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MAGNETIC MONITORING OF THE GASEOUS INTERACTIONS IN Sm-Fe-Ta-BASED ALLOYS

SPREMLJANJE MAGNETNEGA VEDENJA ZLITIN NA OSNOVI Sm-Fe-Ta MED HIDRIRANJEM IN NITRIDIRANJEM

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Understanding the interactions with hydrogen and nitrogen that happen during processing of a SmFe material is essential if we want to achieve the best magnetic properties. The magnetic behaviour of $Sm_{13.7}Fe_{86.3}$ and $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ materials during the hydrogenation-disproportionation-desorption-recombination (HDDR) and subsequent nitriding processes was investigated using a specially designed vibrating-sample magnetometer (VSM) modified with a high-temperature (up to 1000 °C) vacuum-gas system. The attritor-milled-compacted powder samples were mounted in the VSM and heated at 4 °C /min in flowing hydrogen at 1 bar to 750 °C, held there for an hour and then 2 hours under vacuum, before being cooled to room temperature at 4 °C/min. The nitriding process of the samples was preformed at slightly higher heating rate of 5 °C/min at 1 bar. The samples were heated to 500 °C and held there for 4 hours before they were cooled to room temperature. The results show that the initial absorption of hydrogen results in an increase in magnetization as well as Tc and that the sluggish disproportionation of the Sm_2Fe_{17} phase in the $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ sample is due to dissolved Ta. The monitoring of the nitriding process shows the increase in the magnetization as the sample picks up the nitrogen at around 250 °C. If the sample was previously HDDR-ed the nitrogen uptake goes very smoothly, whereas on the other hand if the samples are not HDDR processed, the nitrogen reaction consists also of decomposition of $SmFe_2$ and $SmFe_3$ phases.

Key words: SmFeN, hydriding, nitriding

Nitridi na osnovi SmFe so zaradi svojih odličnih intrinzičnih lastnosti deležni velike pozornosti, saj so velik potencial kot trdomagnetni materiali. Vendar pa zlitina sama po sebi še ni magnet. Šele s pozornim procesiranjem v vodiku in dušiku dobimo material z uporabnimi magnetnimi lastnostmi. Magnetno vedenje zlitin s sestavama $Sm_{13,7}Fe_{86,3}$ in $Sm_{13,8}Fe_{82,2}Ta_{4,0}$ smo opazovali v magnetometru s tresočim vzorcem (VSM) v pretoku vodika in dušika. Vzorce smo segrevali s hitrostjo 4 °C/min v vodiku in 5 °C/min v dušiku. Procesna shema postopka HDDR (hidrogenacija-disproporcionacija-desorpcija-rekombinacija) je naslednja: Vzorce smo segreli na temperaturo 750 °C, jih tam obdržali 1 uro, nato pa še 2 uri v vakuumu preden smo jih ohladili na sobno temperaturo. Nitridiranje, ki smo ga prav tako izvedli v VSM, je potekalo pri temperaturi 450 °C 4 ure, nato pa smo vzorce ohladili na sobno temperaturo. Začetna absorpcija vodika je povzročila povečanje magnetizacije in Curiejeve temperature vzorca. Reakcija z vodikom se nadaljuje z razpadom materiala oz. faze Sm_2Fe_{17} pri približno 600 °C. Ker se Ta delno raztaplja v fazi Sm_2Fe_{17}, se je razpad le-te zgodil pri višji temperaturi, kar je v skladu z našimi prejšnjimi rezultati. Efekt vgrajevanja dušika v kristalno celico, ki se prične pri 250 °C, se kaže v povečevanju magnetizacije vzorca. Pri vzorcih, obdelanih po postopku HDDR, je potekal proces nitridiranja enakomerno in brez posebnosti. Vzorci, neobdelani po postopku HDDR, pa kažejo drugačen odziv. Proces nitridiranja je v temperaturnem območju med 150 °C in 350 °C sestavljen iz dveh dodatnih procesov, ki smo jih pripisali razpadu faz $SmFe_2$ in $SmFe_3$.

Ključne besede: SmFeN, hidriranje, nitridiranje

1 INTRODUCTION

Because of their excellent intrinsic magnetic properties a lot of research work has been done on SmFeN-type materials [1] over the last decade. A lot of investigations on phase composition [2,3,4], gaseous interactions [5,6,7] and magnet processing [8,9,10] were undertaken in order to understand the material and produce good magnetic properties.

The ability of these intermetallic compounds to absorb certain gasses, such as hydrogen or nitrogen, makes them particularly interesting; however, not just because of their hydrogen storage properties but because of the significant changes in intrinsic magnetic properties that occur with the absorption of hydrogen or nitrogen. For example, hydrogen absorption in Sm_2Fe_{17} increases the Curie temperature by about 140 K, and nitrogen absorption by even more, about 360 K. Furthermore, hydrogen can be used to obtain a fine-grained microstructure via the hydrogenation-disproportionation-desorption-recombination (HDDR) process, which when combined with the nitrogen absorption increases the coercivity.

The vibrating-sample magnetometer (VSM) plays a central role in measuring the magnetic properties of rare-earth transition-metal magnets, however the VSM has rarely been used to monitor changes that occur with these materials when they are subjected to different temperature and atmospheric conditions. The magnetization changes that take place with these kinds of materials, whether they are heated in hydrogen or nitrogen, are usually relatively large, and a VSM is ideally suited to such measurements.

2 EXPERIMENTAL

$Sm_{13.7}Fe_{86.3}$ (SmFe) and $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ (SmFeTa) cast alloys were produced by conventional induction melting by Less Common Metals. For the investigations in hydrogen the samples were crushed to a lump form and further reduced in size using a vibro-mill. For the investigations in nitrogen the material was first crushed and then further reduced in size by milling in hexane using an attritor mill for 30 minutes, in the inert atmosphere of a glove box, so as to produce a particle size of approximately 10 μm. All the thermo-magnetic experiments in hydrogen and nitrogen were performed using a Lakeshore 7303 VSM, modified with a high-temperature (up to 1000 °C) vacuum-gas system, offering the possibility to monitor the magnetic behavior of the samples during the hydriding or the nitriding process. The hydriding consisted of heating the samples in hydrogen to 750 °C at 5 °/min. Prior to heating in hydrogen the VSM's sample tube was twice evacuated to $8\cdot10^{-2}$ mbar. The cycles were repeated two times: Cycle 1 and Cycle 2. The nitriding of the milled-only samples, and the samples previously HDDR processed consisted of heating them in nitrogen to 450 °C at 5 °C/min.

3 RESULTS AND DISCUSSION

3.1 Experiments in hydrogen

Figure 1 shows the results from the SmFe alloy. For Cycle 1 (the black line) we see an initial drop in magnetization with temperature up to 125 °C, at which point we observe a rapid increase in magnetization - despite an increasing temperature. At 170 °C the magnetization ceases to increase any further, and from then on we observe a steady decline in the magnetization for about the next 200 °C, with the T_C of the hydrided Sm_2Fe_{17}-type phase found at 254 °C and that of the $SmFe_3$ phase at 386 °C. From this minimum in the magnetization further heating causes a steady increase between 398 °C and 505 °C before a more rapid increase takes place up to 598 °C. The magnetization of the sample then decreases at an increasing rate until the end of the experiment at 750 °C. Cycle 2 (the dark-gray line) contains the same basic reactions and T_Cs as Cycle 1 but with some significant differences. The initial hydrogenation reaction has clearly divided into two separate reactions. As with Cycle 1 the magnetization then decreases and the hydrided Sm_2Fe_{17}-type phase has its T_C again at 254 °C. At ~380 °C there is almost no indication of any T_C, however, there is still clear evidence for a smaller disproportionation reaction associated with the $SmFe_3$ phase. Compared to Cycle 1, the main disproportionation reaction of the Sm_2Fe_{17}-type phase is now much faster.

Figure 2 shows the results from the SmFeTa alloy. Although similar to the SmFe alloy in their basic forms, it exhibits some important differences. The initial hydrogenation reaction remains single-stage for both cycles, with the second cycle seeing the start of the reaction at a higher temperature: Cycle 1, 141 °C; and Cycle 2, 160 °C. After a peak in the magnetization the curves indicate a T_C for the material as follows: Cycle 1, 250 °C; and Cycle 2, 257 °C. In the high-temperature part of the graph it is clear that the Cycle-1 curve is very different from the subsequent one. Not only does it exhibit a T_C at 388 °C and a subsequent disproportionation beginning at 402 °C, but the main disproportionation of the Sm_2Fe_{17}-type phase is much slower with the peak in the magnetization not occurring until 702 °C, in comparison with 660 °C for Cycle 2 and less than 600 °C for all of the SmFe-alloy cycles.

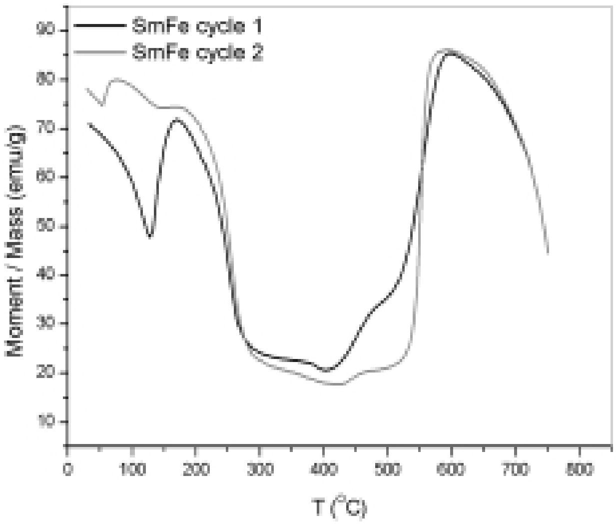

Figure 1: The curve representing the moment/mass in Cycle 1 and Cycle 2 vs. temperature for the SmFe sample in hydrogen

Slika 1: Krivulja moment/masa za vzorec SmFe v vodiku v odvisnosti od temperature

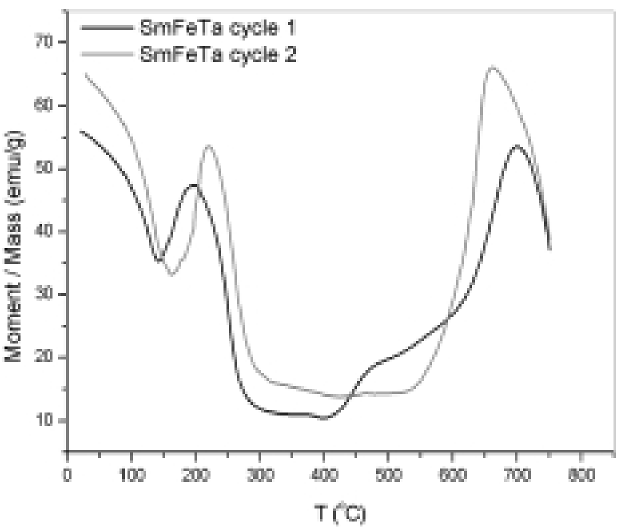

Figure 2: The curve representing the moment/mass in Cycle 1 and Cycle 2 vs. temperature for the SmFeTa sample in hydrogen

Slika 2: Krivulja moment/masa za vzorec SmFeTa v vodiku v odvisnosti od temperature

The hydrogenation of the Sm_2Fe_{17}-type phase of the $Sm_{13.7}Fe_{86.3}$ (SmFe) material depends on the number of the HDDR cycles to which the material has been subjected. The initial absorption reaction is a surface-dependent process, which explains the shift from an initial single absorption at 125 °C to a two-stage absorption at 54 °C and 149 °C. The three-component $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ (SmFeTa) material behaves in a more consistent way with the second HDDR cycle delaying the onset of the hydrogenation. Additional differences were found in the T_Cs of the hydrided Sm_2Fe_{17}-type phases for SmFe and SmFeTa. For both cycles we obtained a value of 254 °C - in almost exact agreement with Xiang-Zhong et al [12] - for the SmFe material, but for the SmFeTa material the T_C increased after the first cycle: from 250 °C during Cycle 1 to 257 °C. Such a result suggests that the material may not have been fully hydrided during the first cycle and/or a significant change had taken place in the material after the first HDDR cycle. Between 300 °C and 400 °C the SmFe and SmFeTa materials behave in a very similar manner. Both materials show evidence for the presence of the $SmFe_3$ phase with a T_C at 386 °C (SmFe) and 388 °C (SmFeTa). The fact that these T_Cs are 9 °C and 11 °C above the reported value for $SmFe_3$ [5] suggests that the material still contains some hydrogen at the onset of the disproportionation at 398 °C (SmFe) and 402 °C (SmFeTa). It is also clear that the HDDR cycling reduces the amount of $SmFe_3$ phase present. For both materials there is practically no evidence for the existence of this phase after the first HDDR cycle.

The disproportionation of the $SmFe_3$ phase overlaps to some extent with the onset of the disproportionation of the Sm_2Fe_{17}-type phase. Nevertheless, for the SmFe material we can easily see the effects of repeated HDDR cycling. During the first cycle the reaction begins at about 500 °C and reaches a maximum rate of 0.93 emu g^{-1} $°C^{-1}$ at 554 °C before tailing off with a maximum in the magnetization at 598 °C. From this point on the magnetization is solely a consequence of the presence of iron and if the experiment were continued beyond 750 °C we would see the T_C of the iron at 768 °C. The second cycle produced almost identical disproportionation reactions with a maximum rate of 3.44 emu g^{-1} $°C^{-1}$, at 550 °C. This small difference in the point of maximum-magnetization increase of only 4 °C for the SmFe material is in stark contrast to the difference between the first and second cycles for the SmFeTa material. During Cycle 1 for the SmFeTa we see a much slower start to the reaction with a peak in the disproportion rate of 0.39 emu g^{-1} $°C^{-1}$ at 663 °C. Cycle 2 has a peak reaction rate of 0.79 emu g^{-1} $°C^{-1}$ at 617 °C - some 46 °C lower. The difference in the temperature of maximum disproportionation rate for the SmFe and SmFeTa alloys on the first cycle is just over 100 °C, very similar to the result we obtained previously using a gas-flow-analysis technique [13].

The slower disproportionation reaction of the SmFeTa material, particularly during Cycle 1, suggests that the tantalum must be stabilizing the Sm_2Fe_{17}-type phase. The difference in the disproportionation reaction between Cycle 1 and Cycle 2 for the same material suggests that the tantalum plays a less important role after the completion of the first cycle. This is also born out by the initial hydriding behavior of the SmFeTa. During Cycle 1 we obtained a T_C of 250 °C while heating the sample in hydrogen, the next cycle gave us a value of 257 °C - whereas the values obtained for the SmFe material stayed the same for both cycles - suggesting that some alteration in the chemistry had occurred. These observations are in very good agreement with our earlier EDX studies on these materials [13], which indicated that the initial concentration of tantalum dissolved in the Sm_2Fe_{17}-type phase was 2.0±0.1 atomic %. After a single HDDR cycle this same phase contained only 1.2±0.1 atomic % of dissolved tantalum, however, it now had Ta_3Fe_7 nano-precipitates distributed within the phase.

3.2 Experiments in nitrogen

The in-situ magnetic changes during the nitrogenation for SmFe are presented in **Figure 3**. The difference in magnetic behavior between the milled-only and the milled+HDDR-ed material is obvious. The milled+HDDR-ed material reacts with nitrogen in a very straightforward way. The magnetization of the material decreases with increasing temperature and the Curie temperature of the Sm_2Fe_{17} phase is observed at 141 °C. The magnetization continues to decrease up to the temperature of 240 °C, when the nitrogen starts to diffuse into the 2:17 lattice. Because of lattice expansion the magnetization starts to increase and reaches a maximum rate of 0.47 emu g^{-1} $°C^{-1}$ at 360 °C. The end temperature of the experiment was based on our previous investigations, in which we discovered that 450 °C is the optimum nitriding temperature. It is clear that the reaction is close to completion at 450 °C. The nitrogen behavior of the milled-only sample differs from the milled+HDDR-ed sample in several aspects. The slight initial magnetization increase at 102 °C is due to the thermal relaxation of the magnetic moments in the material. As the temperature increases the material demagnetizes and the Curie point of the Sm_2Fe_{17} phase is observed at 141 °C. The magnetization increase at around 250 °C, attributed to the absorption of nitrogen into the 2:17 phase, overlaps with an additional process, which gives rise to the magnetization changes in the region between 150 and 300 °C. As a consequence the initial nitrogen absorption temperature for this material cannot be determined. After the magnetization reaches a minimum at 290 °C a steady increase is observed, but with a slower rate (0.20 emu g^{-1} $°C^{-1}$) than the milled+ HDDR-ed material.

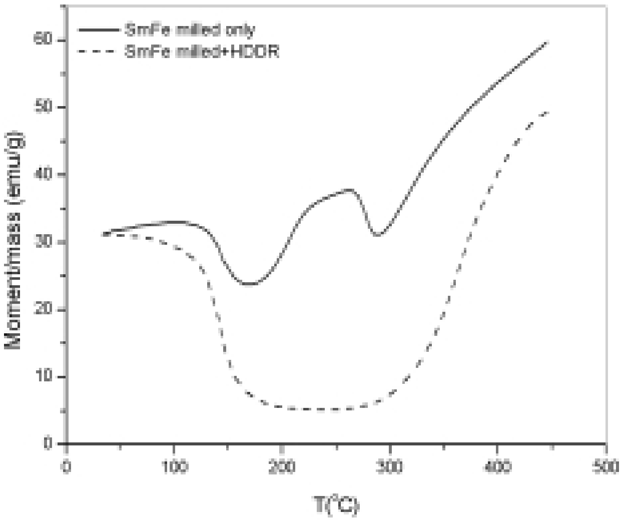

Figure 3: The curve representing the moment/mass vs. temperature for the milled-only and milled+HDDR-ed SmFe samples in nitrogen

Slika 3: Krivulja moment/masa za vzorec SmFe (samo mlet in mlet + obdelan po postopku HDDR) v dušiku v odvisnosti od temperature

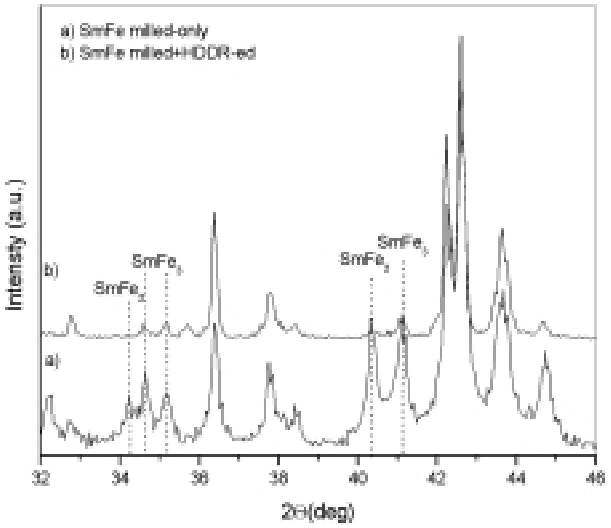

Figure 5: XRD patterns for the SmFe sample: a) milled only, b) milled+HDDR-ed

Slika 5: Rentgenska difraktograma za vzorec SmFe: a) samo mlet, b) mlet + obdelan po postopku HDDR

The SmFeTa alloy presented in **Figure 4** reacts with nitrogen in a very similar way to SmFe alloy. The magnetization of the HDDR-ed material decreases with increasing temperature, and the Curie temperature is observed at 150 °C. The nitrogen absorption starts at 225 °C and reaches a maximum rate of 0.29 emu g^{-1} °C^{-1} at 350 °C. At 450 °C the magnetization is still increasing. The behavior of the milled-only material while heating in nitrogen again differs from the milled+HDDR-ed material, which behaves in a similar way to the binary alloy. The magnetization in the temperature region between 150 °C and 350 °C shows two peaks, one at 225 °C and the next one at 280 °C. After the magnetization reaches minimum at 305 °C it starts to increase again with rate 0,39 emu g^{-1} °C^{-1}, until 400 °C, where it stabilizes.

The different behavior of the milled-only and milled+HDDR-ed material can be explained by taking several factors into consideration. The first difference between them is in the microstructure. The milled-only material is not homogeneous, and it has a lot of irregularities that result from previous material preparation methods such as casting and milling. The grain size of the milled-only sample is large in comparison with the HDDR-processed material, which is a relatively homogeneous sample with a uniform sub-micron grain

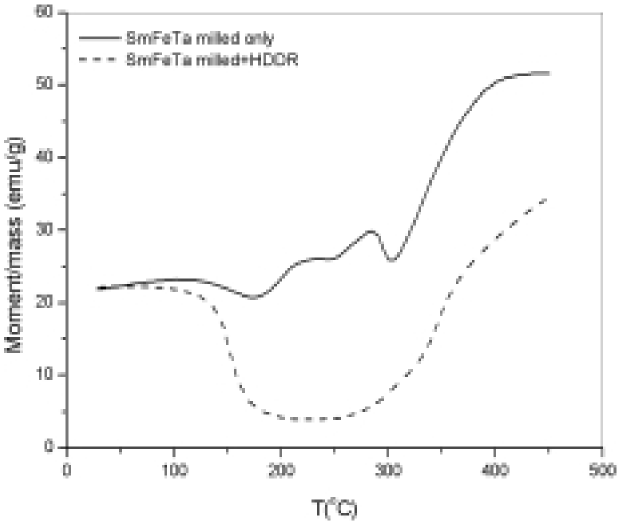

Figure 4: The curve representing the moment/mass vs. temperature for milled-only and milled+HDDR-ed SmFeTa samples in nitrogen

Slika 4: Krivulja moment/masa za vzorec SmFeTa (samo mlet in mlet + obdelan po postopku HDDR) v dušiku v odvisnosti od temperature

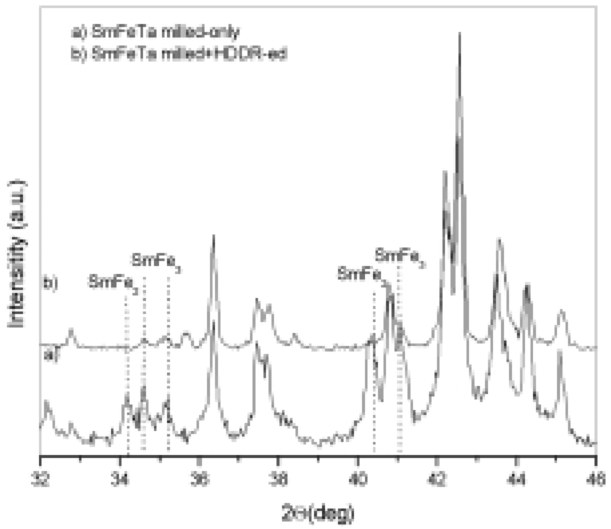

Figure 6: XRD patterns for the SmFeTa sample: a) milled only, b) milled+HDDR-ed

Figure 6: Rentgenska difraktograma za vzorec SmFeTa: a) samo mlet, b) mlet + obdelan po postopku HDDR

size. Therefore, one explanation is in the different characteristics of the samples before and after the HDDR processing. But this is not the only difference between the milled-only and milled+HDDR-ed samples. They also differ in terms of their phase composition. From our previous experiment in hydrogen it is clear that the HDDR process reduces the amount of $SmFe_3$ phase in both the SmFe and SmFeTa samples. In order to thoroughly investigate the phase composition the milled-only and milled+HDDR-ed samples were examined using XRD. The patterns are presented in **Figures 5 and 6**. The a) patterns present the phase composition of the milled-only samples. The peaks of the Sm_2Fe_{17} phase as well as the peaks from $SmFe_2$ and $SmFe_3$ phases are observed for both the SmFe and SmFeTa samples. The pattern of the milled+HDDR-ed sample differs from the milled-only. The peaks of the Sm-rich phases have shrunk significantly which leads us to believe that the different behavior during nitrogenation is due to the disproportionation of the Sm-rich phases ($SmFe_2$ and $SmFe_3$), which are present in the as-cast material. These phases decompose during heating in nitrogen to SmN and αFe, which gives rise in the increase in the magnetization. It was previously reported that these phases decompose in nitrogen at temperatures above 450 °C [14]. It was also reported that the reaction of the Sm-rich phases is particle-size dependent [5,6]. Therefore, we believe that because of the very fine powder the phases react and decompose in nitrogen at even lower temperatures than have been reported so far. The nitrogen absorption process for the Sm_2Fe_{17} phase in the milled-only samples overlaps with the disproportionation of the Sm-rich phases, therefore, the process is not so clear as with the samples which were previously HDDR processed.

4 CONCLUSIONS

By using a VSM, a device that can be accurately calibrated in terms of both the temperature and the magnetic moment of the sample, we have a method that can give us precise information about chemical reactions that result in changes to the magnetic state of iron as well as the T_Cs of phases as they absorb and desorb hydrogen or nitrogen.

The behavior in hydrogen depends on the number of cycles to which the material is subjected. The elimination of Ta from the 2:17 phase shifts the disproportionation reaction to lower temperatures.

The behavior during nitriding depends on the sample processing as well as the sample composition. The reason for the different nitrogen behavior between the milled-only and milled+HDDR-ed material is the removal of the Sm-rich phases during the HDDR process, as well as grain refinement and homogenization.

Acknowledgements

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