Alloyed Alchemy

A CENTURY OF MAGNETIC MATERIALS

by Greg Grant

A century has passed since the Swiss-French physicist, Charles Guillaume, developed the alloy Invar. This was the beginning of an industry that has changed our world immeasurably, giving us much improved communications, entertainment and, most recently, medical imaging techniques.

Magnets and magnetism literally make much of our world possible, yet few technical subjects have been so much retarded by their history. First studied by Thales of Miletus around 585 B.C., magnetite or lodestone as it was more commonly known, would remain the only magnetic substance until the coming of iron, the first of the ferromagnetic materials. Iron, in its turn, would become the only soft ferromagnetic substance in general use until the latter part of the 19th century, when tungsten steel was produced in Germany.

Another material under investigation at this time was iron powder. Charles Fritts and Oliver Heaviside independently investigated this substance as a basis for low-loss inductor cores. Fritts looked into their possible application in motors and dynamos whilst Heaviside, using cores fashioned from iron filings bound with wax, attempted to improve the performance of telephone coils. This was the beginning of what would later grow into the ferrite and micropowder industry of today.

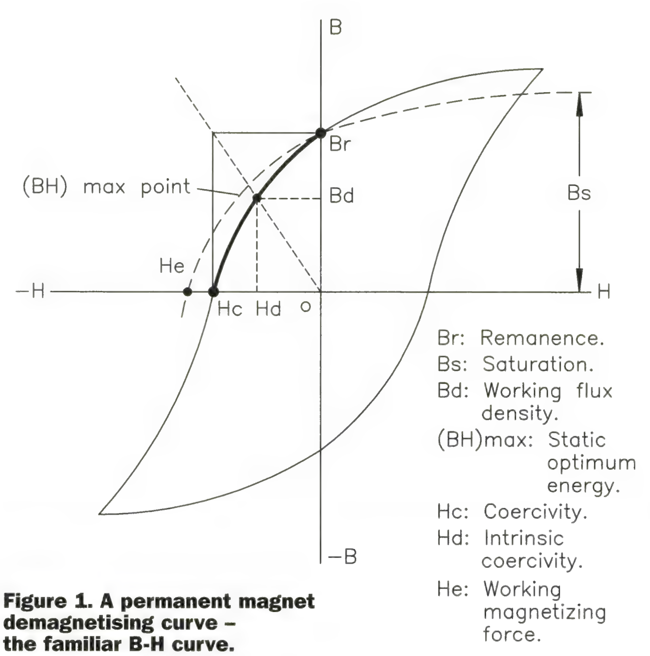

Figure 1. A permanent magnet demagnetising curve – the familiar B-H curve.

In 1890, the Scottish engineer, James Ewing, Professor of Applied Mechanics at Cambridge, discovered the phenomenon of Hysteresis, from the Greek word Husterikos, meaning 'coming late', where the magnetic induction of a material lags the changing magnetic field. The curve, long familiar to all electrical, electronic and communications engineers and shown in Figure 1, showed that the phenomenon might be explained by means of the interaction between (permanent) magnets.

Six years later, the Swiss-French physicist, Charles Guillaume, developed the alloy Invar, the result of an exhaustive study of ferronickel alloys. The new material was so named because of the invariability of its dimensions when heated.

Composed of iron, 36% nickel and 0·2% carbon, Invar is frequently used for the bi-metallic strips in thermostats, the metal-to-glass seals in lamps, in the balance springs of watches and in the Housekeeper seals of the few electronic valves still manufactured. Guillaume followed Invar with Elinvar, another name with a purpose, this time to emphasise the new alloy's low coefficient of elasticity. A meld of nickel, chromium and steel, this elastically invariable material is widely used in scientific instruments.

Thanks to Guillaume's pioneering efforts, the past century has seen enormous strides in the development of metallic alloys with extraordinary magnetic properties. As Figure 2 shows, from the turn of the present century onwards, magnetism generally and magnetic materials particularly, have advanced as rapidly as the two main 20th century developments, aircraft and electronics.

As the century opened, Ewing published a paper in which he suggested that all ferromagnetic atoms and molecules could be regarded as tiny basic magnets, able to rotate on their own axes in an applied magnetic field. He also developed a magnetometer for measuring the properties of ferromagnetic metals as well as the Ewing Curve Tracer and the Ewing Permeability Bridge. In the latter, the flux of an iron sample is balanced against that of a standard bar magnet of similar dimensions. The magnetising force of the test bar is varied until it balances that of the known bar, the permeability being estimated from the value of the force.

By 1902, the British metallurgist, Robert Hadfield, the inventor of manganese steel, had noted

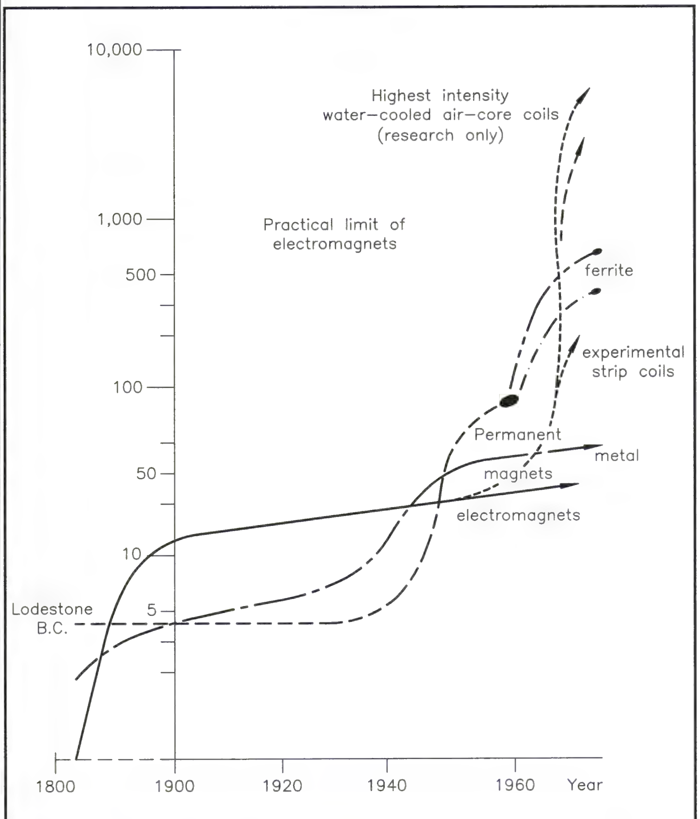

Figure 2. Magnetic material developments in the first sixty years of the present century.

the excellent performance of the silicon steels, which gave a threefold reduction in eddy current and hysteresis losses compared with soft iron sheet. In fact, it was because of such properties that Hadfield, among others, developed these alloys further.

In the following year, the first permanent magnet made without ferromagnetic material appeared, produced by the German chemist and mining engineer, Fritz Heusler. Composed of 10-30% manganese and 9-15% aluminium, the remainder being copper, it was a most effective material.

Later, Heusler replaced the copper with 86% silver to create Silmanal, which, not surprisingly, was expensive. Nevertheless, it was an excellent material, having a far higher coercivity than any other magnet then available. The copper could equally well be replaced by antimony, boron, bismuth or arsenic.

In 1907, magnetic theory took a considerable step forward, with the development of the Domain Theory of ferromagnetism by the French physicist, Pierre Weiss. In it, he explained how metals such as iron form tiny domains of a given polarity and, when these domain poles are aligned, they produce a strong magnetic force.

Nine years later, Permalloy, nickel combined with iron, was discovered at the Bell Laboratories in the United States, and the Japanese physicist, Kotaro Honda, added cobalt to tungsten steel to produce a magnet of considerable strength.

Hearing is Believing

In 1919, the German electronic physicist, Georg Barkhausen, developed a method of actually demonstrating domain movement. He placed a microphone close to a sample of iron undergoing magnetisation.

By slowly and smoothly increasing the magnetising field, Barkhausen found that magnetisation took place in VERY small steps. And you could HEAR those steps, for his microphone fed an amplifier-loudspeaker system which produced a steady series of clicks, the result of the domain nature of the material.

Here, in what came to be known as the Barkhausen Effect, was the first tentative proof that Pierre Weiss had been correct in his analysis of magnetism's nature.

The increasing demand for long distance telephone services had resulted in the discovery that the main factor limiting longer circuits was line capacitance. Telecommunications engineers realised that the problem could be considerably reduced by placing inductors, termed loading coils, at regular intervals along the lines.

The first practical application of the loading coil took place in 1902, when they were inserted in a ten-mile length of telephone cable between New York and Newark, New Jersey. Subsequent trials convincethe American Telephone and Telegraph Company (AT&T) to extend their use, and in 1912, the 235-mile long New York-Washington line was equipped with loading coils.

The British Post Office (BPO) too, were keen on loading coils and in 1915, looped backwards and forwards, the 110-mile circuits on the London-Birmingham cable, producing equivalent lengths of 220, 440, 660 and 880 miles.
By the insertion of inductance coils at 2·5 miles spacing, commercial conversation was obtained up to 600 miles.

Loading coils had to meet stringent specifications such as negligible leakage flux to avoid crosstalk, no hysteresis or eddy current losses and have a permeability of between 10 and 100. The early ones were air-cored but it soon became apparent that new materials would be required to meet the increasingly stringent requirements. This led to the development of magnetic powders. Another spur to better electronic materials was the increasing improvements in valve amplifier and filter design at this time.

In 1926, the first commercial Permalloy was produced, containing 21·5% iron and 78·5% nickel. Once again, it was developed at the Bell Telephone Laboratories by a team led by the Swedish-American metallurgist and electrical engineer, Gustav Elmen, who discovered that almost all alloys of iron with cobalt or nickel were strongly ferromagnetic compared to other substances.

The alloys Elmen helped to develop had very high permeabilities in weak fields and were much used in undersea cable loading coils, where the technique was to use permalloy ribbon wound around the core of the cable which neutralised much of the lime's inherent capacitance.

Consequently, signalling speeds rose to around 400 words per minute and for some years thereafter, all submarine cables were of this type of construction. Later, under such tradenames as Mumetal, Superalloy and Permalloy C, this composite was used in Interstage and Pulse transformers. Later still, they would be exploited further in powder form.

Elmen himself devoted the rest of his career to magnetism. He left the Bell Laboratories in 1941 to set up the Magnetism Unit of the Naval Ordnance Laboratory in Washington DC. He remained the Unit's director until a year before his death.

New Materials and Techniques

1930 to 1939 was the decade of major investigation into the magnetic properties of materials generally.

In ferromagnetic substances, which is the name given to the property of greatly increasing the magnetic flux when a magnetising force is applied, the way the atoms bond to form the solid means that the neighbouring atom's dipoles line up in the same direction, as in Figure 3.

This is what characterises the ferromagnetic materials such as nickel, iron and cobalt from the diamagnetic and paramagnetic substances such as mercury and copper, platinum and aluminium.

Figure 3. The dipole arrangements in ferromagnetic.

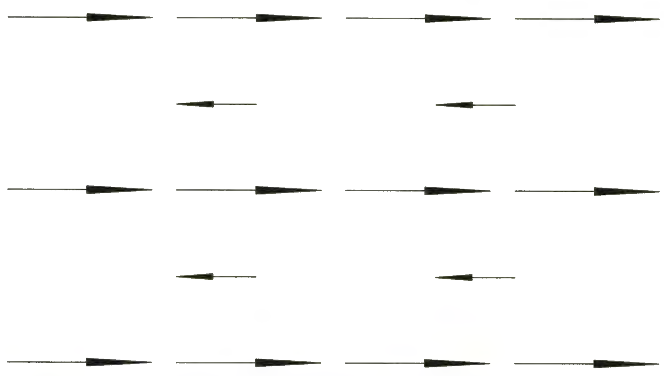

Figure 4. The dipole arrangements in ferrimagnetics.

Ferrimagnetics, or ferrites as they are more commonly known, are different again, as shown in Figure 4. Although arranged in the same manner as antiferromagnetic substances, their dipoles are not the same size and so do not cancel each other out. They are, in short, ceramics, and so their bonds are ionic, resulting from the electric forces of attraction between positive and negative ions.

In 1932, the French physicist, Louis Neel, demonstrated that there was a fourth type of magnetism, which he termed antiferromagnetism.

In such substances, two interlaced atomic lattices have magnetic fields acting in opposite directions, as shown in Figure 5. Five years later, Neel succeeded to the Chair of Physics at the University of Strasbourg, formerly held by Pierre Weiss, where he continued the latter's research into magnetic materials.

One early success of the period was Kato's Oxide, a mixture of iron and cobalt oxides held together by an adhesive, developed by Y. Kato and T. Takei, to produce the first modern ferrite ceramic magnet.

A compound of 50% iron oxide and 50% cobalt iron oxide, the material was sintered at 1,000°C and cooled in a magnetic field from 300°C.

The Americans also developed a similar material some two years later, which they termed Vectolite. It used less cobalt and around 30% iron oxide, which gave a more consistent performance, delivering nearly twice the coercivity level with much lower remanence and energy product.

The British developed a plastic-bonded version of this material, which they termed Caslox.

In 1931, the American physicist, Francis Bitter, developed a technique of covering the surface of a ferromagnetic with a colloidal suspension of magnetic material. The boundaries of the domains were then revealed under the microscope. These Bitter Patterns, as they came to be known, illustrated the boundary of the magnetic domains, the particles gathering there because the magnetic field was at its strongest. The technique was subsequently used in detecting cracks and imperfections in ferromagnetic materials. Here was further proof of Weiss' Domain Theory, demonstrated by what amounted to a refined and sophisticated update of the early iron filings patterns first used by the great Faraday.

Undoubtedly, the development of the 1930s, however, was the Alnico alloys, which brought considerable improvements in permanent magnets.

Developed in the Netherlands, their major constituents were, as their name implies, aluminium, nickel and cobalt in various proportions. To these were added small quantities of one or more of such elements as copper, iron and titanium. In fact, this last group are often referred to by their trade name of Ticonal.

All of these alloys are tremendously hard, their method of production being to place them in a strong magnetic field during heat treatment. This produces a metallic structure which has directional characteristics, that is, a piece of metal will 'align' itself in the direction of the magnetic field.

These materials have a high retentivity, and are used in loudspeakers, magnetrons and other devices requiring strong permanent magnets. Indeed, such components became more cost effective after the introduction of these alloys. Alnico is usually accompanied by a number, for example, Alnico V, a version containing 8% aluminium, 14% nickel, 24% cobalt, 3% copper and 51% iron, which gives stronger permanent magnets than earlier versions.

Another magnetic material produced at this time was Remalloy, a cobalt-nickel-iron-molybdenum combination possessed of mechanical springiness and capable of being produced in thin sheets. Until quite recently, it was common throughout Britain as the diaphragm in virtually every telephone handset.

The 1940s was a decade of rapid magnetic material development. Philips of Eindhoven were very active in magnetic research, and a team of their physicists further developed the Barium ferrites.

In 1946, crystal orientation along a preferred axis was introduced, a technique which virtually trebled the magnetic strength of some alloys. Many present-day magnets are of this type still.

Two years later, Louis Neel continued his investigation into magnetic materials, this time, ferrites, of which magnetite is but one example.

Magnetite has three iron atoms and four oxygen atoms. Neel established that the effects of two of the atoms cancel, leaving the third to produce the magnetic field. He termed such materials perrimagnetic, and since they were electrically non-conducting and so impervious to stray currents, they subsequently became widely used throughout the modern industrial world.

Among their applications are permanent magnet loudspeakers and microphones, as a coating material for magnetic tape, as memory stores in computers and finally, as passive elements in high frequency, low-loss electronic devices. Neel's work led to further developments in micropowder magnets by his team at Grenoble university, in conjunction with the French manufacturing combine, Societé Ugine.

At this time, permanent magnet improvements were almost entirely due to the use of alloys of ever-increasing complexity, there being some 60 different such alloys available with a broad variety of magnetic properties. A decade later, however, this 60 had become 250 or thereabouts.

Throughout the early 1950s, magnetic materials research was largely driven by the demand for television receivers on the one hand and the exacting requirements of the defence industries on the other.

Consequently, the research that had produced the low-loss ferrites was extended, culminating in the discovery of the Ferrimagnetic Garnets in France and the United States in 1956.

By the early 1960s, barium ferrite material was commercially available and by the end of the decade, the Bell Laboratories began to look into the magnetic storage of computer data.

A team led by Andrew Bobeck investigated single-crystal substances whose magnetic domains could be reduced to the size of minute cylinders in the presence of a magnetic field. They could also be readily manipulated by magnetic techniques, and so the presence or absence of a 'bubble' could be used to represent the binary arithmetic that is the staple diet of computers.

The magnetic bubble memory enjoyed considerable success in the computer field for some years until, in the late 1970s, semiconductor memories began

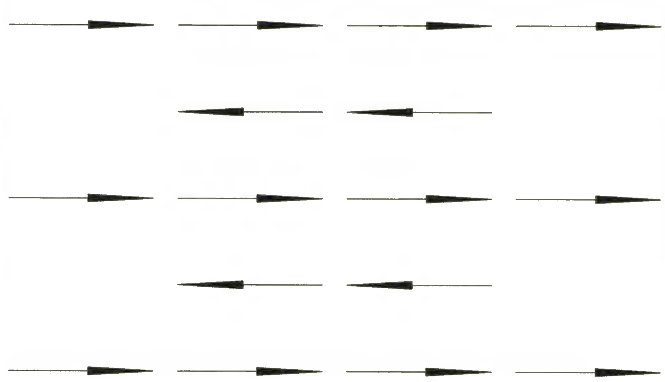

Figure 5. The dipole arrangements in antiferromagnetics.

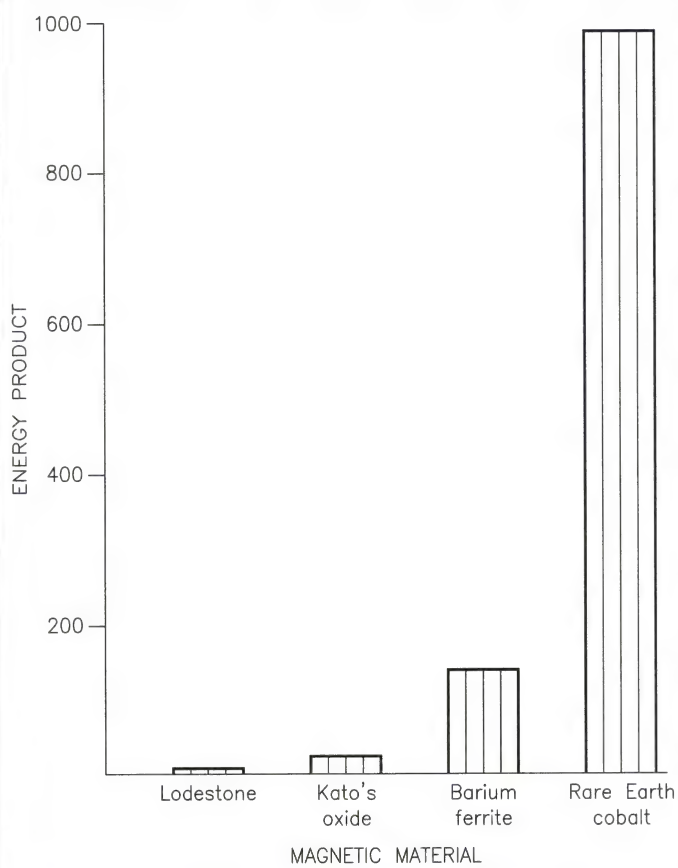

Figure 6. A comparison of Energy Product of some recent magnetic materials against that of the original magnetic material: Lodestone.

to seriously challenge their storage capacity. Today, of course, semiconductor memories have triumphed totally.

It was in the 1970s too, that the rare earth-cobalt magnets appeared, they being a very considerable improvement on almost everything that had gone before.

One way of judging the quality of a magnetic material is to compare its Energy Product against that of the original magnetic substance, Lodestone.

Devices made from Kato's Oxide, for example, gave some four times the energy product of the original base material, whilst the barium ferrites gave seven times the energy product of Kato's Oxide.

The rare earth-cobalt magnets, on the other hand, gave more than seven times the energy product of the barium ferrites or over 200 times the energy product of the original magnetic material!

The Naked Truth

One of the most important recent developments where magnetism is concerned, is Nuclear Magnetic Resonance or NMR, which was brought about by advances in two distinct fields of research, magnetic materials and particle physics.

Superconducting materials were first discovered in 1911, by the Dutch physicist, Kamerlingh Onnes. Having liquified helium, he used it in an experiment with a solid mercury wire and discovered that, at a temperature of 4·2K above absolute zero, the wire's electrical resistance disappeared.

There, broadly, matters rested for some time, since the problem with superconductivity was that it could not be satisfactorily explained theoretically. Moreover, as the few experimenters in this field discovered, stunning laboratory discoveries could not be translated into worthwhile applications in other fields either.

Particle research, on the other hand, had long been considered esoteric, not exactly the sort of field that would bring much benefit to mankind, aside from advancing his knowledge of the structure of matter.

In 1946, however, two physicists, the Swiss Felix Bloch and the American Edward Purcell, changed this perception altogether. Independently, they discovered that chemical substances can absorb some microwave frequencies when they are placed in a powerful, steady and above all, uniform, magnetic field.

Eleven years later, three American physicists, John Bardeen, Leon Cooper and John Schrieffer, put forward what came to be known as the 'BCS' theory to explain the phenomenon of superconductivity. This assumed the existence of coupled electrons, termed Cooper Pairs, which do not undergo scattering through collision with atoms in the conductor.

The way was now open to create magnets composed of superconducting materials, cooled by liquid helium, which could generate the sort of fields Bloch and Purcell had spoken of in their research.

Therefore, if a scanner could be built producing the required field, NMR could become a useful diagnostic tool, as microwaves are much less energetic then X-rays. They are, therefore, excellent at detecting light atoms, which are plentiful in the human body.

Figure 7 illustrates such a scanner. The patient lies within the field generated by the superconducting magnets and the particular point the clinician wishes to study is selected by varying the magnetic field strength in three dimensions, utilising coils above, below and along the axis of the magnet.

The RF, i.e. microwave, field makes the hydrogen atoms spin, which reveals the hydrogen distribution throughout the body, thus displaying different body tissues in a manner less hazardous than X-rays.

Magnetic Resonance Imaging, as the technique is known, will grow apace, not least, because of continually emerging evidence of the damaging nature of X-rays. A recent study in the United States, for example, points to X-rays being the major cause of breast cancer in women up to the mid-1970s, largely because the radiation doses were frequently 50 to 100 times those used presently.

The present century opened with new magnetic materials heralding enormous future developments. Currently, other new materials, the superconductors, are hinting at what the future may bring. The century ahead, therefore, may well prove to be even more magnetic than the present one has been.

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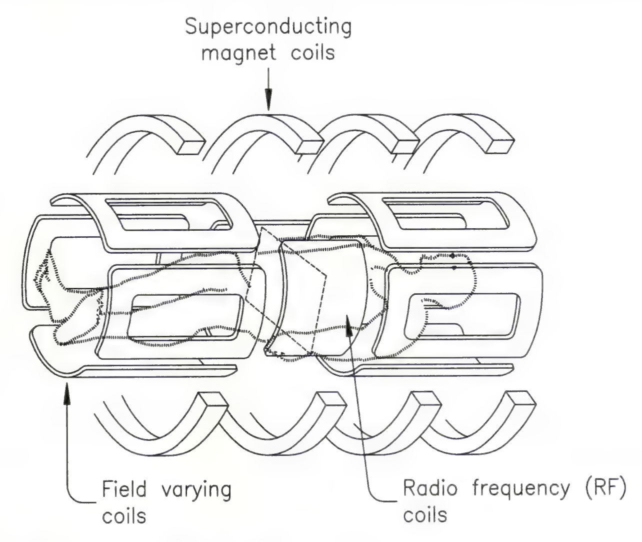

Figure 7. The Nuclear Magnetic Resonance (NMR) scanner, with a patient undergoing a 'scan'.