

A Study on the Magnetic Properties of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type Material Produced by a Combination of HDDR Process and Nitrogenation

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The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials were prepared by the combination consisting of the HDDR (hydrogenation, disproportionation, desorption, and recombination) process and nitrogenation or by the conventional way consisting of nitrogenation only, and the magnetic and thermomagnetic properties of the materials were investigated. The magnetic characterization of the prepared $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials was performed using a VSM. Thermal stability of the materials was evaluated using a DTA under Ar gas atmosphere. The thermomagnetic characteristics of the materials were examined using a Sucksmith-type balance. The previously HDDR-treated $\text{Sm}_2\text{Fe}_{17}$ parent alloy was found to be nitrogenated more easily compared to the ordinary $\text{Sm}_2\text{Fe}_{17}$ alloy. The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination method showed a high coercivity (12.9 kOe) even in the state of coarse particle size (around 60 μm). It was also revealed that the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination has higher thermal stability with respect to the material produced by the conventional way. The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination showed an unusual TMA tracing featured with a low and constant magnetisation at lower temperature range and a peak just before the Curie temperature. This thermomagnetic characteristic was interpreted in terms of the competition between two counteracting effects; the decrease in magnetisation due to the thermal agitation at an elevated temperature and the increase in magnetisation resulting from the rotation of magnetisation of the fine grains comparable to a critical single domain size due to the decreased magnetocrystalline anisotropy at an elevated temperature.

1. Introduction

Since the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ in 1983, an extensive research effort has been made to search for new potentially useful hard magnetic materials. This search effort has brought to light a number of interesting new materials including $\text{RE}_3(\text{Fe},\text{M})_{29}$ compounds [1-3] and $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ [4-8] or $\text{Sm}_2\text{Fe}_{17}\text{C}_x$ [9-12]. Among the new potential materials, the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material has been considered to be a promising candidate for a useful permanent magnetic material because of its superior hard magnetic properties. This material is usually prepared by a solid-gas reaction between the finely milled $\text{Sm}_2\text{Fe}_{17}$ alloy and nitrogen gas. Unfortunately, this preparation route is so sluggish and not favorable in economic point of view. Therefore, a variety of effort has been made to find a cost-effective preparation route of the material. In the mean time, it has been well known [13-16] that the HDDR (hydrogenation, disproportionation, desorption, and recombination) process can transform easily the Nd-Fe-B-type material with coarse microstructure to the material with fine microstructure. This HDDR behavior has been found to take place in $\text{Sm}_2\text{Fe}_{17}$ alloy as well [17, 18]. Applying the HDDR process to the $\text{Sm}_2\text{Fe}_{17}$ parent alloy prior to the nitrogenation may result in a fine microstructure containing a great grain

boundary area which can act as an effective diffusion path for the nitrogen atom during the nitrogenation. It is, therefore, expected that the HDDR process can be used as an effective pre-treatment for an easy preparation of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material.

In the present study, the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material has been prepared using the combination consisting of the HDDR process and nitrogenation and its magnetic and thermomagnetic properties have been investigated and compared with those of the material produced by a conventional method consisting of nitrogenation only. The thermal stability of the material produced by the combination has also been examined.

2. Experimentals

$\text{Sm}_2\text{Fe}_{17}$ parent alloy for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material was produced by an induction melting of the high purity component elements, Sm (99.95%) and Fe (99.99%) under an Ar gas atmosphere. Composition of the alloy used in the present study was 10.1 at.% Sm and 89.9 at.% Fe, and this was slightly iron-excess with respect to the 2:17 stoichiometry. This iron-excess composition was chosen to avoid the formation of unnecessary Sm-rich phase such as SmFe_3 . The prepared alloy ingot was homogenised at

1000°C for 2 weeks under Ar gas atmosphere. In order to prepare the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material using the combination of HDDR and nitrogenation, the homogenised alloy was crushed into a powder with particle size of around 60 μm and then subjected to HDDR process. Hydrogenation of the alloy was carried out by heating the sample under hydrogen gas (H_2 pressure: 1.4 bar) up to disproportionation temperature of 750°C, at which the sample was held for 2 hrs for the disproportionation. Recombination of the disproportionated material was achieved by evacuating the system for 2 hrs at the same temperature. After completion of the recombination, the sample was furnace-cooled down to 450°C. As soon as the temperature arrived at this point a nitrogen gas was introduced into the system for nitrogenation, and the HDDR-treated material was nitrogenated (N_2 pressure: 1.8 bar) for 12 hrs at this temperature. Meanwhile, the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material was also prepared by a conventional way consisting of nitrogenation only. The homogenised alloy was crushed into a powder with finer particle size of around 20 μm and then nitrogenated (N_2 pressure: 1.8 bar) straightaway at 450 °C or 475°C. Magnetic characterisation of the prepared $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials was performed using a VSM after pulsing (45 kOe). Thermomagnetic characteristics of the materials were examined using a Sucksmith-type balance [19] with an applied field of 0.8 kOe. Phase analysis of the materials under various conditions was performed by an XRD ($\text{Cu K}\alpha$). Thermal stability of the prepared $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials was evaluated using a DTA under Ar gas atmosphere.

3. Results and Discussion

3.1 Formation of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase

The formation of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ was assessed by thermomagnetic analysis (TMA) using the Sucksmith-type balance. The TMA tracing for the material prepared by the conventional way at 450°C for 17 hrs is shown in Fig. 1. As can be seen, two deflections take place on heating at around 120°C and around 470°C, respectively (see (a) in Fig. 1). The deflection appeared at lower temperature corresponds to the Curie temperature of the non-nitrogenated $\text{Sm}_2\text{Fe}_{17}$ phase and the one at higher temperature to the Curie temperature of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase. This result indicates that full nitrogenation has not been achieved under the condition used. In order to prepare a fully nitrogenated material by the conventional way, the powder material was nitrogenated at slightly higher temperature of 475°C for 12 hrs, and the TMA tracing for this material is also presented in Fig. 1. It appears that only one deflection is observed at around 470°C (see (b) in Fig. 1) corresponding to the Curie temperature of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$, and this indicates that the material was fully nitrogenated under the condition used. The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials were also prepared by the combination consisting of HDDR process and nitrogenation. The HDDR treated material was nitro-

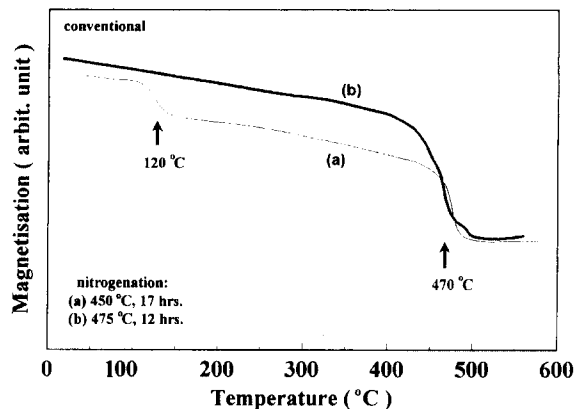


Fig. 1. TMA tracings for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials produced by the conventional way.

genated at 450°C for 12 hrs. TMA tracing for this material is shown in Fig. 2. It appears that the material produced by the combination shows a significantly different behaviour on heating in the TMA tracing. On heating the magnetisation remains unexpectedly almost constant up to around 375°C, from which it begins to increase and shows a peak just below the Curie temperature of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase. This unusual behaviour is to be discussed in detail in section 3.4. Formation of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase in this case can be confirmed clearly by the TMA tracing on cooling. As can be seen, the material has been fully nitrogenated under the condition used. It should be noted that the particle size of the material for the combination method (60 μm) is much coarser than that for the conventional way (20 μm). It can be concluded, therefore, that the combination consisting of HDDR and nitrogenation leads to a much easier preparation of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material with respect to the conventional way. This may be attributed to the greater grain boundary area due to the fine microstructure obtained by the HDDR treatment.

3.2 Magnetic properties of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials

The magnetic properties of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials

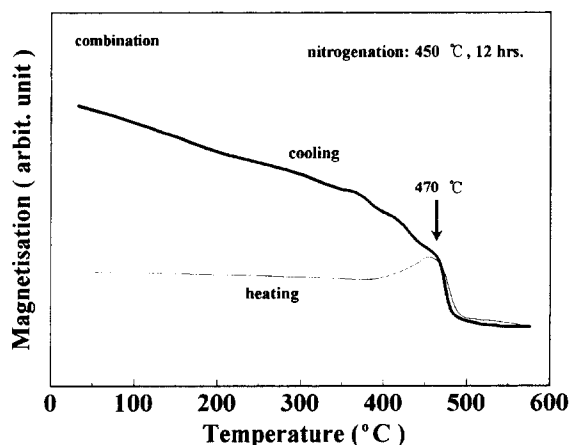


Fig. 2. TMA tracings for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination.

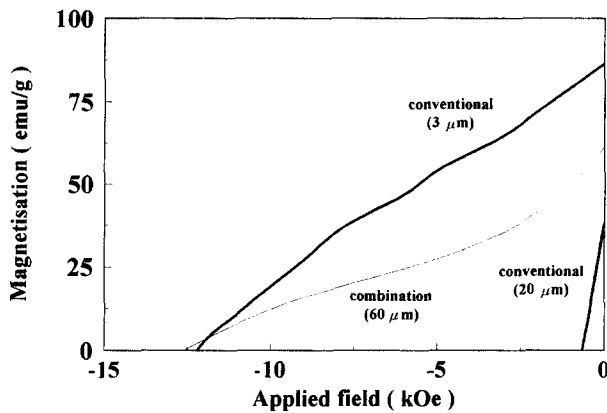


Fig. 3. Demagnetisation curves of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials produced by different ways.

prepared by the combination or the conventional way were measured using a VSM and the results are shown in Fig. 3. The powder materials used for measuring the magnetic properties have different particle size according to the preparation route. The material produced by the combination has particle size around $60 \mu\text{m}$ and the one by the conventional way has $20 \mu\text{m}$, respectively. It can be seen that the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination has high coercivity (12.9 kOe) even in the state of coarse particle size. Whereas the material produced by the conventional way exhibits very low coercivity even though its particle size is much smaller with respect to the material produced by the combination. The high coercivity of the material produced by the combination even in the state of coarse particle can be explained by the microstructure of particle consisting of very fine grains comparable to its critical single domain size ($0.3 \mu\text{m}$) due to the HDDR process. The low coercivity of the material produced by the conventional way may be attributed to the particle consisting of probable single grain ($20 \mu\text{m}$) far greater than the critical single domain size. However, the coercivity of this material may probably be enhanced if the particle size is further reduced. The demagnetisation curve of the material milled down to around $3 \mu\text{m}$ is also shown in Fig. 3. The coercivity is found to be as high as the value of the material produced by the combination. It can be concluded, therefore, that the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination can have high coercivity (12.9 kOe) even in the state of coarse particle size, and this is very useful feature in practical point of view. It has also been found that the coercivity of the material produced by combination depends on the HDDR condition as shown in Fig. 4. The peak coercivity of the material disproportionated for 1 hr. appears to be much lower than that of the material disproportionated for 2 hrs. This may be attributed to the incomplete disproportionation of hydrogenated material during the HDDR treatment.

3.3 Thermal stability of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials

It should be interesting to see if there is a difference in

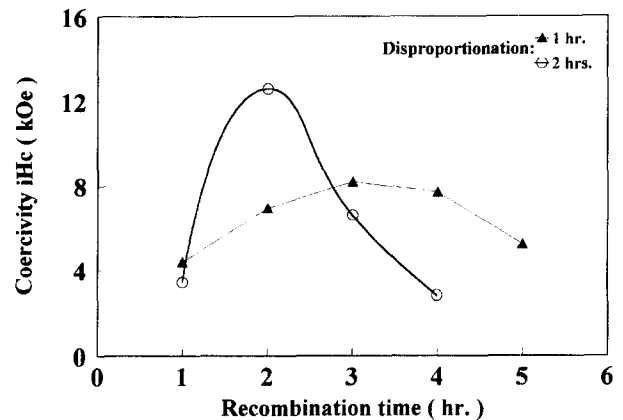


Fig. 4. Variation of intrinsic coercivity as a function of recombination time during the HDDR for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials produced by the combination.

thermal stability of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material depending on the preparation method. Fig. 5 shows the DTA tracings carried out under Ar gas for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials produced by different ways. On heating from room temperature up to 800°C a sharp exothermic peak appears at 620°C or 660°C , respectively. These exothermic peaks are corresponding to the disproportionation of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material into a mixture of SmN and α -iron. This was confirmed by XRD (Fig. 6) performed on the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material (conventional) heated up to 700°C and then cooled under Ar gas. The present results indicate that the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination has higher thermal stability with respect to the material produced by the conventional method.

3.4 Thermomagnetic characteristics of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials

It should be noted here that as stated earlier in Fig. 1 and Fig. 2 the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination method shows a distinct TMA tracing from that of the material produced by the conventional way. Magnetisation of the material remains almost constant up to around 375°C and then shows a peak just before the

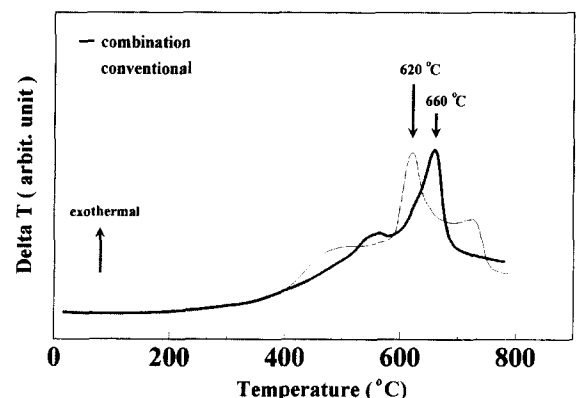


Fig. 5. DTA tracings for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials produced by different ways.

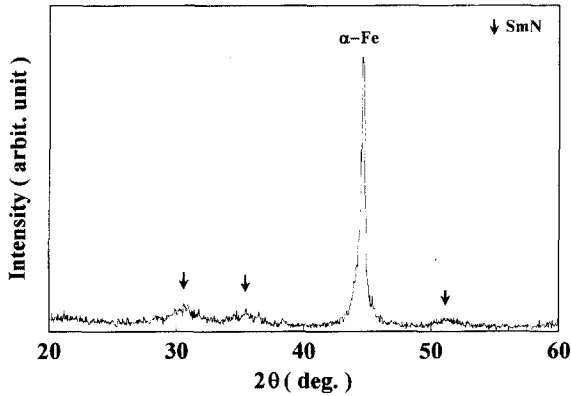


Fig. 6. X-ray diffraction spectrum for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material (conventional) heated up to 700°C .

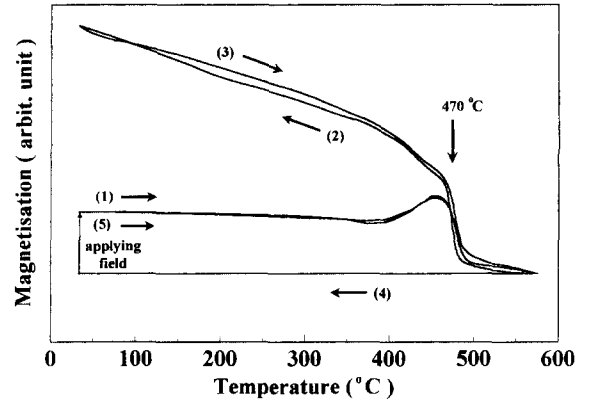


Fig. 7. TMA tracings for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material (combination) under various conditions; (1) first heating, (2) cooling under applied field, (3) second heating after cooling under applied field, (4) cooling without applied field, and (5) second heating after cooling without applied field.

Curie temperature (see (1) in Fig. 7). The TMA tracing on cooling from above the Curie temperature is found not to trace the change observed on heating. Instead a typical ferromagnetic behaviour, in which a magnetisation increases gradually with decreasing temperature, is observed (see (2) in Fig. 7). The sample cooled down to room temperature under the applied field after the first run was subjected again to the second heating TMA, and it appears that the obtained tracing is different from that of the first run, rather almost identical to that during the cooling under applied field (see (3) in Fig. 7). It should be interesting, then, to examine the TMA tracing on the second heating for the sample cooled down from above the Curie temperature without applied field after the first run, and the result of this run is also shown in Fig. 7. It is notable that the TMA tracing on the second heating after

cooling without applied field shows an almost identical tracing to that of the first heating (see (5) in Fig. 7).

We here explain the distinct TMA character of the material produced using the combination in a way proposed by the model shown in Fig. 8. In order to well understand the thermomagnetic character of the material produced by the combination, it is important to notice the microstructural and magnetic domain feature of the material. It is obvious [17, 18] that each particle of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination method may consist of very fine grains comparable to its critical single domain size (around $0.3 \mu\text{m}$) due to the previous HDDR treatment. The microstructure and domain structure

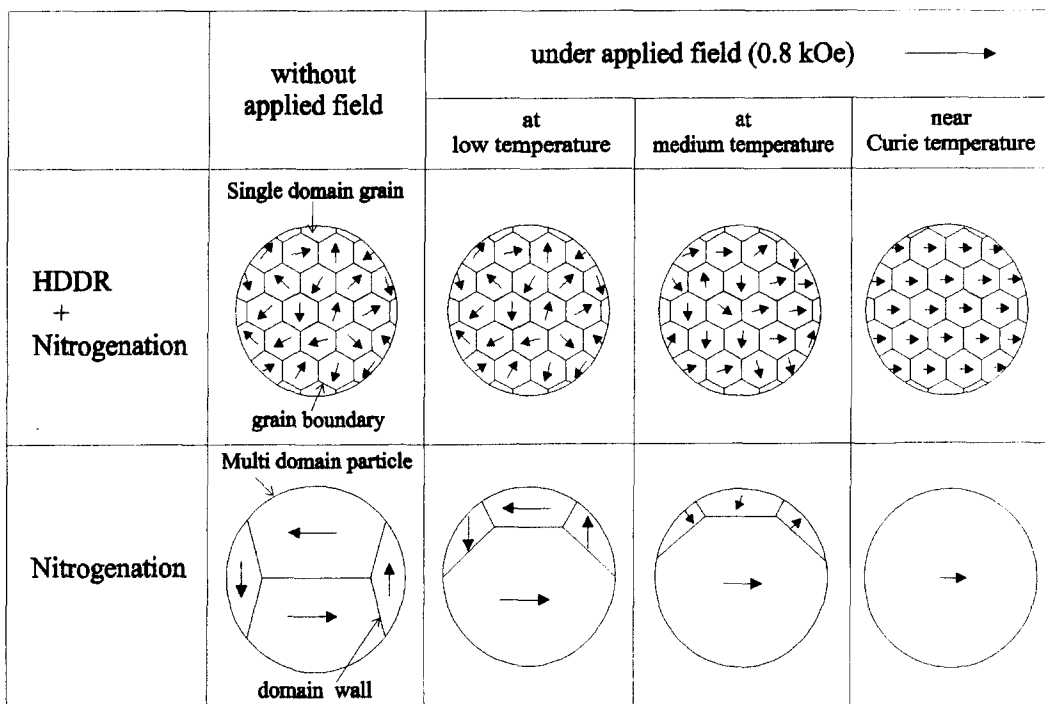


Fig. 8. Schematic diagram showing the change of magnetic domain structure during the TMA.

of the material produced by the combination is, therefore, expected to be like that proposed in Fig. 8, in which the magnetisation of each grain points randomly. When this material is placed under a weak applied field (0.8 kOe) at lower temperature, little magnetisation may be observed because there is no magnetic domain wall to move and the applied field is too weak to rotate the magnetisation of grains along the applied field. The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material is known to have an exceptionally high magnetocrystalline anisotropy [20]. When the material is heated up to a moderate temperature under applied field, two effects counteracting each other will take place. There will be a decrease in magnetisation due to a thermal agitation of the magnetic moment. At the same time, as the temperature increases the magnetocrystalline anisotropy will be reduced and this will give rise to an easy rotation of magnetisation of the grains along the applied field, leading to an increase in magnetisation. These two effects counteract each other, thus no significant magnetisation change may be observed up to a moderate temperature. If the sample is heated further toward the Curie temperature, the magnetisation of each grain will be reduced further, and at the same time the magnetisation rotation along the applied field may become much easier and a significant increase in magnetisation may take place. The latter may be dominant in the competition at an elevated temperature, thus leading to an increase in magnetisation. When the sample is heated close to the Curie temperature the magnetisation decrease due to the thermal fluctuation may become more dominant, and this may be responsible for the appearance of a peak just below the Curie temperature as shown in Fig. 2 or Fig. 7. It can be said, therefore, that the magnetisation increase just below the Curie temperature is a different kind of manifestation of the Hopkinson effect [21].

The TMA tracing of the cooling under applied field showed a different behaviour from that of the heating, and this can be explained in the way described below. When the sample is heated above the Curie temperature the atomic moments of the material will be arranged in a paramagnetic mode. If the sample is cooled down, these randomly oriented moments will be aligned along the applied field on cooling through the Curie temperature. As the temperature decreases, every magnetisation of grains tends to turn back to its nearest easy magnetisation direction. This means that magnetisations of all grains distribute more or less in favourable fashion with respect to the applied field. A great degree of alignment of each grain magnetisation may, therefore, be maintained throughout the cooling. Under this circumstance, the magnetisation increase on cooling due to the reduced thermal agitation may be dominant. This phenomenon may explain the typical gradual increase in magnetisation on cooling under applied field as shown in Fig. 7.

The TMA tracing for the sample previously heated above the Curie temperature and then cooled without

applied showed an identical result with that of the first heating of TMA. In this particular case, the atomic magnetic moments in each grain orient its easy magnetisation direction on cooling through the Curie temperature and the magnetic domain structure at room temperature may become random, which may be the same as that before subjecting to the first run. Thus, the second heating TMA tracing should show an identical trend with that of the first run as shown in Fig. 7. It seems that there is a small increase in magnetisation on applying the field ((1), (5) in Fig. 7), and this may be attributed to the fact that some of the recombined grains may be large enough to have magnetic domain walls in them. These domain walls may be moved easily by the applied field.

The thermomagnetic characteristic of the material produced by the combination was compared with that of the material produced by the conventional way. The TMA tracing performed under the same condition for the material produced by the conventional way showed different trend from that of the material produced by the combination. The TMA tracing for the conventionally prepared material showed a typical ferromagnetic character as shown in Fig. 9. The TMA tracings on the second heating appeared to show identical results with that of the first run regardless of whether the sample was cooled under or without applied field after the first run.

In this material each particle may consist of a large single grain containing multiple magnetic domains, and its domain magnetisation before subjecting to TMA may be distributed randomly as suggested in Fig. 8. When this material is placed under applied field, the domain wall may be moved easily and the favourably oriented domain may grow and predominate in the domains. This will result in a significant magnetisation on applying magnetic field at room temperature. As the temperature increases, the two counteracting effects discussed previously, of course, compete with each other. However, the increase in

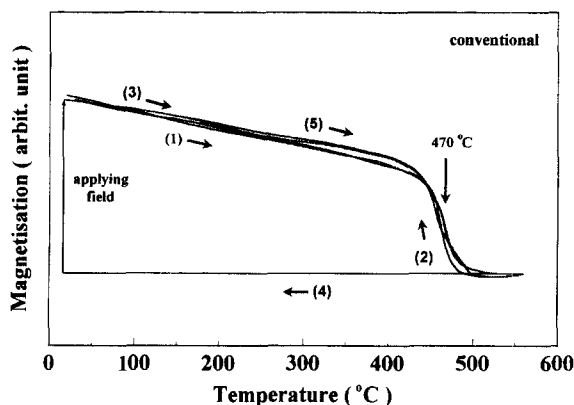


Fig. 9. TMA tracings for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material (conventional) under various conditions; (1) first heating, (2) cooling under applied field, (3) second heating after cooling under applied field, (4) cooling without applied field, and (5) second heating after cooling without applied field.

magnetisation resulting from the magnetisation rotation of each domain due to the decrease in magnetocrystalline anisotropy at an elevated temperature may not be significant. The reason for this can be explained as follows. As soon as the magnetic field is applied at room temperature the domain walls move and majority of the region in the particle may be occupied by the favourably oriented domain. Magnetisation of the grown favourable domain may be almost parallel to the applied field as suggested in Fig. 8. Thus, the contribution to magnetisation increase due to the magnetisation rotation may be resulted mainly from the unfavourably oriented small domains. This contribution may be very small, thus the magnetisation decrease due to the thermal agitation at an elevated temperature may become dominant all the way. This may explain the typical TMA tracing of the first run as shown in Fig. 1 or Fig. 9. The identical TMA tracing on the second heating after the cooling from above the Curie temperature under the applied field can be explained in the same way as discussed previously for the material produced by the combination. The TMA tracing on the second heating after the cooling without applied field also shows an identical trend as shown in Fig. 9. This can be explained easily by considering the fact that on cooling from above the Curie temperature without applied field the magnetic domain structure returns to its initial pattern before subjecting to the first run because of the absence of constraining applied field.

4. Conclusions

The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ materials were prepared by the combination consisting of HDDR process and nitrogenation or by the conventional way, and their magnetic and thermomagnetic properties of the materials were investigated. The previously HDDR-treated $\text{Sm}_2\text{Fe}_{17}$ parent alloy was found to be nitrogenated more easily compared to the ordinary $\text{Sm}_2\text{Fe}_{17}$ alloy. The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination method showed a high coercivity (12.9 kOe) even in the state of coarse particle size (around 60 μm). It was also revealed that the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination has higher thermal stability with respect to the material produced by the conventional way. The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ material produced by the combination showed an unusual TMA tracing featured with a low and constant magnetisation at lower temperature range and a peak just before the Curie temperature. This thermomagnetic characteristic was interpreted in terms of the competition between two counteracting effects; the decrease in magnetisation due to the thermal agitation at an elevated temperature and the increase in magnetisation resulting from the rotation of magnetisation of the fine grains comparable to a critical single domain size due to the decreased magnetocrystalline

anisotropy at an elevated temperature.

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