

# **MANUFACTURE OF MODERN PERMANENT MAGNET MATERIALS**

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## **ABSTRACT**

Every commercially successful permanent magnet material since 1950 has been manufactured via powder metallurgy. Furthermore, the focus of current research into new magnetic materials is based on processes that require fine particulates at one or more stages of manufacture. Such products include exchange coupled hard and soft magnetic phases, unique metallurgical structures created at the atomic level and interstitial elements that can only be diffused over short distances typical of small particles, small diameter fibers or thin sheets. While forming particulates involves well-established practices, obtaining optimized exchange coupling is proving difficult. An even greater challenge is consolidation of the nanoparticulate into bulk magnetic structures while maintaining the nano-structure and introduction and maintenance of magnetic domain alignment.

## **INTRODUCTION**

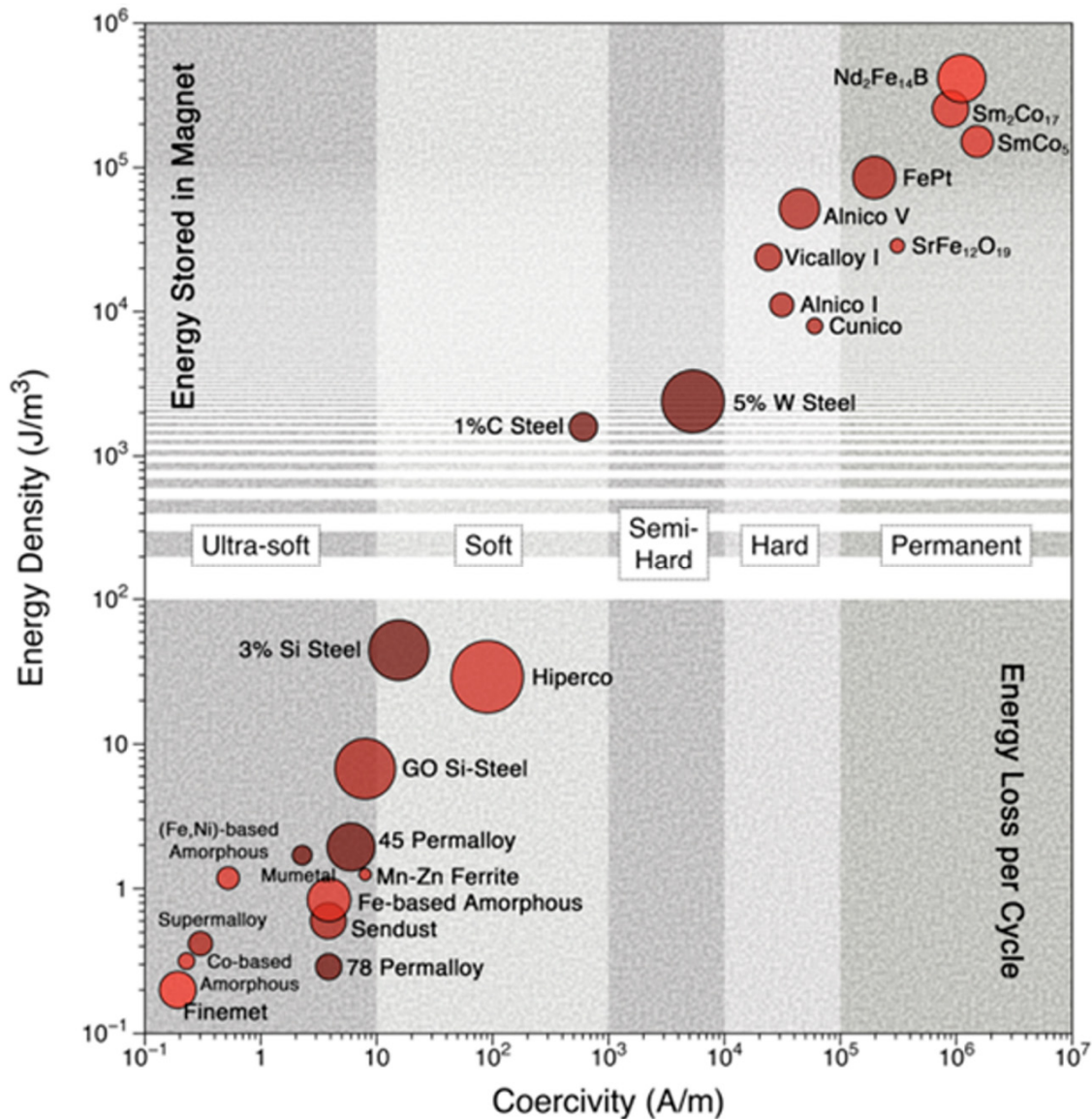
Permanent and soft magnetic materials have undergone radical development since they were first employed in motors in the 1800s. For example, Hitachi reports a greater than 90% reduction in the mass of 5 HP induction motors primarily as the result of a) improved soft and permanent magnetic materials and b) optimized motor designs based on these improved materials.<sup>1</sup> Key metrics of performance are not the same for permanent magnets (PM) and soft magnetic materials. This has led to compositionally different materials with benefits specific to the type of product. Soft magnetic materials emphasize ease of magnetic reversal while permanent magnets require resistance to demagnetization.

Furthermore, the shape and configuration of these materials in an application require different processing methodologies. For example, motor laminations are manufactured by rolling of malleable steel alloys to thin gauge, then cutting or stamping the profile of the rotor or stator, and stacking the laminations to achieve adequate axial length. The malleability of the alloy has been a key manufacturing criterion. On the other hand, most permanent magnets are made via powder metallurgy for at least some part of their manufacturing process.

There are, however, numerous cross-over materials. Examples include soft magnetic composites (SMCs) which are made via powder metallurgy and soft magnetic powder cores (iron, ferrite, silicon-iron, molybdenum permalloy and 50/50 NiFe) - all made from powders. Conversely some permanent or semi-hard magnets are made via rolling, extrusion or mechanical working of bulk alloy (PtCo, MnAlC, NdFeB+Cu, FeCrCo, Vicalloy). The focus of this paper is on differentiating the current and potential manufacturing methods and identifying challenges to obtaining acceptable magnets from newly developed materials.

## **DISCUSSION**

Several authors have presented charts exemplifying the improvement in soft and PM materials that have taken place over time. One such chart, Figure 1, created by Matt Willard of Case Western Reserve University<sup>2</sup>, is rich with information. A similar chart but with timeline is from Coey.<sup>3</sup>



**Figure 1.** Attributes of permanent and soft magnetic materials (Prof. M. Willard)<sup>2</sup>

Soft magnetic materials, used as a carrier of magnetic flux and frequently utilized in rotating machinery, benefit from low hysteresis loss via a low coercivity ( $H_{cB}$ ), high permeability (ease of flux-carrying), and high electrical resistivity to reduce eddy current losses. On the other hand, permanent magnets benefit from high resistance to demagnetization (high  $H_{cJ}$ ) along with a high  $B_r$  (measure of magnetic strength).

This discussion will concentrate on permanent magnetic materials – the upper half of Figure 1. Uses for permanent magnets can be subdivided several ways. A practical differentiation is:

- 1) To provide flux density in a region around the magnet such as for sensing or holding applications. These applications benefit from high values of  $B_r$  (magnetic strength), but do not require high  $H_{cJ}$  (resistance to demagnetization).

- 2) To provide a temporary storage of energy such as in a motor or generator, in which the application requires magnets with high resistance to demagnetization and high Maximum Energy Product  $(BH)_{\max}$  (“energy density” as shown in Figure 1).

The development of permanent magnets has been focussed on increasing these two key characteristics: Maximum energy product,  $(BH)_{\max}$  and Resistance to demagnetization,  $H_{cJ}$ , primarily for the benefit of motor and generator applications. These two applications represent approximately 70% of ferrite and rare earth magnet usage (on a weight basis) and range from MEMS devices to hard disk drive voice coil motors to large systems of many 100 horsepower.

**Table 1.** Development of key permanent magnet figures of merit (edited from reference 3)

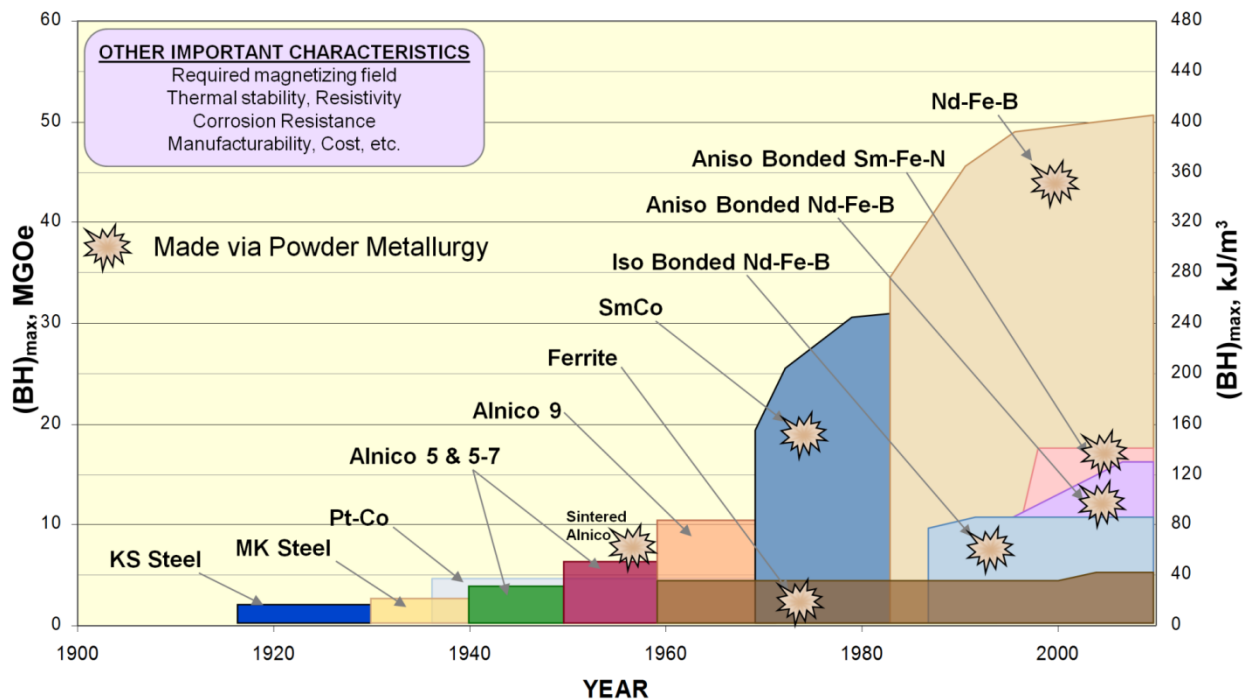
<b>Material</b>	<b>First Reported</b>	<b><math>(BH)_{\max}</math> MGOe</b>	<b><math>H_{cJ}</math> Oe</b>
Remalloy	1931	1.1	230
Alnico	1931	1.4	490
PtCo	1936	7.5	4,300
Cunife	1937	1.8	590
Cunico	1938	1.0	450
Alnico (field treated)	1938	5.5	640
Vicalloy	1940	3.0	450
Alnico, DG	1948	6.5	680
Ferrite, isotropic	1952	1.0	1,800
Ferrite anisotropic	1954	3.6	2,200
Lodex®	1955	3.5	940
Alnico 9	1956	9.2	1,500
RECo <sub>5</sub>	1966	16.0	20,000
RECo <sub>5</sub>	1972	22.0	25,000
RE <sub>2</sub> (CoFeCuZr) <sub>17</sub>	1976	32.0	25,000
RE <sub>2</sub> TM <sub>14</sub> B	1984	26.0	25,000
		35.0	11,000
RE <sub>2</sub> TM <sub>14</sub> B	2010	30.0	35,000
		52.0	11,000

All the materials listed in this table are still commercially produced with the exception of Lodex (environmental and safety issues associated with mercury and lead) and CuNiFe/CuNiCo (replaced by the functionally similar FeCrCo or eliminated by product redesign for performance optimization).

## CURRENT MANUFACTURING PROCESSES

Up through the development and application of alnico magnets, products were metal alloys manufactured using traditional foundry techniques. During the development of alnico, trials were successful in making alnico magnets via powder metallurgical techniques. That is, the cast alloy was crushed and pulverized, blended with additives including lubricants, pressed in conventional compaction dies and liquid phase sintered. Both types of product (cast and sintered) are still globally manufactured. Larger magnets and more complex shapes are made via sand-casting and smaller, simpler parts are made via powder press and sinter.

The next permanent magnet material discovered after alnico to become a commercial success (mid 1950s) was ferrite which is a brittle ceramic, not a metal alloy. For the first time, magnets would not be made in a foundry – ferrite required traditional powder metallurgy (P/M). In 1966-67  $\text{SmCo}_5$  magnets were invented and manufactured using powder metallurgy. Between 1972 and 1975, a higher energy  $\text{Sm}_2\text{Co}_{17}$  type of magnet was developed. It too used powder metallurgy for manufacturing. Then in 1984, commercial production of neodymium iron boron ( $\text{NdFeB}$ , “neo”) commenced using powder metallurgy. Neo can also be made by hot rolling of the alloy when copper is added to improve malleability as was done by Seiko Epson for the manufacture of watch motor magnets. Neo can also be made by hot pressing such as the Magnequench MQ2 and MQ3 products. In the early 1990s  $\text{SmFeN}$  was invented. It is made by nitrogen interstitial infusion into  $\text{SmFe}$  fine alloy powder and is a suitable material for bonded magnets – especially injection molded – but decomposes above  $450\text{ }^\circ\text{C}$  preventing consolidation to full density by all methods tried to-date.



**Figure 2.** Development of Permanent magnets (maximum energy product) over time. Magnetic materials manufactured by powder metallurgy are indicated.

### DOMAIN ALIGNMENT

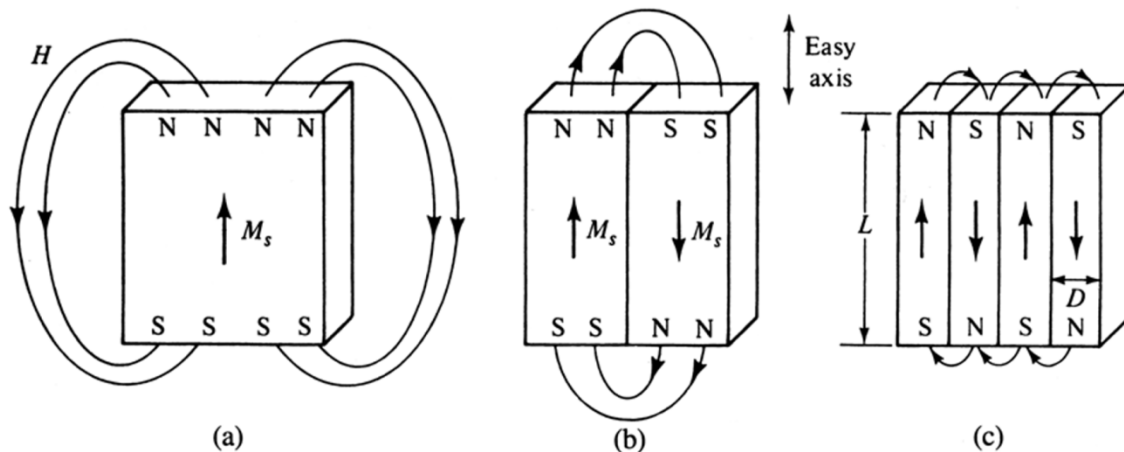
The source of the magnetic field originates in an imbalance of electron spins in atoms, especially in the 3d and 4s sub-shells. This imbalance is strong in the naturally ferromagnetic elements iron (Fe), cobalt (Co)

and nickel (Ni). When these elements are combined with other elements in a crystalline structure, there exists in some crystals an arrangement wherein the magnetic field from each atom aligns with that of its neighbors amplifying the magnetic effect in what is called exchange interaction leading to strong magneto-crystalline anisotropy. Each crystal has a preferred direction of magnetization, usually along the “c” axis as in tetragonal (NdFeB,  $\text{Sm}_2\text{Co}_{17}$ ), hexagonal (ferrite) and rhombohedral ( $\text{SmCo}_5$ ) crystals. The c-axis becomes the easy axis of magnetization.

The procedure for making magnets calls for reducing the bulk chunk alloy into particles each of which consists of only one direction of magnetization. Roughly half of the domains within each particle will point in one direction while the other half point in the opposite direction resulting in no net external field. These particle sizes are approximately 1 micron diameter for ferrite, 3 microns for NdFeB and 4 to 5 microns for SmCo – all measurements equivalent spherical diameter as measured by Fisher Sub-sieve Sizer (FSSS). (Laser-measured dimensions, D-50, are typically about 20% greater).

To manufacture bulk magnets, it is necessary to consolidate the powder into a “green” compact while aligning each particle to have mutually parallel easy axes of magnetic alignment. This is done by applying a magnetic field prior to and during compaction. The applied field magnetizes each particle and then the applied field interacts with the magnetic particles causing them to rotate into alignment. Green compacts are then liquid phase sintered to full density (99+ of theoretical). Sintering results in physical shrinkage of about 15% linearly, 30% volumetrically. Remarkably, the alignment is maintained during sintering and well-manufactured product is 96 to 97% of perfect alignment.

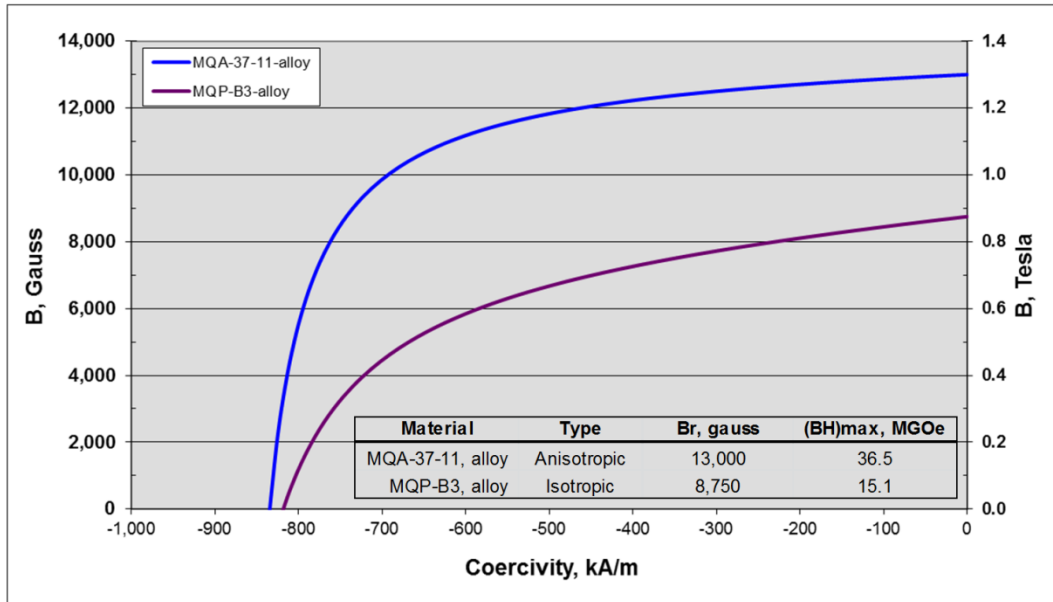
As most will recall from childhood while learning about magnets, like poles repel and unlike poles attract. In the structure of the magnet, there exist numerous domains aligned parallel to each other with north poles next to each other and south poles adjacent to each other. This is the magnetized, higher energy state and domains will try to reduce this energy by some of them rotating as shown in Figure 3, until roughly half are pointed in one direction and half in the opposite direction. In permanent magnets there are two mechanisms by which domains are prevented from rotating.<sup>4</sup> For  $\text{SmCo}_5$  the primary mechanism is *nucleation controlled* pinning. The primary mechanism for ferrite, NdFeB and  $\text{Sm}_2\text{Co}_{17}$  magnets is *domain wall* pinning. These mechanisms are not mutually exclusive and most materials will exhibit some degree of each.



**Figure 3.** Magnetostatic energy and domain structure. Domain rotation results in net zero external field. Bloch walls between domains prevent easy domain rotation, enhancing coercivity.<sup>5</sup>

The importance of domain alignment becomes obvious when we consider the effect of mis-alignment on the resultant external field. Magnetic fields are vectors, that is, they have magnitude and direction. The

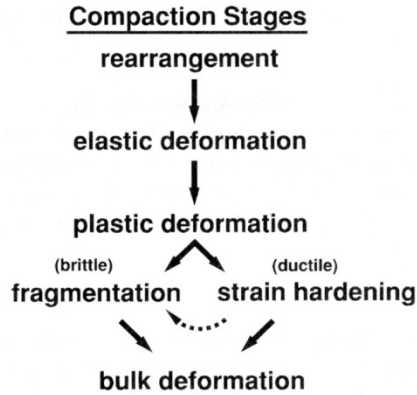
net magnetization in the designed alignment is proportional to the cosine of the angle of mis-alignment of each domain, integrated over all domains. A randomly oriented (isotropic) matrix of domains will produce about 63% of the  $B_r$  of a fully oriented matrix. Energy product is proportional to the square of  $B_r$  and will be about 40% ( $0.63 \times 0.63 = 0.40$ ) of the fully aligned product. Therefore the strongest and presumably best products result from well-aligned domain structures in a fully dense magnet. A comparison of second quadrant hysteresis curves for aligned and un-aligned magnets is presented in Figure 4.



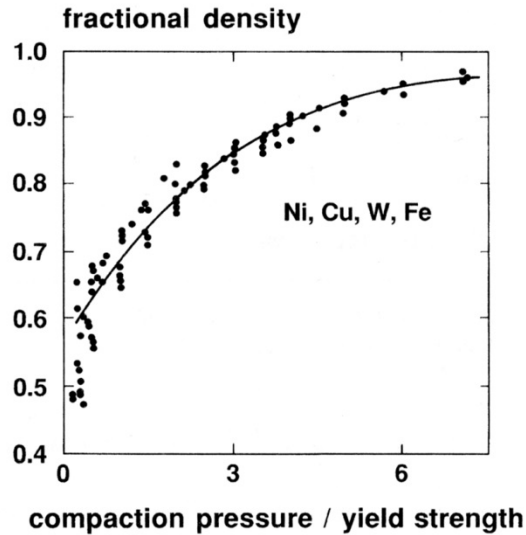
**Figure 4.** Effect of domain orientation on magnet properties of NdFeB. Source data from Magnequench catalogs. Per the catalog data,  $B_r$  of the isotropic alloy, MQP-B3 is 67% of the anisotropic MQA-37-11; energy product of MQP-B3 is 41% of the anisotropic material.

## THE CONSOLIDATION CHALLENGE

According to extensive studies, when compacted, cold powders approach a maximum practically attainable density that is considerably below theoretical – regardless of material.<sup>7-11, 13-14, 16-17</sup> Even superplastic alloys require the addition of modest heating to permit defect slip to achieve densification. This is a problem for permanent magnet powder raw materials which exhibit high hardness.



**Hot compaction** benefits from a lowering of the yield strength of the main alloy or additive constituents.

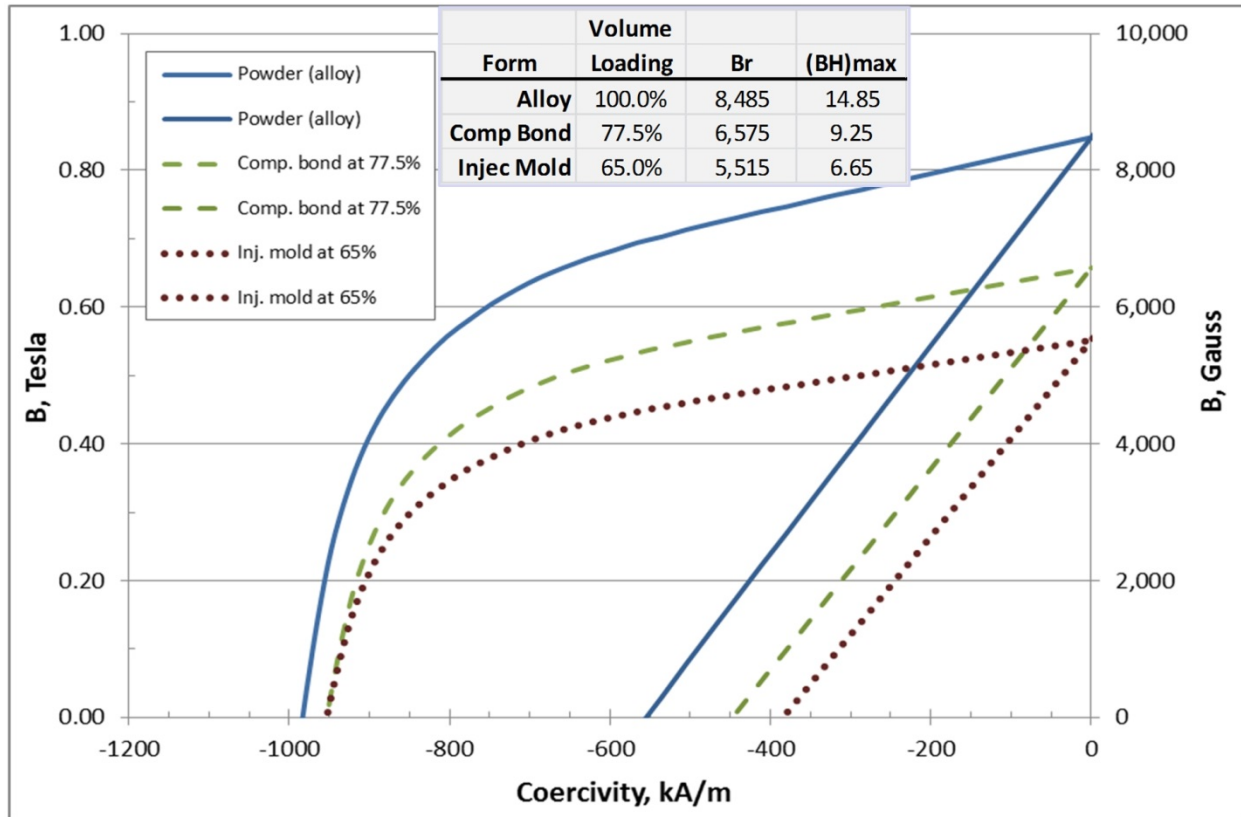


**Figure 5.** Limits to compaction of cold powders <sup>6</sup>

There are several reasons why a well-consolidated magnet is beneficial. Among these are:

- A Fully dense magnet presents a minimum surface to volume ratio minimizing corrosion.
- Full density means that 100% of the volume is magnetic material, thus maximizing magnetic field output (see Figure 6).
- Non-magnetic binders, typically a thermoplastic such as polyamide (PA) or polyphenylene sulfide (PPS) have maximum use temperatures that are often lower than the maximum use capability of the magnetic phase.

Non-magnetic diluents in bulk magnets include non-magnetic binders (plastic or metal) and trapped/encapsulated air. Figure 6 shows the dramatic reduction in residual induction ( $B_r$ , magnetic strength) as a result of a non-magnetic binder – epoxy for the compression bonded magnets and polyamide for the injection molded magnets. The reduction in maximum energy product is tabulated in the chart.



**Figure 6.** Magnetic properties as a function of volumetric loading: alloy, compression bonded, injection molded.

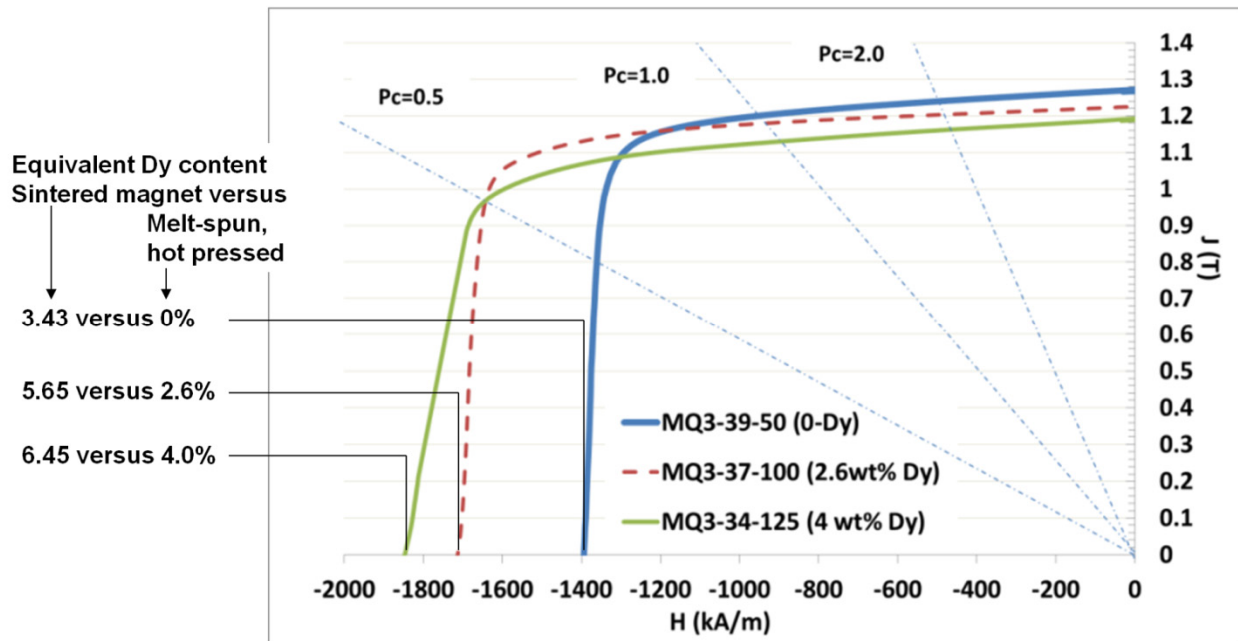
Attempts to achieve full consolidation can result in magnet degradation. One such problem is deterioration of intrinsic coercivity as a result of grain growth during liquid phase sintering. Higher temperature and longer time lead to increased growth. In addition to high temperature sintering, rare earth magnets require phase stabilization achieved by thermal treatment at temperatures just below the sintering temperature (*tempering* or *solution* treatment) and at a lower temperature called *annealing*.

Intrinsic coercivity of NdFeB is greater with reduced microstructure feature size – particle size for P/M processing and crystallite size in melt-spun alloy. NdFeB made via melt-spinning has inherently higher intrinsic coercivity than conventionally cast alloy. Figure 7 is an edited version of a graphic by Magnequench meant to show the improvement in coercivity of hot pressed and die upset magnets, made with melt-spun powder, over conventional liquid phase sintered product – at any specific dysprosium content up to the amounts tested.

Magnequench in the 1980s and 1990s developed processes for hot pressing melt-spun alloy powder, obtaining full density at lower temperature due to the application of uniaxial pressure during thermal treatment. A benefit of lower temperature and shorter times during consolidation is reduced grain growth which results in higher coercivity. This consolidation procedure is called hot pressing to produce a fully dense magnet. Application of higher pressure and temperature results in slightly greater grain growth but also a conversion of isotropic NdFeB into an aligned, anisotropic structure. This specialized hot press process is called die-upset. The creation of the alignment is called magnetic texturing and is achieved in this case, not by application of an external magnetic field, but by directional grain re-structuring which occurs to reduce the stress energy caused by the applied pressure. Liquid phase is present and the



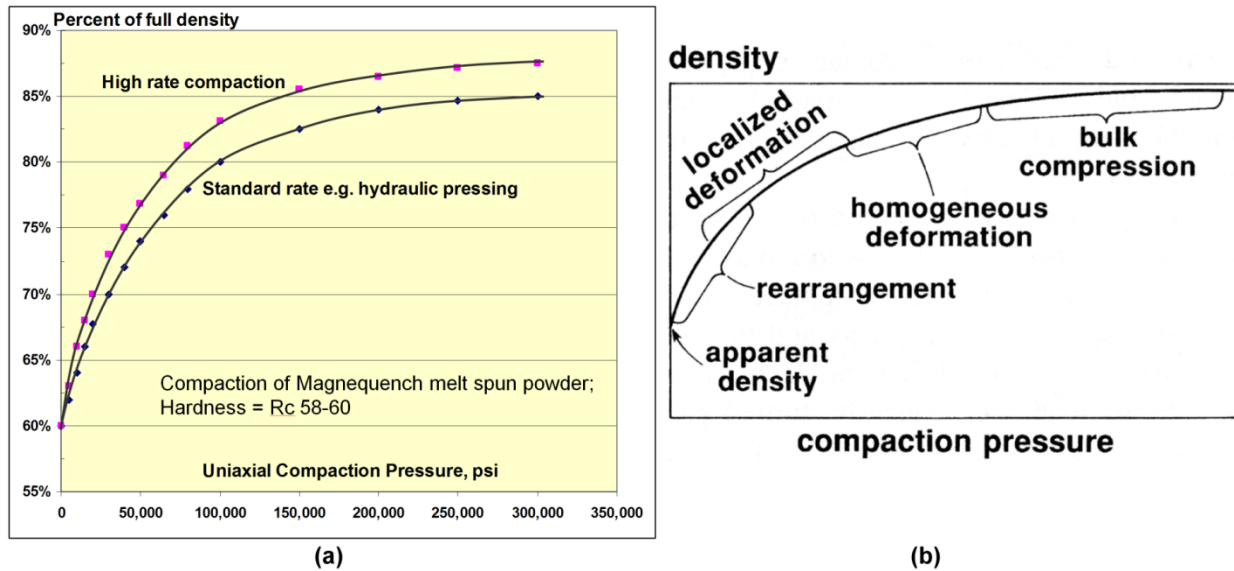
minimal grain growth is due to short exposure to elevated temperature (a few minutes) versus conventional sintered product (60 to 120 minutes).



**Figure 7.** Demagnetization curves of MQ3 magnets with various levels of dysprosium compared to conventional sintered product.

In the late 1980s another consolidation technique was developed called plasma assisted sintering (PAS). In the mid-1990s the name was changed to spark plasma sintering (SPS) and evaluation of this pressing method has extended from ceramics to high strength alloys to magnetic materials, most notably NdFeB. General agreement is that electrically generated plasma probably does not exist. Consolidation takes place by localized heating at contact points between particles with the formation of a minimal amount of liquid phase. Examination of nano-structured materials before and after sintering shows little coarsening. As with hot pressing, this is most likely due to the short time at elevated temperature. Major drawbacks of this process are difficulty in achieving domain alignment and shape/size limitations coupled with set-up time per consolidation run. Furthermore, evidence to-date suggests those materials requiring thermal solution and annealing require the treatments as a separate process subsequent to SPS consolidation, minimized process cost/benefit.

The degree of densification is affected by the rate at which pressure is applied (the rate compaction takes place). Higher compaction rates achieved by high velocity compaction (HVC), explosive compaction, shock consolidation, etc. result in density which is closer to theoretical. However, achievement of near theoretical density is the rare exception and has to-date not worked for permanent magnetic materials.



**Figure 8.** Rate of compaction effect on (a) Magnequench melt spun neodymium-iron-boron powder at 2-3 seconds (hydraulic pressing) and 0.1-0.2 seconds (mechanical impact pressing), no binder; (b) explanation of stages of compaction<sup>6</sup>. Magnequench powder is hard and relatively incompressible.

A continuum of consolidation methods exists between CIP and slow/cold uniaxial pressing and rapid, hot forging and HIP.<sup>7</sup> The following is a partial list with notes.

- Cold compaction (uniaxial and CIP)
  - With binder (bonded magnets)
  - Explosive compaction for slightly higher density
  - Followed by liquid phase sintering (sintered magnets)
- Cold rolling (roll compaction)
  - Very high localized pressure
  - Material must be at least minimally malleable
- Cold forging
  - Very high distributed pressure
  - Material must be at least minimally malleable
- Hot compaction
  - Hot uniaxial pressing; die upset; presence of liquid phase
  - HIP (hot isostatic pressing)
- SPS (spark plasma sintering)
- Friction stir processing
- Hot rolling
- Hot extrusion (or drawing)
- Hot forging

Each process has advantages and limitations regarding: 1) degree of densification, 2) speed of process, 3) integrity (strength) of product, 4) possible shapes and sizes, 5) tool and die wear, etc. Table 2 is an examination of some of the characteristics unique to each method with a rating scale as indicated. Ratings are likely to vary based on characteristics of the powder to be consolidated. The objective of consolidation of nano-particulate powders is rapid processing at as low a temperature as possible – the trade-off being application pressure and temperature.

**Table 2.** Consolidation Map – Methods for consolidating powders: advantages and processing style.

Consolidation Method	Pressure			Temperature		Densification	Grain Growth	Domain Orientation
	Rise Rate	Duration	Concentration	°C	Duration			
CIP	1	2	1	1	2	1	1	B
CIP + sinter	1	2	1	1	5	5	4	B
Cold compaction, uniaxial	2	2	1	1	2	1	1	A
Cold compaction + sinter	2	2	1	5	5	5	4	A
Cold Rolling	3	1	4	1	1	4	2	C
Cold forging	4	2	2	1	2	5	1	C
High Velocity Compaction	4	1	1	1	1	4	1	A
Explosive compaction	5	1	1	1	1	2	1	A
Friction stir welding	2	2	2	2	2	4	3	E
Warm/Hot pressing	2	2	1	4	3	5	3	E
Die upsetting	2	2	1	3	3	4	2	C, D
Hot forging	4	2	2	3	2	5	3	C
Hot rolling	3	1	4	3	2	4	3	C
SPS	1	3	1	4	2	5	2	A, D
HIP	1	5	1	5	5	5	5	B, E

Rating 1 = slow short distributed warm short low minimal  
5 = fast long concentrated hot long high severe

	CODE	Method	Examples
Method of establishing magnetic alignment	A	concurrent magnetic alignment	Traditional ferrite, NdFeB, and SmCo manufacture
	B	pre-alignment (magnetic)	CIP of large magnet forms
	C	work-stress related	Grain oriented silicon-iron; forged or extruded MnAlC; hot rolled NdFeB
	D	liquid phase mass transport	Magnequench die-upset process for NdFeB
	E	none expected, unknown	

## SUMMARY

Numerous methods have been utilized to form permanent magnets. Each method has been selected based on the material’s characteristics and end product requirements. For 150 years, up to the 1990s, material development has focused on the same set of 36 elements of the periodic table. Post 1990 research has shifted more to structure, especially at the nano-scale. Almost without exception, nano-particulates require consolidation to be functional and this has posed severe challenges with each method solving some issues (e.g. densification), but not others (e.g. excessive grain growth). The Consolidation Map provides insight for continuing innovation.

## REFERENCE

1. H. Mikami, “Technologies to Replace Rare Earth Elements”, World Manufacturing Forum, October 17, 2012
2. M. A. Willard, “Stronger, Lighter, and More Energy Efficient: Challenges of Magnetic Material Development for Vehicle Electrification”, *Frontiers of Engineering: Reports on Leading-Edge Engineering from the 2012 Symposium*, National Academies Press: Washington, DC (2013) pp. 57-63.
3. J.M.D. Coey, *Magnetism and Magnetic Materials* Cambridge University Press, 2009, p. 10
4. R. J. Parker, *Advances in Permanent Magnetism*, John Wiley & Sons, Inc., 1990, p. 56-58
5. R. J. Parker, *Advances in Permanent Magnetism*, John Wiley & Sons, Inc., 1990, pp.331-332

6. B.D. Cullity and C.D. Graham, *Introduction to Magnetic Materials*, John Wiley & Sons, Inc. and IEEE, 2009
7. D. Brown, W. Zhensheng, He Feng, D. Miller, J. Herchenroeder, "Dysprosium-free Melt-spun Permanent Magnets", MS&T – COM 2013, Montreal, Canada, October 2013
8. R. M. German, *Powder Metallurgy Science, 2nd ed.*, MPIF, 1994, p.207, p.225
9. S.H. Luk, F.Y. Chan and V. Kuzmich, "Higher Green Strength and Improved Density by Conventional Compaction", *Advances in Powder Metallurgy & Particulate Materials*, compiled by J.J. Oakes and J.H. Reinshagen, Metal Powder Industries Federation, Princeton, NJ, 1998, vol. 3, part 11, pp. 81–99.
10. Rutz, H.G., Hanejko, F.G., "High Density Processing of High Performance Ferrous Materials", *Advances in Powder Metallurgy & Particulate Materials*, Vol. 5, 1994, Metal Powder Industries Federation, Princeton, NJ, pp.117-133
11. S. Kalpakjian, S.R. Schmid, *Manufacturing, Engineering & Technology*, Fifth Edition, Pearson Education, Inc., 2006
12. R.B. Schwartz, P. Kasiraj, T. Vreeland Jr., T.J. Ahrens, "A Theory for the Shock Consolidation of Powders", *Acta metall.* Vol. 32, No. 8, pp. 1243-1252, 1984
13. R.B. Schwartz, P. Kasiraj, T. Vreeland Jr., T.J. Ahrens, "The Effect of Shock Duration on the Dynamic Consolidation of Powders", *Shock Waves in Condensed Matter*, 1983, Elsevier Science Publishers B.V., 1984
14. I. Donaldson, S. Luk, G. Pozmik, K.S. Narasimhan, "Processing of Hybrid Alloys to High Densities", *World Congress on Powder Metallurgy & Particulate Material*, 2002
15. B. Azhdar, "Improved High Velocity Cold Compaction Processing : polymer powder to high performancne parts", *KTH Chemical Science and Engineering*, 2005
16. N. Yavuz, "Mechanics of Dynamic Powder Compaction Process", *Journal of Engineering Sciences*, 1996, pp. 129-134
17. Roll Compacting of Metal Powders, *Metals Handbook*, Ninth Edition, Volume 7, Powder Metallurgy, pp. 401-409
18. H.N.G. Wadley, D.M. Elzey, "Application of Powder Densification Models to the Consolidation Processing of Composites" in *Composite Materials (ICCM VIII)*, eds. S.W. Tsai and G.S. Springer, SAMPE (Covina, CA) 18-B (1991).
19. H. Hofman, P. Bowen, "Powder Technology, Part II : Compaction", Downloaded April 25, 2014: <http://ltp.epfl.ch/files/content/sites/ltp/files/shared/Teaching/Master/06-PowderTechnology/Compaction.pdf>
20. U.S. Patent 3,017,665 : Rolling Mill
21. U.S. Patent 3,124,838 : Apparatus for Compacting Metal and Metal Coated Particles
22. U.S. Patent 3,478,136 : Process for Roll-Compacting of Metal Powder with Flange Lubrication