

EFFECT OF THE MICROSTRUCTURE ON MAGNETIC PROPERTIES OF Nd₂(Fe,Co)₁₄B₁Ga-BASED ALLOYS DURING HDDR PROCESS

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Abstract. Microstructure and magnetic properties of Fe-Nd_{13.5}-Co₁₅-B_{6.8}-Ga_{0.1}-Zr_{0.2-1} alloys during HDDR process were studied. ZrB₂ phase was detected and identified by X-Ray diffraction. Influence of Ga, Zr and Ga+Zr additions on phase relations at different stages of HDDR process was studied by X-ray diffraction and magnetic measurements.

INTRODUCTION

Recently the process based on carefully controlled hydrogenation, disproportionation, desorption and re-combination (HDDR) for producing Nd-Fe-B magnetic powders, used in anisotropic resin bonded magnets, was developed [1]. Additions of Co, Ga and Zr are the most effective for increasing the magnetic anisotropy and coercivity of the powder [1,2]. Anisotropy of the large (0.05-0.1 mm in size) grains results from the orientation memory effect: oriented fine Nd₂Fe₁₄B grains grow from finely distributed disproportionated structure (NdH₂+BFe₂+Fe) and by some mechanisms yet to be established have a common orientation within each grain of the original as cast material [1,2].

As it was proposed in [3], this effect is caused by tiny nuclei of Nd₂Fe₁₄B phase existing in the disproportionated mixture after HD- stage of HDDR process; new fine grains of Nd₂Fe₁₄B grow from these nuclei. As it was proved by X-Ray diffraction [4], some amount of Nd₂(Fe-Co)₁₄B phase exist after HD- stage of HDDR process thanks to Ga additions to Fe-Co-Nd-B alloy. Co additions accelerate forming of Nd₂Fe₁₄B phase in DR- stage of the HDDR process [5].

Mechanism of the Zr influence on the orientation memory effect is not understood quite. It was proposed in [3], that ZrB₂ phase may be responsible for this effect. Small precipitates of Zr-rich phase were found in Nd₂Fe₁₄B grains by transmission electron microscopy (TEM), but the structure of these precipitates was not determined [6,7]. Not only Zr-B₂ phase may exist in these alloys but also ZrB₁₂. Zr-B phases have very high melting points, Metal-B phases are known to be very chemically stable and to be good grain-grow inhibitors in many alloys. So ZrB₂ or ZrB₁₂ phase precipitates may be good centers for nuclei of Fe₁₄Nd₂B phase and may control the grain size in HDDR process.

Co additions, useful for orientation memory effect, stimulate the formation of soft-magnetic (Fe-Co)₂Nd phase, not desirable for hard magnetic materials, Ga (and Al) suppresses its formation and formation of Ga-Fe-Co-Nd phases takes place [8-10]. Some fine Co-containing precipitates were found by TEM in Fe₁₄Nd₂B grains [10].

These precipitates can play a role of centers for Fe₁₄Nd₂B nuclei in orientation memory effect too.

This work is concerned with study of phase relations that can play a role in orientation memory effect, and coercivity too, for Co, Ga, Zr -doped Fe-Nd-B alloys on different stages of HDDR process.

EXPERIMENTAL

The Nd-Fe-B based alloys, given in table I, were melted in vacuum induction furnace and were cast in the form of plate 12 mm thick. Plates were mechanically polished, broken to pieces, annealed in evacuated quartz tubes for 16 hours at 1100° C and rapidly cooled to room temperature. These ingots were disk-milled into the powder with grain size 0.05-0.2 mm (stage 1). The powders were disproportionated at 800-830°C under controlled hydrogen pressure 0.1-1.0 atm. for 1-2 hours (stage 2), 0.5 hour under vacuum at 820-860°C, then cooled in argon stream (stage 3). Stage 2 was fixed by the quenching of the powder in container on the copper surface.

X-Ray diffraction studies were done by numerical diffractometer and accompanied by computer data analysis for stage 1-3 samples. Cu-K_a radiation was used.

Table I. Compositions of alloys, at.% Fe- basis.

alloy N	Nd	Co	B	Ga	Zr
1	13.5	15.0	6.2	1.0	0.2
2	13.5	15.0	6.2	1.0	0.6
3	13.5	15.0	6.2	1.0	1.0
4	13.5	15.0	8.2	1.0	1.0
5	13.5	15.0	6.2	---	0.2
6	13.5	15.0	6.2	---	1.0

RESULTS AND DISCUSSIONS

Fragments of X-ray diffractograms of alloys 1-6 after annealing treatment are shown in fig.1. Between of the main Nd₂Fe₁₄B phase peaks some peaks of minor phases are visible.

The main peak of $\text{Nd-Fe}_4\text{-B}_4$ phase ($2\theta=40.0^\circ$) is practically absent for alloy 6, very small for alloys 2 and 3. Its intensity becomes greater subsequently for alloys 5, 1 and 4. B and Ga additions increase its intensity, but Zr additions diminish.

Peaks of $(\text{Fe-Co})_2\text{Nd}$ phase with cubic structure [8-10] ($2\theta=34.2, 40.3, 42.2^\circ$) were found for all alloys. Their intensity (relative to the peaks of main phase) increases subsequently for alloys 1, 2, 4, 5, 3, 6. B and Ga additions decrease their intensity, but Zr additions increase.

Peaks of ZrB_2 phase have practically the same positions as peaks of $(\text{Fe-Co})_2\text{Nd}$ phase. Above mentioned lines are wider than others, but they must belong to $(\text{Fe-Co})_2\text{Nd}$ phase, because their intensity for alloys 3 and 6 is very high and B additions diminish their intensity.

Peaks of ZrB_2 phase are covered by strong reflexes of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Only a peak at $2\theta=25.2^\circ$ was seen in cases of alloys 3 and 6 near peak 202 of $\text{Fe}_2\text{-Nd}_{14}\text{-B}$ phase, see fig.2.

Additional peaks were found for alloy 3 (and very small - for 1,2,4 alloys). Their positions agree with $(\text{Fe-Co})_{17}\text{Nd}_2$ phase peak positions.

At HD stage of HDDR process X-Ray diffractograms contained intensive peaks of NdH_2 and bcc Fe and relatively weak peaks of Fe_2B , as reported in [1-5], but also peaks of ZrB_2 phase. These peaks were seen at $2\theta=25.2;41.7;51.7;62.5^\circ$. Other peaks were covered by intensive lines of NdH_2 and Fe phases. Intensity of these peaks is of the same order as peaks of Fe_2B phase. Ga addition slightly diminishes their intensity. Some peaks are shown in fig.3.

Peaks of other minor phases (NdFe_4B_4 , $(\text{Co-Fe})_2\text{Nd}$, ZrB_{12} , $(\text{Fe-Co})_{17}\text{Nd}_2$) and of Ga-containing phases were not found on the HD stage (2).

Decrease of the intensity of ZrB_2 phase due to Ga addition may take place because Ga may combine with Zr and Zr-Ga phases may be formed. These phases have more complex structure than ZrB_2 phase, their peaks must be not so intensive as peaks of ZrB_2 , so they may be invisible.

Diffractograms after HDDR process shown in fig.4 contained some minor phase peaks between peaks of main $\text{Fe}_{14}\text{Nd}_2\text{B}$ phase.

Main peak of $\text{Fe}_4\text{B}_4\text{Nd}$ phase ($2\theta=40.0^\circ$) was very small for alloys 2,3, large for 1, 4 and 5 alloys, closed by other intensive peaks for alloy 6.

Peaks of $(\text{Co-Fe})_2\text{Nd}$ phase became more intensive than on fig.1 for alloy 6, for alloys 2-5 their intensity became smaller, for alloy 1 this peak was not observed.

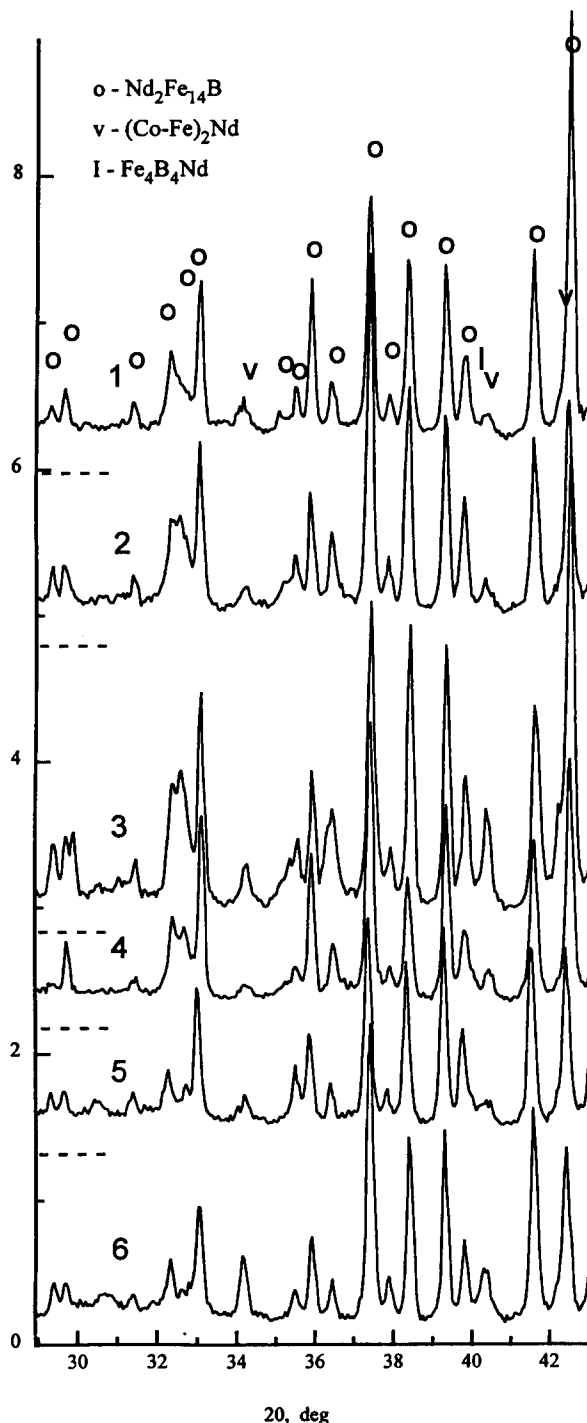


Fig.1. Diffractograms of alloys 1-6 after annealing.

Intensity - in thousands counts.

Broken lines - zero intensity for 1-5 lines.

Visible peak of ZrB_2 phase became more intensive.

Intensive line at $35.0-35.1^\circ$ was seen for Ga-doped alloys (1-4).

Above described phase relations can be understood if we assume, that Zr combines with B forming ZrB_2 phase, that is known to be a very stable compound even at very high temperatures and even in liquid metals and alloys. In this work ZrB_2 phase was identified at all stages of HDDR process, its precipitates may play a role of centers of $Nd_2Fe_{14}B$ phase nuclei on -DD- stage of HDDR process as it was proposed in [3].

Formation of ZrB_2 phase leads to many secondary effects on phase relations.

Since B was taken from the alloy by Zr, deficit of B may take place, and $(Co-Fe)_xNd_y$ phases may appear. Appearance of $Fe_{17}Nd_2$ phase due to formation of ZrB_2 phase was predicted for Zr-doped alloys in [12] and observed in [13].

In our case $(Fe-Co)_2Nd$ phase that was observed in Co doped alloys [8-9], appears in all alloys (1-6). Zr additions stimulated, but B additions suppressed its formation. This can be explained as a result of ZrB_2 phase formation, leading to a shift of alloy point on $(Fe-Co)-Nd-B$ phase diagram to the $(Co-Fe)-Nd$ side. More complex mechanism, based on assumption, that Zr additions make $(Co-Fe)_2Nd$ phase more stable than $Nd_2Fe_{14}B$ phase may take place too. It was found in [14], that Al additions make $(Co-Fe)_2Nd$ phase less stable. But Zr additions may make it more stable.

Ga additions suppressed formation of $(Fe-Co)_2Nd$ phase in alloys 1-6. Similar effect was observed in [10] for Fe-Nd-B-Co-Ga alloys. Another mechanism can explain Ga influence on phase relations in Fe-Nd-B-Co-Zr-Ga alloys too. Some amount of Zr can be connected with Ga forming compounds Zr_xGa_y and shift of alloy point on phase diagram to the $(Co-Fe)-Nd$ side due to ZrB_2 phase formation may be smaller. In this case, the amount of $(Co-Fe)_2Nd$ phase must be diminished by Ga addition, that was seen for alloys 1,3,5,6. Data on alloys 3 and 4 demonstrating, that extra B additions suppress formation of $(Co-Fe)_2Nd$ phase more effectively than Ga additions, agree better with the last explanation.

Magnetic properties of alloys 1-6 after HDDR process (table II) depend on $(Co-Fe)_2Nd$ phase amount. For alloy 1 this phase was not visible after HDDR process; its magnetic properties were the best. iH_c decrease due to large Zr additions was observed in [2,13]. Above described formation of ZrB_2 phase, leading to deficit of B and forming of $(Fe-Co)_xNd_y$ softmagnetic phases, that are not desirable for hard magnets, may be one of the causes of magnetic properties decrease due to large Zr additions. In this case HDDR process must help Zr to take B from the alloy, since at

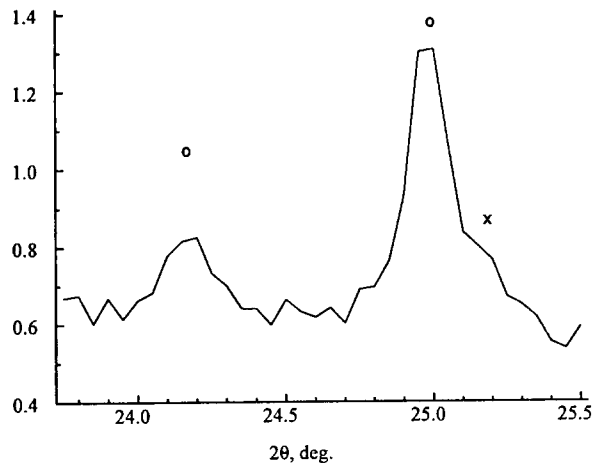


Fig.2. Fragment of diffractogram of alloy 6 after annealing.
Intensity - in thousands counts.
o - $Fe_2Nd_{14}B$, x - ZrB_2

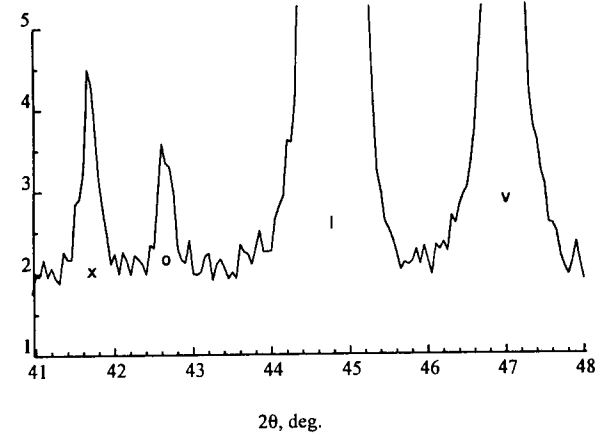


Fig.3. Fragment of diffractogram of alloy 6 on stage 2 (HD).
Peaks of ZrB_2 - x, BFe_2 - o, Fe - I, NdH_2 - v.
Intensity - in hundreds counts.
110 Fe-peak intensity - 7500 counts.

Table II. Magnetic properties of powders after HDDR process.
HD-stage - $810^\circ C, 2h$, -DR stage - $850^\circ C, 0.5h$.

alloy N	B_r , kG	iH_c , kOe	$(BH)_{max}$, MGOe
1	8.8	13.2	15.4
2	8.7	13.6	15.2
3	8.3	12.1	11.2
4	8.4	13.8	14.7
5	8.3	13.9	14.7
6	8.2	10.6	11.9

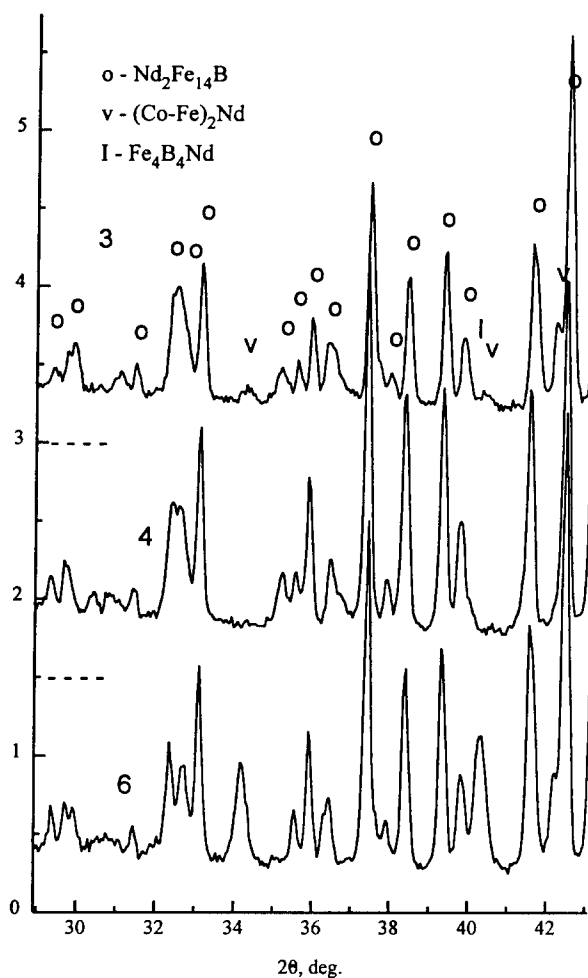


Fig.4. Diffractograms of alloys 3, 4, 6 after HDDR process, described in tab. II. Intensity - in thousands counts. Broken lines - zero intensity for 3, 4 lines.

-DD- stage of HDDR process B exists in compounds Fe_2B and ZrB_2 , but the formation of the last compound is more chemically effective (temperature of its formation (more than 3000°C) is 2 times higher). So, Zr additions must be accompanied by B additions and this is more important for HDDR process magnets.

CONCLUSIONS

ZrB_2 phase was identified by X-Rays diffraction on all stages of HDDR process in Fe-Nd-B-Zr-based alloys. This phase is considered to be the possible centers for nuclei of $\text{Fe}_{14}\text{Nd}_2\text{B}$ phase, that are considered to be the origin of anisotropy memory effect in the Fe-Nd-B based alloys for HDDR process.

Its formation leads to secondary effects on phase relations influencing on magnetic properties in these alloys. Most probably, due to deficit of B, taken from the alloy by Zr, formation of small amounts of softmagnetic $(\text{Fe-Co})_2\text{Nd}$ phase, spoiling magnetic properties, takes place. Zr additions, increasing the B deficit, stimulate its formation, but Ga and B additions, decreasing this deficit, suppress its formation. HDDR process helps forming of ZrB_2 phase, so Fe-Co-Nd-B-Zr-(Ga) alloys for HDDR process must contain a supply of B (or Ga).

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