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# HYDROGEN DECREPITATION AND MAGNETIC PROPERTIES OF $Sm_2Fe_{17}$-TYPE ALLOY MODIFIED WITH A SMALL ADDITION OF Nb

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*Abstract*-The hydrogen decrepitation behaviour of the $Sm_2Fe_{17}$ alloy containing 4at%Nb was examined by means of DTA and SEM metallography, and the magnetic properties of the alloy were studied by means of VSM or TMA. It has been found that a simple hydrogenation and degassing treatment for the alloy caused a poor hydrogen decrepitation. The cycle treatment consisting of repeated hydrogenation and degassing, however, caused a severe hydrogen decrepitation with a combination of intergranular and transgranular failure. The disproportionation temperature of the hydrogenated $Sm_2Fe_{17}$-type alloy was enhanced significantly by small addition of Nb. It has also been found that the Curie temperature of $Sm_2Fe_{17}$ matrix phase in the Nb-containing alloy has been enhanced by the hydrogenation, and this was attributed to the increase in interatomic distance between the neighbouring iron atoms caused by the interstitial occupancy of the hydrogen atom into the $Sm_2Fe_{17}$-type lattice. The magnetisation of the $Sm_2Fe_{17}$ alloy containing Nb was found to be lower than that of the Nb-free alloy, and this was explained by the dilution effect due to the presence of the paramagnetic $NbFe_2$ phase.

## I. INTRODUCTION

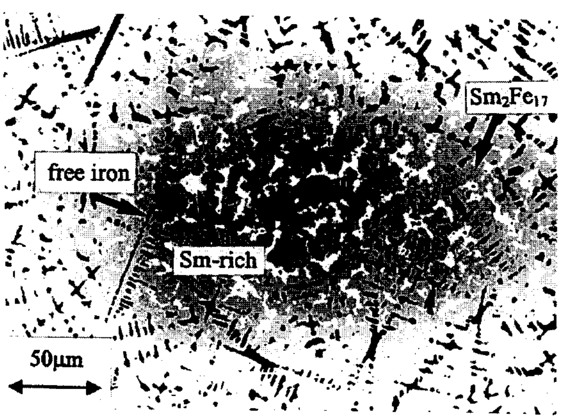
Interstitial $Sm_2Fe_{17}N_x$-type material has been considered to be a potential candidate for the permanent magnetic material because of the high Curie temperature, the improved uniaxial magnetocrystalline anisotropy, and the high saturation magnetisation which are superior or comparable to those of the NdFeB-type material. However, cast $Sm_2Fe_{17}$ alloys, from which interstitial $Sm_2Fe_{17}$ nitride is produced ( see for example reference [1-4]) , exhibit considerable inhomogeneity. This is because the $Sm_2Fe_{17}$ compound is formed by a peritectic reaction between the previously crystallised solid Fe and the liquid Sm-rich phase[5], thus leading to the presence of a considerable amount of free iron in the cast state. This will reduce dramatically the intrinsic coercivity of the interstitial nitride unless removed by a proper treatment prior to the nitriding process. The free iron is removed generally by an annealing at high temperature for a prolonged period, and this is a costly and time-consuming process. In order to overcome this practical difficulty, a modification of the cast structure of the $Sm_2Fe_{17}$ alloy by a substitution of M (M=Nb, Ta) for Fe in the alloy has been investigated[6,7]. In the present study, an $Sm_2Fe_{17}$ alloy has been modified by a small addition of Nb in an attempt to reduce the structural inhomogeneity in the cast alloy. The modified as-cast alloy will, therefore, be used directly for the production of $Sm_2Fe_{17}N_x$-type material without the necessity of a homogenising treatment which is an essential and time-consuming process for the conventional alloy. The hydrogen decrepitation behaviour and the magnetic properties of the modified alloy have been investigated. The present study has been carried out as a precursor to the study on the effect of previous hydrogenation treatment on the formation of $Sm_2Fe_{17}N_x$-type material.

## II. EXPERIMENTAL WORK

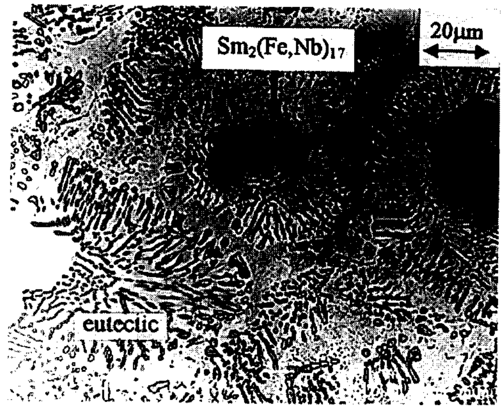
Induction melted alloys with the compositions Sm 10.5%, Fe 89.5% and Sm 10.2%, Fe 85.8%, Nb 4% (atomic %) were supplied by Rare Earth Products (Widnes, UK). The microstructure of the alloys was examined using a SEM and the phase analysis of the alloys was performed by means of X-ray microanalysis (EDX). The hydrogenation behaviours of the alloys were investigated using a DTA under hydrogen (HDTA) at a hydrogen pressure of ~1 bar, and the desorption was studied by means of mass spectrometry. The cast alloy was subjected to a hydrogenation and a degassing treatment: The hydrogenation was carried out at room temperature or at 300°C, and it was followed by a degassing treatment at 450°C (under vacuum better than 0.05 mbar). For a cycle treatment, the hydrogenation and the degassing were repeated up to four times. The hydrogen decrepitation behaviour of the alloy was investigated by means of a SEM. The hydrogen desorption behaviour of the alloy was investigated using a mass spectrometer. The particle size and its distribution of the pulverised powders were determined by means of laser particle size analysis. The magnetic properties of the as-cast or the hydrogenated material were characterised by means of VSM (vibrating sample magnetometer) or TMA (thermomagnetic analysis). For VSM measurement, the specimens were magnetised using a pulse magnetiser with field strength of 40 kOe, and then subjected to the measurement along the magnetised direction. X-ray diffraction analysis was performed using CrKα radiation.

## III. RESULTS AND DISCUSSION

The microstructures of the as-cast Nb-free or -containing alloys examined by a SEM are shown in Fig.1. It is apparent that the microstructure of Nb-free alloy consists of three phases (Fig.1 (a)). The $Sm_2Fe_{17}$ phase and the dendritic free iron are clearly visible, and a small amount of unreacted Sm-rich phase is also observed. Meanwhile, the microstructure of the Nb-containing alloy consists largely of a mixture of $Sm_2(Fe,Nb)_{17}$ matrix and eutectic phase. The X-ray microanalysis (EDX) showed that the matrix phase had a chemical composition of $Sm_2(Fe,Nb)_{17}$ stoichiometry and the eutectic was a mixture of the $Sm_2(Fe,Nb)_{17}$ phase and $NbFe_2$ Laves phase. It is worth noting that there is little evidence for the presence of free iron in the as-cast Nb-containing alloy. It is suggested, therefore, that the as-cast Nb-containing alloy can be used directly for the production of $Sm_2Fe_{17}N_x$-type material without the necessity of a homogenising treatment which is an essential and time-consuming process for the conventional alloy. The beneficial effect of the niobium additions is in agreement with previous studies[6]. The compositional analysis of the phases in the alloys obtained by means of EDX are summarised in Table 1.




(a)




(b)

Fig.1. SEM Photographs showing the microstructures of the as-cast $Sm_{10.5}Fe_{89.5}$ (a) and $Sm_{10.2}Fe_{85.8}Nb_4$ (b) alloys.

Table 1. Chemical compositions of the phases in the as-cast $Sm_{10.5}Fe_{89.5}$ and $Sm_{10.2}Fe_{85.8}Nb_4$ alloys.

| alloy | phase | | Sm | Fe | Nb | possible stoichiometry |
|---|---|---|---|---|---|---|
| | | | (at %) | | | |
| Nb-free | matrix | | 12.0 | 88.0 | | 2 : 17 |
| | free iron | | | 99.5 | 0.5 | |
| | Sm-rich | | 95.6 | 4.4 | | |
| Nb-containing | matrix | | 10.8 | 86.6 | 2.6 | 2 : 17 |
| | eutectic region | light | 11.4 | 85.1 | 3.5 | 2 : 17 |
| | | grey | | 65.2 | 34.8 | 1 : 2 |

Fig.2 shows the DTA trace carried out for the as-cast Nb-free or -containing alloys under hydrogen gas (hydrogen pressure : ~ 1 bar). On heating from room temperature to 850°C, two exothermic peaks appear at around 270°C and 570°C for Nb-free alloy and at around 250° and 740°C for Nb-containing alloy. The peaks appearing at the lower temperatures correspond to the initial hydrogen absorption and the higher temperature peaks to the disproportionation of the hydrogenated alloy into a mixture of Sm hydride and free iron. It can be seen that the hydrogen absorption temperature is not influenced significantly by the addition of Nb. It is worth noting, however, that the disproportionation temperature is increased significantly from around 570°C to around 740°C by the small addition of Nb.

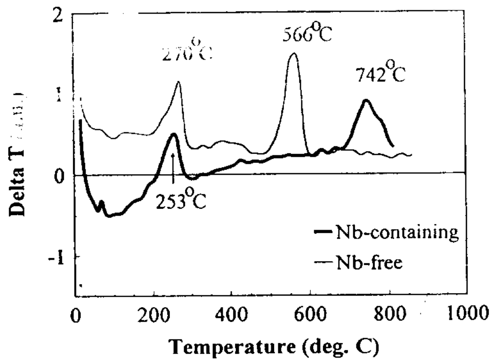



Fig.2. HDTA trace for $Sm_{10.2}Fe_{85.8}Nb_4$ alloy.

Hydrogen desorption behaviour of the alloy investigated using a mass spectrometer is shown in Fig.3. The as-cast alloy powder (mean particle size : 72 μm) was in-situ hydrogenated in the spectrometer under hydrogen gas (hydrogen pressure : ~1 bar) prior to carrying out the desorption spectrometry. It appears that the hydrogen desorption takes place from ~150°C, most rapidly at ~250°C and it is completed at ~450°C.

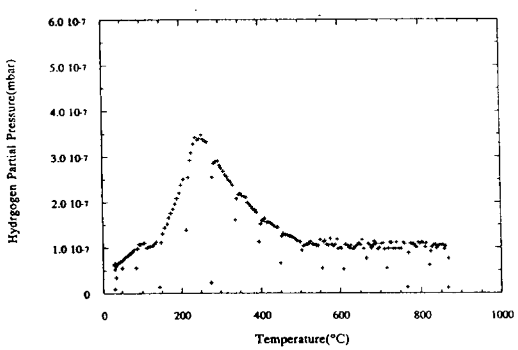



Fig.3. Mass spectrometry result showing the hydrogen desorption behaviour of the hydrogenated $Sm_{10.2}Fe_{85.8}Nb_4$ alloy.

In order to study the possible hydrogen decrepitation behaviour of the Nb-containing alloy used in the present study, the as-cast material was hydrogenated and degassed under various conditions and the morphology of the particles was examined by a SEM. The hydrogenation and the degassing conditions were based on the HDTA (Fig.2) and the mass spectrometry (Fig.3) results. Thus, the hydrogenation and degassing treatment were carried out at 300°C and 450°C, respectively. Fig.4 shows the morphology of the bulk alloy subjected to hydrogenation at 300°C for 1 hour under hydrogen gas (15 bar) and then subjected to a degassing treatment at 450°C for 4 hours under rotary pump vacuum (better than 0.05 mbar). The hydrogenated material was smeared lightly before the SEM observation It is apparent that the bulk alloy has been fractured by the hydrogenation and degassing treatment, but only intergranular cracking has occurred and there is no evidence for cracks within the matrix grains (transgranular cracks).

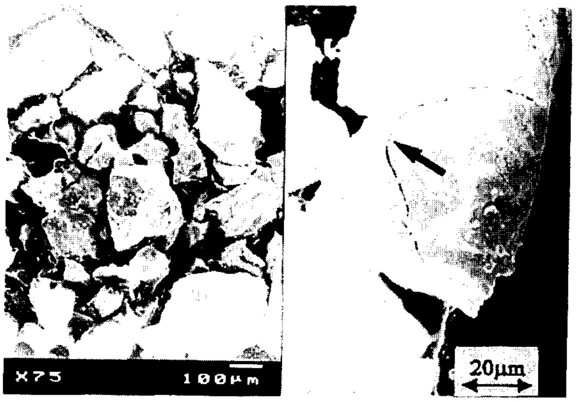
(a)　(b)

Fig.4. SEM photographs showing the morphology of the $Sm_{10.2}Fe_{85.8}Nb_4$ alloy subjected to one cycle hydrogenation and degassing treatment (a) general view (b) close examination.

The bulk alloy subjected to cyclic hydrogenation and degassing treatment (CHD) (hydrogenation at 300°C for 1 hour under hydrogen gas (15 bar) and then degassing at 450°C for 4 hours under vacuum, this cycle being repeated four times and final state of the alloy was in the hydrogenated condition) shows a clear combination of intergranular and transgranular cracking as shown in Fig.5. The bulk alloy samples subjected to less than four of these cycles showed only intergranular cracking similar to that shown in the Fig.4. The decrepitation behaviours of the alloy hydrogenated and degassed under various conditions are summarised in Table 2. It can be seen that an effective decrepitation of the alloy can be achieved only employing the CHD treatment with the number of cycles greater than four, and it will be seen that the production of fine powder for nitrogenation is facilitated significantly by employing the CHD treatment.

Table 2. Decrepitation behaviour of the alloy hydrogenated under various conditions.

| hydrogenation | | | degassing | | | number of cycle | crack |
|---|---|---|---|---|---|---|---|
| temp (°C) | pressure (bar) | time (hr) | temp (°C) | pressure (mbar) | time (hr) | | |
| 300 | 1 | 4 | | | | | intergranular |
| 300 | 15 | 4 | | | | | intergranular |
| 300 | 15 | 4 | 450 | 0.04 | 4 | 1 - 3 | intergranular |
| 300 | 15 | 4 | 450 | 0.04 | 4 | 4 | intergranular, transgranular |




(a) (b)

Fig. 5. SEM photographs showing the morphology of the $Sm_{10.2}Fe_{85.8}Nb_4$ alloy subjected to four cycle hydrogenation and degassing treatment. (a) general view (b) close examination (transgranular cracks indicated by arrows).

Fig. 6 shows the particle size distributions of the as-cast and the CHD treated Nb-containing alloys pulverised for 30 min. It appears that the particle sizes of the pulverised materials exhibit an irregular distribution in which a continuous and finite variation of particle sizes within a considerably broad range. It is clear, however, that the overall particle size of CHD treated material is significantly finer than that of the as-cast material. The mean particle sizes of the CHD treated and the as-cast materials were measured to be around 43 μm and 72 μm, respectively. This results indicate that The CHD treatment can be used as an effective means of powder preparation for the production of $Sm_2Fe_{17}N_x$-type materials.

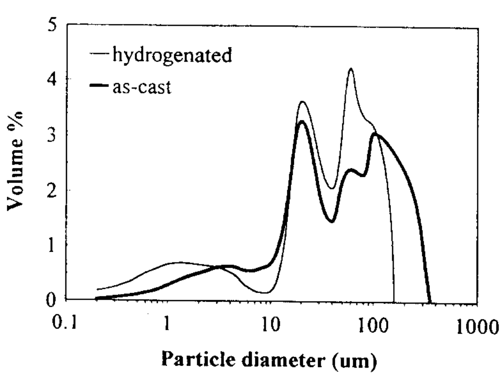



Fig.6. Particle size distributions of the as-cast and the cycle hydrogenated $Sm_{10.2}Fe_{85.8}Nb_4$ alloys pulverised for 30 min.

Fig. 7 presents the TMA traces for the as-cast and the CHD treated Nb-containing alloys. It is found that the Curie temperature of the $Sm_2Fe_{17}$-type matrix phase in the Nb-containing alloy is increased up to 231°C by the hydrogenation. The Curie temperature of $Sm_2Fe_{17}$-type alloy is believed to be related closely to the interatomic distance dependence of Fe-Fe exchange interaction. The relatively short distance between the nearest neighbouring iron atoms in the $Sm_2Fe_{17}$-type phase gives rise to a negative exchange interaction, thus low Curie temperature[8]. The introduction of interstitial hydrogen atom may lead to increase in the interatomic distance between neighbouring iron atoms, thus the increase in the exchange interaction. This increase in the exchange interaction may lead to the enhancement of the Curie temperature. X-ray diffraction analyses presented in Fig.8 show that the major reflections from the CHD treated alloy shift toward lower angles with respect to those from the as-cast alloy, indicating that the lattice of $Sm_2Fe_{17}$-type matrix phase has been expanded by the hydrogenation. The lattice expansion may result from the interstitial occupancy of hydrogen atoms into the lattice, and this supports the increase in interatomic distance between neighbouring iron atoms.

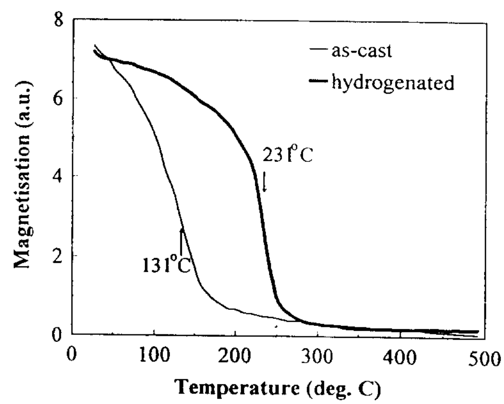



Fig.7. TMA results for the as-cast and the hydrogenated $Sm_{10.2}Fe_{85.8}Nb_4$ alloys.

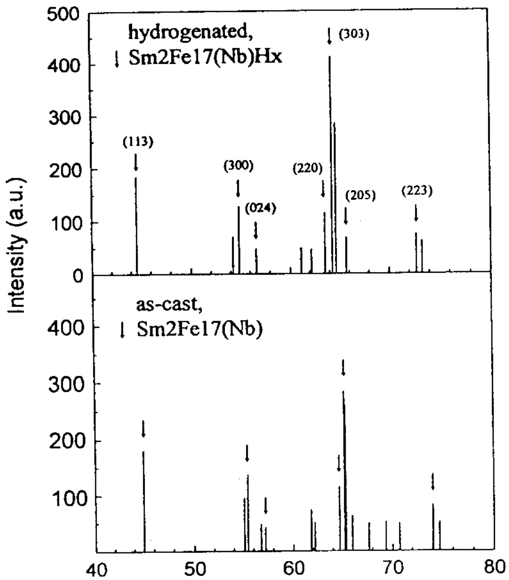



Fig.8. X-ray diffraction analyses of the as-cast and the hydrogenated $Sm_{10.2}Fe_{85.8}Nb_4$ alloys.

Fig.9 shows the 1st and 2nd quadrant of the hysteresis loop obtained by a VSM for as-cast Nb-free or -containing alloys. It appears that the magnetisation of the $Sm_2Fe_{17}$ alloy is deteriorated slightly by the small addition of Nb, and this may be attributed to the dilution effect of the magnetisation due to the presence of the paramagnetic $NbFe_2$ phase in the Nb-containing alloy.

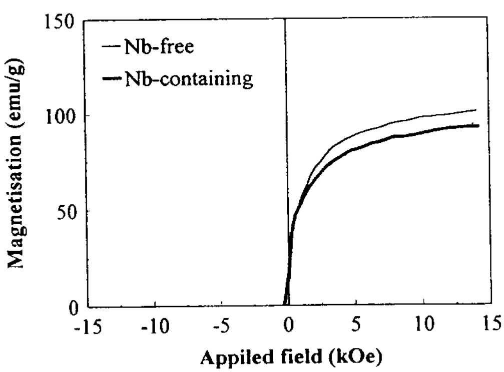



Fig.9. The 1st and 2nd quadrant of the hysteresis loops for the as-cast Nb-free or -containing alloys.

## IV. CONCLUSION

The hydrogen decrepitation behaviour and the magnetic properties of the $Sm_{10.2}Fe_{85.8}Nb_4$ alloy have been investigated, and it has been found that a simple hydrogenation and degassing treatment for the alloy caused a poor hydrogen decrepitation. The cycle treatment consisting of repeated hydrogenation and degassing, however, caused a severe hydrogen decrepitation with a combination of intergranular and transgranular failure. The disproportionation temperature of the hydrogenated $Sm_2Fe_{17}$-type alloy was enhanced significantly by small addition of Nb. It has also been found that the Curie temperature of $Sm_2Fe_{17}$ matrix phase in the Nb-containing alloy was enhanced substantially by the hydrogenation, and this was attributed to the increase in interatomic distance between the neighbouring iron atoms caused by the interstitial hydrogen atoms into the $Sm_2Fe_{17}$ -type lattice. The magnetisation of the $Sm_2Fe_{17}$ alloy containing Nb was found to be lower than that of the Nb-free alloy, and this was explained by the dilution effect due to the presence of the paramagnetic $NbFe_2$ phase.

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