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Study on the Formation and the Magnetic Properties of $Sm_2Fe_{17}N_x$-type Interstitial Material

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In the present study, the $Sm_2Fe_{17}N_x$-type interstitial materials have been prepared by reaction between Nb-free or Nb-containing Sm_2Fe_{17}-type alloy and N_2 gas. Nitrogenation behaviour of the Sm_2Fe_{17}-type material and disproportionation characteristics of the nitrogenated materials have been studied by means of differential thermal analysis (DTA) and thermopiezic analysis (TPA). Magnetic properties of the produced $Sm_2Fe_{17}N_x$-type interstitial materials were characterised in vibrating sample magnetometer (VSM) or thermomagnetic analyser (TMA). Epoxy-bonded or Zn-bonded $Sm_2Fe_{17}N_x$-type magnets were prepared, and their magnetic properties were investigated. It has been found that nitrogenation kinetics of the Sm_2Fe_{17}-type alloy is improved significantly by the Nb-substitution for Fe in the alloy. The Nb-substitution is also found to enhance thermal stability of the $Sm_2Fe_{17}N_x$-type interstitial material. Hard magnetic properties of the interstitial materials produced from Nb-free or Nb-containing alloy is high enough (intrinsic coercivity : over 7 kOe) for application as bonded permanent magnets. The good hard magnetic properties of the interstitial material are maintained in the epoxy-bonded magnet. Intrinsic coercivity of the Zn-bonded magnets is improved significantly as post-bonding annealing time increases.

1. Introduction

In recent years there has been a considerable interest in the $Sm_2Fe_{17}N_x$-type interstitial compound due to its high hard magnetic properties [1, 2]. The compound has a high Curie temperature (~470 ℃) [3], a high saturation magnetisation (1.5 T at 300 K) [3], and a high uniaxial magnetocrystalline anisotropy field (14 T at 300 K) [4]. This material has thus shown a potential for application as permanent magnetic material as in the case of $Nd_2Fe_{14}B$ compound, and a great deal of effort has been devoted to the production of permanent magnets using the $Sm_2Fe_{17}N_x$ interstitial compound [5-7]. The $Sm_2Fe_{17}N_x$ interstitial compound is prepared usually by a solid-gas reaction between Sm_2Fe_{17} alloy and N_2 gas or mixed gas of N_2 and NH_3 at elevated temperature. The Sm_2Fe_{17} alloy, from which the $Sm_2Fe_{17}N_x$-type interstitial compound is produced, has considerable amount of α-iron in cast condition, and this will reduce the intrinsic coercivity of the produced $Sm_2Fe_{17}N_x$-type interstitial compound unless removed prior to the nitrogenation. Addition of small amount of refractory element, such as Nb and Ta, to the Sm_2Fe_{17} alloy has been known to suppress the formation of primary α-iron during solidification, instead, lead to primary crystallisation of Sm_2Fe_{17} phase [8, 9].

In the present study, the $Sm_2Fe_{17}N_x$ interstitial compound has been prepared by reaction between the Sm_2Fe_{17}-type alloy with or without Nb and N_2 gas. One aim of the present work is to investigate the effects of Nb-substitution for Fe in Sm_2Fe_{17}-type alloy on the formation and disproportionation characteristics of the $Sm_2Fe_{17}N_x$-type interstitial material. This article has also discussed some of the results of investigating magnetic properties of the $Sm_2Fe_{17}N_x$ interstitial material prepared from the Nb-free or Nb-containing alloy and the epoxy-bonded or Zn-bonded magnets produced from it.

2. Experimental Work

Sm_2Fe_{17}-type and Nb-substituted Sm_2Fe_{17}-type alloys were prepared using an induction melting at 1400 ℃. Chemical compositions of the alloys are shown in Table Ⅰ. The as-cast Nb-free Sm_2Fe_{17} alloy was annealed at 1000 ℃ for 10 days under argon to remove an α-iron, and the Nb-containing alloy was subjected to annealing at 1000 ℃ for shorter period of 40 hours. These annealing removed completely the α-iron existed in as-cast state (This was confirmed by X-ray microanalysis in SEM and the result is not shown). The annealed alloys were pulverised for 1 hour under cyclohexane to avoid oxidation. Particle size of the powder determined by SEM was found to be 20-60 μm. $Sm_2Fe_{17}N_x$-type interstitial material was prepared by nitrogenating the pulverised material under N_2 gas (nitrogen pressure: ~1 kg/cm^2) at 430° or 475 ℃. Nitrogenation behaviour of the Sm_2Fe_{17}-type alloys and the disproportionation characteristics of the nitrogenated materials were studied by means of differential thermal analysis (DTA) and thermopiezic analysis (TPA) [10]. The TPA is a variation of thermal analysis in which a small quantity of powder sample (~60 mg) placed in a small volume chamber (~8 cc) with a solid-state pressure sensor and the chamber is filled with required gas. The sample is heated by a microprocessor-controlled furnace, and the pressure change in the sealed chamber is monitored by the pressure sensor while following a fixed heating profile. Typical heating rate in TPA is 5 ℃/min, and isotherm at certain temperature was also carried out.

Table Ⅰ. Chemical compositions of alloys (wt %)

alloy	Sm	Fe	Nb
Nb-free	23.25	balance	
Nb-containing	22.72	balance	5.00

The magnetic properties of the produced $Sm_2Fe_{17}N_x$ interstitial material were characterised by means of vibrating sample magnetometer (VSM) or thermomagnetic analyser (TMA). Prior to VSM measurement, the nitrogenated materials were milled finely using a ball mill for 24 hours, and the milled powder (average particle size was determined by SEM to be around 3 m) was bonded using candle wax. Epoxy-bonded magnets were prepared by well mixing the milled powder with 3 wt % fluid epoxy resin and then compressing the mixture into pellets using a metal die (compressing pressure: 500 kg/cm^2). The pellets were cured at room temperature for 24 hrs. Density of the epoxy-bonded magnets was 5.56 g/cm^3. Zinc-bonded magnets were prepared by well mixing the milled powder and zinc metal powder (particle size less than 45 μm) and then pressing the mixture into pellets using a metal die (compressing pressure: 1500 kg/cm^2). The prepared pellets were annealed at 430 ℃ for 1-4 hrs under nitrogen gas (N_2 pressure: 1 kg/cm^2). Density of the Zn-bonded magnets annealed at 430 ℃ for 1-4 hrs was 6.31 g/cm^3.

3. Results and Discussion

In an attempt to investigate the nitrogenation characteristics of the Sm_2Fe_{17}-type alloys with or without Nb alloys, TPA was performed for the pulverised alloy powders. Some typical TPA traces for the Nb-free or Nb-containing alloy powder obtained by continuous heating at 5 ℃/min in 0.8 kg/cm^2 of N_2 are shown in Fig. 1. As can be seen, these nitrogen TPA traces for the powder show a broad region of nitrogen absorption from around 430 ℃ to around 730 ℃. These wide ranges of temperature cover both the nitrogenation stage and the disproportionation stage. Of particular note is that pressure drop due to these reactions appears to be greater for the Nb-containing alloy with respect to the Nb-free alloy, and this phenomenon is discussed in more detail afterward (see Table Ⅱ and Fig. 4).

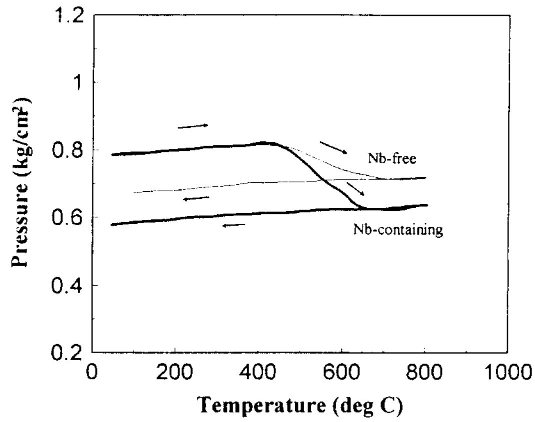

Fig. 1. TPA traces for Nb-free or Nb-containing alloy powder (heating rate at 5 ℃/min in 0.8 kg/cm^2 of N_2).

The above TPA results suggest that the two types alloys show different nitrogen absorption characteristics. It is of particular importance to understand the disproportionation character of $Sm_2Fe_{17}N_x$-type interstitial materials for the development of $Sm_2Fe_{17}N_x$-type bonded magnets. The major difficulty which is encountered in the investigation of disproportionation characteristic of the $Sm_2Fe_{17}N_x$ interstitial material using TPA is the observation that the nitrogenation and the disproportionation take place together at certain range of temperature as seen in the above results. When one examines the disproportionation characteristics, it is important, therefore, to use a proper experimental means, in which the nitrogenation stage and the disproportionation stage can be observed separately. For this purpose, a DTA tracing under nitrogen was undergone. Alloy powder was heated at rate of 5 ℃/min under nitrogen in DTA. The initial nitrogen pressure for DTA run was 0.8 kg/cm^2, and this was increased with heating up to 1.6 kg/cm^2 by thermal expansion at 800 ℃. Some DTA tracings are shown in Fig. 2. In the DTA trace, three distinct exothermic peaks appear. The large and broad exothermic peak appeared at middle temperature range of the trace may be correspond to the nitrogenation, and the peak at higher temperature to the disproportionation. There is another small exothermic peak at lower temperature, which is yet to be identified. It appears that the disproportionation for the Nb-containing alloy starts at slightly higher temperature (around 660 ℃) with respect to the Nb-free alloy (around 620 ℃). We note here that in this DTA run the material was heated continuously, so the material was not believed to be fully and optimally nitrogenated during heating up to the disproportionation temperature. Determination of disproportionation temperature using not optimally nitrogenated material can be misleading. We thus prepared fully nitrogenated materials by heating the Nb-free or Nb-containing alloy powders at 475 ℃ for 12 hrs or at 430 ℃ for 9 hrs, respectively. Materials processed under these conditions were confirmed to be fully nitrogenated by TMA (see Fig. 5). The fully nitrogenated materials were then subjected to DTA, and the results are shown in Fig. 3. The exothermic reaction taking place at higher temperature corresponds to disproportionation of the nitrogenated material, and it appears that the nitrogenated Nb-free alloy begins to disproportionate from around 610 ℃ and the nitrogenated Nb-containing alloy from around 660 ℃. This DTA results lead us to conclude that the disproportionation temperature of $Sm_2Fe_{17}N_x$-type interstitial material may be enhanced slightly by the Nb-substitution for Fe in Sm_2Fe_{17}-type alloy.

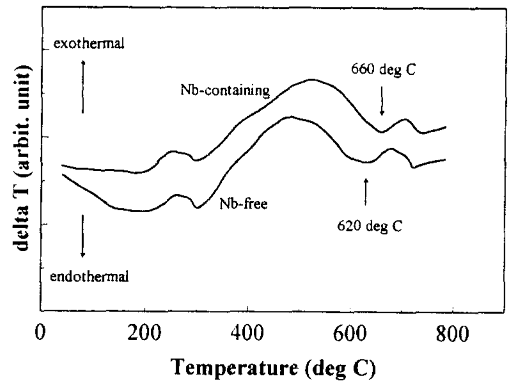

Fig. 2. DTA traces for Nb-free or Nb-containing alloy powder (heating rate at 5 ℃/min in 0.8 kg/cm^2 of N_2).

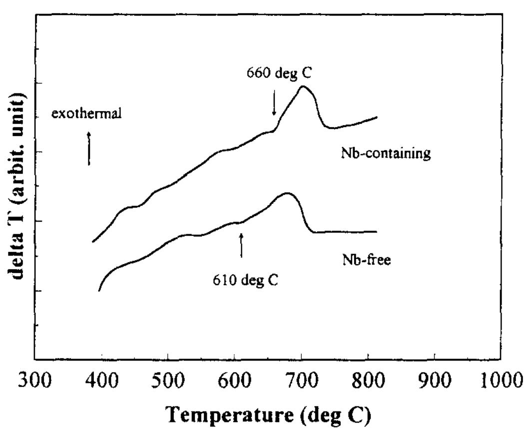

Fig. 3. DTA traces for fully nitrogenated Nb-free or Nb-containing alloy powder.

In the above TPA results (Fig. 1), we have seen that the nitrogen absorption characteristics appears to be different for the different types of alloys, and this suggests that Nb substitution may influence the nitrogenation kinetics of the Sm_2Fe_{17}-type material. We have investigated the effect of Nb-substitution on the nitrogenation kinetics using TPA. The pulverised alloy powders were heated under N_2 gas up to 430 ℃ or 475 ℃, and then held at these temperatures for isothermal heating. During the isothermal heating, variation of N_2 gas pressure was monitored as a function time. Some isotherms are shown in Fig. 4. It appears that nitrogen absorption takes place more rapidly in Nb-containing alloy than in Nb-free alloy. These results clearly indicate that the Nb-substitution can improve substantially the nitrogenation kinetics. of particular note in Fig. 4 is that pressure drop due to nitrogen absorption for the Nb-containing alloy is much greater than for the Nb-free alloy. This observation was also confirmed by an experiment measuring the weight gain due to nitrogen absorption by means of microbalance. The powder material of Nb-free or Nb-containing alloys was nitrogenated at 475 ℃ for 12 or at 430 ℃ for 9 hrs, respectively, and the weight gain due to nitrogen absorption was measured. Assuming that whole material was composed of Sm_2Fe_{17} or $Sm_2(Fe, Nb)_{17}$ stoichiometry in each alloy, we calculated the quantity of absorbed nitrogen and it is expressed as x-value as shown in Table II. It is quite surprising for the Nb-containing alloy to have such a high nitrogen content, x-value around 4.8. The precise reason for the extraordinarily high nitrogen content in the $Sm_2(Fe, Nb)_{17}N_x$-type interstitial material is not well understood at the present time.

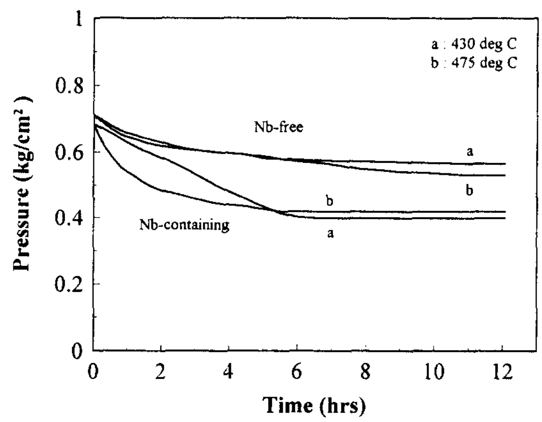

Fig. 4. Isotherms for Nb-free or Nb-containing alloy powder at elevated temperatures.

Table II. Nitrogen contents in $Sm_2Fe_{17}N_x$-type interstitial materials.

alloy	Nb-free	Nb-containing
x-value in $Sm_2Fe_{17}N_x$ or $Sm_2(Fe, Nb)_{17}N_x$	2.8 ± 0.5	4.8 ± 0.5

Fig. 5 shows the TMA result for the nitrogenated materials. The Nb-free alloy was nitrogenated at 475 ℃ for 12 hrs, and the Nb-containing alloy at 430 ℃ for 9 hrs. These TMA tracings exhibit a characteristic of a materials with single magnetic phase, of which Curie temperature is around 470 ℃ or around 460 ℃. This magnetic phase with Curie temperature of around 470 ℃ or 460 ℃ may be $Sm_2Fe_{17}N_x$ or $Sm_2(Fe, Nb)_{17}N_x$ interstitial materials. There is no deflection at around 130 ℃ corresponding to the Curie temperature of unreacted 2:17-type phase in the TMA traces. The present results indicate that the materials have been fully nitrogenated under the condition used in this study.

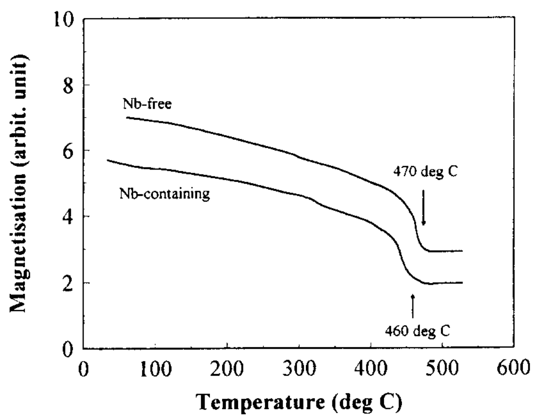

Fig. 5. TMA results for nitrogenated materials.

Recently there has been a considerable effort aimed at establishing an effective way of producing the $Sm_2Fe_{17}N_x$ interstitial material, and hydrogen treatments, such as previous hydrogenation prior to the nitrogenation [9, 11, 12] or HDDR process [13], have been found to be an useful preparation route of the $Sm_2Fe_{17}N_x$-type interstitial material. It is, therefore, worth to examine the hydrogen absorption characteristics of the Sm_2Fe_{17}-type alloys. The TPA trace for the reaction between the finely milled Nb-free or Nb-containing alloy and H_2 are shown in Fig. 6. Unlike the TPA traces of the same material heated in nitrogen, which show wide range of temperature covering both the nitrogenation reaction and the disproportionation reaction, the TPA traces in hydrogen show a clear two-stage absorption process: The first stage corresponds to hydrogen absorption and the second to disproportionation of the intermetallic into SmH and α-iron. For the Nb-free alloy, hydrogen absorption is found to take place most rapidly at around 270 ℃. Subsequent heating leads to gradual desorption of hydrogen from the hydrogenated material, and this desorption continues up to around 550 ℃, where most of the hydrogen is desorbed and only small quantity of hydrogen is retained in the material. Further heating this material above 550 ℃ leads to disproportionation into Sm hydride and α-iron. This reaction appears to take place most rapidly at around 600 ℃ and accompany a massive hydrogen absorption. The general trend for the Nb-containing alloy appears to be similar. Of particular note in these results is that the disproportionation temperature of the hydrogenated Sm_2Fe_{17}-type material is enhanced significantly by the Nb substitution for Fe in the alloy. This observation is in a good agreement with the previous result obtained from DTA [14].

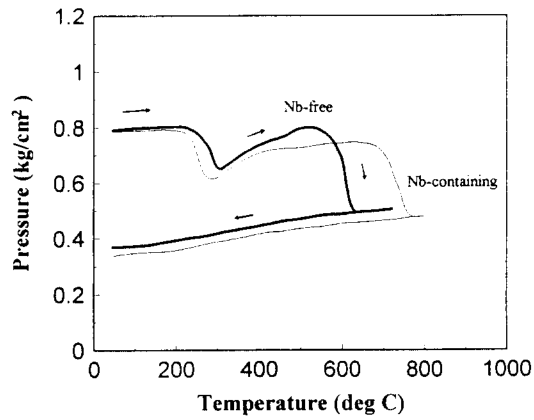

Fig. 6. TPA trace for finely milled Nb-free or Nb-containing alloy in hydrogen.

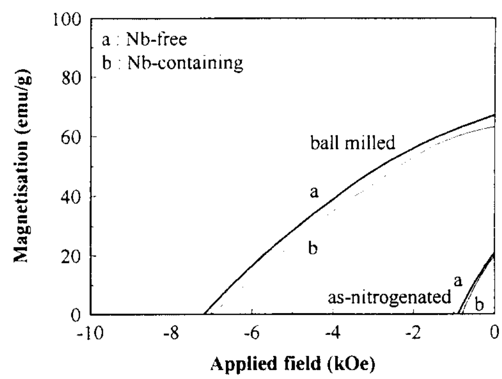

Fig. 7. Demagnetisation curves of nitrogenated materials.

The magnetic properties of nitrogenated Nb-free or Nb-containing alloys were characterised in VSM, and the results are shown in Fig. 7. The Nb-free alloy were nitrogenated at 475 ℃ for 12 hrs, and the Nb-containing alloy at 430 ℃ for 9 hrs. Some of the nitrogenated materials were milled for 24 hours under cyclohexane using a ball mill. Shown in the Fig. 7. are demagnetisation curves of the nitrogenated materials under as nitrogenated or subsequently ball milled condition. As can be seen, the as-nitrogenated material shows poor hard magnetic properties, while the ball milled material appears to have reasonably high hard magnetic properties (intrinsic coercivity of over 7 kOe). Remanence and intrinsic coercivity of the ball milled material produced from Nb-containing appears to be slightly lower than those of the material from Nb-free alloy. The lower remanence of the material produced from Nb-containing alloy may be attributed to the presence of nonmagnetic $NbFe_2$ phase. The degradation of remanence and intrinsic coercivity due to Nb-substitution is negligible in practical point of view. The ball milled materials are thought to be suitable for application as resin-bonded or soft metal-boned magnets.

Fig. 8 shows the second quadrant demagnetisation curve of 3 wt% epoxy-bonded isotropic Sm_2 (Fe, Nb)$_{17}$N$_x$ magnet produced from Nb-containing alloy. The hard magnetic property of the nitrogenated material is maintained without any significant degradation. Fig. 9 shows variation of the second quadrant demagnetisation curve of 20 wt% Zn-bonded isotropic Sm_2 (Fe, Nb)$_{17}$N$_x$ magnets as a function of post-pressing annealing time at 430 ℃. It appears that remanence of the bonded magnets is not improved significantly. Intrinsic coercivity is, however, enhanced significantly as the annealing time increases, and this may be explained by the formation of a paramagnetic Zn_xFe_y secondary phase between the Sm_2 (Fe, Nb)$_{17}$N$_x$ particles [5, 7] and improvement of surface smoothness by the annealing.

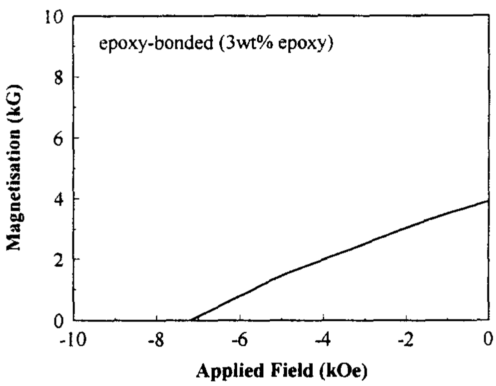

Fig. 8. Demagnetisation curve of epoxy-bonded isotropic Sm_2 (Fe, Nb)$_{17}$N$_x$ magnet.

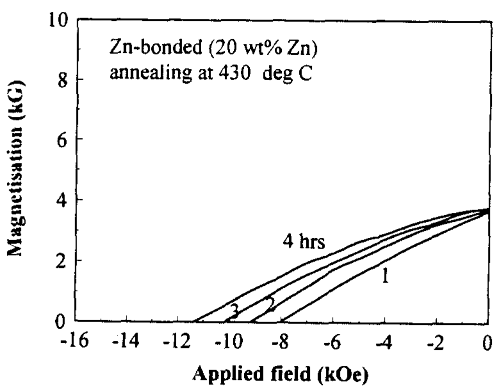

Fig. 9. Demagnetisation curves of Zn-bonded isotropic Sm_2 (Fe, Nb)$_{17}$N$_x$ magnets.

4. Conclusion

$Sm_2Fe_{17}N_x$-type interstitial materials have been prepared by reaction between Nb-free or Nb-substituted Sm_2Fe_{17}-type alloy and N_2 gas. Nitrogenation behaviour of the Sm_2Fe_{17}-type materials and disproportionation characteristics of the nitrogenated materials have been studied. Magnetic properties of the produced $Sm_2Fe_{17}N_x$-type interstitial materials and epoxy- or Zn-bonded magnets produced from them were investigated. It has been found that nitrogenation kinetics of the Sm_2Fe_{17}-type alloy is improved significantly by the Nb-substitution for Fe in the alloy. The Nb-substitution is also found to enhance thermal stability of the $Sm_2Fe_{17}N_x$-type interstitial material. Hard magnetic properties of the interstitial materials produced from Nb-free or Nb-containing alloy is high enough (intrinsic coercivity: over 7 kOe) for application as bonded permanent magnets. The good hard magnetic property of the interstitial material is maintained in the epoxy-bonded magnet. Intrinsic coercivity of the Zn-bonded magnets is improved significantly as post-bonding annealing time increases.

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