

## Study on the Effects of Hydrogen Decrepitation on the Formation of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type Material

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In an attempt to find an effective production way of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material, the  $\text{Sm}_2\text{Fe}_{17}$ -type alloy with chemical composition of Sm 22.7 wt.%, Fe 72.3 wt.%, Nb 5.0 wt.% was subjected to a HD (hydrogen decrepitation) treatment prior to a nitrogenation, and its effect on the formation of the nitride material was investigated. The nitrogenation behaviours of the alloy were investigated using a TPA (thermopiezic analysis), TMA, and DTA under nitrogen gas, and XRD. It has been found that the previous HD treatment significantly facilitated the formation of  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type nitride, and this was accounted for by the clean surface and the finer particle size of the powder caused by the HD treatment. It has also been found that the hydrogen atoms existing in the initial HD-treated alloy were removed almost completely during the nitrogenation. The heat output associated with the nitrogenation of the previously HD-treated alloy was found to be significantly smaller than that of the as-cast alloy.

### 1. Introduction

Coey *et al.* [1, 2] discovered that the magnetic properties of a  $\text{Sm}_2\text{Fe}_{17}$  compound, which has the highest iron content of the stable compounds in the Sm-Fe system, can be changed dramatically to a magnetically hard one by an interstitial addition of a nitrogen atom. Thus obtained  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material has overall magnetic properties comparable to those of the Nd-Fe-B-type counterpart. In the period since the discovery of the nitride material, a variety of research efforts have been made to improve the magnetic properties and to develop an effective production routes [3-7]. More recently, two Japanese companies announced [8, 9] that they were going to introduce the injection moulded bonded anisotropic  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type magnet with energy product of 10~13 MGOe into market very soon. It is more likely, therefore, that this announcement may trigger off an extensive research activity in the field of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type magnetic materials. The  $\text{Sm}_2\text{Fe}_{17}$  nitride is prepared usually by a solid-gas reaction between the  $\text{Sm}_2\text{Fe}_{17}$  alloy and nitrogen gas at an elevated temperature. It is generally understood that one of the difficulties encountered in producing the nitride material is the poor kinetics of the nitride formation reaction. The  $\text{Sm}_2\text{Fe}_{17}$  alloy is, therefore, processed into a powder-like material in order to improve the reaction kinetics, and the present author reported [10, 11] that the hydrogen decrepitation (HD hereafter) treatment was an effective way of producing fine powder of the  $\text{Sm}_2\text{Fe}_{17}$  alloy. In the present study, in an attempt to find an

effective production way of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material, the  $\text{Sm}_2\text{Fe}_{17}$ -type alloy was subjected to a HD treatment prior to a nitrogenation, and its effect on the formation of the nitride material has been investigated.

### 2. Experimental Procedures

The alloy used in the present study has a chemical composition of Sm 22.7 wt.%, Fe 72.3 wt.%, Nb 5.0 wt.%. The as-cast alloy was subjected to a hydrogen decrepitation prior to nitrogenation. It was reported [10, 11] previously that the  $\text{Sm}_2\text{Fe}_{17}$ -type alloy exhibited a severe decrepitation only when the alloy was hydrogenated and then degassed repeatedly. In the present study, the alloy was hydrogenated (hydrogen pressure: 15 bar) at 300°C for 1 hour and then degassed at 450°C for 4 hours under vacuum, and these treatments were repeated four times to cause a severe decrepitation. After the HD treatment the material was kept in hydrogen-in state unless stated otherwise. The HD-treated alloy was pulverised for 1 hour using an automatic agate pulveriser in a glove box filled with high purity nitrogen gas (oxygen content in the glove box: less than 150 ppm). The as-cast alloy was also pulverised under the same condition for comparison. The mean particle size of the pulverised HD-treated or as-cast alloy measured by means of a laser particle size analysis were 43.6  $\mu\text{m}$  and 71.9  $\mu\text{m}$ , respectively. The obtained powder materials were then nitrogenated at 475°C under nitrogen gas (nitrogen pressure: ~1 bar). The nitrogenation behaviours of the alloy

were investigated using a TPA (thermopiezic analysis), TMA and DTA under nitrogen gas. The magnetic properties of the nitride material were characterised by means of VSM. Prior to the VSM measurement, the powder sample was wax-bonded and then magnetised using a pulsing field of 45 kOe.

### 3. Results and Discussion

Fig. 1 illustrates the TPA traces for the as-cast or HD-treated alloy powders (mean particle size: 71.9  $\mu\text{m}$  and 43.6  $\mu\text{m}$ , respectively) undertaken under nitrogen gas (nitrogen pressure:  $\sim 1$  bar) to show the reactivity between the  $\text{Sm}_2\text{Fe}_{17}$  alloy under different conditions and nitrogen gas. It appears that for the as-cast alloy, the nitrogen pressure in the reaction chamber begins to decrease from around 290°C and a rapid drop is observed from 480°C. These temperature may be corresponding to the points at which the as-cast alloy begins to absorb the nitrogen and most rapidly, respectively. Meanwhile, for the HD-treated alloy, the pressure drop occurs from around 170°C, and surprisingly a rapid increase in pressure is observed from around 250°C up to around 450°C. This pressure increase may be due to the desorption of hydrogen from the hydrogenated alloy. The pressure increase is stopped at around 450°C and then followed by a rapid decrease, indicating that the hydrogen desorption is almost completed at 450°C and the nitrogen absorption takes place rapidly above the temperature. It can be seen from these results that the HD treated alloy can pick up the nitrogen at significantly lower temperatures with respect to the as-cast alloy. This suggests that the HD treatment to the  $\text{Sm}_2\text{Fe}_{17}$  alloy prior to the nitroge-nation may facilitate the formation of  $\text{Sm}_2\text{Fe}_{17}$ -type nitride.

Fig. 2 shows the TMA results for the materials nitroge-nated at 475°C for 4 hours using an as-cast (a) or HD treated (b) alloy powders. It appears that for the material produced from the as-cast alloy two deflections are observed at around 150°C and around 470°C, respectively.

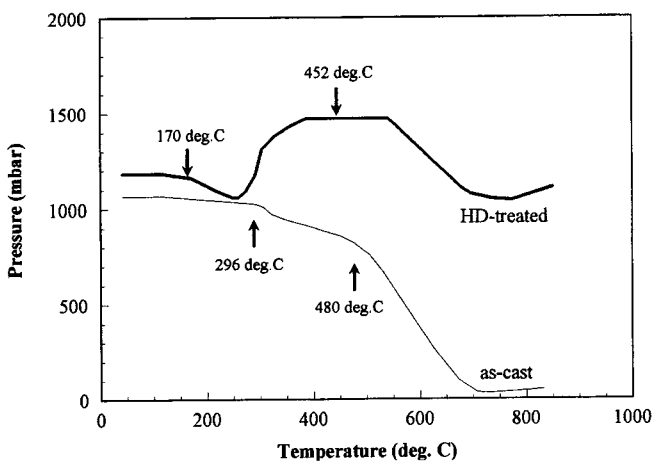


Fig. 1. TPA trace for the as-cast or HD treated alloy under nitrogen.

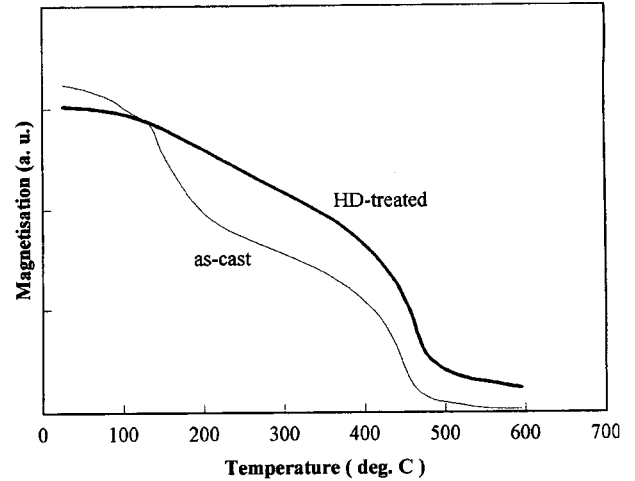


Fig. 2. TMA results for the nitrogenated materials nitrogenated for 4 hours at various temperatures using the as-cast (a) or HD treated (b) alloy powder.

Those reflections may be corresponding to the Curie temperatures of the unreacted  $\text{Sm}_2\text{Fe}_{17}$  phase and the formed  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type nitride, respectively. Meanwhile, for the materials produced using the HD-treated alloy, only one deflection at around 470°C appears, indicating that the alloy has been fully nitrogenated under the condition used. These results, together with the results of TPA shown in Fig. 1, indicate clearly that the previous HD treatment may facilitate the formation of  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type nitride.

Fig. 3 shows the XRD spectra for the materials nitroge-nated under identical condition (475°C for 4 hours) using the as-cast or HD-treated alloy. Also included in Fig. 3 is the spectrum for the as-cast alloy for comparison. It can be seen that the nitride produced from the HD-treated material has major diffraction peaks moved toward lower angle with respect to the as-cast alloy. This indicates that the HD-

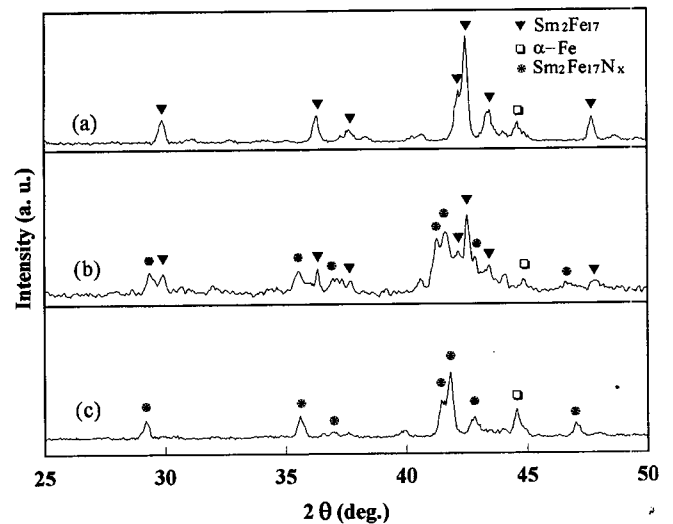


Fig. 3. XRD spectra for the materials nitrogenated under identical condition; (a) as-cast, (b) nitrogenated using the as-cast alloy, and (c) nitrogenated using the HD-treated alloy.

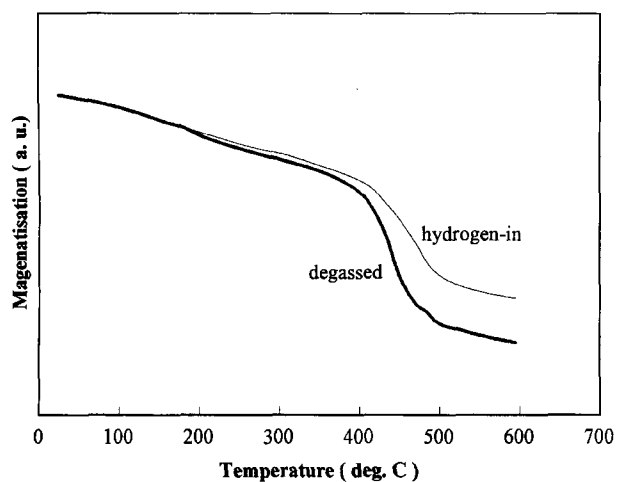


Fig. 4. TMA results for the materials nitrogenated at 475°C for 4 hours using the HD treated material with hydrogen-in or the one with hydrogen-out.

treated alloy has been fully nitrogenated under the condition used. Meanwhile, the material nitrogenated using the as-cast alloy shows split diffraction peaks. This indicates that the material has been partially nitrogenated, and the unreacted  $\text{Sm}_2\text{Fe}_{17}$ -type and formed  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type phases coexist. These results also confirm that the previous HD treatment may facilitate the formation of  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material.

It may be interesting to see whether the presence of hydrogen atoms in the initial HD-treated material prior to a nitrogenation affects the formation of nitride. The HD-treated material under hydrogen-in or degassed state was nitrogenated at 475°C for 4 hours, and TMA was performed for the nitrogenated materials (Fig. 4). It is worth noting that the TMA curves show no significant difference between the two materials. This result indicates that the presence of hydrogen atom in the HD-treated  $\text{Sm}_2\text{Fe}_{17}$ -type parent alloy prior to the nitrogenation may not influence significantly the nitrogenation reaction of the alloy. It can be concluded, therefore, that the easier formation of nitride caused by the previous HD treatment may be due simply to the decrepitation, which provides a clean surface and a finer particle size, rather than the presence of the hydrogen atoms in the alloy.

The fact that easier formation of the nitride from the HD-treated alloy may be due to the decrepitation providing a clean surface and a finer particle size is also evidenced by the TMA results for the materials nitrogenated at 475°C for 4 hours using the HD-treated materials with or without the pulverisation (for 1 hour) prior to the nitrogenation (Fig. 5). As can be seen in Fig. 5, it is apparent that the material nitrogenated after the pulverisation shows substantially higher degree of nitrogenation with respect to the material without pulverisation. These results demonstrate clearly that the easier nitride formation of the HD-treated alloy may be due mainly to the clean surface and finer size of particles, rather than the presence of the hydrogen atoms.

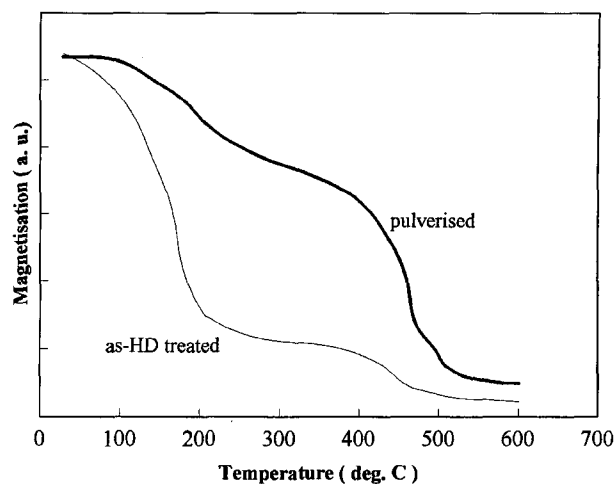


Fig. 5. TMA results for the materials nitrogenated at 475°C for 4 hours using the HD treated material with or without pulverisation.

It was revealed in Fig. 1 that the hydrogen atoms existing in the HD-treated alloy were desorbing on nitrogenation. It is, therefore, interesting to see if some of the hydrogen atoms still exist after the completion of nitrogenation. The nitride produced from HD-treated alloy (under hydrogen-in state) was subjected to a mass spectrometry under vacuum and the partial pressures of nitrogen and hydrogen gas were measured during heating. As can be seen in Fig. 6, it appears that the partial pressure of hydrogen is negligibly low, indicating that the hydrogen atoms picked-up on HD treatment has been removed almost completely during the nitrogenation.

As revealed above, the hydrogen atoms picked-up in the HD-treated alloy are removed during the nitrogenation. This indicates that the hydrogen desorption and nitrogen absorption during the nitrogenation may probably take place almost simultaneously. It can be expected, then, that the heat associated with the nitrogenation may be different depending on the initial state of the parent alloy. As-cast or HD-treated (hydrogen-in) alloy was subjected to DTA

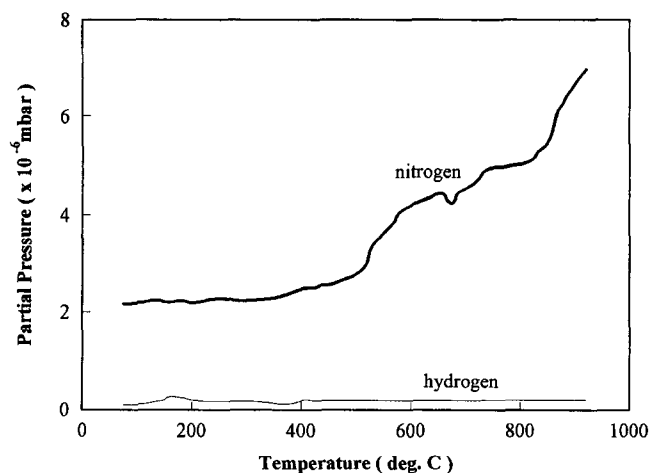


Fig. 6. Mass spectrometry results for the nitride produced from HD treated material.

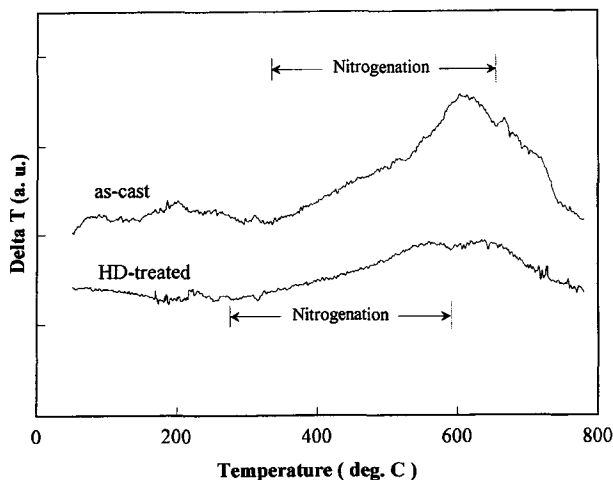


Fig. 7. DTA traces under nitrogen gas for the as-cast or the HD treated material.

under nitrogen gas, and the results are shown in Fig. 7. As can be seen, the heat output (the area under the curve corresponding to nitrogenation) associated with the nitrogenation of HD-treated material appears to be significantly smaller with respect to the as-cast alloy. This is of significance in practical point of view. The nitrogenation of  $\text{Sm}_2\text{Fe}_{17}$  alloy evolves generally a great heat, and the temperature of the sample during the nitrogenation increases unintentionally beyond the required temperature due to the heat evolved. This excessive heating may easily cause a disproportionation of the formed nitride, thus a great difficulty in the control of process variables is usually associated. The problem associated with the over-heating may be more severe in particular in the mass production of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material. It is notable, therefore, that the previous HD treatment may possibly suppress the over-heating in the mass production of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material, and thus give rise to an easy control of the nitrogenation process.

The second quadrant demagnetisation curve of the mate-

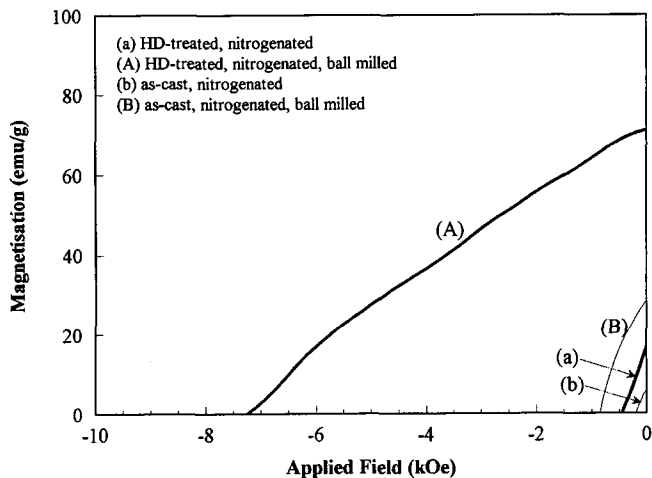


Fig. 8. Demagnetisation curves for the nitrides under various conditions.

rials nitrogenated at  $475^\circ\text{C}$  for 15 hours using the HD-treated or as-cast alloy was measured by means of VSM, and the results were shown in Fig. 8. Both of the materials produced from the HD treated or as-cast alloy exhibit poor coercivities at the as-nitrogenated state. The coercivity of the material from the HD-treated alloy was, however, improved markedly by a post-nitrogenation milling (ball milling for 24 hours). This was not the case for the material produced from the as-cast alloy. The poor coercivity of the as-nitrogenated material from the HD-treated alloy may be due to the excessively coarse particle size far larger than the critical single domain size of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material. Meanwhile, the poor coercivity of the nitride produced using the as-cast alloy at the as-nitrogenated state or even after the milling (ball milling for 24 hours) may be due simply to the incomplete nitrogenation.

#### 4. Conclusions

A HD treatment was applied to the  $\text{Sm}_2\text{Fe}_{17}$ -type alloy prior to the nitrogenation and its effect on the formation of  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type material has been examined. It has been found that the previous HD treatment significantly facilitated the formation of  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -type nitride, and this was accounted for by the clean surface and the finer particle size of the powder caused by the HD treatment. It has also been found that the hydrogen atoms existing in the initial HD-treated alloy were removed almost completely during the nitrogenation. The heat output associated with the nitrogenation of the previously HD-treated alloy was found to be significantly smaller with respect to the as-cast alloy.

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