

Extending the limits of the Sm₂Co₁₇ system

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Summary

The theoretical limit of energy product for the Sm₂Co₁₇ system has been previously calculated at 34 MGOe (270 kJ/m³). Arnold Magnetic Technologies has been delivering material near this limit for the last three years and with the recent introduction of RECOMA[®] 35E is right at that limit. In order for further improvements both composition and process challenges must be overcome to produce a coherent system that can deliver remanences in excess of 1.2T while still delivering intrinsic coercivity high enough to be of commercial interest versus existing products such as RECOMA 33E. Developing alloys with greater magnetic remanence creates increasingly narrow process windows, and requires stringent control throughout manufacturing.

Introduction

Perhaps the first modern permanent magnet material was Alnico. Invented in 1931 as an alloy of aluminum, nickel and iron, it evolved through extensive research over a period of 40 years into a family of materials ranging from Alnico 1 with energy product of less than 1.5 MGOe (12 kJ/m³) to Alnico 9 with energy product as high as 11.5 MGOe (92 kJ/m³). The improved energy products were primarily the result of increased coercivity due to the introduction of directional grain growth (shape anisotropy) and addition of increasing amounts of cobalt and titanium.

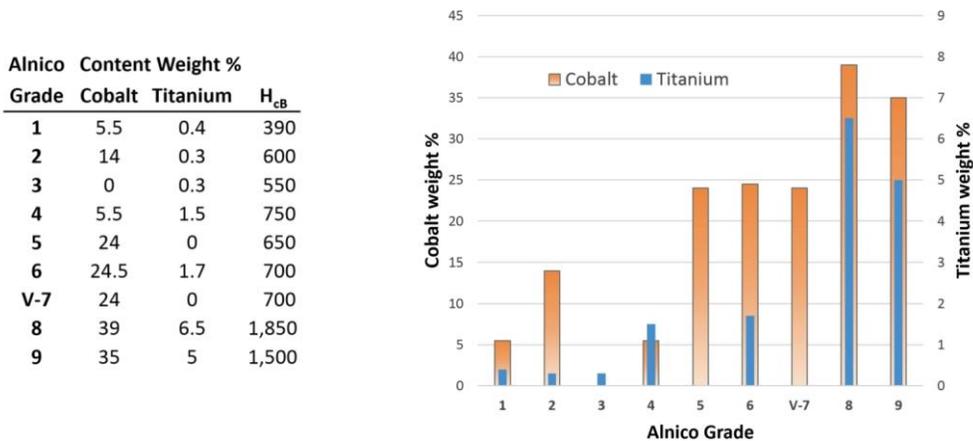


Figure 1. Changes in Alnico composition resulted in improved coercivity and energy product, up to 11.5 MGOe (92 kJ/m³) for Alnico 9.

When hard ferrite (ceramic) magnets were commercialized in the mid-1950s, research on Alnico did not stop. When SmCo_5 was invented in 1965, research on Alnico did not stop. However, research efforts eventually diminished ~1975 as new approaches to making better Alnico were exhausted and when SmCo 2:17 was introduced commercially.

The second major permanent magnet invention of the 20th century was hard ferrite. Development of ferrite magnets occurred rapidly. The material costs were so low and the resistance to demagnetization adequately high that no significant improvement in performance was considered imperative and no improvements were made, until after 45 years of production, with the introduction of LaCo-ferrite grades shortly after year 2000. Since then three series of improved LaCo-ferrite have been introduced, pushing the energy product to 5.5 MGOe (44 kJ/m³) and the intrinsic coercivity to 5500 Oe (438 kA/m). It appears that ferrite may now be reaching the limits of its potential.

After ferrite came SmCo. SmCo_5 was the natural continuation of research conducted globally combining rare earth elements (REEs) especially yttrium with transition metals (TM), especially cobalt. Any one of numerous researchers might have claimed the invention of SmCo_5 , though credit is generally given to Karl Strnat. Strnat, working with Al Ray and Herb Mildrum at the University of Dayton continued the development, seeking to reduce or eliminate the need for cobalt. By 1975 $\text{Sm}_2\text{Co}_{17}$ had been developed with higher energy product and a high anisotropy field (H_A).

$\text{Sm}_2\text{Co}_{17}$ benefited from a modest reduction of cobalt from 65 to ~50 weight percent with substitution by iron which increased residual induction (B_r) providing higher energy product. To achieve adequate coercivity required the addition of copper and zirconium, each serving to modify the structure to provide domain pinning, copper in the grain boundary phase and zirconium through the development of the lamella structure. Both Cu and Zr reduce the magnetization, so optimized compositions are necessary. Thermal processing is also more difficult than for SmCo_5 and it took several years for the material to become widely produced and utilized.

In 1978, the price of cobalt increased 6.5x in a matter of months resulting in dramatic price increases for SmCo magnet products and initiating a search for rare earth magnets based on iron, a widely available and inexpensive element. Numerous laboratories were combining REEs with Fe, but resulting materials exhibited low coercivity until, by accident, Norman Koon and Badry Das, working at the US Naval Research Laboratory (NRL) added a modest amount of boron in an attempt to make rapidly quenched RE-Fe amorphous. The resulting material, produced in early 1980, exhibited both moderate B_r and H_{cJ} and resulted in US patents being issued to the US Navy: for the composition and the hard magnetic powder (RE-Fe-B, US 4402770 and Re.34322) and for the production process for making the alloy (melt-spinning and subsequent anneal, US 4533408 and Re.34322).

However, the US Navy does not commercialize inventions and it remained for both M. Sagawa at Sumitomo and J. Croat at General Motors to optimize composition and provide practical manufacturing processes for sintered magnets (Sagawa) and powder for bonded magnets (Croat). Credit for first commercial sintered magnet product went

to Crucible Magnetism (November 1984). The first major application for NdFeB was in hard disk drives (HDDs), a market that was rapidly growing concurrent with the introduction of NdFeB. By 1990, it was reputed that 75% of NdFeB was going into the voice coil motors (compression bonded magnets) and the spindle drive motors of HDDs (sintered magnets).

The invention and rapid commercialization of NdFeB had a chilling effect on research for improved SmCo. Indeed, a survey of professional society publications shows almost no reference to SmCo from the period 1984 through the late 1990s while research into NdFeB was extensive and continues to the present. However, starting in 1998 there has been a renewed interest in exploring the performance limits of SmCo compositions especially in light of the temperature-performance limitations of NdFeB magnets (Figure 2). Indeed, about half of the references to this paper are from the period 1998 to 2015.

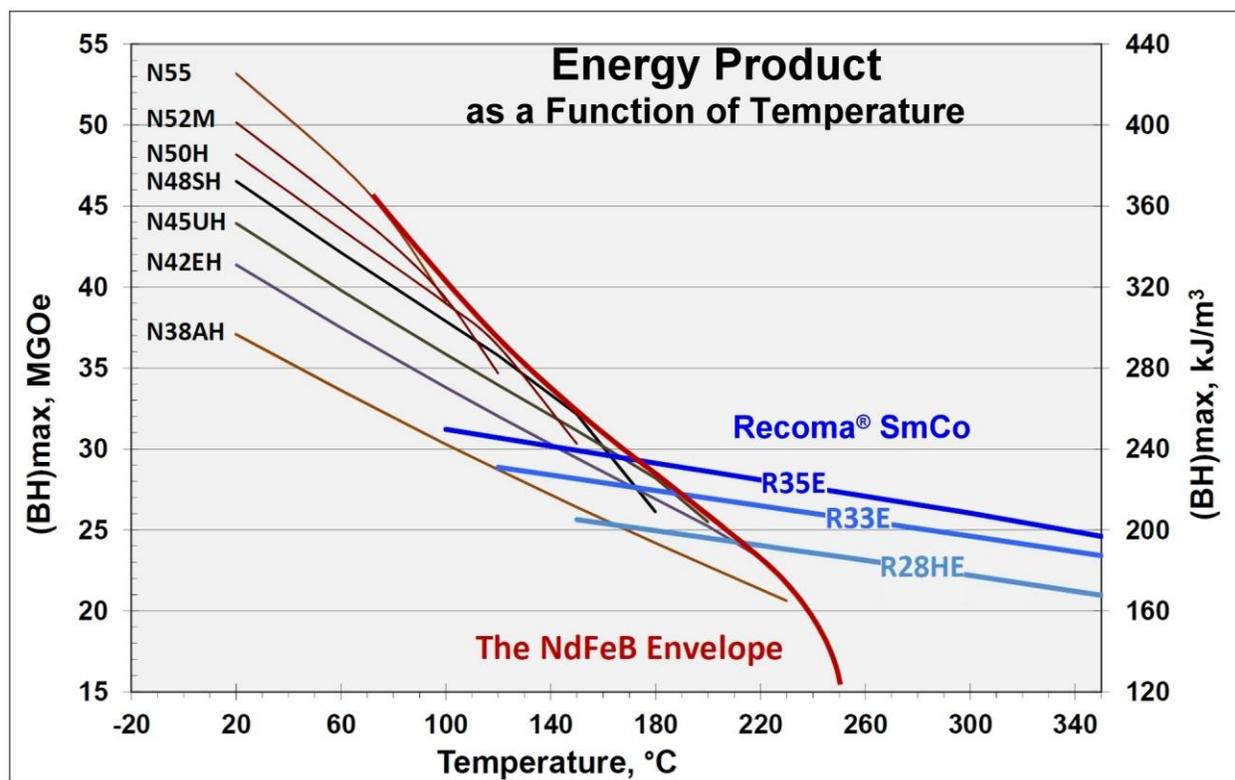


Figure 2. NdFeB magnets, regardless of composition, reach a temperature where irreversible loss will occur. Each grade reaches that point at a different coercivity and energy product. Plotting several grades creates an “envelope” above which SmCo magnets are superior performers. Three Recoma[®] grades are plotted for comparison.

With turmoil in the rare earth industry, there has also been interest in improved non-rare earth magnets, for example Alnico and the LaCo-ferrite magnets. Research in existing materials has benefitted from a lack of progress in development of new magnet compositions. None of these comments is meant to detract from the efforts of researchers or laboratories who have steadfastly sought improved magnetic performance. And some success has been achieved by nitride magnets, especially SmFeN. More recently, Fe₁₆N₄, which has been in the lexicon of magneticians for

several decades, has been improved in performance to levels approaching that of Alnico.

Arnold Magnetic Technologies manufactures SmCo magnets and has for several decades. It is only natural that we should make efforts to improve upon its performance, especially now with a lack of a significant new magnet material and recognition of the limitations of competing magnetic products.

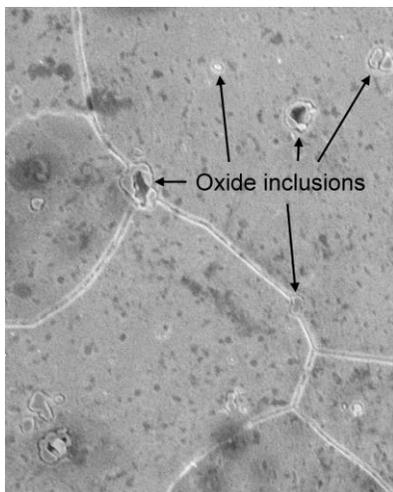
Making better SmCo

Several issues are recognized as important to the quality of magnets in general and SmCo specifically. Some are obvious; some less so. They are listed below and each will be discussed and include a list of references.

- Contamination: e.g., oxygen and carbon
- Alignment: particle alignment during compaction
- Elemental substitution: Fe, Ni or Mn for Co; Pr, Nd, Y for Sm, Ti for Zr
- Starting alloy condition: solidified grain structure; homogeneity
- Thermal process: solution treatment; quench rates
- Microstructure development

CONTAMINATION

It is difficult to totally eliminate some contaminants and unless they contribute to the field strength or pinning of the domains, they are likely to be at least a diluent and at worst bind with Co, Fe, or Sm reducing the magnetic field-generating alloy. Oxygen and carbon are the most pernicious contaminants. One weight percent oxygen binds with 6.2 weight percent samarium. Sm_2O_3 is distributed throughout the grain structure though some concentration at grain boundaries and triple junctions is evidenced (Figure 3). To compensate for the samarium bound with oxygen requires very careful control of oxygen in the raw materials and pick-up during processing and a base-adder trial is typically conducted to establish the exact amount of excess samarium in the formulation to balance the oxygen in the system.



of alignment. Figure 2 from reference 6. **Figure 3.**
Microstructure showing location of

Carbon is also a potential problem. Small amounts of excess carbon reduce sintering temperature and improve demagnetization hysteresis loop shape. However, controlling the exact amount present in the alloy system is challenging. Further, carbon binds preferentially with zirconium to form ZrC , arguably requiring a compensatory addition of Zr. The binding ratio is 7.6 weight percent zirconium per weight percent carbon. Carbon is present in small percentages in the raw materials, but

additional amounts can be added via organic processing lubricants during milling or pressing and from organic vapors in the vacuum sintering process through atmospheric contamination.

Contamination references: 8, 9, 26, 39, 40.

ALIGNMENT

Maximum Br requires that all grains are aligned in one direction. This is achieved during manufacture by reduction of the alloy to a particle size wherein each particle contains only one crystal. In $\text{Sm}_2\text{Co}_{17}$, this (maximum allowable) particle size is approximately 4-5 microns FSSS (7-10 microns laser particle size analysis). Smaller particles improve the “perfection” of this crystal structure (one crystal per particle) but increase the oxygen pickup during processing and can make alignment more difficult. Larger particles can be used but increasingly risk multiple crystal orientations.

Prior to and during compaction of the alloy particles, domain orientation is impressed via an external magnetic field. Orienting torque is applied due to the reaction of the magnetized particle’s field with the applied orienting field. In order for this field interaction to occur the applied field must be adequately strong to achieve magnetization of the particles. Compaction creates misalignment forces on the particles. The three methods of compaction are:

- Axial (parallel)
- Transverse (perpendicular)
- Isostatic

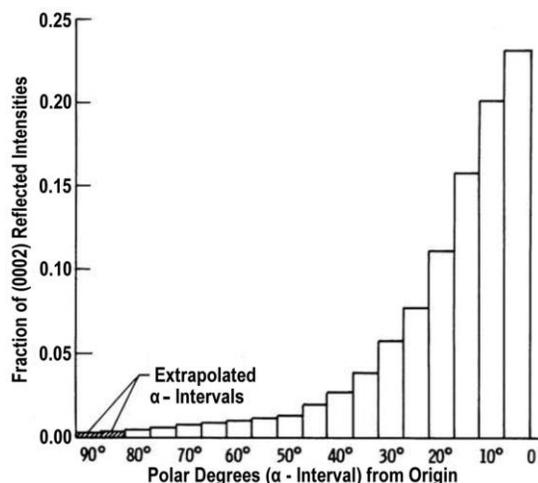


Figure 4. Result of the x-ray determination

Isostatic pressing compacts the powder with minimum misalignment of the grains. Transverse pressing is almost as effective. Axial/parallel pressing results in the most misalignment during compaction. It is remarkable that the magnetic alignment remains essentially unchanged or even slightly improved during volume contraction of 25% during liquid phase sintering.

How does one measure degree of perfection of domain alignment? The preferred method is the Schulz XRD crystallographic determination with an example of tabulated results shown in Figure 4.

Grain alignment references: 6, 14, 15, 39, 44, 47, 60, 81, 99, 109, and 110

ELEMENTAL SUBSTITUTION

Optimal magnetic properties of SmCo 2:17 have been achieved using a quinary alloy represented by the formula $\text{Sm}(\text{Co}_a \text{Fe}_b \text{Cu}_c \text{Zr}_d)_z$ where “z” is somewhat less than 8.5 (=17/2). For example a typical formula as reported by de Campos et al is $\text{Sm}(\text{Co}_{0.66}\text{Fe}_{0.2}\text{Cu}_{0.1}\text{Zr}_{0.04})_8$ [40]. Iron has been substituted for cobalt at 5 to 20 weight percent. A 5 weight percent grade produces excellent high temperature capability while a 20 weight percent material maximizes magnetic strength. If 20 weight percent is good, would 25 weight percent produce even higher magnetic strength? What is the limit of iron substitution?

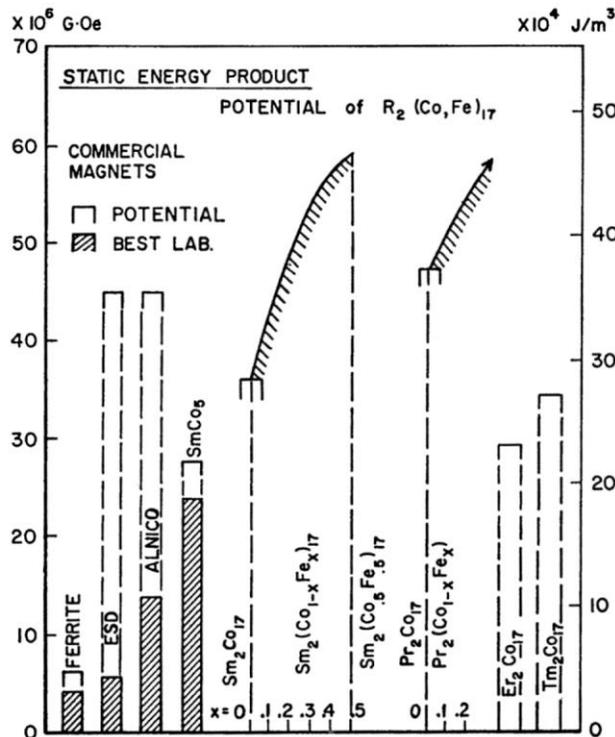


Figure 5. Energy product potential of permanent magnets including SmCo with the addition of iron. Hard Magnetic Properties of Rare Earth-Transition Metal Alloys, Strnat [35].

Thermal processing of the SmCo alloy becomes more difficult as the iron content increases (see section on thermal processing). Even more importantly, the intrinsic coercivity decreases more-and-more rapidly as iron content rises above 19 weight percent (Figure 6) although Liu and Ray show mH_c (i.e., H_{cJ}) rising again above $b=0.30$ (mole ratio). There is a more thorough discussion about iron content, “z” value and microstructure development in Ray [15]. In the extreme, total substitution of iron for cobalt has been found to not work as $\text{Sm}_2\text{Fe}_{17}$ has a planar rather than uniaxial anisotropy.

Furthermore, as iron is increased, the familiar phase diagram for SmCo changes [26, 87, 88] and copper and zirconium must also be adjusted to maintain the composition “in balance” for optimum microstructural development and properties [23, 57, 59, 69, 71, 72, 80, 107]. Morita shows us the change to the phase diagram resulting from

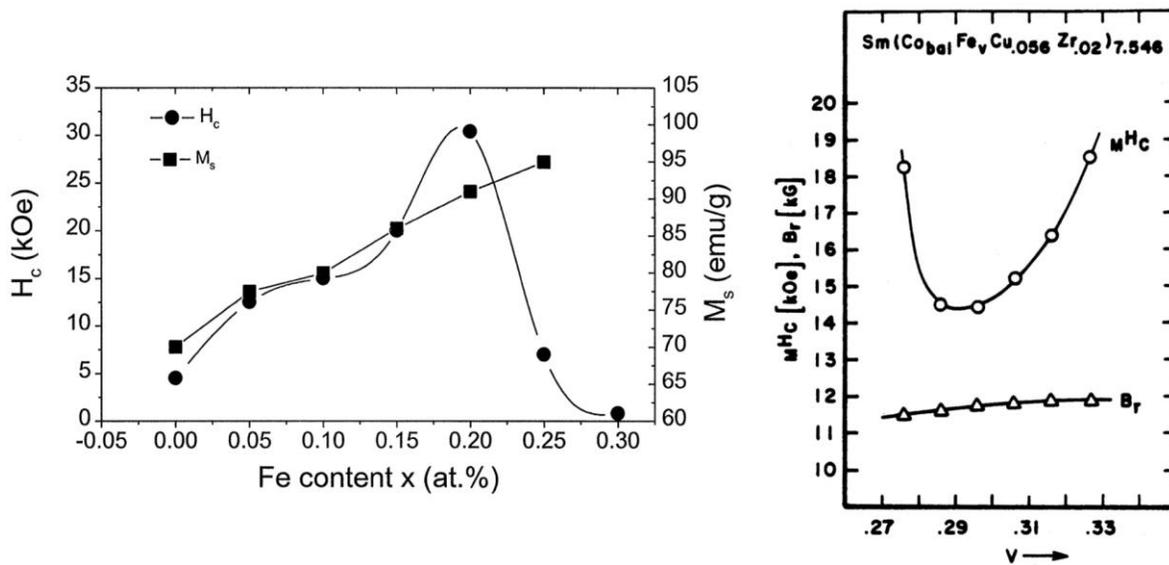


Figure 6. Fe content versus coercivity reaches minimum and then rises. Left chart is from Tang et al [72]; right chart is from Liu and Ray [107]

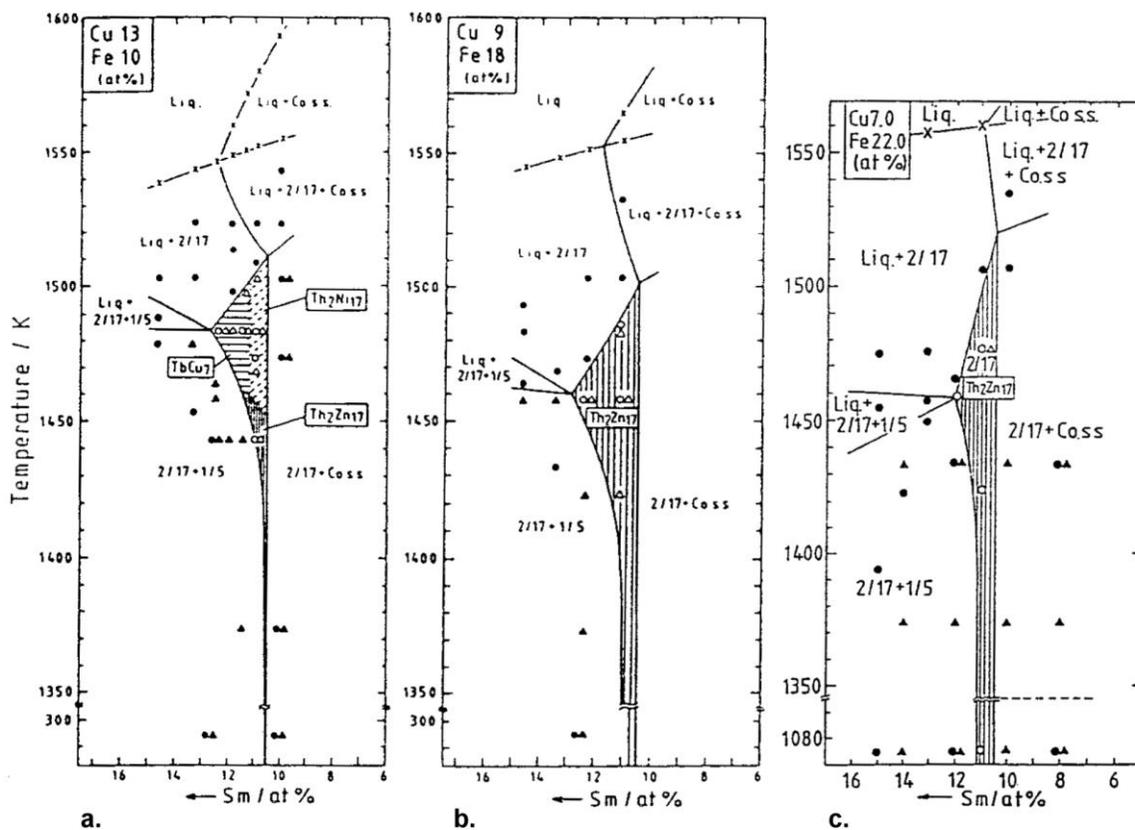


Figure 7. Effect on the SmCo phase diagram due to changing Cu and Fe content [87].

Changes of Fe and Cu (Figure 7). The heavily cross-hatched area is the solution treatment region with hexagonal SmCo stable at higher temperatures and the rhombohedral form stable at lower temperatures. With changes in iron, copper and

zirconium, the size and shape of the region changes as does the stable phase locations within the region. References show these phase diagram regions in detail such as Chin in 1989 [26] and Morita in 1987 [88] and 1989 [87].

Elements other than iron have been introduced into the chemistry in substitution for cobalt. Common substitutions include nickel and/or manganese [55,72,93]. To-date, these substitutions have not produced substantive improvements in commercial magnet properties due to trade-offs between magnetic field strength, resistance to demagnetization, or alloy chemical stability (e.g., corrosion resistance).

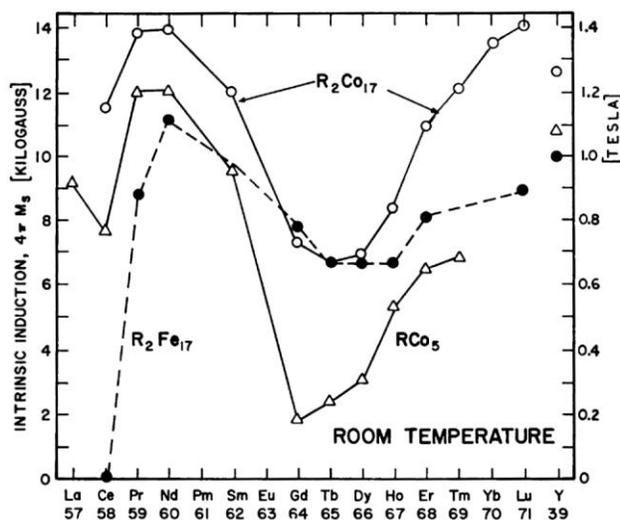


Figure 8. Substitution of rare earth elements in RCo_5 and R_2Co_{17} compounds [35]

Other rare earth elements (REEs) can be substituted for Sm (Figure 8). The most desirable substitute from a cost and availability standpoint is cerium. Resulting magnet performance, especially coercivity, is inferior to commercial SmCo but is adequately high to be interesting due to lower material cost and abundant Ce supply [61,92,93].

Strnat teaches us that Pr and Nd in 2:17 compounds should have higher magnetization than Sm (Figure 8). And in the 1:5 SmCo alloys Pr has been substituted for up to about half of the samarium with a concomitant increase in energy product from 22 up to 25 MGOe (200 kJ/m^3). Unfortunately, the presence

of Pr reduces intrinsic coercivity and destabilizes the alloy increasing corrodibility. When Pr replaces all the Sm in $PrCo_5$ it facilitates decomposition.

“The affinity for oxygen of the different RE elements varies significantly, with the light RE being less stable than the heavy RE and Y. Among the former, Sm, Nd and Ce act relatively much better than La and Pr (whose presence as an alloying constituent has been known to cause sintered magnets to age unacceptably fast and, eventually, to crumble).”

Rare Earth-Cobalt Permanent Magnets, K.J. Strnat in *Ferromagnetic Materials*, section 2.3.3. Chemical stability problems, Vol. 4, Edited by E.P. Wohlfarth and K.H.J. Buschow, Elsevier Science Publishers B.V., 1988 [95]

During the development of $Sm_2(Co,Fe,Cu,Zr)_{17}$ numerous refractory elements were tried before settling on zirconium as optimum. Examples of alternatives are V, Ti, Hf, and Mo. In trials, zirconium produced the greatest increase in coercivity with the least reduction in magnetization and the majority of research has been based on optimizing zirconium content or adjusting zirconium content to compensate for other alloy changes.

Elemental substitution references: due to the large number, they are divided into categories as follows.

- Iron substitution for cobalt: 3, 16, 21, 22, 23, 43, 45, 57, 58, 59, 61, 67, 69, 71, 78, 79, 86, 91, 94, 101, 107, 108.
- Ce, Pr, Nd, Y substitution for samarium: 61, 82, 90, 92, 93, 108
- Cu, Zr, Ti, Hf and miscellaneous: 17, 23, 27, 28, 29, 32, 40, 53, 56, 57, 59, 68, 69, 71, 72, 76, 77, 79, 80, 91, 100, 107, 112

STARTING ALLOY CONDITION

At least three conditions of the alloy have been investigated relevant to improving magnetic performance: 1) grain size (sometimes incorrectly called particle size in the literature); 2) homogeneity of the alloy composition and structure usually as the result of a solution treatment after melting and casting; and 3) alloy (crystal) structure as the result of the melt/cast process such as a structured grain growth from controlled bulk mold casting, medium-fine growth from strip casting or an extremely fine microstructure from melt spinning. Earliest efforts were often targeted at solution treating the cast alloy to ensure an homogenous phase structure which would fracture and mill into single crystal (one direction of alignment) particles with adequately high magnetic properties to facilitate magnetic alignment during compaction or for use as a bonded magnet powder such as reported by Shimoda et al [16,78,101]. It has been found that SmCo alloy cast and cooled under controlled rates yields a suitable microstructure for subsequent milling and alignment during compaction avoiding the additional solutionizing step.

Strip casting for thermally induced controlled crystal growth has been investigated. It has been shown to improve the starting crystal structure of NdFeB magnet alloy and in combination with HD, results in improved magnetic properties of the finished magnets. Sakaki claims that for the SmCo system there is improved crystal growth and more uniform milled particles resulting in better grain alignment in the magnet [73,96]. Thus either bulk casting or strip casting can be used to produce alloy though the bulk cast method is less capital-intensive. A brief on-line search yielded 18 published papers regarding melt spinning of Sm-TM magnet alloys. All of the identified references included variations in chemistry or thermal processing which is not a direct comparison of melt spinning to bulk casting or strip casting. However, each method was reported capable of producing adequate magnetic properties. The confounding of alloy cast method with compositional variations might benefit from additional designed experiments.

The milling process must be optimized relevant to particle shape and size. Presumably particles with a lower aspect ratio and a smooth outer surface would align better in compaction, especially axial (parallel) pressing. Hydrogen decrepitation (HD) has been evaluated [111]. However, the inherent brittleness of the SmCo crystal structure permits easy pulverizing. No advantage was found to justify the extra processing steps and costs associated with HD.

Milling of the cast alloy to fine particle size has been accomplished via ball (or attritor) milling and via fluid bed jet milling. Ball milling efficiency is improved in the presence of liquid carriers and surfactants. These organic materials introduce a small residual amount of carbon which can, if not sufficiently removed or controlled, produce variable sintering effects plus the dilution effect of the ZrC non-magnetic phase. Further, particle size distribution in ball milling is broader than that obtained via jet milling since the process does not provide for elimination of the super fines or the less-milled larger particles. Super-fines oxidize more easily introducing the dilution effect of non-magnetic Sm_2O_3 while larger particles may not be single crystal (single magnetic alignment direction) reducing the vector sum of magnetization.

Fluid bed jet milling has a cut-off for large particles controlled by a variable speed rotating "squirrel-cage" at the gas/particle exit. Small particle content is eliminated using one or more stages of cyclone separation upon exhaust from the mill. The result is a narrower particle size distribution with minimal contamination from organics. Both ball/attritor milling and fluid bed jet milling must be controlled to minimize oxygen pickup. The milled powders are sensitive to oxidation especially in the presence of high relative humidity.

Starting alloy condition references: 16, 73, 78, 96, 101, 111

THERMAL PROCESS

Although hot pressing of SmCo has been reported, standard powder metallurgical processes are used for the commercial manufacture of SmCo magnets. Once the powder has been aligned and compacted, it must be densified via liquid phase sintering. This is accomplished in either a vacuum or inert atmosphere furnace. In laboratory or small-scale production helium tube furnaces have been utilized to sinter and control-cool magnets. Large scale production coupled with the operational problems of large tube furnaces and increasing expense of helium dictate the use of vacuum furnaces to accomplish densification and phase development.

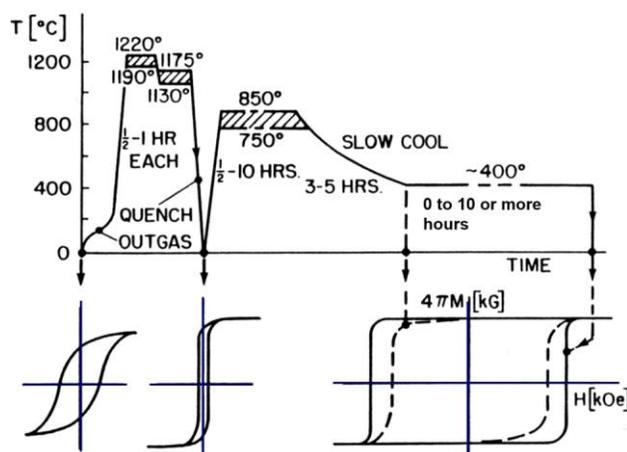


Figure 9. Sinter, solution and tempering thermal treatment as described in Strnat [95] showing development of the hysteresis loop shape.

Samarium has a relatively high vapor pressure such that at and near sintering temperature it volatilizes from the magnet surface. Sintering is therefore a compromise of maximum densification in a vacuum to avoid trapped pores coupled with partial pressure inert gas (argon) to suppress volatilization. Each manufacturer has no doubt optimized around a suitable combination of time/temperature/partial pressure. One method has the furnace operate at a vacuum until shortly after the onset of sintering at which point the furnace is switched to partial pressure adequate to

suppress samarium vaporization [45,74,95].

Subsequent to densification, the crystal structure requires homogenization (solution treatment). The complexity of this is illustrated by Morita et al in Figure 7. Phase diagrams have been generated for several composition variants and these show the change in shape and stable phases in the sinter and solution treatment temperature region.

Tempering is achieved in three stages. Stage one is an extended hold at or near 850 °C. Stage two is a ramp from 850 to 400 °C over an extended period and can be accomplished as one continuous ramp or as a stepped process. The final, stable structure is developed ~400 °C [95].

Ray in "Metallurgical behavior of Sm(Co,Fe,Cu,Zr)_z alloys" [62] describes the thermal development of the SmCo microstructure (Figure 10).

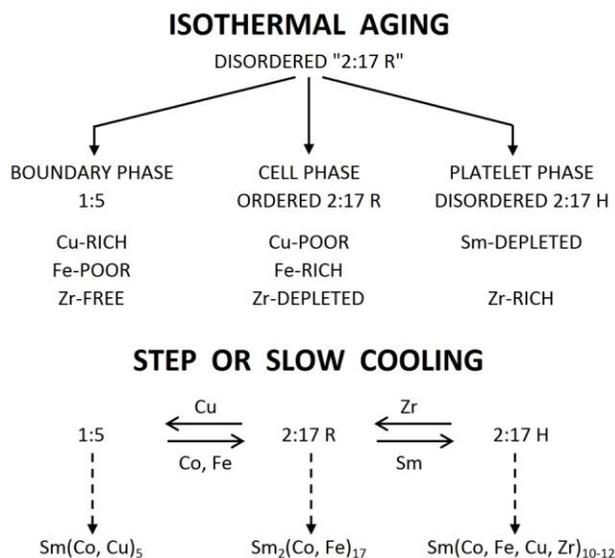


Figure 10. "Proposed reactions for a Sm(Co,Fe,Cu,Zr)_z alloy that has been homogenized at 1100-1200 °C, and quenched to room temperature. Isothermal aging at 800-850 °C creates the three phases of the cell structure (1:5, ordered 2:17 R, and 2:17 H). Step or slow cooling (800-400 °C) promoted diffusion across the phase boundaries." [62]

Thermal process references: 7, 11, 15, 16, 24, 30, 31, 33, 55, 57, 58, 69, 72, 73, 74, 78, 80, 84, 89, 95, 101, 107, 115

MICROSTRUCTURE DEVELOPMENT

The final structure of SmCo 2:17 has been extensively reported. Although additional phases have been proposed/reported [20, 26, 40], the structure is fundamentally the 2:17 rhombohedral phase, a hexagonal Sm(Co,Cu)₅ cell boundary phase and the Zr-rich lamella structure. Coercivity is developed as the result of both the Sm(Co,Cu)₅ cell boundary and the Zr-rich lamella phases. Ray [62] provides in Figure 10 an explanation for the phase development.

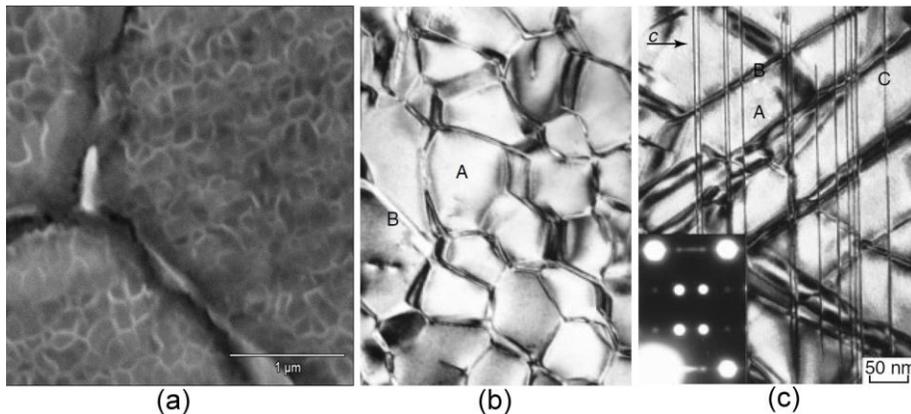
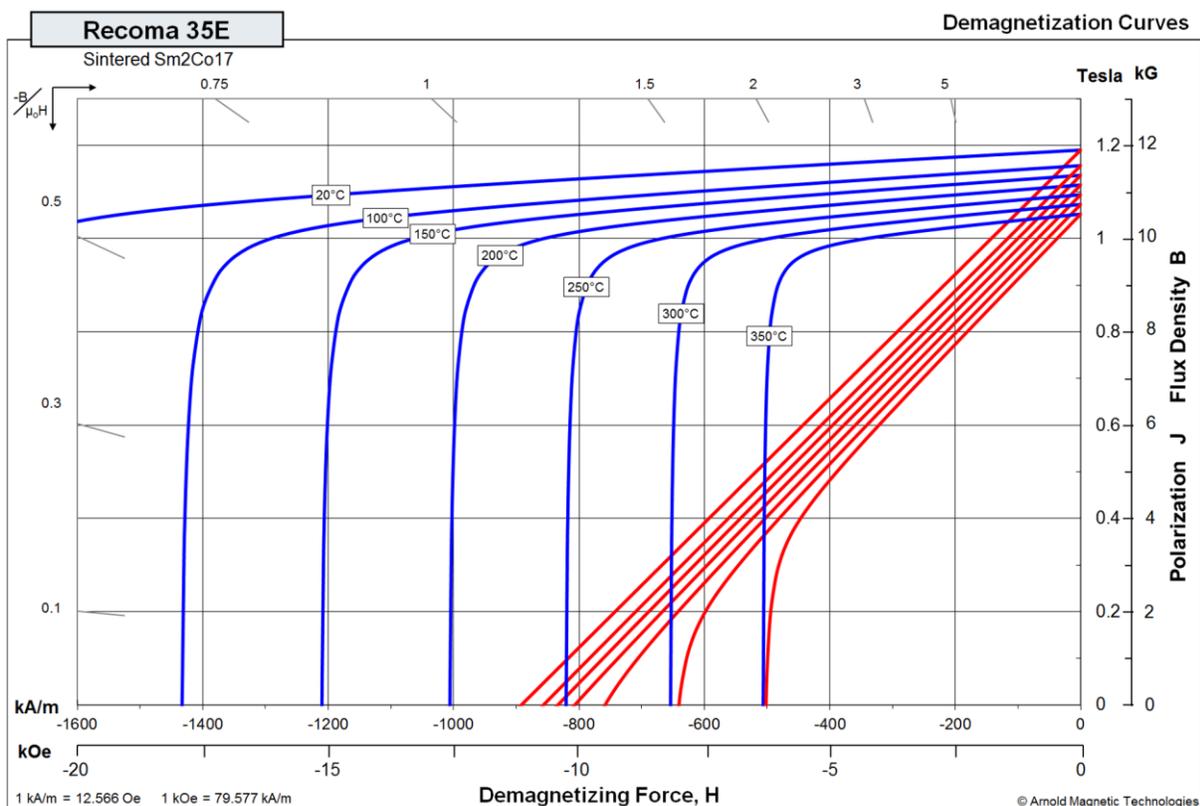


Figure 11. Cellular and lamella microstructures. (a) SEM image showing the cellular microstructure [66]. (b) TEM image showing cellular microstructure [97]. (c) TEM image showing the main phase A, the cell boundary phase B and the Zr-rich lamella phase C [97].

Microstructure development references: about 75% of the references discuss microstructural development therefore a number list of references is not included here.

RESULT OF CONTINUED PROCESS IMPROVEMENT

As a result of continued efforts to optimize the chemistry and manufacturing process of SmCo 2:17, Arnold introduced RECOMA[®] grade 33E in 2014 and recently introduced RECOMA[®] grade 35E, shown here, which exhibits a remarkable combination of high energy product, high intrinsic coercivity and “square loop” shape.



Summary

The spectrum of magnetic materials has seen few new industrially interesting entrants since the advent of NdFeB and since its introduction followed so soon after the commercialization of SmCo, there remains more opportunity to find optimization and improvements in the SmCo system than in other, more-thoroughly investigated materials. The chemistry of SmCo suggests several paths to increasing the energy density. However, many of the changes made to increase energy product also remove process aids whose function has to be replaced by subtle composition adjustment and more sophisticated thermal processing - which becomes ever-more demanding as a result. Modern equipment and a thoughtful examination of every step of the process have resulted in a strategy that can reliably deliver commercializable materials with energy product beyond previous limits. Combined with the natural high-temperature performance of SmCo, this creates compelling new products for the market.

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