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Viewpoint article

Reaction sintering as a high-throughput approach for magnetic materials development

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ABSTRACT

Experimental high-throughput approaches based on diffusion couples in reaction crucibles recently have been successfully introduced in the research of magnetic materials. However, sometimes this method is limited out of thermodynamic and kinetic reasons, e.g. when melting point reduction does not occur. Liquid and solid state reaction sintering is an advanced powder based approach suited for (1) discovering novel phases, (2) verifying and specifying phase equilibria in systems with existing information and (3) realization of phases difficult to obtain by conventional metallurgy. Therefore, reaction sintering delivers significant contribution for accelerated materials discovery and development in the research of magnetic materials.

1. Introduction

For efficient energy conversion in high-power motor and generator applications novel hard magnetic materials filling the gap between hard ferrites and Fe-Nd-B in the performance-cost landscape are required [1–4]. The vast number of as yet unexplored multi component systems gives hope that such materials still can be discovered. Key for the successful mining for such novel hard magnetic phases is the application of an efficient screening concept.

High-throughput materials science in general is an approach to speed up discovery, study and design of novel and known materials. The approach aims to identify optimum parameters or base materials by systematic altering and analysis in parallel. A prominent effort is the Materials Genome Initiative [5–7] that relies on high-throughput computation (phase diagrams, reaction kinetics, influences of additives on intrinsic material parameters) supplemented by experiments and use of extensive data bases.

Recently, computational and experimental high-throughput methods have found their way into the research of magnetic materials to scan efficiently through multi component systems in search for novel hard magnetic phases within reasonable time. Computational high-throughput screening (HTS) is based on ab-initio modeling of phase stabilities and intrinsic magnetic properties [8–10]. Experimental HTS is based on thin film [11,12] and bulk approaches [13–15]. The approaches make use of thin film libraries and heterogeneous non-equilibrium states, respectively. Lately, the study of non-equilibrium phenomena has developed into an active and exciting field for material design, which can provide new insights into phase equilibria and thermodynamics [16].

In this viewpoint article, reaction sintering is introduced as an advanced highly efficient synthesis tool kit for accelerated magnetic materials discovery and development.

2. Strategy of bulk high-throughput screening and processing

The bulk high-throughput approach previously developed and introduced by the authors is well-suited to scan rapidly through multi component systems [13]. The strategy of this multilevel approach is illustrated in Fig. 1.

To handle the large number of prospective systems, a prioritization tool has been developed. It is based on the fact that the probability of a ternary or higher component system to form intermetallic phases is reflected in the number of phases that each of its boundary systems form. For ranking the systems a phase index has been established which has been additionally combined with the raw materials cost index and other physical principles.

To scan systematically and quickly through the systems of the prioritization list for novel hard magnetic phases, the reaction crucible method has been established. Instead of time-consuming exploration of the corresponding phase diagrams, the method makes use of heterogeneous non-equilibrium states or diffusion couples. They are based on the formation of concentration gradients between different elements (e.g. transition metals, rare earth metals, additives) due to thermodynamically guided diffusion processes. As only transition metal rich intermediate phases are interesting candidates for permanent magnets, one sample (the corner of the transition metal) is enough to cover the most relevant part of the corresponding system. Of course, there is still a slight probability to miss phases due to kinetic issues.

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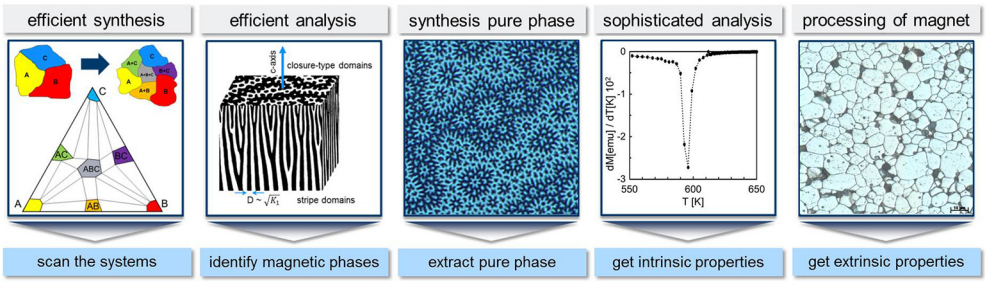

Fig. 1. Strategy of high-throughput screening and processing (multilevel approach).

To identify promising hard magnetic phases their typical domain pattern (stripe domains, closure-type domains) is analyzed by a combination of different microscopy techniques. The domain patterns further allow direct determination of the corresponding intrinsic magnetic properties. From domain contrast and domain width saturation polarization J_s and magnetic anisotropy constant K_1 can be deduced. When the domain structure is observed as a function of temperature, the Curie temperature T_C is obtained from the temperature dependence of J_s. From the intrinsic properties the hysteresis properties (coercivity H_c, remanence J_r, maximum energy product $(BH)_{max}$) of a bulk permanent magnet based on the identified novel phase can be theoretically estimated. From this, the material's expected industrial relevance can be approximated.

Once an interesting novel hard magnetic phase has been discovered, it has to be synthesized in larger volumes. Finally, an optimal processing route is required to process the novel phase into a bulk permanent magnet and combine its favorable intrinsic magnetic properties with a suitable microstructure.

The efficiency of the reaction crucible approach has been demonstrated for well-known systems like binary Co-Sm and Fe-Nd-B. Also with the approach several hundred systems have been screened for novel hard magnetic phases. More than 15 interesting phases could be discovered so far. However, for numerous systems this method is not the best suited one due to thermodynamic and kinetic reasons, e.g. when melting point reduction is missing. Here, reaction sintering represents a promising alternative.

3. Reaction sintering

Reaction sintering is a powder based technique which is already well-established in adjacent science fields, e.g. ceramics [17]. Recently reaction sintering has been successfully applied to hard magnetic materials [13]. Reaction sintering uses a powder mixture of the elements (powder particle size < 500 μm) involved in a specified system. As novel hard magnetic phases are expected to be rich in transition metals (e.g. >50 at.%), a transition metal rich composition (e.g. >50 at.% Fe) is chosen. The powder mixture is compacted in order to achieve a proper connection between the different powder particles. The resulting green compact is sintered in inert gas atmosphere at elevated temperatures (800 °C – 1200 °C) for several hours (3 h – 96 h). Sintering allows each particle of an element (e.g. Fe) in contact with a particle of another material (e.g. additives) to form a diffusion couple on a small scale (Fig. 2), as long as the system has not yet reached the homogenized state. This heterogeneous non-equilibrium state with its many different local element concentrations (still Fe rich) can be used as high-throughput method to search for new phases. At the contact interfaces (solid-liquid, solid-solid) different diffusion couples can be generated containing stable intermediate equilibrium phases provided that phase formation is allowed by reaction kinetics.

An example for such restrictions is described for the system Cu-Zn in [18]. Although the approach is not eligible for completeness, numerous different intermediate phases in the Fe-rich corner of a given system will still exist in parallel in the sample, so that the probability to find novel hard magnetic phases is rather high. Depending on whether a liquid is formed or not during sintering, reaction sintering is called liquid phase sintering or solid state sintering. Examples for liquid phase and solid state sintering are ternary Fe-Nd-B and binary Fe-Ti, respectively.

In the case of Fe-Nd-B melting point reduction due to Nd ($T_m = 1024$ °C) provides a large-area reaction zone and guarantees fast diffusion processes. In the sample (sintering at 1150 °C for 6 h) most Fe rich phases in the vicinity of the initial powder mixture composition are detected (Fig. 3a and inset). Here, remnants of elemental Fe particles are surrounded by a sequence of intermetallic phases consisting of $Fe_{17}Nd_2$ (close-by) and hard magnetic $Fe_{14}Nd_2B$. So, the Fe-content of the compounds decreases with increasing distance from the Fe particle. It should be noted that occurrence of Fe_2B and FeB cannot be confirmed

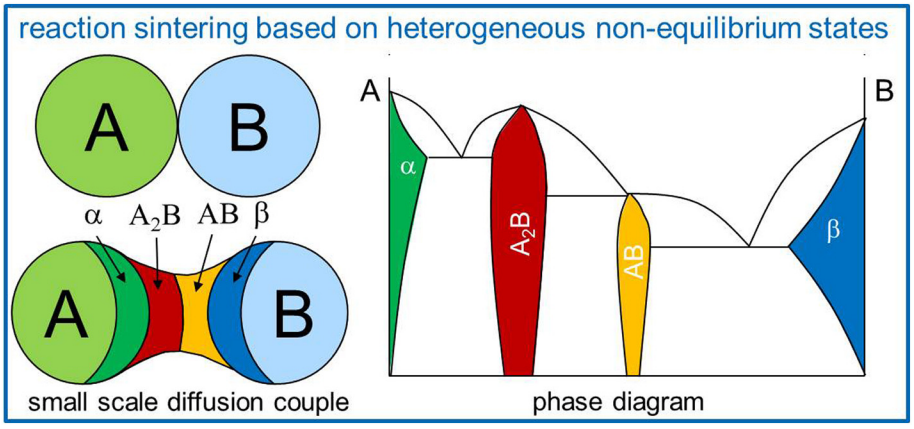

Fig. 2. Illustrating the principle of reaction sintering based on heterogeneous non-equilibrium states. In between two particles A and B the intermediate phases occurring in the corresponding phase diagram (here: A_2B, AB) may be formed, provided that reaction sintering is interrupted in time for preventing the specimen from reaching the homogenized state. It should be noted, that it may occur, that some stable phases do not form due to kinetic reasons [18].

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