Phase transition behaviour and corrosion resistance of $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{1.425}\text{B}_{0.075}$ and related compounds

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The global permanent magnet markets are several billion dollars a year. Anisotropic NdFeB magnets, the strongest ones, are made by sintering or by hot pressing of amorphous ribbons. Our aim is to obtain anisotropic bulk material by casting and applying a thermo-mechanical treatment. $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$ was found to be a promising composition with a nearly complete phase transition between 850°C and 1080°C. The time temperature transition behaviour of $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$ was investigated. First thermo-mechanical experiments were made. The orientation of the crystallites is caused mainly by plastic deformation and not by uniaxial pressure.

Introduction

A promising group of permanent magnet materials, $\text{Nd}_2\text{Fe}_{14}(\text{B},\text{C})$ was discovered some years ago [1,2]. The main limitation of these compounds is their relatively low Curie temperature (e.g. 312°C for $\text{Nd}_2\text{Fe}_{14}\text{B}$ and 262°C for $\text{Nd}_2\text{Fe}_{14}\text{C}$). Small amounts of Co increase the Curie temperature significantly [3]. The $\text{Nd}_2\text{Fe}_{14}\text{C}$ compound undergoes a solid state transformation from the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure (Φ) at lower temperatures to the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure (with interstitial C atoms; Δ) at higher temperatures [4].

Contrary to $\text{Nd}_2\text{Fe}_{14}\text{B}$ the corresponding Carbide is formed peritectically. The primary crystallized phase in these as-cast alloys is γ -iron [5]. Our aim is to use this solid state transformation to obtain high coercivity bulk material without having to use the powder metallurgical route.

Experimental details

The alloys were prepared by arc melting from starting material of at least 99.9% purity. We started with an excess of Nd of 3% to equalize evaporation losses during arc melting. After melting the samples were wrapped in tantalum foil, sealed into an evacuated quartz tube and annealed at different temperatures. Afterwards the samples were characterized by x-ray powder photographs (Jagodzinski-type) and standard metallographic techniques. Samples of the composition $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$ were plastic deformed (20-30%) during recrystallization and afterwards tested for anisotropy by means of x-ray diffraction. A series of $\text{Nd}_{2.5}\text{Fe}_{13}\text{Co} - \text{C} - \text{B}$ compounds with different C/B ratios was investigated with regard to corrosion resistance, Curie temperature (T_C), saturation magnetization (σ_s) and lattice constants (for details see ref. 6). Corrosion resistance was measured in atmosphere at 60°C and 100% humidity.

Results and Discussion

A corner of the pseudo ternary phase diagram $\text{Nd}_{2.5}\text{Fe}_{13}\text{Co} - \text{C} - \text{B}$ was investigated. The solid state transformation occurs over a large temperature range. $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$ was found to be a promising composition with a nearly complete phase transition between 850°C and 1080°C. At 1080°C

the equilibrium phases are free iron, Δ and a Nd-rich phase, while at 850°C the equilibrium phases are Φ and Nd-Carbides/Borides. The time temperature transition behaviour of $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$ was investigated (fig. 1). The bulk material is first annealed for 15 min at 1150°C, i. e. above the peritectic temperature. The structure then consists mainly of dendrites of free iron with a Nd-rich phase in the space between. The desired tetragonal phase starts forming immediately at a subsequent annealing at around 850°C at the interfaces between these two phases. After 15 min more than 50 % of the material consist of this phase. A small amount of Δ is formed around the iron grains. The formation of new Φ phase can only occur by the diffusion of iron atoms through the already formed intermetallic phases to the Nd-rich phase, therefore long annealing times (several days) are required afterwards to eliminate free iron. At 800°C the diffusion slows down the formation of Φ , while at 900°C and at 950°C the Δ phase becomes more stable.

Table 1: Saturation magnetization, Curie-temperature and amount of corroded surface of several samples.

Composition	σ_s [Am^2/kg]	T_C [K]*	Corr [%]
$\text{Nd}_2\text{Fe}_{14}\text{B}$		570	67
$\text{Nd}_2\text{Fe}_{13}\text{CoB}$		631	69
$\text{Nd}_2\text{Fe}_{13}\text{CoC}_{0.2}\text{B}_{0.8}$		621	52
$\text{Nd}_2\text{Fe}_{13}\text{CoC}_{0.4}\text{B}_{0.6}$		617	60
$\text{Nd}_2\text{Fe}_{13}\text{CoC}_{0.6}\text{B}_{0.4}$		617	57
$\text{Nd}_2\text{Fe}_{13}\text{CoC}_{0.8}\text{B}_{0.2}$		620	35
$\text{Nd}_2\text{Fe}_{13}\text{CoC}_{0.9}\text{B}_{0.1}$		615	
$\text{Nd}_2\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$		606	
$\text{Nd}_2\text{Fe}_{13}\text{CoC}$		606	3
$\text{Nd}_{2.5}\text{Fe}_{13}\text{CoB}$	133	629	62
$\text{Nd}_{2.5}\text{Fe}_{13}\text{Co}(\text{C}_{0.3}\text{B}_{0.7})_{1.5}$	141	625	49
$\text{Nd}_{2.5}\text{Fe}_{13}\text{Co}(\text{C}_{0.6}\text{B}_{0.4})_{1.5}$	139	615	42
$\text{Nd}_{2.5}\text{Fe}_{13}\text{Co}(\text{C}_{0.8}\text{B}_{0.2})_{1.5}$	113	605	7
$\text{Nd}_{2.5}\text{Fe}_{13}\text{Co}(\text{C}_{0.95}\text{B}_{0.05})_{1.5}$	116	612	9
$\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{1.5}$	128	612	10
$\text{Nd}_{2.5}\text{Fe}_{14}(\text{C}_{0.95}\text{B}_{0.05})_{1.5}$	136	576	4
$\text{Nd}_{2.5}\text{Fe}_{12}\text{CoV}(\text{C}_{0.95}\text{B}_{0.05})_{1.5}$	114	579	8
$\text{Nd}_{2.5}\text{Fe}_{12}\text{CoNi}(\text{C}_{0.95}\text{B}_{0.05})_{1.5}$	123	605	0
$\text{Nd}_{2.5}\text{Fe}_{11}\text{Co}_2\text{Ni}(\text{C}_{0.95}\text{B}_{0.05})_{1.5}$		684	0

* T_C is underestimated with respect to equilibrium conditions

The material can be deformed during the formation of the intermetallic phases. The Φ phase prefers growing in x-y-direction. Therefore the crystallites formed at the iron/Nd-rich interfaces are flat crystals with the c-axis perpendicular to these interfaces. In case of plastic deformation the crystallites break into platelets and align with the ab plane parallel to the flow direction. This was observed in the surface region of a sample deformed during the first minutes of the annealing at 850°C. X-ray analysis yields an amount of oriented crystals of 65%. The determining factor for preferred orientation in this alloy is therefore the plastic deformation and not the pressure during recrystallization as described for Nd-Fe-B alloys [7]. A

Fig.1: The formation of the Φ -phase and the Δ -phase at different temperatures.

still present problem is the migration of the nearly liquid Nd-rich phase during deformation. Possible techniques to prevent this are the deformation at lower temperatures and/or the use of an iron shell (as described in ref. 8).

The results of the corrosion experiments and the determination of T_C and σ_s are listed in table 1. The corrosion resistance of $\text{Nd}_{2.5}\text{Fe}_{13}\text{CoC}_{0.95}\text{B}_{0.05}$ is far better than that of Nd-Fe-B magnets. The Curie temperature amounts to 339°C. The composition $\text{Nd}_{2.5}\text{Fe}_{12}\text{CoNiC}_{0.95}\text{B}_{0.05}$ shows no corrosion under these experimental conditions. Its Curie temperature is 332°C. The saturation magnetization for isotropic bulk material amounts to 116 Am²/kg for the Ni-free composition and 123 Am²/kg for the Ni-containing compound. It is to mention that Ni seems to stabilize the Δ phase, therefore the Ni-containing compound was annealed at 800°C to avoid a large amount of Δ phase. A variation of the C/B ratio with C/B>9/1 has a small effect on corrosion and magnetization behaviour and on lattice constants but it has a strong effect on the phase transition behaviour. Therefore the Δ stabilizing effect of Ni can be overcome by a slightly higher B content.

These are important results for applying a thermo-mechanical treatment. Further investigations to obtain anisotropic bulk material are in progress.

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