

ADAPTING THE HDDR PROCESS AND NdFeB-BASED PERMANENT-MAGNET ALLOYS FOR FACTORY PRODUCTION

PRODUKCIJA NdFeB MAGNETOV S POSTOPKOM HDDR, PRIREJENIM ZA INDUSTRIJSKO UPORABO

Paul John McGuinness¹, Spomenka Kobe¹, Irena Škulj²

¹ Ceramics Department, Institut 'Jožef Stefan', Jamova 39, 1000 Ljubljana, Slovenia

² School of Metallurgy and Materials, The University of Birmingham, Birmingham B15 2TT, United Kingdom
paul.mcguinness@ijs.si

Prejem rokopisa - received: 2001-05-21; sprejem za objavo - accepted for publication: 2001-06-13

As part of a NATO Science-for-Peace industry-based project we studied the effects of Pr and Zr substitutions to a basic Nd₁₅DyFe₇₆B₈ alloy in order to develop a material and a process which could be easily transferred to factory production. We processed the materials using a conventional hydrogenation-disproportionation-desorption-recombination (HDDR) process and a simple rotary-pump-type vacuum. The Pr and Zr substitutions were observed to have a positive and cost-effective influence on the coercivity of the processed powders: the optimum Pr substitution was the replacement of three-quarters of the Nd, and for Zr a much smaller 0.1 atomic % was found to be the best. Microstructural observations of the as-cast structures revealed significant differences between the Zr- and Pr-substituted materials and the additive-free NdDyFeB alloy, but post-HDDR microstructures were all very similar and provided little help for optimising the processing conditions. By combining the substitutions of Pr and Zr in a relatively rare-earth-rich alloy we were able to produce a coercive powder of >1000 kA/m and have a process which can now be quickly and easily transferred to the factory.

Keywords: HDDR, NdFeB, permanent magnet, coercivity, praseodymium, zirconium

V okviru projekta NATO Science for Peace smo izvedli naslednjo raziskavo. Študirali smo vpliv Pr in Zr na magnetne lastnosti materiala Nd₁₅DyFe₇₆B₈ ter na parametre postopka HDDR, ki bi bil uporaben tudi v industriji. Materiale smo procesirali s konvencionalnim postopkom hidrogenacije, disproporcionacije, desorpcije in rekombinacije imenovanim postopek HDDR, pri katerem smo vakuum dosegli z enostavno rotacijsko črpalko. Ugotovili smo, da Pr in Zr pozitivno vplivata na koercitivnost, pa tudi na zniževanje stroškov produkcije. Najvišje koercitivnosti smo dosegli z zamenjavo treh četrtin Nd s Pr ter z zamenjavo 0,1 at. % Fe z Zr. Pri opazovanju mikrostruktur litih zlitin smo v zlitinah s Pr in Zr, v primerjavi z originalno zlitino NdDyFeB, opazili določene razlike. Te razlike pa so postale manj očitne, ko smo med seboj primerjali zlitine, že obdelane po postopku HDDR.

S kombinacijo različnih substitucijskih dodatkov Pr in Zr osnovni zlitini, smo s postopkom HDDR naredili magnetne prahove s koercitivnostmi višjimi od 1000 kA/m. Pogoje postopka HDDR smo priredili tako, da bi bil prenos postopka v industrijo čim bolj enostaven.

Ključne besede: HDDR, NdFeB, trajni magnet, koercitivnost, prazeodim, cirkonij

1 INTRODUCTION

The hydrogenation-disproportionation-desorption-recombination (HDDR) process is now a well-established method for producing highly coercive powders from NdFeB- and SmFe-based alloys. The process is based on the formation of a RE-TM (rare-earth-transition-metal) hydride which at higher temperatures has a tendency to disproportionate into a mixture of RE-hydride and iron; subsequent desorption of the hydrogen using a vacuum at high temperatures causes the RE-hydride to desorb and the RE, iron and boron—in the case of NdFeB-based alloys—to recombine with a sub-micron microstructure. Gutfleisch and Harris¹ have comprehensively reviewed this area in an article on hydrogen-assisted processing. With respect to the chemistry of the processed materials, additions of small amounts of Zr to sintered, melt-spun and HDDR-processed NdFeB-based magnets have been reported to improve coercivity², corrosion resistance³ and the

degree of anisotropic growth⁴. In all cases it is reported that the amount of added Zr can be critical for achieving good properties. Substitutions of Nd by Pr have been less-thoroughly investigated, particularly with respect to the HDDR process. Kim and Jeung⁵ reported modest coercivities of just 4.8 kOe (380 kA/m) in alloys based on PrFeBCoZrGa while a recent study by Faria et al⁶ suggests that total replacement of Nd by Pr in a Pr_{13.7}Fe_{63.5}Co_{16.7}B₆Zr_{0.1} material leads to the development of highly anisotropic material with reasonable coercivities of >700 kA/m.

In this paper we report on the effect of Zr substitutions, in the range 0 to 2 % (all percentages refer to atomic percent, unless otherwise stated), to a basic cast alloy with the approximate composition Nd₁₅DyFe₇₆B₈. We also present results for Pr substitutions in the range 0 to ~15 %, for the same basic composition. Zr is always added at the expense of Fe, and Pr replaces Nd. Based on the results from individual substitutions we have also looked at a combination of Zr

and Pr substitutions in order to optimise the properties of the magnets in terms of coercivity. Effects on the remanence or the degree of anisotropic growth for our powders are neither presented nor discussed, the processing conditions we used led to the production of powders that exhibited an isotropic character and the loop shapes obtained were typical of isotropic HDDR-processed powders.

The results reported in this paper come from an industry-based project, the aim of which was to develop HDDR-based technology and alloys in the laboratory that could be easily transferred to factory production. For this reason we chose to carry out the experiments in an environment that approximates to that encountered in a factory: we used as-cast materials in relatively large quantities and processed them in a reactor equipped only with a conventional rotary pump. Handling of the materials after the HDDR process and the bonding of the powders into test magnets were also performed in a manner similar to that encountered in a large-scale manufacturing process.

2 METHODS AND MATERIALS

Alloys, in 5-kg batches, were supplied by Less Common Metals Ltd, UK. The ingots were prepared in rectangular water-cooled copper moulds and the compositions of all the materials are given in **Table 1**. No homogenisation treatments were applied to any of the castings.

Table 1

Alloy	Composition
A	Nd ₁₃ Fe ₈₁ B ₆
B	Nd _{14.7} Fe _{77.3} B _{8.0}
C	Nd ₁₆ Fe ₇₆ B ₈
D	Nd ₁₅ Dy _{1.0} Fe ₇₆ B _{8.0}
E	Nd _{14.8} Dy _{1.0} Fe _{76.0} B _{8.1} Zr _{0.1}
F	Nd _{14.6} Dy _{1.0} Fe _{75.8} B _{8.3} Zr _{0.3}
G	Nd _{15.2} Dy _{1.0} Fe _{74.8} B _{8.3} Zr _{0.7}
H	Nd _{15.4} Dy _{1.0} Fe _{73.3} B _{8.3} Zr _{2.0}
I	Nd _{14.7} Fe _{77.3} B _{8.0}
J	Nd _{7.4} Pr _{7.3} Fe _{77.3} B _{8.0}
K	Pr _{14.7} Fe _{77.3} B _{8.0}
L	Nd ₁₅ Dy _{1.0} Fe _{75.9} B ₈ Zr _{0.1}
M	Nd _{11.25} Pr _{3.75} Dy _{1.0} Fe _{75.9} B ₈ Zr _{0.1}
N	Nd _{7.5} Pr _{7.5} Dy _{1.0} Fe _{75.9} B ₈ Zr _{0.1}
O	Nd _{3.75} Pr _{11.25} Dy _{1.0} Fe _{75.9} B ₈ Zr _{0.1}
P	Pr ₁₅ Dy _{1.0} Fe _{75.9} B ₈ Zr _{0.1}

Pieces of alloy taken 1 cm from the mould wall were polished and investigated with optical and scanning electron microscopy. Quantitative EDX analysis was used to determine the chemical composition of the different phases in the materials.

To produce the coercive powders in our factory-like environment the as-cast alloys were crushed to <5 mm and two samples of 18 g each, held in separate

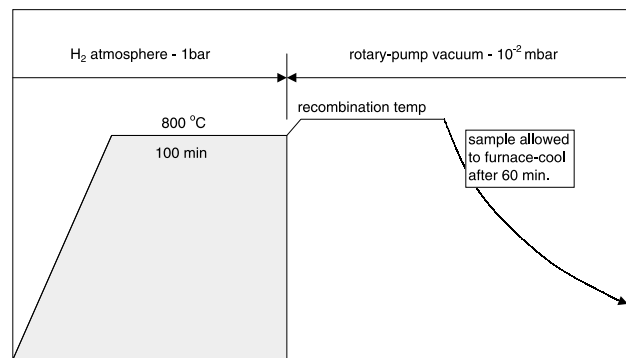


Figure 1: Temperature-gas-processing scheme for HDDR experiments

Slika 1: Shema postopka HDDR (temperatura-tlak)

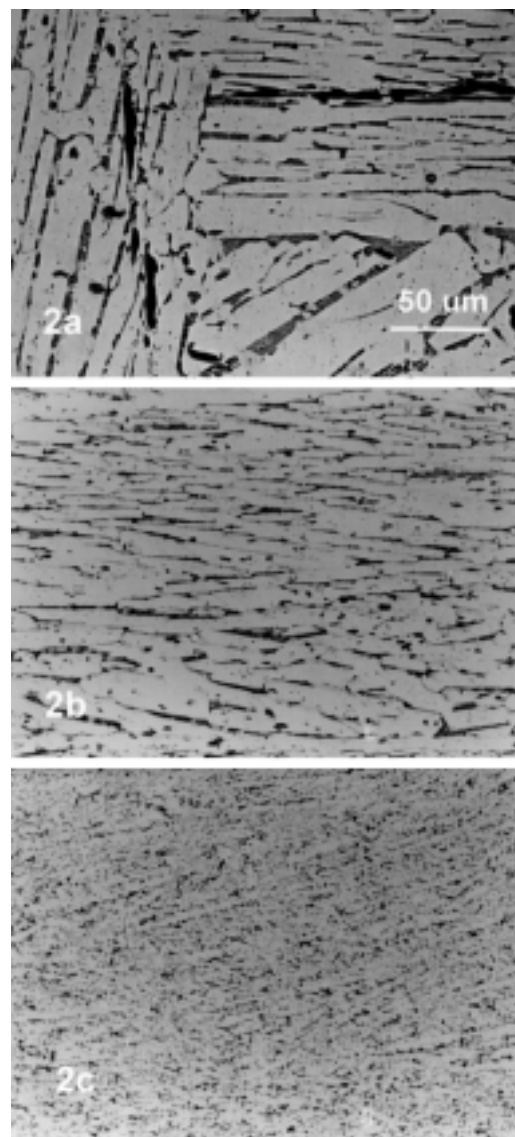


Figure 2: Optical micrographs of as-cast alloys D, E and H

Slika 2: Mikrostruktura litih zlitin D, E in H, posneta z optičnim mikroskopom

a (D) - Nd₁₅Dy₁Fe₇₆B₈; 2b (E) - Nd_{14.8}Dy₁Fe₇₆B_{8.1}Zr_{0.1}; 2c (H) - Nd_{15.4}Dy₁Fe_{73.3}B_{8.3}Zr₂

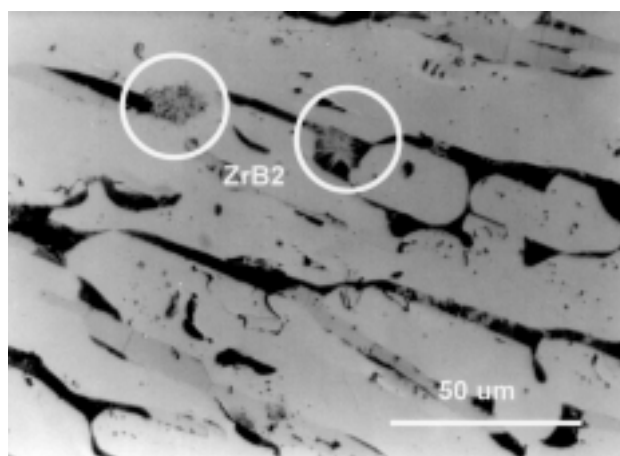


Figure 3: High-magnification image of alloy E showing ZrB_2 phase
Slika 3: SEM posnetek zlitine E, ki prikazuje ZrB_2 fazo, posneto pri visoki povečavi

containers in the hot zone, were HDDR processed in a rotating furnace during each processing run. The rotating furnace was capable of operating between 1 bar over-pressure and 10^{-2} mbar vacuum with the temperature controlled by a conventional PID controller. The temperature-gas-processing scheme used in this series of experiments is shown in **Figure 1**.

After removing the processed powders from the furnace the material was gently re-crushed using a mortar and pestle to $<250 \mu m$ (the only step carried out in a <5 -ppm-oxygen glove-box) and then bonded in a phenolic resin (Novolak). This bonding material was supplied in the form of a white-yellow powder with a particle size which is 90% $<45 \mu m$. Five mass % of this powder was mixed with the HDDR powder and the resulting blend was pressed at $\sim 160^\circ C$ to produce cubic test samples with a volume of approximately $1 cm^3$. Prior to measurement the samples were pulsed in a magnetic field of ~ 5 Tesla and the demagnetisation curves determined with a room-temperature permeameter.

3 RESULTS

Optical micrographs of as-cast samples D (0 % Zr), E (0.1 % Zr) and H (2.0 % Zr) are shown in **Figures 2a, 2b and 2c**. The photographs are low-magnification (100x) images, chosen to show the overall microstructure of the sample. A reduction in the grain size with increasing amounts of Zr is evident. **Figure 3** is a high-magnification image of sample E and shows the presence of the star-like ZrB_2 phase. Quantitative measurements on the H alloy suggest that the boride phase constitutes some 5 volume % of this particular alloy. Cast alloys I (Nd:Pr 100:0), J (Nd:Pr 50:50) and K (Nd:Pr 0:100) are shown in **Figures 4a, 4b and 4c**. Pr appears to have some effect on reducing the grain size but mostly it seems to encourage the development of an increasingly rectangular morphology.

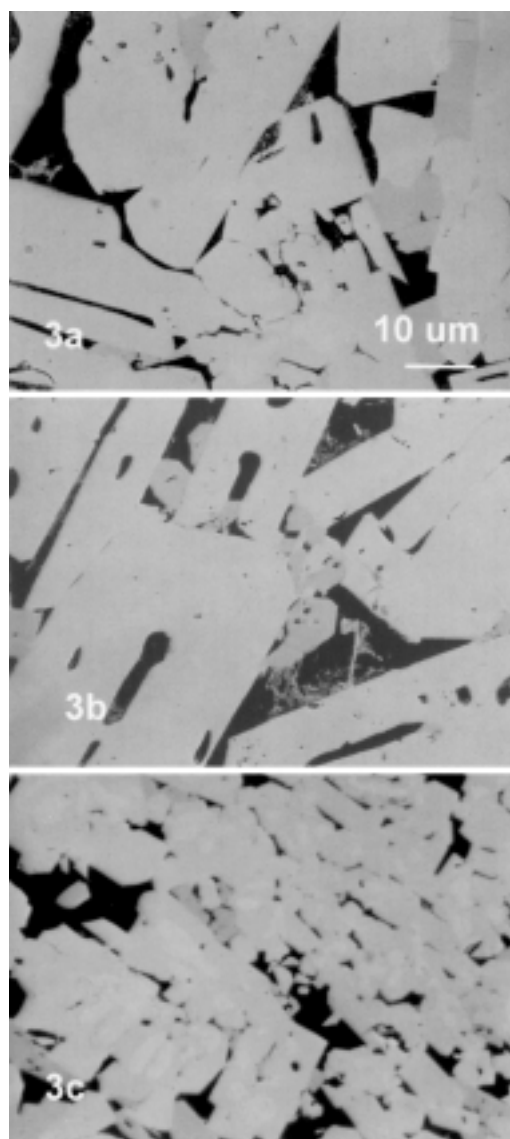


Figure 4: Optical micrographs of as-cast alloys I, J and K
Slika 4: Mikrostruktura litih zlitin I, J in K, posneta z optičnim mikroskopom

3a (I) - $Nd_{14.7}Fe_{77.3}B_8$; 3b (J) - $Nd_{7.4}Pr_{7.3}Fe_{77.3}B_8$;
 3c (K) - $Pr_{14.7}Fe_{77.3}B_8$

An elemental analysis of the J material using quantitative EDX showed that although we had a 50:50 split in terms of overall composition, the Pr and Nd do not distribute evenly between the three major rare-earth-containing phases. The observed elemental concentrations are shown in **Table 2**.

Table 2

$RE_2Fe_{14}B$ phase (%)	$REFe_4B_4$ phase (%)	RE-rich phase (%)
Nd 6.8	Nd 12.2	Nd 40.4
Pr 5.4	Pr 9.6	Pr 59.6
Fe 87.8	Fe 78.2	-

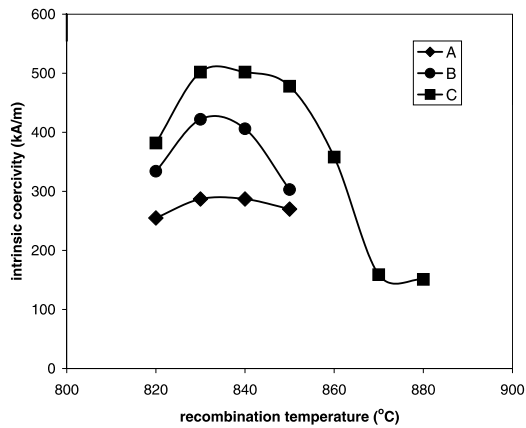


Figure 5: Coercivity v. recombination temperature for ternary NdFeB-type alloys

Slika 5: Grafični prikaz odvisnosti koercitivnosti od temperature rekombinacije za ternarne zlitine NdFeB

Initial HDDR-processing experiments were carried out on NdFeB materials that did not contain either Zr or Pr. Samples were recombined from 820 to 880 °C and the results for the three materials: A, B and C, are shown in **Figure 5**.

The coercivities for HDDR powders produced from the alloys D to H are shown in **Figure 6**. The graph shows us that Zr substitution results in an increase in the maximum coercivity when small substitutions (0.1 to 0.7 %) are made, however, 2.0 % provides no advantage over the Zr-free sample.

Alloys containing various amounts of Pr (I, J and K) were processed under the same HDDR conditions with recombination temperatures ranging from 820 to 900 °C, the results are shown in **Figure 7**. As with the substitution of Zr we see benefits: an improvement in the coercivity, which is linked to increasing substitutions of Pr, and a significant broadening of the processing window, also linked to more Pr.

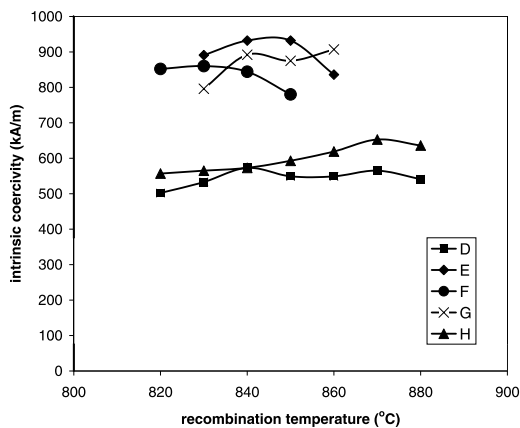


Figure 6: Coercivity v. recombination temperature for Zr-doped NdDyFeB alloys

Slika 6: Grafični prikaz odvisnosti koercitivnosti od temperature rekombinacije za zlitine NdDyFeB, dopirane z Zr

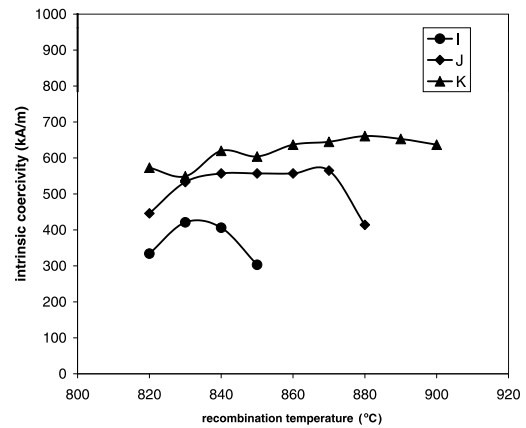


Figure 7: Coercivity v. recombination temperature for Pr-substituted NdDyFeB alloys

Slika 7: Grafični prikaz odvisnosti koercitivnosti od temperature rekombinacije za zlitine tipa NdPrDyFeB

The final group of processed materials, samples L to P, represents materials with 0.1 % Zr and Nd:Pr ratios: 100:0 (L), 75:25 (M), 50:50 (N), 25:75 (O) and 0:100 (P). Samples were recombined at temperatures from 820 to 880 °C and the results are shown in **Figure 8**.

4 DISCUSSION

Substitutions of Zr and Pr have a significant influence on the microstructure of the as-cast materials. Zr tends to reduce the grain size, and at the 2 % level it has largely destroyed the classical columnar microstructure so typical of NdFeB-based cast materials. Such a difference in the initial structure would suggest that the post-HDDR structure would also be very Zr-content dependent, however, our microstructural observations were not able to confirm this. The situation is similar with Pr substitutions. The as-cast microstructure undergoes a progressive change, with increasingly angular grains being observed for the high-Pr-content

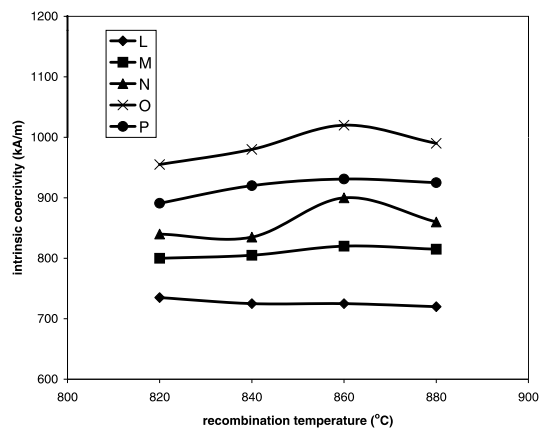


Figure 8: Coercivity v. recombination temperature for NdPrDyFeBZr-type alloys

Slika 8: Grafični prikaz odvisnosti koercitivnosti od temperature rekombinacije za zlitine tipa NdPrDyFeBZr

alloys. However, HDDR-processed materials containing various amounts of Pr all look pretty much the same, except in the case of very high recombination temperatures when all compositions exhibit some very large grains.

The first experiments on the ternary NdFeB alloys show the effect of increasing the rare-earth content—more rare earth, more coercivity (**Figure 5**). Because of our low-vacuum processing conditions and some air-handling of the powders the amount of oxygen absorbed by the alloys is relatively high—typically 0.3-0.5 weight %, depending on the composition—and so a rare-earth-rich material is required to develop acceptable coercivities.

Based on the results obtained with our ternary alloys we selected a second series of alloys containing 15 % Nd, 1 % Dy and a range of Zr substitutions from 0.1 % to 2.0 %. Dy is a very common substitution element in both sintered and melt-spun materials, it is well known to enhance the coercivity of NdFeB-based materials by increasing the anisotropy field. Unfortunately, as it couples anti-ferromagnetically with Fe this also leads to reductions in the magnetisation and, consequently, lower values for the remanence. The Zr, we know from our earlier studies ⁷, can enhance the coercivity and under certain conditions it can provide a wider processing window in terms of the range of optimum recombination temperatures. In this series of experiments we found that a substitution of 0.1 % Zr gave us good coercivities and provided an acceptable window in terms of compositional variation and recombination temperature. However, by the time the substitutions reached levels of 2 % Zr we were already beginning to see a detrimental effect on the coercivity (Fig.6). This effect is almost certainly linked to the development of the large amounts of ZrB₂ that we observed, affecting the stoichiometry of the system—particularly with respect to boron—and degrading the properties in this way.

In our third series, Pr was substituted for half and for all of the Nd in a basic ternary alloy in order to determine what advantage—if any—a change in rare earth could provide. The results show an approximately 50 % improvement in coercivity and a tremendous increase in the range of temperatures where we can achieve optimum coercivities (**Figure 7**). Both of these factors are very important for industrial production. At this point it is often useful to discuss the microstructures of the processed materials: can we use microstructures to explain why the coercivity of the K (Nd:Pr 0:100) alloy is twice that of the I (Nd:Pr 100:0) alloy at a recombination temperature of 850 °C; is the 40 % drop in coercivity of the J (Nd:Pr 50:50) alloy between recombination temperatures of 870 and 880 °C reflected in some sort of microstructural change? Unfortunately, unlike the case of the as-cast microstructures, there is little or no difference to be observed in the post-HDDR state, irrespective of whether we change the chemistry or

the recombination temperature. Of course at very high recombination temperatures we do observe what has been termed "explosive grain growth", but in general the microstructures observed using scanning electron or optical microscopy are not very useful in helping us to refine the process and achieve better properties. It has been reported for the case of PrFeCoBZr and NdFeCoBZr alloys ⁶ that the different coercivities can be explained by a "distinctly different morphology" which exists when Pr is substituted for Nd, but we were unable to observe any such differences in our materials—which, it must be pointed out, did not contain any cobalt—under our processing conditions. Our observation that the materials which contain Pr rather than Nd are relatively insensitive to high recombination temperatures is, however, in broad agreement with those who have reported slower kinetics for Pr-based materials ⁸; and the better coercivities can be largely attributed to the 30 % higher anisotropy field of the Pr-based RE₂Fe₁₄B phase ⁹. Having said this, Pr substitution is less effective than it might be. We observed that the Pr has a preference for the RE-rich phase over the RE₂Fe₁₄B phase (**Table 2**), where its anisotropy-field-enhancing properties could be put to better use. Although it is always possible that Pr could have a positive effect on coercivity as part of a microstructural improvement related to the RE-rich phase we have not been able to see any features that could champion Pr as a RE-rich-phase-improving element.

In the fourth stage of our investigation we looked at a further refinement of the optimum Pr substitution and to see whether it was possible to combine the beneficial effects of Zr and Pr. **Figure 8** suggests that it is, and that the optimum Pr substitution for Nd—for the case of our materials processed under the conditions in our laboratory—is three-quarters; however, we know from other experiments carried out on the same alloys under high-vacuum conditions ¹⁰ that it is also possible to obtain the best results for the all-Pr alloy. Since the more Pr is substituted for Nd the higher would be the anisotropy field of the RE₂Fe₁₄B phase we would expect the all-Pr material to give the highest coercivity, but this assumes that all other things are equal, and because of the radically different processing environments this is very unlikely to be the case. Nevertheless, the significant substitution of Nd by Pr appears to be a wholly beneficial exercise, boosting coercivity and, perhaps surprisingly, reducing the material costs. At the time of writing (April 2001) Pr metal with a purity of 99 % is around three-times cheaper than the equivalent Nd. This is a topsy-turvy situation: Pr is three-times less abundant than Nd in the earth's crust—and there is no reason to suspect that this will ever change. The big factor affecting the relative prices is demand. Nd (magnets and capacitors) like Y (phosphors), Eu (phosphors), and Dy (RE magnets) is a much-sought-after material which can command a high price, in contrast, Pr—and most of the

other rare earths—are viewed as by-products. This means Pr is cheap—at least until someone decides to use lots of it. But if RE₂Fe₁₄B-type magnets were based on (Nd_{0.75}Pr_{0.25})₂Fe₁₄B the rare-earth metals would be consumed in a proportion which matches their abundance, and artificially low (and high) prices—at least as far as Nd and Pr are concerned—would no longer exist. There would also be less of a need to use Dy because Pr would provide, at this Pr-additive level, almost twice the anisotropy-field increase resulting from the typical Nd₁₄DyFe₇₇B₈-based Dy-substituted alloys, and without the unfortunate side effect of anti-ferromagnetic coupling. Of course this would leave plenty of unwanted Dy on the shelf—and so its price would, presumably, drop.

The other important points to note from Figure 8 are that the positive effects of Pr and Zr are cumulative, both substitutions appear to act independently with 0.1 % Zr together with 11.25 % Pr (O) producing a higher coercivity than the individual substitutions could achieve on their own, and that we retain the wide temperature-processing window which is vital for industrial production.

Any discussion of the properties of HDDR-processed powder must always emphasise that the results are very dependent on the equipment used. There are many factors to consider, these include: the capacity and efficiency of the pump; the amount of material processed in a single batch; the temperature homogeneity; and the ability of the furnace to cope with the endothermic reactions that take place. To suggest that we have solved all the problems associated with producing a 1000-kA/m magnet in the factory would be wrong, but we have shown that under conditions which would not be difficult to obtain in a factory we can generate very high coercivities given the right composition of the alloy. The process of up-scaling, first to 10-kg batches and then onto larger amounts, remains a task for the manufacturer.

5 CONCLUSIONS

Our investigation of Pr and Zr substitutions to NdDyFeB-based alloys that were processed using the HDDR technique allows us to draw a number of conclusions:

- Our factory-like processing conditions require plenty of rare-earth metal to be used in the starting material.

We needed 16 % rare earth to achieve properties above 1000 kA/m.

- Small substitutions (<1 %) of Zr increase the coercivity. The formation of the ZrB₂ phase seems to play an important role here. Larger substitutions (≥2 %) show no improvement. The formation of the ZrB₂ phase seems to play an important role here, too.
- Substituting three-quarters—or perhaps more—of the Nd with Pr results in very significant increases in coercivity and a broadening of the processing window in terms of recombination temperature.
- When we take into account the benefits in terms of coercivity and price, Pr looks to be an element which should play a larger role than it has so far in REFeB-based magnets.

Acknowledgements

The Ministry of Science and Technology of the Republic of Slovenia is gratefully acknowledged for the provision of research funds. Much of this work was carried out as part of the NATO Science-for-Peace Programme, Project No: SA.SfP_-972428(98)CDW373.

6 REFERENCES

- ¹ O Gutfleisch and IR Harris, Proceedings of the 15th International Workshop on Rare-Earth Magnets and their Applications, Dresden, Germany, 1998, 1, 487
- ² PJ McGuinness, C Short, AF Wilson, and IR Harris, *J. Less-Common Metals* 184 (1992) 243
- ³ S Kobe Beseničar, J Holc, G Dražič and B Saje, *IEEE Trans. Magn.* 30 (1994) 2, 693
- ⁴ T Takeshita and R Nakayama, Proceedings of the 10th International Workshop on Rare-Earth Magnets and their Applications, Pittsburgh, USA, 1990, 51
- ⁵ YB Kim and WY Jeung, *J. Appl. Phys.*, 83 (1998) 11, 6405
- ⁶ RN Faria, DN Brown and IR Harris, *J. Alloys and Comps.*, 296 (2000), 219
- ⁷ PJ McGuinness, I Škulj, A Porenta and S Kobe, Proceedings of the 15th International Workshop on Rare-Earth Magnets and their Applications, Dresden, Germany, 1(1998), 553
- ⁸ AC Neiva, AP Tschiptschin and FP Missell, *J. Alloys and Comp.* 217 (1995), 273
- ⁹ S Hirose, Y Matsuura, H Yamamoto, S Fujimura, M Sagawa and H Yamauchi, *J. Appl. Phys.* 59 (1986), 873
- ¹⁰ O Gutfleisch and A Bollero, Private Communication