

# SURFACE COATING OF HDDR PROCESSED NANOCRYSTALLINE POWDERS

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**Keywords:** Ni-Fe-B POWDERS Nickel-Iron-Boron, HDDR processes, Hydrogen Disproportionation Desorption Recombination PROCESSES, nanocrystalline powders, surface protection, surface coating, coercivity, high coercivity, RE magnets, Rare Earth magnets, magnetic properties, coated powders

**Abstract:** Chemical surface modification can be used as a method for corrosion protection of sensitive powders based on intermetallic alloys between rare earth and transition metals /1/. Surface coating is used for preventing fine powders, based on Nd-Fe-B,  $\text{Sm}_2\text{Fe}_{17-x}\text{Ta}_x$  and  $\text{Sm}_2\text{Fe}_{17-x}\text{Ta}_x\text{N}_{3-\delta}$  prepared by HDDR processing and mechanically alloying, from hydrolysis. Powders coated by chemisorbed organic substance, after exposing to a humid atmosphere, do not show any chemical or physical change.

Different coating agents were used and the sufficient amount of various materials was optimised with the emphasis on minimising their quantity. Simple experiment shows that the surfactant is successfully chemisorbed on the powder surface and that the coated powders are hydrophobic indefinitely.

Magnetic properties were measured on samples after they were exposed to the same corrosion tests. Measurements on coated and bonded samples were compared with the measurements of non-coated samples. By using Auger electron spectroscopy the thickness of the coating was controlled. In order to distinguish the nature of the bonding between the powder surface and the surface-active substance FT-IR spectroscopy in absorbance and diffuse reflection modes was used.

The protection of the fine particles is based on the formation of a covalent bond between the hydroxyl groups at the particle surface and the surface-active substance. The monomolecular layer of organic substance does not damage the magnetic properties of the powder, but successfully protects the powder against humidity.

## Površinska zaščita nanokristaliničnih prahov pripravljenih po HDDR postopku

**Ključne besede:** Ni-Fe-B prahovi Nikelj-Železo-Bor, HDDR procesi z vodikovo disproporcionalno desorpcijsko rekombinacijo, prahovi nanokristalinični, zaščita površin, prekrivanje površin, koercitivnost, koercitivnost visoka, RE magneti zemelj redkih, lastnosti magnetne, prahovi prekriti

**Povzetek:** Kot zaščito pred korozijo občutljivih prahov na osnovi intermetalnih zlitin redkih zemelj in elementov prehoda je mogoče uporabiti kemijske metode površinskega prekrivanja prahov. Tako prekrivanje smo uporabili za prahove na osnovi Nd-Fe-B,  $\text{Sm}_2\text{Fe}_{17-x}\text{Ta}_x$  in  $\text{Sm}_2\text{Fe}_{17-x}\text{Ta}_x\text{N}_{3-\delta}$ , ki so bili izdelani po HDDR postopku in s postopkom mehanskega legiranja oziroma visokoenergijskega mletja. Prahove smo prekrivali z organskimi sredstvi s kemisorbcijo in po korozijskih testih ti prahovi niso kazali nobenih kemijskih ali fizikalnih sprememb.

Uporabili smo različna sredstva in optimizirali njihovo količino. Enostaven laboratorijski poskus nam je pokazal, da je organsko sredstvo vezano na površino prahov s kemisorbcijo in da je prekrit prah trajno hidrofoben.

Prahovom smo izmerili magnetne lastnosti po korozijskih eksperimentih in jih primerjali z prahovi, ki so bili izmerjeni takoj po HDDR postopku in so bili brez zaščite. Za oceno debeline površinske plasti smo uporabili Augerjevo spektroskopijo. Naravo vezi med površino prahu in površinsko aktivnim sredstvom smo določali z uporabo FT-IR spektroskopije v absorpcijski in difuzijski refleksiji.

Ugotovili smo, da zaščita finih prahov temelji na tvorbi kovalentne vezi med hidroksilnimi skupinami na površini prašnih delcev in površinsko aktivne snovi. Zelo tanka plast organske substance ne poslabša magnetnih lastnosti prahov vendar pa zelo učinkovito zaščiti njihovo površino.

### Introduction

Several routes can be used to prepare high coercivity Nd-Fe-B powders, which can be used as a basic material for bonded magnets. For achieving high coercivities, in addition to composition the average particle size, grain size and its distribution are the most important parameters. Single domain sized grains (~300 nm) are preferable. For the production of nanocrystalline powders, in addition to melt spinning, the hydrogenation, disproportionation, desorption, recombination (HDDR) process /1,2/ and intensive milling /3/ can be used

successfully as preparation methods for obtaining nanocrystalline powders without any further milling. It is well known that magnetic powders based on rare-earth and transition metals are very sensitive to the atmospheric conditions and one of the tasks of many researchers was, and still is, to improve the properties of the basic material by lowering the sensitivity of the bulk powder itself. The addition of small quantities of Co and Al improved the corrosion resistance of Nd-Fe-B magnets /4/. Also refractory elements like Zr /5,9/ and V /6/ or  $\text{ZrO}_2$  can achieve this in sintered magnets /7,8/ and HDDR processed powders /10/. The addition of Zr

or  $ZrO_2$  has been the subject of our further research /11/, together with the study of additional improvement of corrosion resistivity in powders, which is the basis of this paper.

Based on the results achieved with other materials /12/ and our preliminary experimental results, the idea was to improve the basic resistivity of Nd-Fe-B powder not only with additives, but also by coating individual particles with a very thin protective layer of organic molecules. It is important that the magnetic properties of the powders processed either by the HDDR processing route or intensive milling (IM) should not be damaged by the coating process. The resistivity against corrosion should be improved to the extent that very fine powders can be handled without any protective atmosphere in the production environments and that this procedure also should not significantly increase the production costs.

Surface modification of powders is based on the formation of a covalent bond between the hydroxyl groups that are usually present at metal or metal oxide surfaces, and surface modifying agents, such as long-chain carboxylic acids or silanes. The surface-active agent is first physically adsorbed onto the powder surface while during heating, condensation takes place, resulting in the formation of a covalent bond. After the reaction, the powder surface is covered with a monomolecular layer of organic molecules.

## Experiment

Different powders:  $Nd_{16}Fe_{76}B_8$ ,  $Nd_{15}Dy_1Fe_{76}B_8$ ,  $Nd_{15}Dy_1Fe_{75.3}Zr_{0.7}B_8$  were produced from 5 kg batches by HDDR processing. The compositions were chosen on the basis of our previous work /10/. For HDDR processing the alloys were exposed to a hydrogen atmosphere in a specially constructed rotating furnace. Detailed processing parameters were published previously /13/. After HDDR processing the resulting powder was hand crushed and coated with a thin organic layer. Silanes were used for this purpose. The experimental procedure is published elsewhere /14/. Coated and non-coated powders prepared by different routes and with different compositions were exposed to atmospheric conditions as well as more severe corrosive tests in a humidity chamber (Weiss) (95 % relative humidity and 40°C, 8 hours; ~ 40 % relative humidity and 25°C, 16 hours) in accordance with the DIN 50017 standard. The weight increase was followed and after the corrosion tests were completed, magnetic properties were measured and compared with the properties of the basic powders. The morphology of the powders was observed using a JEOL 840A SEM. The surface of the coated powders was analysed using high-resolution field emission AES (Microlab 310-F VG Scientific) combined with XPS. AES analysis was performed under standard conditions: a primary electron beam of 5 keV and the current between 1 and 10 nA. AES point analyses were performed on different grains of powder. Points for AES analysis were selected from SEM images with magnifications between 200 and 1000. XPS (X-ray Photoelectron Spectroscopy) of the same sample was used to determine the chemical state of the silicon. For XPS analysis  $MgK\alpha$  radiation was used. In order to

determine the nature of the bonding between the powder surface and the surface-active substance, FT-IR spectroscopy (Digilab FTS-80 spectrometer) in absorbance and diffuse reflection modes was used.

## Results and discussion

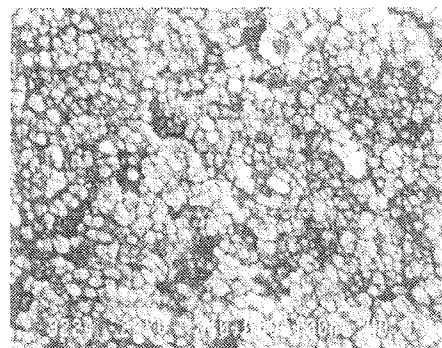


Fig. 1. SEM image of HDDR processed powder ( $Nd_{15}Dy_1Fe_{75.3}Zr_{0.7}B_8$ ).

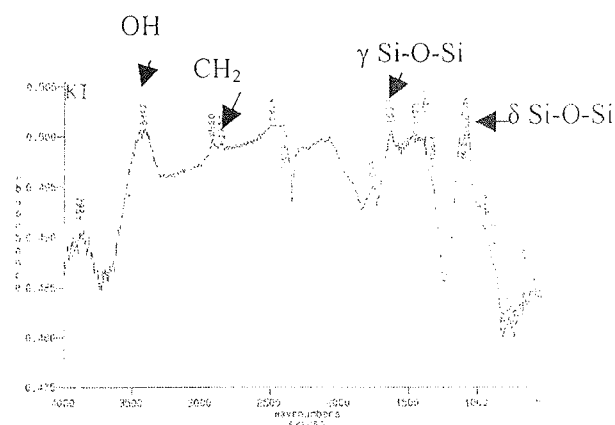


Fig. 2. FT-IR spectrum of the coated powder.

Figure 1 shows a SEM image of the HDDR processed powder. The thin organic layer cannot be seen from this image, but a simple experiment shows that the surfactant is successfully chemisorbed on to the powder surface. If the powder is mixed with water, uncoated powder sinks immediately, but coated powder is hydrophobic and therefore floats on the water. Powders coated by chemisorbed silanes are hydrophobic indefinitely, while powders with only physisorbed organic molecules are not sufficiently resistant to the water and sink after a finite time. It is known from previous work that if the temperature used for the chemical reaction is too low, the water molecules replace the organic molecules /12/. With AES analysis the presence of C and Si on the powder surface was detected. Adsorbed carbon from the air was removed from the sample surface by Ar ion sputtering. XPS analysis of the same sample

showed that peaks of Si 2s at 153.1 eV and Si 2p at 101.4 eV correspond to Si in silanes. Further analyses showed besides Si (2p 101.4 eV) also Fe (3s 92.6 eV), which indicates the thickness of the organic layer on the surface of the Nd-Fe-B powder. AES and XPS analyses show that the coated powder is covered with an ultra thin layer of organic material and one can estimate the thickness of this coating as a monolayer.

By using FT-IR spectroscopy on the powders observed in absorbency and diffuse reflection modes, we expected that the vibrational modes observed in the measured spectra could help to differentiate between species which are present on the surface and in the bulk of the crystallites. In order to distinguish between the surface of the powders with respect to the bulk, we measured the diffuse reflectance spectra of the powders. Polycrystalline samples were simply mixed with KBr without applying pressure, which may cause grinding and crushing of the powder particles. In such a way, the surface of the particles remained unaffected and the inner part of the bulk of the crystallites did not become exposed to infrared radiation when examined in the diffuse scattering mode. The spectrum obtained is shown in Figure 2. We can estimate the characteristic peaks for Si-O-Si groups ( $\gamma$  and  $\delta$ ), as well as CH<sub>2</sub> groups, which must be the consequence of some remaining organic surface modifying agent's groups not used for the reaction. This can only indicate that the number of OH<sup>-</sup> groups on the powder surface was a minimum, but enough for the reaction and consequently for the protection of the powder with a mono-molecular layer.

Nanocrystalline powders with highly reactive surfaces react with the atmosphere immediately and most likely form a passivated surface of a thin NdO<sub>x</sub> or/and Nd<sub>2</sub>O<sub>3</sub> layer, corrosion does not proceed any further. Coated powders with silane showed a marginal weight gain (less than 0.01 %) in the first 50 hours of exposure to the severe corrosion conditions with complete passivation afterwards. One can conclude that not a 100 % coating of particles was achieved and those uncoated particles oxidise, which contributes to the observed weight gain.

Magnetic properties of the HDDR processed powders measured before the corrosion tests (844 kA/m) compared to the properties of the powders coated with silane and measured after the test (860 kA/m) show that coercivity did not change as a result of the chemical treatment. This makes the use of tested organic substances suitable for the coating of nanocrystalline Nd-Dy-Fe-B powders with a very thin (~10 nm) protective layer and without damaging the magnetic properties. With the very high resistance to corrosion of the coated surface in the first 20-hours free handling of the powder in laboratory atmospheric conditions (~ 40 % R.H.) is possible.

This is of great importance in the production where the handling of sensitive powders in the air without any consequences would contribute to the lowering of production costs. The above results imply that the starting powder is covered with a thin layer of hydroxyl groups that enable the adhesion of silane molecules to the

powder's surface. Presumably the Nd-rich phase has to be the reacting precursor for hydrolysis of the particle's surface. Even with very careful handling of the powder in a protective atmosphere and/or liquid, a very small number of OH- groups in a protective gas or organic liquid are always present. It is not clear yet, if these groups adhere onto the extremely sensitive powder from the surrounding in spite of the very careful handling in the protective atmosphere throughout the processing. It seems to be more likely, that these groups proceed from the organic liquid used as a solvent for silane. According to the proposed reaction schemes, during the subsequent heating in vacuum, condensation takes place (water or alcohol molecules are eliminated) and the covalent bond forms.

## Conclusion

Coating achieved by the chemical reaction between the Nd-Fe-B powder's surface and silane molecules is a very powerful method for the protection of sensitive nanocrystalline powders. HDDR processed powders coated with stearic acid show a marginal weight gain (less than 0.01%) in the first 50 hours of exposure to the severe corrosion conditions. The weight increase after the corrosion test of the more sensitive mechanically milled powders coated with silanes shows a weight increase in the first few hours which is lower than 0.05%, suggesting that this coating has excellent prospects. The magnetic properties are not damaged and the coating enables free handling of the powder for at least 20 hours in air. The results achieved could be of great importance in production where the handling of sensitive powders in air without any significant degradation would contribute to a lowering of production costs.

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