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Reaction Characteristics of the $Sm_2Fe_{17-x}Ga_x$ ($x = 0, 2$) Alloy with Hydrogen and Methane Gas

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The Ga-stabilised Sm_2Fe_{17}-type alloy can hardly be disproportionated under ordinary HDDR condition. The HDDR characteristics of Ga-substituted Sm_2Fe_{17}-type alloy were examined, and, in particular, the effect of particle size on the disproportionation of the Ga-substituted alloy was investigated in detail. The reaction characteristics of the Sm_2Fe_{17}-type alloys with or without Ga-substitution with methane (CH_4) gas are also examined. The Ga-stabilised Sm_2Fe_{17}-type alloy was able to be disproportionated significantly on heating up to 800 °C under hydrogen with normal pressure. The particle size influenced significantly on the disproportionation of the Ga-substituted alloy, and the material with finer particle size (< 40 μm) was fully disproportionated on heating up to around 800 °C under hydrogen gas with normal pressure. The Ga-substituted alloy has a very sluggish recombination kinetics with respect to the alloy without Ga-substitution. The $Sm_2Fe_{17}C_X$-type carbide was stabilised significantly by the Ga-substitution for Fe in the parent alloy. While the $Sm_2Fe_{17}C_X$ was disproportionated below 800 °C the Ga-stabilised $Sm_2Fe_{15}Ga_2C_X$ carbide remained intact even on heating up to 800 °C.

1. Introduction

Together with the $Sm_2Fe_{17}N_X$ material, the $Sm_2Fe_{17}C_X$ material is considered to be a promising candidate for permanent magnet due to its high hard magnetic properties [1-5]. The ternary carbide can be prepared by a standard alloying technique (melting of constituent elements). The material can also be prepared by a solid-gas reaction between Sm_2Fe_{17} alloy and hydrocarbon such as methane, acetylene, butane, and so on. It has been well known that HDDR treatment can be used as an effective way of not only enhancing the reaction kinetics between the Sm_2Fe_{17}-type alloy and gas and also improving the coercivity of carbide by obtaining a fine grain structure [6]. As with the $Sm_2Fe_{17}N_X$ material, the main drawback of the $Sm_2Fe_{17}C_X$ material is known to be a poor thermal stability. Extensive research effort has been made to enhance the thermal stability, and it is found that the $Sm_2Fe_{17}C_X$ phase can be stabilized by a partial substitution of Fe by Ga [7-9]. The Ga substitution, however, leads to a highly enhanced stability of the 2 : 17 phase under hydrogen gas, and this causes some difficulty in application of the HDDR; the Ga-stabilised 2 : 17 phase is so stable that the phase can hardly be disproportionated under ordinary HDDR condition. It has been reported recently that the Ga-stabilised 2 : 17 phase can be disproportionated successfully with high hydrogen pressure (10 bar) [10]. The principal purpose of the present study is to investigate the effect of particle size on the disproportionation of the Ga-stabilised 2 : 17 phase. The effect of Ga-addition on the HDDR characteristics of the Sm_2Fe_{17} alloy and reaction characteristics of the alloy with methane (CH_4) gas are also examined in this article.

2. Experimental Work

Sm_2Fe_{17} and Ga-substituted $Sm_2Fe_{15}Ga_2$ alloys were prepared by an induction melting of constituent elements with high purity under Ar gas atmosphere. Prepared alloys were homogenised at 1000 °C for 1 week under Ar gas. Homogenised alloys were processed into powder with various particle sizes. HDDR characteristics and the reaction characteristics of the materials with CH_4 were examined by means of differential thermal analyser (DTA), thermopiezic analyser (TPA), and X-ray diffractometer (XRD) with Cu-Kα radiation. The DTA and TPA experiments were undertaken in a mode of closed system. Reaction chamber charged with powder sample was evacuated and then filled with hydrogen or methane gas (gas pressure : 1.8 kgf/cm^2). The system was closed throughout the experiment and the sample was heated with a heating rate of 7 °C/min.

3. Results and Discussion

Fig. 1 shows the DTA traces for the alloys (40~60 μm) with or without Ga-substitution undertaken under hydrogen gas. For the alloy without Ga-substitution, two clear exo-

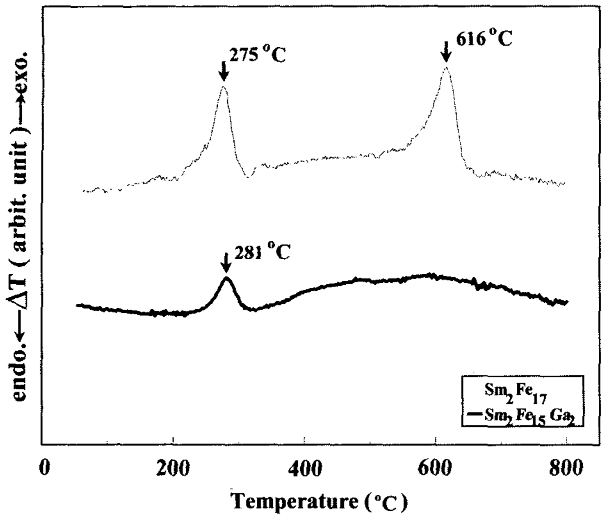

Fig. 1. DTA traces for the Sm_2Fe_{17} and $Sm_2Fe_{15}Ga_2$ alloy powders (40 μm~60 μm) under H_2 gas.

thermic peaks appear, and they are considered to be corresponding to the hydrogenation of Sm_2Fe_{17} alloy (275 °C) and to the hydrogen-assisted disproportionation of the 2 : 17 phase (616 °C). For the alloy with Ga-substitution, however, only an exothermic peak due to the hydrogenation is clearly observed at slightly raised temperature compared to the alloy without Ga-substitution, and an obvious thermal event corresponding to a disproportionation is hardly observed. This is simply because the Sm_2Fe_{17} phase was highly stabilised by the Ga-substitution.

The above DTA result seems to indicate that the Ga-stabilisd Sm_2Fe_{17}-type alloy would not be disproportionated at all in hydrogen gas. It is not clear, however, whether the Ga-stabilisd Sm_2Fe_{17}-type alloy is not disproportionated actually or it is disproportionated but with small heat flow. The precise dsproportionation behaviour can be examined better with TPA. The TPA results performed under hydrogen gas for the alloys are shown in Fig. 2. It appears that

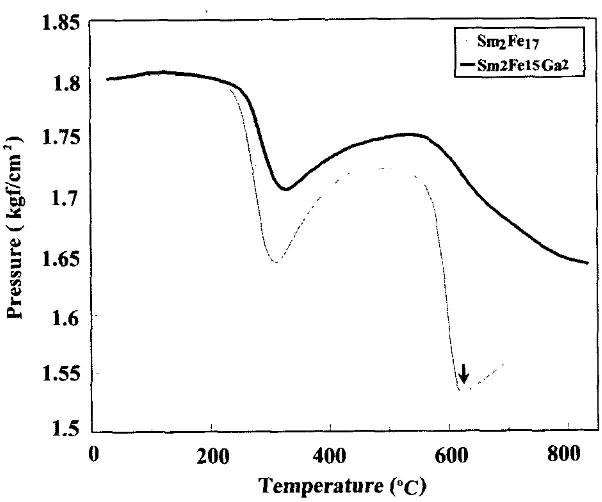

Fig. 2. TPA traces for the Sm_2Fe_{17} and $Sm_2Fe_{15}Ga_2$ alloy powders (40 μm~60 μm) under H_2 gas.

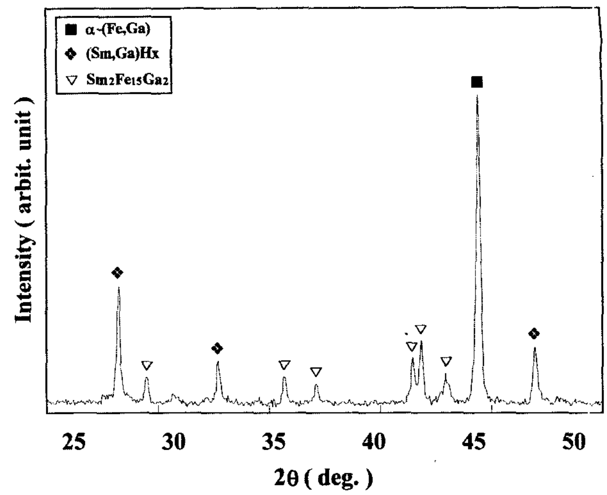

Fig. 3. XRD spectrum for the $Sm_2Fe_{15}Ga_2$ alloy powder (40 μm~60 μm) heated up to 800 °C under H_2 gas.

two pressure drops take place on heating for both the alloys, each of which is corresponding to hydrogenation and disproportionation, respectively. It is notable that while the alloy without Ga-substitution shows a rapid pressure increase (from around 620 °C) after the pressure drop due to disproportionation the alloy with Ga-substitution shows a slow but significant pressure drop from around 560 °C, and it is continued up to above 800 °C. These results indicate that the Ga-substituted alloy is quite stable and disproportionated very slowly even at higher temperature. It should be noted, however, that there is a considerable pressure drop from around 560 °C, and this indicates that the Ga-substituted alloy has been disproportionated to a great extent on heating up to 800 °C. This fact is also confirmed by XRD phase analysis of the alloy heat up to 800 °C under hydrogen gas. As can be seen in Fig. 3, a significant amount of disproportionated phases of (Sm,Ga)H_X and α-Fe are observed. This indicates that the alloy has been disproportionated considerably. Correlating this result with that of DTA shown in Fig. 1, it can be said that the Ga-stabilised alloy can be disproportionated significantly on heating up to 800 °C under hydrogen with normal pressure and the heat flow associated with disproportionation may be considerably small compared to the alloy without Ga-substitution. It can also be said that the TPA may be a more efficient tool for an investigation of disproportionation behaviour with respect to the DTA.

The above results indicate that the Ga-substituted alloy is disproportionated significantly on heating under hydrogen with normal pressure. It is expected that the disproportionation of the alloy may be influenced profoundly by its particle size. The disproportionation characteristics of the Ga-substituted alloy with different particle size was examined using DTA and TPA under hydrogen gas with normal pressure (1.8 kgf/cm^2). In DTA result (Fig. 4) an immediate thermal event associated with disproportionation is hardly observed here again even for the alloy with very fine parti-

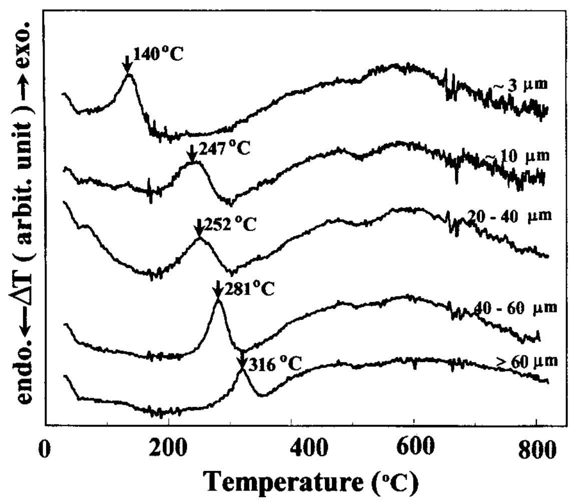

Fig. 4. DTA traces for the $Sm_2Fe_{15}Ga_2$ alloy powders with various particle sizes under H_2 gas.

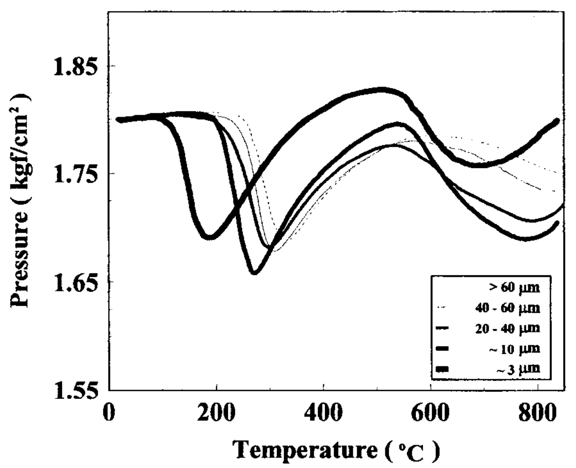

Fig. 5. TPA traces for the $Sm_2Fe_{15}Ga_2$ alloy powders with various particle sizes under H_2 gas.

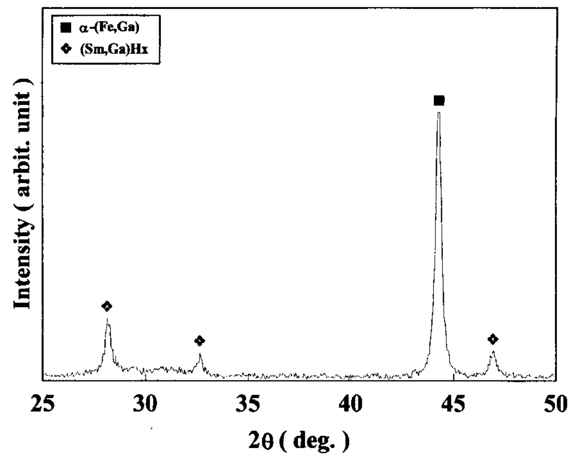

Fig. 6. XRD spectrum for the $Sm_2Fe_{15}Ga_2$ alloy disproportionated for 30 minutes at 800 °C (particle size : 20 μm~40 μm).

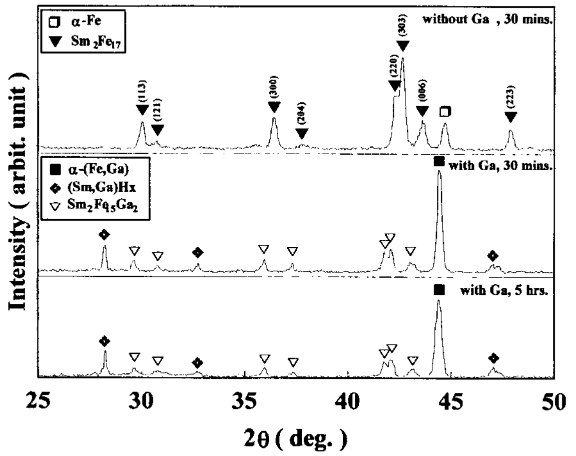

Fig. 7. XRD spectra for the Sm_2Fe_{17} and $Sm_2Fe_{15}Ga_2$ alloys recombined at 800 °C.

cle size (average size : around 3 μm). As stated earlier, the likelihood of disproportionation can be examined more precisely by TPA. As can be seen in the TPA results shown in Fig. 5, for all the materials two typical pressure drops appear. The pressure drop at higher temperature is, needless to say, due to disproportionation. Of particular note in these TPA results is that for the materials with particle size greater than 40 μm the pressure drop has not been finished up to 800 °C. However, for the materials with particle size smaller than 40 μm the pressure drop has been completed at or below around 800 °C, after that the pressure increases rapidly. These results may indicate that the material with finer particle size can be fully disproportionated on heating up to around 800 °C under hydrogen gas with normal pressure. XRD phase analysis for the alloy with finer particle size (20~40 μm) heated up to 800 °C under hydrogen gas also evidenced for this fact as shown in Fig. 6.

The fully disproportionated Ga-substituted alloy with finer particle size was recombined under vacuum and its recombination characteristics was compared with that of the alloy without Ga-substitution. Recombination characteristics of the fully disproportionated alloys examined by XRD are shown in Fig. 7. As can be seen, the fully disproportionated alloy without Ga-substitution has been nicely recombined within 30 min. On the contrary, for the Ga-substituted alloy a significant amount of disproportionated phases still exist even after long period of recombination (5 hrs). This indicates that the Ga-substituted alloy has a very sluggish recombination kinetics with respect to the alloy without Ga-substitution. Other research group reported that the Ga-substituted alloy disproportionated under high pressure hydrogen (10 bar) was completely recombined within a practically reasonable time [10]. This suggests that the recombination characteristics of the Ga-substituted alloy may be influenced significantly by the hydrogen pressure on disproportionation

The Sm_2Fe_{17}-type alloy is carburised into $Sm_2Fe_{17}C_X$-type material using the reaction mainly with a methane gas. The reaction characteristics of the alloys with or without Ga-substitution with methane gas were examined by TPA,

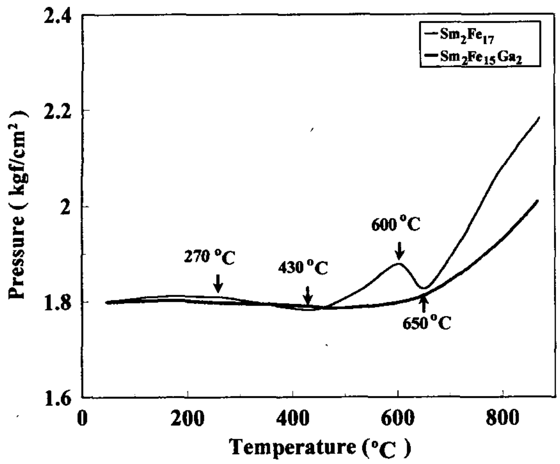

Fig. 8. TPA traces of Sm_2Fe_{17} and $Sm_2Fe_{15}Ga_2$ alloy powder (particle size : 40 μm~60 μm) under CH_4 gas.

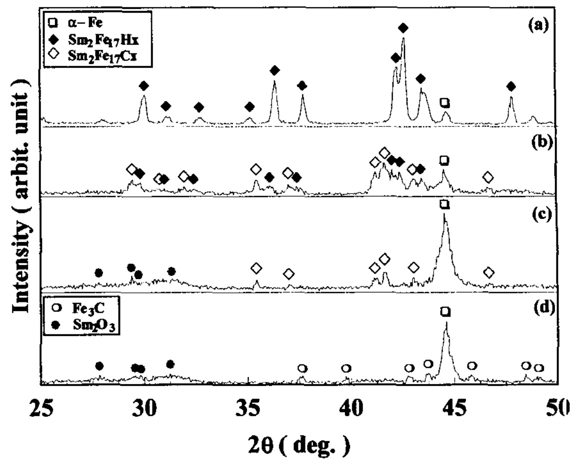

Fig. 9. XRD spectra for the Sm_2Fe_{17} alloy heated in CH_4 gas under various conditions.

and they were compared with each other. Fig. 8 show the TPA results for the alloy powders (40~60 μm) under CH_4 gas (pressure : 1.8 kgf/cm^2). As can be seen, for the alloy without Ga-substitution the pressure begins to decrease from around 270 °C up to around 430 °C, and then increases up to 600 °C. The pressure decreases again in the temperature range of 600 °C to 650 °C, after that it increases very rapidly. The methane gas is known to decompose intrinsically at around 650 °C [11]. It is thought, however, that the gas in contact with the Sm_2Fe_{17}-type alloys is decomposed into a mixture of hydrogen and carbon at significantly lower temperature of around 270 °C. The alloy powders is thought to act as a catalyst for the decomposition reaction of the methane gas. As can be expected from the decomposition reaction of methane ($CH_4 \rightarrow C + 2H_2$), decomposition of 1 mole methane produces 2 mole of hydrogen. This means that the pressure in the reaction chamber of TPA should be increased from around 270 °C. The TPA result shows, however, that pressure in the chamber decreases instead. We interpret this pressure decrease in a way that the hydrogen gas resulting from the decomposition of methane is absorbed into the alloy to form a $Sm_2Fe_{17}H_X$ hydride as soon as the decomposition takes place. This interpretation is evidenced by a phase analysis (Fig. 9(a)) of the material heated up to 430 °C. The pressure increase appeared in the range of 430° to 600 °C may be due mainly to dehydrogenation of the $Sm_2Fe_{17}H_X$ into $Sm_2Fe_{17}H_y$ (x > y). It is also supposed that at upper part of the temperature range some of Sm_2Fe_{17}-carbide ($Sm_2Fe_{17}C_X$) may be formed. Presence of a mixture of $Sm_2Fe_{17}H_y$ and $Sm_2Fe_{17}C_X$ in the alloy heated up to 590 °C (Fig. 9(b)) evidences for this interpretation. The rapid pressure drop observed in the range of 600° to 650 °C may be due to the disproportionation of $Sm_2Fe_{17}C_X$, which absorbs additional hydrogen. This explanation is evdenced by the phase analysis of the alloy heated up to 640 °C (Fig. 9(c)). $Sm_2Fe_{17}C_X$ and greater amount of α-Fe are observed, and this α-Fe may result mainly from the disproportionation of $Sm_2Fe_{17}C_X$. Some of Sm_2O_3 is also observed in the sample, and this may be formed by the oxidation of SmH_X when it was exposed to air. Finally, the rapid pressure increase from 650 °C may be due mainly to the intrinsic decomposition of methane gas. The material heated up to 800 °C consists of a mixture of α-Fe, Fe_3C and Sm_2O_3 (from oxidation of SmC_X) which resulted from full disproportionation of $Sm_2Fe_{17}C_X$ (Fig. 9(d)).

Meanwhile, as also shown in Fig. 7 the reaction characteristics of the Ga-substituted alloy with methane are different from those of the alloy without Ga-substitution. Main difference is that there is no distinctive pressure change up to around 650 °C and no pressure drop due to the disproportionation of carbide is found in particular. The alloy heated up to 450 °C exists as $Sm_2Fe_{15}Ga_2H_X$ (Fig. 10(a)), and the material heated up to 600 °C consists of a mixture of $Sm_2Fe_{15}Ga_2H_X$ and $Sm_2Fe_{15}Ga_2C_X$ (Fig. 10(b)). It is notable that the carbide is still observed even in the sample heated up to 800 °C together with a greater amount of α-(Fe,Ga) (Fig. 10(c)). This α-(Fe,Ga) is supposed to result mainly from the disproportionation of the $Sm_2Fe_{15}Ga_2H_X$ rather

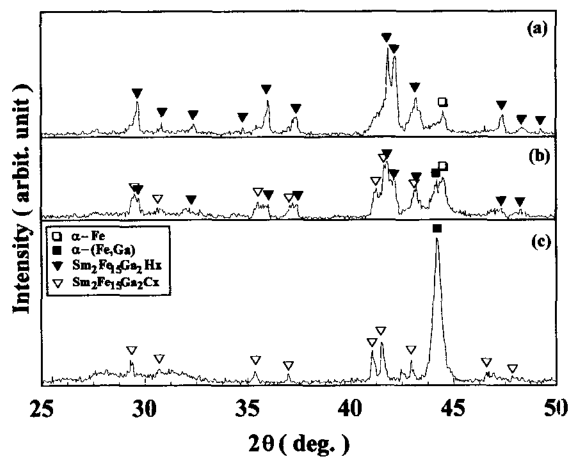

Fig. 10. XRD spectra for the $Sm_2Fe_{15}Ga_2$ alloy heated in CH_4 gas under various conditions.

than the carbide. These results indicate that the $Sm_2Fe_{17}C_X$-type material is stabilised significantly by the Ga-substitution for Fe in the parent alloy.

4. Conclusions

The Ga-stabilised Sm_2Fe_{17}-type alloy was able to be disproportionated significantly on heating up to 800 °C under hydrogen with normal pressure and the heat flow associated with disproportionation was considerably small compared to the alloy without Ga-substitution. The disproportionation behaviour of the Ga-substituted alloy could not be examined properly by DTA, and TPA was found to be a more efficient tool for this purpose. The particle size influenced significantly on the disproportionation of the Ga-substituted alloy, and the material with finer particle size ($< 40\ \mu m$) was fully disproportionated on heating up to around 800 °C under hydrogen gas with normal pressure. The Ga-substituted alloy has a very sluggish recombination kinetics with respect to the alloy without Ga-substitution. The $Sm_2Fe_{17}C_X$-type material was stabilised significantly by the Ga-substitution for Fe in the parent alloy. While the $Sm_2Fe_{17}C_X$ was disproportionated below 800 °C the Ga-stabilised $Sm_2Fe_{15}Ga_2C_X$ carbide was not disproportionated even on heating up to 800 °C.

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