀土后的含铁废水或废渣的处理、钕铁硼废料的直接回用和再生等的研究状况进行了综述, 比较了各种工艺的优缺点, 并就钕铁硼废料中的稀土和铁资源回收利用的研究提出了建议, 可为实现钕铁硼废料的更高效综合利用、减少二次污染提供借鉴。

关键词: 钕铁硼废料; 铁; 回收; 稀土; 综合利用

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钕铁硼是一种性能优越的磁性材料, 在众多领域都有广泛的应用[1]。钕铁硼在生产加工过程中会产生约 30% 的废料, 此外在应用过程中磁性材料自身或随设备报废也会产生大量废料。这些废料中含有 20%~30% 的稀土元素, 其余主要是铁, 具有较高的利用价值。对钕铁硼废料进行资源化再利用, 可以减少固废污染, 同时降低稀土生产成本, 利于实现稀土矿产资源的可持续利用。

目前对钕铁硼废料进行资源化利用的相关研究很多, 其中火法工艺尚未实现工业化[2,3], 而湿法工艺应用较广泛, 其基本流程是先将废料溶解, 然后进行稀土与铁的分离、稀土酸溶液的除杂净化, 最后将稀土沉淀后进行灼烧, 得到稀土氧化物。

采用全溶法时通常不进行废料的预处理, 直接用酸将稀土与铁完全溶出。因酸溶液中铁浓度较高, 后续可用硫化物将铁沉淀[4], 也可将稀土以复盐[5~9]、氟化物[10]、草酸盐[11,12]或磷酸盐[13,14]等形式沉淀, 或采用萃取的方法[15~19]使稀土与铁分离。

采用优溶法时通常要进行废料的预处理, 如自然氧化[20]、氧化焙烧[21~26]、硫酸化[27~31]、氯化[32,33]、硝酸化[34]、电解[35]等, 然后用酸或水将废料中的稀土优先溶出而与大部分的铁分离。酸溶液中仍残留少量的铁, 可以使用氧化剂如 H_2O_2[36]、MnO_2[37]、$NaClO_3$[38~40]等, 或采用电化学[41]的方法将残留的铁尽可能地全部氧化为三价, 然后调节溶液的 pH 值将其水解生成 $Fe(OH)_3$ 沉淀而除去。

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净化后溶液中的稀土离子可用草酸、碳铵[42]等进行沉淀,再经灼烧即可得到稀土氧化物。

这些工艺通常仅回收了钕铁硼废料中的稀土和钴[12,39,43~45]等稀贵金属,而其中占废料总重约70%的铁则未加以综合利用和合理处置,往往形成酸性废水或废渣污染水源、占用土地,造成了环境污染。

目前对钕铁硼废料中铁资源回收利用的研究较少,多是将铁随稀土一并加以回收利用,而铁单独回收制得的产品则价值偏低,故未引起人们足够的兴趣。本文综述了目前钕铁硼废料处理过程中对其中的铁资源进行回收利用的相关研究。

1 稀土与铁共回收工艺

1.1 湿法工艺

该法是将钕铁硼废料溶解之后,向溶解液中加入含 CO_3^{2-}、OH^-、$C_2O_4^{2-}$ 等的沉淀剂或采用电化学的方法,使稀土和铁同步或分步沉淀下来加以回收利用。

Lai 等[46]用盐酸溶解钕铁硼油泥,并用 H_2O_2 将 Fe^{2+} 氧化,然后用氨水做沉淀剂将稀土、铁与钴元素一起沉淀回收,工艺简单,沉淀效率高,沉淀经高温分解制得的复合粉体产品可满足制备二次钕铁硼的需要[47]。田忆兰等[48]用盐酸溶解钕铁硼废料,并用 H_2O_2 将 Fe^{2+} 氧化,然后利用尿素来沉淀稀土和铁元素,通过调节温度来改变尿素的水解速度,进而控制沉淀过程的速度,沉淀产物经灼烧可得铁与稀土的混合氧化物,流程简单,产品纯度和收率都比较高。刘敏等[49,50]将钕铁硼油泥用盐酸溶解,用 H_2O_2 氧化 Fe^{2+} 后,采用两步共沉淀法回收钕铁硼废料中的稀土和铁元素。沉淀物经加热分解得到钕铁混合氧化物,后续可用于制备钕铁硼。Liu 等[51]将钕铁硼废料经氧化焙烧后与草酸溶液进行反应,得到草酸稀土为主的固体沉淀物和含草酸铁的浸出液。沉淀物经焙烧后得到稀土氧化物,而浸出液中加铁粉还原,可制备出 $FeC_2O_4 \cdot 2H_2O$。

He 等[52]用磷酸做浸出剂选择性地浸出钕铁硼油泥中的铁,生成的 $REPO_4$ 沉淀用稀盐酸溶解后再用草酸沉淀稀土,经焙烧可得稀土氧化物,而磷酸浸出液可用草酸沉淀出 $FeC_2O_4 \cdot 2H_2O$,磷酸在回收铁的过程中再生。

共沉淀法避免了稀土与铁的分离过程,工艺简单,流程较短,元素回收率高,实现了有价元素的同步回收,但只能得到铁与稀土的混合物,应用范围较窄;分步沉淀法过程稍复杂,但选择性地分离了稀土和铁,可实现稀土和铁的高值回用。另外,由于两种方法都需要用酸将钕铁硼废料溶解再进行沉淀反应,故不管用哪种沉淀剂,最终还是会产生一定量的含盐废水。

兰超群[53]用氢氟酸将超细钕铁硼废料中的稀土转化为稀土氟化物沉淀,而铁则溶于氢氟酸溶液中,再通过电沉积的方式回收铁,同时再生氢氟酸溶液回用于溶解废料,整个过程没有废弃物和污染物的排放,实现了资源循环利用和回收过程零废排放的目的。

1.2 火法工艺

火法工艺依据钕铁硼废料中的稀土元素在高温条件下能与某些固态或气态的提取剂反应生成对应的化合物或合金等,再通过简单的物理方法或较清洁的化学方法将其与硼铁等分离,如氧化法[54~58]、氯化法[59~63]、液态合金提取法[64~66]等,无复杂的原料处理过程,流程较短,对环境无不良影响,缺点是在高温下进行,能源消耗大。利用这些方法回收稀土后,铁最终形成金属或 Fe-B 合金,附加值高,但目前鲜见对此铁金属或合金进行利用的相关研究。也可将钕铁硼废料中的铁以挥发性的 $Fe(CO)_5$ 的形式与稀土分离,同步回收铁并将稀土富集于残渣中。Miura 等[67]对钕铁硼粉末废料进行加氢歧化处理,得到 α-Fe/Fe_2B/NdH_2(或氧化钕)纳米复合粉体,再以硫为催化剂进行羰基化反应,铁元素提取率显著提高。李博等[68]将钕铁硼废料进行氧化焙烧后用饱和的硫酸盐溶液处理,再对焙砂进行热还原,所得还原块料与 CO 进行合成反应,生成的五羰基铁可用于生产高附加值的微米级羰

基铁粉。该方法羰基化反应时间较长,使生产效率低下,且使用了 CO,生产上操作较困难。

2　回收稀土后的废水或二次废渣的再利用工艺

湿法工艺处理钕铁硼废料后会产生含铁盐的酸性废水或含 Fe_2O_3、$Fe(OH)_3$ 的二次废渣,较直接的应用是将废水用于蒸发浓缩结晶出铁盐[69],也可将废渣应用到其他需要铁源的相关工艺中[70],Fe_2O_3 渣还可直接作为炼铁的原料[30,34,71]。Liu 等[72]以 NdFeB 废磁体中回收稀土后的废液为原料制备了 α-Fe_2O_3 纳米颗粒,对亚甲基蓝具有良好的吸附性能。Itoh 等[32]的研究表明,NdFeB 废料用 NH_4Cl 选择性氯化分离稀土后的铁基固体残渣具有良好的电磁波吸收性能,可作为电磁波吸收剂再利用。

若将二次废渣进行转化,则可用于制备铁矾[73]、铁氧体、氧化铁红等。吴冕等[74]使用硫酸浸取钕铁硼二次废料,通过黄铵铁矾法使得酸浸液中的铁以斜六方体形貌的黄铵铁矾的形式沉淀,而与少量稀土以及其他元素分离,对后续稀土元素的富集以及采用沉淀法与其他元素进行分离有很大意义。钟晓林等[75]以回收稀土后的钕铁硼废渣为原料,用硫酸浸出其中的铁,在溶液中用铁屑将 Fe^{3+} 还原为 Fe^{2+},净化除杂后按比例加入 $MnSO_4$ 和 $ZnSO_4$,用碳酸氢铵将各组分沉淀下来,经过干燥、研磨、焙烧等过程即可制得粒径约为 50 nm、近球形的 Mn-Zn 铁氧体微粉,活性高、纯度高。宋宁等[76]以钕铁硼二次废渣为原料,用硫酸浸出其中的铁,经净化和重结晶后得到硫酸亚铁溶液,按配方加入锰盐和锌盐,用碳铵和氨水为沉淀剂,共沉淀出的前驱体经微波干燥、煅烧得到 Mn-Zn 铁氧体微粉,再经烧结即可得到纯度高、活性好的 Mn-Zn 铁氧体,其主要成分的含量与原配方相比偏差小。梁浩等[77]将钕铁硼废料优溶液中的 Co、Zn、Cu 等元素萃取分离出来,添加配料,经共沉淀、焙烧制粉,再与优溶渣混合焙烧制粉,制得了尖晶石型铁氧体磁粉,该方法最大限度地利用了钕铁硼废料中回收稀土后的各种组分。王兴尧等[78]用盐酸浸取钕铁硼二次废料,然后用有机萃取剂萃取浸取液中的铁,再用氨水进行水热反萃沉淀,经洗涤、烘干、研磨得到深红色的纳米氧化铁红粉末。肖景波等[79]用硫酸对钕铁硼废料酸浸渣进行循环浸出,浸出液进行还原、分步沉淀,依次得到碳酸稀土、硫化钴和氢氧化亚铁,氢氧化亚铁最终制成氧化铁红工业颜料,该方法同时也实现了对钕铁硼废料酸浸渣中微量稀土和钴元素的有效分离和富集,各种资源得到了综合利用。这些方法多为湿法工艺,流程长,在充分利用废水或废渣的过程中还是会不可避免地产生新的废水。

3　钕铁硼废料回用和再生技术

依据钕铁硼废料来源和氧化程度的不同,可以分别采取不同的处理方法进行再生或直接回用,如制备磁粉、烧结磁体、粘结磁体和热压磁体等,铁与稀土都可得到最大限度的回收利用。

烧结钕铁硼磁体机械加工过程产生的块状废料,氧化程度不高,仍基本保持原有的成分、微结构和一定的磁性,如果用复杂的工艺流程溶解、分离提纯、回收其中的有价元素则从工艺和经济上都显得不合理。未被氧化的烧结钕铁硼磁体废料可经清洗、去皮等处理后送回熔炼或制粉工序[80]进行再利用,该方法不需要复杂的前处理,可沿用原有的磁体制备工艺,因此生产上更为方便可行。轻微氧化的钕铁硼磁体废料则需进行再生处理以满足应用的性能要求。目前常用的再生技术有氢处理技术[81~83]、掺杂法[84~86]、熔盐溶解氧化物法[87]等,这些方法流程短,工艺环保,但再生后的磁体某些性能仍无法恢复到原磁体的水平。

氧化较严重的钕铁硼油泥废料可用钙热还原法[88~90]制得钕铁硼合金以达到回用的目的,但对还原条件要求比较严格。

4 结语

铁在钕铁硼废料中占有较大的比重,但由于自身的经济价值不明显,故钕铁硼废料中铁的回收利用并未引起人们较多的关注。在现有的钕铁硼废料处理工艺中,湿法工艺流程长,会产生新的废弃物,且多是将铁作为稀土产品的杂质组分废弃,若将铁随稀土一并回收则会降低稀土产品的价值,并且产品利用范围较窄;若将铁作为回收稀土后的二次废物再利用,可充分利用资源,避免造成固液废弃物污染环境,但不会产生显著的经济效益。火法工艺可将铁作为回收稀土的副产品,价值较高而且工艺相对清洁,但设备要求高,能源消耗大,不适宜工业化生产。钕铁硼废料直接回用和再生技术仅适用于氧化程度不高的废料,再生磁体性能的下降也是有待解决的问题。

为高效利用钕铁硼废料中的稀土和铁资源及避免造成废弃物污染环境,今后的研究可从以下几方面入手:(1)火法、湿法、电化学、生物学方法等多种方法联用,使钕铁硼废料处理工艺绿色化,降低处理成本;(2)某些钕铁硼废料中仍存在合金状态的稀土和铁,通常在废料焙烧或酸浸过程中被氧化,其还原性未得到利用,故可考虑在钕铁硼废料处理过程中加以合理利用;(3)拓宽稀土和铁的共沉淀物及回收稀土后的铁渣、含铁废液的应用领域;(4)简化回收稀土后的铁渣和含铁废液的处理流程,降低处理成本,提高再利用的经济效益。

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Current Situation of Iron Recovery and Utilization in NdFeB Waste

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Abstract: Firstly, various wet processes for the recovery of rare earth in Nd-Fe-B waste are briefly introduced. Then it focuses on the research status of the relevant processes of iron resource recovery and utilization in Nd-Fe-B waste, such as co-recovery of rare earth and iron, treatment of iron-containing wastewater or waste slag after recycling rare earth, direct reuse and regeneration of Nd-Fe-B waste are reviewed. This paper compares the advantages and disadvantages of various processes, and puts forward some suggestions on the recycling of rare earth and iron resources in Nd-Fe-B waste, which can provide reference for realizing more efficient comprehensive utilization of Nd-Fe-B waste and reducing secondary pollution.

Key words: NdFeB waste; iron; recovery; rare earth; comprehensive utilization