Gas-Phase Modification of Rare-Earth Intermetallic Compounds

R. Skomski and J.M.D. Coey

Recent work concerning the interstitial modification of permanent magnet alloys based on rare-earth iron intermetallic compounds is reviewed. The crystal structure of the new materials is discussed, then the thermodynamic and statistical aspects of the low-temperature interstitial modification process are considered. Finally, reaction kinetics and thermal stability of the new compounds are discussed and future prospects assessed.

1. Introduction

BINARY rare-earth iron intermetallics have proven unsuitable for permanent magnets, unlike binary rare-earth cobalt compounds. One reason is the shortage of iron-rich phases that can form with the light rare earths. Another is their low Curie temperature, T_C. Whereas T_C increases with cobalt content in R-Co systems, there is a decrease in T_C at the iron-rich end in R-Fe systems. For example, the Curie temperature of Y_2Co_{17} is 1167 K, whereas that of Y_2Fe_{17} is 325 K. The problem is related to the tendency toward antiferromagnetism found in dense-packed iron lattices.

The most iron-rich phase in the binary phase diagrams is R_2Fe_{17}. It has been known for some time that almost any atomic substitution for iron initially raises T_C[1] and that the Curie temperature can be increased by up to about 200 K on hydrogen absorption.[2] Similar increases are achieved by introducing carbon into the melt,[3] which yields a series of ternary compounds $R_2Fe_{17}C_x$ with $x < 1.5$, where the carbon occupies octahedral interstitial sites in the 2:17 structure.[4]

In 1990, a series of interstitial nitrides, $R_2Fe_{17}N_{3-\delta}$, was prepared by a novel low-temperature reaction with a nitrogen-containing gas at temperatures of up to 500 °C.[5,6] The ternary nitrides exhibit a remarkable increase in Curie temperature, about 400 °C above that of the 2:17 parent compounds. Nitro-

R. Skomski and J.M.D. Coey, Department of Pure and Applied Physics, Trinity College, Dublin, Ireland.

gen also occupies the octahedral interstitial sites in the 2:17 structure, coordinated by two rare-earth and four iron atoms.[7,8] A volume increase of about 6% results from the nearly complete occupancy of these sites. Low-temperature interstitial modification of R_2Fe_{17} by reaction with hydrocarbon gases yields ternary carbides that have Curie temperatures that are nearly as high as those of the nitrides.[9] Attempts to introduce quantities of interstitial boron, silicon, or sulfur by gas-solid reaction have proved relatively unsuccessful.[10] On the other hand, it is possible to introduce carbon directly at low temperature from the solid phase.[10,11] Other intermetallic structure types with a similar interstitial site to that in R_2Fe_{17}, notably $R(Fe_{12-x}M_x)$, have been successfully modified with nitrogen[12] or carbon.[13]

The interstitial compounds $Sm_2Fe_{17}N_3$ and $Sm_2Fe_{17}C_3$ have higher Curie temperatures and anisotropy fields than $Nd_2Fe_{14}B$ and higher magnetizations than $SmCo_5$ or Sm_2Co_{17}. The problem now is to develop coercivity and devise a process for making good permanent magnets. Conventional high-temperature powder metallurgy is out of the question, because the new compounds disproportionate when heated above 600 °C. The emphasis falls naturally on bonded magnets produced from coercive nitride or carbide powder.

From $Sm_2Fe_{17}N_{3-\delta}$ powder, both isotropic and anisotropic magnets can be produced by a range of techniques. Nanocrystalline isotropic powder produced by mechanical alloying yields extremely high coercivities, up to $\mu_oH_c = 3$ T.[14] A recent result is the achievement by Street and co-workers of a remanence of 1.4 T in an isotropic nanocrystalline two-phase mixture of exchange-coupled αFe and $Sm_2Fe_{17}N_x$.[52] Despite a low coercivity, the energy product is 206 kJ/m^3. The remanence enhancement is similar to that in nanocrystalline mixtures of $Nd_2Fe_{14}B$ and Fe_3B.[15]

Table 1   Intrinsic magnetic properties of permanent magnet compounds

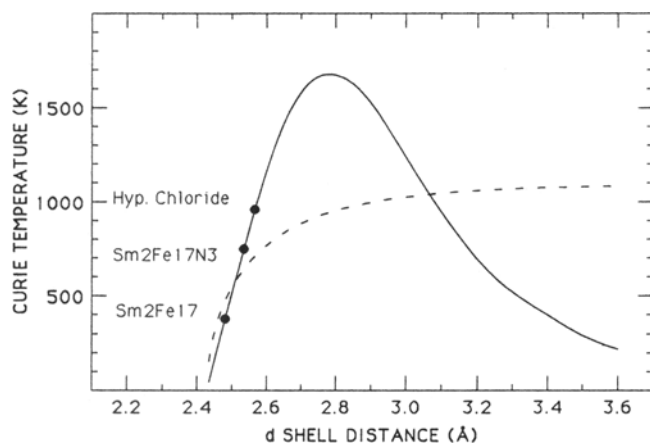|	T_C, K	μ_oM_s, T	B_a, T	$\mu_oM_s^2/4$, kJm^{-3}
SmCo$_5$	1000	1.14	28	259
Sm$_2$Co$_{17}$	1193	1.25	6	311
Nd$_2$Fe$_{14}$B	592	1.60	9	509
Nd$_2$Fe$_{14}$C	535	1.50	10	448
Sm$_2$Fe$_{17}$N$_3$	749	1.54	22	472
Sm$_2$Fe$_{17}$C$_3$	668	1.43	16	407

Fig. 1 Curie temperature as function of lattice expansion. Solid line: Slater-Néel curve. Dashed line: Band-structure limit.

Fig. 2 Sm_2Fe_{17} structure, showing 9e and other interstitial sites.

Anisotropic bonded magnets are usually made from a powder where each particle is a single crystallite that can be oriented with its easy direction along an applied magnetic field. The coercivity of monocrystalline powder tends to be small. Values of $\mu_o H_c$ of up to 0.5 T have been achieved by treatment in pure nitrogen.[16] After heat treatment of the milled powder at 700 °C in vacuum before nitriding, values of $\mu_o H_c$ of up to 2 T are achieved.[16]

Resin bonding has been carried out for mechanically alloyed or aligned monocrystalline powders. The best reported energy products are 87 kJ/m^3 for isotropic[17] and 136 kJ/m^3 for anisotropic magnets.[18] The coercivity of the $Sm_2Fe_{17}N_3$ may increase tenfold or more with zinc bonding. However, the value of remanence of metal-bonded magnets is their weak point so far. It is related to the presence of rather large quantities of nonmagnetic phases such as Fe_3Zn_7 and imperfect space filling of the oriented powders.

This article reviews several aspects that are relevant for the production of interstitially modified magnets. Crystal structure and equilibrium properties, as well as reaction kinetics and thermal stability, are discussed. Conclusions are drawn concerning the permanent magnetic properties and the processing behavior of the new materials. Most of the emphasis is on Nitromag, $Sm_2Fe_{17}N_x$, because that is where the most progress has been made.

2. Background

The effect of interstitial atoms on the Curie temperature is essentially due to the lattice expansion they provoke; the chemical nature of the interstitial is less important than its influence on lattice volume.[19] The simplest way to express the expansion-induced increase of the Curie temperature, which reflects the volume dependence of the exchange interactions, is to use the classic Slater-Néel curve.[19] Using band structure considerations given in Ref 20, a curve is obtained[21] that is qualitatively similar to the Slater-Néel curve, except for large
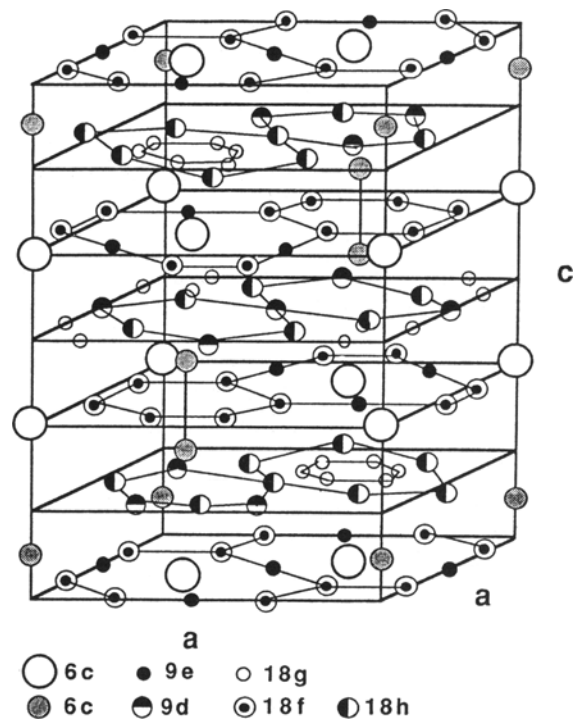
lattice expansions where all electrons are localized. Figure 1 shows that it is worthwhile trying to insert interstitial atoms with larger volumes such as boron, silicon, or chlorine into the octahedral sites.

Besides the increase in Curie temperature, there are other beneficial effects of the interstitial on the intrinsic magnetic properties. Like iron itself, iron-rich intermetallics are generally weak ferromagnets with an incompletely filled $3d\uparrow$ subband; consequently there is some scope for increasing the iron moment via d band narrowing or further exchange splitting. This is precisely what happens as the lattice expands.[22,23] For example, the zero-temperature moment of Y_2Fe_{17} rises from 32.8 to 38.1 μ_B on nitrogenation, compared with 39.4 μ_B expected for a strong ferromagnet with fully exchange-split bands.[19] The effect of lattice expansion outweighs that of N-Fe hybridization, and useful increases in magnetization are achieved at room temperature, partly due to the increase in the intrinsic iron moment and partly due to the large increase in T_C.

The third effect of the interstitials is to modify the crystal field experienced by the rare earth. According to the disposition of interstitials around the rare earth, the electric field gradient A_{20} may be positive or negative. In $R_2Fe_{17}N_3$, it is negative, which means that rare earths such as Sm with a positive quadrupole moment exhibit the uniaxial anisotropy required of permanent magnets. The contribution to the magnetocrystalline anisotropy from the rare earth far outweighs that of the iron sublattices, and anisotropy fields in the range 14 to 26 T have been reported for $Sm_2Fe_{17}N_{3-\delta}$.[18,24,25] Some of the variation is due to different compositions of the samples and some to different methods of measurement.
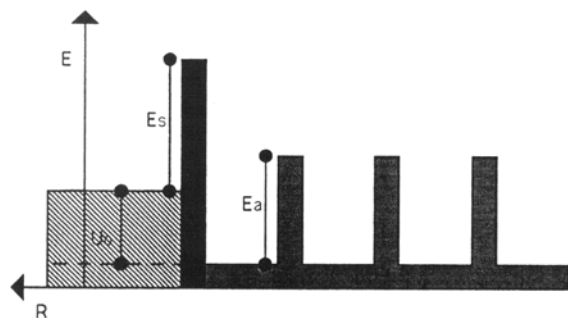
Fig. 3 Schematic of the interstitial modification process.

3. Crystal Structure

Intermetallic structures are composed of approximately close-packed arrays of the constituent atoms. Interstitial modification on a large scale is possible only by small atoms, which can diffuse through the lattice and find interstitial sites large enough to accommodate them and satisfy their bonding requirements. The size of the interstices must be sufficiently large. The octahedral interstitial sites are better than the tetrahedrals because they are usually much bigger. Neighboring atoms may be displaced to accommodate the interstitial, but this increases the net reaction energy, U_o, and the interstitial solubility is reduced. Metals are electropositive, consequently, electronegative elements have a favorable reaction energy, but the electronic structure of the host is also an important consideration. Of all the elements in the periodic table, only hydrogen and chlorine and the light 2p elements at the end of the first period (B, C, N, O and F) have sufficiently small atomic radii ($R < 1$ Å). Hydrogen is small enough to fit into tetrahedral as well as octahedral interstices, particularly if its single electron is partly delocalized. Boron (s^2p) has a preference for trigonal prismatic coordination, whereas carbon (s^2p^2) and especially nitrogen (s^2p^3) prefer octahedral sites. Oxygen and fluorine are strongly electronegative and tend to form ionic compounds.

The R_2Fe_{17} binary compounds crystallize in the rhombohedral Th_2Zn_{17} structure for rare earths lighter than Gd (Fig. 2) and in the hexagonal Th_2Ni_{17} structure for rare earths heavier than Dy; both structure types are found for R = Gd, Tb, Dy, and Y.[26] The crystal symmetry is unaffected by low-temperature gas-phase interstitial modification. The possible interstitial sites in the Th_2Zn_{17} structure are shown in Fig. 2. The 9e octahedral sites have two rare earth and four iron neighbors; the hexagonal 3b sites have two rare earth and six iron neighbors, and the surrounding ring of six tetrahedral 18g sites have two rare earth and two iron neighbors.

Hydrogen site occupancy has been determined in $R_2Fe_{17}H_x$ with R = Ce, Nd,[27] and Pr.[28] It occupies both 9e and 18g sites, with a preference for the octahedral sites and no more than two tetrahedral sites in a six-membered ring being occupied. Carbon has been shown to occupy octahedral sites in $Nd_2Fe_{17}C_{0.5}$.[4] A definitive structure study of $Pr_2Fe_{17}N_{2.9}$[8] shows that nitrogen occupies 9e sites only. Other neutron diffraction studies on $Nd_2Fe_{17}N_x$[23,29-31] situate the nitrogen mainly or exclusively on 9e sites.
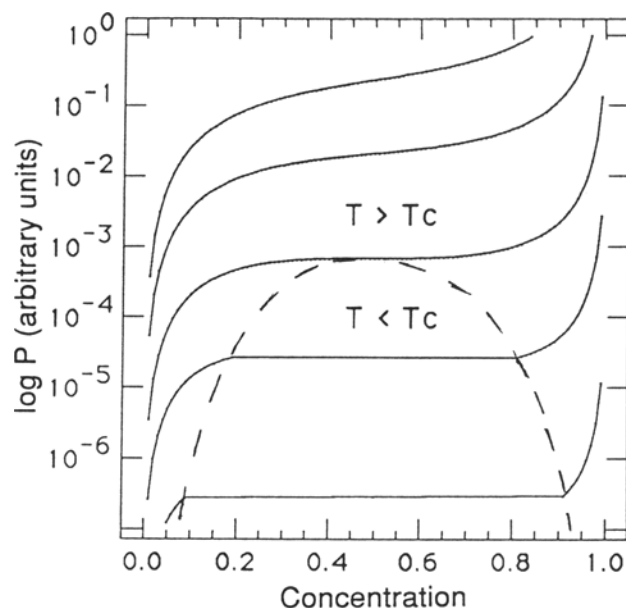

Fig. 4 Schematic phase diagram for a lattice gas.

Most authors report a maximum nitrogen occupancy of less than 3 per formula, consistent with exclusive 9e site occupancy. Exceptions are Iriyama et al.[32] and others[33] who claim to make $Sm_2Fe_{17}N_x$ with x of 6 or even more after treatment in hydrogen or ammonia, but no structural data to situate the nitrogen are yet available on these materials. The observed volume expansion appears to be inconsistent with interstitial nitrogen occupancy in the 2:17 structure much greater than three.

If the R_2Fe_4 octahedron is considered to be one key to successful nitrogenation, then it is possible to predict to a certain extent which structure types are likely to form interstitial nitrides. For instance, compounds with a tetragonal $ThMn_{12}$ structure such as $Nd(Fe_{11}Ti)$ are able to accommodate up to one nitrogen per formula unit on the 2b sites. However, the size of the interstitial site is only *one* factor; chemical affinity often outweighs the size effect. For instance, the solubility of nitrogen in Sm_2Co_{17} is lower compared to that in Sm_2Fe_{17}, in spite of the equivalent crystal structure. A possible reason for this behavior is the slightly higher electronegativity of cobalt.[11]

4. Equilibrium Thermodynamics

Formation of interstitially modified intermetallics by low-temperature reaction is schematically illustrated in Fig. 3. A gas or a solid source is used, which decomposes at the intermetallic surface to release the required atoms. They must first overcome a surface or interface barrier before entering the intermetallic lattice to occupy interstitial sites, provoking a local lattice expansion. Once inside the intermetallic, the atoms diffuse under the influence of the chemical potential, ultimately attaining an equilibrium state.

The process may be roughly parameterized in terms of four energies: U_o, the total reaction energy that includes terms of different sign due to dissociation of the source reagent and af-
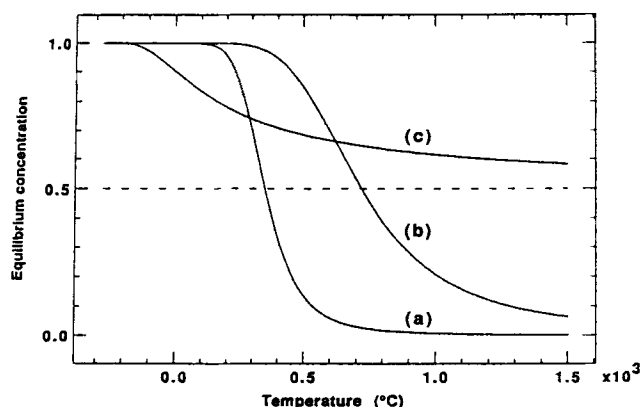
Fig. 5 Temperature dependence of the equilibrium interstitial concentrations for different types of interaction. (a) Gas-solid reaction (atomic gas). (b) Gas-solid reaction (molecular gas). (c) Solid-solid interaction.

Fig. 6 Equilibrium interstitial concentration for the $N_2Sm_2Fe_{17}$ interaction.

finity of the intermetallic for the interstitial atom, as well as a smaller elastic term; U_1, the interatomic elastic and electronic interaction of the interstitial atoms within the intermetallic; E_s, the surface barrier to penetration; and E_a, the activation energy for diffusion.

The equilibrium state of the interstitially modified compound depends on the net reaction energy, U_0, and on the interatomic interaction energy U_1. A key issue is whether the equilibrium state is a uniform solid solution or a mixture of phases, one nitrogen-rich, the other nitrogen-poor.

It turns out that phase segregation (Fig. 4) occurs below a certain critical temperature $kT_0 \approx 4\ U_1$.[34] The interatomic interaction is mainly due to long-range elastic strain:[35] the occupation of a given interstitial site slightly increases the size of the neighboring interstices whose occupation now becomes energetically more favorable.

Most of the evidence available for $Sm_2Fe_{17}N_{3-\delta}$ favors a random solid solution at the temperatures used for nitrogenization (400 to 500 °C). The evidence can be summarized as follows:

• Intermediate lattice parameters for intermediate nitrogen content[36,37]

• Intermediate Curie temperatures for intermediate nitrogen content[37]

• Variable environments of the rare earths as probed by nuclear magnetic resonance (NMR)[38]

• Homogenization experiments[39]

• Domain size observations[11,40]

Much of the evidence to the contrary appears in systems where the surfaces are nitrogen-rich or in polydisperse powder where the small grains are more thoroughly nitrided than the large ones. Besides, nonlinear mapping of the nitrogen concentration, e.g., due to optical transitions, may mimic a discontinuous nitrogen content. Another reason to believe that U_1 may be negligible is the relatively low concentration of interstitials, 3:19, so the size of the neighboring interstices is only slightly
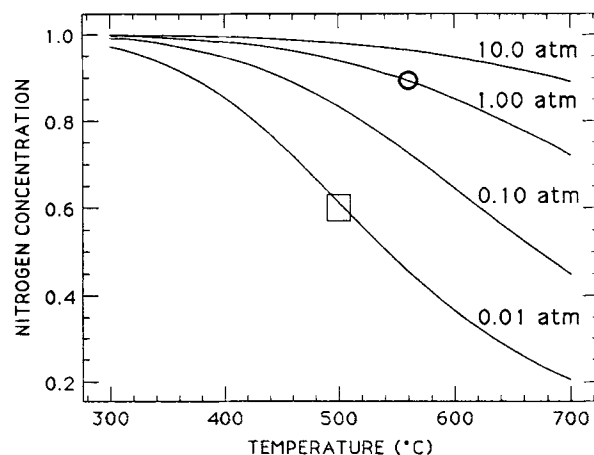
modified. The classic two-phase system is PdH_x where the critical temperature T_0 is 292 °C. A crude estimate of T_0 in the $Sm_2Fe_{17}N_{3-\delta}$ system is 200 K.[36]

The equation of state gives the equilibrium interstitial concentration $c_0(P,T)$ as a function of temperature and pressure. Equations of state can be easily obtained if U_1 is neglected. Using a lattice gas, partition functions and equations of state have been obtained by counting all energetically equivalent states.[10,11,36,41] Results are given for interstitial modification reactions involving a monatomic gas, a diatomic gas, and a solid.

In the case of a hypothetical reaction with a monatomic gas, the result is:

$$c_0 = \left\{1 + (kT/v_0P)\exp(U_0/kT)\right\}^{-1}$$

where v_0 is a cell volume on the order of 1 Å^3.

For the reaction with a diatomic gas such as N_2 or H_2:

$$c_0 = \left\{1 + \sqrt{(13kT/v_0P)}\exp(U_0/kT)\right\}^{-1}$$

This expression reduces to Sieverts' square-root law, $c \approx \sqrt{P}\exp(U_0/kT)$, in the low-concentration limit. The theory can be extended to allow for more than one interstitial site, with a different parameter, U_{0i} for each. The value of U_0 for N_2 and Sm_2Fe_{17} is -57 kJ/mole.[41] Finally, in the case of a solid-solid reaction, the expression for the equilibrium concentration becomes independent of pressure:

$$c_0 = \{1 + \exp(U_0/kT)\}^{-1}$$

The equilibrium concentration is highest for solid-solid reactions for a given value of U_0, essentially because of the lower entropy of a solid compared to a gas. The high-temperature limit is $c = 0.5$. Some typical results for concentration as a function of temperature are shown in Fig. 5 and 6.

These considerations suggest that a low-temperature solid-solid reaction is a worthwhile route for interstitial modification. On reacting Sm_2Fe_{17} with graphite, lattice expansion of up to 5% has been achieved.[10] In fact, the standard reactions for interstitial carbonation using hydrocarbon gases[3] are
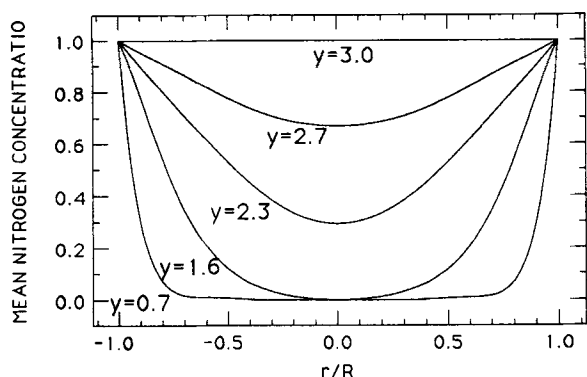
Fig. 7 Concentration profiles for intermediate nitrogen concentration.

Fig. 8 Stability curve for $Sm_2Fe_{17}N_3$.

probably solid-solid reactions, because the reagents decompose at the surface to leave a thin film of solid carbon, which then diffuses into the intermetallic.

5. Reaction Kinetics

The loading proceeds from the surface of the intermetallic by diffusion. Consequently, the surface energy barrier, E_s, which strongly depends on the powder processing, decides the temperature above which the gas atoms can enter the intermetallic lattice. The initial stages may involve rapid diffusion along easy pathways such as microcracks or grain boundaries,[18,42,43] but ultimately the diffusion has to proceed through the bulk of each crystallite. The simplest theoretical approach that provides some insight into the problem is to solve the diffusion equation $\partial c/\partial t = D\nabla^2 c$ for spherical particles subject to the boundary condition $c = c_o$ at the surface.[36,41] Some results for different stages of incomplete nitrogenation described by an average concentration $\langle c \rangle$ are shown in Fig. 7. Simple diffusion in particles always leads to "bathtub" profiles with positive curvature. There is some evidence that these profiles are found in incompletely nitrided grains.[11,42] It may be noted that grains with an average composition $Sm_2Fe_{17}Fe_{2.3}$ have a core with $c \approx 0.3$, when $c_o = 1$ at the surface. These poorly nitrided cores act as soft centers for nucleation of reverse domains.[44]

The diffusion constant D has been measured in several ways.[7,41] Most reliable are perhaps the measurements made during the initial stages of nitrogenation when $\langle c \rangle = 6c_o\sqrt{(\tau/\pi)}$, where the reduced time τ is defined as $\tau = Dt/R^2$ for spherical grains of radius R. For particles of general shape, R is replaced by $A/3V$, where A/V is the area-to-volume ratio. In the initial stage, the absorption is therefore proportional to $\sqrt{t}$, and is independent of particle shape. Assuming the diffusion is thermally activated so that $D = D_o \exp (E_a/kT)$, the constants derived from the $\sqrt{t}$ dependence at different temperatures are $D_o = 1.0$ mm^2/s and $E_a = 133$ kJ/mole for nitrogen in Sm_2Fe_{17}.[36] Other values of D_o and E_a have been reported,[7,45] but there is agreement that the bulk diffusivity at 500 °C is approximately 10^{-15} m^2/s. D is independent of concentration provided the interatomic interactions of the interstitial atoms can be neglected.
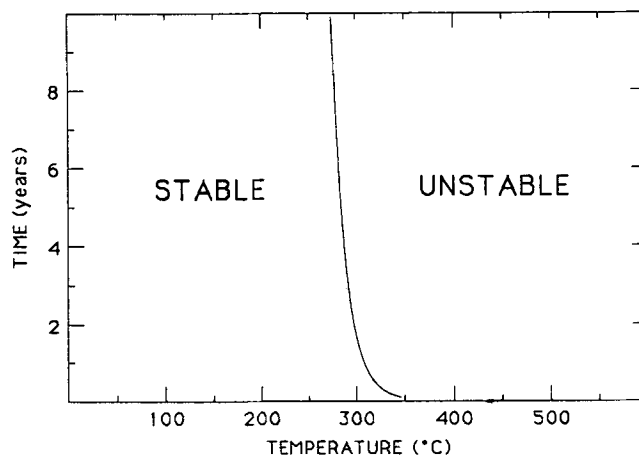
From these values, the times necessary to nitrogenate particles to a desired extent can be derived, given the temperature and their effective radius. It takes 1.5 h, for example, to achieve $\langle c \rangle = 0.87$ ($y = 2.6$) at 500 °C in particles of effective radius 5 μm. Values of D_o and E_a are similar in 1:12 structure compounds.[36]

There are reports that the nitrogenation reaction can be accelerated by pretreatment with hydrogen,[43,46,47] or the use of ammonia,[18,32] or by increasing the nitrogen pressure.[48] Some of these effects may be explained by the hydrogen decrepitation effect,[49] which dissociates the crystallites within a powder particle along the grain boundaries. The expansion produced by nitrogenation may have similar effects.[50]

6. Thermal Stability

From the energetical point of view, the disproportion of the rare-earth intermetallic lattices, in particular $Sm_2Fe_{17}N_3$, and the formation of ionic compounds like SmN is more favorable than interstitial modification. At some point, the lattice dilation[36,41] and the chemical affinity between rare-earth and interstitial atoms will render the interstitial intermetallic unstable. The disproportionation rate is determined by the diffusivity of iron, which increases rapidly with temperature. The disproportionation behavior of $Sm_2Fe_{17}N_x$ can be summarized as follows. The nitride cannot be produced at temperatures above 600 °C. High-temperature processing is impossible. At sufficiently low temperatures, $Sm_2Fe_{17}N_x$ can remain in a quasistable state practically indefinitely.

There are different ways to estimate the temperature below which $Sm_2Fe_{17}N_3$ can be regarded as stable.[11] Assuming a single decomposition mode, which may correspond to the diffusion of the iron atoms, it can be estimated that the nitride disproportionates at 700 °C after a few seconds, at 500 °C after a few hours, and at 300 °C after a few years (Fig. 8). The corresponding room-temperature value is on the order of 10^{15} years; consequently, $Sm_2Fe_{17}N_3$ can be considered as stable for practical purposes at temperatures up to about 250 °C.

7. Perspectives

The Curie temperature and anisotropy field of $Sm_2Fe_{17}N_3$ are more attractive than those of $Nd_2Fe_{14}B$ for permanent magnetic applications. No existing processing route can be applied for magnetic fabrication because of the instability of the nitride at temperatures above 600 °C. The prospects of Nitromag therefore depend on the development of an effective processing route that yields magnets with a useful energy product at an acceptable cost. The best energy product, reported for fine powder, is 240 kJ/m^3.[51] Superior coercivity has been achieved at temperatures above 150 °C.[47] Problems remain with achieving acceptable densities with zinc-bonded magnets, or producing orientable coarse powder with sufficient coercivity for resin-bonded magnets. However, published results are encouraging, and it is likely that with suitable additives and better control of process parameters that these problems will be overcome. Already, mechanical alloying exists as a process for producing material that can be bonded to make useful isotropic magnets, and the performance of isotropic nanocrystalline material may be extended by forming two-phase nanoscale mixtures of $Sm_2Fe_{17}N_3$ and αFe.[52]

8. Conclusions

On a broader scale, gas-phase or solid phase interstitial modification offers a route for synthesizing a wide range of new intermetallic derivatives. The limits of the process are still being defined, but it has already significantly expanded the horizons for magnetic materials with nitrogen and carbon. Other physical properties (mechanical, thermal, and optical) are altered by interstitial modification, and in the future, some of these changes may also find practical uses.

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