

Nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ prepared by mechanical alloying and subsequent heat treatment

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Abstract

Sm–Fe alloy was prepared by mechanical alloying of the elemental metals, and the $\text{Sm}_2\text{Fe}_{17}$ phase was obtained through properly crystallizing the Sm–Fe alloy. Subsequently, the nitrogenation behaviour of the $\text{Sm}_2\text{Fe}_{17}$ phase was investigated. The results show that nitrogenation consists of the following processes: incubation period, coexistence of $\text{Sm}_2\text{Fe}_{17}$ and nitride phase, and transformation of the residual $\text{Sm}_2\text{Fe}_{17}$ into nitride phase. During nitrogenation, small amounts of very fine α -Fe particles segregate. After nitrogenation, the metastable phase formed during crystallization disappears; this is attributed to the nitrogen-induced transformation of the hexagonal $\text{Sm}_2\text{Fe}_{17}$ phase into the rhombohedral one.

1. Introduction

Since the appearance of Nd–Fe–B permanent magnets in 1983, the interstitial hydride, carbide and nitride of iron-based rare earth intermetallic compounds produced by both alloying and gas–solid reaction have caused great interest in the scientific and technological world [1–3], because they have potentially excellent magnetic properties. The interstitial H, C and N atoms do not change the crystal structure of the parent compounds markedly, but significantly affect the magnetic interaction by increasing the volume of the crystal cell. The influence will be greater in the case where the intermetallic compound has a high iron content and a low Curie temperature. On the other hand, nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ can change the easy-plane magnetic anisotropy into an easy-axis anisotropy, and raise the Curie temperature and the intrinsic coercive force strikingly. Therefore it seems fairly attractive to study these materials.

Recently, Coey *et al.* [4] reported the results of treatment (in ammonia and N_2) of $\text{Sm}_2\text{Fe}_{17}$ alloys prepared by the melting technique. Schnitzke *et al.* [3] reported the magnetic properties of nitrogenated $\text{Sm}_2\text{Fe}_{17}$ alloys prepared by mechanical alloying. In the present paper, the nitrogenation behaviour of Sm–Fe alloys produced by mechanical alloying is investigated.

2. Experimental details

Powders of 99% pure samarium and 99.5% pure iron were mixed in the ratio $\text{Sm}_2\text{Fe}_{17}$ and sealed under argon atmosphere in a hardened steel vial. The mechanical alloying was performed in a Spex 8000 mixer-mill.

Portions of the mechanically alloyed sample were wrapped in tantalum foils, and put into a quartz tube for crystallization in a vacuum of 5×10^{-5} Torr. A small piece of a rare earth metal was also placed into the tube in order to reduce oxidation. Subsequently, the crystallized samples were transferred to a stainless steel container for nitrogenation. With either flowing N_2 at $P=0.3$ MPa or N_2 at $P \approx 1$ MPa at rest, the results of the nitrogenation reaction were not different.

The structures of the as-milled, crystallized and nitrogenated samples were examined by X-ray diffraction in a Rigaku D/max- γ A diffractometer with Cu $K\alpha$ radiation. The above-mentioned powders were also investigated by scanning electron microscopy, transmission electron microscopy and Auger electron spectrometry. After nitrogenation the phase in the sample, as tested by X-ray diffraction, was found to be the fully changed nitride, written as $\text{Sm}_2\text{Fe}_{17}\text{N}_x$. It has been reported that, after full nitrogenation, the value of x is between 2.0 and 2.6 [4].

3. Results and discussion

The X-ray diffraction patterns of the Sm-Fe powders milled for various times are presented in Fig. 1. It can be seen that the resultant phases are amorphous Sm-Fe and α -Fe. Figure 2, curve c, shows the X-ray diffraction

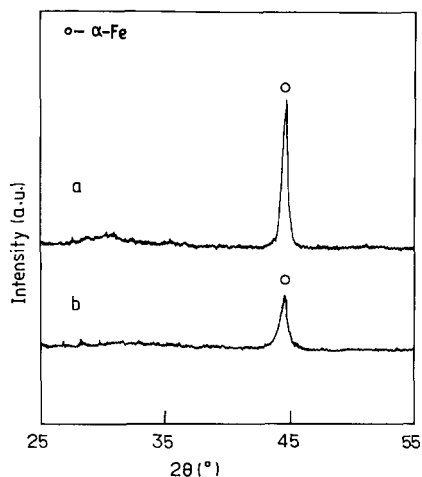


Fig. 1. X-ray diffraction patterns of samples after milling for 5 h (curve a) and 8 h (curve b).

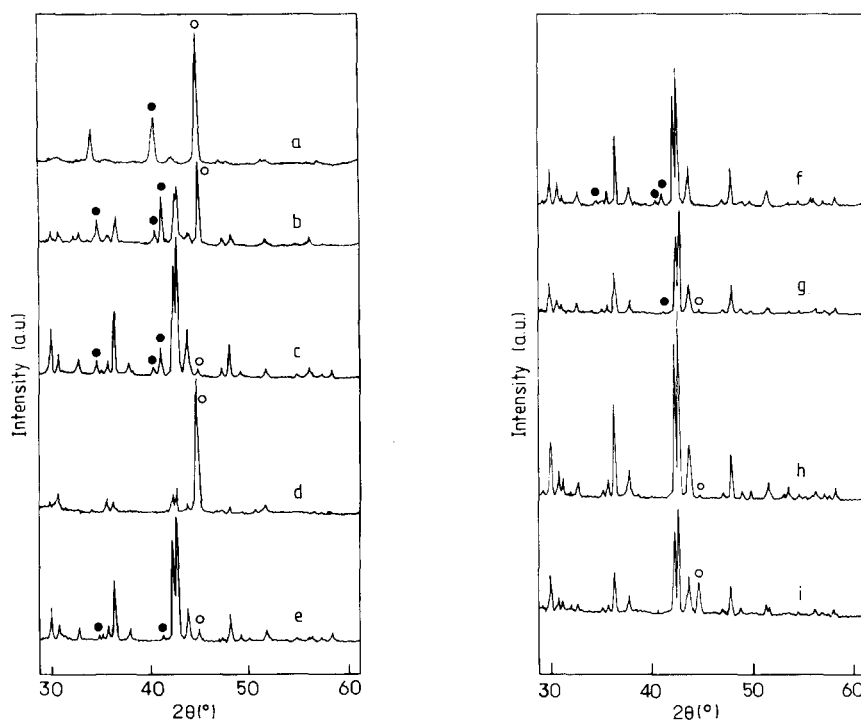


Fig. 2. X-ray diffraction patterns of as-milled samples crystallized in various conditions: curve a, 400 °C for 4 h; curve b, 600 °C for 4 h; curve c, 700 °C for 4 h; curve d, 800 °C for 10 min; curve e, 800 °C for 0.5 h; curve f, 800 °C for 1 h; curve g, 800 °C for 2 h; curve h, 840 °C for 2 h; curve i, 880 °C for 2 h; ●, metastable phase; ○, α -Fe.

pattern of the properly crystallized sample. The peaks corresponding to α -Fe have become very weak. The nitrogenation experiments were then performed on such crystallized samples. In Fig. 3 are shown the Auger depth profiling results of the samples after full nitrogenation. It is obvious that the distribution of Sm, Fe and N atoms is homogeneous through the whole sample surface investigated.

3.1. Incubation period of the nitrogenation process

At a temperature of 460 °C, when the purified N_2 gas was admitted to the crystallized Sm_2Fe_{17} powders, the nitrogenation started after a period of time rather than immediately, and this period of time is here referred to as the incubation period. Figure 4, curve a, shows the X-ray diffraction pattern of the as-crystallized (before nitrogenation) powder, whereas Fig. 4, curve b, shows the pattern of the crystallized powder after "nitrogenation" (4 h at 460 °C) which indicates no formation of nitrides. It is suggested that there exists an incubation period for real nitrogenation. This seems analogous to the first absorption of hydrogen (namely, activation) for hydrogen storage

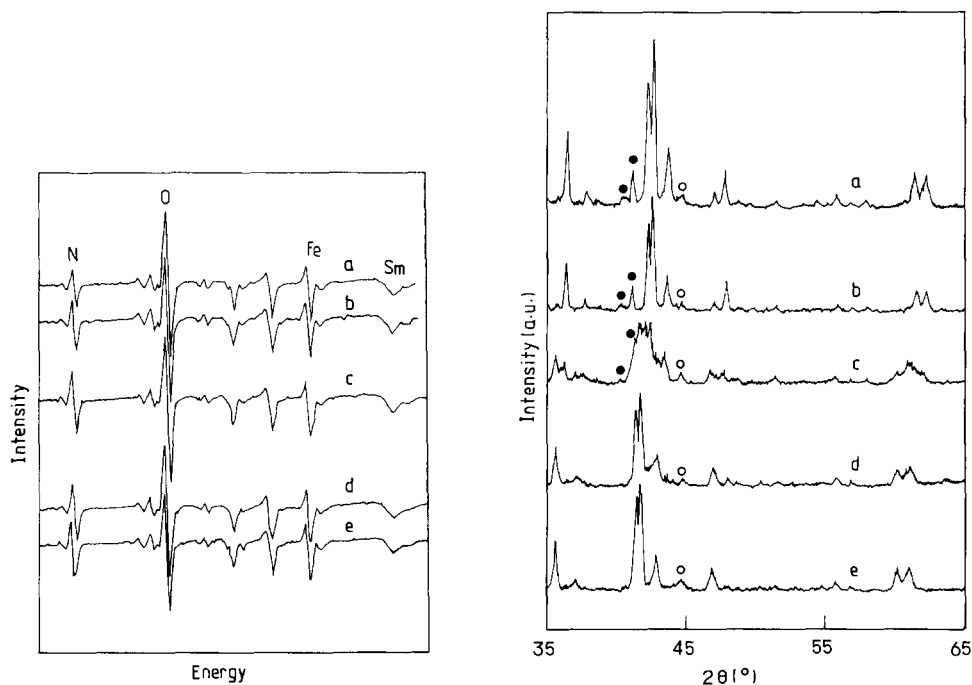


Fig. 3. Auger depth profiles of as-milled Sm-Fe alloy, Ar^+ bombarded for 0 min (curve a), 20 min (curve b), 30 min (curve c), 40 min (curve d) and 50 min (curve e).

Fig. 4. X-ray diffraction patterns of samples nitrogenated in various conditions: curve a, as crystallized; curve b, 460 °C for 4 h; curve c, 460 °C for 4.5 h; curve d, 460 °C for 5 h; curve e, after full nitrogenation; ●, metastable phase; ○, α -Fe.

materials. Taking LaNi_5 as an example, the transformation of LaNi_5 to LaNi_5H_6 can start only when LaNi_5 alloy has been kept in hydrogen atmosphere under a pressure higher than the equilibrium value for a period of time. However, after activation, LaNi_5 alloy shows characteristic hydrogenation kinetics, and the incubation period no longer exists [5]. As to the incubation period for the hydrogenation of LaNi_5 alloy, Lue *et al.* [6] suggested that it takes a period of time to produce adequate fresh surfaces which catalyse the decomposition of H_2 and make it possible for the hydrogenation to proceed. On the other hand, Schlappbach *et al.* [7] thought that there exists some residual O_2 in the H_2 gas which results in oxidation of some La atoms on the surfaces, so that nickel atoms segregate out in the form of fine particles and catalyse the decomposition of H_2 . The incubation period, according to these authors, is the time needed for the segregation process of the nickel particles.

The sites occupancy of nitrogen atoms in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ alloy has been deduced from high resolution neutron diffraction data [8], namely, nitrogen atoms exist in the 9e octahedral interstices lying in the *c* planes that contain the rare earths, which is coordinated by two samarium atoms and four iron

atoms. The nitride has a structure that is derived from that of the parent compound $\text{Sm}_2\text{Fe}_{17}$, but its volume expands by 5–6% [4].

Since nitrogen in the nitride of $\text{Sm}_2\text{Fe}_{17}$ is present in the form of atoms, the nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ may consist of the following sequences: (1) N_2 decomposes into nitrogen atoms on the surfaces of $\text{Sm}_2\text{Fe}_{17}$ particles ($\text{N}_2 \rightarrow 2\text{N}$); (2) nitrogen atoms diffuse to the 9e octahedral interstices of $\text{Sm}_2\text{Fe}_{17}$; (3) $\text{Sm}_2\text{Fe}_{17}$ transforms into the corresponding nitride phase.

The N_2 molecule is rather stable; the energy barrier for its decomposition is 235 kJ mol^{-1} . At a temperature of 460°C , the energy is not high enough to decompose N_2 . However, in consideration of the fact that the nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ can take place at 460°C , it is concluded that the surfaces of $\text{Sm}_2\text{Fe}_{17}$ particles must have catalysed the decomposition of N_2 by lowering the energy barrier. Therefore the existence of the incubation period can be interpreted as follows: the oxidation of the particle surfaces made them lose the catalytical function and it takes a period of time for N_2 to contact fresh surfaces of $\text{Sm}_2\text{Fe}_{17}$ particles, either by diffusion through the oxidation layers, or by cracking of the surfaces caused by the expansion of the crystal cell because of the introduction of a small number of nitrogen atoms. However, further studies are needed to clarify the mechanism.

The incubation period is closely related to the surface conditions of $\text{Sm}_2\text{Fe}_{17}$ particles. It is found that the incubation period of the sample exposed to air for a longer time is longer than that of the sample exposed to air for a shorter time. Even for the partially nitrogenated sample, as shown in Fig. 4, curve c, there still existed an incubation period when it was renitrogenated after it had been exposed to air for a period of time. This indicates that the surface condition is important in determining the incubation period.

After the incubation period the nitrogenation can be completed within not too long a time, such as 1 h. The nitrogenation process is not reversible at least at room temperature; this is, when placed in vacuum at room temperature, the fully nitrogenated sample does not decompose into the $\text{Sm}_2\text{Fe}_{17}$ phase and N_2 gas.

3.2. Phase transformation during nitrogenation

The experimental results indicate that the nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ is a phase transformation process, *i.e.* the transformation of $\text{Sm}_2\text{Fe}_{17}$ phase into its corresponding nitride phase, as shown in Fig. 4. During the nitrogenation process, the $\text{Sm}_2\text{Fe}_{17}$ phase and the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase coexist (see Fig. 4, curve c). As stated above, N_x stands for the saturated amount of nitrogen in the nitride phase rather than for the variation of nitrogen atoms absorbed by $\text{Sm}_2\text{Fe}_{17}$ during the nitrogenation process. As nitrogenation progresses, there is an increment in the amount of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase and a decrement in the amount of $\text{Sm}_2\text{Fe}_{17}$ phase (Fig. 4(d)). Eventually, the $\text{Sm}_2\text{Fe}_{17}$ phase transforms into the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase (Fig. 4, curve e). This indicates that, during nitrogenation, the distribution of nitrogen atoms in the $\text{Sm}_2\text{Fe}_{17}$ alloy is not homogeneous. Some crystal cells are fully occupied by

nitrogen atoms to form the saturated nitride phase, but others are free of nitrogen atoms and remain $\text{Sm}_2\text{Fe}_{17}$ phase. In other words, the individual cells do not contain the average number of nitrogen atoms, for if they do there will be just one set of diffraction peaks in the X-ray diffraction pattern, and the positions of the peaks will shift to low diffraction angles as nitrogenation proceeds. However, as a matter of fact, there are two sets of diffraction peaks in the X-ray diffraction pattern; this is powerful evidence for the conclusion that the number of nitrogen atoms in crystal cells is either the saturated value or zero. With nitrogenation progressing, the number of cells occupied by nitrogen atoms increases, and the number of cells free of nitrogen atoms decreases. However, the existence of the residual nitrogen-free phase will lower the intrinsic coercive force, because it does not show uniaxial magnetic anisotropy.

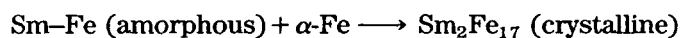
3.3. Segregation of fine α -Fe during nitrogenation

The crystallized sample still contains a small number of α -Fe particles (Fig. 4, curve a) which remain unchanged during the incubation period (Fig. 4, curve b). However, as nitrogenation proceeds, the widths of diffraction peaks of α -Fe increase (Fig. 4, curves c–e), indicating that during nitrogenation new, much finer, α -Fe particles segregate out. When studying the variation of nitrogenation of Y_2Fe_{17} with temperature, Coey *et al.* [4] found that high temperature (850 °C) leads to the decomposition of $\text{Y}_2\text{Fe}_{17}\text{N}_{3-\delta}$ into YN and α -Fe. Apparently, this is not analogous to our results. In our experiment, the segregation of α -Fe was accompanied by the formation of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$. Therefore it is suggested that the increment of α -Fe during nitrogenation does not result from the decomposition of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$.

The segregation of α -Fe particles during nitrogenation may be interpreted from the so-called surface segregation phenomenon [9]. During nitrogenation, on the surfaces of $\text{Sm}_2\text{Fe}_{17}$ particles, the residual oxygen in N_2 reacts with samarium atoms to form Sm_2O_3 which is very fine and possesses an amorphous structure. Therefore elemental iron is formed and segregates into very fine α -Fe particles which are finer than either the α -Fe particles formed during crystallization at excessively high temperature (Fig. 2, curve i) or those formed by decomposition of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ [4].

3.4. Disappearance of the metastable phase formed during crystallization

The crystallization of mechanically alloyed Sm–Fe alloy can be represented by the following solid state reaction:



It can be seen from Fig. 2 that, as crystallization proceeds, the fraction of α -Fe decreases but the fraction of $\text{Sm}_2\text{Fe}_{17}$ increases. After proper crystallization, the α -Fe phase almost disappears (see Fig. 2, curves c, g and h).

However, in some cases, as shown in Fig. 2, apart from the diffraction peaks of α -Fe and $\text{Sm}_2\text{Fe}_{17}$, three other peaks are visible on the X-ray

diffraction pattern of the samples after crystallization. When the temperature rises from 400 to 700 °C, the peaks (corresponding to the filled circles in Fig. 2) become more and more obvious. When the as-milled sample crystallized at 800 °C, these peaks are visible in the early stage, but vanish gradually as crystallization progresses, so it seems that these peaks correspond to a metastable phase. Calculations show that these peaks correspond to the $\text{Sm}_2\text{Fe}_{17}$ phase with the hexagonal $\text{Th}_2\text{Fe}_{17}$ structure.

Intermetallic compounds of the R_2Fe_{17} (where R is a rare earth metal) type may have two different structure types, *i.e.* the hexagonal $\text{Th}_2\text{Ni}_{17}$ structure type and the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure type; the only difference lies in the manner of layer stacking along the *c* axis, the former being BCBCBC..., whereas the latter is ABCABC.... For the R_2Fe_{17} alloys in which the atomic number of the rare earth is lower than that of dysprosium, the $\text{Th}_2\text{Zn}_{17}$ type is the stable structure type, but beyond $\text{R} \equiv \text{Dy}$ the stable structure is the $\text{Th}_2\text{Ni}_{17}$ type.

On the other hand, after nitrogenation, even when performed at temperatures lower than the crystallization temperature, the metastable phase formed during crystallization always disappears. Figure 4, curve a, shows the X-ray diffraction pattern of the crystallized (700 °C, 4 h) sample with some indications of the presence of the metastable phase. After full nitrogenation at 460 °C, the diffraction peaks of the metastable phase vanish (Fig. 4, curve d). However, during the incubation period, the diffraction pattern of the metastable phase remains unaltered in comparison with that of the as-crystallized sample (Fig. 4, curve b). In the middle stage of nitrogenation, the traces of the metastable phase are still visible (Fig. 4, curve c). In addition, regardless of the small amount of the $\alpha\text{-Fe}$ phase before and after nitrogenation, the metastable phase formed during crystallization always vanishes after full nitrogenation. This suggests that the appearance or disappearance of the metastable phase is irrelevant to the $\alpha\text{-Fe}$ phase.

Coene *et al.* [10] have studied $\text{Y}_2\text{Fe}_{17}\text{C}_x$ ($0 \leq x \leq 1.6$) alloy by X-ray diffraction and high energy electron diffraction techniques. Their results show that the carbon atoms can induce the structure to change from the hexagonal $\text{Th}_2\text{Ni}_{17}$ structure type to the rhombohedral $\text{Th}_2\text{Zn}_{17}$ type, *i.e.* the $\text{Y}_2\text{Fe}_{17}\text{C}_x$ with low carbon content has the $\text{Th}_2\text{Ni}_{17}$ structure type, but $\text{Y}_2\text{Fe}_{17}\text{C}_x$ with high carbon content has the $\text{Th}_2\text{Zn}_{17}$ structure type.

The structure of the above-mentioned metastable phase has not been determined. However, from the computation of the positions of the diffraction peaks, the disappearance of the metastable phase after nitrogenation and the results of Coene *et al.*, it may be deduced that the metastable phase is $\text{Sm}_2\text{Fe}_{17}$ with $\text{Th}_2\text{Ni}_{17}$ structure. After nitrogenation, the hexagonal $\text{Sm}_2\text{Fe}_{17}$ transforms into the rhombohedral $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ because of the high nitrogen content.

It is interesting that, when the as-milled sample crystallizes in an argon atmosphere, the above-mentioned metastable phase generally no longer appears. So far, this cannot be interpreted reasonably.

4. Conclusions

The Sm-Fe alloy prepared by mechanical alloying consists of an amorphous Sm-Fe phase and the α -Fe phase. After proper crystallization, the Th₂Zn₁₇-type Sm₂Fe₁₇ phase with very little α -Fe phase can be obtained. In some cases, a metastable phase forms during crystallization, and it is probably Sm₂Fe₁₇ with the hexagonal Th₂Ni₁₇ structure. After nitrogenation, the metastable phase vanishes, possibly because of the structural transformation from the Th₂Ni₁₇ type into the Th₂Zn₁₇ type caused by the introduction of N atoms. Nitrogenation is a phase transformation process consisting of the following stages: incubation period, coexistence of Sm₂Fe₁₇ and Sm₂Fe₁₇N_x and, finally, the transformation of the residual Sm₂Fe₁₇ into Sm₂Fe₁₇N_x. The existence of the incubation period can be interpreted as being due to surface oxidation. During nitrogenation, very fine α -Fe particles segregate, and this may be explained by the surface segregation phenomenon.

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