MAGNETS: HISTORY, THE CURRENT STATE AND THE FUTURE

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Abstract

The paper outlines the history of development of magnets, from magnetite ore, through to the production of steel, Alnico, ferrite, samarium and neodymium magnets. The directions of further research on the improvement of the magnetic properties of magnets in the future are also discussed.

Keywords: Magnets, magnetic materials, magnetic properties

1. INTRODUCTION

Magnetic materials can be divided into two main types: so called soft magnetic materials (with coercivity H_c below 0.4 $A \cdot m^{-1}$) and hard magnetic materials, characterized by a high coercivity value. The latter are used for the construction of permanent magnets, which are important elements of instruments and devices commonly used both in everyday life and in many branches of industry, as well as in scientific research. For example, magnets can be found both in telecommunications and information technology equipment and measuring and control instrumentation, as well as in current generators and electric motors. They are also a basis for electro-acoustic devices and different types of sensors. The scale and variety of uses of magnets can be evidenced by their world's production volume, which amounts to several hundred thousand tons a year. The manufacture of hard disk drives alone is at a level of about 300 million items per year, while considering the fact that a contemporary motor car is equipped, on average, with 35 electric motors, at an annual global car production of about 70 million this is tantamount to 2 billion motors with magnets a year.

Therefore it is extremely important, not only from the scientific, but also from the economic point of view, to search for new magnet materials with increasingly better service parameters (i.e. having both high remanence B_r and coercivity H_{cB} and magnetic energy density $(BH)_{max}$ values, as well as good temperature stability of these values), with maintained availability of raw-materials and their relatively low price. The present paper has made a review of the development of magnetic materials over centuries, starting from prehistoric times, through the present time, up to the materials of the future.

2. THE MAGNETITE ERA

The magnetite (Fe_3O_4) ore was the first natural magnet, known already in antiquity (China, Greece). At that time (in about 2500 BC), the phenomenon of attraction of iron pieces by forces coming out of magnetite ore was observed [1, 2]. Ancient legends say, among other things, about pulling out to a distance of iron parts from hulls the ships sailing past the islands situated between Ceylon and Sumatra, as described by e.g. Ptolemy (in about 100-178 BC). There were also stories about nails pulled out from shepherds' sandals, disarming and immobilizing of knights, or about means enhancing the magnet action force (e.g., by rubbing the magnet with iron filings), as well as inhibiting it (such as garlic, onion, or a time of the day).

At different times and different places, where magnetite ore was found, it was called, either: the Magnesia stone, the stone of Lydia, Horus' bone in ancient Egypt; loadstone in England; aimant ("loving stone") in France; or ts'u she in China.

According to Chinese sources, as early as in about 3000-2500 BC [3], one of the first applications of magnetite ore was in the compass, as the indicator of the North-South direction of the Earth's field. **Fig. 1** shows compasses in the form of a balancing spoon made of magnetic ore, lying on a smooth copper or bronze plate (**Fig. 1a**), a floating fish (**Fig. 1b**), and a turtle rotating around the vertical axis (**Fig. 1c**). At that time, as the indicator of the position of the Earth's magnetic poles, magnetic ore was used primarily for magnetizing by rubbing of iron needles intended to be used in a compass.

a) b) c)

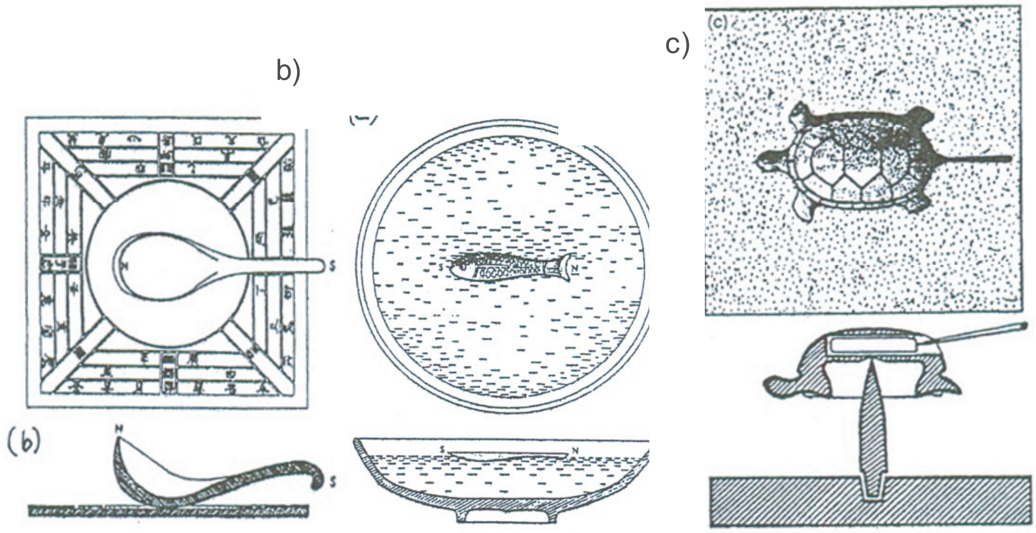

Fig. 1 A model of the first in the world Chinese Si Nan compass from the period of the Han dynasty (around the 3rd century BC) in the shape of a spoon made of magnetic ore, lying on a smooth bronze plate (a), a floating fish (b), and a turtle rotating around the vertical axis (c)

In Europe, on the other hand, as the beginning of the history of development of the study of magnets, the information about Thales of Miletus (approx. 624-546 BC), as reported by Aristotle (approx. 384-322 BC) in his treatise "*De anima*", should be regarded. According to this information, "the magnet has a soul, because it attracts iron". A similar view is also expressed by Plato (427-347 BC) in his dialogues Ion and Timaeus. Unfortunately, these are not quite correct attempts to interpret the observed phenomena.

Also Roman poet an philosopher Titus Lucretius Caro (97-55 BC), in his wok „*De rerum natura*”, gives a fairly large coverage to the phenomena of attraction of iron by the magnet (called therein a stone). The magnetic stone and its "liking" for iron is also written by Plinius the Elder (23-79 AD) in his Natural History (Book XXXVII). Saint Augustine, on the other hand, in his work entitled "*De civitate dei*" written in the years 413-426 AD described the experience of attracting iron rings by magnet stone. These were the first interesting experiences leading to the discovery of the phenomenon of magnetic induction. An important period in the history of research on magnets were the centuries from 13th to 17th. Associated with this period are names, such as Petrus Peregrinus (the second half of the 13th century, likely to be identified as Peter of Maricourt [4]), Giambattista della Porta (1535-1615) [5] and William Gilbert (1544-1603) [6].

In his letter "*On the magnet*" sent in August 1269 to his friend, he introduced, among other things, the term "magnet poles" and gave a description of the compass. Also Giambattista della Porta in his work entitled „*Magiae naturalis*” gave much coverage to magnets, e.g. the sources of magnetic interactions, the division of a magnet (magnet ore) into parts, the description of scales as used for the measurement of the forces acting between magnets, or the use of fine iron filings for the observation of the magnetic field around a magnet.

William Gibert of Colchester, an English physicist and Queen Elizabeth I's own physician, achieved the world's fame after publication of his work „*De magnete…*” in 1600 in London. An important achievement of Gilbert was the development of a theory based on performed experiments with a magnetic needle placed on the surface of a sphere cut out from magnetic ore, called the *terrella*, saying that the Earth is a large spherical magnet (**Fig. 2**). Gilbert also discussed to a little greater extent the methods of permanent magnetizing of iron bars intended, inter alia, for compass needles. In particular, he described the method of unidirectional rubbing of an iron specimen surface with magnetite, and the forging of thin iron wire positioned in the Earth's magnetic field in the Nord-South direction followed by prolonged magnetizing it in the Earth's magnetic field (without plastic deformation). He also recommended the use of the hardening of iron, in today's sense, which had a martensitic structure after this treatment, resulting in a slight increase in coercivity. The first magnetic measurements of magnetic ore were made by H. Du Bois and E.T. Jones [7] in 1896. They only measured the coercivity H_{cJ} and remanence J_r, which amounted to, respectively: 4.0 $kA \cdot m^{-1}$ and 0.44 T.

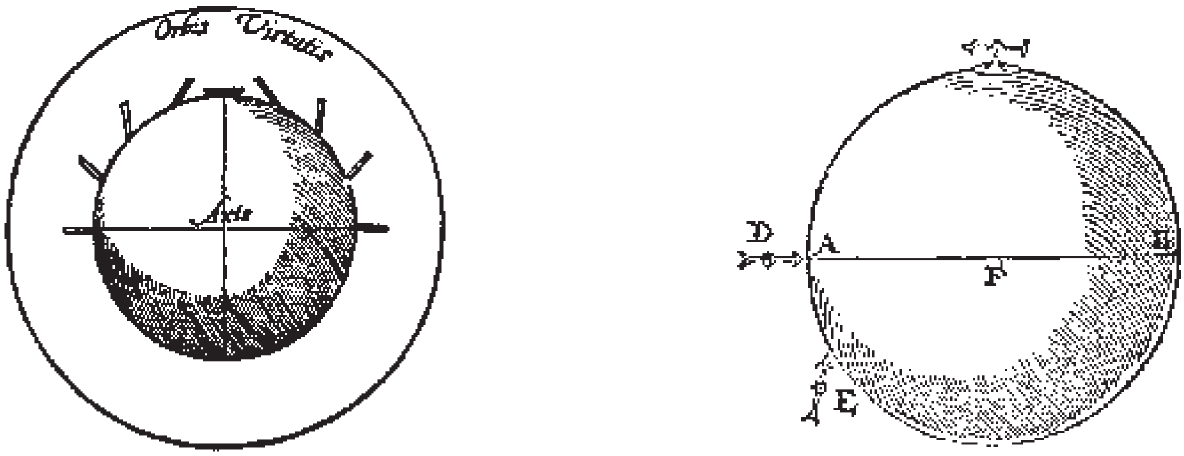

Fig. 2 William Gilbert's terrella - a scale model of the magnetic Earth made from a loadstone

3. THE STEEL ERA

The double touch method of making magnets from iron bars, as described by Gilbert, was continued in England in the 30s of the 18th century by Servington Savery [8]. This method involved touching a surface being magnetized with one pole of magnetite ore, and then repeated rubbing along the whole needle length. This activity was repeated many times until complete magnetization.

A further significant progress in making artificial magnets was achieved by Gowin Knight (1713-1772), who was a well-known British manufacturer of magnets of hardened steel. In this method, two inclined magnets were placed with the opposite poles in the middle of a steel plate being magnetized. The magnets were then shifted away from each other. This operation was repeated many times, while only changing the plate surface. This method of producing magnets was called the method of divided touch.

In 1750, John Michell (1727-1793), an English physicist and astronomer [9], developed a method of making magnets from steel by using a modification of the method of divided touch (the method of variety of double touch). In this method, a hardened steel plate to be magnetized is placed between two non-magnetized bars. Magnetizing is done with two inclined magnets, as in the method proposed by John Canton, by repeated rubbing the hardened steel surfaces to and fro.

As John Michell noted, the developed method enabled magnets to be produced not only from soft iron, but also from hardened steel, which retained magnetization considerably longer.

Equally important and interesting work on magnet production was conducted not only in England, but also in France (H. L. Du Hamel (1700-1782) and in Russia (F. U. T. Aepinus (1724-1802).

A significant progress was made in England in the 18th century with the development of magnets from carbon steel containing 1.0 to 1.5 wt.% C. Unfortunately, no good magnetic properties were achieved (a coercivity of

H_{cB} = 3.8 kA·m^{-1}). Whereas, as reported by G. Hannack [10], Remy in Germany and Böhler in Austria demonstrated in the years 1883-1885 that the best magnet steels contained 0.6 % of carbon and from 5 % to 5.5 % (w/w) of tungsten (H_{cB} = 5.6 kA·m^{-1}, B_r = 1.03 T, $(BH)_{max}$ = 3.1 kJ·m^{-3}).

Also Maria Skłodowska-Curie (the two-time Nobel Prize winner: in physics in 1903 and in chemistry in 1911), better known for the discovery of polonium and radium and research on radioactivity, devoted her first scientific studies in 1898 to the measurements of the magnetic properties of tungsten steel [11].

In 1885, Hopkinson [12] first gave the magnetic properties of hardened chromium steel (6.0 wt.% Cr). He achieved H_{cB} = 4.8 kA·m^{-1}, B_r = 0.95 T, $(BH)_{max}$ = 3.0 kJ·m^{-3}. Whereas, in 1892 Hadfield [13] stated that with a chromium content of up to 28 % (w/w) the magnetic properties of steel increased, while above this value, decreased.

In this group of martensitic magnet steels, steels of a cobalt content from 3 to 30 wt.% were developed in the 20s of the 20th century. Magnets of a cobalt content of 30 % had the following magnetic properties: H_{cB} = 19.9 kA·m^{-1}, B_r = 0.9 T, $(BH)_{max}$ = 7.5 kJ·m^{-3}.

4. MULTICOMPONENT ALLOYS - THE ERA OF ALNICO MAGNETS

The understanding of the microstructural bases of precipitation hardening enabled Köster [14] in 1932 to develop alloys not containing carbon, namely: Fe-Co-W and Fe-Co-Mo. Work was also conducted on the technology enabling the making of magnets with a low cobalt content (Fe-Cr-Co alloys with 8-12 wt.% Co) or not containing this element (Mn-Al-C alloys and Fe-Al-C alloys) having good magnetic properties.

Studies carried out in the years 1935-1939 showed that a good material for magnets were the alloys of iron with platinum, iron with palladium and cobalt with platinum [15]. Thus, we quote here as an example, that the Fe-Pt alloy has a coercivity of H_{cB} = 390 kA·m^{-1}, a remanence of B_r = 1.04 T, and $(BH)_{max}$ = 160 kJ·m^{-3}. While magnets of poorer magnetic properties, but well plastically deformable are provided by the following alloys: Cu-Ni-Fe (Cunife), Cu-Ni-Co (Cunico) and Fe-V-Co (Vicalloy) [16].

The history of modern magnets started in 1932, when Mishima [17] demonstrated that the carbon-free ternary alloy 25 at.% Ni, 10 at.% Al and the balance of Fe exhibited a higher coercivity and did not require hardening. The coercivity of these alloys amounted to above 50 kA·m^{-1}, and the energy product, 10 kJ·m^{-3}. These magnets were improved in the years 1932-1968 by adding cobalt, which substituted for part of the iron, and the addition of copper, whereby a coercivity of H_{cB} = 110-140 kA·m^{-1}, a remanence of B_r = 1.0-1.1 T and $(BH)_{max}$ = 60-75 kJ·m^{-3} were obtained. A significant achievement in the production of Alnico magnets was the application of heat treatment in a magnetic field by Oliver and Shedden [18]. Thus, anisotropic magnets of better properties in the direction of magnetic field action were made. Alnico magnets were also made by sintering powdered alloys (which is a method frequently used in the production of complex shape and small-sized magnets). Also powders bonded with a plastic and then pressed were used for magnets.

A high interest of industry was also aroused by the alloys of platinum with iron and cobalt thanks to their high coercivity value of H_{cB} = 125 kA·m^{-1}, remanence of B_r = 0.58 T and $(BH)_{max}$ = 24.4 kJ·m^{-3}. An extensive discussion of research on the crystalline structure and magnetic properties of Alnico alloys is provided in the study by McCurrie [19].

5. THE ERA OF MAGNETICALLY HARD FERRITES

Introduced in the 50s of the last century, despite their poorer service parameters (but a simpler manufacturing technology) compared to Alnico magnets, ferrite magnets, mainly barium ($BaFe_{12}O_{19}$) or strontium ferrite oxides, in terms of the number of tons produced yearly, have become the basic materials used in industry. On an industrial scale, barium ferrite is produced by the synthesis of barium oxide and ferric oxide, followed by pressing and preliminary sintering and then grinding again in ball mills down to a particle size of approx. 1 μm, pressing and final sintering. Whereas, magnets with anisotropic properties are pressed in a magnetic field before sintering. The anisotropic properties of barium ferrite are as follows: H_{cB} = 250 kA·m^{-1}, remanence up to 30 T, and the energy product $(BH)_{max}$ up to 340 kJ·m^{-3}.

In 1954, the world's production of ferrite magnets amounted to about 6000 tons, while in 1985, over 200 000 tons. A reasonably complete review of the basic properties of ferrites is provided in the study by Stäblein [20].

6. THE LAST HALF CENTURY - SAMARIUM AND NEODYMIUM MAGNETS

According to the view taken by Livingston [2] in his research on rare-earth magnets, which was initiated by Strnat [21], three periods should be distinguished:

- the first period encompassing rare-earth (R) elements with 3d transition metals (Fe, Ni, Co);
- the second development period involving magnets of rare-earth elements with cobalt (so called 2-17 compounds); and
- the third period initiated in 1984 with the development of Nd-Fe-B magnets.

In the first group of magnets, the rare-earth metal Sm forms the $SmCo_5$ compound with cobalt [22]. The second group includes magnets (with a higher cobalt content) of a rare-earth element - transition metal type, i.e. Sm_2Co_{17} [23]. The basic magnetic properties are as follows: the coercivity of $SmCo_5$ equals 1.5 MA·m^{-1} and $(BH)_{max}$ = 160 kJ·m^{-3}; whereas for Sm_2Co_{17}, H_{cB} = 1.7 MA·m^{-1}, while $(BH)_{max}$ is much higher, amounting to 215 kJ·m^{-3}. Sm-Co magnets are manufactured by the powder sintering method. The third group includes $Nd_2Fe_{14}B$ magnets [24, 25]. An important advantage of these magnets, from the practical point of view, are high magnetic parameters: H_{cB} = 1.25 MA·m^{-1}, B_r = 1.22 T and $(BH)_{max}$ = 450 kJ·m^{-3}. Comprehensive information on these magnets are provided, e.g., in the study of Livingston [2].

Also, an important group is made up by Sm-Fe-N magnets, and in particular $Sm_2Fe_{17}N_3$ ones [26]. Introducing nitrogen atoms to the Sm_2Fe_{17} compound considerably increased the saturation magnetization, i.e. from 1.09 T to 1.52 T. A further improvement was possible by introducing a second phase with a high saturation magnetization value (e.g. α-Fe , for which B_s = 2.15 T) to the magnet. Thus, magnets were obtained, which had two phases: the magnetically hard phase $Sm_2Fe_{17}N_3$ and the soft phase α-Fe.

A discussion of the hitherto existing state of research on Sm-Fe-N magnets is provided in the study of Katter [27]. In view of the fact that forming more perfect $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_3$ phases is a difficult (or even impossible) task, the further studies were geared towards improving the microstructure. Thus, magnets of a nanocrystalline structure (with grains in one of the nanometric directions) were formed. So, single-phase and diphase (nanocomposite) [28, 29] and, a little later, anisotropic diphase nanocrystalline [28] magnets were produced. Contemporary magnets, such as Sm-Co or Nd-Fe-B, are manufactured in the sintering process. Whereas, nanocrystalline-structure magnets are obtained in the process of prolonged grinding of a mixture of powders of elements (mechanical alloying, MA) or a ready-made alloy (mechanical milling MM), by rapid cooling from the liquid state, by the hydrogenation, disproportionation, desorption and recombination (HDDR) method, the great plastic deformation of the solid material (serve plastic deformation, SPD) and, in the next stage, the controlled crystallization of phases enabling a structure of nanocrystalline grains to be formed.

7. CONCLUSIONS

Currently, we know and manufacture magnets of various types and different properties (**Fig. 3**). The question that arises is: do we have to search for new materials for magnets? The response to this question is neither easy nor simple, as we still do not know many materials that we need or will need. For example, we do not currently know a magnet that retains its properties up to a temperature of 500 °C. Also, there is no magnet with a saturation induction above 2.7 T. New applications of magnets are likely to emerge, when they are associated with mechanical or electrical properties. We are also of the opinion that the development of magnets in the future should involve a further reduction of the crystalline structure grain size. Interesting is and will be the magnetism of carbon, which has been intensively studied in recent years.

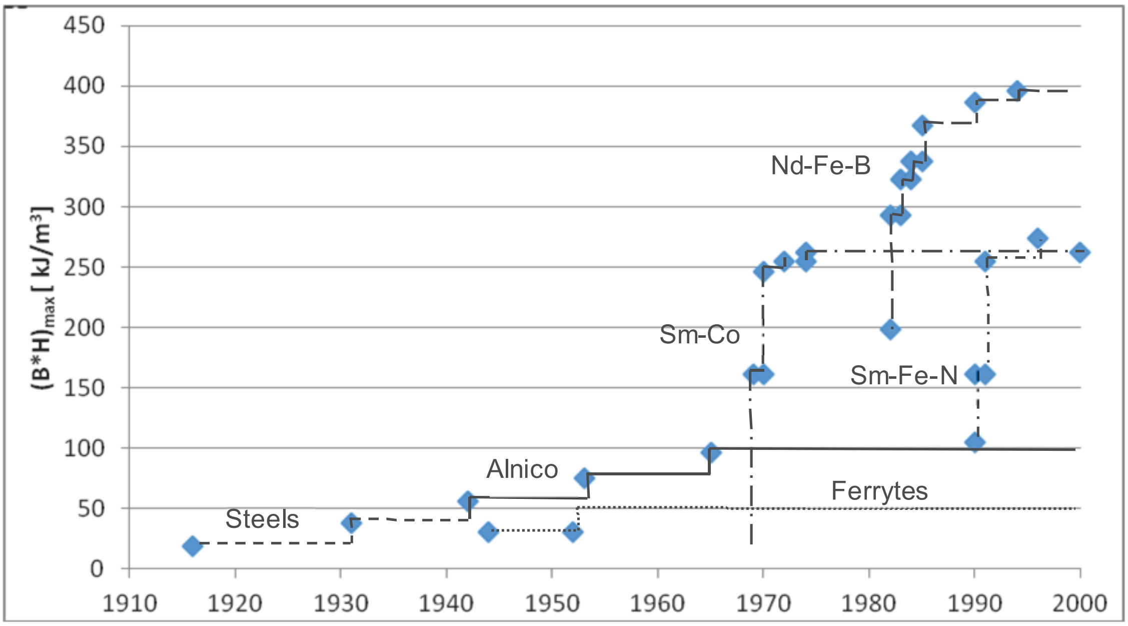

Fig. 3 Examples of the permanent magnets manufactured on an industrial scale over the last century with the increasing value of the magnetic energy density (*BH*)max, as the measure of their magnetic quality

The economic factor, too, is not without significance here. It is due to the low manufacturing prices (raw-material and production costs) that ferrite magnets have still played the leading role, despite the 50 years that have passed since they were first introduced and many new materials that have been developed during this time. Although they do not have record high magnetic properties, the price of their unit magnetic energy is by approx. 10 times lower compared with Nd-Fe-B magnets. The role of Sm-Co magnets is also decreasing, since Nd-Fe-B magnets are considerably cheaper than they, with comparable magnetic properties.

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