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Methods of Characterization of Multiphase Nd-Fe-B Melt-Spun Alloys

A. Grujić [1], V. Ćosović [1], J. Stajić-Trošić [1], A. Maričić [2], N. Talijan[1*]

[1] Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, Belgrade, Serbia

[2] Technical Faculty Čačak, Svetog Save 65, Čačak, Serbia

Abstract:

Nanocomposite permanent magnetic materials based on Nd-Fe-B alloys with a low Nd content are a new type of permanent magnetic material. The microstructure of these nanocomposite permanent magnets is composed of a mixture of magnetically soft and hard phases providing the so called exchange coupling effect. Beside the optimization process parameters, methods of characterization have a very impotrant role in the design of an optimal magnetic matrix of multiphase melt-spun Nd-Fe-B alloys. Different methods and techniques of characterization were used for observation and study of the microstructure evolution during crystallization. A summary results of measurements using different methods of characterization are presented to enable a better insight into relations between the microstructure and magnetic properties of the investigated melt-spun Nd-Fe-B alloys.

Keywords: *Melt-spun Nd-Fe-B; Phase composition; Magnetic properties; XRD; MS ^{57}Fe; VSM.*

1. Introduction

The interest in researching nanostructural permanent magnetic materials of rare-earth-transition-metals-type has been accelerated and especially stimulated by an exceptional progress in materials synthesis and new methods and techniques of characterization. The activities in this research area are directed towards nanocomposite permanent magnetic Nd-Fe-B materials that are composed out of two phases, the hard magnetic one and the soft magnetic one, with the exchange coupling effect existing between them. This multiphase magnetic material is the result of the crystallization process of melt-spun Nd-Fe-B amorphous alloys with a low Nd content. Nanocomposite materials obtained in this way are characterized by high magnetic energy despite the fact that the content of the hard magnetic $Nd_2Fe_{14}B$ phase in the alloy amounts to 15 mass%.

There are many different research attempts aimed at improving the magnetic properties of this type of nanocomposite magnetic materials, with the methods and techniques of characterization being crucial for crystallization process and its directing towards optimal composition of nanocomposite materials which results in high magnetic properties.

*) Corresponding author: cmm@tmf.bg.ac.yu

2. Experimental

The investigated Nd-Fe-B alloy with a low Nd content was prepared by rapid quenching (R/Q) in optimally selected cooling rate under Ar atmosphere [1]. In the presented research different methods of analysis were used. The temperature behavior aimed at selection of a favorable regime of heat treatment of the investigated melt-spun alloy was examined by differential thermal analysis (DTA). The phase transformation in the function of cooling rate and heat treatment regime for defined initial chemical composition of melt-spun Nd-Fe-B alloy were investigated by determining the phase composition, by application of X-ray diffraction analysis (XRD) and with Mössbauer spectroscopic (MS) phase analysis. For determining the critical temperature of phase and magnetic transformations, thermomagnetic measurements were carried out. The thermomagnetic (TM) curves were completed with hysteresis loops in stages before and after TM treatment. Magnetic properties in the function of the investigated parameters were measured on a VSM (vibratory sample magnetometer) with a magnetic field strength of 50 kOe.

Comparison of the experimental results obtained by different investigation techniques enabled more complete comprehension of the crystallization process and phase composition during heat treatment. The importance of the selected methods of characterization is presented through experimental results.

3. Results and discussion

Investigation of thermal behavior in order to select and define optimal heat treatment regime was done using thermal analysis. Thermal behavior of the synthesized alloy in "as-quenched" state was tested at temperatures between 20^0C and 900^0C with different heating rates - 10, 20 and 30^0 C/min. DTA curves reached by different heating rates are presented on Fig 1. Comparing experimental data for DTA curves and data from literature, it was observed that main phase transformations occur between 580^0C and 700^0C. In previous research on series tested by DTA analysis, XRD analysis was done for final temperatures on DTA curves [1].

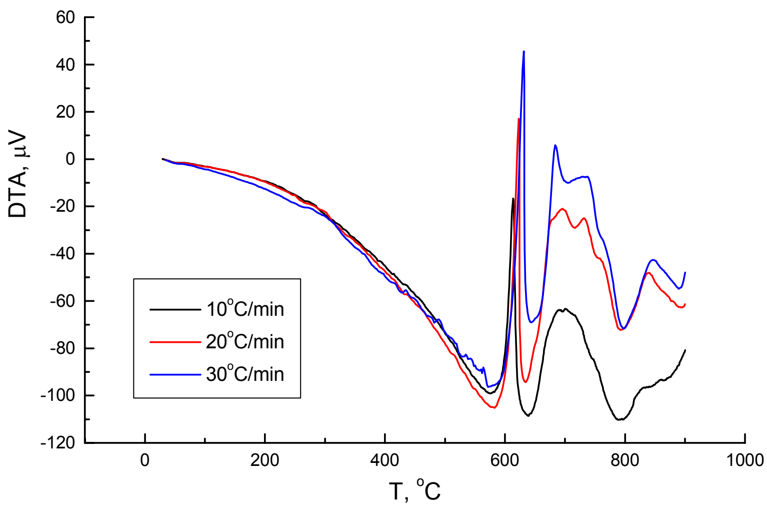


Fig. 1 DTA curves of "as quenched" $Nd_{4.5}Fe_{77}B_{18.5}$ alloy synthesized with different heating rates

It was experimentally proved [2,3,4] that there is no definite crystallization flow during heat treatment which is characteristic of the multiphase rapid quenched Nd-Fe-B alloy.

For the investigated Nd-Fe-B alloy with a reduced amount of Nd (4.5 at. %) some researchers, on the basis of experimental research claimed that crystallization occured by forming of a metastable phase $Nd_2Fe_{23}B_3$. Further heating lead to the decomposition of $Nd_2Fe_{23}B_3$ and the amount of Fe_3B increased with precipitation of the $Nd_2Fe_{14}B$ phase [2,5]. Practically, between 600^0C and 700^0C, Fe_3B and $Nd_2Fe_{14}B$ phases exist together with $Nd_2Fe_{23}B_3$ and α-Fe phases. Those phase transformations occur in a short period, together with increasing of the temperature of heat treatment.It was observed that in this temperature interval density of Fe_3B particles is increased, and their distribution in the magnetic matrix is increased [5]. This is very important for definition of the formation of nano composites of $Fe_3B/Nd_2Fe_{14}B$. According to Hono [3,4], the size, density and uniformous distribution of hard magnetic phase $Nd_2Fe_{14}B$ depends on the density of grains of the Fe_3B soft magnetic phase (phase with high magnetic saturation).

On Fig 2. DTA curves of tested R/Q $Nd_{4.5}Fe_{77}B_{18.5}$ alloys, treated at 600^0C, 660^0C and 700^0C during 5 minutes are given. The first crystallization peak on DTA curves (temperatures between 590^0C and 600^0C) corresponds to crystallization of the soft magnetic phase with high magnetization of the Fe_3B phase assured by XRD analysis and Mössbauer ^{57}Fe spectroscopic analysis (Table I). The second obvious peak corresponds to crystallization of the $Nd_2Fe_{14}B$ hard magnetic phase. Several more peaks with lower intensity can be noted on DTA curves corresponding to other phases, mainly α-Fe and boride phase, identified by XRD and MS analysis (Tab. I).

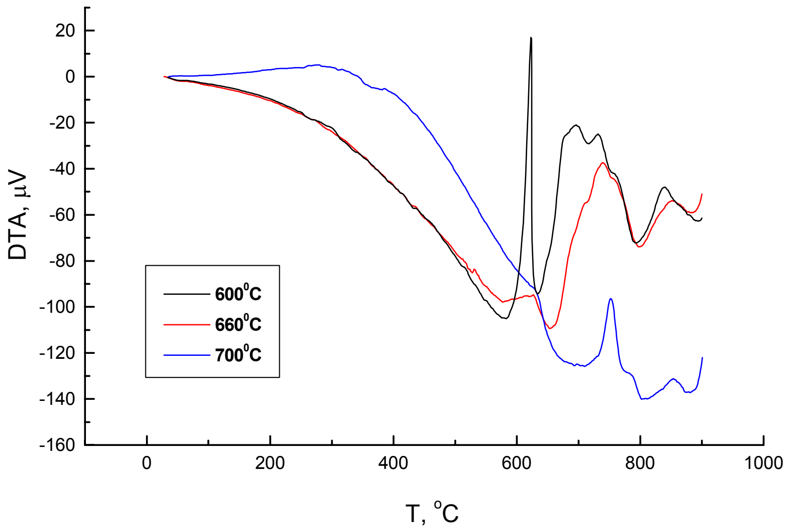


Fig. 2 DTA curves of "as quenched" $Nd_{4.5}Fe_{77}B_{18.5}$ alloy treated at different temperatures

According to a correlation of DTA results, the results of phase analysis and measured magnetic properties, optimal phase composition, maximal values of magnetic properties are reached for the alloy treated at 660^0C during 5 minutes in the researched temperature interval (600^0C-700^0C).

The results of XRD analysis of the treated sample of $Nd_{4.5}Fe_{77}B_{18.5}$ at the optimal temperature (660^0C) during 5 minutes are shown on Fig. 2. After optimal heat treatment, Fe_3B, $Nd_2Fe_{14}B$, ferromagnetic $Fe_{77.2}Nd_{22.8}$ and α-Fe phases were identified using XRD analysis. Compared to the temperature of heat treatment of 600^0C where metastable $Nd_2Fe_{23}B_3$ is identified by diffraction peaks on the XRD difractogram, the existance of the

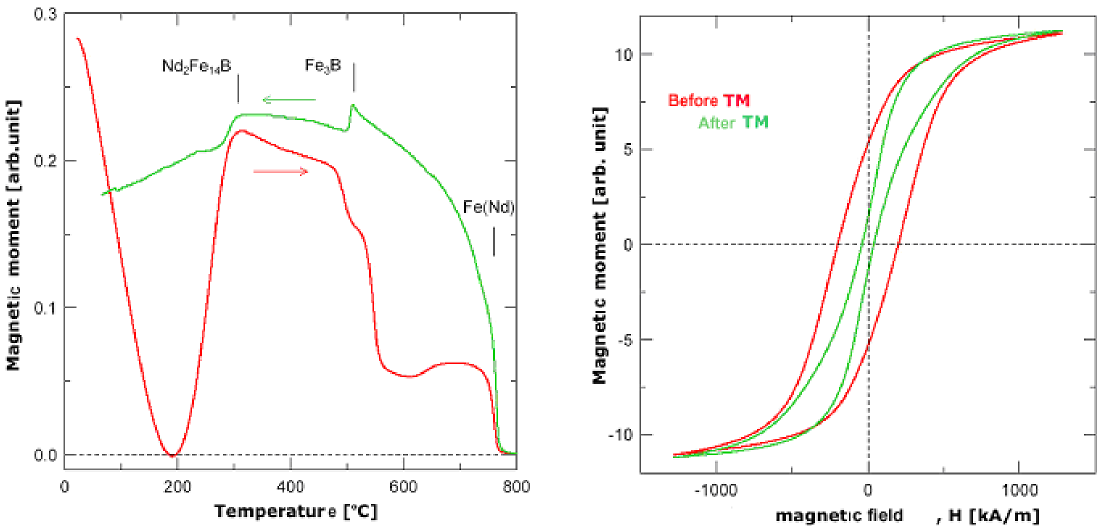
$Nd_2Fe_{14}B_3$ phase in traces might be claimed for the sample treated at 660^{0}C. Metastable phase $Nd_2Fe_{23}B_3$ crystallizes interphase, and during further crystallization flow, it decomposes to other phases: soft magnetic phase of high magnetization Fe_3B, with further heating, precipitation of $Nd_2Fe_{14}B$ is increased, and the α-Fe phase crystallizes in a lower percent. Increase of the amount of the main magnetic phase - $Nd_2Fe_{14}B$ with increase of the temperature of heat treatment between 600^{0}C and 660^{0}C influences an increase of the coercitive force and increasing of maximal magnetic energy.

Tab. I Phase composition before and after thermomagnetic measurements based on results of XRD and MS analysis for the tested $Nd_{4.5}Fe_{77}B_{18.5}$ alloy

PHASE COMPOSITION						***Magnetic properties (VSM)***		
XRD analysis		***MS ^{57}Fe analysis***				***Hc kOe***	***Br kG***	***$(BH)_{max}$ MGOe***
Before TM	***After TM***	***BeforeTM***	***mas %***	***After TM***	***mas %***			
Fe_3B $Nd_2Fe_{14}B$ α-Fe $Fe_{77.2}Nd_{22.8}$	Fe_3B $Nd_2Fe_{14}B$ α-Fe Fe_2B FeB $Nd_{1.1}Fe_4B_4$	Fe_3B $Nd_2Fe_{14}B$ α-Fe Fe-Nd ferro $Nd_{1.1}Fe_4B_4$	39 6 2 49 4	Fe_3B $Nd_2Fe_{14}B$ α-Fe Fe_2B FeB $Nd_{1.1}Fe_4B_4$	67 0 16 12 2 3	2.8	10.9	10.7

For better insight in the crystallization flow during heat treatment, analysis of the phase composition was done using Mossbauer spectroscopic phase analysis. Table I contains the results obtained for the investigated alloy after optimal heat treatment (660^{0}C) as well as phase composition of this alloy after maximal temperature of heat treatment (800^{0}C) during thermo magnetic measurements. By analyzing MS spectra, relative amounts of identified phases: $Nd_2Fe_{14}B$ – 6 mass %, Fe_3B – 39 mass %, $Nd_{1.1}Fe_4B_4$ – 4 mass %, α-Fe – 2 mass % and whole set of Fe-Nd magnetic phases with 49 mass % were observed. The existence of a boride phase is the consequence of the fact that in investigated alloy amount of boron is over 4.2 at. %. A comparison of the measured values for magnetic properties with the results of phase analysis(Table I) enables the conclusion that due to a significant amount of soft magnetic phase of high magnetization Fe_3B (39 mass%) nanocomposite with main magnetic phase $Fe_3B/Nd_2Fe_{14}B$ was formed. From SQUID hysteresis the reduced remanent ratio (Mr/Ms) was calculated for optimally heat treated alloy (660^{0}C, 5 minutes) as 0.58, and it is higher than the theoretical limit (0.5). The exchange coupling effect between grains of the Fe_3B soft magnetic phase and the $Nd_2Fe_{14}B$ hard magnetic phase significantly influences the increase of remanence.

According to experimental results of the research of thermal behavior, it was observed that multiphase Nd-Fe-B alloys are very sensitive to heat treatment, and at the same time phase transformations. The influence of heat treatment on the phase and magnetic transformations is followed by thermo magnetic measurements and MS phase analysis before and after TM measurements.



(a) (b)

Fig. 3 a)Thermomagnetic curves and (b) appropriate hysteresis of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy,after annealing at. 660^{0}C, 5 min and after TM measurements

On Fig 3.(a) thermomagnetic curves for R/Q $Nd_{4.5}Fe_{77}B_{18.5}$ after heat treatment on the optimal temperature of 660^{0}C during 5 minutes are shown. Magnetic behavior during heat treatment is illustrated on appropriate hysteresis on Fig 3.(b) for states before and after TM measurements. The hysteresis loop before TM measurements for the optimally heat treated alloy completely corresponds to optimal phase composition and measured magnetic properties shown in Table 1. The shape of the hysteresis curve after the border temperature of thermomagnetic measurements (800^{0}C) is shown on Fig 4. and shows a significant decrease of hard magnetic properties as a consequence of antiferomagnetic behavior which was caused by thermal decomposition of phases responsible for forming of optimal magnetic microstructure. Results of MS phase analysis after TM measurements and relative mass ratios of identified phases reached by calculation of MS spectra (Table 1.), show complete decomposition and disappearing of the $Nd_2Fe_{14}B$ hard magnetic phase phase and significant increase of the amount of the soft magnetic phase, which directly influences magnetic properties.

XRD analysis after TM measurements identified a significant increase of soft magnetic phases of Fe_3B, α-Fe, Fe_2B, FeB and the boride phase (Table 1.) which is one more experimental proof for the loss of magnetic properties caused by thermal decomposition of phases responsible for optimal magnetic properties with increase of the temperature of heat treatment above the optimal value.

4. Conclusion

Experimentally obtained value of Br and the calculated relative remanence ratio (Mr/Ms=0.58) indicate that nanocomposite Fe_3B /$Nd_2Fe_{14}B$ was formed after optimal selected heat treatment. Experimentally determined remanence ratio Mr/Ms for alloys with a low Nd content correspond with the theoretical considerations for this type of R/Q Nd-Fe-B alloys predicting the possibility of enhancement of magnetic properties despite the reduced rare earth content.

Correlation of the experimental results, gained by the selected methods of characterization, has laid the foundation for a better understanding of a new magnetic concept of interactive intergranular effects, especially from the point of view of the role of the interactive mehanism of chemical and magnetic stability of sinthesized nanocomposite magnets.

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Садржај: *Нанокомпозитни перманентни магнетни материјали засновани на Nd-Fe B легурама са ниским садржајем неодијума представљају нови тип перманентних магнетних материјала. Микроструктура ових нанокомпозитних перманентних магнета састоји се из смеше магнетно меке и магнетно тврде фазе између којих се јавља "exchange coupling" ефекат. Осим оптимизације процесних параметара, методе карактеризације имају веома велику улогу у дизајнирању оптималног магнетног матрикса вишефазних melt-spun Nd-Fe-B легура. Различите методе и технике карактеризације коришћене су за посматрање и проучавање еволуције миктроструктуре током кристализације. Сумарни резултати мерења, добијени применом различитих метода карактеризације, приказани су ради бољег увида у повезаност између миктроструктуре и магнетних својстава истраживане melt-spun Nd-Fe-B легуре.*
Кључне речи*: Melt-spun Nd-Fe-B, Фазни састав, магнетна својства, XRD; MS ^{57}Fe; VSM.*