Optimizing the microstructure of sintered Nd-Fe-B magnets via the application of scandium hydride

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Abstract. This paper is focused on optimizing the microstructure of near-stoichiometric Nd2Fe14B-based magnet by grain boundary structuring via the application of ScHx (0.5 and 1 wt.%) added to the matrix powder mixture at the fine milling stage. Scandium is assumed can acts as component, which restricts the Nd2Fe14B-phase grain growth and by analogy with titanium, niobium, molybdenum and vanadium alloying for Nd-Fe-B compositions, Sc improves the corrosion resistance and technological stability of magnets. The base alloy having the composition (wt.%) Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Nb-0.5, Fe-balance was prepared by strip-casting technique and subjected to hydrogen decrepitation during heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h dwell at this temperature. The scandium hydride was prepared by direct reaction of Sc with hydrogen using a Sieverts apparatus. The microstructure, phase composition and distributions of REM and Sc for the prepared magnets were investigated by SEM/EDX method.

It was found that the total REM content in the main magnetic (Nd, Pr, Dy)2Fe14B phase of both magnets was 11.8 at % and as well as the scandium content was nearly identical. Sc mainly was observed as individual phases. The Sc content in them for magnets prepared with 0.5 and 1.0 wt.%ScHx is 15 and 38 at.%, respectively. In this case, the chemical composition of the phase in the magnet prepared with 0.5 wt % ScHx corresponds to that of Laves phase, whereas for the magnet with 1.0 wt % ScHx, the iron content in the phase is less than 10 at %. The R-rich phase was found is enrich in Nd and Pr. The further experiments with ScHx should be performed in varying boron content in the magnets.

1. Introduction
Sintered Nd-Fe-B magnets find wide applications for technology owing to the high maximum energy product \( (BH)_{\text{max}} \), residual inductance \( (B_r) \), and magnetization coercive force \( (H_c) \). Aside from their use in hard disc drives (HDDs), head driving voice coil motors (VCMs), and magnets for positioning optical pickups such as CDs or DVDs, they are indispensable materials for small, high-performance, highly-efficient drive units including servo motors for industrial appliances, DC brushless motors for hybrid vehicles, air conditioners, and motors for home electric appliances such as washing machines, and a number of innovative applications [1-7].
Scandium is assumed can acts as component, which restricts the Nd$_2$Fe$_{14}$B-phase grain growth and by analogy with titanium, niobium, molybdenum and vanadium alloying for Nd-Fe-B compositions, Sc improves the corrosion resistance and technological stability of magnets. This paper deals with the effect of ScH$_x$ compound, which was added (0.5 and 1 wt.%) to the matrix powder mixture at the fine milling stage, on the microstructure, phase composition and magnetic characteristic of near-stoichiometric Nd$_2$Fe$_{14}$B-based magnet.

2. Experimental
The base alloy having the composition (wt.%) Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Nb-0.5, Fe-balance was prepared by strip-casting technique and subjected to hydrogen decrepitation during heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h dwell at this temperature. The ScH$_x$ compound was prepared by direct reaction of Sc with hydrogen using a Sieverts apparatus. The ScH$_x$ compound(0.5 and 1 wt.%) and hydrogen-decrepitated strip-cast alloy were mixed and subjected to fine milling for 40 minutes till reaching an average particle size of 3 μm using a vibratory mill and isopropyl alcohol medium. After wet compaction of the pulp in a transverse magnetic field of 1500 kA/m, blanks of magnets were sintered at T = 1080 °C for 2 h and subjected to an optimum heat treatment (HT) at 500 °C for 2 h. The high-resolution field emission gun-scanning electron microscope QUANTA 450 FEG equipped with an EDX APOLLO X microprobe was used for the investigation of microstructure and chemical composition of the samples. The grain size of Nd(R)$_2$Fe$_{14}$B phase was evaluated using the automatic image analysis, when the ferret max of grains was measured. Magnetic properties of the permanent magnets were measured using the automatic hysteresisgraph at room temperature (RT). To analyze magnetic properties of magnet at higher temperatures up to 150 °C, we used vibrating sample magnetometer (VSM) Microsense EV9 embedded with the oven working in the temperature range from RT to 700 °C. However, for these measurements the dimensions of the magnet were reduced to 1×1×1 mm due to small space in the oven and in order not to saturate VSM highly sensitive for detection of thin films and other magnetic materials owing lower magnetization. Maximal applied magnetic field of VSM is 1920 kA/m (2.4 T) at RT and 1800 kA/m (2.25 T) when using the oven.

3. Results and discussion
3.1 Study of microstructure and phase composition
The microstructure of both types of the sintered magnets prepared from the powder mixture with 0.5 and 1 wt.% of ScH$_x$ compound is shown in figures 1 and 2, where the analyzed phases are indicated. Chemical composition of theses phases is summarized in table 1, where the mean values obtained from three analyses are given for phases 1 and 3. The stoichiometric composition of matrix grains in the both samples is close to that of the Nd(R)$_2$Fe$_{14}$B phase (Phase 1 in Fig. 1 and Fig. 2). The several intergranular Nd-rich phases at multiple 2-14-1 grain junctions, which contained ~58 to 71 wt.% Nd and ~19 to 23 wt.% Pr, were observed (phase 2 in figures 1 and 2). The scandium content at these phases was variable. Some small intergranular phases in triple junctions (phase 5 in figures 1 and 2) were characterized by the increased Fe-content in comparison to the phase 2, which could be affected by the composition of surrounding material (the analyzed area is smaller than the EB spot size). Other found phases in the structure of both magnets were REM-(Fe)-based oxides between grains of the samples (phase 3 in figures 1 and 2). It can be seen that black particles are placed between the matrix grains (phase 4 and 6). According to the spot chemical analysis, these could be the compound based on Sc-Nb-(B). In case of the magnet with 0.5 wt.% of ScH$_x$, the particles are in the needle-shaped form. The higher content of ScH$_x$ addition led to the formation of the plate-shaped particles. The increased content of Sc was observed only at the intergranular phases, i.e. no significant diffusion of Sc to matrix 2-14-1 grains was realized during the sintering and subsequent heat treatment.
Figure 1. The microstructure of Nd-Fe-B sintered magnet prepared from the powder mixture with 0.5 wt.% of ScHₓ addition and marked analyzed phases.

Table 1. Chemical analysis of Nd-Fe-B sintered magnet prepared from the powder mixture with 0.5 wt.% of ScHₓ addition.

| Area/phase | Oₓ | Dyₓ | Alₓ | Nbₓ | Scₓ | Prₓ | Ndₓ | Feₓ | Coₓ | Cuₓ |
|------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Area       |    |     |     |     |     |     |     |     |     |     |
| Phase 1    | 0.8| 0.3 | 0.3 | 0.1 | 0.1 | 0.2 | 5.2 | 22.4| 69.3| 0.6 | 0.2 |
| Phase 2.1  | 0.0| 0.0 | 0.1 | 0.2 | 0.2 | 19.2| 59.4| 20.4| 0.5 | 0.3 |
| Phase 2.2  | 0.4| 0.3 | 0.3 | 0.4 | 19.9| 57.9| 19.6| 4.6 | 0.5 | 0.6 |
| Phase 2.3  | 0.0| 0.0 | 0.3 | 0.2 | 22.8| 71.4| 4.6 | 0.5 | 0.2 |
| Phase 3    | 14.1| 1.5 | 0.2 | 0.3 | 6.9 | 10.8| 29.2| 36.3| 0.4 | 0.3 |
| Phase 4.1  | 0.2| 0.2 | 13.2| 8.0 | 7.5 | 21.1| 48.9| 0.6 | 0.4 |
| Phase 4.2  | 0.4| 0.2 | 14.6| 6.6 | 5.9 | 20.2| 51.3| 0.5 | 0.4 |
| Phase 4.3  | 0.6| 0.2 | 10.8| 5.2 | 7.7 | 23.1| 51.7| 0.5 | 0.3 |
| Phase 5.1  | 0.6| 0.1 | 0.3 | 0.2 | 14.4| 35.4| 39.1| 0.8 | 9.0 |
| Phase 5.2  | 2.0| 0.5 | 0.9 | 0.5 | 12.4| 34.1| 48.5| 0.6 | 0.5 |
| Phase 5.3  | 0.0| 0.3 | 0.2 | 0.2 | 16.7| 44.0| 29.1| 0.8 | 8.9 |

Figure 2. The microstructure of Nd-Fe-B sintered magnet prepared from the powder mixture with 1 wt.% of ScHₓ addition and marked analyzed phases.
Table 2. Chemical analysis of Nd-Fe-B sintered magnet prepared from the powder mixture with 1 wt. % of ScH₅ addition.

| Area/phase | O_K | Dy_M | Al_K | Nb_L | Sc_K | Pr_L | Nd_L | Fe_K | Co_K | Cu_K |
|------------|-----|------|------|------|------|------|------|------|------|------|
| Area       | 1.3 | 0.3  | 0.4  | 0.8  | 7.2  | 24.2 | 64.8 | 0.6  | 0.4  |
| Phase 1    | 0.8 | 0.2  | 0.3  | 0.3  | 6.2  | 22.3 | 68.9 | 0.6  | 0.3  |
| Phase 2.1  | 4.8 | 0.1  | 0.3  | 0.9  | 20.6 | 68.7 | 3.8  | 0.5  | 0.3  |
| Phase 2.2  | 0.3 | 0.1  | 0.1  | 0.2  | 19.3 | 65.2 | 14.3 | 0.4  | 0.1  |
| Phase 2.3  | 0.0 | 0.1  | 0.7  | 1.0  | 18.3 | 61.7 | 17.4 | 0.6  | 0.2  |
| Phase 3    | 25.4| 1.0  | 0.1  | 0.1  | 14.7 | 15.1 | 38.3 | 4.8  | 0.3  | 0.2  |
| Phase 4.1  | 1.8 | 0.2  | 1.3  | 53.5 | 8.0  | 21.0 | 13.4 | 0.5  | 0.3  |
| Phase 4.2  | 0.0 | 0.2  | 14.3 | 9.2  | 9.6  | 26.2 | 37.2 | 1.0  | 2.4  |
| Phase 4.3  | 0.0 | 0.2  | 10.0 | 6.2  | 8.3  | 23.9 | 48.7 | 0.9  | 1.9  |
| Phase 5.1  | 1.1 | 0.5  | 0.5  | 0.4  | 13.4 | 36.4 | 46.2 | 0.6  | 0.9  |
| Phase 5.2  | 1.2 | 0.2  | 0.1  | 0.3  | 19.1 | 41.4 | 36.8 | 0.7  | 0.3  |
| Phase 5.3  | 0.4 | 0.3  | 0.1  | 0.2  | 11.7 | 31.3 | 51.2 | 1.0  | 3.9  |
| Phase 6.1  | 0.4 | 0.1  | 44.0 | 27.7 | 5.5  | 12.0 | 9.6  | 0.3  | 0.4  |
| Phase 6.2  | 0.2 | 0.2  | 28.7 | 17.8 | 7.5  | 18.6 | 26.0 | 0.5  | 0.5  |
| Phase 6.3  | 0.7 | 0.2  | 22.7 | 19.4 | 10.2 | 24.5 | 21.0 | 0.7  | 0.7  |

The distribution of Sc, B, Nb, Cu and Co in matrix grains and in the intergranular phases was studied using x-ray mapping – see figures 3 and 4. The scandium was preferentially found at intergranular phases, because Sc does not diffuse into 2-14-I grains despite to the small atomic radius (among rare-earth metals) [8]. It is evident that Sc-based phases (black particles) are characterized by the increased boron and niobium contents. This fact corresponds with the assumption that scandium and niobium react during sintering and heat treatment with boron to form boride at grains boundaries. However, this phenomenon must be investigated in detail. Co and Cu distribution over the matrix grains is nearly homogeneous. Some Nd-rich phases contain a higher amount of Cu in comparison with other intergranular phases.

Figure 3. X-ray elemental mapping of Sc, B, Nb, Cu and Co in matrix grains and in the intergranular phases of Nd-Fe-B sintered magnet prepared from the powder mixture with 0.5 wt.% of ScH₅ addition.
The effect of Sc-based particles on the microstructure of sintered magnets is analogous to that of Ti, Nb, Mo, which form borides at grain boundaries [9-13]. These particles effectively restrict the grain growth during sintering and heat treatment, which can favor the high coercivity. The grain size distribution in the sintered magnets prepared from powder mixture with 0.5 and 1 wt. % ScHₓ is shown in figure 5. The mean grain size of both sintered magnets was nearly identical and achieved the value of $7 \pm 3 \mu m$. However, the major difference in the microstructure of both magnets consisted in the grain size fraction. The higher content of ScHₓ caused that the proportion of small grains ($\leq 4 \mu m$) was two-times increased and the size distribution was more uniform.

**Figure 4.** X-ray elemental mapping of Sc, B, Nb, Cu and Co in matrix grains and in the intergranular phases of Nd-Fe-B sintered magnet prepared from the powder mixture with 1 wt.% of ScHₓ addition.

**Figure 5.** The grain size distribution in the sintered magnets prepared from powder mixture with (a) 0.5 wt.% and (b) 1 wt.% of ScHₓ addition.

### 3.2 Magnetic properties

The magnetic properties of sintered magnets prepared with 0.5 and 1 wt.% of ScHₓ addition from VSM are given in table 3 and table 4, respectively. It is obvious from these results that the values of magnetic properties of both magnets are nearly identical at all temperatures, i.e. the amount of added ScHₓ compound did not affect the magnetic characteristics.
Table 3. Magnetic properties of Nd-Fe-B sintered magnet prepared from the powder mixture with 0.5 wt.% of ScH₃ addition.

| B_r  | cH_J | cH_B | T      | α (B_r) | β (H_B) | Temperature range |
|------|------|------|--------|---------|---------|------------------|
| (T)  | (kA/m) | (kA/m) | (°C) | (% / °C) | (% / °C) | (°C)             |
| 1.04 | 716  | 477  | 20    | -0.03   | -0.83   | 20 - 50          |
| 1.03 | 557  | 358  | 50    | -0.22   | -0.71   | 20 - 100         |
| 0.86 | 318  | 231  | 100   | -0.33   | -0.83   | 20 - 100         |
| 0.59 | 183  | 135  | 150   | -0.33   | -0.83   | 20 - 150         |

Table 4. Magnetic properties of Nd-Fe-B sintered magnet prepared from the powder mixture with 1 wt.% of ScH₃ addition.

| B_r  | cH_J | cH_B | T      | α (B_r) | β (H_B) | Temperature range |
|------|------|------|--------|---------|---------|------------------|
| (T)  | (kA/m) | (kA/m) | (°C) | (% / °C) | (% / °C) | (°C)             |
| 1.08 | 716  | 477  | 20    | -0.15   | -0.83   | 20 - 50          |
| 1.03 | 557  | 358  | 50    | -0.29   | -0.76   | 20 - 100         |
| 0.83 | 318  | 223  | 100   | -0.35   | -0.75   | 20 - 100         |
| 0.59 | 195  | 139  | 150   | -0.35   | -0.75   | 20 - 150         |

The series of J-H curves for both sintered magnets measured using the VSM in dependence on temperature are documented in figure 6. The shape of the curves at 20 °C showed two magnetization reversals starting at about ±278 kA/m. This step could be caused by the effect of surface layer of small samples. The smaller the sample, the higher the surface fraction and its effect.

![Figure 6. VSM J-H curves of the Nd-Fe-B sintered magnet prepared from the powder mixture with (a) 0.5 wt.% and (b) 1 wt.% of ScH₃ addition depicted as a function temperature.](image)

4. Conclusions

The detailed investigation of microstructure and magnetic properties of Nd-Fe-B sintered magnets prepared from the powder mixture with 0.5 and 1 wt.% of ScH₃ addition and subjected to optimum heat treatment has been performed. After the decomposition of ScH₃ during the sintering process, the free scandium probably reacted with niobium and boron to form needle-shaped and plate-shaped boride particles at the grain boundaries, which could effectively restrict the grain growth during the heat treatment. The scandium was preferentially found at intergranular phases, because Sc does not diffuse into 2-14-1 grains despite to the small atomic radius (among rare-earth metals). The effect of
the amount of used ScHₓ addition in powder mixture on magnetic characteristics was not demonstrated.

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