Preparation and characterisation

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Modern high performance magnets are based on nanocrystalline materials. The excellent magnetic properties of these materials are determined by a specific chemical and phase composition and, to a great extent, by a particular nanometer-scale (crystallite sizes in the range of 10^1 - 10^2 nm) microstructure. Therefore, one on the most important stages for the development and optimisation of nanocrystalline magnetic materials is the study of the structure as well as the understanding of the phase formation mechanisms in these materials. Here, preparation and characterisation of magnetic bulk nanocrystalline materials is reviewed (for the preparation of film systems see e.g. the presentations by N. M. Dempsey, J. Bachmann). Principle synthesis methods including mechanical ball milling, melt spinning and hydrogen-assisted processing are applied to R-Fe-B (R = Nd, Pr) and Fe-Pt alloys with the aim to produce permanent magnets with a high remanence and high coercivity. The use of x-ray diffraction for the study of the structure as well as advanced microstructure imaging techniques is discussed. Differential scanning calorimetry (DSC) is applied for the study of phase transformations and for the analysis of the thermal properties of the materials.

1. PREPARATION

1.1. Mechanical ball milling

Mechanical alloying, or more generally mechanical ball milling, is the process when mixtures of powders (of different metals or alloys/compounds) are milled together. Frequently the term *mechanical alloying* is used to emphasise the fact that material transfer is involved during processing, whereas milling of (already alloyed) powders having uniform composition with the aim of e.g. crystallite size reduction and/or mechanically inducing other transformations is termed *mechanical milling* [1]. Mechanical alloying is a complex process and involves the optimisation of a number of variables to achieve a desired structure, phase composition and microstructure. The most important parameters are: type of mill, milling container, milling time and speed, type and size of the grinding medium, ball-to-powder weight ratio, milling atmosphere, process control agents and temperature of milling.

Mechanical alloying of elemental Nd, Fe and B powders leads to the formation of a layered microstructure of Fe and Nd with B particles remaining undeformed and embedded in the

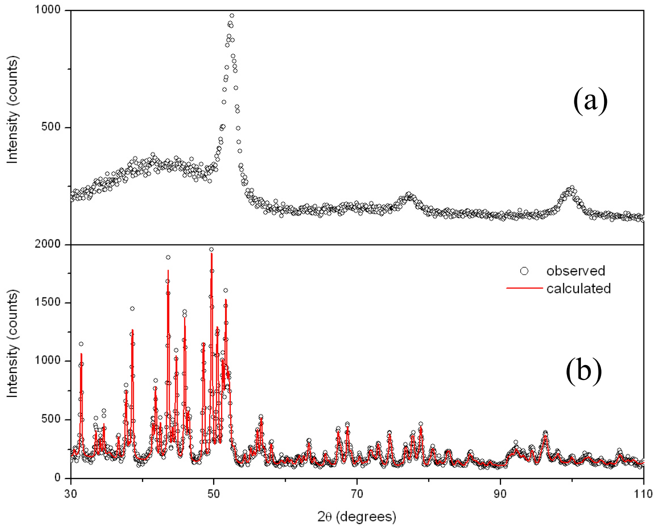

Fig. 1. *X-ray diffraction pattern of an alloy with the composition close to* $Nd_2Fe_{14}B$ *milled in a planetary ball mill for 60 h (a) and an example of a Rietveld refinement plot for this alloy after subsequent heat treatment at 650°C/30 min. Open circles and the full line represent observed and calculated x-ray diffraction profiles, respectively.*

interfaces [2]. In contrast, mechanical ball milling of the $Nd_2Fe_{14}B$ compound crushed into coarse powder, sometimes with the additional elemental Fe or Co powders, leads to the formation of a mixture of an amorphous phase and nanocrystalline Fe (Fig. 1a). In both methods, heat treatment at relatively low annealing temperatures of 600-700 °C and short reaction times of 5-30 min are required for the formation of the hard magnetic $Nd_2Fe_{14}B$ phase (Fig. 1b), which is due to the extremely fine distribution of the reactants.

A variation of milling is *cryomilling* in which the milling operation is carried out at cryogenic temperatures. The method is indispensable for processing powders of ductile components, where the effect of cold welding between the powder particles and the grinding medium should be minimised. It allows to avoid the use of process control agents often leading to powder contamination. This method has been successfully used to prepare nanocrystalline Fe-Pt (x = 40-60) alloys [3].

1.2. Melt spinning

In the melt spinning method, a molten alloy is injected through an opening of a crucible onto a rapidly rotating wheel, as a rule, made out of material heaving high heat conductivity (Fig. 2). During this process solidification rate may reach about 10^5-10^6 K/s and, as a result, ribbons or flakes (due to high brittleness Nd-Fe-B ribbons are frequently fragmented) with thickness of about 30-50 μm are thrown off the wheel surface. The process is usually carried out in inert atmosphere (e.g. Ar or He).

The structure and magnetic properties of rapidly quenched Nd-Fe-B alloys depend on the quenching rate, which is determined by the wheel rotation speed, injection conditions (type and pressure of the inert gas, crucible opening size, distance between the crucible and the wheel etc.) and temperature of the melt. The method mostly used for the production of rapidly quenched

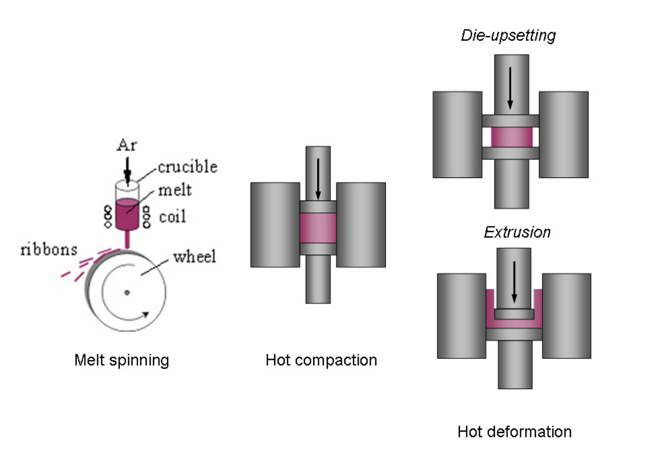

Fig. 2*. Schematic representation of the melt spinning, hot compaction and hot deformation techniques.*

Nd-Fe-B alloys is “overquenching” followed by heat treatment during which coercivity is developed. By overquenching materials with partially amorphous structure, similar as that shown in Fig. 1a, are obtained. Optimally annealed overquenched Nd-Fe-B ribbons have grain structure with crystallite size in the range of 20-50 nm, i.e. below critical single-domain particle size of the $Nd_2Fe_{14}B$ compound (200-300 nm [4]). This method is applied for commercial production of magnet powders suitable for the manufacture of bonded magnets.

1.3. Hot deformation

Nd-Fe-B materials produced by the melt spinning and by mechanical ball milling are magnetically isotropic. Therefore, in the absence of exchange coupling between crystallites, the remanence-to-saturation ratio M_r/M_s is limited to 0.5 [5]. One of the methods for obtaining anisotropic magnets with maximised energy density from nanocrystalline Nd-Fe-B alloys is the hot deformation (Fig. 2). Prior to the hot deformation a highly dense almost isotropic precursor is obtained by the hot compaction (T = 675-750 °C). A grain alignment along the c-axis of the tetragonal $Nd_2Fe_{14}B$ phase (easy magnetisation direction) perpendicular to the plastic flow is achieved after high temperature (700 -800 °C) compressive deformation (die-upsetting). The key for the hot workability is the presence of a rare earth rich grain boundary phase, which is liquid at the deformation temperature. Alternatively, hot extrusion may be performed, which results in obtaining ring magnets with a radial texture.

1.4. Sintering

Sintering is a conventional powder metallurgy method for the production of textured $Nd_2Fe_{14}B$-type and $Sm(Co,Cu,Fe,Zr)_z$ magnets. Because the compositions of recent high energy density Nd-Fe-B magnets are close to stoichiometry, conventionally cast materials would contain a high proportion of Fe-dendrites due to the peritectic nature of the formation of the $Nd_2Fe_{14}B$ phase. Fe is detrimental to the crushability during jet milling and to the magnetic properties of the magnet. The “strip casting” method, in which alloys are cast onto a rotating water-cooled wheel, suppresses the formation of free α-Fe and leads to a fine grained microstructure with grain sizes ranging from 5-60 μm. Pulverisation is usually achieved by jet milling where an ultrasonic flow of inert gas induces mechanical collisions of the particles. The particles are subsequently aligned in large magnetic fields (~ 1 MA/m), densified and subjected to the liquid-phase sintering (at around 1000 °C). Anisotropic, sintered $Nd_2Fe_{14}B$-type magnets with energy products (BH)max exceeding 400 kJ/m^3 are now produced routinely in industry using these techniques.

1.5. Hydrogen-assisted processing methods

Hydrogen Decrepitation

Hydrogen decrepitation is usually used in the production of fully dense sintered Nd-Fe-B magnets. Decrepitation means the self-pulverisation of large metal particles into powder. It relies on the fact that the bulk alloy consists of the matrix phase, $Nd_2Fe_{14}B$, and a Nd-rich, grain boundary eutectic which readily absorbs hydrogen at room temperature and at hydrogen pressures < 1 bar. This results in the formation of neodymium hydride and the subsequent differential expansion results in the decrepitation of the bulk material. The initial failure is predominantly intergranular in nature and the exothermic nature of the reaction causes the alloy to heat up and hydrogen is absorbed subsequently by the matrix phase to form a $Nd_2Fe_{14}BH_x$ solution.

HDDR

The Hydrogenation Disproportionation Desorption Recombination (HDDR) process is a strikingly simple method for producing magnetically highly coercive rare-earth transition metal powders (e.g. of $Nd_2Fe_{14}B$-type) by utilising a fully reversible hydrogen gas-induced chemical reaction. Unlike the HD-process, the HDDR route involves heating the bulk alloy in around 1 bar of hydrogen to about 800 °C. The first stage of the HDDR-process is the absorption of hydrogen by the Nd-rich phase at the grain boundaries essentially to form $NdH_{2.7}$. The next stage is the formation of the $Nd_2Fe_{14}BH_x$ interstitial solution. This is followed by a complete hydrogen desorption with further increasing temperature before the disproportionation reaction is triggered. In the case of $Nd_2Fe_{14}B$, the HDDR reaction can be described as: $Nd_2Fe_{14}B + (2 \pm x)\, H_2 \Leftrightarrow 2NdH_{2\pm x} + 12Fe + Fe_2B \pm \Delta H$. As in mechanically alloyed or melt spun materials, the coercivity in HDDR processed materials arises from the fact that final grain sizes are significantly smaller than or comparable to the critical single-domain grain size. The crucial difference, however, to the former two methods is that with the HDDR process it is possible to produce directly highly anisotropic magnet powders without the mechanical deformation necessary for example for melt-spun materials. Here "anisotropic powder" means that the magnetically easy axes (c-axes) of the $Nd_2Fe_{14}B$ grains are aligned in the multigrain powder particles. Consequently, compact textured magnets can be produced by aligning these anisotropic powder particles in a magnetic field.

2. CHARACTERISATION

2.1. X-ray diffraction

The purpose of this presentation is to illustrate the potential of x-ray powder diffraction in materials characterisation and give a brief description of the methods for the determination of the phase composition, microstructure parameters (crystallite size and lattice strain) and chemical ordering.

Traditionally phase identification is based on a comparison of the observed data with interplanar spacings d and relative intensities I of known phases. Quantitative phase analysis assumes that the integrated intensity of Bragg reflections is proportional, among all the intensity factors, to the volume fraction of a phase in a multi-phase mixture. The analysis is, however, extremely complicated or not possible at all when a severe overlap of diffraction peaks and/or peaks of different phases occurs. For instance, in the case of Nd-Fe-B alloys, x-ray structure analysis is complicated due to several reasons: in the Nd-Fe-B system the formation of several equilibrium and non-equilibrium phases is possible. Due to low crystal symmetry and large lattice constants, x-ray diffraction patterns contain a large number of overlapping diffraction lines, often of low absolute intensity (Fig. 1). In $L1_0$-based alloys, diffraction lines of the phases suffer from a severe overlap due to the nanocrystalline nature of the materials and/or rather close cell dimensions [7]. Evidently, these reasons complicate an extraction of detailed crystal structure information as well. Hence, the determination of peak position and intensity independently of each other is not an appropriate approach in these cases.

An advanced method for analysing diffraction data was proposed by Rietveld [8, 9]. It is based on a whole-pattern fitting with parameters of a model function depending on the crystallographic structure, instrument features and some numerical parameters. With such an approach, even the overlapping peaks contribute information about the structure to the refinement. The aim of the Rietveld analysis is to find a set of parameters that describe the observed diffraction pattern as good as possible. These include lattice constants, phase fraction, degree of texture, site occupation parameters (used for the determination of the degree of chemical order) and profile broadening parameters.

The broadening of x-ray diffraction lines arises due to both physical (specimen-related) and instrumental (geometrical) factors [10, 11]. Once the instrumental broadening is “removed”, the analysis of the physically broadened line profile can be made. In general, the physical broadening contains contributions from the small size of the crystallites (coherently scattering domains) and lattice strain (often denoted as microstrain or lattice distortion) caused by e.g. the presence of lattice defects. In order to separate the contributions from crystallite size and lattice strain to the overall breadth the modified Williamson-Hall analysis [12], the so-called "average size-strain" method of Langford [13] can be applied.

Neutron diffraction can also be used for the characterisation of materials [14]. As compared to x-rays, neutrons offer the advantage of being weakly absorbed by materials, i.e. their penetration depth is large, in the order of centimetres. The neutron scattering amplitude does not show a strong dependence on the atomic number, thus providing a possibility to locate light atoms or distinguish neighbouring atoms in the periodic table. Moreover, the interaction of the magnetic moment of neutrons with unpaired electrons enables the investigation of magnetic structures.

2.2. Differential scanning calorimetry

A critical step towards understanding the phase formation in various materials is to characterise their thermal properties [15, 16]. Differential scanning calorimetry (DSC) has proven to be a very useful tool in this effort. By determining the rate of heat flow into a sample, DSC provides quantitative thermodynamic and kinetic information about physical or chemical changes occurring in the material. The latter alter the enthalpy and/or heat capacity of the material, which in turn results in the release or the absorption of heat. Thus, DSC enables determination of transition temperatures and transition heats of such processes as melting, crystallisation, solid-state transitions, chemical ordering, spin-reorientation transitions, chemical reactions etc. as well as kinetics of these processes (e.g. Kissinger method [17, 18]). Also second order-type transitions, such as ferromagnetic Curie transition, can be detected by abrupt variations in heat capacity.

2.3. Imaging techniques

In electron microscopy, a focused beam of electrons is used to examine objects on a very fine scale. This examination can yield information about topography, microstructure, chemical composition and crystallographic information. Whereas transmission electron microscopy (TEM) is applied for the investigation of very thin samples with resolution down to atomic scale, scanning electron microscopy (SEM) can be used for imaging surface features of massive samples. The process of image formation is fundamentally different between the two techniques; for more details the reader is referred to Ref. [19]. In contrast to TEM, sample preparation for SEM is less complicated. At the same time, high resolution SEM allows observation of crystallites in the range of about 20-30 nm [7, 20]. Secondary electron mode in SEM provides a three-dimensional perspective, whereas the use of backscattered electrons allows detecting the contrast between areas with different chemical compositions.

Atomic force microscopy (AFM) is another scanning probe technique. It relies on attractive forces that are generated between electron clouds of atoms of a specimen and a vibrating cantilever, when these are brought in close proximity, and yields information about sample topography. AFM can be used for imaging non-conductive samples at near-atomic resolution. Magnetic force microscopy (MFM) relies on a principle similar to AFM. The MFM technique is based on the detection of the magnetostatic interaction between a sample and a small ferromagnetic tip and is used for observation of magnetic domains [21].

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