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Nanostructured electronic and magnetic materials

R V RAMANUJAN

School of Materials Engineering, Nanyang Avenue, Nanyang Technological University, Singapore 639 798
e-mail: ramanujam@ntu.edu.sg

Abstract. Research and development in nanostructured materials is one of the most intensely studied areas in science. As a result of concerted R & D efforts, nanostructured electronic and magnetic materials have achieved commercial success. Specific examples of novel industrially important nanostructured electronic and magnetic materials are provided. Advantages of nanocrystalline magnetic materials in the context of both materials and devices are discussed. Several high technology examples of the use of nanostructured magnetic materials are presented. Methods of processing nanostructured materials are described and the examples of sol gel, rapid solidification and powder injection moulding as potential processing methods for making nanostructured materials are outlined. Some opportunities and challenges are discussed.

Keywords. Nanomaterials; electronic materials; magnetic materials; magnetic media; materials processing; powder processing.

1. Introduction

Nanostructured materials (nanomaterials) are materials possessing at least one length scale on the order of a billionth of a meter. They manifest extremely fascinating and useful properties, which can be exploited for a variety of structural and non-structural applications (Inoue 2001). Nanostructured materials can possess improved properties such as high strength, improved hardness, ductility in normally brittle materials, wear-resistance, erosion-resistance, corrosion-resistance and higher chemical activity (Edelstein & Cammarata 1998). Nanomaterials can be much more formable than their conventional, commercially available counterparts. Research on nanomaterials research literally exploded in mid-1980's in the US.

Nanomaterials have numerous commercial and technological applications in areas like analytical chemistry, drug delivery, bioencapsulation, and in electronic, magnetic, optical and mechanical devices. Although there is much literature available on nanomaterials, in this paper, specific examples are chosen which are considered to be of near-term commercial value. The paper discusses the applications of nanomaterials in electronics and magnetic devices, and finally a summary of processing methods is presented.

2. Nanocrystalline materials in electronics

Nanostructured systems are useful in tailoring the magnetic, optical and electronic properties of materials. It is obvious that nanostructured materials will have an increasing impact on electronics, since the drive for increasingly smaller dimension in electronics translates into the requirement for higher functionality, increased memory density, and higher speed. The hope of utilizing effects obtained with an additional tenfold reduction in dimension drives the study of nanoscale devices based on new operating principles. Advantageous manipulation of the properties of materials can be made by systematic nanoscale variation of composition.

Quantum effect devices or single electron devices are of great potential utility for future electronic circuits. For example, one class of devices operates on the interference effect typical of wave phenomena in modifying electron transport. These devices tend to be analogs of microwave or optical devices such as waveguides, modulators, or interferometers. All of these devices rely on the elimination of scattering in order to preserve the phase of the electron wave. This requires combination of highly ordered crystals, with tailored electronic and magnetic properties, low temperatures, and small dimensions. Below are some examples of practical applications:

2.1 *Next generation computer chips*

With convergence as one of the main drivers in the microelectronics industry, smaller and better performance electronic devices are undoubtedly required. A significant reduction in size of a microprocessor means a considerable increase in the operating speed. However, researchers are faced with several technological impediments to these advancements, namely, lack of the ultrafine precursors to manufacture these components; poor dissipation of the tremendous amount of heat generated by these microprocessors due to faster speeds; and poor reliability (short mean time to failure). Ultra-high purity, nanocrystalline starting materials can help the industry to overcome these barriers with better thermal conductivity, and longer lasting, durable interconnections.

2.2 *Phosphors for high definition TV*

Better resolution of television screens could be achieved by reducing the size of the phophors, which make up the pixels. Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide, and lead telluride synthesized by the sol–gel technique are noteworthy candidates for improving the resolution of monitors. It was envisioned that through the use of nanophosphors, the cost of these displays could be made much more affordable so as to enable them to be purchased by an average household.

2.3 *Low cost flat-panel displays*

A huge market in the portable computer industry is represented by flat-panel displays. Japan has become the market leader primarily because of its research and development efforts on the materials for such displays. Nanocrystalline phosphors again play a major part in enhancing the resolution of these display devices. In addition, much higher brightness and contrast could be expected from flat panel displays constructed out of nanomaterials due to their enhanced electrical and magnetic properties.

2.4 *Large electrochromic display devices*

There is a class of materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through the materials, or by the application of electric field. An electrochromic device utilizes such materials. Nanocrystalline materials such as tungsten oxide gel are used in very large electrochromic display devices. The reaction governing electrochromism, which basically is a reversible coloration process under the influence of an electric field, is the double-injection of ions and electrons, which combine with the nanocrystalline tungstic acid to form a tungsten bronze.

These devices could be used in public billboards and ticker boards to convey information. They are quite similar to LCD displays, and they change colour when a voltage is applied. When the voltage polarity is reversed, the colour is bleached. The resolution, brightness, and contrast of these devices are greatly dependent on the tungstic acid gel grain size, and this is where nanotechnology comes into play.

3. Nanostructured magnetic materials

Many of our modern technological devices rely on magnetism and magnetic materials; these include electrical power generators and transformers, electric motors, computers, and components of sound and video reproduction systems (DeCristofaro 1998). Novel nanomagnetic materials are interesting from the point of view of the relationship between microstructural features and magnetic properties. Such features include particle size and distribution, chemical inhomogeneities, crystalline defects, crystallographic texture examples being (a) nanocrystalline soft magnetic materials produced from amorphous precursors, (b) two-phase nanoparticles with high moment cores and high resistivity ferrite shells, and (c) spring exchange magnetic materials (Kneller 1991; Wu *et al* 2001). Areas of topical interest include soft and hard magnets, hard magnetic nanoprticles, magnetic recording media and magnetic multilayers.

3.1 *Basic principles guiding the synthesis of nanomagnetic materials*

All ferromagnetic materials below the Curie temperature are composed of small-volume regions, called domains, in which there is a mutual alignment in the same direction of all magnetic dipole moments. Within these domains, the spontaneous magnetization present is equal to the saturation magnetization of the material, and so the individual domains are fully magnetized at all times. In the absence of an applied field, there is no net magnetic moment or field generated by the material because the magnetization direction of each domain is randomly oriented. During magnetization of the material, domains whose magnetization directions have a component in the direction of the applied field will grow at the expense of those that do not. Once all the unfavorably oriented domains have been eliminated by domain wall movement, the magnetization direction of the single domain that remains will be rotated so as to be parallel to that of the applied field and saturation is thus achieved. As the magnetic field is reduced by reversal of field direction, the curve does not retrace its original path. A hysteresis effect is produced and forms a hysteresis loop, this loop is a key tool in the quantitative analysis of permanent magnet performance. These loops are a graphical representation of the relationship between an applied magnetic field and the resulting induced magnetization within a material. The field that is generated by the magnetized material (B_i)

when added to that of the applied field (H) is known as the normal induction (B_n) or simply B. Since this induction has two components, it is defined as:

$$B = B_i + H.$$

The loops show the properties of the magnetic material as it is magnetized and demagnetized. When a magnetic field is applied to unmagnetized material, the intrinsic induction (B_i) is established within it, parallel to the applied field. If H is sufficiently strong, the magnet will become fully magnetized at the saturation flux density (B_{sat}). When the field is reduced to zero, the magnet returns to the residual value or remanence (B_r), as long as the magnet is within a closed magnetic circuit. Some of these magnetic properties can be improved with nanostructured magnetic material and thus the next section will discuss nanostructured magnetic materials.

3.2 *Nanostructured magnetic materials*

Magnetic nanoparticles show a variety of unusual magnetic behaviour compared to bulk materials, mostly due to surface/interface effects, including symmetry breaking, electronic environment/charge transfer, and magnetic interactions. Futhermore, since nanophase particles can be as much as 50% surface material, new magnetic properties characteristic of surfaces and interfaces become important and may be of practical value.

3.2a *Soft magnetic materials:* Soft magnetic nanocrystalline alloys have high coercivity and low remanence magnetization. Two important factors to improve the remanent magnetization are the nanocrystalline grain size and the degree of coherence across interphase boundaries (this should be sufficient to enable adjacent phases to be exchange coupled). Soft magnetic materials can be used for data storage applications that are dependent on the microstructure and geometry of the material (McHenry *et al* 1999). Magnetic films are used in a variety of applications, including recording media and heads, magneto-optical storage, and sensors. The behaviour of the magnetic domains and single domain particles, magnetoresistance, and magnetic anisotropy of the films are influenced by factors that include the grain size and orientation, the presence of the non-magnetic phases at grain boundaries, non-magnetic interlayers, and magnetostriction.

Another form of nanostrucutured magnetic materials is useful in power electronics and sensors. Such materials can be obtained by crystallising precursors cast as amorphous alloy ribbons. The amorphous ribbons typically crystallise in two stages: a magnetically desirable *bcc* (Fe, X) phase appears first, followed by a boride phase, the presence of which is deleterious to good, soft magnetic behaviour. In the optimised chemistries, the separation between the two crystallisation events is very large ($\sim$ 150 K), so that crystallising heat treatments may be conducted above the temperature for the first event, while safely avoiding the onset of the other. Attractive soft magnetic properties were observed for nanocrystalline Fe-base alloys obtained by crystallization of an amorphous ribbons alloy ribbon produced by rapid solidification. In particular, the crystallization of amorphous Fe–Si–B alloys containing Nb and Cu results in the formation of a nanoscale *bcc* structure and the *bcc*/amorphous alloys exhibited good soft magnetic properties of 1·2 to 1·4 T for saturation induction (B_s) and 10×10^4 for effective permeability (μ_c) at 1 kHz. Higher Fe content amorphous alloys of type Fe–M–B (M $=$ Zr, Hf, or Nb) were subsequently studied and mixed phase nanocrystalline/amorphous alloys were found to exhibit excellent soft magnetic properties.

The mechanisms proposed for good soft magnetic properties of nanoscale *bcc* Fe–M–B alloys are as follows.

(i) High B_s resulting from the increased Fe content and the magnetic coupling between the nanoscale *bcc* particles via the ferromagnetic amorphous phase;
(ii) reversible magnetization due to magnetic homogeneity from the nanocrystalline *bcc* Fe phase being smaller than the width of magnetic domain walls;
(iii) stability of the nanocrystalline structure enhanced by the enrichment of solute elements in the amorphous phase,
(iv) reduction of the saturated magnetostriction, λs, resulting from the redistribution of the solute elements between the nanocrystalline *bcc* and amorphous phases.

The addition of Co to these alloys can enhance the values of B_s and μ_c and balancing additions of Zr and Nb can achieve nearly zero λs.

3.2b *Hard magnetic materials:* Magnetic induction can be improved by utilizing exchange coupling in magnetically hard and soft phases. Nanoscale two-phase mixtures of hard and soft magnetic phases can exhibit values of remanent magnetization, Mr, significantly greater than the isotropic value of 0·5, Ms. This “remanence enhancement” is associated with exchange coupling between the hard and soft phases which forces the the magnetization vector of the soft phase to be rotated to that of the hard phase. Two important requirements for alloys to exhibit remanence enhancement are a nanocrystalline grain size and a degree of coherence across interphase boundaries sufficient to enable adjacent phases to be exchange coupled.

While the very low losses of the nanocrystalline soft magnetic materials are dependent on the nanometer grain size for their properties, the hard magnetic nanocrystalline alloys with remanence enhancement provide greater flexibility in processing, especially with powder materials. These remanence enhanced nanocrystalline hard magnetic alloys may find many applications as permanent magnet components.

3.3 *Some applications of nanostructured magnetic materials*

3.3a *Storage applications:* The route to progress in memory technology is cost reduction and the development of ever faster, more compact, and less power consuming memory systems, with greater storage capacity. Theory shows that all these benefits can be obtained by reducing the size of the basic storage cell, hence it is natural to suppose that nanotechnology will eventually play a fundamental role. However, it is imperative that the system must also include a means for writing and reading the cells efficiently. This is the most demanding aspect of memory design. For instance, very compact memories based on scanning tunnelling microscopy employs storage cells approaching the size of a single atom. One formidable challenge to this is designing sufficiently fast and reliable read/write mechanisms. One probable route by which nanostructure research could lead to a successful memory technology would be via nanoelectronics research resulting in the development of an ultrahigh-density, VLSI technology

3.3b *Giant magneto resistance (GMR) recording head:* Magnetic recording essentially involves detecting changes in the direction of magnetization in the storage medium. Small magnetic fields immediately above the regions of magnetization changes are associated with this divergence. These stray fields are read by inducing signals or resistance changes in the head as the storage medium is moved past them. This is called magnetoresistive effect, and it is useful for sensing magnetic fields such as those in the magnetic bits of data stored on a computer hard drive.

In order to store the magnetic transitions at high densities (e.g. 10^4 cm^{-1}), several constraints are imposed on the storage media and on the write and read heads. Just take the case for storage media. With a high storage density, the distance between magnetization reversals become very small. This produces strong demagnetising fields on the stored 'bit'. For stable storage, the coercive force, must be high enough to withstand these demagnetising stray fields.

Another consideration is to ensure sufficient stray field for detection of the transition, a high remanence is thus required. A storage medium with both high coercive force and saturation magnetization would seem to be required. High permeability and high data rates ($>$ 100 MHz) place additional constraints on the write head materials, e.g., eddy currents need to be avoided. Nanostructured structures promise to solve all these constraints on media and read heads. Specially prepared layers of nanometer-thick magnetic and non-magnetic films were found to exhibit the giant magnetoresistance (GMR) effect. In 1991, it was demonstrated by IBM Almaden research center that the GMR effect could be observed in easily made samples. It also discovered that a special kind of GMR structure, a spin valve, could sense very small magnetic fields. A new era involving the use of GMR in the read heads for magnetic disk drives has begun.

In the spin valve GMR head shown in figure 1, the copper spacer layer is about 2 nm thick and the Co GMR pinned layer is about 2·5 nm thick. It is important to control these layers thickness with atomic precision. This novel read head has extended magnetic disk information storage from 1 to $\approx$ 20 Gbits in 1998. One future application of GMR that is contemplated by

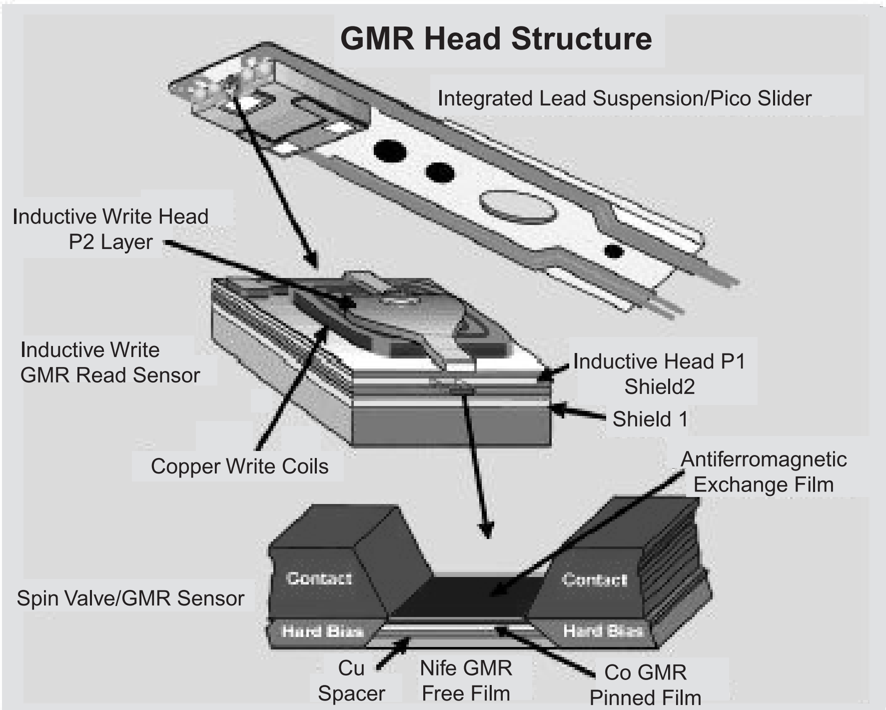

Figure 1. IBM commercial GMR read head.

researchers is non-volatile magnetic random access memory (MRAM). What is interesting about this MRAM is that, not only has the material size requirement per bit been dramatically reduced, but also the memory access time has dropped from typically a few milliseconds to nanoseconds. In addition, due to GMR effect inherent resistance to radiation damage, these memories are expected to be used for space and defence applications. Thus the GMR effect indeed could be exploited for many exciting applications thanks to its properties. However, a challenge to GMR device performance would be the signal-to-noise ratio. In-plane GMR device performance suffers from low signal-to-noise ratios as the device lateral dimensions get smaller than 1 micron. Research on vertical GMR devices that give larger signals as the device dimensions shrink are underway. As an illustration, at 10 nm lateral size, GMR devices could provide signals in excess of 1 V and memory densities of 10 Gbit on a chip. This is comparable to that stored on conventional magnetic disks. If successful, the chip would eliminate the need for magneto-mechanical disk storage with its slow access time in milliseconds, large size, weight, and power requirements.

3.3c *High power magnets:* The magnetic strength of a material is measured in terms of coercivity and saturation magnetization values. These values increase with decrease in grain size and increase in the specific surface area of the grains. Magnets made of nanocrystalline yttrium-samarium-cobalt grains possess very fascinating magnetic properties due to their extremely large surface area. Some typical applications include quieter submarines, automobile alternators, land-based power generators, motors for ships, ultra-sensitive analytical instruments, and magnetic resonance imaging in medical diagnostics.

4. Processing methods

4.1 *Processing of nanocrystalline materials*

A summary of some common techniques of processing nanomaterials is presented in table 1. Nanocrystalline materials have many good properties but they have some drawbacks where the

Table 1. Methods to synthesize nanocrystalline materials.

Starting phase	Techniques	Nature of product
Vapour	Inert gas condensation	3D
	Physical vapour deposition – evaporation and sputtering	1D
	Plasma processing	
	Chemical vapour deposition	3D
	Chemical reactions	3D
Liquid	Rapid solidification	3D
	Electrodeposition	1D, 3D
	Chemical reactions	
Solid	Mechanical attrition	3D
	Devitrification	3D
	Spark erosion	3D
	Sliding wear	3D

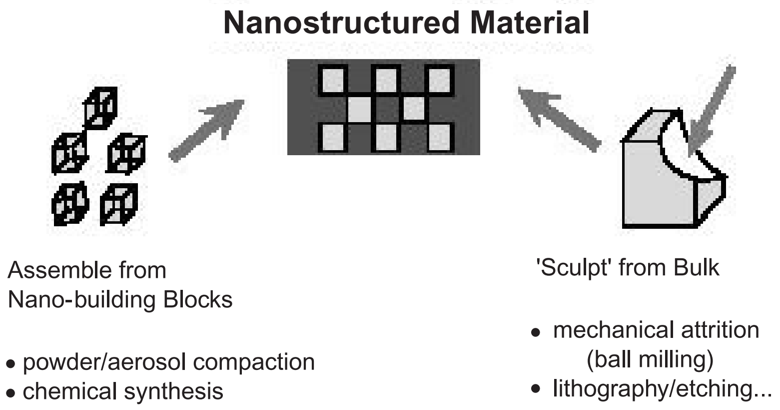

Figure 2. Ways to make nanostructured material.

cost of production is very high. Two common ways of thinking about making nanomaterials are presented in figure 2. Some cost-effective processes of manufacturing nanocrystalline materials have been proposed (Cahn 1991; Lall 1992):

(i) *Plasma processing:* A non-transferred arc thermal plasma reactor has been used to vaporize coarse metal powders. A supersonic nozzle is used to quench the powder, and the powders are collected in a filter system that can be sealed and dismantled in a glove box. A drawback of the process is oxidation during fine powder handling.

(ii) *Combustion process:* The combustion process utilizes oxidizers and fuels. In controlled environments, high temperatures can be generated by the exothermic redox reactions between decomposition products of the oxidizer and the fuel. Owing to the fast heating and cooling, there is nucleation of crystallites but little growth, resulting in nanocrystalline ceramics. Some of the process features are as below.

  (a) It is a versatile process leading to the synthesis of single phase, solid solutions, and composites as well as complex compound oxide phases.
  (b) It uses cheap raw materials.
  (c) It is a scalable and high production rate process.
  (d) The products are of high purity and loosely agglomerated, resulting in high sinterability.

(iii) *Mechanical alloying:* A high-energy ball milling process has been used to produce nanostructured powders.

(iv) *Supercritical fluid:* The production of nanostructured particles or their films depends upon the substantial change in solubility of a solute in a solvent, at the supercritical point (temperature and pressure) of the solvent.

(v) *Sol–gel method.*
Processing techniques that can be scaled up to mass production are as follows.

  (a) Powder synthesis techniques – Magnetic nanocrystals may be synthesised as free-standing powders or nanoencapsulates that must then be compacted to form a bulk alloy with nanocrystalline grains. An example is carbon arc synthesis which is the primary method used in nanoencapsulates, nanotubes and endohedral fullerenes. This technique allow for the production of metal or metal carbides nanoparticles with protective coatings.

(b) Rapid solidification processing – Amorphous alloys to be produced by a variety of rapid solidification processing routes with cooling rates $> 10^4$ K/s for eutectic alloys.

(c) Solidification processing of bulk amorphous alloys – Bulk amorphous alloys are formed by more conventional solidification routes at slower cooling rates.

(d) Crystallisation of amorphous precursors – Bulk alloys with nanocrystalline grains can also be produced by solid state (crystallisation) of an amorphous precursor.

4.2 *Crystallization from the amorphous phase*

One of the popular methods used in producing nanocrystalline materials is by first making an amorphous phase of appropriate chemical composition. This amorphous phase is then subjected to certain elevated temperatures, above the primary crystallization temperature but below the secondary crystallization temperature, in controlled time. Doing so yields nanocrystalline grains with amorphous intergranular material. By and large, the crystallization process is done by annealing in an inert gas furnace. However, there are a few exceptions: Nanocrystalline Finemet of $\simeq 15$ nm nanocrystallite size has been produced by laser annealing of the amorphous precursor. This technique offers some flexibility as compared to conventional furnace-annealing techniques. The use of flash annealing of a melt-spun Finemet precursor has also been reported. Very fine nanocrystalline grain size achieved by this process has resulted in enhanced soft magnetic properties.

4.3 *Rapid solidification techniques*

High enough cooling rates during solidification can be achieved when two important requirements are satisfied. The solidification rate, R, during ideal cooling is related to the section thickness, z (in mm) through the relation: $R = 10^4 z^{-2}$, suggesting that the solidification rate increases by two orders of magnitude for a decrease in section thickness by one order of magnitude. Hence, it is imperative that the molten metal be delivered in a stream which is thin enough in at least one dimension and has high surface area to volume ratio to allow rapid heat removal. Second, to rapidly remove heat, contact area between the melt and the cooling medium needs to be maximized by rapidly increasing the liquid alloy surface area. This could be achieved by spreading the melt as thin layers on a substrate, or by physically disintegrating the melt into small droplets by atomisation. It is obvious that the molten metal can be delivered in the form of either droplet, cylindrical stream or ribbon stream and the melt stream can be cooled by gas, liquid, or solid.

Rapid solidification methods could be classified into three broad categories as follows

(i) *Spray methods:* The melt is fragmented into droplets prior to quenching. Powder is produced by this method. The mechanism of atomisation and the means of cooling can be different in different techniques. Some atomisation methods are by gas, water, ultrasonic, rotating, soluble gas, electrohydrodynamic, spark erosion, and twin roll means.

(ii) *Chill methods:* The continuity of the melt is preserved up to and during quenching. This is achieved by bringing the melt into contact with a chilling substrate. Various methods involve injecting the melt into a die cavity, forming the melt into a thin section by forging between a hammer or piston and an anvil, extruding the melt on to a chilled surface or extraction of the melt by contact with a rotating disc. Some chill methods are by using dies, piston and anvil, twin roller quenching, free flight melt spinning, chill block melt spinning, planar flow casting, and melt overflow.

(iii) *Surface methods:* The material acts as a heat sink – rapid melting and solidification take place at a limited depth at the surface. This method has also been referred to as self-quenching, laser annealing, laser glazing etc. An extremely high power density of laser or electron beam, typically of the order of 10^6 W/cm^2 is concentrated on the alloy surface. There are two ways of performing this surface treatment. One is where the surface is rapidly scanned in a direction perpendicular to the beam, while other is where the material is not moving. Cooling rates of 10^6–10^8 K/s have been reported.

As an example, consider the production of the amorphous soft magnetic materials precursor, which can be in bulk form, patterned magnetic arrays or thin substrate form. Thin amorphous cobalt based alloy strips are generally manufactured by the liquid quenching method which resorts to the single roll technique. The extremely small thickness of less than $4{\cdot}8\,\mu$m resulting from the substrate method notably enhances soft magnetic properties such as permeability and core loss in the high frequency range. Additionally, magnetic cores and electromagnetic apparatus can be produced from thin Co-based amorphous alloy strips. One of the technical challenges faced is that of making the layers thinner than $5\,\mu$m. These thin strips contain relatively numerous pinholes because they entrain bubbles during the reduction of plate thickness and, therefore, pose problems of practicability as well as adaptability for higher frequencies.

Iron-based alloys are also of considerable interest (Yoshizawa *et al* 1988; Yoshizawa 2001). Production of thin soft magnetic alloy strips of Co-based alloys, comprises the following steps: (a) ejecting molten alloy through a nozzle onto the surface of a rotating cooling member, and (b) rapidly quenching the alloy thereby producing thin amorphous alloy. It is also possible to produce thin Co-based amorphous alloy strips of thickness less than $4{\cdot}8\,\mu$m.

The Co soft magnetic material is used in noise filters, saturable reactors, miniature inductance elements for abating spike noise, mains transformers, choke coils, zero-phase current transformers, magnetic heads etc., i.e., devices which are expected to exhibit high levels of permeability at high frequencies.

The method for the production of thin soft Fe-based magnetic alloy strips consists of rapid quenching of the molten alloy and heat-treating the quenched alloy strip at a temperature exceeding the crystallization temperature of the alloy. Specifically, materials of high permeability are effectively used in various magnetic parts such as current sensors in zero-phase current transformers and noise filters. In the case of a noise filter, for example, a switching power source is widely used as a stabilizing power source for electronic equipment and devices. In the switching power source, adoption of a measure for the abatement of noise constitutes an important task. High-frequency noise having a switching frequency as its basic frequency and noise in the MHz range issuing from a load such as, for example, the logic circuit of a personal computer poses a challenge.

4.4 *Sol–gel synthesis as a processing method*

Sol–gel synthesis is widely used due to some advantages such as those listed below.

(i) Produces materials (both metals and ceramics) at low temperatures (around 300°C *vis-à-vis* about 1500°C for conventional techniques).
(ii) Able to produce in large quantities (commercially viable) relatively cheaply.

(iii) Can synthesize many materials.
(iv) Co-synthesize two or more materials simultaneously.
(v) Coat one or more materials onto other materials (metal or ceramic particulates, and three-dimensional objects).
(vi) Produce extremely homogeneous alloys and composites.
(vii) Synthesize ultra-high purity (99·9999%) materials.
(viii) Tailor the composition very accurately right from the early stages of the process, because the synthesis is actually carried out at atomic level.

The sol–gel process is able to control the microstructure of the final products accurately and thus control the physical, mechanical, and chemical properties of the final products.

4.5 *Powder injection moulding*

Powder injection moulding is the combination of metal injection moulding (MIM) and ceramic injection moulding (MIM) (Lall 1992). Powder injection moulding is a productive and widely used technique for shaping plastics. However, there are several properties of metals and ceramics, such as high strength, high stiffness, high operating temperature, which have strong advantages over polymers. Besides, metals and ceramics exhibit electrical, magnetic and thermal properties not possible with polymers. Thus, powder injection moulding (PIM) has been used for the production of metallic and ceramic products, exploiting benefits that have been proven over the decades in plastic injection moulding.

Powder injection moulding process consists of four major steps, namely feedstock, injection moulding, debinding and densification as shown in figure 3. In the first stage, a feedstock is compounded from the powder and a binder system. The second stage requires the aid of an

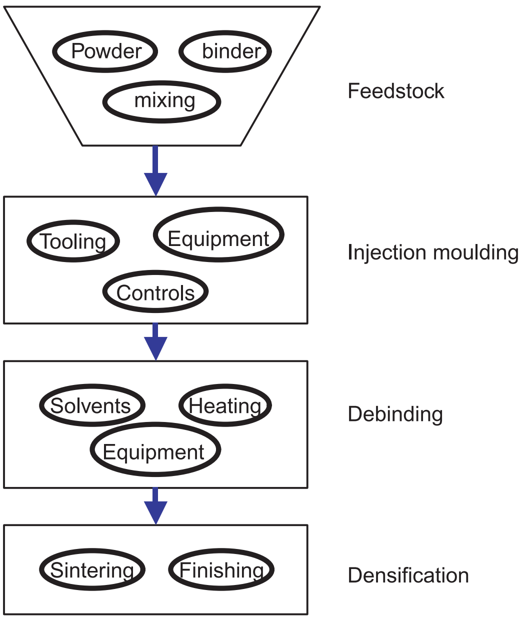

Figure 3. Flow chart for the PIM process showing the four major process steps.

Figure 4. Powder injection moulding machine.

injection moulding machine (see figure 4) to produce the “green” moulds. Removal of the binder yields the third stage. Sintering and finishing which is the final stage in PIM gives the final product.

As a technology, PIM has been around for some time. There are five factors that impact on the selection of PIM for any application as shown in figure 5. These are a large selection of

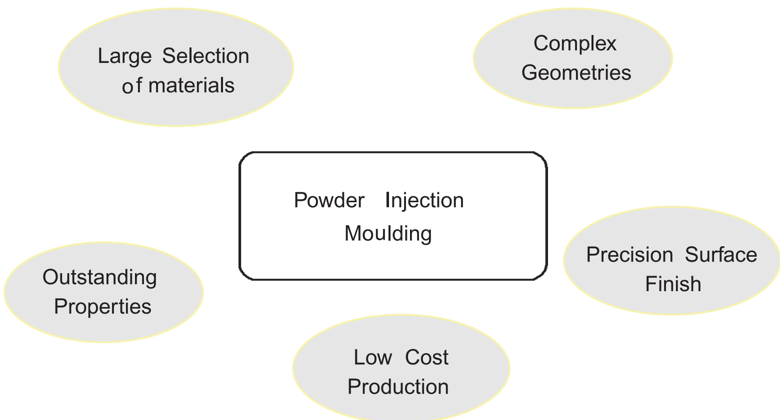

Figure 5. Five important factors for the selection of PIM.

materials, complex geometries, surface finish, outstanding properties and relatively low cost production. Using PIM to make products with magnetic properties is one of the key applications of PIM. The next section will give a brief description of powder injection moulding of conventional magnetic materials.

5. Powder injection moulding of conventional magnetic materials

A large number of amorphous alloys have been prepared by various rapid solidification techniques. Among amorphous alloy systems, iron- and cobalt-based amorphous alloys have been used in application of magnetic materials. Powders for rapid solidification are produced mainly by inert gas atomization and centrifugal atomization. Both processes produce spherical particles in the size range 20 to 100 μm in diameter by employing cooling rates up to 10^6 K/s. However, for nanostructured magnetic materials, the particle size should range from 1–100 nm.

Conventional magnetic materials used in powder injection moulding can be amorphous. Amorphous magnetic materials, which impose less obstacles to the movement of magnetic domain boundaries and have low hysteresis losses, and high permeability, have been developed for various electronic devices such as sensors and motors.

Although powder injection moulding of conventional magnetic materials can produce complex shape, good surface finish and good dimensional control, because of the amorphous phase structure, it cannot obtain other advantages which nanostructured magnetic materials possess, as will be highlighted in the next section. For example, sensors made by nanocrystalline materials can exhibit improved sensitivity compared to sensors made from amorphous materials. Advantages and applications of powder injection moulding of nanostructured magnetic materials will also be presented in the following section.

6. Powder injection moulding of nanostructured magnetic materials

By the use of the powder injection moulding technique with nanostructured magnetic materials, the following advantages can be obtained:

(a) High shape complexity: PIM can produce more complex parts than either investment casting or traditional press and sinter techniques.
(b) High density: PIM parts produced with our feedstock will have density levels between 97·5 and 99·5%. These levels typically exceed traditional press and sinter techniques, and are comparable to investment casting.
(c) High performance: Nanocrystalline magnetic materials are exceptionally strong, hard, and ductile at high temperatures. They have lowest energy losses (narrowest B/N hysteresis loop), high permeabilities and exhibit nearly or exactly zero magnetostriction.
(d) Low cost: Cost savings can be realized by eliminating machining operations, secondary coining operations or surface impregnation.

7. Potential applications of PIM to nanostructured materials

7.1 *High-sensitivity sensors*

Sensors employ their sensitivity to the changes in various parameters they are designed to measure. The measured parameters include electrical resistivity, chemical activity, magnetic permeability, thermal conductivity, and capacitance. All of these parameters depend greatly on the microstructure (grain size) of the materials employed in the sensors. A change in the sensor's environment is manifested by the sensor material's chemical, physical, or mechanical characteristics, which is exploited for detection. For instance, a carbon monoxide sensor made of zirconium oxide (zirconia) uses its chemical stability to detect the presence of carbon monoxide. In the event of carbon monoxide's presence, the oxygen atoms in zirconium oxide react with the carbon in carbon monoxide to partially reduce zirconium oxide. This reaction triggers a change in the sensor's characteristics, such as conductivity (or resistivity) and capacitance. The rate and the extent of this reaction are greatly increased by a decrease in the grain size. Hence, sensors made by nanocrystalline materials are extremely sensitive to the change in their environment. Typical applications for sensors made out of nanocrystalline materials are smoke detectors, ice detectors on aircraft wings, automobile engine performance sensor etc.

7.2 *Solenoid assembly*

The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains). The key properties of the solenoid assembly, made of iron-nickel steel by PIM, are magnetic permeability and magnetic strength. With nanostructured iron-nickel steel, high magnetic permeability and magnetic strength are achieved and value-added products to both producers and consumers are, possible.

Figure 6 is a schematic of a solenoid with a metal housing and a moving piston, which is held in position by a spring. As the solenoid is energized, a magnetic flux is generated in the surrounding materials. Since the lines of force run across the air gap, the movable piston is pulled axially, overcoming the spring force. When de-energized, the system loses its magnetic field and the spring pushes the piston back into the original starting position. Such a device can be used to perform a number of short-stroke functions. This includes opening and closing valves and switches.

7.3 *Comparison with other forming processes*

Section 8 enumerates the advantages of powder injection moulding over other conventional processes as shown in table 2.

8. Opportunities and challenges in PIM of nanomaterials

The foremost area of opportunity is the control of the particle preparation process so that size is reproducible. This requires creation of narrow size range particles that can be prepared by

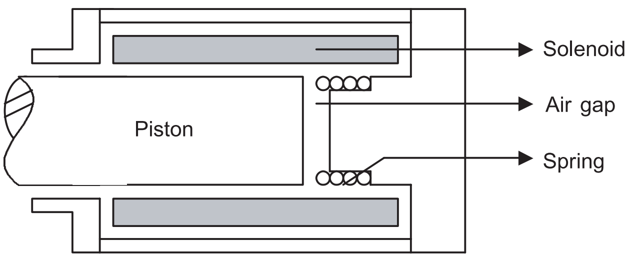

Figure 6. Schematic of a solenoid unit.

Table 2. Comparison of PIM with other conventional processes.

Process	Limitations	PIM advantage
Die casting	Lower strength alloys	Numerous high strength materials
Investment casting	Labour intensive process	Highly automated process
	Costly process	Lower costs
	Requires secondary machining	No secondary operations needed
Machining	Complex shapes require numerous machining centers	Mold the part net shape
	Significant material waste	Virtually no material waste
	Design limitations	Ideal for complex shapes
	Difficult to machine hard materials	Wide range of available materials
Powder metal press & sintering	Low material densities	High densities 97%–99·7%
	Limited part complexity	Ideal for complex shapes
	Secondary machining operations often required	No secondary operations needed
	Impregnation required to weld or plate	Can be welded or plated

processes as described earlier. In most studies, the size of the primary particles depends on material properties and the temperature/time history.

The second area of opportunity is process control. In the concept of a process control methodology, the nature of chemical processes makes it imperative to have means of effectively monitoring and initiating change in the process variables of interest. Accordingly, those involved with production of nanoparticles would monitor outputs, make decisions about how to manipulate outputs in order to obtain the desired behaviours, and then implement these decisions on the process.

A third area of opportunity is the process and product relationship that leads to continuous uniformity. That is, the specification setting by product users that must be available to relate to process control in manufacturing. Here, nanoparticle formulation and the process used to prepare the particles must be linked and interactive.

Achieving implementation in the industrial market will require close attention to resolving the challenges in the three areas summarized above. In addition, there remains a large gap between the cost of preparing conventional materials and that of preparing nanoparticles. This will remain a challenge for the future if nanomaterials are to be competitive.

9. Summary

Specific examples of the use of nanostructured electronic and magnetic materials have been cited and potential applications of PIM of nanomagnetic material are discussed. Processing techniques which are scalable to industrial practice are cited and comparative advantages have been outlined. The case of powder injection moulding of both conventional and nanomagnetic materials is discussed and it appears that the most significant areas of application for this technology are high-sensitivity sensors and solenoid assemblies. However, controlling the particle preparation process, process control, process and product relationship that leads to continuous uniformity are the opportunities as will as the challenges in the technology.

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References

Cahn R W (ed.) 1991 *Materials science and technology; A comprehensive treatment. Vol 15: Processing of metals and alloys* (Weinheim: VCH)

DeCristofaro N 1998 Amorphous metals in electric power distribution applications. *MRS Bull.* 23: 50–56

Edelstein A S, Cammarata R C (eds) 1998 *Nanomaterials: Synthesis, properties and applications* (London: Inst. Phys.)

Inoue A 2001 Bulk amorphous and nanocrystalline alloys with high functional properties. *Mater. Sci. Eng.* A304–306: 1–10

Kneller E F 1991 The exchange spring magnet: A new material principle for permanent magnets. *IEEE Trans. Magnet.* 27: 3588–3600

Lall C 1992 Soft magnetism: Fundamentals for powder metallurgy and metal injection moulding. (Princeton, N J : Metal Powder Industries Federation) pp 90–92

McHenry M E, Willard M A, Iwanabe H, Sutton R A, Turgut Z, Hsiao A, Laughlin D E 1999a Nanocrystalline materials for high temperature soft magnetic applications. *Bull. Mater. Sci.* 22: 495–501

McHenry M E, Willard M A, Laughlin D E 1999b Amorphous and nanocrystalline materials for applications as soft magnets. *Prog. Mater. Sci.* 44: 291–433

Wu Y Q, Ping D H, Murty B S, Kanekiyo H, Hirosawa S, Hono K 2001 Influence of heating rate on the microstructure and magnetic properties of Fe3B/Nd2Fe14B nanocomposite magnets. *Scr. Mater.* 45: 355–362

Yoshizawa Y, Oguma S, Yamauchi K J 1988 New iron based soft magnetic alloys composed of ultrafine grain structure. *J. Appl. Phys.* 64: 6044

Yoshizawa Y 2001 Magnetic properties and applications of nanostructured soft magnetic materials. *Scr. Mater.* 44: 1321–1325