

ANALYSIS OF CORROSION PROPERTIES OF MELT SPUN Nd-Fe-B RIBBONS COATED BY ALUMINA COATINGS

ANALIZA KOROZIJSKIH LASTNOSTI HITRO STRJENIH Nd-Fe-B-TRAKOV, OPLAŠČENIH Z ALUMINIJEVIM OKSIDOM

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We have coated Nd-Fe-B melt spun powders, used for the production of bonded magnets via the sol-gel route by Al₂O₃. Topography and chemical composition of as-spun and protected ribbons was compared by Auger electron spectroscopy, X-ray photoelectron spectroscopy, secondary electron spectroscopy and electron diffraction spectroscopy. To determine the corrosion properties, we have conducted a Highly accelerated stress test, at 110 °C and 90 % humidity, followed by measuring the weight change. To confirm the effectiveness of the coated layer, magnetic properties were compared with a vibrating sample magnetometer. Al₂O₃ coatings resulted in superior corrosion resistance and magnetic properties and thus expanding the applicability of bonded magnets to severe atmospheric conditions.

Keywords: Nd-Fe-B, bonded magnets, HAST, Al₂O₃ coatings

S sol-gel metodo smo oplaščili hitro strjene Nd-Fe-B-trakove za uporabo pri izdelavi plastomagnetov. Za analizo topografije in kemične sestave hitro strjenih in oplaščenih trakov smo uporabili Augerjevo elektronsko spektroskopijo, rentgensko fotoelektronsko spektroskopijo, spektroskopijo sekundarnih elektronov in elektronsko difrakcijsko spektroskopijo. Za določitev protikorozijske učinkovitosti oplaščenja smo izvedli pospešeni stresni preizkus pri temperaturi 110 °C in 90-odstotni vlažnosti, čemur je sledila analiza masnih izgub. Z vibracijskim magnetometrom smo primerjali magnetne lastnosti prahov pred oplaščenjem in po njem. Oplaščenje z Al₂O₃ se je izkazalo kot izvrstna protikorozijska zaščitna materiala, ki je odlično zaščitila tudi magnetne lastnosti. Aplikacije plastomagnetov se s tem lahko razširijo tudi na področja, ki zahtevajo zahtevnejše atmosferske razmere, tj. pri višjih temperaturah in visoki vlažnosti.

Ključne besede: Nd-Fe-B, plastomagnetni, HAST, oplaščenje z Al₂O₃

1 INTRODUCTION

Nd-Fe-B magnets market continues to grow¹. They possess a high magnetic energy product, a combination of a high remanence (B_r) and sufficient coercivity (H_{cl}), a much desired property allowing miniaturization and diversification of application. Automotive industry, hard drives, or wind turbines are just an example of application where their use can be found².

Nd-Fe-B magnets can be produced by sintering or by bonding. Sintered magnets possess magnetic properties as high as with a B_r up to 1.4 T and an H_{cl} up to 2500 kA/m³. Machining is used to give the magnets their final shape. In contrast to sintered magnets, bonded Nd-Fe-B magnets are produced by blending various polymer binders, such as epoxy or nylon, where melt-spun ribbons play the role of raw material⁴. The blend is cast moulded or injection moulded into final shape. Therefore, bonded magnets are chosen when complex shapes are demanded, with the advantage of being less expensive than sintered magnets. The magnetic properties of bonded magnets are, however, inferior to those of sintered magnets. Commercial bonded magnets have a B_r up to 0.7 T and an H_{cl} up to 1400 kA/m.

Nd-Fe-B magnets are very susceptible to corrosion, mainly due to the high rare-earth content in the grain-boundary phase⁵. Susceptibility to corrosion is naturally increased at elevated temperatures and especially in humid environments, affected by rare-earth elements. This restricts not only their range of applications, but can also damage the magnetic material during the moulding process⁶⁻⁸.

Adjusting the composition, by adding Co, Ga or TiC to the melt-spun ribbons^{9,10} improves the corrosion resistance, but it also affects the magnetic properties, by reducing either the H_{cl} or B_r – or both of them. However, even with an optimized composition, additional corrosion protection is necessary. Attempts to protect the surface of ribbons have been reported, such as direct surface oxidation during rapid solidification, electroplating, chemical vapour deposition and applying thin films of SiO₂, TiO₂ and MgO via the sol-gel route^{11,12}. But, difficulties from the perspective of process control and mass production appear. Applying a thin film of SiO₂ or TiO₂ through a sol-gel route offered very good corrosion resistance, especially for TiO₂. The MgO thin film was investigated in strongly acidic media, and good corrosion resistance was reported, but with no corrosion

test in a humid environment. MgO has the same disadvantage as rare-earth elements, since both react rapidly in the presence of humidity.

The sol-gel approach was to some extent put to one side in the past, since the chemical reagents (precursors) used to be extremely expensive. But now, sol-gel precursors are increasingly widely used and more commercially available, while the price of Nd-Fe-B raw material has become extremely expensive and Nd-Fe-B magnets are in greater demand for use at high temperatures. As a result, the sol-gel approach is becoming very interesting from the commercial perspective.

In this paper we present an investigation of sol-gel-applied coatings of Al_2O_3 , which were applied directly to the melt-spun ribbons. This method has several advantages over the coating of final products or other coatings, reported by other authors. Firstly, the ribbons are protected from oxidation during transport; secondly, such a coating offers better protection to the final magnets because each piece of melt-spun ribbon is coated; and thirdly, it tends not to reduce the overall Br of the final magnet, which is a problem associated with coating the outside of an already-bonded magnet. Such a coating can provide a much better corrosion-resistant protection than the standard protective film, usually applied around the final-shaped bonded magnet. A protective layer can be scratched off the magnet by force during transport or while installing the magnet into the final application. The same surface scratching does not damage the bonded magnets where the coating has been applied to each individual powder particle, since all the powder particles are coated.

We have investigated the influence of applied coatings on the corrosion resistance of powders in high humidity, using the Highly accelerated stress test (HAST) ¹³. The presence of the coating layers was determined by electron diffraction spectrometry (EDS), and X-ray photoelectron spectroscopy (XPS). The appearance of the surface of the samples was analysed by scanning electron microscopy (SEM) before and after the HAST using secondary electron imaging (SEI) as well as backscattered-electron imaging (BEI). The magnetic properties of the samples before and after exposure to the HAST were analyzed with a vibrating-sample magnetometer (VSM).

2 EXPERIMENTAL

MQB commercial melt-spun ribbons, put through a sieving analysis, in the mesh between 100 μm and 250 μm were selected for the experimental work. We chose this size range because this is the standard size for the production of bonded Nd-Fe-B magnets. We analysed the powders using a SEM JEOL 7200. The samples for the SEM analysis were prepared by mixing the powder of selected size with acrylic resin, which was followed by the standard metallographic procedure of grinding

and polishing. The result was a metallographic sample that contained a large number of powder particles, where we could observe the cross-section of the particles.

This was followed by the sol-gel process; the details of the sol-gel process are presented in **Figure 1**. The powders were first degreased and cleaned in isopropanol (IPA) and acetone, then dried at 60 °C, 1 h. 0.5 g of Al_2O_3 precursor, aluminium isopropoxide was added to 100 mL of IPA, respectively. 10 g of MQB powder in were added to 100 mL of IPA and stirred. The mixture of precursor and IPA was then slowly added to a mixture of MQB powders and IPA, while stirring to ensure an even distribution of precursor, powder and IPA. No water was added to promote the chemical reaction. The mixture of powder, aluminium isopropoxide and IPA was stirred for 10 min, and then the IPA was removed from the powders. The powders were then dried at 60 °C for 15 min,

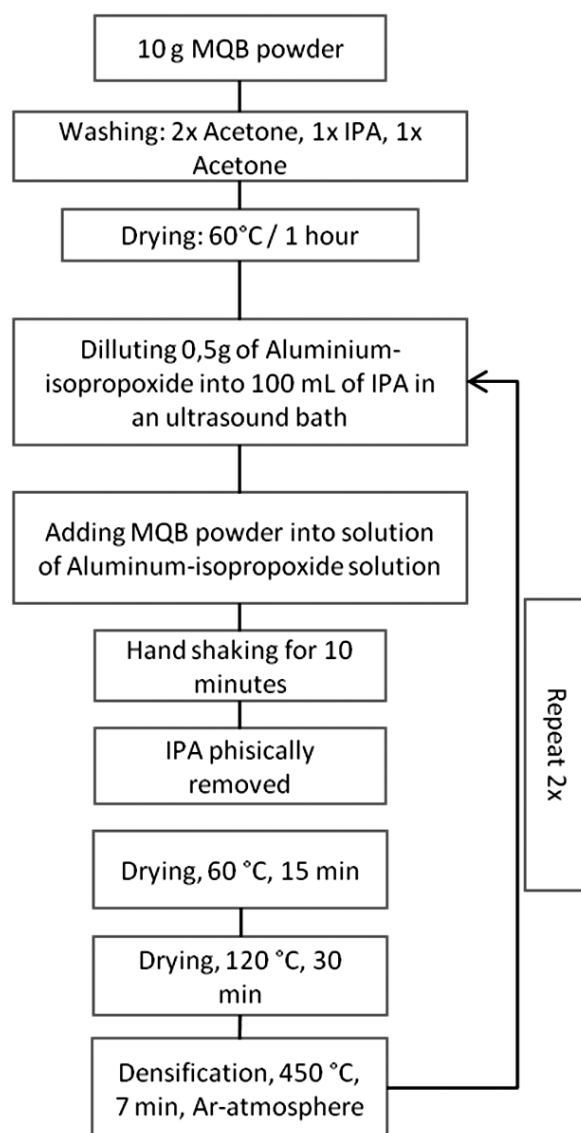


Figure 1: Scheme of the sol-gel process
Slika 1: Shema sol-gel procesa

followed by additional drying at 120 °C for 30 min. The coated powders were then put in a glass tube under an argon atmosphere and heated to 450 °C for 7 min to densify the Al₂O₃ coating. Three coatings were applied by repeating the above-described process two more times. This treatment was applied because we wanted to thicken the Al₂O₃ coating and to ensure that all the particles were covered with Al₂O₃, leading to full coverage of the surface.

The presence of the coating layer was confirmed by XPS spectrometer produced by Physical Electronics Inc., model TFA XPS. The Al monochromatized source of X-ray light with the power of 200 W was used. The energy of the X-ray beam was 1486.6 eV. The analysis area was 0.4 mm in diameter. The energy scale was aligned to the carbon C 1s spectrum at 284.8 eV. Main peaks in this spectrum are O 1s, C 1s, Al 2p, Al 3s and Fe 2p. Unfortunately the Nd 3d peak at binding energy of 980 eV was not possible to identify in this spectrum due to strong overlap with oxygen KLL peak at this energy. Also the boron peak B 1s at energy of 190 eV is not visible due to low sensitivity of B in XPS spectroscopy.

We also took advantage of the XPS and used it to perform a profile analysis on the Al₂O₃ coated particles in order to determine the thickness of the Al₂O₃ coating layer. The sputtering rate was estimated to be about 2 nm/min on the Ni layer of known thickness. Relative sensitivity factors provided by instrument producer were used to calculate elemental concentrations. The analysis depth of the XPS method is about 3–5 nm.

HAST followed the XPS analysis to determine the corrosion behaviour of the uncoated and coated particles. The HAST experiment was performed in an industry-standard HAST chamber, type Kambič. The conditions of the corrosion test were 110 °C, 90 % humidity, and the duration of the corrosion test was set to 192 h (8 d). The powders were carefully weighed to (2 ± 0.01) g before the HAST test, with an accuracy of ±0.1 mg, and placed in separate Al₂O₃ vessels. During the corrosion test, the powders were removed from the HAST chamber every 48 h, with the purpose of following the corrosion rate. After each removal the vessels containing the powders were dried at 120 °C, for exactly 30 min, then weighed. This step was repeated until the final 192 h. Weight change was calculated as a weight increase expressed in a mass fraction (*w*%) using the equation:

$$(\text{mass}(x\text{ h}) - \text{mass}(0\text{ h})) / \text{mass}(0\text{ h})$$

with *x* being the number of hours inside the HAST chamber.

We also used the SEM to observe the surface topology of the MQB powders to compare the effect of temperature and humidity on coated and uncoated particles.

VSM measurements were conducted on a Lakeshore 7307 VSM, which was used to compare the magnetic properties of the as-spun and the sol-gel-coated ribbons with the ribbons subjected to the HAST test.

3 RESULTS AND DISCUSSION

The SEM analysis of the selected powders showed that the actual size distribution is larger. The reason for that can be seen in **Figure 2**. The powder particles are far from being spherical; rather they are thin, elongated particles of irregular shape.

Following the SEM analysis the particles were cleaned. In this way we were hoping to remove all the dust, grease, and at least partially also the Nd-oxide layer from the surface. Cleaning the surface was also necessary as part of the preparation for coating via the sol-gel route.

EDS analysis of the sol-gel-processed powders showed the presence of aluminium. The results are given in **Table 1**. **Figure 3** presents a SEI image of the coated powders, with spots indicating the points of EDS analyses. The oxygen content cannot be determined using EDS, for the reasons already mentioned. Also, it is

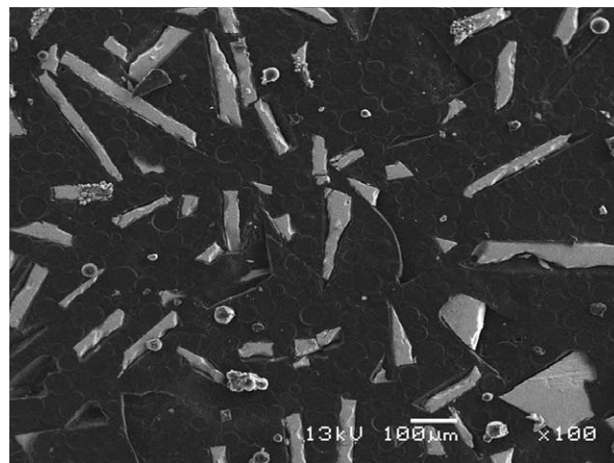


Figure 2: SEI image of MQB as-spun ribbons
Slika 2: SEI-posnetek MQB hitro strjenih trakov

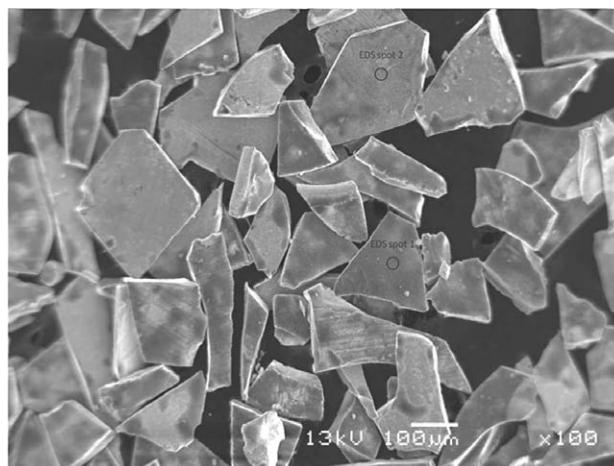


Figure 3: SEI image of Al₂O₃ sol-gel-processed powder, with marked spots for EDS analysis

Slika 3: SEI-posnetek prahu, oplaščenega z Al₂O₃ po sol-gel metodi, z označenimi točkami, kjer so bile izvedene EDS-analize

clear that the aluminium concentration varies a lot, probably for the same reasons as mentioned in the previous section for SiO₂ coated particles. Nevertheless, aluminium was present at all the measured points, from which we concluded that the particles were fully covered.

Table 1: Results from the EDS analysis of Al₂O₃ sol-gel-processed powder

Tabela 1: Rezultati EDS-analize prahu, oplaščenega z Al₂O₃ po sol-gel metodi

Element	spot 1 (x/%)	spot 2 (x/%)
Al	14.8	3.53
Fe	73.77	82.43
Nd	11.43	14.04

To prove the presence of an Al-oxide structure on the particle surfaces we used XPS. Since XPS can be used for depth-profile analyses we tried to determine not only the composition of the top layer, but also to determine how thick the oxide layer is. The results of the depth profile by XPS are presented in **Figure 4**. It is clear that Al and oxygen are present in high concentrations throughout the measured depth profile. There is also some Nd present in the top layer. In contrast, iron is not present in the top layer; its concentration rises slowly towards the end of the measured profile.

From this we could draw two conclusions. First, Al-oxide of some sort is present throughout the measured profile. The most probable composition of this oxide is Al₂O₃, since it is the product of the sol-gel reaction. Second, the measured compositions are rather stable throughout the measured profile. This is attributed to the diameter of the sputtering beam, which was estimated to be 0.4 mm and the possible tilt angle of the measured particle to the sputtering beam. First is beyond the size range of the measured powder (0.1–0.25 mm), meaning that the sputtering might have been conducted on neighbouring powder particles, resulting in a very stable, and misleading, concentration depth profile. The

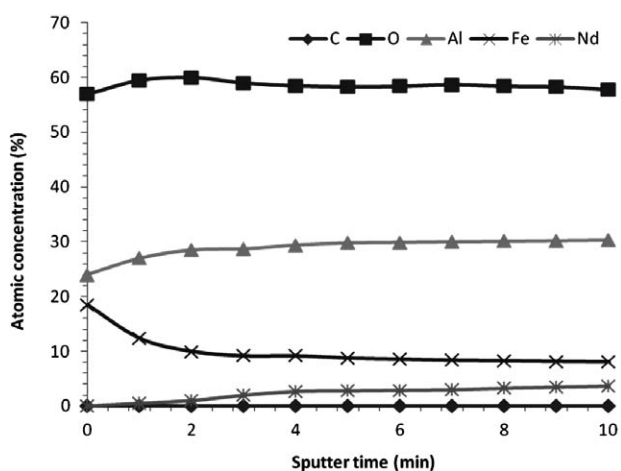


Figure 4: XPS depth profile on Al₂O₃ coated powder
Slika 4: Profilna XPS-analiza prahu, oplaščenega z Al₂O₃

tilt angle is difficult to control, since we are dealing with rather small particles, which align randomly. So, we could have been sputtering a particle, which was not exactly perpendicular to the sputtering beam, causing a seemingly thicker layer of elements than they actually are. On the other hand, it could mean this is the actual depth profile, meaning the oxide layer is thicker than the measured profile.

3.1 HAST

Uncoated, and Al₂O₃-coated particles were put through the HAST, as described previously. The mass change in the mass fractions (%) is given in **Figure 5**. All the particles gained weight rapidly during the first 48 hours. However, the mass increase of the uncoated particles was much higher than that of all the coated particles. The Al₂O₃ coated only once provided good corrosion protection, but Al₂O₃ was clearly more effective. After the first 48 h the rate of oxidation of the Al₂O₃ coated particles was still approximately three times slower than that of the uncoated particles.

It is unknown to us, why the weight increase rate in the first 48 h is much higher than in the following time. It could be possible that moist oxidized the Nd-Fe-B flakes in case of uncoated particles, while in the case of sol-gel coated particles some moist diffuses into the gelated coating, due to H₂O deprivation inside the coated layer. Second option is that some water diffused through the coating layers under the effect of high pressure and temperature. It would be impossible to evaporate this water during drying. But it is difficult to provide information, whether this water formed to create oxides. If it did, we should observe some spalling behaviour of the coating layer on the SEI images on **Figure 5**. But no spalling was found.

The SEM images shown in **Figure 6** reveal the difference between the uncoated and coated particles. The uncoated particles are clearly corroded, while the Al₂O₃

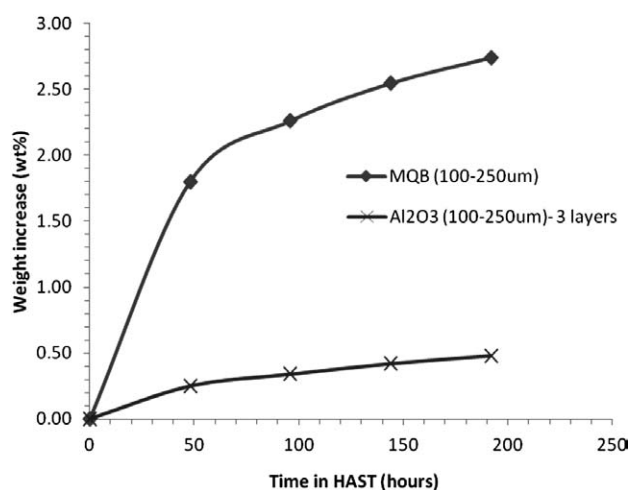


Figure 5: Effectiveness of the Al₂O₃ coating during the HAST
Slika 5: Učinkovitost Al₂O₃ oplaščenja po HAST-u

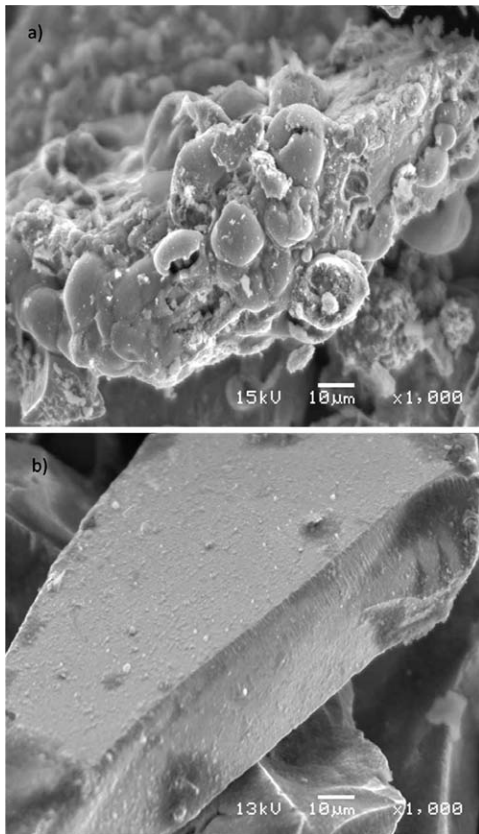


Figure 6: SEI images of particles after HAST: a) uncoated, b) Al₂O₃ – three times coated

Slika 6: SEI-posnetki prašnih delčkov po HAST-u: a) neoplaščeni, b) oplaščeni z Al₂O₃ (3-krat)

coated particles look unaffected by the conditions of the test. The Al₂O₃ particles that were coated three times, in particular, do not look any different than prior to the HAST experiment. Also, we could not spot any spalling behaviour.

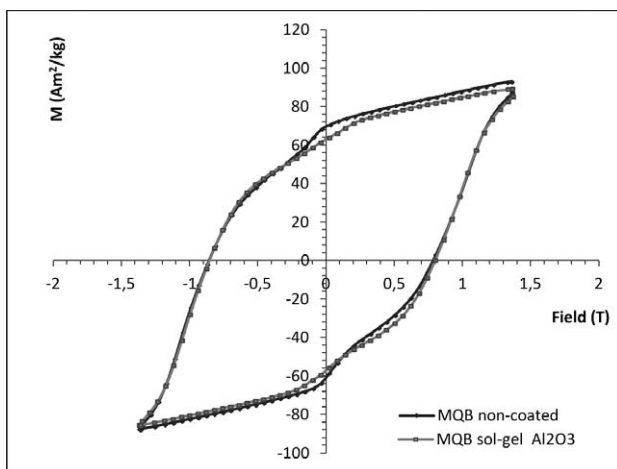


Figure 7: VSM comparison of magnetic properties between powders prior to the HAST

Slika 7: Primerjava magnetnih lastnosti neoplaščeni in oplaščeni prahov pred HAST-om

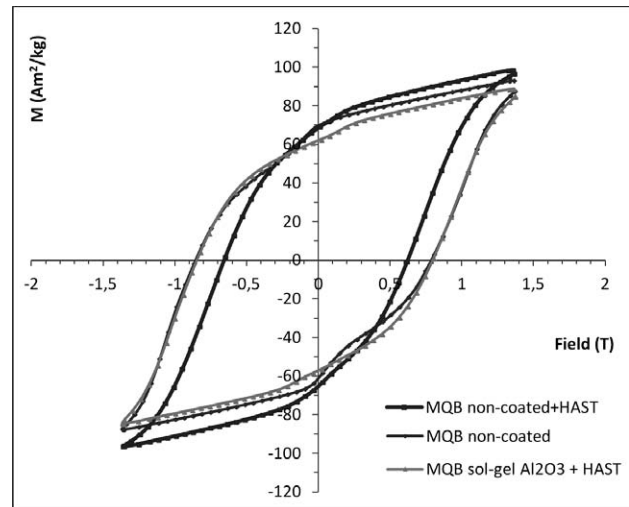


Figure 8: VSM measurements of the uncoated powder and coated powders after the HAST

Slika 8: Primerjava magnetnih lastnosti neoplaščeni in oplaščeni prahov po HAST-u

3.2 VSM measurements

We measured uncoated and Al₂O₃ coated MQB powders before and after the HAST. The results presented as a $B - H$ curve, normalized to sample mass can be seen in **Figures 7 and 8**. For a clearer view, **Figure 7** contains only the results of the powders prior to the HAST, while **Figure 8** represents powders after the HAST test, and the MQB powder prior to HAST test, as a comparison. The H_{cl} is plotted on the x-axis, while the B_r is plotted on the y-axis.

As can be seen in **Figure 8**, the MQB uncoated and Al₂O₃ coated samples' magnetic properties are practically identical.

As for the H_{cl} of the uncoated powder, it dropped by 20 % after the HAST. This drop in H_{cl} can be attributed to corrosion, which changes the microstructure of the affected particle. Al₂O₃-coated powder lost magnetic none of the magnetic properties after the HAST, showing the coating layer to be extremely effective.

4 CONCLUSIONS

1. We have successfully coated Nd-Fe-B powders with Al₂O₃ using the sol-gel process.
2. VSM measurements proved the effectiveness of Al₂O₃ coating, since magnetic properties remained as prior to the HAST test.
3. The sol-gel coating technique of Al₂O₃ proved to be a reliable and non-complicated process for enhancing the corrosion properties of the Nd-Fe-B powders, suitable for mass production.
4. This method is unique compared to other techniques, since it protects all the individual magnetic powder particles, making the corrosion protection much more reliable. Thus, the magnetic raw material is protected

from atmospheric conditions throughout the production process, starting with the transport of the powder, the moulding, installing into the final application, and use during the final application.

5. With the price of used metal alkoxide precursor falling rapidly, this process offers a commercially affordable corrosion-protection route for Nd-Fe-B melt spun ribbons used in bonded magnets.
6. We have demonstrated that the application of bonded magnets can be expanded to high-temperature and high-humidity environments, ranging up to 110 °C and 90 % humidity.

Acknowledgments

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