REEgain Milestone 2, TP3

PART A: Corrosion in NdFeB magnets

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Introduction to the report

The report focuses on the evaluation of corrosion mechanisms on NdFeB-magnets from a microstructural viewpoint. Correlating inner magnet structure with corrosion mechanisms.

The microstructure of NdFeB-magnets makes the compound prone to corrosion attacks, and the lifetime is closely linked to degradation from corrosion and the choice of coating strategy.

The report has severed as a basis for the work done towards TP3, Milestone 3:coating strategies and the future work to be done in TP3 leading towards Milestone 4: designing combined stress testing for magnet component lifetime assessment.

This report does not address the microstructure and the expected corrosion properties of the permanent magnets developed in RP1/TP2 of the REEgain project. This will be addressed in a later issues PART 2 report.

Corrosion, an electrochemical reaction

In general, corrosion can be seen, as an electrochemical reaction were the metal is oxidized through an electrical cell formed by a fluid on the surface of the metal.

In the below example the fluid is water (H_2O) and the metal is iron (Fe).

Cathode:
$O_2(g) + 2H_2O + 2e^- \rightarrow 4OH^-$

Anode:
$Fe \rightarrow Fe^{2+} + 2e^-$
$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$
("rust")

$O_2(g)$ $4OH^-$ $Fe(OH)_2$ $2OH^-$

$2e^-$ Fe^0 Fe^{2+}

Metal
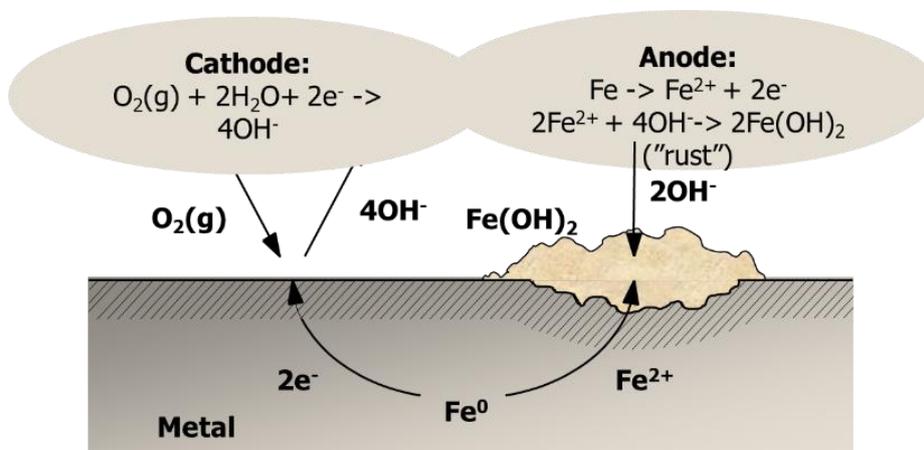
Figure 1: Electro chemical corrosion process.

At the cathode, oxygen (O_2) is reduced and forms hydroxide ions when reacting with water (H_2O), the hydroxide ion hereafter reacts with the oxidized iron to form iron hydroxides (formation of rust).

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Corrosion types

General corrosion
General corrosion results in a uniform surface attack of the corroding metal. An example is corrosion of unprotected mild steel, or oxidation of galvanized steel. The corrosion rate of uniform corrosion attacks is often predictable and it is therefore possible to predict remaining lifetime of parts with uniform corrosion.

Pitting corrosion
Pitting corrosion is defined as a localized corrosion attack resulting in cavities (holes) are produced in the metal. The corrosion type is typically seen on stainless steel were the corrosion is initiated by a local breakdown of the passive film on the steel. Opposite to uniform corrosion it is not possible to predict the corrosion rate of pitting corrosion.

Selective corrosion
Selective corrosion is the corrosion of on phase of a material in a specific environment. Selective corrosion is seen on brass parts were the β-phase corrodes when exposed to an ammonium-containing environment, while the α-phase is unaffected.

Galvanic corrosion
Galvanic corrosions is seen when two electrochemical dissimilar metals (metals with different electrode potential) is connected. For harsh environments as outdoors, high humidity and offshore environments galvanic corrosion is prone to occur even with a difference in electrode potential of just 0,15V, while the difference must be minimum around 0,25V in normal environments as eg. warehouses .for galvanic corrosion to occur.
The bigger the difference in standard electrode potential is, the higher is the affinity for galvanic corrosion-

Intergranular corrosion
Intergranular corrosion is confined to the grain boundaries of the metal. The corrosions type can be seen on stainless steel after heat exposure were chrome carbides precipitates in the grain boundaries and thereby depletes chrome from the nearby grain areas resulting in corrosion attacks in these areas.

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Corrosion and the microstructure of NdFeB-magnets

NdFeB magnets has been found to consist of 3 phases with different chemical composition and therefore also contains 3 phases with different affinity to corrosion.

$Nd_{1+\varepsilon}Fe_4B_4$ = η-phase < 1%

Nd-rich = n-phase ~ 5 %, "grain boundary phase"

$Nd_2Fe_{14}B$ = Φ-phase ~ 94 %
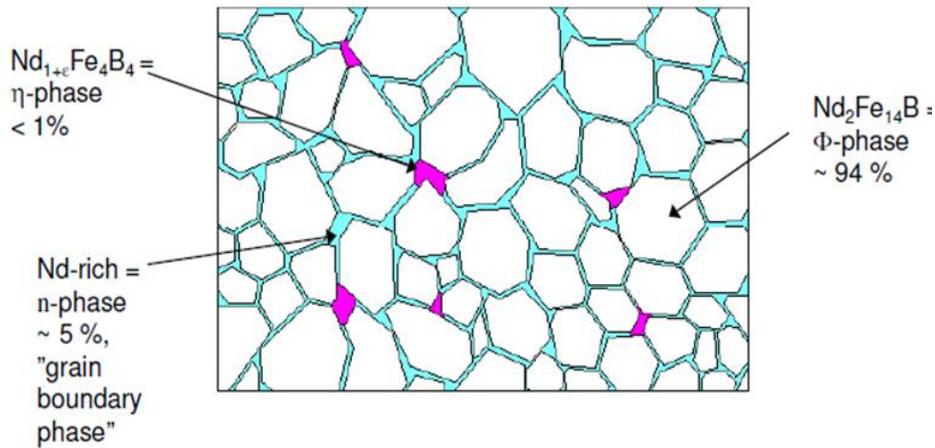
Figure 2: η phase > n phase > φ phase [Sugimoto et al. (1987)]

10 µm	EHT = 20.00 kV	Signal A = SE1	Mag = 11.02 K X	
	WD = 13.0 mm			
	I Probe = 200 pA	File Name = sample1-4.jpg	Chamber = 1.75e-003 f	
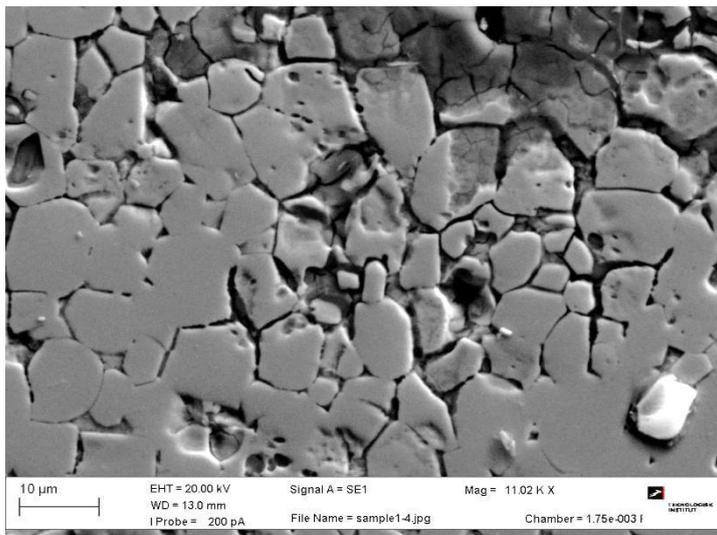
Figure 3: Scanning Electron Microscope picture of corroded NdFeB magnet

Approximately 5% of the microstructure consists of a neodymium rich phase while the major part approximately 94% consists of an iron rich phase.

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Material	E_{SHE} , V
Gold	1.68
Iron	-0.41
Neodymium	-2.25
Magnesium	-2.38

Figure 4: Standard electrode potential [Handbook of chemistry and physics, 58th edition]

Looking into the standard electrode of neodymium it is found that neodymium has a standard electrode potential on level with that of magnesium, and is therefore highly prone to corrode in moist environments. The difference in corrosion potential of iron and neodymium is 1,8V, which indicate a severe affinity for galvanic corrosion between the two elements.

In the galvanic series for seawater magnesium is placed as one of the most least noble metals, presumable neodymium would share that position with magnesium if exposed to seawater.
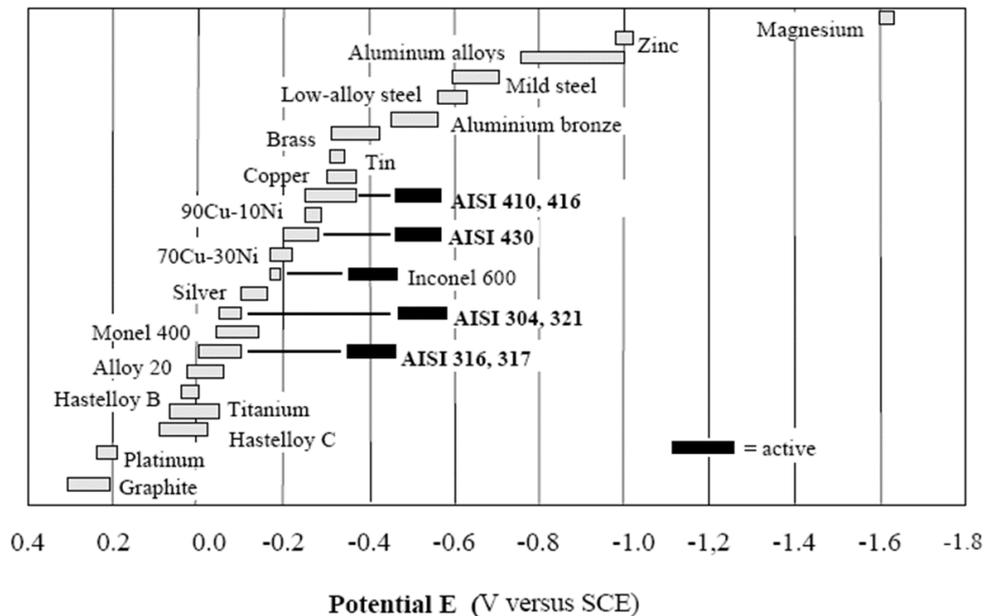
The microstructure of the NdFeB magnet combined with the difference in electrode potential of the phases results in an internal galvanic cell when exposed to moist. The result being galvanic corrosion between the phases in the microstructure, with the neodymium rich phase being the phase that will corrode.
The effect is a corrosion mode that appears intergrannular because the corroding element (Nd rich phase) is located in the grain boundaries.

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As result the $Nd_2Fe_{14}B$ grains were the surrounding Nd-rich particles have corroded will loosen from the magnet and the magnet will start to lose its structural integrity.

Effect of grain size

In the article "Grain growth effect in the corrosion behavior of nanocrystalline NdFeB magnets" [1]. As described in the article the magnetic properties of NdFeB magnets are influenced by the microstructure, particularly the grain size. Small and homogeneous grain sizes were reported to be favorable in order to obtain optimum magnetic properties and minimum deformation stresses.

As corrosion of magnets is of the major issues when designing systems using permanent magnets, it is therefore relevant to assess the influence of grain size on corrosion of neodymium magnets.

For the tests described in the article samples with different grain size were prepared by annealing hot pressed magnet samples at 800ºC for 0,5, 1, and 6h. the grain size of the hot pressed magnet and the annealed samples were determined by scanning electron microscope and estimated to be 100. 230, 330 and 600nm (fig.5).
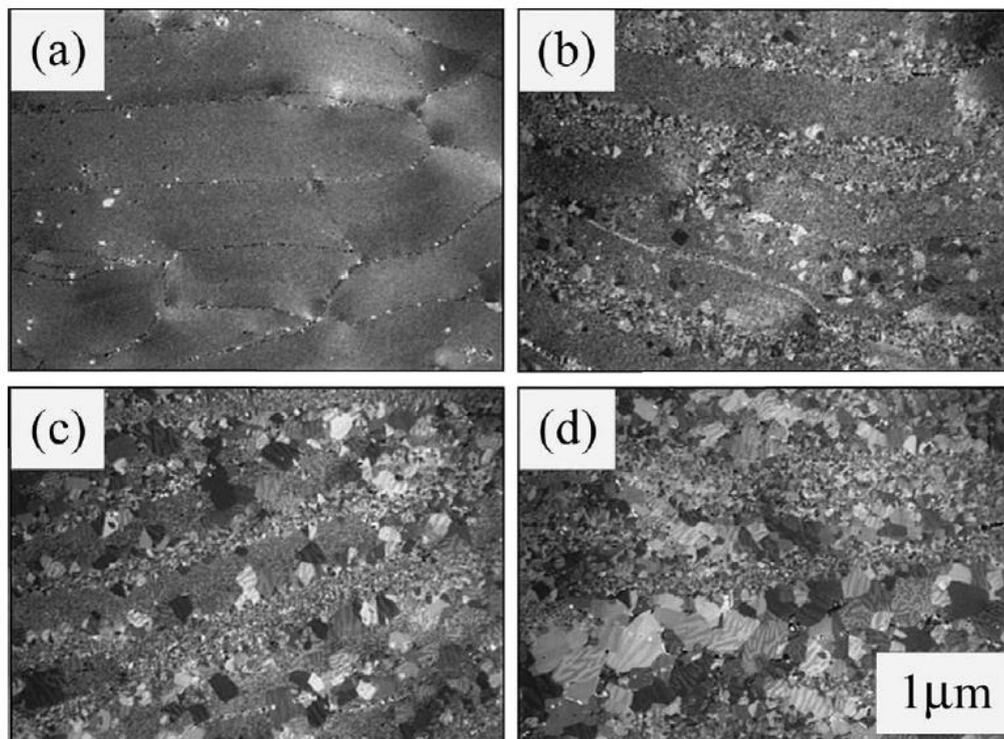
Figure 5: Kerr-effect micrographs for polished NdFeB magnets hot pressed (a) and annealed at 800ºC for 0,5h (b), 1h (C) and 6h (d) [1]

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The corrosion rate was hereafter determined by exposing the samples to a N_2-purged 0,1M H_2SO_4 solution at 25ºC, while measuring the dissolution behavior of the samples by on-line inductively coupled plasma (ICP). Furthermore the corrosion rates were measured gravimetrically with an accuracy of ±10µg

The test showed a clear difference in the corrosion behavior as a effect of the grain size. The corrosion rate of the annealed magnet with a mean grain size of 600nm is significantly lower than that of the hot pressed sample with a 100nm grain size(fig.6). The result were further confirmed by the results of the gravimetric measurement that showed similar results.
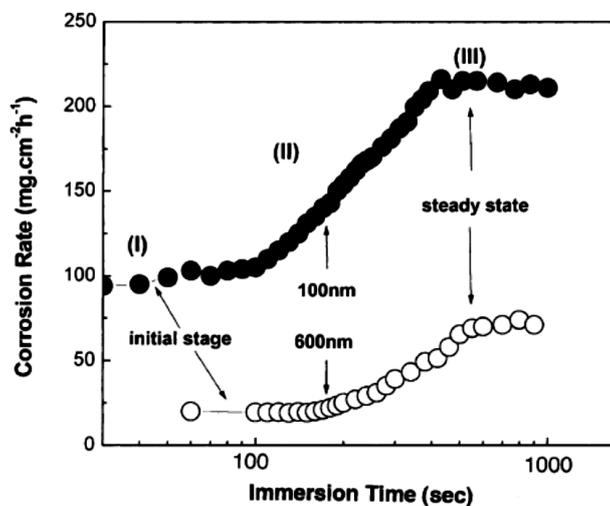
Figure 6: Corrosion rates measured by ICP solution analysis for NdFeB-magnets with grain sizes of about 100 and 600nm [1].

Effect of magnetic field on corrosion of NdFeB magnets

Several articles addresses the effect on corrosion rate by applying an magnetic field to the magnet during the corrosion testing even though most investigations has been done on non-magnetized samples.

The weight loss of magnetized and non-magnetized samples were tested in a 3.5% NaCl solution [2]. The study revealed a larger weight loss on the magnetized samples than on the non-magnetized. Samples were immersion tested for 5, 15, 20, 30, 40 and 60 days, for each interval 6 magnetized and 6 non-magnetized samples were removed from the test solution and the average weight loss determined. The result of the test is illustrated in figure 7.

As the corrosion process is an electrochemical process it is likely that it is affected by the presence of a magnetic field. The magnetic field on the magnetized samples is

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evaluated to facilitate the oxygen transport on the surface of the magnets, and thereby the magnetization increases the initial corrosion process of the magnet.

With longer immersion time corrosion product will attached to the surface due to the magnetization this will result in corrosion conditions similar to that seen with crevice corrosion. With crevice corrosion, the lack of fluid movement results in a sour environment with an increased aggressiveness.
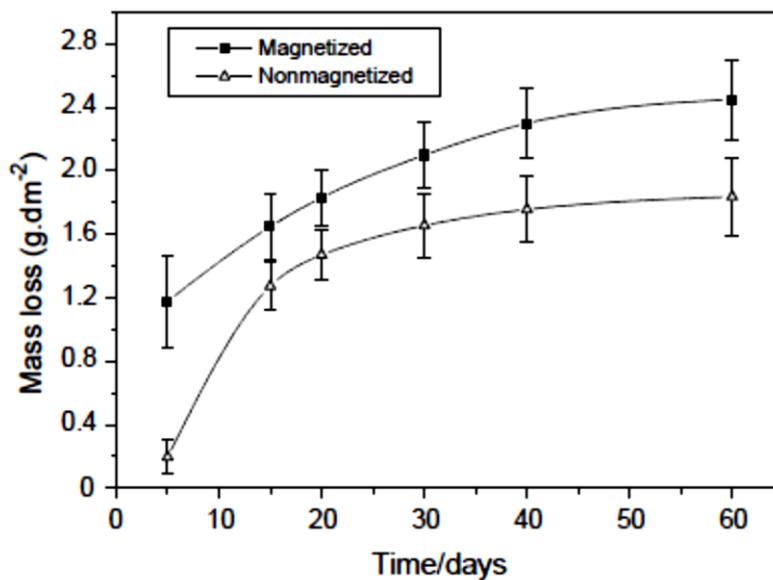
Figure 7: Weight loss results for magnetized and non-magnetized samples after various times of immersion [2].

In [3] magnetized and non-magnetized samples were exposed to a 0,005M H_2SO_4 solution. Also in these experiments the influence of a magnetic field was observed and recorded by depth measurements made on samples after 1 days exposure in the above mentioned solution.

For the non-magnetized sample the corrosion attach occurred nearly homogeneous at only at the rim a slightly enhanced dissolution was observed. On the magnetized sample the corrosion attack were strongly localized leaving the rim, with high magnetic flux, area more or less unaffected (fig.8)
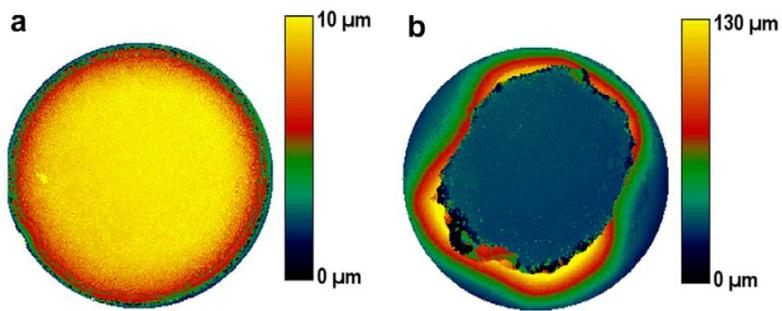
Figure 8: Surface depth profiles of the pole facesof NdFeB cylenders after 1 day immersion in 0,005M H_2So_4 in the (a) non-magnetized and (b) magnetized state[3].

Figure 9: Photograph of the pole pace of a magnetized NdFeB cylinder after 1 day of free corrosion in 0,005M H_2SO_4[3].

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Conclusion

The build-up of the microstructure of NdFeB results in a microstructure prone to internal galvanic corrosion between the phases in the microstructure.
The poor corrosion abilities of the magnet itself means that it can only be used with sufficient surface treatment or in capsulation. The way corrosion progresses through the magnet also suggests that a barrier type of surface treatment will be the most viable type of treatment.

The grain size is found to affect the corrosion rate of the NdFeB magnets with larger grains resulting in lower corrosion rates. However this might be in conflict with the production processes and the magnetic properties of the magnets.

The magnetization of tested samples is also found to affect both the localisation of corrosion attacks and the strength of the attack.
Today most corrosion testing is done on non-magnetized samples due to practical circumstances, however this practice should be revised to support testing og magnetized samples.

References

[1]   A.A. El-Moneim, A.Gebert, F. Schneider, O.Gutfleisch, L.Schultz; Corrosion Science 44 (202) 1097-1112
[2]   I. Costa, M.C.L. Oliveira, H.G. de Melo, R.N.Faria; Journal of Magnetism and Magnetic Materials 278 (2004) 348-358
[3]   Ralph Sueptitz, K. Tschulik, M. Uhlemann, M- Katter, L. Schultz, A. Gebert; Corrosion Science 53 (2011) 2843-2852