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PROCESSING Sm-Fe(Ta)-N HARD MAGNETIC MATERIALS

PROCESIRANJE TRDIH MAGNETOV NA OSNOVI Sm-Fe(Ta)-N

Kristina Žužek, Paul J. McGuiness, Spomenka Kobe
Institute Jožef Stefan, Ljubljana, Jamova 39, Slovenia

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SmFe based alloys interstitially modified with nitrogen are potential candidates for high energy permanent magnets. In order to obtain the optimum properties a thorough understanding of the starting material and processing parameters is required. The microstructures of two cast alloys of composition $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ and $Sm_{13.7}Fe_{86.3}$ were carefully examined with a SEM equipped with EDX and the exact stoichiometries of the phases were determined. The SmFeTa material was found to contain significant amounts of $TaFe_2$, as well as the Sm_2Fe_{17}, $SmFe_2$, $SmFe_3$ phases observed in the SmFe material but without the α-iron dendrites which are characteristic of the latter material. Hydrogen absorption-desorption studies carried out on both materials have demonstrated the increased resistance to decomposition of the $Sm_2(FeTa)_{17}$ material, requiring an additional 150°C for the reaction to go to completion. The optimum conditions necessary to provide the highest coercivities using the conventional HDDR process combined with pre-milling were investigated. The coercivities obtained after using the HDDR process and subsequent nitriding without any pre-milling were 680 kA/m for the SmFeTaN and 360 kA/m for the SmFeN samples. Significantly higher coercivites of 1000 kA/m for SmFeN and 1275 kA/m for SmFeTaN were achieved by reducing the particle size with milling prior to the HDDR process. The better coercivities obtained with the Ta containing sample were found to be due to the presence of a much smaller amount of αFe. The milling prior to the HDDR treatment improves the coercivity because of the small particle size, which prevents the grains growing too large, with their consequent very negative effect on the coercivity.

Key words: SmFeN, Ta, HDDR, milling

Zlitine na osnovi sistema Sm-Fe, intersticijsko modificirane z dušikom, imajo velik potencial kot trajni magnetni materiali. Optimalne magnetne lastnosti lahko dosežemo s pravilno obdelavo zlitine, ki pa temelji na poznavanju materiala. Primerjali smo zlitini sestave $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ in $Sm_{13.7}Fe_{86.3}$. Fazno sestavo smo preučevali z elektronsko vrstično mikroskopijo in EDX analizo. SmFeTa zlitina vsebuje $TaFe_2$ fazo, poleg nje pa tudi Sm_2Fe_{17}, $SmFe_2$, $SmFe_3$ faze, ki so prisotne tudi v SmFe zlitini z izjemo, da SmFe zlitina namesto $TaFe_2$ vsebuje dendritsko αFe. Študirali smo procese absorbcije in desorbcije vodika. Ugotovili smo, da Ta stabilizira Sm_2Fe_{17} fazo, saj je bila temperatura razpada te faze za 150°C višja od temperature, pri kateri je razpadla Sm_2Fe_{17} faza iz binarne zlitine. Poiskali smo optimalne pogoje postopka HDDR, ki so nam dali najboljše rezultate na področju magnetnih lastnosti. Koercitivnosti prahov dobljenih po tem postopku in nadaljnjem nitriranju, so 680 kA/m za $Sm_{13,8}Fe_{82,2}Ta_{4,0}N_x$ in 360 kA/m za $Sm_{13,8}Fe_{86,3}N_x$. Občutno višje koercitvnosti smo dosegli z mletjem materiala, ki smo ga izvedli pred postopkom HDDR, t.j. 1275 kA/m za $Sm_{13,8}Fe_{82,2}Ta_{4,0}N_x$ in 1000 kA/m za $Sm_{13,8}Fe_{86,3}N_x$. Razliko v višji koercitivnosti sestave s Ta, gre pripisati manjši vsebnosti α-Fe. Višje koercitivnosti pred mletega materiala pa dejstvu, da v majhnih delcih rast velikih zrn, ki imajo negativen vpliv na koercitivnost, ni možna.

Ključne besede: SmFeN, Ta, HDDR, mletje

1 INTRODUCTION

SmFeN magnets have received considerable attention since their discovery in 1991[1] Their intrinsic properties are comparable with, or better than, those of magnets based on $Nd_2Fe_{14}B$, and so they have the potential to take a significant share of the rare earth permanent magnet market. SmFeN magnets are open to a number of possible processing routes, for example, mechanical alloying[2,3], melt spinning[4,5] and conventional powder metallurgy[1,6] however the HDDR process[7,8] appears to be the most promising.

The addition of a third element, in this case Ta, is primarily intended to reduce the incidence of α-iron which typically constitutes some 25% of the phases present[9] in the as-cast binary alloy. The α-iron can be removed by an extended vacuum or inert gas heat treatment, however this is expensive, environmentally detrimental and can cause problems with maintaining precise composition as a result of samarium evaporation. The addition of 4-5% Nb[10] or Ta[11] or 1% Zr[12] to the SmFe material allows the primary crystallisation of α-iron to be avoided.

Effects of reducing the particle size in combination with the HDDR process have been noted by other workers, Müller et al[13] found that by milling after the HDDR process was completed a remarkable increase in coercivity could be observed. This increase was attributed to the well known effects of size reduction as a result of milling. They also found milling prior to the HDDR process had a minimal effect unless an additional 5 wt% of samarium was added. In this case the improvement was attributed to a more even microstructure not possible with larger particles due to having grain formation begin earlier in the centre of the large particles. Gebel et al[12] also used vibration milling under toluene to produce fine powders prior to applying the HDDR process as part of their experimental procedure.

In this paper we have investigated the effects of a Ta addition on the hydrogen absorption behaviour as a function of temperature using Thermopiesic Analysis

(TPA) and Gas Flow Analysis (GFA). We have also produced magnets using powders with a variety of pre-milling times combined with a conventional HDDR and nitriding process to assess the benefits of the Ta addition.

2 EXPERIMENTAL

Both the SmFe and SmFeTa cast alloys were produced by conventional induction melting methods in 5 kg batches by Less-Common Metals Ltd. Small pieces of approximately 0.5 cm^3 were cut from similar parts of each alloy and mounted and polished for metallographic examination. The results of this examination have been published previously[14] and the analyses on the Sm_2Fe_{17} phase showed that 2-3% of Ta is dissolved in this phase. As cast materials were also investigated using x-ray diffractometry to determine their lattice parameters.

The hydrogen absorption, desorption and disproportionation behaviour of the SmFe and SmFeTa alloys was observed using Thermopiesic Analysis (TPA) and Gas Flow Analysis (GFA). The difference between these two methods is in the measured quantity. In the case of TPA it is the pressure of hydrogen, and with the GFA it is the differential hydrogen flow. Schematic diagrams of both pieces of equipment are shown in **Figure 1**. The TPA is a device, which measures the changes in pressure with the sample held within a fixed volume. As the material absorbs H_2 the pressure is observed to fall, subsequent hydrogen desorption causes a pressure increase. It is important to note that these changes take place against a constantly increasing background of pressure due to the increasing temperature of the experiment. The GFA, in contrast, is a constant pressure system. Gas is allowed to flow into the system at a constant rate, typically 50 ccm/min, this flow is set by a mass flow controller. The exhaust gas flow is measured in a similar way and by taking the difference between the flow-in and the flow-out it is possible to calculate ΔQ, the amount of the gas being absorbed or desorbed at any particular stage of the experiment. In both cases, experiments were undertaken between room temperature and 800°C.

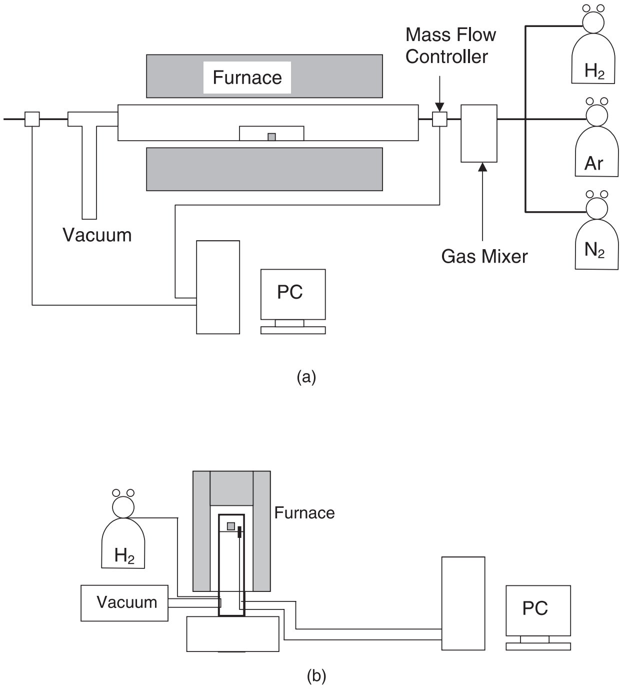

Figure 1: The schemes of GFA (a) and TPA (b) processes
Slika 1: Shematični prikaz GFA (a) in TPA (b) procesa

In order to assess the effect of Ta on the magnetic properties of a $Sm_2Fe_{17}N_x$ type permanent magnet, materials were processed using a HDDR based procedure. The ingot material was crushed to a particle size of less than 1 mm and then reduced further by milling. The milling was carried out in an attritor mill for times of between 1 and 60 minutes, under hexane, in the inert atmosphere of a glove box. The particle size of the attritor milled powder was determined using a Fisher sub sieve sizer. An investigation of the size distribution of the powders was undertaken with a scanning electron microscope. The HDDR processing was carried out in a rotating furnace capable of operating between 1 bar over pressure and a vacuum of 10^{-2} mbar. The initial stages of the HDDR processing were carried out in pure H_2. Samples were heated at 5°C/min to 750°C and then held at this temperature for 60 mins. The second, recombination, stage was carried out under vacuum for a further 60 mins using temperatures 740 and 820°C. All samples were subsequently nitrided at 450°C for 4 hours in a flow of nitrogen gas. Permanent magnet bonded samples were produced by mixing the powder with epoxy resin. These samples were measured at room temperature in a conventional permeameter after pulsing the magnets in a field of 5 T.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction experiments

Results of the lattice parameter refinement calculations can be seen in **Table 1**. These refinements reveal that the presence of Ta in the Sm_2Fe_{17} phase, in agreement with Saje et al[15], causes a significant lattice expansion. The volume of the 2:17 unit cell for the SmFeTa alloy, being in this case, some 0.42% greater than that of the binary SmFe; although this is somewhat smaller than the 0.7% expansion reported by Gutfleisch et al[16] for a 4%Nb alloy.

The changes in hydrogen pressure during heating at 5K/min, for both alloys, can be seen in **Figure 2**. The first absorption events for the binary and Ta substituted alloys are observed at temperatures between 50 and 250°C and are the result of interstitial absorption of hydrogen into the Sm_2Fe_{17}, $SmFe_2$ and $SmFe_3$ phases. $SmFe_2$ absorbs hydrogen at temperatures between 120-160°C and the hydride decomposes immediately to SmH_x and αFe[17]. Because the onset temperatures for ini-

Table 1: Lattice parameter measurements of 2:17 phase in SmFe and SmFeTa
Tabela 1: Parametri osnovne celice 2:17 faze v SmFe in v SmFeTa zlitini

SmFe alloy				**SmFeTa alloy**			
Phase	a(Å)	c(Å)	V(Å^3)	Phase	a(Å)	c(Å)	V(Å^3)
2:17	8.545±0.992	12.428±0.004	785.812±0.364	2:17	8.558±0.002	12.441±0.005	789.096±0.005

tial hydrogen absorption depend very much on the surface conditions, it would be wrong to suggest that the different behaviour of the materials is a result of the Ta substitution. Above 150°C we observe a multistage desorption. With the help of the GFA data we can interpret this multistage desorption in terms of a continuous loss of hydrogen from the 2:17 phase combined with the desorption of hydrogen from the $SmFe_3H_X$ phase at ~245°C. The desorption from the $SmFe_3H_X$ phase takes place over approximately 10°C after which the hydrogen loss from the 2:17 hydride continues for both materials up to ~440°C. At this point a second absorption is observed to take place until the temperature reaches ~500°C. This second absorption is clearly defined and is a consequence of the decomposition of $SmFe_3H_X$ to SmH_X and αFe. Further heating brings about a third desorption stage, but here there is a significant difference in the behaviour of the two alloys. The binary material begins absorbing at ~550°C because of the $Sm_2Fe_{17}H_X$ decomposing to SmH_X and Fe whereas the Ta substituted material remains undecomposed until a temperature of ~700°C is reached.

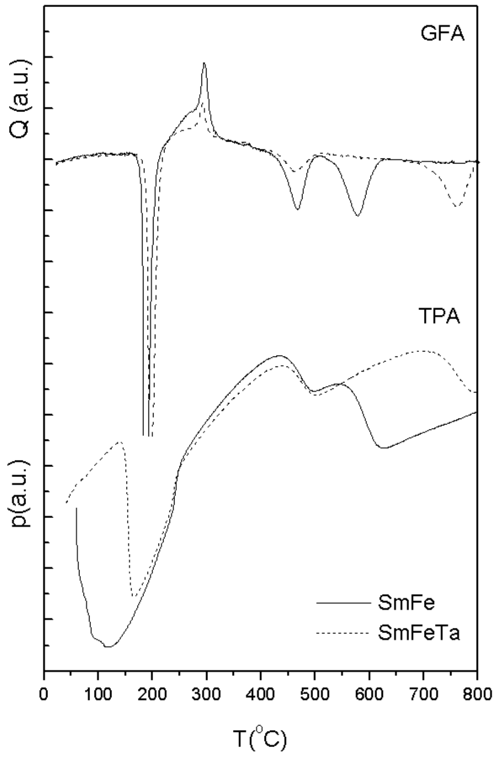

Figure 2: TPA and GFA curves for as cast SmFe and SmFeTa alloys, showing their behaviour during HDDR process
Slika 2: TPA in GFA krivulje za zlitini SmFe in SmFeTa, ki ponazarjata interakcije z vodikom med procesom HDDR

3.3 GFA investigations

The hydrogen absorption and desorption events were also observed by measuring the difference in hydrogen flow (ΔQ) at different temperatures **(Figure 2)** using the GFA. The first absorption peak was observed to begin at ~170°C for both alloys. The reaction proceeds rapidly and appears to come to completion prior to the onset of the desorption stage at ~220°C. This desorption corresponds to loss of interstitial hydrogen from the 2:17 phase and at ~280°C an increased rate of desorption indicates loss of hydrogen from the $SmFe_3H_X$ phase as well. At ~400°C we observe the beginnings of the $SmFe_3$ decomposition stage which takes place over the same temperature range for both materials, the process being largely completed at ~510°C. As with the TPA experiments we observe striking differences in the behaviour of the materials at higher temperatures. For the binary material the decomposition of the 2:17 phase extends from ~520°C to ~630°C, while with the Ta substituted sample it takes place from 680°C to 800°C, which is more than 150°C higher.

If we compare the results obtained with the TPA and the GFA it is clear that the different experimental methods give very comparable results. The discrepancies in the initial absorption are frequently observed and can be attributed to the variation in surface condition of the starting materials. The desorption of hydrogen from the $SmFe_3H_X$ phase is very clearly demonstrated by the GFA and the larger peak obtained for the binary material corresponds with the relatively larger amounts of $SmFe_3$-type phase observed in the binary material. Both methods clearly show the decomposition of the $SmFe_3H_X$-type phases in both alloys between ~420 and ~520°C and the substantial difference in the temperature of decomposition for the $Sm_2Fe_{17}H_X$ and $Sm_2(FeTa)_{17}H_X$ phases at higher temperatures.

3.4 Magnet processing

The results of a Fisher Subsieve Sizer (FSSS) particle size analysis on the SmFe and SmFeTa materials milled for between 1 and 60 mins can be seen in **Figure 3**. The measurements indicate that the average size of the particles decreases rapidly with milling time at least for the first 10-15 mins before settling at a size of approximately 3-4 μm. Obviously the FSSS measurements only give us an indication of the average particle size of the powder.

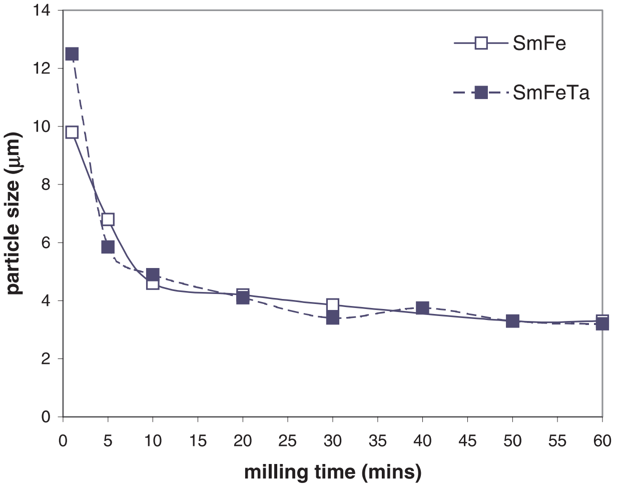

Figure 3: The particle size in dependence of milling time for SmFe and SmFeTa alloys

Slika 3: Velikost delcev v odvisnosti od časa mletja za zlitini SmFe in SmFeTa

Information relating to the spread in the particle size is not provided by such a measurement. However, SEM micrographs of both SmFe and SmFeTa powders (**Figure 4**) show that the size distribution for the two materials is relatively narrow and basically similar for both materials for the same milling times.

Figure 5 shows the effect of pre-milling time on SmFe and SmFeTa processed at recombination temperatures of 740°C and 820°C. Both materials show a sharp increase in coercivity with relatively short milling times when a recombination temperature of 820°C is used. This is particularly so for the SmFeTa material. In comparison, milling time appears to have relatively little effect when the lower recombination temperature is used. In other words, while the coercivity of the materials processed at the higher temperature depends very much on the particle size of the starting material, the coercivity of the low recombination temperature samples is to a much greater extent, particle size independent. The explanation for this observation lies in the grain size of the recombined materials. The grains in the samples processed at the lower temperature grow relatively slowly and so the size of the particles, which contain these grains, is relatively unimportant. In the case of the higher temperature processing, where very significant grain growth can take place, particle size is critical, since grains can grow to quite large sizes in large particles, but are obviously re-

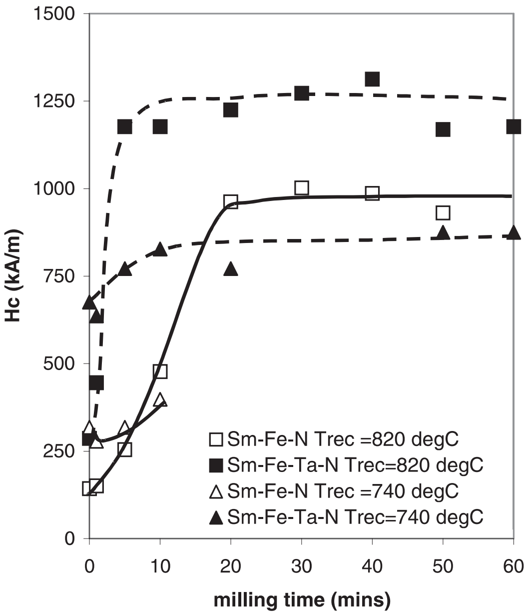

Figure 5: Variation in coercivity with milling time for SmFe and SmFeTa materials recombined at 740°C and 820°C

Slika 5: Koercitivna sila v odvisnosti od časa mletja za vzorca SmFe in SmFeTa, ki sta bila rekombinirana pri 740°C in 820°C

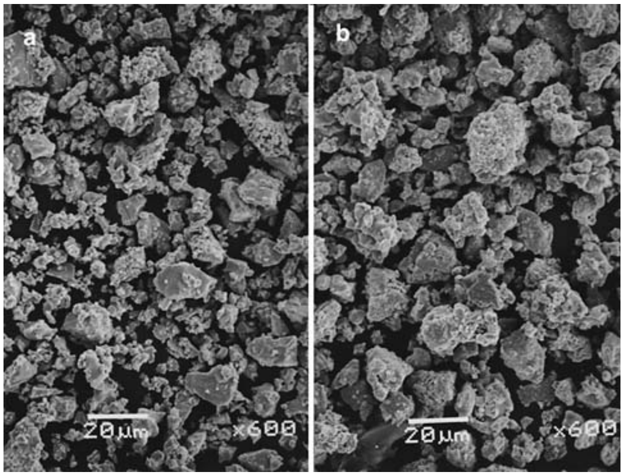

Figure 4: SEM micrographs of the SmFeTa (a) and SmFe (b) powders milled for 20 mins

Slika 4: SEM posnetek vzorcev SmFeTa (a) in SmFe (b) mletih v attritor mlinu 20 min

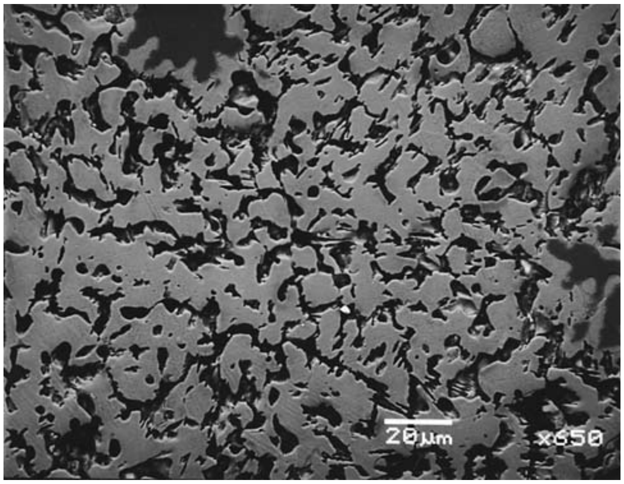

Figure 6: SEM micrograph showing big grains (>20 μm) of Sm_2Fe_{17} phase (grey)

Slika 6: SEM posnetek, ki prikazuje zrna Sm_2Fe_{17} faze (sivo) velikosti >20 μm stricted just to the size of the particle with small particles. In other words, it is impossible, for example, to have a grain size larger than 1μm in a particle with size 1μm. The 820°C recombination temperature causes rapid grain growth and the resulting coercivities in the non pre-milled (1mm) material are low as a result of this grain growth. But with a particle size reduction to 4-5μm a considerable increase in the coercivity is observed because the particle size is now in a position to restrict the grain size.

The SEM micrograph in **Figure 6** shows the presence of grains substantially larger than 5μm in the non pre-milled starting material recombined at 820°C. Such grains could not exist in the pre-milled material simply because of the physical dimensions of the particles. This being the case, it would seem that in order to achieve the highest coercivities for SmFe based HDDR materials it is critical to restrict the grain growth by restricting the particle size.

4 CONCLUSIONS

The introduction of Ta has a very significant and beneficial impact on both the cast material and the final nitrided HDDR product. The enhanced values of coercivity in the SmFeTa material indicate the critical importance of Ta in reducing as far as possible any free iron in the material. The Ta containing alloy was observed to be significantly more stable in terms of the resistance of the 2:17 hydride phase to disproportionation. This can be attributed to the dissolution of small amounts of Ta into the 2:17 phase increasing its stability with respect to decomposition in a hydrogen atmosphere.

Milling of the material before the HDDR treatment reduces the particle size and prevents the grains from growing to a size when they may have a detrimental effect on the coercivity. The low recombination temperature samples are largely particle size independent, but the case of the high temperature processing, particle size is critical.

ACKNOWLEDGEMENT

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