Kovine, zlitine, tehnologije / letnik 28 / 1994 / številka 4 / strani 567 do 570

Use of the HDDR Process in Preparation of Zirconia Doped Nd-Dy-Fe-B High Coercivity Powder

HDDR postopek kot metoda za pripravo visoko koercitivnih Nd-Dy-Fe-B prahov

S. Kobe Beseničar,* B. Saje, G. Dražič, Jožef Stefan Institute, Ljubljana, Slovenia

The present paper deals with the use of the HDDR process as the preparative method for obtaining zirconia doped high coercive Nd-Dy-Fe-B powders. The influence of the dopant and of the processing parameters on the HDDR mechanism and the magnetic properties of the powders obtained, was studied. The material was characterized by magnetisation measurements at various stages of the HDDR process. Electron microscope studies on the Nd-Dy-Fe-B powders were performed to observe the influence of zirconia addition on the crystallisation during the recombination process.
Key words: Nd-Fe-B magnets, coercivity, processing.

HDDR postopek (Hidrogenacija Disproporcionacija Desorpcija Rekombinacija) smo uporabili kot metodo za pripravo finih visoko koercitivnih Nd-Dy-Fe-B prahov dopiranih s cirkon oksidom. Študirali smo vpliv dopanta in procesnih parametrov na mehanizem poteka HDDR postopka in na končne morfološke in magnetne lastnosti tako dobljenih prahov. Vzorce smo karakterizirali na različnih stopnjah HDDR postopka z magnetnimi meritvami. Prahove smo opazovali z elektronskim mikroskopom in študirali vpliv cirkonovega oksida na potek kristalizacije med postopkom rekombinacije.
Ključne besede: Nd-Fe-B magneti, koercitivnost, procesiranje.

Introduction

One of the well known methods for preparation of isotropic Nd-Fe-B coercive powders is the HDDR process, as reported in several papers[1-4]. It was also established previously that an anisotropic powder can be produced by the addition of small amounts of Zr to the initial composition. The intrinsic coercivities of powders prepared by this method are reported to be up to 1100 kA/m (13.8 kOe)[5,6].

In our previous work the beneficial influence of zirconia on the microstructure and consequently on the magnetic properties and corrosion resistance of sintered Nd-Dy-Fe-B magnets was reported[7,8].

The purpose of the present work was to prepare high coercive Nd-Dy-Fe-B powders by the HDDR processing route, using the same composition of the basic alloy, together with the addition of 1 wt.% of ZrO_2, as previously employed[8]. High coercivity powders were intended for use as the basic material for the preparation of resin bonded magnets. This paper only deals with the powder processing and its characterization.

Experimental

The basic alloys for the HDDR process were prepared by arc melting the alloys NdFe, DyFe, FeB and Fe powder in a pure Ar atmosphere. The alloy composition was $Nd_{15-x}Dy_xFe_{76}B_8$ ($0<x<3$). In order to prevent oxidation, a Ti sponge was used as a getter for oxygen. 1 wt.% of zirconia was added before arc melting. The melted buttons were then subjected to HDDR processing. They were treated in hydrogen at room temperature (20kPa) first and then heated to different temperatures between 750°C and 850°C and exposed to further hydrogenation for two hours. A thermopiezic (TPA) analysis and DTA analyses were performed to follow the absorption process. The procedure was followed by evacuating the system and after exposing the samples to maximum temperature and high vacuum (10^{-3} Pa) for one hour they were furnace cooled[6].

Samples were lightly crushed and the powders obtained were characterized by magnetic measurements. For the mass magnetization measurements a DSM8 magnetometer - susceptometer was used; the intrinsic coercivity measurements were performed using a permeameter. Comparability of the measurements was attained by using always the same quantity of examined powder and binding material (epoxy) (wt.% 85/15). Samples were pulsed in a field of 4000 kA/m and demagnetized with a field of cca 2000 kA/m. Powders were observed by means of a SEM/EPMA (JEOL JXA 840 A). Phase analyses were performed using a TEM (JEOL 2000 FX).

Results and discussion

Figure 1 shows the demagnetizing curves of powders obtained by the HDDR process at different temperatures. Samples with and without zirconia addition are compared. The basic composition of those samples is $Nd_{15}Dy_1Fe_{76}B_8$. Z0 samples are without zirconia addition and Z1 with 1 wt%

* dr. Spomenka KOBE BESENIČAR,
Inštitut Jožef Stefan, Jamova 39, 61000 Lj.,

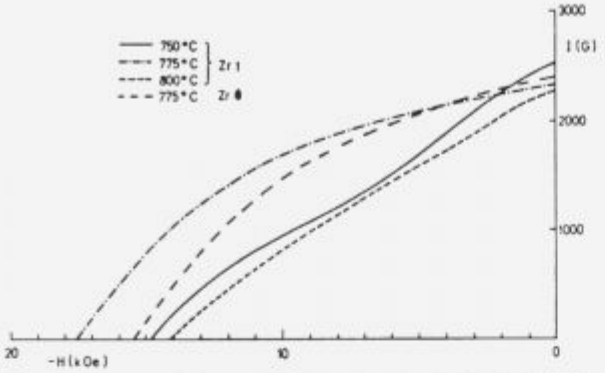


Figure 1: Demagnetizing curves of powders obtained by the HDDR process at different temperatures. Samples with and without zirconia are compared.

Slika 1: Demagnetizacijske krivulje prahov, dobljenih po HDDR postopku pri različnih temperaturah. Primerjava vzorcev z in brez dodatka cirkon oksida.

of zirconia additive. A maximum value of the intrinsic coercivity of 1400 kA/m (17.5 kOe) was attained when samples with the addition of zirconia were processed at 775°C. This value exceeds the coercivity of samples without zirconia and processed under the same conditions for about 13 % of the value obtained with samples without additive. At 750°C the poorer magnetic properties obtained were attributed to the presence of free iron. Grain growth at 800°C causes a decrease in coercivity.

Figure 2 shows the difference in the mass magnetization between samples with and without ZrO_2 addition processed at different temperatures. Several experiments in two different laboratories showed reproducible results. Samples with zirconia addition revealed a higher magnetization at lower temperature (750°C) than samples free of this additive. In **Figure 3** the SEM micrographs of the samples without addition of zirconia (A) and with zirconia addition (B) are shown. Both samples were processed under the same conditions. They were treated at 750°C. There is obvious difference in the grain size, which is around 0.3 μm in the samples without ZrO_2 addition and in the range between 0.3 μm and 1 μm in the samples with the additive. The most probable reason for the recombination process starting at lower temperatures and consequently the higher magnetization of doped samples, lies in the different reaction kinetics of zirconia doped samples. At temperatures of the recombination

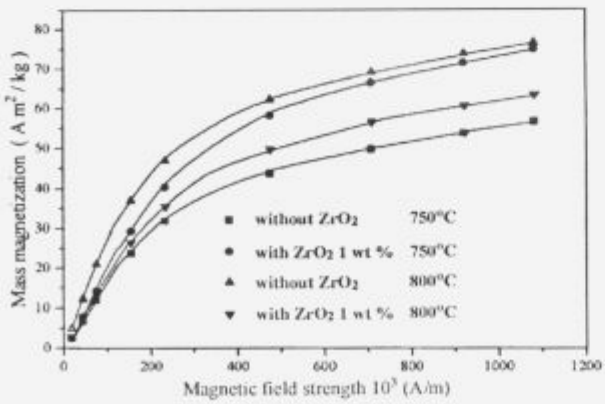
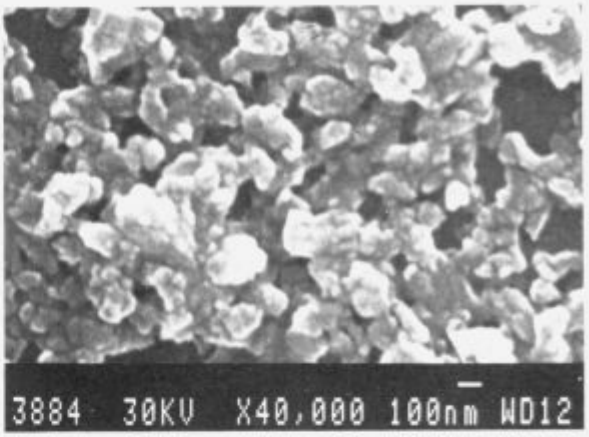
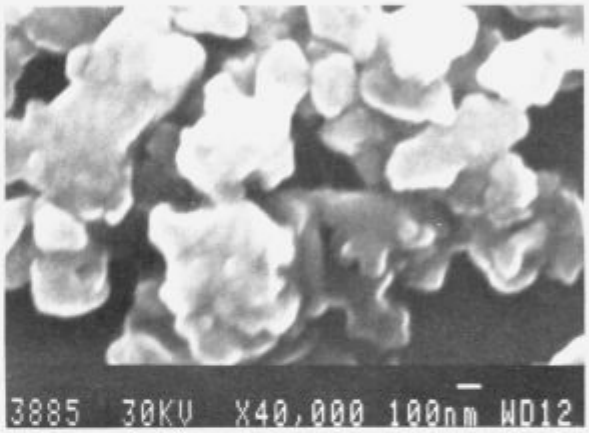


Figure 2: Mass magnetization measurements of samples with and without ZrO_2 addition, processed at different temperatures.

Slika 2: Magnetizacija vzorcev z in brez dodatka cirkon oksida, pripravljenih pri različnih temperaturah, kot funkcija jakosti magnetnega polja.



A



B

Figure 3: SEM micrographs of the samples processed under the same conditions (750°C): A - without zirconia, B - with zirconia addition.

Slika 3: SEM posnetki vzorcev pripravljenih pri enakih pogojih (750°C): A - brez cirkon oksida, B - s cirkon oksidom.

process higher than 750°C the mass magnetization is normally always higher in samples free of additive.

Our TEM observations confirmed the presumption about different reaction kinetics of zirconia doped samples. When the samples are exposed to the recombination process at 750°C, nano crystals of Nd rich phase which occurs within the origin grains are at least an order of magnitude smaller in the case of zirconia free samples (2 nm) (**Fig. 4A**) than in the case of samples with zirconia addition (up to 20 nm) (**Fig. 4B**).

In addition the crystallites of hard magnetic phase within the origin grains are at least an order of magnitude bigger in zirconia doped samples (**Fig. 5B**) comparing to the zirconia free sample (**Fig. 5A**), where nano crystals do not exceed 10-20 nm.

In **Figure 6** EDX spectra of 2-14-1 phase in samples without (A) and with zirconia (B) addition are shown. The $Fe_{K_\alpha}/Nd_{L_\alpha}$ peak-height ratio is lower in the case of sample (A) (cf. **Fig. 5**) indicating that several small Nd-rich particles were also present in the analysed volume. In the case of sample B, the particle size of Fe-rich phase is large enough to obtain just the spectrum of this phase without the interference from Nd-rich phase.

TPA analysis of the absorption process showed the disproportionation starting at higher temperature and proceeding slower in zirconia doped samples (**Fig. 7**). These results were confirmed also with a DTA analysis (**Fig. 8**). It is obvious that disproportionation of the samples without zirconia addition starts at lower temperature.

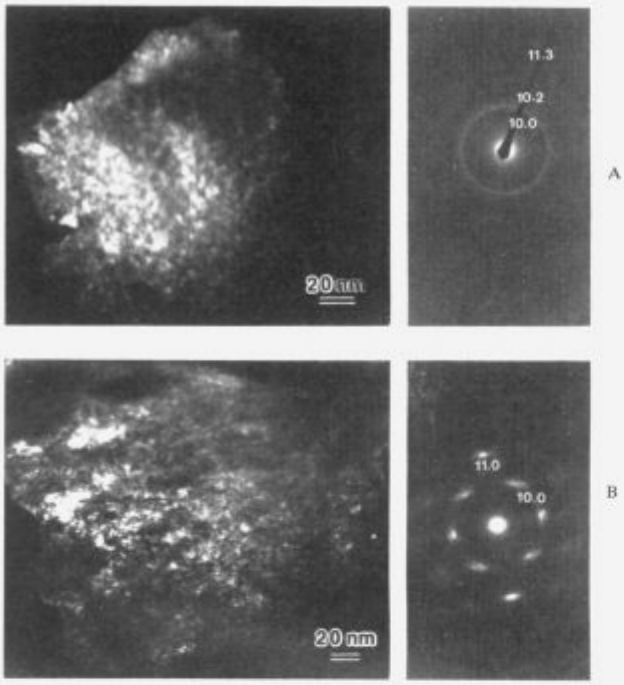


Figure 4: TEM micrographs (dark field) and corresponding diffraction patterns of NdDyFeB samples - Nd rich phase: A - zirconia free, B - zirconia added.

Slika 4: TEM posnetki (temno polje) in odgovarjajoči difraktogrami vzorcev NdDyFeB - faza bogata z Nd: A - brez cirkon oksida, B - z dodatkom cirkon oksida.

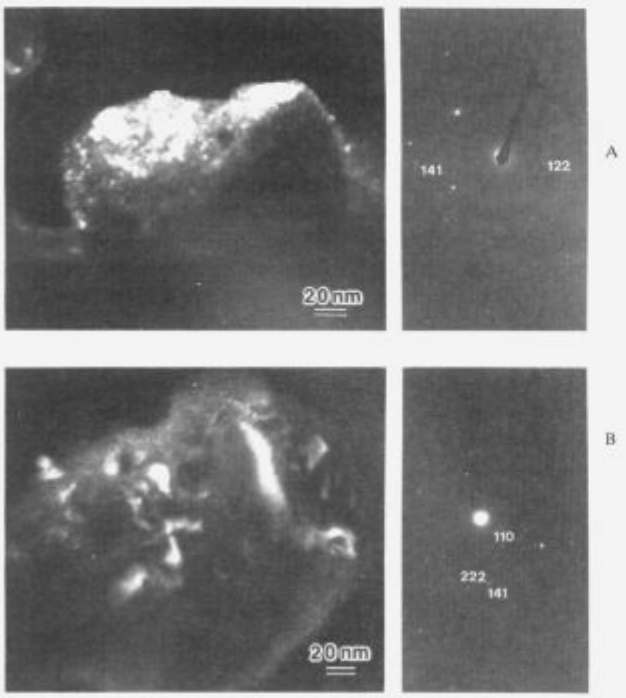


Figure 5: TEM micrographs (dark field) and corresponding diffraction patterns of NdDyFeB samples - $Nd_2Fe_{14}B$ phase: A - zirconia free, B - zirconia added.

Slika 5: TEM posnetki (temno polje) in odgovarjajoči difraktogrami vzorcev NdDyFeB: faza - $Nd_2Fe_{14}B$ A - brez cirkon oksida, B - z dodatkom cirkon oksida.

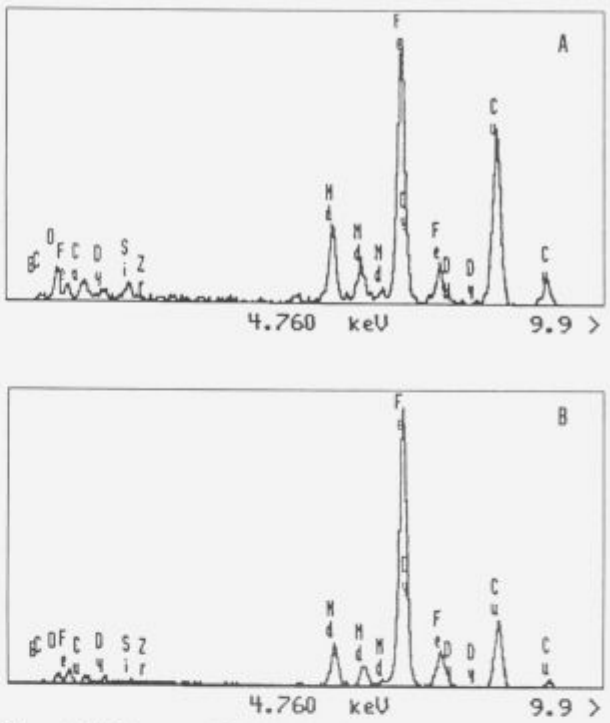


Figure 6: EDX spectra of 2-14-1 phase in samples without A and with B zirconia addition.

Slika 6: EDX spektri 2-14-1 faze v vzorcih brez A in z dodatkom cirkon oksida B.

A tentative explanation is that the statement about the local stabilization of 2-14-1 phase with respect to disproportionation, when elements such as Zr are added to the basic alloy[9] could be also transmitted in the case of zirconia addition. With the addition of zirconia the so called cells remain unaffected by the disproportionation and they act as nucleation centres in the recombination process. This model which explains anisotropy of such powders can tentatively also explain our TEM observations. A certain texture structure of the Nd-rich crystals formed during the recombination process in zirconia doped samples was detected (**Fig. 4B**, diffraction pattern). In the samples without ZrO2 addition the structure consists of randomly oriented nano crystallites (**Fig. 4A**). A detailed analysis with TEM on solid samples will give us more information about phase composition. There are

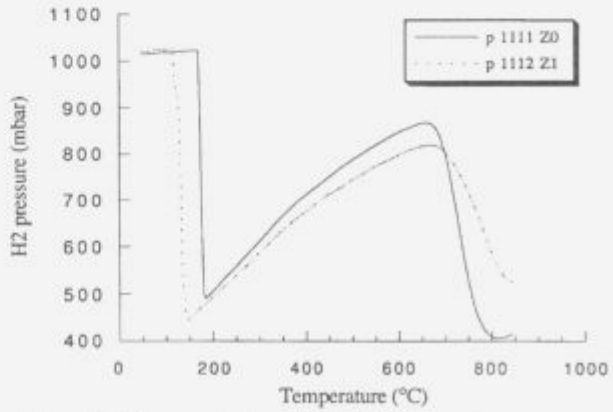


Figure 7: TPA traces for zirconia free (Z0) in zirconia added (Z1) $Nd_{11}Dy_1Fe_{82}B_6$ samples.

Slika 7: TPA analiza vzorcev $Nd_{11}Dy_1Fe_{82}B_6$: Z0 - brez cirkon oksida, Z1 - z dodatkom cirkon oksida.

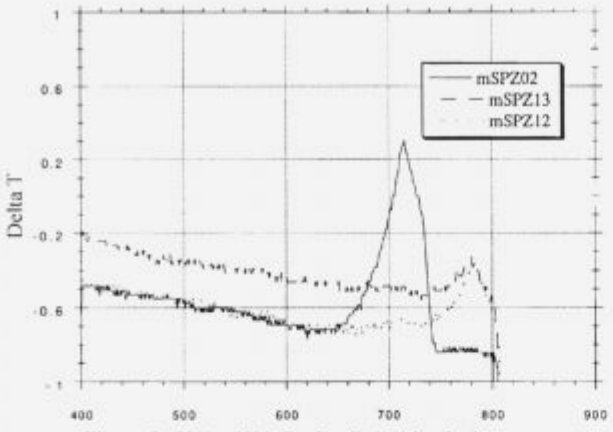


Figure 8: DTA of $Nd_{15}Dy_1Fe_{76}B_8$ in 1 bar hydrogen (note: graphs are not calibrated to the mass)

Slika 8: DTA analiza vzorca $Nd_{15}Dy_1Fe_{76}B_8$ pri 1 bar vodika (grafi niso kalibrirani na maso).

some indications about the presence of a phase based on Fe and Zr and this will also help us to explain the results of our first TEM analyses.

On the basis of these results, one can conclude that the HDDR processing route for the preparation of high coercive zirconia doped Nd-Dy-Fe-B powders reaches its optimum at 775°C for the present processing conditions (temperatures tested were: 750°C, 775°C, 800°C, 850°C). Further work will study the preparation of anisotropic magnets by different established techniques.

Acknowledgment

The financial assistance of the Ministry of Science and Technology and the British Council, UK are gratefully acknowledged. Part of the work was performed at the University of Birmingham, School of Metallurgy and Materials. Authors (S. Kobe Beseničar and B. Saje) would like to thank Prof. I. Rex Harris for his guidance and fruitful discussions. Prof. I. Rex Harris is also gratefully acknowledged for his critical review of the manuscript. The assistance of Mr. F. Dimc for the magnetic measurements and Mr. Z. Samardžija for SEM observations are gratefully acknowledged.

References

[1] T. Takeshita, R. Nakayama, *Proceedings of the 10. International Workshop on Rare Earth Magnets and their Applications*, Kyoto, (1989) 551

[2] P. J. McGuiness, X. J. Zhang, X.J. Yin, I.R. Harris, *J. Less Common Metals*, 158 (1990) 359

[3] I. R. Harris, P. J. McGuiness, *J. Less Common Metals*, 172 (1991) 1273

[4] X. J. Zhang, P. J. McGuiness, I. R. Harris, *J. Appl. Physics*, 68(8) (1991) 5838

[5] T. Takeshita, R. Nakayama, *Proceedings of the 11. International Workshop on Rare Earth Magnets and their Applications*, Pittsburgh, PA, (1990) 7

[6] P. J. McGuiness, C. L. Short, I. R. Harris, *IEEE Trans. on Magn.*, 28, (1992) 5, 2160-2162

[7] S. Beseničar, B. Saje, G. Dražič, J. Holc, *JMMM* 104-107, (1992) 1175

[8] S. Kobe Beseničar, J. Holc, G. Dražič, B. Saje, *IEEE Trans. on Magn.*, 30, 2, (1994) 693-696

[9] I. R. Harris, *Proceedings of the 12. International workshop on rare-earth magnets and their applications*, Canberra (1992) 347