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Single-phase $Nd_2Fe_{14}B$ by co-reduction

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Abstract

Single-phase $Nd_2Fe_{14}B$ offers the possibility of improving the corrosion behaviour and the magnetic properties of sintered NdFeB magnets in combination with an appropriate sintering additive by forming a two-phase magnet. Furthermore, the single-phase $Nd_2Fe_{14}B$ is suitable for the manufacturing of resin-bonded magnets produced by, for instance, the hydrogenation, disproportionation, desorption and recombination process. In view of this background the coreduction process has been improved for the production of single-phase $Nd_2Fe_{14}B$. Single-phase $Nd_2Fe_{14}B$ is obtained by choosing appropriate raw materials and performing the co-reduction process in a controlled way. X-ray diffraction analysis showed the hard magnetic phase $Nd_2Fe_{14}B$ and only traces of $NdFe_4B_4$, but no α-Fe and Nd-rich phase. Some α-Fe precipitates were identified by metallographic examination and scanning electron microscopy with energy-dispersive X-ray analysis.

1. Introduction

The rare earth metals form numerous intermetallic compounds with nearly all elements of the periodic table except the noble gases and the elements of the 4 B, 5 B and 6 B group. Most of these are incongruently melting alloys with a very narrow compositional range at room and also at elevated temperature. These combined facts require special care and the application of special metallurgical methods whenever the production of such intermetallics in single-phase form is wanted. For scientific investigations, the annealing of the as-cast specimens over several hundred to several thousand hours is standard in such cases.

The hard magnetic rare earth transition metal intermetallics, especially, have attained considerable technical importance. Examples are the alloys based on the intermetallics $Nd_2Fe_{14}B$ [1], $SmCo_5$ [2], Sm_2Co_{17} [3], or the recently developed alloy $Sm_2Fe_{17}N_x$ [4]. In the case of the hard magnetic compound $Sm_2Fe_{17}N_x$, a single-phase Sm_2Fe_{17} is the precursor for nitrification. NdFeB alloys for the powder metallurgical route of making magnets always contain a neodymium-rich phase and the intermetallic $NdFe_4B_4$. Of these, only the Nd-rich phase is necessary in the final permanent magnets. It separates the $Nd_2Fe_{14}B$ crystallites magnetically and assists, by virtue of its low melting point, the consolidation and densification of the pressed, green magnet bodies. In addition, unwanted α-Fe or Nd_2Fe_{17} may also be present in the as-cast alloys and should be avoided by all means [5, 6]. The main

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disadvantages of the NdFeB magnets are their susceptibility to corrosion [7–9] and their low Curie temperature [10]. Accordingly a two-phase magnet based on the single-phase $Nd_2Fe_{14}B$ and an appropriate sintering additive should be aimed at. Then the temperature stability will be improved by an advanced microstructural morphology [11].

The attainment of a nearly single-phase microstructure with only small amounts of the Nd-rich phase and other compounds can be facilitated when the molten alloy is rapidly solidified, which results in a microcrystalline or even amorphous solidification product [12, 13]. But the practical application of such a material is limited to resin-bonded magnets, and the melt spinning technique is a costly process. A recently developed simple method for the production of microcrystalline NdFeB alloys to be used in isotropic and anisotropic resin-bonded magnets is the hydrogenation, disproportionation, desorption and recombination process based on the single-phase $Nd_2Fe_{14}B$ intermetallic compound [14].

Consequently the target of the present investigation was the optimization of the co-reduction process for the production of single-phase $Nd_2Fe_{14}B$.

2. Experimental details

The materials were prepared in laboratory batches of 2.5–5.0 kg each by the co-reduction process. During the coreduction process there is a simultaneous reduction of rare earth and transition metal oxides in the presence of a transition metal powder. The reducing agent is calcium metal. The principle of the co-reduction process will be described below by means of the production of single-phase $Nd_2Fe_{14}B$.

For the production of $Nd_2Fe_{14}B$ the raw materials Nd_2O_3, Fe_2O_3, B_2O_3, iron metal powder and calcium metal are used. In the case of standard NdFeB alloys, a raw material mixture without Fe_2O_3 is usually applied. The ingredients are intensively blended, pressed into tablets and put into a crucible. The crucible, made of a heat-resistant Fe–Cr–Ni steel, is sealed by welding a lid on top and is inserted into a reaction furnace. The reduction and diffusion process is performed as follows.

First the reaction mixture is degassed by evacuating the crucible and the furnace at room temperature. Then the furnace is heated under vacuum to about 800 °C. Again a degassing of the reaction mixture can be observed. At a temperature above 400 °C the exothermic reaction occurs between the calcium and the added oxides. When the exothermic reaction is finished the furnace is heated to a temperature of 1200 °C. After completion of the reduction and diffusion process the crucible is cooled to room temperature. The lid is removed from the crucible. The reaction material consisting of CaO, a certain excess of calcium and the desired alloy is taken out of the crucible and crushed. The excess of calcium metal, which is necessary for the co-reduction process, and the CaO formed are chemically transformed into $Ca(OH)_2$ by reacting with water. The leached alloy powder is filtered, washed and finally dried in a vacuum drier.

The co-reduction reaction was investigated by temperature measurements during the reduction and diffusion process. The progress of the formation of the NdFeB alloys was analysed by interrupting the co-reduction process at different stages. For characterizing the reaction products and for obtaining evidence of the formation of the single-phase intermetallic compound we used X-ray diffraction analysis, metallographic and scanning electron microscopy (SEM) investigations.

3. Results and discussion

The co-reduction process was investigated with regard to its ability to produce single-phase $Nd_2Fe_{14}B$. First the progress of the co-reduction reaction was analysed for the composition Nd 16.7 / Fe 77.0 / B 6.3 (at.%) using a reaction mixture without Fe_2O_3. The reaction products were characterized by metallographic observation, X-ray diffraction analysis and SEM investigation.

Figure 1 illustrates a temperature profile of the reaction with a raw material mixture of the composition Nd 16.7 / Fe 77.0 / B 6.3 (at.%) without Fe_2O_3, as measured in the crucible during the reduction and diffusion process. The resulting different phase compositions of the reaction mixture as a function of time are given in Table 1.

After a first degassing of the raw material mixture at room temperature, a further desorption of adsorbed air and moisture is observed during heating to about 800 °C. According to the X-ray diffraction analysis, a first reaction between the calcium metal and the oxides was determined at 560 °C by identifying CaO. Later on the spontaneous ignition of the mixture takes place at 640 °C.

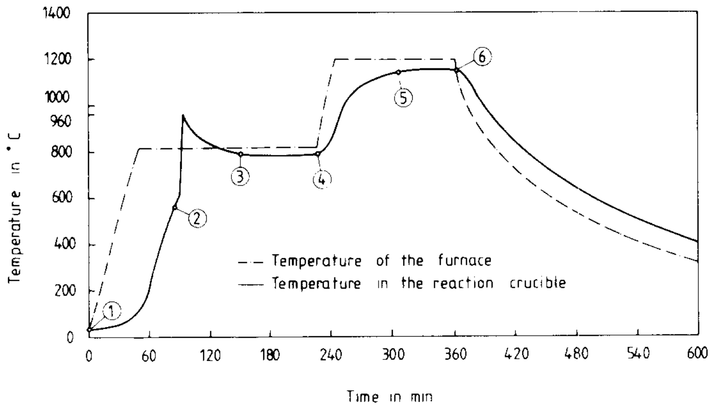


Fig. 1. Temperature profile of the co-reduction reaction with a raw material mixture of Nd 16.7 / Fe 77 / B 6.3 (at.%) without Fe_2O_3 as a function of time.

TABLE 1

Phase compositions of the raw material and of the reaction mixture as a function of time analysed by X-ray diffraction and SEM with EDX analysis. The numbers 1–6 refer to the various stages indicated in Fig. 1.

1	2	3		4		5		6	
Nd_2O_3	Nd_2O_3	$Nd_2Fe_{14}B$	+ + +	$Nd_2Fe_{14}B$	+ + +	$Nd_2Fe_{14}B$	+ + +	$Nd_2Fe_{14}B$	+ + + +
α-Fe	α-Fe	$NdFe_4B_4$	+	$NdFe_4B_4$	+	$NdFe_4B_4$	+	$NdFe_4B_4$	(+)
B_2O_3	B_2O_3	Nd-rich phase	+ +	Nd-rich phase	+ +	Nd-rich phase	+	Nd-rich phase	(+)
Ca	Ca	α-Fe	+ +	α-Fe	+ +	α-Fe	+	α-Fe	(+)
	CaO	Ca CaO		Ca CaO		Ca CaO	Ca CaO		

+ + +–+ + + + = matrix phase
+–+ + = secondary phases
(+) = impurities

Nd_2O_3 is thermodynamically much more stable than B_2O_3, and calcium metal melts at 839 °C. From these facts we can assume that the exothermic reaction starts in the solid state, probably as an interface reaction between the B_2O_3 and the calcium metal. This reaction also causes the sharp increase of the temperature to 960 °C after the ignition of the raw material mixture.

When the exothermic reaction is finished, $Nd_2Fe_{14}B$, $NdFe_4B_4$, neodymium metal alloyed with 3–10 wt.% Fe, and unalloyed α-Fe were found in the reaction mixture by X-ray diffraction and energy-dispersive X-ray (EDX) analysis. Corresponding to the binary Nd–Fe phase diagram, the neodymium when alloyed with about 10 wt.% Fe melts at 685 °C, the eutectic temperature. Binary Nd–Fe alloys with 3–10 wt.% Fe have liquidus temperatures between 685 °C and 900 °C. Hence, a liquid Nd-rich phase is formed during the exothermic reduction reaction, which promotes the formation of the intermetallics $Nd_2Fe_{14}B$ and $NdFe_4B_4$. Subsequently a decrease of the concentration of the unalloyed α-Fe precipitates is observed during the isothermal stage at 800 °C, this means that the α-Fe is partially dissolved in the liquid Nd-rich phase. The $NdFe_4B_4$ concentration does not change considerably, which means that the diffusion is too slow for an adjustment of the concentration. So at the end of this reaction stage, the reaction mixture is composed of $Nd_2Fe_{14}B$ and substantial amounts of $NdFe_4B_4$, the Nd-rich phase and also α-Fe precipitates. Therefore a further homogenization treatment is required. For this purpose the reaction mixture is heated up to 1200 °C. During the heating treatment at 1200 °C, the concentration of $NdFe_4B_4$, Nd-rich phase and α-Fe is diminished but without formation of further phases. This suggests that the homogenization is achieved not only by increasing the temperature but, more importantly, by the presence of the low melting Nd-rich phase. The higher temperature improves the wetting of the grains by the Nd-rich phase and hence its distribution in the reaction mixture. This, in turn, leads to enhanced dissolution of the α-Fe and $NdFe_4B_4$ intermetallic and the formation of the hard magnetic $Nd_2Fe_{14}B$ compound by an accelerated diffusion process.

In view of the progress of the alloy formation during the coreduction process the task was to optimize the coreduction for the production of single-phase $Nd_2Fe_{14}B$ in pure form. In this case the peritectic melting point, the very narrow compositional range, and the lack of the Nd-rich phase have to be considered.

The single-phase $Nd_2Fe_{14}B$ requires theoretically 26.7 wt.% Nd. Figure 2 shows the relationship between the neodymium content applied in the raw material mixture and the neodymium concentration analysed in the final NdFeB product. A very narrow compositional range demands accurate analysis of the losses during the whole co-reduction process including the chemical leaching. The most important losses observed for the rare earth component are due to the formation of hydroxides or oxihydrates. These are partially dissolved during the chemical leaching or remain in the alloy and cause an increasing oxygen content. In view of these losses, an excess of 1.5 wt.% Nd has to be used to obtain the stoichiometric $Nd_2Fe_{14}B$ composition.

The maximum reaction temperature can be adjusted to a certain value by adding, for instance, Fe_2O_3 to the raw material mixture. Figure 3 illustrates the linear increase of the reaction temperature with increasing Fe_2O_3 content. The importance of the grain size of the raw materials was also investigated. Figure 4 demonstrates a metallographic cross-section of a coreduced $Nd_2Fe_{14}B$ sample produced with an Fe powder of a grain size larger than 75 μm. A homogeneous distribution of unalloyed α-Fe grains was observed in this case.

$Nd_2Fe_{14}B$ melts peritectically at 1180 °C. At the melting point the following equilibrium exists:

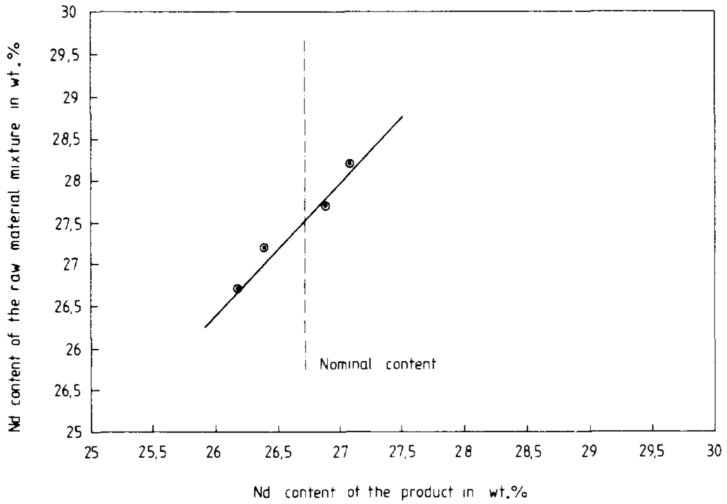


Fig. 2. Neodymium content of the raw material mixture as a function of the analysed neodymium concentration in the final product.

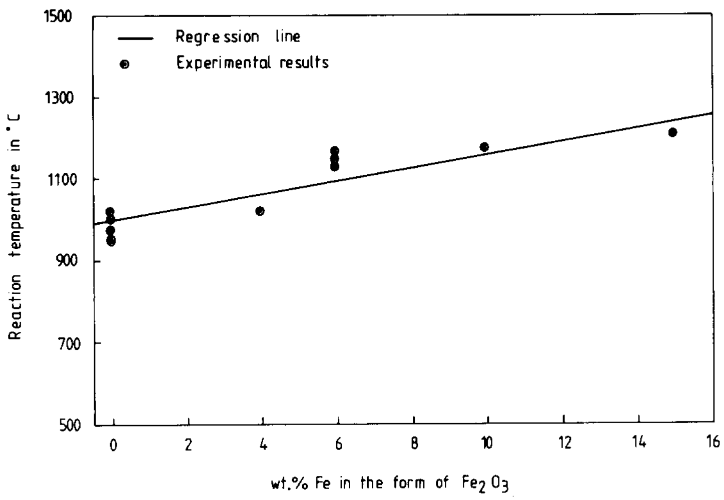


Fig. 3. Reaction temperature during the exothermic reduction reaction as a function of the iron content in form of Fe_2O_3.

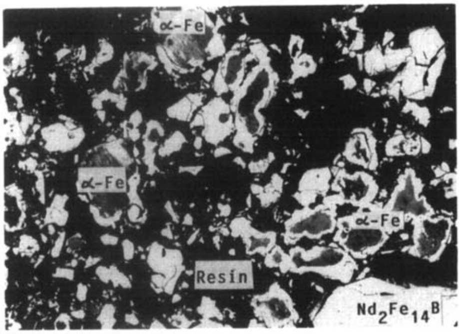


Fig. 4. Metallographic cross-section of co-reduced, single-phase $Nd_2Fe_{14}B$ produced with a raw material mixture with an iron powder larger than 75 μm, 100:1.

$$Nd_2Fe_{14}B \rightleftharpoons L_{Nd\text{-rich}} + \alpha\text{-Fe} \tag{1}$$

However, the precipitation of α-Fe has to be avoided, because it affects the hard magnetic properties. The desired formation of single-phase $Nd_2Fe_{14}B$ can be obtained from a thermodynamic standpoint only by a solid-state reaction. But then the formation of the stoichiometric $Nd_2Fe_{14}B$ composition has to occur only by solid-state diffusion without the support of the low melting Nd-rich phase. In view of this complication, the diffusion has to be enhanced by raising the temperature during the reduction and diffusion process as high as possible, but without heating to the peritectic melting point of the intermetallic compound, and by minimizing the diffusion length.

The reaction temperature was therefore adapted to the peritectic melting point of the $Nd_2Fe_{14}B$ phase of 1180 °C by adding 6 wt.% of the total iron content in form of Fe_2O_3. The measured reaction temperature is then close to 1110 °C. The grain size of the iron metal powder should be less than 75 μm, otherwise a homogeneous distribution of unalloyed α-Fe grains is found in the final alloy.

Figure 5 represents the temperature profile of an adjusted composition of the raw material mixture with respect to the grain size of the raw materials, the rare earth content, and the Fe_2O_3 content. It is obvious that during the whole co-reduction process the temperature in the crucible stays below the peritectic melting point of the $Nd_2Fe_{14}B$ intermetallic.

According to the X-ray diffraction analysis, no α-Fe was present and there was only a very weak diffraction line of $NdFe_4B_4$. The metallographic cross-section of this material given in Figs. 6(a) and 6(b) shows in most parts of the sample single-phase $Nd_2Fe_{14}B$ without any $NdFe_4B_4$, α-Fe and Nd-rich phase (Fig. 6(a)). Only a few precipitates of α-Fe (Fig. 6(b)) or

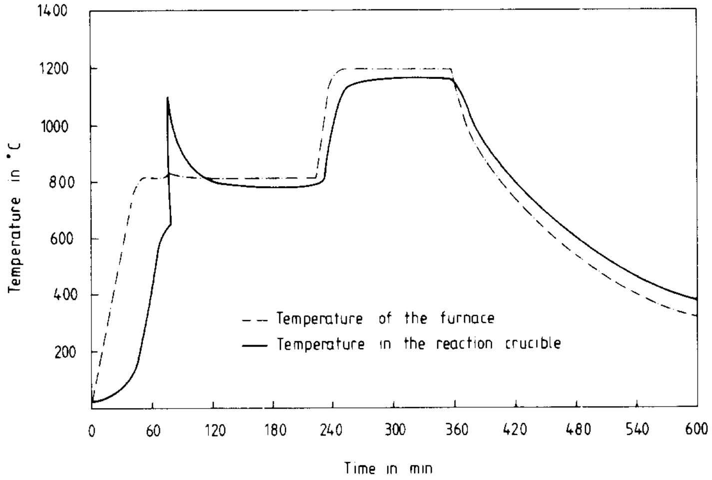
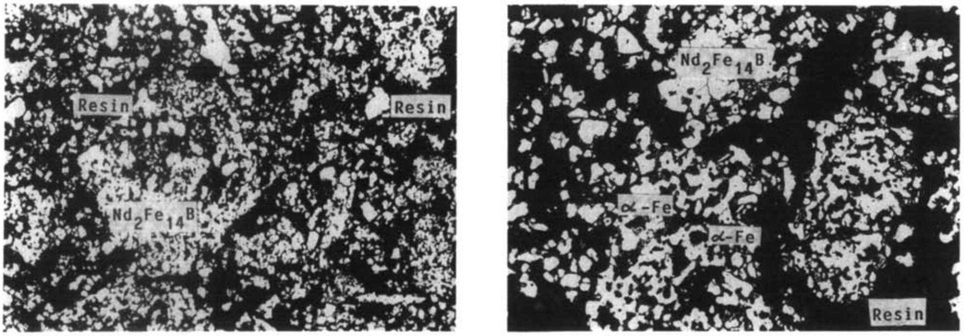


Fig. 5. Temperature profile of the co-reduction reaction with an adjusted raw material mixture for making single-phase $Nd_2Fe_{14}B$ as a function of time.



(a) (b)

Fig. 6. Metallographic cross-section of co-reduced single-phase $Nd_2Fe_{14}B$ produced by an adjusted raw material mixture: (a) 100:1; (b) 200:1.

TABLE 2

Typical chemical composition of the co-reduced single-phase $Nd_2Fe_{14}B$

	Nd	SE	Fe	B	Ca	O	C	H
Wt.%	27.3 ±0.3	27.5	Bal. ±0.3	1.0	<0.1 ±0.05	<0.3	<0.05	<0.1

$NdFe_4B_4$ grains could be identified by SEM with EDX analysis and metallographic observation. A typical chemical composition of the co-reduced single phase $Nd_2Fe_{14}B$ is shown in Table 2.

We thus find that single-phase $Nd_2Fe_{14}B$ can be obtained by the co-reduction process, by selecting the appropriate raw materials, adding a certain amount of Fe_2O_3 and using a certain excess of Nd.

4. Summary

The progress of the co-reduction process was investigated step by step. Subsequently the co-reduction process was adjusted to produce a single-phase $Nd_2Fe_{14}B$. The co-reduction process was characterized by temperature measurements during the reduction and diffusion steps. For determining the phase composition of the co-reduced reaction products and for obtaining evidence of the formation of a single-phase intermetallic compound we employed X-ray diffraction and SEM with EDX analysis.

In NdFeB alloys of high neodymium concentration the presence of the Nd-rich phase has an important role not only in the manufacturing of NdFeB magnets but also for the production of the alloy itself by coreduction. The Nd-rich phase, by virtue of its low melting point, assists the formation of the $Nd_2Fe_{14}B$ phase and accelerates the homogenization of the NdFeB alloys.

In manufacturing single-phase $Nd_2Fe_{14}B$, the absence of the Nd-rich phase has to be compensated for by minimizing the diffusion length and raising the reaction temperature to close to the peritectic melting point of the intermetallic phase $Nd_2Fe_{14}B$. This is achieved by selecting appropriate raw materials, by adding a certain amount of Fe_2O_3 and by applying a certain excess of neodymium. The results obtained in the course of the present investigation prove that single-phase $Nd_2Fe_{14}B$ with only traces of α-Fe and $NdFe_4B_4$ can be manufactured by the co-reduction process.

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References

1 M. Sagawa, F. H. Setsuo and M. Yutaka, *Eur. Patent, 01.01532*, 1983.

2 K. Strnat, G. Hoffer, J. Olson, W. Ostertag, J. J. Becker, *J. Appl. Phys., 38* (1967) 1001.

3 T. Yoneyama and S. I. Tomizawa, *Patentschrift DE 2705384C3*, 1977.

4 J. M. D. Coey, H. Sun *et al. Eur. Patent Application, 0453270 AL*, 1991.

5 J. Fidler and K. G. Knoch, *J. Magn. Magn. Mater., 80* (1989) 1.

6 D. Lemarchand, F. Vial, A. Hanet, B. Labulle and S. Vigier, *IEEE Trans. Magn., 26* (1) (1990) 253.

7 W. Bloch, K. Grendel and H. Staubach, *Proc. 11th Int. Workshop on Rare-Earth Magnets and their Application, Pittsburgh, PA, 1* (1990) 108.

8 A. Hagebe, E. Otsubi and Y. Kinetsu, *Proc. 10th Int. Workshop on Rare-Earth Magnets and their Application, Kyoto* 1989, Vol. 2 p. 383.

9 S. Szymura, H. Bala, G. Pawlowska, Yu. M. Rabinovich, V. V. Sergeev and D. V. Pokrovskii, *J. Less-Common Met., 175* (1991) 185.

10 C. Abache and H. Oesterreicher, *J. Appl. Phys., 57* (1) (1985) 4112.

11 K.-D. Durst, H. Kronmüller and G. Schneider, *Proc. 5th Int. Symp. on Magn. Anisotropy and Coercivity in Re–Transition Metal Alloys, Bad Soden, 1987, Vol. 2* p. 209.

12 J. J. Croat, J. F. Herbst, B. W. Lee and F. E. Pinkerton, *J. Appl. Phys., 53* (1984) 2078.

13 C. Tsung-Yao, *Ph.D.*, University of Texas, Austin, 1989.

14 I. R. Harris and P. J. McGuiness, *J. Less-Common Met., 172–174* (1991) 1273.