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High coercivity powders based on Sm–Fe–Ta–N prepared by a novel technique

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Nitrided Sm_2Fe_{17}-based materials possess excellent intrinsic magnetic properties, and in this study we have investigated two compositions: $Sm_{13.7}Fe_{86.3}$ and $Sm_{13.8}Fe_{82.2}Ta_{4.0}$. The stoichiometry of each phase was determined and the SmFeTa material was found to include Ta_3Fe_7, in addition to the Sm_2Fe_{17}, $SmFe_2$ and $SmFe_3$ phases observed in the SmFe alloy, but without the α-iron dendrites which are characteristic of the binary material. SEM and TEM studies revealed that in the cast structure some 2.0% Ta is initially dissolved in the $Sm_2(FeTa)_{17}$ phase, however, HDDR processing causes the formation of Ta-based precipitates leaving the 2 : 17 with much less dissolved Ta. The HDDR process, with subsequent nitrogenation, was used to prepare coercive powders. The coercivities of these powders were found to be very dependent on HDDR conditions and Ta addition. The highest coercivity achieved was 1280 kA/m for the composition with Ta.

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Because of their excellent intrinsic magnetic properties, SmFeN [1] magnets are being treated as potential candidates for certain types of high-energy permanent magnets. But because of their instability at temperatures above 500°C, where they decompose into αFe and SmN, their production is limited to bonded magnets. The most common processes used for the preparation of the highly coercive powder for bonded magnets are 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 Sm_2Fe_{17} phase is produced by a peritectic reaction resulting in some inreacted αFe (up to 25%) [9] which, because it is magnetically soft, has an adverse effect on the hard magnetic properties. Regardless of the method used for the preparation of the alloy the crystallization of αFe is difficult to avoid. As a result, a long and expensive heat treatment is necessary in order to remove the αFe phase. Previous studies, however, have shown that with the addition of a third element: 4–5% Nb [10] or Ta [11] or 1% Zr [12], the primary αFe crystallization can — to a large extent — be avoided.

The HDDR process used for the preparation of highly coercive powders is bases on the reaction of the alloy with hydrogen at different temperatures. The addition of a third element to the system causes significant changes in the behavior of the material: Ga [13], Zr [14] or Nb [15] have been observed to stabilize the 2 : 17 phase against disproportionation.

In this paper we will attempt to explain the difference between SmFe and SmFeTa alloys, which arises from the different microstructures and phase composition.

1. Experimental procedure

SmFe and SmFeTa cast alloys were produced by conventional induction melting methods in 5-kg batches by Less Common Metals Ltd. The metals were carefully prepared using standard metallographic methods and examined by an energy dispersive x-ray spectroscopy (EDX)-equipped SEM. As-cast materials were also investigated using x-ray difractometry to determine their lattice parameters.

The cast alloys and alloys which have been HDDR-treated once were investigated with TEM in order to explain the different behavior during the HDDR process between the binary material and the Ta-containing material. TEM samples of powdered material were prepared using 3 to 5 wt.% phenol-formaldehyde resin, pressed at 0.5 to 1 MPa and cured at 180°C for a few minutes. The resulting pellet was mechanically very strong, so subsequent grinding, dimpling and ion erosion were without any problems. Due to the high proportion of powder particles, no liguid-nitrogen cooling during the ion erosion process was necessary and no charging effects were observed in the transmission electron microscope. Samples were examined using a Jeol 2000 FX TEM, operated at 200 kV. The chemical composition was investigated using a Link AN-10000 EDX system with an Ultra-Thin Window Si(Li) detector mounted perpendicular to the electron beam. The samples were tilted at an angle of 30.5° during the EDXS spectrum collection. The Ta_3Fe_7 phase from the SmFeTa cast material and the Sm_2Fe_{17} phase from the binary cast material were used as standards for the k-ratio determination. The Cliff–Lorimer [16] method and absorption correction [17,18] were used for the quantitative analysis. The sample thickness, required for the absorption calculations, was estimated using the contamination-spot method.

2. Results and discussion

2.1. *X*-ray diffraction and EDX spectroscopy. The SmFeTa material was found to contain significant amounts of Ta_3Fe_7 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 SmFe material.

Results of the lattice-parameter refinement calculations

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

Analyses of the Sm_2Fe_{17} phase in the SmFeTa sample show that 2–3% of Ta is dissolved in this phase. More detailed information relating to this investigation has been published previously [19]. Results of the lattice-parameter refinement calculations are shown in the Table. These refinements reveal that the presence of Ta in the Sm_2Fe_{17} phase, in agreement with Saje et al. [20], causes a significant lattice expansion. The volume of the 2:17 unit cell for the SmFeTa alloy was observed to be 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. [21] for a 4% Nb alloy.

2.2. TEM investigations. In order to assess the influence of Ta on the different behaviour observed during the HDDR process, both materials were studied using analytical electron microscopy (TEM-EDX). First the SmFeTa cast material was investigated (Fig. 1). The phase composition obtained using SEM-EDX analyses was confirmed. It was found that the 2:17 matrix phase has some Ta dissolved in it. In contrast, Ta can be found in the form of Ta-rich precipitates in the Sm-rich phases $SmFe_2$ and $SmFe_3$. In the $SmFe_2$ phase some planar defects were observed. Using bright-field and dark-field experiments it was confirmed that these defects are most probably antiphase boundaries (APB) (cf. Fig. 1).

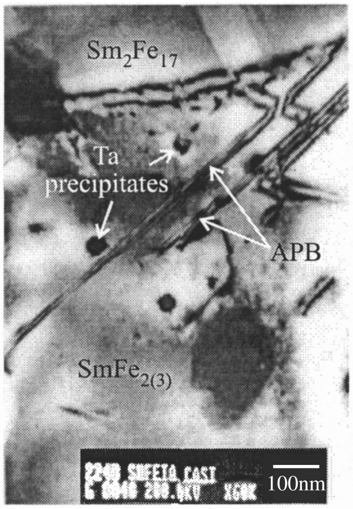

Figure 1. A TEM image of as-cast Sm–Fe–Ta alloy.

Then the SmFeTa sample subjected to the HDDR run (Fig. 2) was investigated and some differences were observed. It was found that the 2:17 matrix phase contains less Ta than the same phase in the cast material. The Ta was found in the form of Ta-based precipitates located within the original 2:17 phase. To find the exact difference in the Ta concentration in the Sm_2Fe_{17} phase between the cast material and in the samples after the HDDR run, we performed rigorous, quantitative EDXS analysis.

During the 5 minutes required for the collection of an EDXS spectrum we observed that the drift of the sample and the sample contamination (carbon build-up) were relatively low. Limited to 300 seconds and taking into account that around 5000 counts per Ta L_α peak for a 3% error limit (at the 95% confidence level) should be used, we found that the foil thickness at the measuring points had to be at least 150 nm. At this thickness the

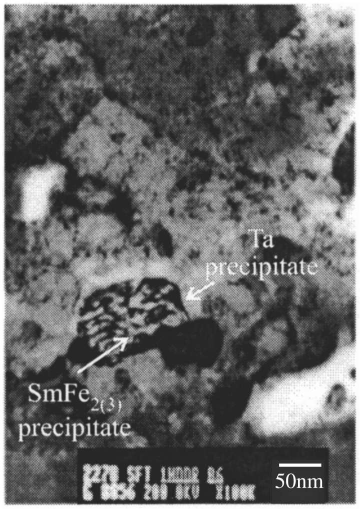

Figure 2. A TEM image of HDDR-processed Sm–Fe–Ta material.

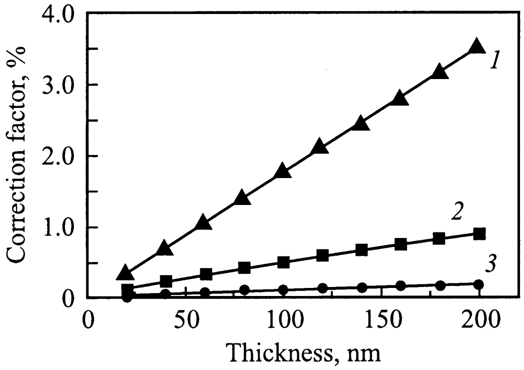

Figure 3. Calculated absorption-correction and sec. fluorescence correction factors vs foil thickness (*1* — absorption-correction factors for Ta, *2* — secondary fluorescence correction factors for Sm–Fe, and *3* — for Fe–Ta).

influence of the amorphous contamination layer, originating from the ion erosion process, is also minimised. In addition, due to the relatively high mass absorption coefficient of Ta L_α lines in Sm (433.9 cm^2/g) [18], the influence of absorption should be tested if the errors are to be kept as low as possible. In Fig. 3, the calculated absorption-correction coefficients for Ta as a function of foil thickness in the Sm_2Fe_{17} phase are shown. For a thickness of around 150 nm, the correction factor is higher than 2.5% and thus absorption should not be neglected. We performed a similar calculation [22] for the secondary fluorescence correction (Fig. 3) and found that the effect is very low, so this type of correction was not used.

From the measured concentrations we calculated the reproducibility (precision, defined as the relative standard deviation of measurements) of the Ta concentration measurements in various phases. It was found that in the Ta_3Fe_7 phase (cast material) the reproducibility was better than 2%, justifying the use of this phase as a standard for Ta. In the $Sm_2(FeTa)_{17}$ phase in the cast alloy the relative standard deviation of measurements was better than 5% and in the same phase in the sample after a single HDDR cycle it was around 12%. The relatively high value of the standard deviation in this case can be explained by the presence of Ta_3Fe_7 nano-precipitates in the analysed volume. After discarding the points where a high concentration of Ta indicates the presence of Ta-rich precipitates, it was found that in the Ta-containing cast material the concentration of Ta in the Sm_2Fe_{17} phase is 2.0 ± 0.1 at.% while after the HDDR process this phase contains 1.2 ± 0.1 at.% of Ta.

In summary, the introduction of Ta has a very significant and beneficial impact on the cast material, magnet-processing problems associated with the presence of iron dendrites are removed due to formation of the Ta_3Fe_7 phase rather than peritectic iron.

The Ta-containing alloy was also 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 2.0% of Ta into the 2 : 17 phase increasing its stability with respect to decomposition in a hydrogen atmosphere. SEM and TEM studies revealed that the Ta is initially dissolved in the $Sm_2(FeTa)_{17}$ phase in the cast structure, however, HDDR process causes the formation of Ta-based precipitates leaving the 2 : 17 phase with 1.2% dissolved Ta.

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