Rare-earth-free magnetically hard ferrous materials

Zefan Shao and Shenqiang Ren

Permanent magnets, especially rare-earth based magnets, are widely used in energy-critical technologies in many modern applications, involving energy conversion and information technologies. However, the environmental impact and strategic supplies of rare-earth elements hamper the long-term development of permanent magnets. Hence, there is a surge of interest to expand the search for rare-earth-free magnets with a large energy product ($BH_{\text{max}}$). Among these rare-earth-free magnets, iron-based permanent magnets emerge as some of the most promising candidates due to their abundance and magnetic performance. In this review, we present a summary of iron-based permanent magnets from materials synthesis to their magnetic properties.

1 Introduction

Permanent magnets have received intense interest due to their applications in energy-critical technologies, such as wind turbine, electric vehicles and information storage.\(^1\)–\(^8\) The essential measure of permanent magnets is the energy product,\(^9\)\(^,\)\(^10\) which is defined as the product of $B$ and $H$ in the second quadrant hysteresis curve.\(^11\)\(^,\)\(^12\) Rare-earth magnets include neodymium magnets and samarium–cobalt magnets.\(^13\)–\(^15\) However, considering the rapidly increasing demand for rare-earth elements in various areas (Fig. 1a), much attention has been focused on searching for new alternative magnets with rare-earth-free elements.\(^16\)\(^,\)\(^17\) The rare-earth-free magnetic materials with high magneto-crystalline anisotropy and energy product exhibit promising potential for use as permanent magnets (Fig. 1b and Table 1).\(^16\)\(^,\)\(^18\)

Among many pursued rare-earth-free elements, iron has been emerging as one of the most promising candidates due to...
its abundance and large saturation magnetization.\textsuperscript{19,20} The ferrites have shown their applications in navigation from ancient times.\textsuperscript{11,21} Iron-based magnets with a large coercivity, such as FePd, FePt, FeCo, Fe\textsubscript{12}N\textsubscript{2}, \textepsilon-Fe\textsubscript{2}O\textsubscript{3}, FeNi and Fe\textsubscript{5}Se\textsubscript{4}, would present great potential for green energy applications due to the coexistence of ferromagnetic and antiferromagnetic coupling.\textsuperscript{22} The magnetization of these magnets is temperature-dependent and shows an abrupt transition point due to the phase transformation.\textsuperscript{23} Alternatively, high coercivity can also be triggered by the dimension and morphology of ferrite hard magnets within the single domain region.\textsuperscript{24} The ferrite magnets could exhibit tuneable coercivity ($H_C$) due to the varied particle size and stoichiometry.\textsuperscript{25} Moreover, magnetic properties can be influenced by the exchange coupling interaction between magnetically hard and soft phases.\textsuperscript{22,23} In this review, we summarize the strategies for the synthetic control of magnetic properties in iron-based magnets.\textsuperscript{14,45}

\section{Preparation and magnetic properties of iron-based ferrous materials}

Iron-based ferrous materials are some of the rare-earth-free hard magnets with a large uniaxial magnetocrystalline anisotropy.\textsuperscript{26} Iron-based magnets, particularly the tetragonal L\textsubscript{1}$_0$ ordered phase, show promising applications in information storage and electrical machine systems due to their large magnetic anisotropy and high coercivity.\textsuperscript{18,53,54} Therefore, intense attention has been focused on the formation of the L\textsubscript{1}$_0$-ordered phase in iron-based magnets.\textsuperscript{25}

\subsection{Iron cobalt hard magnet}

The FeCo alloy, an important magnetic material, is very attractive due to its high saturation magnetization ($M_s$) and Curie temperature ($T_C$) among transition metal alloys, while its small coercive field and low magnetocrystalline anisotropy indicate its soft nature.\textsuperscript{27} However, tetragonal distorted FeCo alloys could turn FeCo alloys into hard magnets with high coercivity.\textsuperscript{16} The theoretical calculations achieved by Wu \textit{et al.} in 2008 showed a giant uniaxial magnetocrystalline anisotropy and saturation magnetization in body-centered-tetragonal FeCo alloys (Fig. 2a).\textsuperscript{57}

The possibility of achieving high magnetocrystalline anisotropy in FeCo alloys was initially inspired by staining metal films on a templated substrate. In 2006, Winkelmann, \textit{et al.} reported the perpendicular magnetic anisotropy induced by pure Fe and Co films grown on Pd (001), showing that the anisotropy energy can be improved by a tetragonal crystal structure.\textsuperscript{28} A suitable range of lattice-parameter ratios, known as $c/a$ values, can promote the formation of tetragonal FeCo, which were proved to be between 1.18 and 1.31 by Warnicke \textit{et al.} in 2007.\textsuperscript{29} The exact prerequisites, obtained using the $c/a$ ratio, promote the synthesis of a tetragonal crystal structure of an FeCo alloy and provide a potential direction for high magnetocrystalline anisotropy. In 2012, Kim and Hong reported that the energy product of FeCo grown on an FePt (001) substrate, as shown in Fig. 2b, can reach 66 MGOe and the maximum

\begin{table}[h]
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\begin{tabular}{|l|l|l|}
\hline
Hard magnet & Magnetocrystalline anisotropy, MJ m\textsuperscript{-3} & Saturation magnetization, kG \tabularnewline \hline
Fe\textsubscript{16}N\textsubscript{2} & 2.0 & 28.3 (ref. 36 and 37) \tabularnewline
L\textsubscript{1}$_0$FeCo & 0.1 & 24.5 (ref. 38) \tabularnewline
L\textsubscript{1}$_0$FePt & 6.6 & 13.8 (ref. 39 and 40) \tabularnewline
L\textsubscript{1}$_0$FeNi & 1.3 & 14.7 (ref. 41) \tabularnewline
L\textsubscript{1}$_0$FePd & 1.8 & 13.7 (ref. 40 and 42) \tabularnewline
Zr\textsubscript{2}Co\textsubscript{11} & 1.1 & 7.8 (ref. 43 and 44) \tabularnewline
MnBi & 1.0 & 8.2 (ref. 45 and 46) \tabularnewline
MnAl & 1.8 & 7.5 (ref. 47 and 48) \tabularnewline
Alnico 9 & 0.2 & 11.2 (ref. 49 and 50) \tabularnewline
Alnico 5–7 & 0.1 & 13.5 (ref. 50 and 51) \tabularnewline
\hline
\end{tabular}
\caption{Magnetic properties of rare-earth-free magnets}
\end{table}
coercivity, guided by a full potential linearized augmented plane wave (FLAPW) method, is 188 kOe. In 2015, Giannopoulos introduced an advanced FeCo ultrathin layer grown on an L10 FePt film, which shows a maximum energy product of up to 50 MGOe and a maximum coercive field of 50 kOe, as shown in Fig. 2c. These discoveries clearly show the potential applications of FeCo alloys in permanent magnets. In 2014, the interstitial boron doped FeCo, introduced by Khan and Hong, indicated that the magnetocrystalline anisotropy constant can reach 0.8 MJ m$^{-3}$ with an estimated energy product of 100 MGOe. The preparation of tetragonal distorted FeCo magnets reported so far has been through similar routes by synthesizing under a high temperature and oxygen-free environment. The average diameter of FeCo particles, synthesized in this method, inevitably increases with the rise of temperature. The magnetic properties, such as coercivity, can be weakened with a large size of FeCo particles. A long-standing challenge of controlling the particle size has been overcome by utilizing an AuCu/FeCo (core/shell) structure (Fig. 2d), introduced by Ren in 2014. This approach presents a tetragonal FeCo microstructure which is induced by the L1$_0$ ordering of the AuCu core, with an average diameter of 10 nm and a significantly high coercivity and magnetization with the values of 846 Oe and 221 emu g$^{-1}$, as shown in Fig. 2e and f.

2.2 Iron platinum and iron palladium hard magnets

Precious metal ferromagnets, such as FePd and FePt, have shown a large magnetocrystalline anisotropy due to their crystal structure. The L1$_0$ ordered FePd and FePt alloys show a large magnetocrystalline anisotropy. The microstructure of hard magnet FePd is dominated by a face-centered-tetragonal lattice.

2.2.1 Iron palladium. Iron palladium (FePd) alloys, achieving high magnetocrystalline anisotropy and energy density, attract intense interest due to their broad applications ranging from data storage to ferrofluids. The colloidal solution synthesis of hard magnetic FePd particles is one of the most studied ones. The formation of a tetragonal FePd lattice, triggered by high temperature sintering, makes the FePd particles exhibit a hard magnetic performance. The phase formation, induced by high temperature conditions, cannot always control the size of annealed FePd nanoparticles during the sintering process. The simultaneous chemical reaction introduced by Chen and Nikles in 2002 was operated in a three-neck flask by the reduction of palladium acetylacetonate and thermal decomposition of iron pentacarbonyl, which achieved an optimal coercivity of 685 Oe as shown in Table 2.

The order parameter $S$, presented in Table 1, was calculated using unit cell parameters $(a, c)$ obtained by X-ray diffraction quantification. The FePd nanoparticles would reach an average diameter of 11 nm after annealing at 773 K for 1 h (Fig. 3a). Meanwhile, the FePd nanoparticles introduced by Sato et al. in 2000 were synthesized by a modified polyol process, showing the thermal treatment effect on magnetic properties. Besides, in 2004 Hou et al. reported monodisperse FePd nanoparticles, controlled by the ratio and type of stabilizer, presenting an average diameter of 13.5 nm and an optimal coercivity of 350 Oe, as shown in Fig. 3b. The exchange-coupling also played an important role in controlling the formation of L1$_0$ FePd. In 2013, Yu et al. reported a one-pot synthesis of L1$_0$ FePd–Fe (Fig. 3c), which was controlled by a thermodynamically stable mixture, with the lattice fringe spacings of 0.27 nm and 0.20 nm (Fig. 3d), indicating an optimal coercivity of 2.6 kOe and a saturation magnetization of 190 emu g$^{-1}$, as shown in Fig. 3e. A eutectic reaction, known as liquid phase transformation, is based on a solid-state eutectic composition with low melting point to minimize energy consumption which leads to a low-cost manufacturing process.

![Fig. 2](image)

**Fig. 2** (a) The calculated total energy ($\Delta E$) and magnetocrystalline anisotropy energy ($E_{\text{MCA}}$) of FeCo along the (001) direction; (b) a schematic illustration of the crystal structure of FeCo/FePt(001); (c) magnetic hysteresis loops for an FeCo/FePt thin film; (d) schematic figure of the AuCu/FeCo (core/shell) nanocrystal synthesis; (e) the TEM image of AuCu/FeCo (core/shell) nanoparticles; (f) the $M$–$H$ loops of L1$_2$ AuCu/FeCo particles. The inset shows the annealing temperature-dependent coercivity of L1$_2$ AuCu/FeCo. Reproduced from ref. 42, 45, 46 and 48 with the permission of AIP Publishing, Elsevier and American Chemical Society.

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<th>Condition</th>
<th>Vacuum</th>
<th>Vacuum</th>
<th>Vacuum</th>
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<td>600</td>
<td>700</td>
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<tr>
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<td>$c$ (pm)</td>
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<td>$S$</td>
<td>0</td>
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<tr>
<td>$H_c$ (Oe)</td>
<td>12</td>
<td>665</td>
<td>548</td>
<td>421</td>
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2.2.2 Iron platinum. Iron platinum (FePt), face-centered-cubic (FCC) phase, can be transformed into a face-centered-tetragonal (FCT) phase with a large magnetocrystalline anisotropy after a high temperature thermal annealing.\(^{75}\) During the past few decades, researchers have developed many synthetic routes to attain FePt with a FCT lattice microstructure, such as one-step thermal synthesis with metal precursors, water-in-oil microemulsion and exchange-coupled assembly. In 1935, L1\(_0\) FePt alloys, with a magnetocrystalline anisotropy of 66 Merg cm\(^{-3}\), were synthesized by Graf and Kussmann.\(^{76}\) The ordered L1\(_0\) FePt alloys can be generated by annealing FCC FePt at a certain temperature which is above the FCT ordering temperature. In 2003, Jayadevan reported a chemical route, achieving the transition of the FCT crystal structure of FePt, with an optimal coercivity of 1.7 kOe at 10 K, as shown in Fig. 4a.\(^{77}\) Through the decomposition of platinum acetylacetonate and iron pentacarbonyl in the presence of oleic acid and oleylamine, monodisperse FePt was successfully prepared in 2000 by Sun et al.\(^{78}\) In 2003, Sun’s group reported fct-FePt (Fig. 4b) nanoparticles obtained from a chemical reaction route, showing a high coercivity of 7.6 kOe (Fig. 4c).\(^{79}\) The chemical synthesis routes for FePt were the dominating routes in the past few decades. Meanwhile, a long-existing challenge is the aggregation of FePt nanoparticles induced by thermal annealing beyond the single-domain region. In 2004, the synthesis of FePt nanoparticles with tunable size was introduced by Chun et al., where the average diameter of FePt was 6 nm (Fig. 4d and e) and the room temperature coercivity reached 13 kOe.\(^{80}\) The transformation of the face-centered-tetragonal phase generated from the disordered FCC crystal structure requires a reaction temperature above 650 °C, while the morphology and structure of FePt nanoparticles are likely to be destroyed during the sintering process due to the relatively high temperature. In 2019, Ren et al. developed an annealing route known as eutectic melt crystallization of ordered L1\(_0\)-FePt to synthesize an ordered face-cubic-tetragonal FePt alloy, as shown in Fig. 4f. The as-synthesized L1\(_0\)-FePt particles exhibited a coercivity of 16 kOe and a saturation magnetization of 33.6 emu g\(^{-1}\) with the optimal energy product reaching 5.0 MGOe, as shown in Fig. 4g-i.\(^{81}\)

2.3 Fe\(_{16}\)N\(_2\)

The Fe\(_{16}\)N\(_2\) magnet, one of the promising permanent magnet candidates, exhibits a giant saturation magnetization.\(^{82}\) The synthesis of bulk \(\alpha''\)-Fe\(_{16}\)N\(_2\) was reported (Fig. 5a).\(^{83}\) In 1972, Kim and Takahashi studied the saturation magnetization and magnetic moment of \(\alpha''\)-Fe\(_{16}\)N\(_2\) which showed a saturation magnetization of 2000 emu cm\(^{-3}\), as shown in Fig. 5b, which is larger than that of FeCo.\(^{84}\) Due to its high magnetic performance, much attention was paid to the exploration of different types of \(\alpha''\)-Fe\(_{16}\)N\(_2\), such as bulk, nanoparticles and thin films. Subsequently, various synthesis routes were reported, such as the preparation of \(\alpha''\)-Fe\(_{16}\)N\(_2\) nanoparticles using compounds containing Fe\(_2\)O\(_3\) and NH\(_3\)-H\(_2\) mixed gas, introduced by Bao and Metzger in 1994.\(^{85}\) These methods mostly produced multiple phases, including \(\alpha''\)-Fe\(_{16}\)N\(_2\), while the magnetic properties can be influenced by the volume ratio of \(\alpha''\)-Fe\(_{16}\)N\(_2\) (Table 3). In 2016, Wang et al. reported a route for the synthesis
of Fe$_{16}$N$_2$ by ball milling and shock compaction, achieving a high saturation magnetization of 210 emu g$^{-1}$ and a large coercivity ($H_C$) of 854 Oe, as shown in Fig. 5c. Fig. 5d suggests that the coercivity of the synthesized free-standing Fe$_{16}$N$_2$ foil can reach 1910 Oe. The value of the magnetic energy product of Fe$_{16}$N$_2$ can reach 20 MGOe at room temperature, proving the potential applications in permanent magnets, as shown in Fig. 5e. Fig. 5f indicates the crystalline structure through the TEM diffraction pattern.

2.4 ε-Fe$_2$O$_3$

Iron oxides exist as different crystalline polymorphs, such as α-, β-, γ-, and ε-Fe$_2$O$_3$. Among these iron oxides, ε-Fe$_2$O$_3$ is of much interest due to its unique magnetic properties. The ε-Fe$_2$O$_3$ formed under exclusively high temperature conditions exhibits potential applications in recording media and micro-wave devices. The silica template methods, depending on the chemical reaction, have been the most common synthesis routes in the past several decades. In 2004, Jin, Ohkoshi and Hashimoto reported nanosized ε-Fe$_2$O$_3$, prepared in a silica matrix, which showed a giant coercive field of 20 kOe at room temperature (Fig. 6a). In 2008, Sakurai et al. introduced an advanced route to synthesize ε-Fe$_2$O$_3$ nanoparticles with an average diameter of 7 nm by combining the reverse-micelle and sol–gel methods (Fig. 6b), as shown in Fig. 6c. In 2012, Namai reported a nanocrystalline ε-Fe$_2$O$_3$ (Fig. 6d), prepared by a nanoscale chemical synthesis in a silica template (Fig. 6e), presenting a large coercivity value of 31 kOe (Fig. 6f). The two-step magnetic transition was dependent on temperature and the external magnetic field. In 2015, Kohout et al. reported 57Fe isotope enriched ε-Fe$_2$O$_3$, prepared by a sol–gel technique in a silica template, which exhibited a coercivity $H_C$ of 21 kOe at 300 K, as shown in Fig. 6g. A significant improvement of

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<th>Table 3</th>
<th>Magnetic properties of Fe$_{16}$N$_2$. Reproduced from ref. 70 with the permission of AIP Publishing</th>
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<td>Species</td>
<td>Site</td>
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<tr>
<td>α$'^{-}$Fe$_{16}$N$_2$</td>
<td>FeI</td>
</tr>
<tr>
<td>α$'^{-}$Fe$_{16}$N$_2$</td>
<td>FeII</td>
</tr>
<tr>
<td>α$'^{-}$Fe$_{16}$N$_2$</td>
<td>FeIII</td>
</tr>
<tr>
<td>α-Fe</td>
<td>—</td>
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<tr>
<td>γ-Austenite</td>
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magnetic properties for ε-Fe₂O₃ was reported by Ohkoshi et al. in 2017. The attained ε-Fe₂O₃, prepared using metal instead of traditional iron ions, showed the highest coercivity of 45 kOe at 200 K, as shown in Fig. 6h.

2.5 FeNi

The L₁₀-FeNi phase, known as tetrataenite [Fe₅₀Ni₅₀], is one of the rare-earth-free magnet candidates. In 1962, Pauleve et al. reported L₁₀-FeNi induced by neutron irradiation and annealed at 593 K under a magnetic field. The order–disorder transition temperature of L₁₀-FeNi is shown to be 593 K, further proved by Reuter et al. in 1989 under electron irradiation. As the atomic jump of nickel in FeNi alloys could take more than 10 000 years at 573 K, L₁₀-FeNi is only found naturally in meteorites. In 2015, Poirier et al. introduced tetragonal L₁₀-FeNi obtained from the meteorite NWA 6259, presenting a large anisotropy field of 14.4 kOe (Fig. 7a). Furthermore, in 2016 Lewis et al. reported tetragonal FeNi that was generated through an annealing protocol and pointed out the crystal structure transition of the FeNi lattice from a cubic to tetragonal unit cell, as shown in Fig. 7b.
FeNi was also presented by Hayashi et al. in 2013. The L1₀-FeNi alloy, prepared by a reductive reaction, showed a maximum coercivity of 220 kA m⁻¹ (2765 Oe). However, the stabilization of tetragonal FeNi alloys is a challenging task. In order to overcome this challenge, Ren introduced a rational epitaxial core/shell design to stabilize tetragonal FeNi nanocrystals (Fig. 7c). The reconstruction of tetragonal FeNi was triggered by the surface stress due to the existence of AuCu cores, as shown in Fig. 7d. The designed FeNi exhibited a large coercivity of 1010.2 Oe and a saturation magnetization of 122 emu g⁻¹, as shown in Fig. 7e.

2.6 Fe₃Se₄
Fe₃Se₄, presenting a NiAs-type structure, has been studied due to its hard magnetic properties. In 1956, Hirakawa suggested that the crystal of Fe₃Se₄ can be magnetized in the c-plane which is similar to Fe₇Se₈. The ferrimagnetism of Fe₃Se₄ was generated by aligned spins within the c-plane. Bishwas reported in 2014 a large increase in the energy product of Fe₃Se₄ up to 0.12 MGOe, as shown in Fig. 8a. The synthesis of Fe₃Se₄ nanostructures doped with manganese has been proved to be a potential strategy to improve magnetic properties, such as the energy product. In 2011, Zhang et al. synthesized Fe₃Se₄ by organic-solution-phase chemical decomposition and showed that its high coercivity is 40 kOe at 10 K (Fig. 8b and c). Among rare-earth-free magnets, Fe₃Se₄-based magnets are of intense interest. However, more advanced strategies aiming to improve Fe₃Se₄ are still urgent.

3 Conclusions
An overview of the existing and advanced manufacturing routes, developed in the past few decades, was explored and reviewed for rare-earth-free iron-based permanent magnets. The utility of versatile properties of iron-based magnets, such as coercivity and energy product, promotes the development of several permanent magnet candidates such as FePd, FePt, FeCo, Fe₃Fe₅N₃, ε-Fe₂O₃, FeNi and Fe₃Se₄. Among the prepared FeCo phase, the optimal estimated energy product and coercivity achieved are 66 MGOe and 188 kOe. For FePd alloys, the maximum coercivity of 2.6 kOe and saturation magnetization of 190 emu g⁻¹ showed the advantages of exchange-coupling. Meanwhile, the eutectic crystallization method indicated an advanced route to minimize the manufacturing procedure. The FePt magnet showed an optimal coercivity of 7.6 kOe with an optimum energy product of 5.0 MGOe. The Fe₃Fe₅N₃ magnet presented a high coercivity of 1910 Oe and energy product of 20 MGOe. The coercivity of ε-Fe₂O₃ prepared in a silica template can be tunable from 31 kOe to 45 kOe. The rare-earth-free magnets, synthesized using iron-based precursors, play an important role in developing permanent magnets. The basic magnetic properties, such as coercivity and energy product, have been widely developed in several iron-based magnetic materials due to iron’s low cost and abundance nature. However, the limitation of low energy product of rare-earth-free Fe-based magnets still poses a significant challenge for its practical applications, while the tunable magnetic properties achieved by doping could be a promising strategy to further improve their energy product. Therefore, the trend of permanent magnet development would focus on high magnetic performance in the foreseeable future accompanied by the extension of materials list.

Conflicts of interest
There are no conflicts to declare.

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Notes and references

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