Final Report Summary - ROMEO (Replacement and Original Magnet Engineering Options)

Executive Summary:
Permanent magnets are vital components in an enormous number of domestic and industrial devices, and they are particularly crucial within the rapidly-developing renewable energy sector, where the motors for electric vehicles and the generators in wind turbines require strong magnets with the ability to operate at temperatures well over 100°C. Currently, these magnets are based on the rare earth elements neodymium and dysprosium, which are predominantly mined in China (>95%). Exports are being restricting as a result of an expanding domestic market and a policy of relocating magnet manufacturing to China, thereby multiplying the costs of raw materials for magnet manufacturers in Europe. The rare-earth crisis is particularly critical for heavy rare earths such as dysprosium that are currently required to assure the high-temperature performance of the magnets. Therefore, the ROMEO project has focused at reducing the European dependence upon the supplies of rare earth metals used to produce magnets by several key
industries. It has more specifically been dedicated to a removal or high reduction of heavy rare earth (HRE) metals in permanent magnets. To this end, attention was placed on:

1) The development of several novel microstructural-engineering strategies in order to eliminate, or drastically reduce the heavy rare-earths (HRE) in high-temperature Nd-Fe-B magnets with improved coercivity and retained magnetisation, which will enable them to be used for applications above 100°C.

2) The development of totally rare-earth-free magnets, aiming at a drastic reduction of Europe’s dependence on Chinese imports while shifting emphasis in magnet manufacturing from a raw-materials-dependent business to one that is essentially knowledge-based, and flourishing in Europe.

The first objective (1) was fully matched within the three years duration of the project. Objective (2) was also achieved, but within relatively modest deviations.

Thirteen partner institutions contributed to the ROMEO project within the frame of a consortium agreement. There was no sub-contracted or associated party. Seven organisations (54%) came from the research and high education sector whereas the other 6 (46%) were from industrial sector. Six European countries were represented. In total, 46 person/year contributed to the project for an overall budget of 3979 746 €. The project was organised in 7 scientific work packages (WP) and 2 WP designed for dissemination and administration purposes.

Drastic reduction of the amount of HRE needed to produce permanent magnets was fully achieved in the scope of objective (1), thanks to the invention of a new and innovative method to promote selective formation of a dysprosium-rich phase in the shell of the hard magnetic grains, with no loss in magnetization within the core of the hard magnetic phase. Current technologies use about 10-11 wt% of Dy, whereas with the new technique, only 0.6 wt% Dy is effective. This reduction by a factor of 16 represents a dramatic decrease in cost of the manufactured magnets, which can be estimated to roughly 40% based on the raw material costs in 2015. Furthermore, the new method is cost-effective, eco-efficient and can be easily implemented in industrial production. It was already tested in realistic industrial conditions to set-up a prototype motor for an electric vehicle and a windmill, respectively. Two patents were filed and more than ten papers were published. Many invitations were sent to the scientific coordinator to present those results at international conferences.

Objective 2) was based on the evident need for a medium-grade permanent-magnet material that can offer properties greatly superior to hard ferrites, yet they can be some 20% less in terms of remanence and coercivity than normal-grade Nd-Fe-B magnets. New materials discovered in ROMEO are:

- YCo5-xFex (0 ≤ x ≤ 0.5) alloy. The average coercivity and maximum magnetization obtained are 0.81 T and 100 Am2/kg, respectively, which indeed enables an important achievement in filling the gap between ferrite permanent magnets and NdFeB magnets. This technology will soon fit into industrial production.
- Heusler alloys: High throughput screening methods based on spin-polarized density functional theory (DFT) and advanced data mining strategies were used to predict novel Heusler or other alloys with targeted properties. One such alloy, Co2MnTi, displays a remarkably high TC and is the first brand new high-temperature ferromagnet that has been designed directly by a machine-learning process.

Thus, the ROMEO project was very successful, first for having achieved its main objectives within a rather short period of 3 years, and second for having demonstrated how European industry may gather to face
unexpected challenges coming from abroad, when the price of raw materials rises under the effect of political issues.

Project Context and Objectives:

1- Objectives of the project

The ROMEO project has focused at reducing the European dependence upon the supplies of rare earth metals used to produce magnets by several key industries like the automotive industry or the manufactures of wind turbines. It has more specifically been dedicated to a removal or high reduction of heavy rare earth (HRE) metals in permanent magnets. To this end, attention was placed on:

1) The development of several novel microstructural-engineering strategies in order to dramatically improve the properties of magnets based purely on light rare earth elements, and more specifically coercivity, which will enable them to be used for applications above 100°C.

2) The development of totally rare-earth-free magnets, aiming at a drastic reduction of Europe’s dependence on Chinese imports while shifting emphasis in magnet manufacturing from a raw-materials-dependent business to one that is essentially knowledge-based, and flourishing in Europe.

The first objective (1) was fully matched within the three years duration of the project. Objective (2) was also achieved, but within relatively modest deviations (see section 5 below).

At a less coarse-grain level, the following goals were targeted:

1-1: Grain-boundary diffusion of heavy rare earths

1-2: Extreme grain-size refinement

1-3: New grain-boundary phases

2-1: High-throughput computational materials discovery, and candidate materials synthesis

2-2: Coercivity development in rare-earth-free materials by grain-boundary engineering which will be explained in more details in the following sections.

2- Scientific and technical background

Permanent magnets are vital components in an enormous number of domestic and industrial devices, and they are particularly crucial within the rapidly-developing renewable energy sector, where the motors for electric vehicles and the generators in wind turbines require strong magnets with the ability to operate at temperatures well over 100°C. Currently, these magnets are based on the rare earth elements neodymium and dysprosium, which are predominantly mined in China (>95%). Exports are being restricting as a result of an expanding domestic market and a policy of relocating magnet manufacturing from a raw-materials-dependent business to China, thereby multiplying the costs of raw materials for magnet manufacturers in Europe. The rare-earth crisis is particularly critical for heavy rare earths such as dysprosium that are currently required to assure the high-temperature performance of the magnets.

Coercivity, or coercive field \( HC \), is a measure of the ability of a permanent magnet to withstand an external magnetic field without being demagnetized. It is, by definition, equal to the value of the external field that modifies the magnetization of the magnet after it was magnetized to saturation or in other words, the resistance the magnet is able to oppose a demagnetizing field. High values are therefore directly linked to the pinning of magnetic domain walls, i.e. the boundaries that separate different magnetization domains in
a ferromagnet. High coercivity is achieved by disruption of the network of magnetic sites, for instance by pre-existing grain boundaries or precipitates. One very efficient way to prepare a permanent magnet with value of HC above 2000 kA/m is to manage selective precipitation of HRE containing phases at grain boundaries. This is where the focus of ROMEO was placed. Another approach is to invent new compositions of magnets that contain no rare earths at all, and show efficient pining of the domain walls thanks to intrinsic heterogeneities of their microstructure.

3- Partners and consortium organisation

Thirteen partner institutions contributed to the ROMEO project within the frame of a consortium agreement. There was no sub-contracted or associated party. The participating organisations are listed below:

1 - Coordinator, Jožef Stefan Institute (JSI), Slovenia, RES
2 - Technical University Darmstadt (TUD), Germany, RES
3 - Institut Néel (CNRS), France, RES
4 - St. Pölten University of Applied Sciences (PUAS), Austria, RES
5 - Trinity College Dublin (TCD), Ireland, HE
6 - Vienna University of Technology (TUW), Austria, RES
7 - KOLEKTOR GROUP d.o.o. (KOL), Slovenia, IND
8 - SIEMENS (SIEMENS), Germany, IND
9 - Vacuumschmelze GmbH & Co. KG (VAC), Germany, IND
10 - VALEO (VALEO), France, IND
11 - DAIMLER (DAIMLER), Germany, IND
12 - Leibnitz Institut Dresden (IFW), Germany, RES
13 - TEMAS AG (TEMAS), Switzerland, SME

As shown in the right hand side column, 7 organisations (54%) came from the research and high education sector whereas the other 6 (46%) were from industrial sector. Six European countries were represented. In total, 46 person/year contributed to the project for an overall budget of almost 4 M€.

4- Work plan of the project

The project was organised in 7 scientific work packages (WP) and 2 WP designed for dissemination and administration purposes:
WP1: Project management
WP2: Materials modelling, which dealt with both objectives 1) and 2)
WP3: Microstructure engineering, which focused at objective 1)
WP4: Novel hard magnets, which was dedicated to objective 2)
WP5: Advanced characterization, which also dealt with both objectives 1) and 2)
WP6: Assessment of manufacturing prospects for new materials
WP7: Assessment of materials for technical and lifetime properties
WP8: Dissemination, exploitation and networking
WP9: Administrative and financial management.

WP1, with 13 p.m involved, was dedicated to the overall management of the project and its scientific coordination, which was taken over under the leadership and responsibility of Prof. Dr Spomenka Kobe by partner institution 1, Jožef Stefan Institute in Ljubljana (Slovenia). This WP was caring for the scientific coordination, reporting and all financial matters.

WP2 (128 p.m) was designed as the background task able to model the materials of interest for the consortium. Led by partner 4, the main objectives of this work package were:
- Explaining the magnets’ intrinsic properties based on electronic structure calculations,
- Modelling the micromagnetic and coercivity properties, which are the bases of the new materials’ functionality,
- Identifying new compounds with permanent magnet potential by high-throughput computational screening.

WP3 (126 p.m) was under the leadership of partner 3 and focused on the development of high-coercivity Nd-Fe-B-based magnets with drastically reduced, or zero, HRE content. The objectives were to:
- Minimise the amount of HRE used to increase the coercivity of Nd-Fe-B-based magnets, through the development of grain-boundary diffusion processing (GBDP),
- Reduce the grain size of Nd-Fe-B magnets while avoiding problems with oxidation,
- Prepare Nd-Fe-B magnets with novel coercivity-enhancing grain-boundary phases.

WP4 (75 p.m) was led by partner 4 with the objective to investigate at least four candidate rare-earth-free magnetic materials which have a uniaxial crystal structure and an anisotropy K1 > 500 kJ m-3. Research prior to the start of ROMEO led to narrowing down the hundreds of known structures to a few promising ones, e.g. Mn3-xM, where M = Ga, Ge, and Al, and tetragonally distorted FeCo-based materials, that were used for theoretical calculations and test structures to validate the material properties.

WP5 (128 p.m) under the supervision of partner 2, was designed in view of a multiscale characterization of the micro- and nanostructures down to the atomic scales and magnetic properties. This work package has provided deep insight into the critical demagnetization processes on a local scale in order to identify the weak link in the microstructure responsible for the nucleation of magnetization reversal.

WP6 (22 p.m) led by partner 9, was focusing on strategic and economic aspects of the project’s materials development by carrying out an assessment of the industrial applicability of the new developed permanent magnet materials based on the results provided from WP3, WP4, WP5 and WP7. In addition to attractive magnetic properties, the newly issued materials developed within the ROMEO project had to be producible on a large scale by European industry in an eco-efficient manner with the potential for subsequent, economically viable recycling.

WP7 (31.7 p.m) was placed under the responsibility of partner 10 and focused on the assessment of materials for technical and lifetime properties in view to:
- Prepare appropriate sintered samples in order to build the project prototypes,
- Prepare appropriate bonded samples in order to build the project prototypes,
• Build and test different electrical machines at the situated prototype level based on sintered magnets or based on polymer-bonded magnets,
• Validate the materials on the applied prototype level under application-related conditions.

WP8 (18 p.m) was for dissemination, exploitation and networking activities. WP9 (17.7 p.m) was giving the administrative support to the scientific coordinator as needed for networking, webbing, reporting and managing the financial support. Both tasks were placed under the responsibility of a SME (partner 13).

5- Main results and deliverables

Drastic reduction of the amount of HRE needed to produce permanent magnets was fully achieved in the scope of objective (1), thanks to the invention by partner 1 of a new and innovative method to promote selective formation of a dysprosium-rich phase in the shell of the hard magnetic grains, with no loss in magnetization within the core of the hard magnetic phase. Current technologies use about 10-11 wt% of Dy, whereas with the new technique, only 0.6 wt% Dy is effective. This reduction by a factor of 16 represents a dramatic decrease in cost of the manufactured magnets, which can be estimated to roughly 40% based on the raw material costs in 2015. Furthermore, the new method is cost-effective and eco-efficient. It can be easily implemented in industrial production. Partner 9 has already tested this achievement in real conditions. Partners 1 and 9 prepared a bench of 550 magnets according to the new state of the art. These magnets were used by partners 10 and 8 to set-up a prototype motor for a car vehicle and a windmill, respectively. Two patents were filed and more than ten papers were published on this subject. Many invitations were sent to the scientific coordinator to present those results at European meetings and international conferences. Coverage by Slovene media, as well as in China, has resulted.

Objective 2) was based on the evident need for a medium-grade permanent-magnet material that can offer properties greatly superior to hard ferrite, yet they can be some 20% less in terms of remanence and coercivity than normal-grade Nd-Fe-B magnets. New materials discovered in ROMEO, which fulfil this gap, are:
- YCo5-xFex (0 ≤ x ≤ 0.5) alloy. The inventive technology together with the Fe addition to the basic YCo5 alloy invented by partner 3 and proceeding between partners 3 and 1 enabled an important achievement in filling the gap between ferrite permanent magnets and NdFeB magnets. The average coercivity and maximum magnetization obtained are 0.81 T and 100 Am2/kg, respectively. Partner 7 is ready for setting up this technology into its production.
- Heusler alloys: High throughput screening methods based on spin-polarized density functional theory (DFT) and advanced data mining strategies were used to predict novel Heusler or other alloys with targeted properties. One alloy, Co2MnTi, displays a remarkably high TC in perfect agreement with the predictions, while the other, Mn2PtPd, is a complex antiferromagnet. It was the first time that a brand new high-temperature ferromagnet has been discovered and designed directly by a machine-learning process. In the case of Mn2PtPd a single phase is found without evidence of decomposition.

6- Resources
In agreement with the Commission, 560.5 p.m were planned and an effective amount of 602 p.m was used to achieve the results of the project. Few shifts were observed between allocated resources and manpower actually used, which are explained in details in the report.

The total budget allocated by the European Commission amounted to 3 979 746 €, which was spent in total as agreed in the contract.

7- Dissemination and exploitation policy after the end of the project

The publication policy of the consortium will not limit itself to the few articles under submission at the present time. More papers should be issued in the coming period. More projects will be based on the results of ROMEO in view of responding to national as well as to European calls. Two such projects are already under evaluation by the European Commission. In Slovenia, the coordinating institution has used ROMEO to support its plans for Smart Specialization. A similar approach holds true for the other partners in their respective countries. Exploitation of the forehand and newly developed knowledge will follow the rules set-up by all partners in the consortium agreement.

8- Other issues

There are no ethical issues attached to ROMEO. Creation of research and management employment by ROMEO was an important issue, resulting in roughly 15 new jobs within 3 years. There was no specific focus on gender balance. Yet, 3 WPs out of 9 had female personnel as a leader.

9- Conclusion

The ROMEO project was very successful, first for having achieved its main objectives within a rather short period of 3 years, and second for having demonstrated how European industry may gather to face unexpected challenges coming from abroad, when the price of raw materials rises under the effect of political issues. We expect that, despite the up-and-downs prices exhibit on the market, such an outstanding consortium of complementary talents will be able to meet again when other challenges of a similar nature will trigger innovation in Europe.

10- Acknowledgements

All partners are most grateful to the European Commission for the substantial financial support offered to the project under Contract n°FP7/NMP/2012/Small/6-309729.

Project Results:
WP2

Introduction
The search for heavy rare earth reduced and rare earth free permanent magnets can be assisted by computer simulation. Computational materials science spans many length scales, ranging from electronic structure computation at the atom level to the computation of the magnetic properties on the scale of the grain size of the material. In addition to numerical simulation, analytic models of magnetization reversal give further insight into how magnetic materials and their structure can be improved, in order to reduce the heavy rare earth content of permanent magnets while keeping reasonable magnetic properties, especially at high temperature. Rare earth free permanent magnets may be realized with new materials. Combining electronic structure calculations with expanding materials databases, search strategies can be applied to find new potential candidate materials for permanent magnets.

The main objectives of the materials modelling work package were to (1) Explain the magnets’ intrinsic properties based on electronic structure calculations, (2) Model the micromagnetics and coercivity, which is the basis of the new materials’ functionality, and (3) Identify new compounds with permanent magnet potential by high-throughput computational screening.

Atomistic modelling/first principle calculations
The key properties of permanent magnets, such as coercivity or remanence, depend on both the intrinsic magnetic properties and the microstructure. First principle simulations of the intrinsic magnetic properties and micromagnetic simulations of the coercive field are essential to understand how to maintain excellent hard magnetic properties with a reduction in heavy rare earth content. Electronic structure calculations were performed using the software package WIEN2K at zero temperature, in order to compute the magnetic moment and the magneto-crystalline anisotropy energy of the rare-earth transition metal compounds RE2Fe14B (RE=Pr,Dy). WIEN2k is a full-potential, linearized augmented plane wave method and includes relativistic effects, such as spin-orbit coupling. In particular, the magneto-crystalline anisotropy energy has been simulated as a function of the lattice parameter changes. Reference materials such as RECo5 (RE=Y, Sm) and Y2Fe14B were taken to test the validity of the used approach. The main properties of interest are the spontaneous magnetization (magnetic moment of each atom) and the magnetic anisotropy energy. A high spontaneous magnetization gives magnetic materials that can deliver strong magnetic fields in a magnetic circuit. A high magneto-crystalline anisotropy energy gives magnetic materials that are stable against high demagnetizing fields. The critical external field which causes demagnetization is the coercive field. It is a key quantity characterizing a permanent magnet.

We have calculated the spontaneous magnetization and the anisotropy energy while changing the values of the “c” and “a” lattice parameters. In a permanent magnet, distortions of the lattice may occur at the surface of the grain where the crystals of the main phase have to match the lattice of the grain boundary phase. The results show that magneto-crystalline anisotropy depends on the lattice spacing. Local changes of the lattice parameter of the order of 0.5 percent may have a strong influence on the magneto-crystalline anisotropy. For RE = Nd and Pr we see considerably large changes in the magneto crystalline anisotropy energy. The anisotropy energy changes by up to ten percent for a two to three percent change in ratio of the lattice constants. Total magnetization though seems to be less sensitive to changes in the lattice. The change in magneto-crystalline anisotropy by lattice distortion is more significant in Pr2Fe14B than in Dy2Fe14B and Y2Fe14B. The change in the spontaneous magnetization was limited to a maximum of two percent for a two to three percent change in ratio of the lattice constants. It is evident that the lattice distortions originated from changes in grain boundaries could influence the local anisotropy field responsible for nucleation and magnetization reversal.

For realizing a rare-earth free permanent magnet MnBi is an interesting material because of its high
Magneto-crystalline anisotropy at elevated temperature. The magneto-crystalline anisotropy increases with increasing temperature. In order to understand this effect we performed electronic structure calculations with the simulation package WIEN2k. The anisotropy and its temperature variation were found to depend on the particular arrangement of the Mn and Bi atoms in the crystal. The numerical results suggest that thermal expansion of the lattice accounts for an increase of the magneto-crystalline anisotropy energy density by about 11 percent when the temperature is changed from 300 Kelvin to 700 Kelvin.

Micromagnetic modelling
The influence of the microstructure such as grain size and grain boundary phases on the magnetic properties can be understood through numerical micromagnetic simulations. Micromagnetism is a continuum theory which describes magnetization reversal on a length scale ranging from a few nanometers to micrometers. Computational micromagnetics or analytical models are especially useful for providing further insight into the magnetization reversal process of grain boundary engineered permanent magnets. In these magnets the grains have a core / shell structure. The core is Nd2Fe14B whereas the shell contains heavy rare earth elements such as Dy and Tb. This approach leads to a considerable reduction of the heavy rare earth content while preserving excellent hard magnetic properties.

We studied the role of grain boundary phases (GB) in multigrain finite element simulations based on microstructures derived from transmission electron microscopy imaging. Special attention was paid to the compositional analysis of GB with a thickness ranging from 2 - 30 nm. This analysis revealed that the majority of grain boundary phases contain about 50 - 70 atomic percent of iron. Finite element micromagnetic simulations have been carried out in order to study the influence of internal demagnetizing fields, determined by the microstructure, on the magnetization switching behavior. Emphasis was placed on the influence of the grain boundary phases and their magnetic properties, due to their substantial influence on the nucleation of reverse magnetic domains and the pinning of domain walls. The strongest reduction of the coercive field is caused by grain boundary phases with soft ferromagnetic properties. Shielding the Nd-Fe-B cores from nucleation sites at the grain boundary with Dy or Tb containing shells, leads to an increase of the coercivity from 2.5 to 3.6 T and 2.5 to 4.3 T, respectively.

During Romeo we developed a micromagnetic solver for large scale simulations of permanent magnets including thermal fluctuations. Classical micromagnetics treats temperature effects with the temperature dependence of the intrinsic magnetic properties, most importantly the anisotropy field. The nucleation of a reversed domain is initiated if the energy barrier that separates the initial magnetic state from the reversed state vanishes under the influence of the external field. With thermal activation the system can hop over a finite energy barrier which leads to a reduction in the switching field. The newly developed method was applied to study the thermal stability of Dy treated grain boundary engineered magnets. The results show that thermal fluctuations reduce coercivity considerably for all the variations of soft magnetic grain boundary phases and Dy containing shells investigated. At a temperature of 300 Kelvin, thermal activation reduces the coercivity by 15%, while at 450 Kelvin the reduction is around 25%. At both temperatures the reduction in coercivity resulting from a soft surface defect in a Nd2Fe14B core is canceled out by a thin (Dy47Nd53)2Fe14B shell covering the core: Despite the presence of a soft magnetic surface defect, the coercivity is similar to a perfect, defect free particle. From the results we can conclude that a hard magnetic shell containing either Tb or Dy with a thickness of 4 nm is sufficient to recover the coercive field of a perfect Nd2Fe14B without any soft magnetic defects. Small imperfections in the hard shell do not deteriorate the effect of grain boundary diffusion. However, as soon as a large continuous area of the
heavy rare earth containing shell is removed, the coercive field drops drastically.
MnAl has gained attention as a possible basis for rare-earth free permanent magnets. Using input from transmission electron microscopy, we built realistic finite element models of key structural features of MnAl. We computed the critical field required to nucleate a reversed domain and the pinning field which is required to push a domain over structural defects. The results show that the maximum expected coercive field in MnAl magnets is $\mu_0H_c = 1.5$ T.

Analytical modelling
A new analytical model of coercivity was developed which shows how magnetization reversal is initiated. The model accurately reproduces the temperature dependence of the coercive field found in bulk magnets that contain dominating second order anisotropy terms. With a soft magnetic surface defect layer with a thickness of 1 nm, the model accurately reproduces the temperature dependence of the coercive field found in the test Pr-Fe-B bulk magnets. Based on the model, a physical picture of magnetization reversal emerges according to which reversal is governed by the activation of a non-homogeneous magnetic configuration, reminiscent of a domain wall.

The model is especially useful to understand and develop novel concepts for grain boundary engineering. The concept of superferrimagnetism to enhance coercivity involves the deposition of a soft magnetic layer at the surface of the hard grains, selected such that the soft-hard intrinsic magnetic coupling be antiparallel, thus the term superferrimagnetic coupling. Without the grain boundary phase magnetization reversal occurs as follows: As the strength of the negative applied field is increased a “critical” volume of reversed magnetization forms at a certain moment, from which reversal expands into the whole grain. When the grain is covered with the superferrimagnetic layer, the reversal process changes because the reversed nucleus has two domain walls, one towards the bulk of the grain and one towards the grain boundary phase. The additional energy associated with the formation of the additional domain wall at the interface between the defect region and the superferrimagnetic layer is a source of coercivity enhancement. Model calculations show that the maximum enhancement of coercivity can reach 50 percent.

The results of the analytical model for new grain boundary concepts are confirmed numerically by numerical Monte-Carlo simulations.

Heusler database mining using ab-initio methods
New candidate phases for permanent magnet materials may be found by high throughput screening methods based on spin-polarized density functional theory and advanced data mining strategies. During Romeo we completed the construction of a Heusler alloys database with electronic structures. This includes calculations of structural, electronic and magnetic properties of existing and hypothetical Heusler alloys, in their full, half and inverse forms. The prototype structures have been constructed by considering all the possible combinatorial compositions compatible with the Heusler formula unit (A2BC) and with elements A, B and C taken among the following elementary elements: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Al, As, B, Ba, Bi, Br, Ca, Cl, Ga, Ge, Hf, Hg, In, Ir, K, La, Li, Mg, Na, Os, P, Pb, Re, Sb, Se, Si, Sn, Sr, Ta, Te, Ti, W.

A web interface provides a tool to automate the calculation of Heusler alloys using the VASP code. Simply enter the atoms for the X,Y and Z atoms and press go, the calculation will be launched on TCD’s super computer and the results will appear in the database. Currently we have 250,000 materials calculated. The database can be searched for specific properties and/or elements based on their stability against
decomposition. Other selection criteria are tetragonal distortion, a prerequisite for establishing a magneto-
crystalline anisotropy, and the high enough critical temperature above which the (anti)ferromagnetic phase
ceases to exist.
We calculated the enthalpy of formation for 250,000 Heuslers and 500,000 binary compounds. By
screening the Heuslers against decomposition into binary phases we predicted 23 new magnetic
materials. Two newly predicted phases have been successfully synthesized in WP4. Among them is a high
performance ferromagnet and a tetragonally distorted anti-ferromagnet.
A key criterion for materials selection is economic cost. Taking into account cost, tetragonal distortion and
power density provides a list of possible candidate materials from the binary database. Using these criteria
we can reduce the number of candidate materials to 270. For these materials we computed the magneto
crystalline anisotropy energy, resulting into seven promising candidates materials.

WP3

WP3 focused on the development of high-coercivity Nd-Fe-B-based magnets with drastically
reduced, or zero, HRE (Heavy Rare-Earth) content. The objectives were to minimise the amount of HRE
used to increase the coercivity of Nd-Fe-B-based magnets, through the development of grain-boundary
diffusion processing (GBDP), grain size refinement, and the use of novel grain boundary phases. Work on
bulk powders and magnets was complemented by studies on thin films that serve as model systems for
microstructure engineering.

Electrophoretic deposition (EPD) followed by grain boundary diffusion was shown to be very effective in
minimising the amount of Dy/Tb required to increase coercivity in commercial sintered Nd-Fe-B magnets.
EPD was used to coat sintered magnets containing no Dy in the basic alloy. Variation of the coating
thickness revealed that a 200-μm-thick layer of DyF3 was the optimum. The coercivity was increased in
such samples by 30 % with only 0.2 mol % of Dy. The EPD process has many advantages with respect to
other coating techniques such as dip-coating: it is very useful for evenly coating the magnet, with the
thickness of HREF3 coating we can tailor the coercivity, it is easy to coat samples with a complicated
geometry, the technique is cheap, fast and reliable, it has a reduced environmental impact since waste is
minimised and extra materials costs associated with the heavy-rare-earth component of the magnets can
be minimised, because of the accurate control of the amount of material deposited on the magnets prior to
the GBDP.

A reduction in grain size of sintered magnets, through the use of He gas during jet milling of the starting
alloy, was shown to be effective in increasing the coercivity of heavy RE free sintered magnets. Replacing
N2 with He as the milling gas leads to an increase in particle speed before collision, resulting in reduced
particle sizes. The particle sizes obtained in this project (D50 = 1.9 - 2.3 μm according to laser diffraction,
1.1 to 1.6 μm according to F.S.S.S.) are the smallest ones for NdFeB powder ever processed at VAC with
an AFG100 jet mill. These particle sizes are more than a factor of two smaller than those achieved with jet
milling under N2. Coercivity HcJ of up to 1600 kA/m was reached in HRE-free magnets produced with He-
milled powders. Imaging of a fracture surface of such magnets revealed an average grain size of about 2
μm. Comparison with previous results showed that the empirical relation that the coercivity HcJ increases
approximately with the inverse square root of the grain size remains valid for these samples with ultra-fine
microstructures. However, the high amount of Nd that was added to reach this level of HcJ leads to a reduction of Br, because the RE rich phase does not contribute to the polarization. The rectangularity of the demagnetizing curves of the samples with the best HcJ among the HRE free magnets is poor. Structural analysis of these samples in WP5 revealed that some relative large grains occurred in the microstructure and that the thickness of the grain boundary phase is relative small between some grains. Both aspects are assumed to have contributed to the observed reduction in the rectangularity of demagnetizing curves.

Surface coating of Nd-Fe-B powders to reduce corrosion during processing was studied. Both Al2O3 and SiO2 coatings were tested and best results were obtained for SiO2 coated powders prepared with the use of TetraEthyl-OrthoSilicate (TEOS). A solution of NdFeB powder, isopropanol, NH4OH and TEOS was mixed and corrosion tests carried out on vacuum dried powders. Corrosion was reduced by 75 % for a period of 8 h, which is enough for the normal processing of Nd-Fe-B powder in production. The technique is simple and cost effective. The flowabillity of the powder was increased by 20 %, which is an important improvement for large-scale production.

Metal-bonding of NdFeB powders was studied for magnet use at elevated temperatures. Magnetic properties comparable to those of polymer bonded magnets were reached in Zn-bonded Spark Plasma Sintered magnets. The optimum results were achieved with the addition of 20-40wt. % of Zn binder, and the use of MQP-B ~250μm in size. Such a combination yields the highest density due to favourable stacking of the particles, which has a substantial impact on remanence. In addition, due to the rapid hot-working cycle, the binder does not penetrate into the hard-magnetic phase and thus does not deteriorate the performance. Magnetic measurements revealed up to 600mT of remanent magnetization, while coercivity is almost fully preserved.

Consolidation of nano-grained Nd-Fe-B materials (HDDR and melt-spun) has been studied with or without the use of a second material which serves first in the compaction process itself, aiding densification, and secondly, can be diffused as a grain boundary phase between main phase grains, to increase coercivity. Spark Plasma Sintering of melt-spun Nd-Fe-B mixed with DyF3 powder was used to produce fully dense magnets. After additional thermal treatment the coercivity increased for 25 % with respect to the starting melt-spun material. Hot compaction and die-upsetting of melt spun and/or HDDR Nd-Fe-B powders blended with Nd and Dy containing low melting point alloys was also studied. It was shown that for hot-compacted magnets, the formation of Dy-rich shells on a nanoscale is possible by adding DyCu to the precursor powder and that Dy diffusion into Nd2Fe14B grains depends on the crystallographic orientation of the grains. Long term annealing at 600 °C enhances diffusion but induces the formation of large Nd-Dy-O rich precipitates close to the flake boundary with c-NdO2 or c-Nd2O3 structure. As a consequence, Dy is partly consumed and not available for the grain boundary diffusion, which limits the increase in coercivity. After die-upsetting, the distinct Dy-rich shells are smeared out due to the elevated deformation temperatures. For small grains this leads to a homogeneous Dy distribution within the full grain volume, which limits the effective increase in coercivity. Milling and the use of Nd-containing ternary eutectics with reduced melting points restricts the distribution to the grain surface and leads to a much higher effective increase in coercivity per wt. % Dy or Tb. Faster die-upsetting reduces the formation of large grains and other phases and therefore increases also absolute values. As a consequence, a better overall performance was obtained in comparison to the
Dy-free reference samples. Surfactant-assisted ball milling of HDDR powers was used to produce ultrafine single crystalline Nd2Fe14B powders (m-HDDR). The powders were blended with Nd-Cu powder of eutectic composition Nd70Cu30 (at. %) and then hot pressed. The thus produced compacts showed a large decrease in magnetisation compared to the non-compacted starting particles. This was attributed to a combination of oxidation of the ultrafine particles with some residual partial pressure of oxygen, and reaction of the particles with residual organic surfactants from the ball milling process. The surfactants were necessary in order to produce the ultrafine particles from the starting HDDR powder. Adding the eutectic to m-HDDR powder and hot pressing led to a further decrease in magnetisation due to the dilution effect. The coercivity of the compacts was not increased by the addition of the Nd-Cu eutectic and it was shown that the eutectic particles did not melt during hot pressing above the eutectic temperature. This was attributed to reaction of the eutectic particles with the residual organic surfactants.

Thin film samples were developed as model systems for the study of microstructure engineering. High rate triode sputtering was used to prepare films of NdFeB, with specific crystallographic texture (isotropic or out-of-plane) and the structure of the as-deposited films (amorphous or crystalline) being controlled with the choice of film deposition temperature. Multilayer samples were prepared with the NdFeB layer in direct contact with either the Ta capping and buffer layers (reference samples) or with intermediate RE-containing layers (samples for grain-boundary diffusion studies). Both continuous multilayer structures, and micro-patterned multilayers, were studied.

In the case of continuous multilayer structures with a Dy layer deposited on an amorphous NdFeB layer, short annealing time (10 min) at 550°C led to a coercivity of 2.7 T, while longer annealing time (1 h) led to a drop in coercivity to 1.3 T. Reference Dy-free samples had a coercivity of 2.2 T, for both annealing times. The increase in coercivity for the short annealing time is due to an increase in the anisotropy field in Dy-containing grain-boundary regions of NdFeB grains while the drop in coercivity for the longer annealing time is attributed to the observed expulsion of RE (Dy and Nd) from the magnetic layer to above the Ta capping layer. A study of the influence of lower annealing temperatures (350-500°C) was carried out on samples in which the Dy layer was deposited onto pre-crystallised NdFeB layers. Optimised annealing led to enhanced coercivity compared to reference Dy-free samples, and the optimum conditions depended on the deposition temperature used to prepare the NdFeB layer, clearly demonstrating the role of the starting microstructure in GBDP.

To increase control of the microstructure in films, a lithography-based process was developed to produce isolated Nd-Fe-B islands of diameter in the range 1 µm to 25 µm. After crystallization of the Nd-Fe-B islands, the Ta capping was etched off, the islands covered with various RE layers (Nd, Dy, Gd), and the dot arrays were then annealed to induce diffusion. While a marginal or a negative effect of annealing on coercivity was systematically observed with Ta and Nd coatings, a coercive field increase is obtained with Dy and Gd coatings, the optimal annealing temperatures being 400°C and 300°C, respectively. The strongest increase in coercivity (80 %) is achieved for Dy (total Dy content corresponding to less than 5 at. % of the overall Nd content), which is explained by an increase in anisotropy field at the surface of Nd2Fe14B grains. A 20 % increase in the coercivity of optimally annealed Gd capped islands is attributed to a manifestation of superferrimagnetism, in which the Gd-containing surface layers are coupled antiparallel to main phase Nd2Fe14B grains. A similar increase in coercivity was achieved in continuous layers, and good quantitative agreement was achieved with simulations (WP2).
There is a huge potential market opportunity for a new material with a suitable combination of coercivity $H_c$, Curie temperature ($T_C$) and remanence ($B_r$), which could fill the gap between Nd-Fe-B and ferrite magnets. The goal is based on the evident need for a medium-grade permanent-magnet material that can offer properties greatly superior to hard ferrite, yet they can be some 20% less in terms of remanence and coercivity than normal-grade Nd-Fe-B magnets. This lack of an appropriate material with a remanence around 0.8-1.0 T and coercivity around 1000 kA m$^{-1}$. The remanence $B_r$ of a magnet cannot exceed $\mu_0 M_s$ ($\mu_0$ is the permeability of free space), and the coercivity $H_c$ of an optimized magnet is usually no more than 25% of the anisotropy field $2K_1 / \mu_0 M_s$. The physics of magnetism means we must focus on transition-metal (TM) based compounds to develop a ferromagnetic material. For a high coercivity we need to consider methods of generating magnetic anisotropy; this could be based on magnetocrystalline anisotropy (like RE-TM magnets), shape anisotropy (like Alnicos), or some other form of anisotropy, such as surface anisotropy, or strain-induced anisotropy. Of these, magnetocrystalline anisotropy is the only one that can produce a truly high performance bulk permanent magnet, though other forms of anisotropy may be exploited to produce mid-range magnets.

The state of the art to find a gap magnet is developing existing CaCu$_5$ phase alloys or find a completely new phase using recently developed methods of high-throughput computational materials discovery. An alternative is to develop coercivity based on the ‘superferrimagnetic’ effect, in which main phase grains are coated with a soft magnetic material that couples antiparallel to the main phase [1]. This approach has been applied to main phase materials with magnetocrystalline anisotropy in WP3, and here we explored its application to RE-free main phases with shape anisotropy.

CaCu$_5$ structure:
The development and optimization of rare-earth-free magnets may be pursued by atomic substitutions in known uniaxial materials with reasonably high Curie temperatures ($T_C$) with a view to reducing materials’ costs or improving processability. Fe-doped YCo$_5$ and LaCo$_5$ are a promising starting point for magnet development because it is entirely free of the critical heavy rare earths, Tb and Dy; Yttrium and Lanthanum are potentially in surplus and substitution of iron for cobalt on 3g sites should increase the saturation magnetization according to calculations. The high coercivity (1.2 T) at room temperature and (1.92 T) at 4 K was obtained with 40 Am$^2$/kg maximum magnetization for ball-milled La$_2$Co$_7$ after annealing in the preheated furnace at 850°C for 3 min and subsequently quenching. The best magnetic properties is obtained with $\mu_0 H_c = 1.08$ T and $\delta s = 80$ Am$^2$/kg for ball-milled LaCo$_4.8$Fe$_0.2$ after annealing in a preheated furnace at 800°C for 3 min and subsequently quenching. However the maximum energy product is obtained 25 kJ/m$^3$ due to the secondary soft ferromagnetic LaCo$_{13}$ phase which creates a step in demagnetization curve [2].

YCo$_5$-xFe$_x$ (0 ≤ x ≤ 0.5) alloy powders are pre- pared by high-energy ball milling and subsequent rapid thermal or vacuum annealing in order to obtain a good energy product. The effects of the two different annealing processes on magnetic and crystallographic properties are compared. The highest $(BH)_{max}$, obtained for YCo$_{4.8}$Fe$_{0.2}$ powders dispersed in epoxy is 81 kJ/m$^3$ with $\delta s = 112$ Am$^2$/kg and $\mu_0 H_c = 0.75$ T with $N = 1/3$. After alignment in 5T the powder value of $(BH)_{max}$ is 140 kJ/m$^3$ with $\delta r / \delta s = 0.65$ due to the enhanced 5 T magnetization of 144 Am$^2$/kg. This energy product is the highest maximum energy product in the literature. Alignment increases the magnetization by 30% after for $x = 0.3$ and $x =$
For other compositions it is less, 5-10%. The coercivity for magnetically aligned $\text{YCo4.8Fe0.2}$ decreases only by 13% from 0.75 T, its room temperature value, to 0.65 T at 400 K demonstrating good temperature stability. The best magnetic properties obtained by rapid thermal annealing under similar conditions ($850^\circ\text{C \ 2 \ min}$) are $(BH)_{max} = 51 \, \text{kJ/m}^3$, $\mu_0H_c = 0.83 \, \text{T}$ and $\mu_{max} = 95 \, \text{Am}^2/\text{kg}$ [3]. In order to prepare pressed magnet and control the reproducibility of ball-milling process, we reproduced vacuum annealed $\text{YCo4.8Fe0.2}$ ($850^\circ\text{C \ for \ 2 \ min}$) in 15 different ball-milling process. The average coercivity and maximum magnetization obtained are 0.81 T and 100 Am2/kg respectively.

Vacuum annealed $\text{YCo4.8Fe0.2}$ powder was pressed into pellets using tungsten carbide pistons with 84% and 66% of crystallographic density, without and with the 0.4 T applied field. The field is obtained with using seven NdFeB N52 magnet rings and one NdFeB Magnet N40 magnet cap with axial magnetization direction through the 3 mm and 10 mm bores, respectively. This array was simulated by MANIFEST program and the maximum field, 0.4 T is found for 15 mm ring height. The maximum energy product of powder ingot, pressed under magnetic field, is 61 kJ/m3 (for N =1/2; p=5000 kg/m3; 66% of density and $\mu_0H=0.4 \, \text{T}$) and it increases from 52 kJ/m3 (for N=1/2; p=6337kg/m3; 84% of density and $\mu_0H=0$). The increase in maximum energy product can be attributed to the enhancement in magnetization (≈ 30%) under magnetic field alignment. Density of the field-aligned magnet was limited by the fragility of the tungsten pistons, but it should be quite possible to achieve higher values for denser magnets under magnetic field. The maximum energy product here reported ($(BH)_{max}$) of 61 kJ/m3, has been achieved in magnet with 66% density, it could be enhanced to values close to 150 kJ/m3 in optimized fully-dense magnets [4].

**MnAl alloy:**

It was shown in 1978 by Ohtani et al. [5], that uniaxially textured MnAl based magnets can be produced by hot extrusion. With this technique bulk permanent magnets were produced with $B_r=0.61 \, \text{T}$, $H_c=0.3 \, \text{T}$ and $(BH)_{max}=55.7 \, \text{kJ/m}^3$. Although this magnet shows a much lower coercivity compared to milled MnAl powders, this result is still the benchmark for anisotropic MnAl based magnets.

Since hot working is normally performed at temperatures above 600°C we prepared an induction melted cylindrical shaped ingot of the composition Mn53Al45C2. After the homogenisation heat treatment at $1100^\circ\text{C}$ for 2 days the whole sample contains only t phase with a coercivitiy of essentially zero and a magnetisation of 0.78 T at an applied magnetic field of 4.8 T.

This is close to the value for the non-deformed bulk sample and indicates that the metastable t phase is, as a consequence of the C doping, stable enough to be processed at temperatures in the range of 700°C for a longer period of time (e.g. 1 h). The coercivity of the hot extruded sample is improved by a factor of 10 compared to the non-deformed prealloy. The large difference of remanence in extrusion and radial direction shows the formation of a uniaxial texture. A degree of texture of 45% was calculated from the values of remanence of both directions. The resulting energy density in the extrusion direction is 16.5 kJ/m3. This might be possible with larger deformation ratios, e.g. an area reduction ratio of 7.4 was used in [5].

Twin-like defects in t-MnAl-C, which has the L10 structure, have been studied using electron backscattered diffraction (EBSD) in as-transformed and in subsequently hot extruded samples. In both states, three distinct twin-like defects were found, whose misorientations were described by rotations of $62^\circ$, $118^\circ$ and $180^\circ$ about the normal to $\{1 \ 1 \ 1 \}$. These are denoted as pseudo twins, order twins and true twins, respectively. The true twins are often observed in this type of material. The order twins formed the boundaries between regions where the c-axes were almost perpendicular to each other and these were thought to form due to the accumulation of strains during the transformation to t from the hexagonal parent
Due to symmetry, pseudo twins necessarily appeared at points where order twins interacted with true twins. The frequency of the different defects was very sensitive to the sample state. As the parent phase E is not involved in the dynamic recrystallization which occurs during hot extrusion, there was a greatly reduced fraction of order twins and pseudo twins in the hot extruded state. The misorientation angle of the magnetically easy \{0 0 1\} axis across the three twin-like defects was 48°, 86° and 75° for pseudo, order and true twins, respectively. The interaction of the three twin-like defects with 180° magnetic domain walls and the resulting effect on the magnetic properties of the material may therefore be different [6].

A new phase: Heusler alloys:
High throughput screening methods based on spin-polarized density functional theory (DFT) and advanced data mining strategies are used to predict novel Heusler or other alloys with targeted properties by Prof. S. Sanvito group. The magnetic ordering temperature, TC, has then been estimated by a regression calibrated on the experimental TC of about 60 known compounds. 26 of these predicted Heusler alloys were prepared by arc melting and structure and magnetic properties were investigated. The structure and magnetic properties of two Heusler are well coherent with DFT calculations. One, Co2MnTi, displays a remarkably high TC in perfect agreement with the predictions, while the other, Mn2PtPd, is a complex antiferromagnet. Co2MnTi crystallises in the regular Fm-3m Heusler structure with no evidence of secondary phases and a lattice parameter of a=5.89 Å in close agreement with theory, a=5.84 Å. The magnetization curve displays little temperature dependence and a saturation moment of 4.29 μB/fu at 4 K, fully consistent with the calculated ferromagnetic ground state. Most notably, the extrapolated TC from the zero-field cooled magnetization curve in a field of 1 T is found to be 938 K, essentially identical that predicted by our regression, 940 K. This is a remarkable result, since it is the first time a brand new high-temperature ferromagnet has been discovered and designed directly by a machine-learning process. Also in the case of Mn2PtPd a single phase is found without evidence of decomposition. The XRD pattern corresponds to a tetragonally-distorted regular Heusler with space group I4/mmm (TiAl3-type) and lattice parameters a=4.03 Å and c=7.24 Å. Our magnetic data show a sharp magnetic transition at ~67 K with very little temperature dependence of the susceptibility. There is probably a second, antiferromagnetic transition marked by a peak in the susceptibility at 350 K. Magnetization curves at room temperature and 4 K show no hysteresis or spontaneous magnetization indicating that the compound is antiferromagnetic at low temperature. However, the search for tetragonal distortion was performed only for the ferromagnetic state. Further analysis for the anti-ferrromagnetic ground state reveals that indeed Mn2PtPd is antiferromagnetic and tetragonal distorted with a c/a ratio of around 1.3 in good agreement with experiments [7].

As an alternative for the Heusler alloys the iron-tin system with the iron rich intermetallic Fe3Sn was investigated. Fe3Sn is ferromagnetic with easy-plane anisotropy. Predictions showed that substitution could lead to a change to uniaxial anisotropy by a variation of the lattice parameters. Different elements for substitution were investigated. The addition of neither B, C, P, Fe2P, Al, Si, In, Bi, Pb, Sb, Ta, Mo nor W to Fe3Sn did result in the changes necessary for inducing the desired change in anisotropy. From the added elements only C and Sb produced single phase material. Carbon did not interact with the Fe3Sn structure at all. The carbon itself formed agglomerations amorphously between the Fe3Sn. Antimony led to the formation of Fe60Sb30Sn10. This resulted in a two phase material with large amounts of solid solution Fe92Sn8 and Fe3(SnSb)2. This phase exhibits a magnetization which is too low for the desired permanent magnet application. All of the additions except for carbon resulted in samples with multiple
phases. Like all measured multiphase material the magnetization deteriorates with the addition of elements other than iron or tin. The carbon addition up to 20 at.% does not significantly change the magnetic properties.

The Fe60Sb30Sn10 phase exhibits a saturation magnetization which is only about half as large as in the Fe3Sn system. The reason for this is that it contains about 20% less iron and it has a different crystal structure than Fe3Sn which leads to a lower ferromagnetic coupling of the iron atoms. This reduction in the magnetization value with respect to Fe3Sn makes that the magnetization of Fe60Sb30Sn10 is too low for the desired permanent magnet application.

Combining shape anisotropy and surface effects:
The idea here is to explore the possibility to produce magnets composed of high magnetisation FeCo grains of anisotropic shape covered with a material that serves to impede magnetisation reversal at the grain surface, either through superferrimagnetism, or by the formation of surface layers with magnetocrystalline anisotropy. Such magnets should have coercivities exceeding those achieved in alnico magnets that depend solely on shape anisotropy. In this study we began by trying to exploit the columnar grain structure achieved in sputtered films, then progressed to studying micro-patterned films and finally we began a study of nano-patterned films which should allow us to produce nano-scaled FeCo features of controlled size, shape and inter-feature spacing, covered with the material of our choice.

Continuous and micro patterned films: Firstly we established that triode sputtering can be used to produce 5 µm thick FeCo films with columnar out-of-plane oriented grains traversing the entire film. We then explored the idea of diffusing REs along the grain boundaries of such films, from under and over layers. In the case of Dy/FeCo/Dy structures, the aim was to produce superferrimagnetic coupling at the surface of the FeCo columnar grains. In the case of Nd/FeCo/Nd structures, the aim was to produce thin Nd-FeCo based surface layers having magnetocrystalline anisotropy. It was established that direct contact between FeCo and pure RE layers should be avoided since the rapid formation of RE-FeCo phases led to significant or indeed complete consumption of the Fe-Co phase.

In order to provide only a small amount of RE element at the surface of the Fe-Co grains, we then included non-magnetic spacer layers of materials known to form eutectic phases with REs, between the FeCo and RE layers. Besides, to reduce the distance over which the RE should diffuse, we reduced the thickness of the FeCo layers, and micro-patterned the films using lift-off. X(RE / M / FeCo / M / RE)yX, where M = Cu or Ag and X = Ta or W, as well as reference X/FeCo/X structures were investigated. Intermixing between Ta and Fe(Co) occurred for annealing temperatures as low as 600°C, leading to a drastic loss in magnetisation and the formation of voids in the magnetic layer. Tungsten proved to be a more reliable choice of buffer and capping layer than tantalum, with no intermixing with Fe(Co), nor void formation, observed in samples annealed at temperatures of up to 700°C. However, no increase in coercivity was achieved when compared to reference W/FeCo/W samples annealed under the same conditions.

Nano-patterned films: With the aim to control better the microstructure achieved, and more importantly to favour the development of coercivity by reducing the size of the TM core to below the critical single domain size, work has begun on the fabrication of nm-sized objects using electron beam lithography. The shape quality of the nano-features produced was shown to depend on the size of the individual features, the inter-feature spacing, and the e-beam dose used to irradiate the resin. Covering of these nano-features with different types of surface layers is now being studied.

References:
WP5

Led by TUD, WP 5 focused on the multiscale characterization of the micro- and nanostructures down to the atomic scales and magnetic properties. This work package provided deep insight into the critical demagnetization processes on a local scale in order to identify the weak link in the microstructure responsible for the nucleation of magnetization reversal.

Advanced electron microscopy techniques were applied for the characterization of the different magnets. Scanning electron microscopy (SEM) including energy dispersive x-ray spectrometry (EDXS) and electron backscatter diffraction (EBSD) was used to identify the present phases and quantify their composition and orientation. For the high resolution analysis of the grain boundaries and the triple pockets transmission electron microscopy was applied including EDXS and electron energy loss spectroscopy (EELS). The EELS technique was also further developed for a reliable quantification of the rare earth content within the sample. Other developments within the project are a focused MOKE setup and high coercivity MFM probes. A variety of magnetic measurements in a wide range of temperature was conducted on many different samples, which were able to identify the dominating magnetization processes. Finally different corrosion tests were made on state of the art magnets as well as the demonstrator magnets.

Task 5.1: Detailed analyses of the RE, TM and light-element concentrations and distribution through the grains (M1 - M36)

EDXS and EELS analysis were applied to investigate compositional variations in the Dy treated Nd2Fe14B magnet. The concentration gradient of the elements from the triple pockets into the adjacent matrix grains was determined. The investigated samples were Nd2Fe14B magnets treated with DyF3 using the GBDP process. The analyzed areas were cut from the very center of the bulk magnet. Purchased DyF3 and NdF3 as well as in-house synthesized Dy2Fe14B and Nd2Fe14B were used as reference materials, from which standard spectra were acquired, which were used for quantitative EDXS and EELS analysis.

Task 5.2: Reliable compositional analyses of nanostructured magnets, a correct interpretation of the EELS spectra (M1 - M36)

A detailed analytical study was performed on Tb4O7-treated Nd2Fe14B magnet fabricated by grain boundary diffusion process (GBDP). The GBDP results in the formation of grains characterized by the
(Tb,Nd)2Fe14B-rich shell surrounding the Nd2Fe14B core. The HRE-rich shell largely increases the coercivity due to the higher anisotropy field of Tb-Fe-B while the remanence is reduced due to the lower magnetic saturation. The motivation behind this study was to characterize in details the distribution of Tb in the microstructure close to the specimen’s surface and in the specimen’s interior. For that purpose several FIB lamellas were cut from the Tb-treated sample and analyzed by TEM techniques. EDXS mapping of the lamellas revealed a distinct core-shell structure with Nd-rich NdFeB cores and Tb-rich shells. The reliable quantification of Tb, Nd and Fe elements by EDXS is compromised by strong peak overlap of the Fe-K and Nd-L spectral lines. Therefore, further analytical study was performed using electron energy-loss spectroscopy (EELS) applying an aberration-corrected scanning TEM (STEM). Although a qualitative determination of the elements present in the Nd-Fe-B-based magnet samples by EELS is relatively straightforward, a reliable quantitative analysis is often hindered by the relatively low signal-to-noise ratio of representative ionization edges, like for example Tb. For that purpose a program was developed which implements a refined background correction, exact cross-section values for the investigated elements and a principle component analysis. By this means reliably quantifiable spectra could be obtained. These confirmed quantitatively the former results. At the outer boarder of the Tb-treated magnet the Tb diffused evenly into the grains and formed homogeneous (Tb,Nd)2Fe14B grains. At a distance of 50 - 100 µm into the grains the Tb formed Tb-rich shells around the NdFeB grains with a transition zone between the Tb-rich and Tb-free areas of 20 nm.

Task 5.3: Characterization of nanograins by Electron Holography (M1 - M36)

Off-axis electron holography (EH) was applied on Tb4O7-treated Nd2Fe14B magnet fabricated by grain boundary diffusion process (GBDP). The GBDP results in the formation of grains characterized by the (Tb,Nd)2Fe14B-rich shell surrounding the Nd2Fe14B core. The HRE-rich shell largely increases the coercivity due to the higher anisotropy field of Tb-Fe-B while the remanence is reduced due to the lower magnetic saturation. To observe the decrease in the magnetic saturation between core and shell, the EH method was applied, since it is the only method that can provide direct information of the local magnetic response in the sample at the nano-scale spatial resolution. Therefore, spatially resolved differences of the in-plane component of the magnetization, in the grains (core and shell), triple pockets and at various interfaces, were imaged and quantified.

Task 5.4: Detailed analysis of texture, grain size, grain-boundary phases and phase distribution (M1 - M36)

Detailed analysis of texture, grain size, grain-boundary phases and phase distribution have been done on different samples. With different SEM and TEM techniques including EBSD and EDXS it was possible to identify the microstructural features which determine the magnetic behaviour of the different phases. On hot pressed samples EDX maps and TEM investigations showed, that the grain boundary diffusion process is applicable with the chosen synthesis route. Fine core-shell structures with Dy-rich shells could be observed within the samples. Different grain boundary and triple-point phases could be identified using FFT electron diffraction analysis. Furthermore a preferential diffusion of Dy into one of two adjacent grains was observed, if one of the grain has a low symmetry orientation towards the grain boundary. Sintered NdFeB samples with different Nd content provided by the project partner VAC were analysed at TU Darmstadt, IFW Dresden and TU Vienna. The samples exhibited different magnetic properties and especially the rectangularity was decreasing with increasing Nd content. The EBSD and microstructural analysis showed that with increasing Nd content the average grain size is becoming smaller which can
account for the observed increase in coercivity. At the same time an increased formation of grains 10-20
times larger than the average grain size was observed with increasing rare earth content. This can be
identified as one of the reasons for the reduced rectangularity. The abnormally large grains switch their
polarity at a much smaller field than the fine grains. This effect was also proven by Kerr microscopy.
Another trend which was observed was that the orientation of the grains is also reduced with increasing
rare earth content, which is also influencing the rectangularity of the hysteresis curves.
Standardized EELS experiments were conducted on grain boundaries (GB) from these heavy rare earth
free (Nd,Pr)-(Fe,Co)-B magnetic samples. For reliable quantitative analysis k-factors for the Fe-L2,3 and
Pr- and Nd-M4,5 were obtained by investigating Nd2Fe14B and Pr2Fe14B standards. High resolution
TEM (HRTEM) and high angle annular dark field (HAADF) imaging attributes the thickness of the GB
phases to range from 2-5 nm. Furthermore two different sets of GB phases were identified, one oriented
perpendicular ("x"-GB) and the other parallel ("y"-GB) to the c-axis of the adjacent hard magnetic grain.
Monte Carlo simulations, using the software package 3D CASINO v.3.2
(http://www.gel.usherbrooke.ca/casino/index.html) have been performed, to study the broadening of the
electron beam in the TEM specimen. The broadening of the electron beam, the tilt of the GB and the
position of the electron beam during the EELS acquisition, leads to a reduction of the Fe content in the GB
of 10 at.%. The resulting Fe content of the x-GB is ~20 at.% and of the y-GB ~50 at.%.

Task 5.5: Magnetic measurements (M1 - M36)
Within the ROMEO project a variety of magnetic measurements in a wide range of temperature was
conducted on many different samples produced in work packages 3 and 4. Based on the results the
fundamental physical processes occurring in the new materials could be explained. The measurements
were distributed between all partners of this task and the results were also included into the work
packages 3 and 4.
Furthermore a focused MOKE setup was developed at CNRS Grenoble in collaboration with Universidade
Federal do Parana, Brazil. With the designed system it is possible to rapidly apply pulsed magnetic fields
up to 10 T in a bipolar fashion and scan large surface areas for their magnetic properties. Initial test
measurements have successfully been carried out on compositionally graded SmCo and NdFeB films. The
system proved to be suitable for high throughput characterization of coercivity in such films. In parallel,
high coercivity MFM probes, based on SmCo coatings, have been developed at CNRS, for MFM analysis
of magnetization reversal under field.

Task 5.6: Corrosion tests (M1 - M36)
Corrosion tests have been performed on the demonstrator NdFeB magnets. These TbF3 EPD and grain
boundary diffusion treated magnets were compared to state of the art sintered magnets with respect to
their corrosion behavior. HAS-, salt spray -, 85/85-test were performed.
The comparison shows for the within the ROMEO project developed HRE-F EPD GBD method the losses
are very similar to the state of the art method.
Under harsh environmental conditions a protective coating of the samples is recommended. The obtained
corrosion properties are much better than for the RE-Fe-B based sintered magnets that are known as low
grades, but it shows also that there is still a potential and a need of improvement for the future.
The following goals were set when the ROMEO project was started

- Goal 1: Eliminate, or drastically reduce, heavy rare earths (HREs) in high-temperature Nd-Fe-B magnets by i) grain boundary diffusion of heavy rare earth elements, ii) extreme grain size refinement, and iii) new grain boundary phases.
  - Desired properties: \( B_r \geq 1.30 \, T, \, H_cJ > 2000 \, kA/m @ 20^\circ C \)
- Goal 2: Develop new RE-free magnets with properties intermediate between Nd-Fe-B and ferrites by i) high-throughput computational materials discovery, and candidate materials synthesis, and ii) coercivity development in rare-earth-free materials by grain-boundary engineering.
  - Desired properties: \( B_r \geq 0.8 \, T, \, H_cJ > 600 \, kA/m @ 20^\circ C \)

Towards goal 2, the development of new RE-free magnets with properties intermediate between Nd-Fe-B and ferrite intensive scientific research was done. Suitable magnets for goal 2 were not obtained for the targeted material systems. Therefore, no improved RE-free magnets based prototype set up in the scope of goal 2 was possible and an assessment of new materials in relation to goal 2 could not be done.

The work was continued with 2-17 based material for polymer bonded samples to assess technological parameters. As a result of the technological parameters assessment of eco manufacturing of polymer bonded magnets it can be said, they are applicable to most of isotropic or anisotropic materials. Project targets in this sense were fulfilled.

Towards goal 1 various approaches e.g. by grain boundary diffusion (GBD) of HRE, by extreme grain size refinement and the testing of new grain boundary phases have been examined. Good results have been achieved by GBD based on sintered permanent magnets (PMs). By this approach it is shown that it is possible to reach the magnetic properties demanded for goal 1. The most promising material was produced by collaboration of VAC, SIEMENS and JSI. Magnetic measurements of those HRE lean magnets gave the highest coercivity values of \( >2.3MA/m \) (without HRE in the bulk base material), well above the envisaged target for goal 1. Also the obtained remanence levels of \( >1.3 \, T \) were well above the target level.

An assessment of eco-efficient production by Sintering/metal forming was done on sintering plus HRE GBD and hot compaction followed by die upsetting or backward extrusion.

Two approaches were examined in detail including various tests:
- In collaboration of Siemens and VAC the HRE GBD was tested based on Tb-Metal layers that were deposited by sputtering to the surface of the samples.
- In collaboration of JSI and VAC the HRE-GBD, based on the electrophoretic deposition (EPD) of HRE, was tested. Based on the results the Tb-F EPD method was also chosen to prepare the demonstrator samples.

Towards assessment of Net-shape processing the following method were assessed:
- Cold isostatic pressing (CIP) alignment factors (AF) \~98\%, not appropriate for the production of small (near) net shape parts
- Axial field die-pressing (AP) AF \~91\%, good defined geometry and (near) net shape production, cost effective method
- Transverse field die-pressing (TP) AF \~96\%, good defined geometry and (near) net shape processing, cost effective method
- The press less process (PLP) AF \~98\%, good defined geometry and (near) net shape processing,
production of PLP parts not so cost effective
Rubber isostatic pressing (RIP) AF ~98%, not appropriate for the production of small (near) net shape parts
Metal injection moulding (MIM) not industrialized, needs more research
Die-upsetting (DU) AF deformation degree dependent ~98 % possible better net shape tolerances, complicated processing -> less economic
Backward extrusion (BE) AF deformation degree dependent ~98 % possible only a near net shape process possible, complicated processing -> less economic
CIP, AP, TP, PLP, RIP and MIM are powder metallurgical based approaches while DU and BE are hot deformation process.
All methods are in principle combinable with HRE GBD post processing.
Hot deformation process (i.e. DU, BE) is only for special geometries, eg. thin walled radial oriented rings the best choice. Better magnetic properties are achieved by the powder metallurgical processed material (particularly if combined with HRE GBD ). Among the different pressing methods the TP and the PLP methods are the best choices if the main selection criteria are small net shape tolerances and good magnetic properties, particularly if combined with HRE GBD.
Materials obtained by HRE GBD of Tb sputtered HRE-free VD238TP magnets showed very good magnetic properties, but were not chosen for the prototype manufacturing. Cost efficiency for high volume manufacturing is not given due to several reasons, e.g. high maintenance of sputter instrument, low throughput (e.g. requirement of high vacuum, slow coating procedure), high consumption of electrical energy. These aspects limit the exploitation of the process for industrial high volume magnet production. A raw material based eco-costs/value ratio (EVR) as Life Cycle Assessment was applied as a method to compare the different magnet production processes. It was shown that HRE GBDP methods provide the lowest raw material based EVRs. However, considering the current price level of RE raw materials the reduction of HREs in high end magnets would not compensate the high production costs of HRE GBDP. Nevertheless, if magnet properties for high end applications are superior the production costs would be secondary. Therefore, the HRE GBD processed magnets are the best choice for prototype validation within the ROMEO project.
An assessment of recycling processes for the magnets developed in this project has been done too. As there is no established recycling route for magnets, different possible routes were discussed and compared with respect of their feasibility for the ROMEO magnets and especially the HRE GBD demonstrator magnets. The most well-known routes for recycling magnets are hydrometallurgy, pyrometallurgy and hydrogen decrepitation (HD). Hydrometallurgy describes the process of dissolving the material in strong acids and subsequent selective precipitation of the desired metals as inorganic salts. These salts can then be reduced back to the rare earth elements and be used in the magnet production. In pyrometallurgy the scrap magnets are remelted and after purification processes the magnet alloy can be reused in the magnet production. For hydrogen decrepitation the magnet is exposed to a hydrogen atmosphere. The hydrogen diffuses along the grain boundaries into the magnet which is decrepitated into fine powder, which can be reintroduced into the magnet production process. In principle all of the discussed methods can be used for recycling the magnets developed within the ROMEO project. For the grain boundary diffused, heavy rare earth containing demonstrator magnet the hydrogen decrepitation was assessed as the most suitable recycling process as it is the only process currently available which could maintain parts of the microstructure achieved by the grain boundary diffusion process. It also is the shortest recycling loop and does not require strong acids like
hydrometallurgy or large amounts of energy for remelting the whole material. The HD process was also successfully tested on sintered magnets which were treated by electrophoresis with TbF3. The tests also showed that no significant amount of hydrofluoric acid is forming during the HD process, which could have been a possible hazard during the process.

For the rare earth free magnets developed, recycling will not be economically feasible as the investigated materials consist of mostly cheap elements like iron, manganese and aluminium.

Bases on the assessment results, for pilot test magnet production with dimensions required for demonstrators, modified VD247TP magnets with a low HRE content were used. EPD of Tb-F onto magnets, which were provided by VAC, was carried out at JSI and subsequent HRE GBDP and final machining took place at VAC.

Performing the grain-boundary diffusion process with terbium fluoride, the question whether some of the undesirable gas products based on fluorine were formed during the heat treatment was addressed. Thermogravimetric (TG) chemical analyses were done where possible fluorine-based compounds should be detected with mass spectrometer. Mass spectrometer measurements did not show any substantial changes in measurements of different ions, connected with fluorine. This is the conformation that the GBDP used for the coercivity improvement does not result in formation of potentially harmful gasses based on fluorine. With such analysis we can confirm safe process in the production line where large amount of TbF3 is heated up to 900 °C.

Lifetime properties were examined too. First highly accelerated stress test (HAST) results indicate that the corrosion stability after coating is still good, under harsh condition a coating is recommended. Further on the electric properties concerning conductivity and eddy currents were examined on the base of the Tb-F EPD GBD treated magnets. No significant difference in eddy current losses and conductivity were exhibited.

The HRE GBD method on the basis of Tb-F EPD coating is in principle applicable on an industrial scale, but it competes with other approaches to do the HRE coating and diffusion that are already implemented in industry. For example at VAC already another method is implemented. Both processes are at the actual price level of the HRE from an economic point of view not competitive but they opened the door to a level of improved magnetic properties that is not accessible by any other method up to now and if the prices for HRE rise again the industrial application of this process on a larger scale can be fast expanded on the basis of the research experience that has been won within this project.

For actual high end applications the HRE GBD is the recommended production method.

The research results and basic properties of the nano crystalline material obtained on the basis of the hot deformation like die-upsetting or backward extrusion process show that also this approach has great potential but up to now it is for production only the second choice except for sample dimensions that can’t be produced by the powder metallurgical approach, like e.g. thin walled radial rings. In principle the potential for improvements of the magnetic properties and saving of RE and HRE is expected to be higher for the nano crystalline material, but research results published up to now show that further research effort on this topic is still needed.

Finally it has to be pointed out that mining and separating RE Elements is not a green technology. Thus any production of permanent magnets containing RE can’t be called a green technology too. But it can be more eco efficient if recycling of the permanent magnets materials will be made possible and more common.
The objectives of WP 7 Assessment of Materials for Technical and Lifetime Properties are the:
- To prepare appropriate sintered samples in order to build the project prototype
- To build and test different electrical machines at the situated prototype level based on sintered magnets (following the VAC /JSI route)
- To validate the materials on the applied prototype level under application-related conditions

Potential Impact:

Technical:
Promising results have been obtained in the final stages of the project, it is therefore too early to find direct impacts of ROMEO. However, with the achievement of goal 1 of the ROMEO project, the following potential impacts are likely to be achieved during the next years:
• availability of high performing materials for transport applications by reducing the need for HREs from Nd-Fe-B magnets by reducing the grain size and optimizing the microstructure. This impact will also extend to other emerging high-tech devices in the renewable energy sector including wind turbines
• enabling a drastic reduction in the industrial use of RE and especially HRE materials for the production of permanent magnets, thereby reducing industry’s environmental impact
• providing industrial partners with significant market advantages
• strengthening the few existing magnet producers in Europe (VAC and KOL), and enable Europe to regain its strong historical position in magnet development and fabrication
• through the research and development of HRE-free permanent magnets, ROMEO will significantly advance the state of European science, introducing new materials, methods, and knowledge.

Socio-economic:
Socioeconomically, the change in market conditions and the emergence of revitalized EU-based activity in permanent magnetism is foreseen to bring back key European-trained scientists, now working in China, Japan, and Singapore, back to Europe – a reversal of the brain drain – where they can rapidly establish development and production facilities that will employ people in knowledge-based jobs. Now, at the very end of the ROMEO project, this impact is not yet measurable as it will take time to develop. However, the promising results obtained within ROMEO have already prepared the development in this direction.

Wider societal implications:
No direct wider societal implications are expected in the short run, they will only develop in the medium to long term with the uptake of ROMEO results in the market.

Main dissemination activities

Website:
The ROMEO website went online on April 11, 2013, with the domain name www.romeo-fp7.eu. The website features a publically accessible area and an intranet section. The intranet section can be left via a logout function, for safety reasons.
A system for the evaluation of the impact of the website has been installed (count of hits for viewing statistics). The website has been constantly maintained and was frequently updated. The click count
system for monitoring of success of dissemination has been frequently used. Links to information relevant for the general scope of ROMEO have continuously been added. The sections "results" and "news" have been filled with information. After project end in formation on the project will further be maintained and be made available by JSI via their website.

Interviews and television:
- TV interview (June 13, 2013) on the Slovenian Television News, by the Coordinator Prof. Dr. Spomenka Kobe of JSI
- interview on ROMEO in the Journal JOM, an official publication of the minerals, metals and materials society of TMS Springer, by the Coordinator Prof. Dr. Spomenka Kobe of JSI
- Boris Saje: participation in expert interview (anonymized) of project “CRM-InnoNet, Substitution of Critical Raw Materials”, November 2013; semi-structured expert interviews with nine industrial companies from different countries - focus on current and anticipated future risks associated with critical raw material applications as well as current risk provision strategies.
- TV Interview on the Slovenian Television in April 2015, by the Coordinator Prof. Dr. Spomenka Kobe
- participation of Boris Saje (Kolektor) in the talk «What would the world like without magnets?» on 7th October, 2015 in Ljubljana, within «Science on the street, knowledge and ideas under drafts» lectures, which are open for public. The talk was about the risks of rare earth supply and how to cope with them.

Sending out of the Newsletter to the selected target groups:
For the targeted dissemination of these results, a ROMEO Newsletter has been produced. It has been put on the ROMEO website in February 2015. It has also been sent to the contacts on the list of target audiences.

Dissemination via TEMAS News Ticker
News about ROMEO results including the ROMEO Newsletter have been published and sent via the TEMAS News Ticker with more than 2000 subscribers (mainly German speaking, from industries and science).

Dissemination via websites:
- News about ROMEO on the JSI Website
- publication of the magnetic database developed in the frame of ROMEO

Talks at events with participation of stakeholders
Several talks and presentations were given by the Coordinator Prof. S. Kobe on the occasion of public events, addressing a wider range of stakeholders.

Organisation of a Workshop in Innovative Materials for Ecologic Vehicles (IMEV):
This event was organised by ROMEO partner Valeo, and was held on November 18, 2015 at the Pôle Universitaire et Technologique de Vélizy-Villacoublay, Université de Versailles Saint Quentin. Several ROMEO partners have given presentations on this event.
Dissemination event including TV and media:
On the occasion of the final ROMEO meeting in Ljubljana on November 26, 2015, a dissemination session with TV and other media was held, which was recognised in media worlds wide only shortly after the event.

Exploitation results
The development of an exploitation plan has begun as foreseen in the DoW. In first instance, the goals of this plan have been settled, communicated to the partners, and accepted:

• Setting out the main exploitation aspects of ROMEO
• Compiling of issues to be addressed by the ROMEO consortium with respect to exploitation activities
• Setting-up and establishing activities to address these issues
• Defining persons, groups or committees responsible to address the issues; decision making
• Definition of a time-line for exploitation activities within ROMEO.

The following items to be frequently checked and discussed (if appropriate) during the project in terms of exploitation have been presented to the partners, and accepted:

• Target audience / main clients for exploitation, exploitable results, key areas of application, markets
• Roadmap
• Risks / uncertainties, mitigation
• Harmonization with checklist of WP6
• Harmonization with dissemination and networking activities
• Harmonization with the ROMEO Consortium Agreement / Grant Agreement, especially for publications and IPR. At the midterm meeting in Dresden it was decided to use common sense with respect to the harmonization of IPR issues with publications. This means that partners involved in publications will check for their own IP situation; if necessary, IP will also be discussed with industrial partners not involved in the publication; this will be considered carefully from case to case by the partners publishing.

It was decided by the partners that no activities regarding exploitation were necessary, because project results have not yet reached a level where this was relevant. However, a permanent screening has been carried out in order to immediately spot any issue arising. At project end there are still no issues to be tackled.

List of Websites:
http://www.romeo-fp7.eu/

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