

Phase monitoring during $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ preparation by the calciothermic reduction–diffusion process

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We have examined the effect of various parameters involved in the preparation of the $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy by the calciothermic reduction–diffusion process. Both Nd_2O_3 and NdCl_3 were utilized as starting raw materials. Shorter reaction times and lower heating temperatures are required for the chloride than for the oxide. Among the characterization techniques used to evaluate the final product, Mössbauer spectroscopy was invaluable for the determination of the $(\text{Nd}_{1.1}\text{Fe}_4\text{B}_4)/(\text{Nd}_2\text{Fe}_{14}\text{B})$ ratio, which should be as low as possible.

1. Introduction

Preparation of the $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy is the first step for manufacturing high-performance Nd–Fe–B magnets [1]. This is usually done by melting pure elements together. An alternative route is offered by the calciothermic reduction–diffusion process [2], which has the advantage of using Nd oxide instead of highly reactive Nd metal as a starting material. In this process, appropriate amounts of Nd_2O_3 , metallic Fe and Fe–B alloy powders are mixed together with metallic Ca (the reducing agent) and heated at temperatures around 1000°C . Since the heat of reaction is small, the resulting alloy remains in powder form, which is advantageous for the subsequent stages of magnet fabrication.

In order to optimize the preparation of the magnet alloy by this method, we have undertaken a systematic investigation of the effect of a number of processing variables on the quantitative yield and various physicochemical properties of the final alloy. The utilization of Nd chloride instead of Nd oxide was also investigated. A commercial molten $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy was used as a reference material.

2. Experimental

The raw materials (99.9% pure Nd_2O_3 , metallic Fe and Fe–B alloy, all from

Alfa Products) were mixed into a homogeneous powder, and 99% pure Ca granules were added in alternate layers. Excess Nd oxide and Ca, relative to stoichiometric amounts, were included in different combinations. This mixture was heated under argon atmosphere at various temperatures for various time lengths. The reacted compact was immersed in distilled water, under Ar atmosphere, and left still for 12–48 h until complete disintegration occurred. Calcium hydroxide resulting from the reaction was removed by repeatedly washing with a 1 : 1 mixture of deionized water and ethyl alcohol. Residual Ca and other oxides were bleached by an acetic acid solution, and the resulting alloy was dried under vacuum. The same steps were followed in experiments using NdCl₃ as a raw material, except that the disintegration took much shorter times due to the high solubility of CaCl₂ in water [3].

Sample characterization included phase analysis (X-ray diffraction and Mössbauer spectroscopy), chemical analysis (optical emission spectrography and EDAX), morphology (optical microscopy and SEM), granulometry (BET, Fisher method, and light scattering) and oxygen determination (LECO-CS244 analyzer).

3. Results

X-ray diagrams showed that all samples were mainly constituted by the required ϕ phase (i.e. Nd₂Fe₁₄B), but powders prepared at temperatures lower than 1100°C also contained α -Fe, Ca(OH)₂ and Nd₂O₃. At this temperature, on the other hand, a minimum reaction time of 5 h was required for the reduction-diffusion process to be completed. Furthermore, the reaction yield is greatly increased by an excess amount of Ca. Thus, we have found that, for 5 h at 1100°C, 1.8 times the stoichiometric weight of Ca (combined with a 20% excess of Nd₂O₃) was necessary to ensure the absence of detectable α -Fe in the final product.

Sun et al. [3] have reported that reaction temperatures and times are lowered if NdCl₃ is used as a raw material. Our results confirmed this: a powder of similar quality as the best one obtained by using Nd₂O₃ was obtained after 3 h at 950°C (with 50% excess Ca and 20% excess NdCl₃). Fig. 1 shows the X-ray diagram for this sample and, for comparison, that of the commercial alloy.

As is well known, the as-prepared Nd₁₅Fe₇₇B₈ alloy contains, in addition to the ferromagnetic ϕ phase, both a Nd-rich phase (NRP) and Nd_{1.1}Fe₄B₄ (η phase). Upon appropriate heat treatment, the former gives rise to an intergranular microstructure which is essential in developing a high coercivity. The latter, in contrast, is a stable, nonmagnetic phase generally believed to be detrimental to magnetic properties; a good Nd-Fe-B magnet alloy is thus expected to exhibit a low η/ϕ volume ratio. This feature cannot easily be evaluated from X-ray diagrams due to strong line overlap, but Mössbauer spectroscopy is well suited for such analysis.

The spectrum of η at room temperature is a doublet with one of its lines well resolved from the magnetically split ϕ -phase spectrum. This is illustrated in fig. 2. All measured spectra were fitted with a superposition of a doublet (typically,

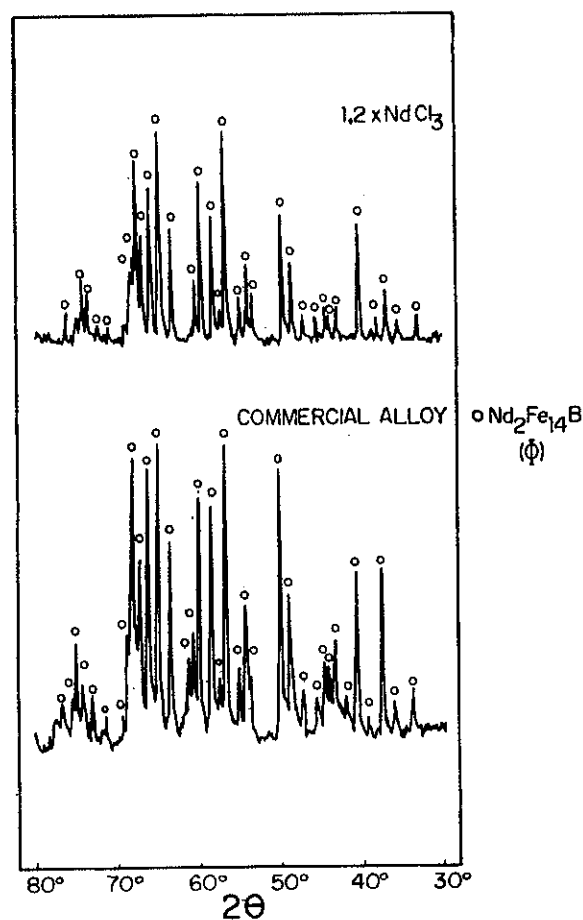


Fig. 1. X-ray diffractograms of Nd-Fe-B alloy prepared from NdCl_3 (top) and commercial molten alloy (bottom).

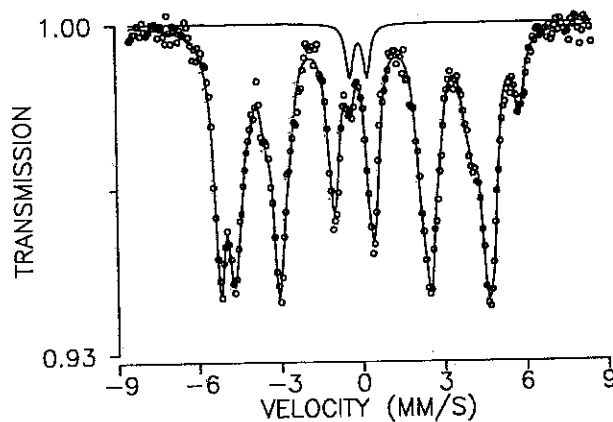


Fig. 2. Mössbauer spectrum of a Nd-Fe-B alloy prepared by reduction-diffusion process, fitted as a superposition of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ spectra. The latter is separately drawn.

QS = 0.6 mm/s [4]) and a set of six magnetic sextets constrained to the 4 : 4 : 2 : 2 : 1 : 1 area ratio characteristic of the Nd₂Fe₁₄B structure. Hyperfine parameters for all sites were left free to vary. Fitted values were consistent with published ones. A further sextet, corresponding to α -Fe, was also included when appropriate. No other Fe-containing phases were found for any sample, indicating the amount of Fe dissolved in the NRP is too low to be detected.

The relative Fe amounts in ϕ and η were found from the respective spectrum areas to be 96.5% (ϕ) and 3.5% (η), for the best samples prepared using either Nd₂O₃ or NdCl₃. These figures compare well with those found for the molten alloy (96.8 and 3.2% respectively). If ϕ and η were the only phases present, a Fe : Nd ratio of 6.78 would result from the above data. A direct determination by EDAX yielded Fe : Nd = 5.79, the discrepancy necessarily being due to the presence of the Nd-rich phase. Combining both data one obtains the following partition of Nd among the three phases: 79.7% in ϕ , 5.4% in η , and 14.9% in the NRP. These figures can unfortunately not be converted to volume fractions, because the structure and composition of the latter phase are not exactly known.

4. Conclusions

Our study has indicated some guidelines for producing Nd-Fe-B alloys for permanent magnets by the reduction-diffusion process. If Nd₂O₃ is used as a raw material, at least 5 h reaction at 1100°C are needed, while NdCl₃ (with 3 h at 950°C) appears to be an interesting alternative. Our results further stress the importance of excess Ca to ensure a complete reaction. Finally, Mössbauer spectroscopy turned out to be invaluable for a full characterization of the resulting product, owing to the great line overlap between ϕ and η phases in X-ray diffractograms.

Acknowledgement

EGG was financially supported by a CNPq-RHAE scholarship.

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