In recent years, the analytical methods using an electron microscope have made huge advances. A lot of progress was made for new high-end analytics due to the development of new detectors, electronics, high-end multi core PCs which can handle new algorithms even in real-time with the measurements. The first results and impressions can be achieved immediately after starting the measurement. This article will show some examples related to the new techniques and will give an impression of EDS, WDS and EBSD related to the examples used.
Energy supply is one of the biggest challenges these days. Fossil fuels are becoming scarce and the CO₂ emission casts a greenhouse effect. The search for advanced materials and new technologies is essential for alternative energies, energy efficiency and sustainable mobility. Energy production with power plants is a promising enterprise. To increase the efficiency of such power plants super magnet materials like Nd₂Fe₁₄B came into focus for this application. They are also used in cars, DVD players and in new kind of refrigerator. Sunlight is another opportunity to get energy from a nearly endless source. The goal is to transform light into electrical energy with a high efficiency. The storage of energy is necessary to bring the energy to the place where it is needed. New batteries like rechargeable Lithium batteries with a high energy density will be in focus.

Applications for the Nd₂Fe₁₄B magnets include motors in cars, medical resonance spectroscopy, industrial motors, DVD players and wind power plants (Huang et al., 1986, Karl J. Strnat, 2008). These magnets possess ten times the energy density of common AlNiCo or hard ferrite magnets. Typically, magnetic materials are produced following a classical sintering process. Two main options for synthesis are possible: from elements and FeNd / FeB pre-sintering process. Two main options for synthesis are possible: from elements and FeNd / FeB pre-sintering process. To get magnets with the highest energy density possible, it is necessary to review and to understand the manufacturing process. It was decided to investigate a sample of NdFeB in three different states of formation:

The first measurement was done on a commercially available sintered magnet. Normally the sintering process is done in a vacuum or in an inert gas atmosphere at 1080°C for 20 to 90 minutes.

The second measurement point was after the magnet was sintered at 1130°C for 5 days to get an initial state.

In the final step it was annealed at 600°C for 2 hours.

The hysteresis curves have shown that the manufacturing process can be simulated in a quite effective way. The characterizations of the intergranular phases in this sintered magnet illustrate the effectiveness of the manufacturing process. The sample was prepared by Schweizer and Goll from HTW Aalen. (Goll et al., 2012; Sun et al., 2007; Fukunaga et al. 2006; Y. Shinba et. al, 2005, A. Kirchner et al. 2004, Sun et al. 2006).

**Conclusion:**

Initial evidence shows that the same processes take place in sintered magnets as in as-cast grain boundary model samples. Different intermetallic phases may occur in the Nd-rich grain boundary area. The post-moderate annealing process, done at a temperature of 600°C, results in a fine eutectic solidification of the material.

1. The Nd₂Fe₁₄B grains correlate with the red areas in the phase map and have a diameter of about 5 to 50 µm. The binder phase is located in the brighter areas between the magnetic grains. Inside these areas, three different compositions were detected automatically by the software. The spherical areas, identified in yellow in the Back Scattered Electron (BSE) image are separated by grey inclusions and contain oxygen. There are no inclusions of Nd-Pr inside the grains. The area between the grains does not show iron.
2. In state 2, the red Nd$_2$Fe$_{14}$B grains have a diameter of about 50 µm. The spherical inclusions are much bigger after sintering at high temperatures and are composed of rare earth oxides. The white areas in the BSE image are related to the Nd-Pr rich binder phase. Inside the binder phase, very small lamella of a Fe rich phase can be seen.

3. The Nd$_2$Fe$_{14}$B grain sizes vary from a few microns up to 100 µm. The little round inclusions inside the magnetic grains and the bigger inclusions in the binder area are rare earth oxides. In the binder area, some irregular iron-free areas seem to be hygroscopic and show a rough surface. The binder phase also contains oxygen-free areas, which are built up of Nd-Pr and rectangular Fe rich phases (marked in phase map).

**WDS investigation on batteries.**

The wavelength dispersive X-ray (WDS) analysis is a technique for high sensitivity and high energy resolution. Sometimes the EDS technique gets to its physical borders. The X-ray will be parallelised using X-ray mirrors or poly capillary. This parallelised X-ray wave will be totally reflected at crystals with different d-values due to Bragg’s law. The scattered X-ray will be measured in a proportional counter. The big advantages of such a parallel beam spectrometer LEXS or TEXS is the small size. These spectrometers can be mounted at any EDS port on a SEM. It is also implemented in the TEAM software and makes all settings simple to operate so that anybody can use the advanced techniques. The energy resolution for C is 5 eV in comparison to the C resolution of 43 eV with EDS.

The effective storage of electrical energy is of main interest and plays a big role. For new mobile technologies, the Li-ion batteries are prospective.
applicants with high energy and power density. The analysis of the microstructure will give clear indications of the power and life expectancy of a battery. The chemical analysis of the element distribution gives the opportunity to characterize the compounds and understand the processes in the battery materials. The diffusion of elements between the cathode and the anode regions is one of the expectancy limitations. To understand these ageing effects, EDS and WDS studies were made.

The principle functionality of a battery is shown in the figure. During charging Li ions diffuse from the cathode area to the anode area and back at the discharging process. With EDS mapping the different phases can clearly be detected. The main components and the fraction are given automatically. The efficiency of a battery depends on the capacity, power, charge and discharge cycles and ion diffusion. The diffusion of other elements than Li plays a big role in the life expectancy of a battery. The element maps show the distribution of each element. The diffusion of main elements C and O can be seen in the elements maps as a kind of dendrites in the separator (C. Hafner et al., 2011, C. Hafner et al., 2011, C. Haffner et al., 2011).

Two problems, from the analytical view, make the investigation of the ageing process difficult. One is a physical problem and cannot be solved using X-ray analytics. Li possess no X-ray spectrum and due to that it is not detectable with any SDD X-ray detector. The second is the very low amount of ions which diffuse through the separator into the opposite area and causes a short circuit. This problem of detecting elements of low concentration can be solved using WDS.

The measurement was done in the separator and the anode areas show in the image. The diffusion zone can be seen in the BSE image of the separator and also in the EDS phase mapping image. The images indicate a gradient from the left to the right side. Two WDS spectra were collected at a brighter position near the cathode area and one position closer to the anode area in the shown separator region. The WDS spectra at the first position show clearly a peak of Ni and Mn. Cu was not detected. At position two there was neither Mn, Ni nor Cu detected.

With a closer look at the anode area the presence of Ni, Mn and Cu can be seen. The spectra of Ni, Mn and Cu were collected at two different positions. One labelled with Anode1 inside a grain with mainly Carbon and a second spot was placed on the border between the grain and phosphates rich area. Inside the grains none of the elements can be found. At the grain boundaries (brighter areas) a small amount of Ni, Mn, and Cu could be measured. This result corresponds to the possibility of diffusion inside the colloidal phosphates and a very slow diffusion into the grains.

**EBSD investigation on CIGS thin layer solar cells and CdTe absorber.**

The electron backscatter diffraction (EBSD) is an upcoming technique to analyse orientation, texture and phase analysis. The latest EBSD detectors Hikari XP has been developed to analyse all kinds of samples. The speed can go up to 650 fps. Using a current of 5 pA or an acceleration voltage of 5 kV 99% of the patterns are indexed correctly. The orientation of the unit cell can be determined with an accuracy of less than 0.1°. The Hikari XP combines a camera for low voltage and high beam current. Because of the smart TEAM software the EBSD technique can
be used in a very easy way. The analysis software possesses a nearly infinite number of functions to get the answer to the related questions.

One of the major sources to replace fossil fuels is the sun. The energy from sunlight was used as long as the earth exists in many different ways. Without the sun, no life would be possible on earth. In recent times, it is often converted into electrical energy to preserve life. Recently we learned more about the opportunities of the photovoltaic process, the direct transformation of light to electrical energy. The first modules used Si single crystals, or polycrystalline Si. The latest development is thin film solar cells with thin layers of compounds containing copper-indium-gallium-selenium. These modules possess an 11% to 13% efficiency but were manufactured with over 19% in the laboratory. The effects of grain boundaries and orientation were studied with the EBSD method to understand problems of the charge carriers diffusing through the layers.

The main parts of a solar cell are two different n- and p-layers. With the help of sunlight, electrons and holes are diffusing into a region of lower concentration. To generate electrical power, metal contacts are put on the front and back of the solar cell. The orientation of the grains inside a solar cell are important for the efficiency. The electrons and holes shall not recombine on their way to the metal contacts. This recombination can happen at grain boundaries related to the kinetic energies of the boundaries between grains with different orientations. Grains are defined by the angle of misorientation between two neighbouring points. In the EBSD software of EDAX the default value of a grain boundary is 5° but can be changed. In case of dislocation inside the crystal low angle grain boundaries are formed. A second type is coincident site lattice grain boundaries (CSL) where a given fraction of atoms share the same position (D. Abou-Ras et al. 2007, D. Abou-Ras et al. 2007, D. Abou-Ras et al. 2007)

The knowledge of grain boundaries with a low recombination potential can help to manufacture solar cells with greater efficiency. The layers of a thin film solar cell are made with a special sputter coater applied in a PVD process. The grain size and orientation can be influenced during processing by pressure and different post processes. (M Nowell, 2009)

Studies of the electrical properties have been reported but in most studies the correlation between orientation and electrical properties cannot be given. In combined investigations of cathodoluminescence (CL) and EBSD, correlation can be detected. The Σ3 CSL grain boundaries are superimposed in red. The CL intensity was measured across the boundaries and plotted in the chart. The highest CL was found across the Σ3 grain boundaries and worse across others. EBSD has the opportunity to determine the CSL twin boundaries in an easy way. The manufacturing can be optimized, thanks to the results.

To visualize the orientation of a unit cell, the sample is defined as a reference system and the direction of the unit cell parallel to the axes of the reference system at each point is colour coded in relation to the orientation of the crystal system. The quality of all related pattern is shown in an image quality map. The different orientations and grains of Cu(In,Ga)
Se2 grains (CIGS) can be seen in the inverse pole figure map. The sample has to be prepared well to get good quality patterns. The phase is known to index the pattern automatically. The indexing and analysis of the patterns is then no problem and the area can be measured in minutes (Abou-Ras et al., 2009).

The cross section of the solar cell is of interest in understanding the electron / hole diffusion. The different grain boundaries can be determined to optimize the diffusion of the charge carrier. A cross section of a CdTe film was prepared and EBSD investigation made. For indexing the different layers, Au, CdTe, CdSe, SnO2/In2O3 (ITO) and glass, were used as given phases.

The EBSD map was measured using Au, CdTe, CdSe, ITO and glass phases of the different layers. The inverse pole figure map and phase map show only used the EBSD informations. The map is not really useable.

The reason for this problem is the near-symmetrical pattern of the different phases. Au, CdTe and In2O3 crystallises in the same cubic point group O3h. The software can’t identify the phase and orientation related to this pattern. If we have a look at a collected pattern from the CdTe area, it can be indexed using each phase.

Superimposed onto the pattern are the calculated reflectors of the three phases, gold left, CdTe in the middle and In2O3 on the right side. Without additional information it is not possible to index the pattern clearly.

With the simultaneous measurement of crystallographic and chemical information this
problem can be solved. Using such a combined EDS / EBSD system (Pegasus) the software collects the pattern and spectra of each pixel. By mixing the EDS elements maps of different elements the distribution of the phases can be seen clearly. The red / green / blue map visualizes the location of the different phases. This information can be used to identify the pattern clearly. The EDS maps allow the software or the user to setup threshold for the element concentrations. If the concentration is higher than the given threshold the software uses the phases containing these elements.

The re-indexing of the pattern shows clearly the phases, grains and its orientations. The data can be analysed for each phase. The orientation maps of the different phases can be separated and analysed in detail. The patterns of the phases are clearly indexed and IPF maps are showing the orientation of each unit cells in the different layers of the cross section.

The complete cross section shows the different grains and orientation. If the IPF map is superimposed on the IQ map, the grain boundaries can be seen. It looks like that perpendicular to the diffusion path of the charge carriers lies a lot of grain boundaries. The
analysis of the kind of grain boundaries is of main interest. The chart indicates a 60° misorientation as a main misorientation between the grains. A 60° misorientation is correlated with a Σ3 twin boundary. These special grain boundaries can be superimposed onto the image quality map and also indicates the perpendicular orientation. A direct comparison of the grain map with Σ3 misorientation and without Σ3 shows clearly the difference. This grain orientation seems to have not so many bad grain boundaries on the way of the charge carriers to the front and back contact.

Literature:
K. J. Strnat, “Modern PermanentMagnets for Applications in Electro-Technology”, Proceedings of the IEEE, Volume 78, Number 6, June 1990, pp. 923, doi:10.1109/5.56908
W. Schatt, „Der allgemeine Herstellungsprozess von FeNdB-Sintermagneten in der Pulvermetallurgieˮ; Kapitel 16, Springer Verlag.
C. Hafner, V. Knoblauch, T. Bernthaler, G. Schneider, „Qualitätsicherung für Lithium-Ionen Batterien mittels Quantitativer Gefügeanalyse“, Tagungsband Metallgraphietagung Karlsruhe (2011)
M. M. Nowell, “Microstructural Characterization of Thin Film Photovoltaics using Electron Backscatter Diffraction”, EDAX Application note

Dr. Felix Reinauer received his doctoral degree in solid state chemistry from the Justus Liebig Universität in Gießen 1998 and was a scientific faculty member at the Rheinisch Westfälische Friedrich Wilhelms Universität in Bonn until he joined EDAX in 2006. His main scientific interests are X-ray and electron crystallography and the whole field of analytical electron microscopy.

Felix.Reinauer@ametek.de

Tomas Vikstrom Biography Tomas Vikstrom has been in the analytical business since 1980 after studying electronics design at the University of Stockholm, Sweden. During the 23 years with EDAX, Tomas has mostly been working as a support/service engineer, but has also during a few years worked with developing computer programs for EDAX systems.