ENERGY CRITICAL MAGNETIC MATERIAL MANUFACTURING PROCESSES

Weimin Yin and Steve Constantinides
Arnold magnetic Technologies
Rochester, NY 14625

ABSTRACT

Soft and Permanent magnetic materials are essential components of many energy-critical applications. Among the uses are electric motors and generators, hybrid vehicle traction drives, transformers, sensors, and microwave beam guidance. Newer materials often require sophisticated and recently invented manufacturing processes to establish and maintain appropriate microstructure, to protect from contaminating reactants and to provide optimal product properties – both magnetic and physical. Traditional manufacturing management often overlooked lower production yield as of lesser importance. However, process yield loss incurs an energy use penalty and consumes larger quantities of increasingly sensitive raw materials. A survey of historic and current magnetic product manufacturing techniques will be presented along with trends in newer technologies.

INTRODUCTION

The global economic bubble burst in 2009. Leading up to it was a period of "irrational exuberance" caused by highly leveraged purchases of homes and consumer goods in general. Strong spending created strong demand for raw materials. Supply of some materials could not keep up with demand causing rapid increases in prices and spot shortages. Some of these materials were also key to energy production, transmission and use and the term Energy Critical Elements (ECEs) was coined most notably in a joint publication of APS and MRS.[1-2] Congressional recognition of elemental criticality resulted in H.R 1022, "Securing Energy Critical Elements and American Jobs Act of 2013". [3]

Energy critical elements also tend to be less common and more expensive.[4] Rare earth elements (REEs) are a majority subset of ECEs, garnering wide news coverage during the last three years due to tensions among China, Japan, the USA and Europe over adequate and uninterrupted supplies of them. One of the major uses for REEs is in the manufacture of permanent magnets: neodymium-iron-boron, samarium cobalt and samarium-iron-nitride. These are the strongest magnets known and required in numerous modern devices to provide small size, light weight and high performance. Attributes vs manufacturing methods of these magnet materials are shown in Table 1.

By one definition “a mineral can be regarded as critical only if it performs an essential function for which few or no satisfactory substitutes exist”. [5] The absence of adequate substitutes for rare earth magnets spawned a host of project activity around discovering new materials either to exceed rare earth magnet performance or to at least fill-in the price/performance gap between readily available ferrite magnets and high performance rare earth magnets.

In the USA, the Department of Energy has promulgated and encouraged research through at least two sub-organizations: EERE for electric vehicles and ARPA-E for energy production, transmission and use. All of the current projects are focused on materials which have exhibited instability at elevated temperature or on nano-structured materials with exchange-coupled phases which structure can be destroyed through grain growth due to processing at elevated temperatures. Methods to consolidate the powders while simultaneously aligning the magnetic domains for maximum output represent the greatest challenges. This review will present representative manufacturing process in permanent magnets industry and examine various options of consolidating novel magnetic materials.

MANUFACTURING PROCESSES

The manufacturing processes for permanent magnets can be split into three main segments: powder preparation, forming and consolidation, and secondary operations such as grinding and coating. A representative manufacturing process of traditional magnets is illustrated in Figure 1.[6]

The alloy power could be produced through mechanical fabrication techniques, including jaw crushing, jet milling and mechanical alloying. Chemical fabrication techniques have also been applied to manufacture magnetic material powder. One of the examples for chemical process is calciothermic reduction used for rare earth magnetic materials.[7] Descriptions of some of the powder preparation processes are presented in Table 2.

Table 1 Existing Permanent Magnet Products

Magnet Product	Manufacturing Method
Alnico	Cast to near net shape, finish grind
	Cast, pulverize, press to shape, sinter, finish grind
Ferrite (Ceramic)	Press & Sinter, finish grind
SmCo (rare earth magnets)	Press & Sinter, finish grind
SmFeN	Injection mold
NdFeB (“Neo”) magnets	Press & Sinter, finish grind
	Melt spin, hot press for isotropic fully dense
	Melt spin, hot press for anisotropic fully dense
	Melt spin, injection mold or compression form and cure
	HDDR to produce powder (alternative to melt spin) for bonded magnets
	Strip cast, pulverize for bonded magnets

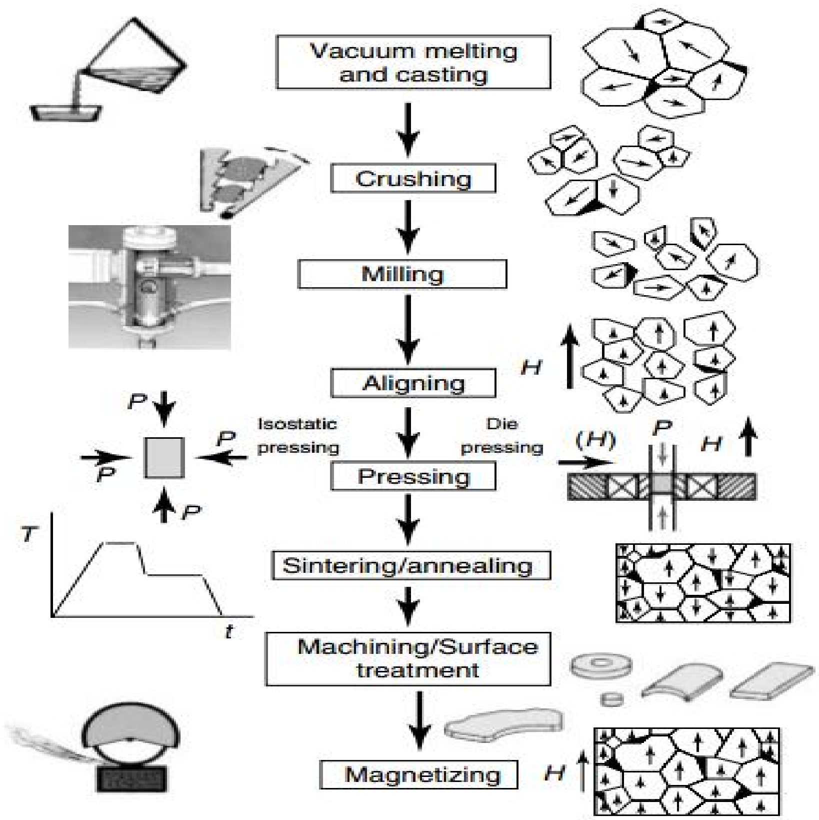

Figure 1 A typical process of manufacturing traditional energy critical permanent magnets.[6]

The prepared powder must then be pressed to form a "green" compact for further processing such as sintering or processed using a combination of pressure and heat to achieve consolidation. As shown in Fig 1, either cold isostatic pressing (CIP) or axial die pressing could be used to press a green compact. The alignment of powder particles is critical as the magnetic moment needs to align to certain orientation to achieve good magnetic properties. Hence each particle must consist of single crystal grain for best magnetic domain alignment. In general alloy powders with a particle size in the range of 1 to 7 microns meet this condition. [6-8] In the case of epoxy bonded magnets, the powder might be more coarse (5 to 150 microns) and a thermal cure completes the magnet processing.

After the powder has been compacted to maximum density and thermally processed, one or more finishing operations are likely. These include machining to finish dimensions via slicing, grinding, core drilling, diamond wheel or wire sawing. If the magnet is to be coated, edges must be rounded (honed) usually by vibratory tumbling. Finish coatings include conversion coatings, epoxy spray, electrophoretic e-coating, nickel plating, aluminum ion vapor deposition and others.

CONSOLIDATION OF TRADITIONAL MAGNETIC MATERIALS

Multiple methods for powder compacting have been used in manufacturing anisotropic permanent magnets and they most involve aligning the particles so that in the finished part all the magnetic domains are pointing in a prescribed direction. The first method is called uniaxial pressing in either axial (parallel) or transverse (perpendicular) coordination between aligning field and applied pressure. Powder is placed into a cavity in a tool on the press and punches enter the tool to compact the powder. Just prior to compaction, an aligning field is applied. The compaction "freezes-in" this alignment. In axial (parallel) pressing, the aligning field is parallel to the direction of compaction. In transverse (perpendicular) pressing, the field is perpendicular to the compaction pressure. Frequently the small powder particles are elongated in the direction of magnetic alignment and transverse pressing yields better alignment, thus higher energy product. Compacting powder in one of these hydraulic or mechanical presses limits the shape to simple cross-sections that can be pushed out of the die cavity.

A second compaction method is called isostatic pressing wherein a flexible container is filled with powder, the container is sealed, an aligning field is applied, and the container is placed into the isostatic press. Using a fluid, either hydraulic fluid or water, pressure is applied to the outside of the sealed container, compacting it equally on all sides. There are two main advantages to making magnet blocks via isostatic pressing: 1) very large blocks can be made – frequently up to 100 x 100 x 250 mm – and 2) since pressure is applied equally on all sides, the powder remains in good alignment producing the highest possible energy product. Typically the green compact is around 60-70% of theoretical density and hence the sintering process is necessary to achieve full density.

Table 2 Powder preparation process of permanent magnetic materials.

Powder Preparation	**Example Application**	**Comments**
Alloy cast and pulverization	Sintered Alnico	Cast alnico is made by casting to near net shape; sintered alnico is more useful for smaller magnets
Alloy atomization	Sintered, hot pressed Bonded Neo magnets	Atomized alloys such as neodymium-iron-boron
Melt spinning	Bonded and hot pressed Neo magnets	Similar to atomization, but alloy powder is cooled much more rapidly resulting in an isotropic, thin flake material (20-30μ)
HDDR (of rare earths)	Sintered Neo magnets	Used especially to reduce Neo cast alloy to fine particles for easier milling;
Mechanical Alloying	Nano-structured magnetic powders	Usefulness still being evaluated especially in alloys under development
Ceramic raw materials calcining	Ferrite (ceramic) magnets	Calcined particles are milled to ~1 micron diameter for pressing and sintering
Powder grinding and milling	Required to reduce each particle in size until it consists of one magnetic domain orientation	Particles are aligned during compaction to provide maximum magnetic output
Chemical production of nano-particulates	Attempts to form nano-structured powders (nano-particulates) for enhanced magnetic properties, especially through exchange coupling	Nano-particulates have been formed of several alloys, but additional development is required to achieve stable high performance
Mechanical Alloying	Common method to mill alloy to fine powder simultaneously creating alloy with nano-structure	Has been used with many materials but is energy intensive and less efficient than some competitive processing methods such as jet milling versus melt spinning

For rare earth materials, the green compact is heated to a sintering temperature above the solidus, and sintering proceeds in the presence of a liquid phase. This is called "liquid phase sintering". [9] For rare earth magnets, the sinter step has to be carried out in a vacuum or an inert gas atmosphere to prevent oxidation. Liquid-phase sintering is generally regarded as proceeding in a sequence of overlapping dominant stages: (1) rearrangement of the solid phase driven by capillary stress gradients, (2) densification and grain shape accommodation of the solid phase involving solution-precipitation, and (3) final stage densification driven by residual porosity in the liquid phase in which Ostwald ripening dominates the microstructural evolution. Besides the sintering process to achieve full density, post-sintering heat treatment has been used to develop proper intermetallic phases and optimal permanent magnet properties. The magnets shrink about 15-20% linearly in the thermal process and usually exhibit a rough surface and only approximate dimensions right after heat treatment, requiring a finish grind to final dimensions.

Table 3 Consolidation process and its applications in permanent magnetic materials

Forming and Consolidation	**Example Application**	**Comments**
Press & Sinter	Sintered Neo, SmCo or ferrite	Powder is compacted to a preform with adequate strength for handling and transporting to the furnace for sintering. Compaction is either uniaxial or isostatic (CIP). Powder is almost universally aligned so magnetic domains are co-parallel.
HIP	Seldom if ever used for commercial magnets	Powder must be sealed within a "canister". After HIPing, the can must be removed. Process is long and inefficient.
Forging (cold and hot)	Currently being evaluated for magnet manufacture	Many magnet materials are extremely hard (Rc 57-61) with minimal elongation resulting in fracture of particles. Hot forging is more likely to succeed than cold. Soft alloys may be cold forged with success.
Roll forging	Currently being evaluated for magnet manufacture	May prevent grain growth of nano-structured materials while permitting consolidation
Rolling (Hot and Cold)	Nano-structured magnetic powders	Commonly used for semi-hard, malleable materials such as FeCrCo and Vicalloy. Was used for a time by Seiko-Epson to form Neo magnets in thin sheet form for stamping into magnets for watch motors. Copper sometimes added to increase malleability.
Friction Stir Processing	Currently being evaluated for magnet manufacture	May prevent grain growth of nano-structured materials while permitting consolidation
MIM and CIM	In common use for powdered metal parts; not yet used for magnets	Has the capability of producing complex part shapes and sintering to near net shape reducing machine costs and material waste.
Hot Extrusion	Has been performed in labs and in production such as of MQ-2 and MQ-3 products from Magnequench and Daido.	MQ-2 parts are fully dense but magnetically isotropic. MQ-3 is formed by pressing hotter and at higher pressures. The resulting magnets exhibit domain alignment.

CONSOLIDATION OF NOVEL MAGNETIC MATERIALS

Great efforts have been made to develop rare-earth free permanent magnetic materials, such as MnAlC tetrataenite FeNi, Iron nitrides and Cobalt carbides.[10] While these materials look very promising, consolidation of the powders present a significant challenge.

The traditional consolidation processes, which work well for current rare earth magnetic materials, don't work for the novel materials. The typical cold consolidation such as uniaxial compaction reaches a limiting density well below theoretical. Liquid phase sintering process results in inevitable grain growth and hence changes the characteristics from those associated with nanostructure. Therefore, development of a densification process for this class of materials is vital to the success of production of novel and sustainable permanent magnetic materials.

The challenge to these magnetic materials is to consolidate to full density while retaining the appropriate nanostructure and achieving co-parallel domain alignment. Since most compaction ceases prior to achieving full density, a second term is introduced: consolidation. A set of options is shown in Table 3. Powder can be consolidated by a variety of techniques, including cold-pressing followed by high temperature sintering, cold and hot extrusion and hot isostatic pressing.[11-13] The essence of these consolidation techniques is to apply high pressure and high temperature to achieve full density. Less common consolidation techniques are spark plasma sintering or microwave and laser assisted sintering, which involves respectively the use of pulsed electric current, microwave and laser irradiation to fully densify the powder consolidation. These techniques are carried out at relatively lower temperatures and for a shorter time than in the conventional sintering process. Therefore, they show potential to achieve fast and full densification of nanostructured materials while minimizing grain growth.

The characteristics of each consolidation process have been summarized in Table 4. Due to space and time constraints only the following methods will be described and compared: conventional room temperature uniaxial compaction, hot pressing, roll forging, friction stir processing and explosive compaction.

Table 4 Characteristics of different consolidation processes

Method of Consolidation	**Temperature**	**Rate of pressure application**	**Maximum Pressure**
Uniaxial pressing, hydraulic	Low	Slow	Mod. To High
Uniaxial pressing, mechanical	Low	Moderate	Mod. To High
Uniaxial pressing, explosive compaction	Low	High	High
Magnetic Dynamic Compaction	Low	Very High	Very High
Cold rolling	Low	Moderate	High
CIP	Low	Slow	Moderate
Hot pressing	Warm to Hot	Slow	Low to Mod.
HIP	Hot	Slow	Mod. To High
Friction stir processing	Low to warm	Moderate	High
Roll forging	Low	Moderate	High
Cold extrusion	Low	High	High
Hot extrusion	Hot	High	Mod. To High
Hot rolling	Hot	Moderate	Moderate

Uniaxial compaction is routinely performed using hydraulic, mechanical or hybrid presses. Normal compaction pressures range from 200 to 400 MPa (30-60 ksi). Pressures up to 1900 MPa (280 ksi) have been used to compact products such as soft magnetic powder cores. Press pressure is generally a compromise between maximum compacted density and excessive tool wear observed from application of high pressure. All the common permanent magnet powders are both very hard and very abrasive.

Hot pressing is a manifestation of stress-enhanced densification, which is performed in rigid dies using uniaxial pressure (Figure 2). [11] Graphite dies have been widely used due to their stability at high temperature. They allow induction heating and are not expected to create a contamination issue for materials such as MnAlC and cobalt carbides. Other die materials include refractory metals such as molybdenum alloys and ceramics such as alumina or silicon carbides.

During hot pressing, an axial load is applied and the initial densification is achieved through particle contacts. As the effective stress falls below yield strength, further densification depends on grain boundary and volume diffusion rates and hence the consolidation temperature is a critical factor. However grain growth of nanocrystalline materials occurs at a relative moderate temperature and hence the window of pressing temperature is in a narrow range. In the meantime, consolidation takes a significant period of time which further makes it difficult to achieve full density without significant grain growth. Vacuum or inert gas environment is often selected to prevent reaction of nanostructured powder and minimize contamination of the compact as well as to prevent deterioration of the tooling.

Powder forging, shown in Figure 2(a) can provide large deformation at low temperature, which is desirable to consolidate nanostructured powders without causing grain growth. Among different forging techniques, roll forging might be the most promising process to fully consolidate a preform of novel magnetic materials. As shown in Figure 2(b), it is a process for reducing the cross-sectional area of bars or billets by passing them between two driven rolls that rotate in opposite directions and have one or more matching groves in each roll. Roll dies designed for forging the required shape are bolted to the roll shafts, which rotate in opposite directions during operation. Roll dies usually occupy about one-half the total circumference; therefore, at least some forging action takes place during half of the revolution.

Friction stir processing is an emerging technique based on the principles of friction stir welding. It is displayed in Figure 2 (c). The basic concept of friction stir processing is remarkably simple. A rotating tool with pin and shoulder is inserted in the material and traversed along the line of interest. The heating is localized and generated by friction between the tool and the work piece, with additional adiabatic heating from metal deformation. A processed zone is produced by movement of material from the front of the pin to the back of the pin. Friction stir processing has been successfully applied in eliminating inhomogeneous microstructure in powdered aluminum alloys. With its severe plastic deformation and minimum amount of heat generated, it is being explored as a valid approach to consolidate the emerging nanostructured magnetic materials.

Explosive compaction (Figure 2(d)) delivers a high strain rate that can be used to consolidate powders.[11, 14] This rapid consolidation technique can provide good particle bonding, especially if the shock wave produces short term melting at the particle contacts. Even though the heating can form a thin liquid layer, the time at temperature is very short. Consequently, nanostructured powders could be densified and exhibit high self-quenching rate, leading to preservation of the nanostructure. This technique has been successfully applied to consolidation of ceramics and intermetallics, which are hard and brittle, similar to nanostructured magnetic material. For Si_3N_4 and SiC, densification to 96% of theoretical density is possible using high peak pressure and heated powders. The densification event occurs in approximately 4 μs. The density of the consolidated material increases with the shock wave energy per unit of compact mass.

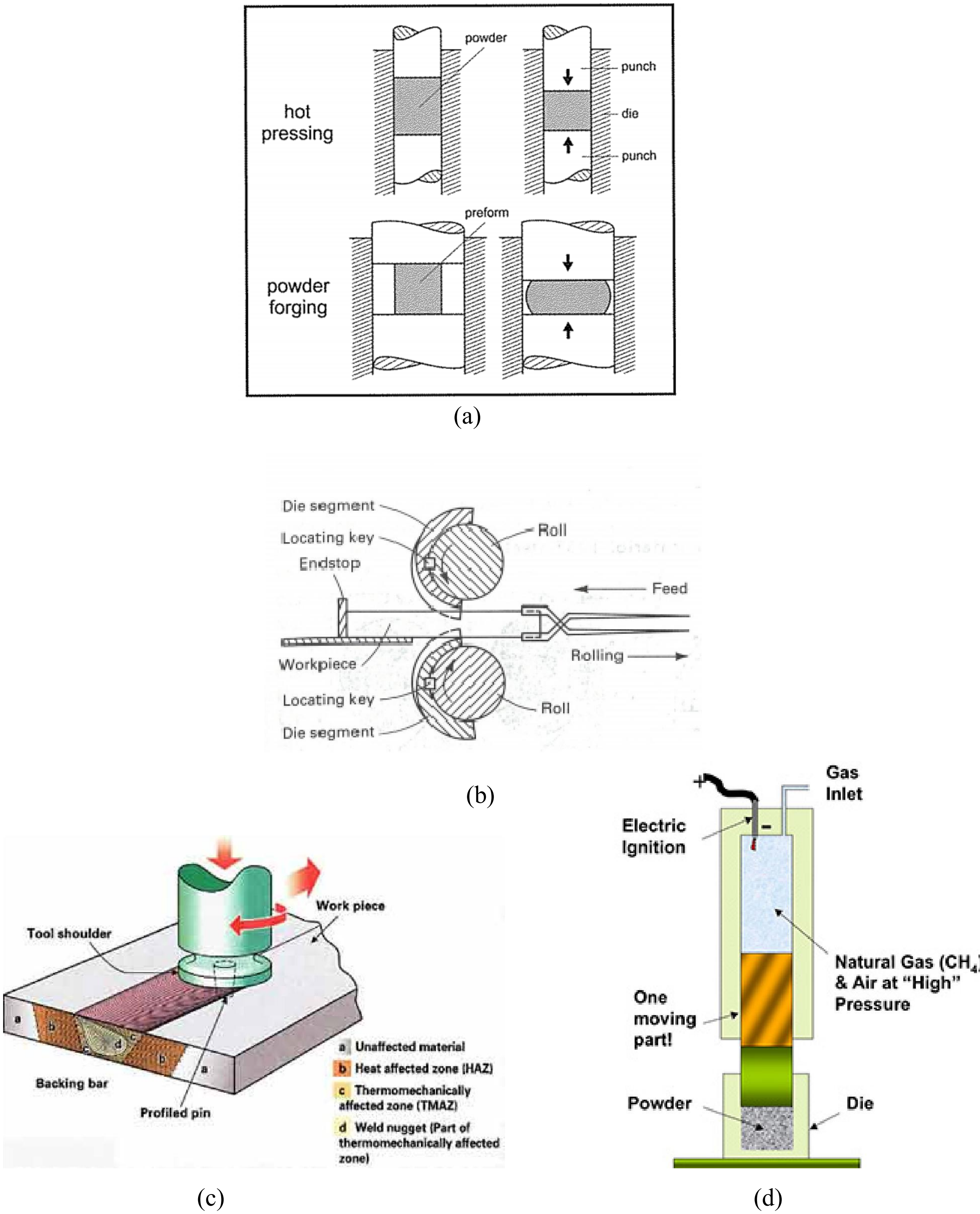

Figure 2 Examples of consolidation techniques: (a) hot pressing and hot forging (b) roll forging (c) friction stir processing (d) explosive compaction.[11, 14-16]

The techniques for eliminating porosity by various consolidation processes exhibit an interplay between time, temperature and pressure. While both pressing temperature and pressure are critical to achieving full density, the time at elevated temperature has to be short enough to avoid grain coarsening. Pressure application rate (PAR) is introduced to define how fast to reach the full pressure. High pressure application rate at modest pressing temperature may prove desirable for consolidation of nanostructured materials. With that in mind, a consolidation process map has been created to evaluate the various consolidation methods, as shown in Figure 3. The consolidation processes can be divided into three groups: (1) low consolidation temperature, slow pressure application rate and modest pressure; (2) high consolidation temperature, slow pressure application rate and modest pressure and (3) modest consolidation temperature, fast pressure application rate and high pressure.

Most powders can be fully consolidated by a combination of thermal softening and external stress. Without thermal softening, it may be impossible to fully consolidate nanostructured materials using either of CIP, uniaxial mechanical and cold extrusion pressing alone (Group 1). On the other hand, thermal mechanical processing at high temperature (Group 2) is capable to achieve full density, yet grain growth seems to be certain due to the extended period of time at elevated temperature. Considering both densification and grain coarsening, explosive compaction and friction stir processing (Group 3) stand out as having the best potential for successful consolidation. The evaluation of consolidation processes on densification and microstructure stability leads to an overall estimation on different processes, shown in Figure 4. Despite the complication of densification and microstructure stability, this evaluation could provide a road map to develop thermal mechanical process to fabricate the novel magnetic materials. The degree of densification and grain growth can be better predicted with further investigation on diffusion, creep and plasticity behavior of the novel magnetic materials.

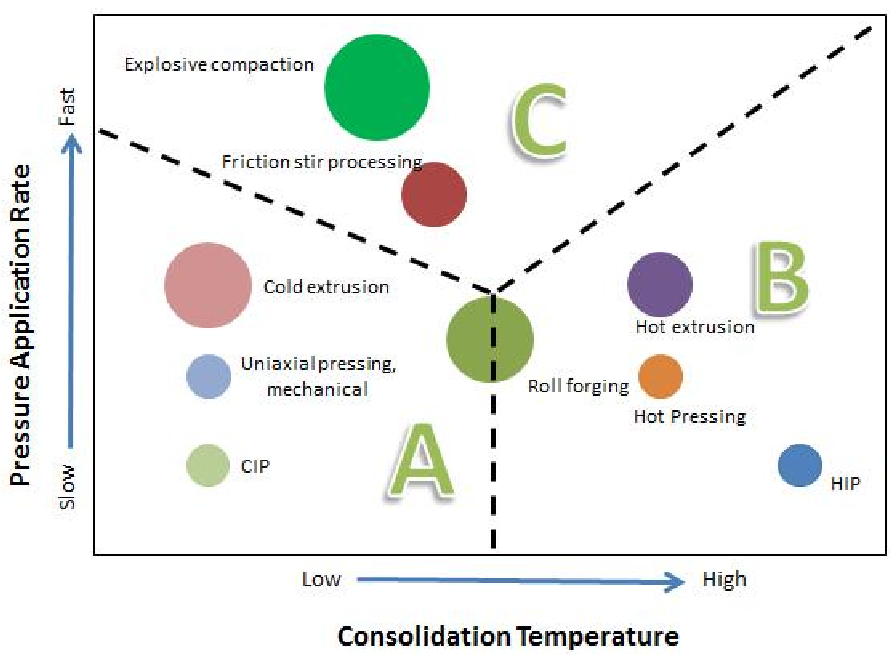

Figure 3 Consolidation process map: Bubble size represents magnitude of consolidation pressure; all data points are shown for illustration. A: insufficient for consolidation; B: microstructure unstable; C: potential for full density and stable microstructure.

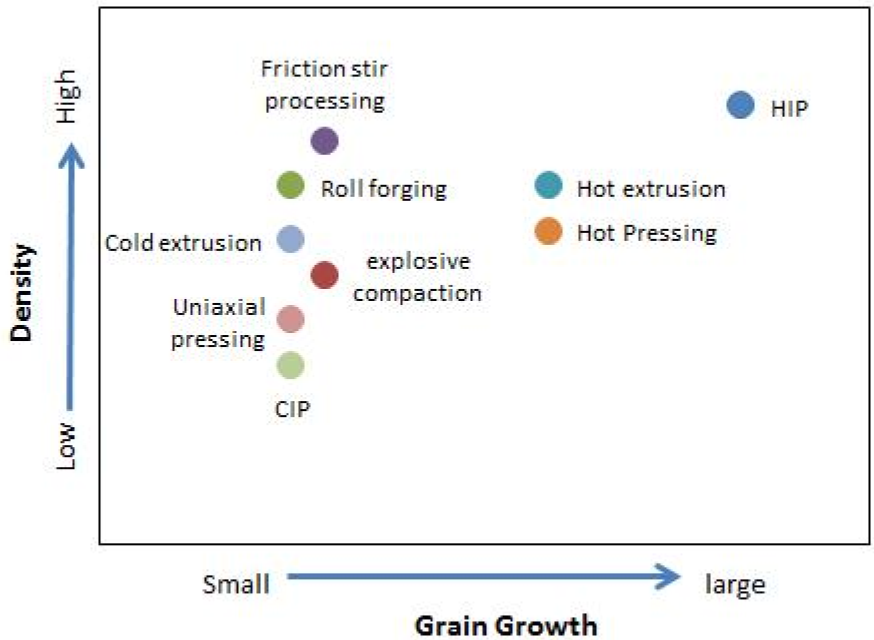

Figure 4 Evaluation of consolidation options regarding the impacts of consolidation processes on densification and grain structure stability of nanostructured materials.

SUMMARY

Permanent magnets have become increasingly important to energy-related applications with examples being wind turbines and electric vehicle traction drive motors. To provide sustainable growth, development of a new class of robust high-energy product magnets will remain an important pursuit in scientific research and the magnetic manufacturing industry. Novel techniques including physical metallurgy, sputtering and wet chemistry are being studied to produce ultra-fine or nanostructured exchanged-coupled magnetic materials. In the meantime, evaluating existing methods and exploring new approaches to consolidate the new class of magnetic powders is a priority of this development.

Regardless of the processing route used, the key to successful consolidation of nanocrystalline materials is to achieve full densification with minimal grain growth and/or undesirable microstructural transformations. Consolidation of nanostructured phases is extremely difficult. Therefore, either enormous pressures have to be applied or heat must be employed to soften the material so that plastic deformation can occur. Material flow by diffusion helps to remove porosity. However the diffusional process does not only assist particle bonding and densification, but also causes grain coarsening to occur. Therefore, successful processing of nano-particulate and nano-structured powders will require a combination of moderate temperature, high pressure and fast pressure application rate.

ACKNOWLEDGEMENTS

This work has been supported in part by the U.S. Department of Energy's Advanced Research Project Agency – Energy (ARPA-E) under Grants DE-AR0000186 and DE-AR0000192.

REFERENCES

1. Energy Critical Elements: Securing Materials for Emerging Technologies, Report by the APS Panel on Public Affairs & the Materials Research Society, February 18, 2011, www.aps.org/about/pressreleases/elementsreport.cfm
2. Critical Materials Strategy, U.S. Department of Energy, December 2011, p.115
3. www.govtrack.us/congress/bills/113/hr1022/text
4. Strategic & Critical Minerals – A Global Perspective, Jonathan Price, Nevada Bureau of Mines and Geology, September 30, 2011, http://dnr.alaska.gov/commis/priorities/Slides/JonanthanPrice.pdf
5. Strategic and Critical Metals in Alaska: a mining industry perspective, Curt Freeman, Avalon Development Corp., 2012 Strategic and Critical Minerals Summit, University of Alaska – Fairbanks, November 30, 2012
6. W. Rodewald, "Rare-earth transition-metal magnets", *Handbook of Magnetism and advanced magnetic materials*, edited by H. Kronmuller and S. Parkin, John Wiley & Sons, Ltd. 2007, vol 4: Novel Materials.
7. K.J. Strnat, "Rare earth – Cobalt permanent magnets", *Ferromanetic Materials*, vol. 4 edited by E.P. Wohlfarth and K.H.J. Buschow, Elsevier Science Publishers B.V. 1988.
8. H.R. Kirchmayr, "Permanent magnets and hard magnetic materials", *J. Phy. D: Appl. Phys*, 1996, vol. 29, pp. 2763-2778.
9. S.J. Kang, "Liquid phase sintering", *Sintering of advanced materials: fundamentals and process*, edited by Z.Z. Fang, Woodhead Publishing, 2010. Cambridge, UK.
10. L. H. Lewis and F. J.imenez-Villacorta, "Perspectives on permanent magnetic materials for energy conversion and power generation", *Metall. and mater. Trans. A,* 2013 vol.44, no.1 supplement, pp. 2-20.
11. R.M. German, *Powder metallurgy and particulate materials processing*, 2005, Metal Powder Industries Federation, Princeton, NJ.
12. S.H. Whang, *Nanostructured metals and alloys*, 2011, Woodhead Publishing, Cambridge, UK
13. C.C. Koch, Nanostructured materials: processing, properties and potential applications, 2002, William Andrew Publishing, Norwich, NY.
14. J. Herchenroeder, D. Miller, N.K. Sheth, M.C. Fooand K. Nagarathnam, "High performance bonded neo magnets using high density compaction" *J. App. Phys*., 2011, vol. 109(7A), pp.743.
15. Metals Handbook Ninth Edition, vol. 14 Forming and Forging, ASM International, 1988 Metal Park, Ohio.
16. W M Thomas, S W Kallee, D G Staines and P J Oakley, "Friction Stir Welding - Process variants and developments in the automotive industry", 2006 *SAE World Congress*, 3-7 April 2006, Detroit, Michigan, USA.