

OXYGEN PICK UP DURING Nd-Fe-B MAGNET PROCESSING UNDER CONTROLLED ATMOSPHERE

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ABSTRACT

In this work, the oxygen contamination of Nd-Fe-B type magnets during controlled atmosphere processing is characterized in the main stages of the powder metallurgical route including the sintering. Three different protective media for ball milling were tested: container filled with high-purity argon; container partially filled with toluene, and the container filled with toluene plus argon, respectively. The oxygen pick-up of an as-pressed compact before heating was also analyzed. The results indicate a final content around 0.2 %wt of O₂, being the high-temperature sintering where most of oxygen contamination occurs.

1. INTRODUCTION

The magnets based on transition metal/rare-earth systems such as the alloys of the Sm-Co and the Nd-Fe-B family, have reached a stage of significant commercial and scientific development. The elevated magnetic properties of these types of materials, however are directly linked to their composition, processing parameters, and strongly dependent of the oxygen content in the final product.

The processing of permanent magnets of the Fe-Nd-B system can be conducted both by powder metallurgy route (PM) and hot-deformation of the as-cast ingots, being this latter a promising alternative low-cost process¹. The better magnetic performance however, is attained by PM via, which is critical what concerns the oxygen contamination of the free Nd or the Nd-rich phases present in the ternary magnetic composition. These phases, solid during the powder production and liquid at sintering temperature, have in both conditions high reactivity, requiring a special environmental control in order to limit the oxygen pick-up. The negative influence of the oxygen during Nd-Fe-B magnets processing might be understood by some correlated aspects: The initial formation of an oxide film on the surface of the powder reduces the bulk mass transport between particles during sintering. That demands

an increase of the temperature or in the heating time in order to attain a better sintering². And by the reduction of the amount of Nd-rich liquid phase, due the formation of Nd₂O₃ or Nd(OH)₃ at the sintering temperature. The presence of such oxides results in a low density material^{3,4}. It is important to point that the liquid in this system has an importante role in the sintering process, acting both as an easy diffusion medium and as an efficient porous filler. In the final magnet, the oxidation also acts negatively on the magnetic properties by changing the main phase composition what reduces the local magnetic anisotropy⁵.

Some addition of doping elements to the ternary basic alloy have been proposed in the literature in an attempt to reduce the oxidation rate^{6,7}, although it is accepted that a totally oxide free rare-earth magnet, is evidently, rather impossible. In this work, the oxygen contamination of Nd-Fe-B magnets production, in laboratorial scale, is followed by means of measurements of O₂ contents after the mean steps of the PM route.

2. EXPERIMENTAL

2.1 Powder Production

The magnet processing followed a suitable powder metallurgy route as schematically presented in the diagram of Figure 1.

The ingots secked the Sumitomo composition (Nd₂Fe₁₄B), being the crushing done manually. Around 30 grams of the coarse powder (< 200 µm) was then ball milled by making use of three different protective media: 1 - milling container filled with high-purity argon; 2 - container partially filled with toluene (80% of the volume) and 3 - container filled with toluene plus argon. The rotation inputted was 36 rpm and the balls (stainless steel) had 6 mm diameter.

These media conditions are illustrated in Figure 2. The argon gas and the organic solvent toluene are widespread used in laboratorial practice as a protective medium to avoid contact of the metals powder with the air during comminution. The tests here aim to check their efficacy in processing such a high reactive element as rare-earth.

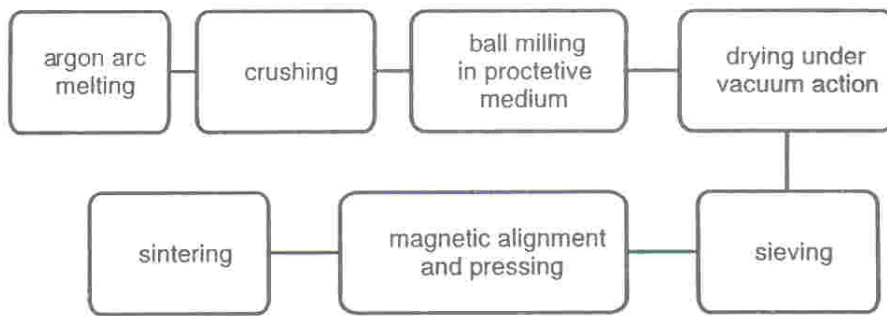


Figure 1 - Production sequence of permanent magnets based on rare-earth-transition metals.

After 3 hours of milling, the final powder in the three conditions were vacuum dried and sieved, in a argon filled glove-box, to an average grain size laying around 3 μm . For alignment the powder was magnetically oriented by the action of an external capacitor discharge field of 3.7 T and uniaxially pressed to a cylindrical form (ϕ 12 x 14 mm at 200 MPa).

The oxygen contamination was evaluated by a LECO 36 gas analyzer at three different stages of the process:

- 1 - during the milling (different milling times);
- 2 - during the air exposure of the green compacts (0 to 180 minutes of air exposure);
- 3 - after sintering.

The evaluation 2 was conducted in order to characterize a possible oxidation during the time necessary to handle the material, i.e.; to align, to press and introduce the briquette into the sintering chamber, since those procedures are ordinary done under air contact.

2.2 Sintering

Before heating, the chamber was evacuated to a vacuum better than 10^{-4} Mbar. This vacuum was hold until the

temperature achieved 900 $^{\circ}\text{C}$ and then the chamber was filled with high-purity argon to atmospheric pressure and kept in this condition during the whole sintering process i.e., 1070 $^{\circ}\text{C}$ for 1 hour. This procedure was chosen to minimize the oxidation and avoid the evaporation of Nd. The complete sintering cycle for magnet production is shown in Figure 3. In this work the path 1-2-3 was employed. The sintering apparatus setup is shown in Figure 4. A more detailed description of the powder production and sintering parameters may be found in references 8 and 9.

3. RESULTS AND DISCUSSION

Figure 5 presents the results of the oxygen pick up as a function of the milling time, for the three environmental conditions. As expected, in all tests the oxygen content increases with the milling time, nevertheless, the conjugated medium (argon + toluene) presented the lowest contamination, close to the best results obtained by others investigators^{9,10}. This condition showed good reproducibility and became the current procedure in our processing route.

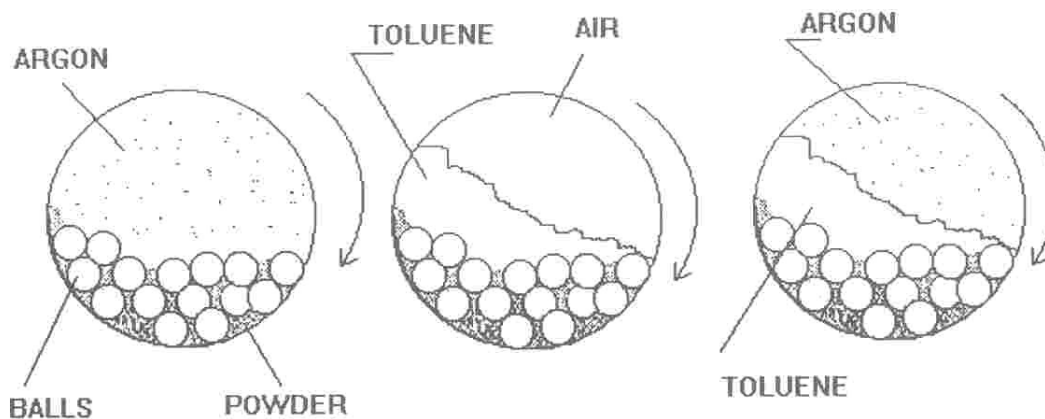


Figure 2 - Ball milling in protective media.

An important aspect concerning processing, although hardly ever considered, is the unavoidable air exposition of the powder during the alignment, pressing and handling of the compact into the furnace before the vacuum system is shifted on. Figure 6 presents the oxygen content evolution for a green compact during the air exposure (milled in toluene + argon).

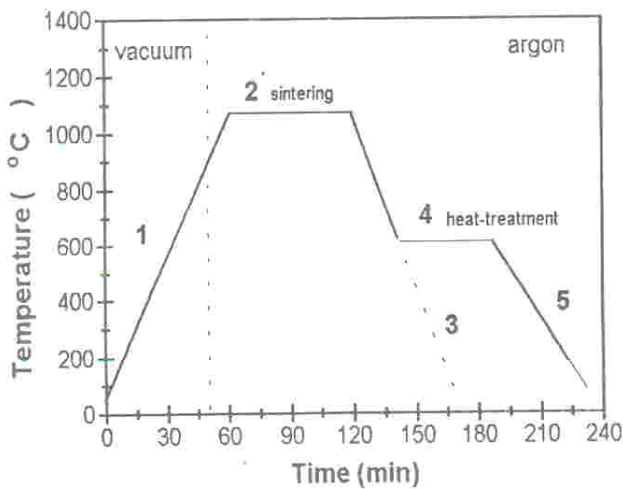


Figure 3 - Sintering thermal cycle and atmosphere. In this work path 1-2-3 was followed.

The data point to a fast oxidation in the first minutes with a tendency to stabilization at values around 2,700 ppm. Ordinary, in laboratorial conditions, the time for these procedures was counted as being around 7 minutes per sample. If we take into account that we have to fill the chamber by making briquette after briquette, the overall time before sealing the chamber becomes a great figure for a wide production.

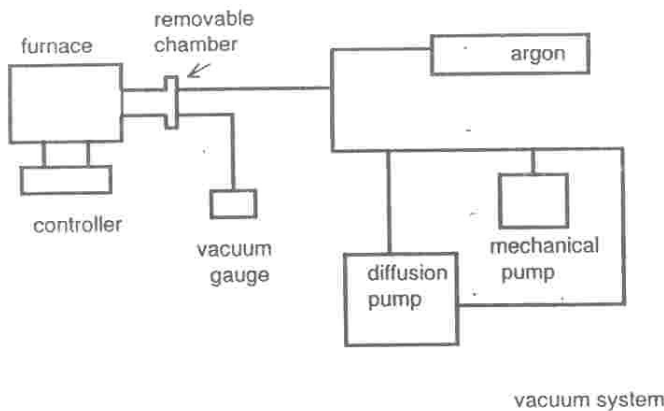


Figure 4 - Vacuum sintering apparatus setup

So, the oxygen concentration of the compact before heating is at least in the range of 420 - 1,000 ppm for an ordinary sequence time. After the sintering, the analysis showed a value of 2,343 ppm of O₂ in the sample, indicating that in despite of the atmosphere control, sintering at high temperature increases the contamination in an order of 1,000 ppm.

It is worth to stress that in industrial scale production, some cares carried out in this work are not practicable in economic terms.

If we follow the processing route as presented on Figure 1, from the starting alloy to final product, more than 2,300 PPM of O₂ are picked up into the composition, what evidently acts negatively on the magnetic performance of these materials.

4. CONCLUSIONS

The data presented in this work reflect the amount of /oxygen contamination of the Nd-Fe-B magnet during the processing in an ordinary laboratorial scale. The results point to the impracticability of getting oxygen-free magnets. Improvement may be done by additional protective procedures, which must be essentially related to improvement of the atmosphere control during the sintering. The high temperature necessary in this stage is also taken as the main factor for oxide formation.

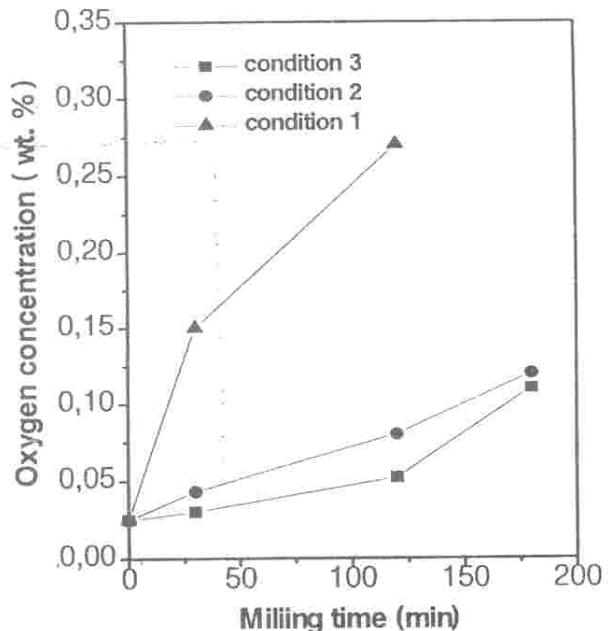


Figure 5 - Oxygen pick up during milling for the three experimental condition.

The time spent in alignment, pressing and to evacuation of the chamber was also found to be a very important parameter which has to be taken into account.

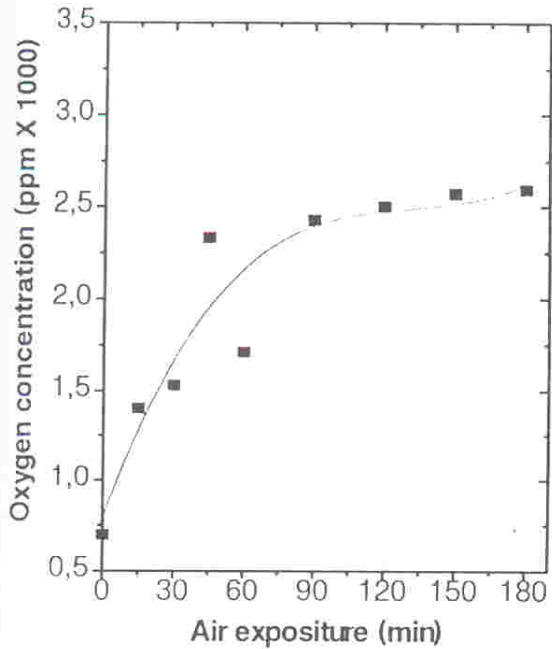


Figure 6 - The green compact oxygen pick up during air exposure (uniaxially pressed at 120 MPa).

5. REFERENCES

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