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Structure and properties of a novel boride $(V_{0.92}Fe_{0.08})_2FeB_2$ with partially ordered U_3Si_2-type

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ABSTRACT

X-ray single-crystal structure analysis was performed for the novel compound $V_{1.84}Fe_{1.16}B_2 \equiv (V_{1-x}Fe_x)_2FeB_2$ at $x = 0.08$ (*P4/mbm*; a = 0.555931(9) nm, c = 0.306781(5) nm; U_3Si_2-type). Consequently, structural identity is obvious between $(V_{0.92}Fe_{0.08})_2FeB_2$ and the precipitates $V_{\sim 2}Fe_{\sim 1}B_2$ earlier identified in the UGISTAB215XH permanent magnet. Magnetic and ^{57}Fe Mössbauer studies of $(V_{0.92}Fe_{0.08})_2FeB_2$ reveal a magnetically ordered ground state with $T_c \sim 110$ K. Mössbauer spectra point towards a ferrimagnetic spin arrangement.

Enthalpy of formations (DFT calculations) for (Fe,V), VB, V_3B_2, and the hypothetical solution $V_{3-x}Fe_xB_2$ ($x<1.5$) clearly document that the tie-line between (Fe,V) and VB is more stable than the continuous solid solution of the U_3Si_2-type phase. This explains the experimental observation that (i) binary V_3B_2 only dissolves a minor amount of Fe (replacing V), and that (ii) binary V_3B_2 and isotypic $V_{1.84}Fe_{1.16}B_2$ appear as independent phases in the ternary phase diagram.

Calculation of the electron localization function elf yielded a very high value ($\Upsilon \sim 0.75$) between boron atoms documenting strong covalent bonding. The Young's modulus E (from nano-indentation) for $V_{1.84}Fe_{1.16}B_2$ is 442 GPa. The higher anisotropy in the ternary boride V_2FeB_2 is concluded from the significantly higher difference between C_{11} and C_{33} in V_2FeB_2 (192.1 GPa) with respect to V_3B_2 (117.0 GPa).

1. Introduction

The present paper intends to shed light on a ternary compound that was revealed in a careful evaluation of the phase relations in the ternary system V-Fe-B at 1080 °C by Homolova et al. [1–3]. In contrast to earlier findings of Kuzma and Starodub [4], this compound appeared as a novel phase (labelled as "T-phase" [1] of unknown crystal structure) with a very narrow homogeneity region around the chemical composition V32Fe28B40 (in at.%). The interest in the system V-Fe-B came from the facts that vanadium and boron are important alloying constituents in the production of creep resistant modified ferritic and austenitic steels to suppress the so-called type IV cracking and to extend the creep life [5]. Furthermore vanadium as a strong boride-former improves hardness and wear resistance [6,7]. To the best of our knowledge, the T-phase, although an important alloy constituent, has neither been characterized with respect to crystal structure nor to physical properties.

Independently, Bras et al. [8] identified via Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray (EDX) analyses of the UGISTAB215XH permanent magnet (Nd13.5Dy1.5Fe67Co5V4B8Aℓ1 in at.%) a V-rich boride precipitate $V_{3-x}Fe_xB_2$ inside the hard magnetic phase; these precipitates enhanced the hard magnetic coercivity [9]. From the tetragonal lattice (a = 0.556 nm, c = 0.306 nm) and EDX-composition the formula V_2FeB_2 (ratio V: Fe ≅ 2) was attributed, which suggested a connection to binary V_3B_2 by V/Fe substitution [8].

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Based on the findings of Kuzma and Starodub [5], a thermodynamic analysis of the phase relations in the system V-Fe-B has been performed by Tojo et al. [10]: this Calphad treatment (from a time when the T-phase still was un- discovered) was backed by Density Functional Theory (DFT) calculations of the enthalpies of formation of the binary borides pertinent to the ternary system. A more recent Calphad calculation [1] integrated the T-phase according to the experimental data of Homolova et al. [2,3]. However, neither crystallographic details of the structure of the $(V,Fe)_3B_2$ phase nor its identity with the T-phase have been elucidated yet. Consequently a detailed structure analysis became the subject of the present work together with a characterization of chemical bonding, band structure, magnetic properties and hardness of the $(V,Fe)_3B_2$ compound. Particularly enthalpy of formation data for $(V,Fe)_3B_2$ in comparison with binary V_3B_2 from DFT calculations are of interest.

2. Experimental details

2.1. Transmission electron microscopy (TEM); electron microprobe (EMPA), X-ray structure analyses and hardness measurements

For TEM investigation of the crystal structure of the T-phase in comparison with V_3B_2 we used two alloys, prepared and labelled by Homolova et al. [1]: alloy 2 (67Fe-15V-18B in at.%, annealed at 1353 K, 60 days, for the T phase) and alloy 4 (13Fe-62V-25B, annealed at 903 K, 190 days, for the V_3B_2 phase), respectively. Samples were polished using standard procedures, microstructures and compositions were checked by scanning electron microscopy (SEM) using a TESCAN LYRA 3XMU FEG/SEM×FIB microscope operated at 20 kV and equipped with an Oxford Instruments X-Max80 energy dispersive X-ray (EDX) analyser. A Philips CM12 STEM transmission electron microscope (TEM) operated at 120 kV with an EDAX EDX analyser was employed to get information about crystal symmetry and lattice parameters of selected phases. Thin foils for the TEM study were prepared by twin jet electropolishing with 5 vol% of acetic acid plus 95 vol% of perchloric acid.

Single crystal (SC) specimens suitable for X-ray structure determination were extracted from the alloy (see insert on microstructure in Fig. 1), which was situated on the tie-line between the T-phase and (Fe,V) and which had an overall composition V42Fe40B18 (in at.%). The alloy was immersed in concentrated HCl which quickly dissolved the (Fe,V)-matrix exposing well crystallized material of the ternary boride. Rather “spherical” single crystal fragments with “diameters” in the range of 30–60 μm were selected for X-ray analyses and were inspected on an AXS D8-GADDS texture goniometer, which assured high crystal quality, unit cell dimensions and Laue symmetry of the single crystal specimens prior to X-ray intensity data collection at room temperature on a four-circle APEX II diffractometer equipped with a CCD area detector and an Incoatec Microfocus Source IμS (30 W, multilayer mirror, Mo-$K\alpha$; $\lambda = 0.071069$ nm; detector distance of 3 cm; full sphere; $2° < 2\theta < 70°$). Besides the general treatment of absorption effects using the multi-scan technique (SADABS; redundancy of integrated reflections >8) [11], no individual absorption correction was necessary because of the rather regular crystal shape and small dimensions of the investigated specimens ($30 \times 35 \times 50$ μm). The crystal structure was solved applying direct methods (Program SHELXS-97) and refined against F^2 (Program SHELXL-97-2) within the program WINGX [12]. Finally the crystal structure was standardized with the program Structure Tidy [13].

After the single crystals were successfully selected, the rest of the residue was analyzed by X-ray powder diffraction with Ge-monochromated Fe-$K\alpha_1$ radiation ($\lambda = 0.1936042$ nm) employing a Guinier-Huber image plate recording system. Rietveld refinements were performed using the program FULLPROF [14], whilst precise lattice parameters were obtained by a least squares fit with the program STRUKTUR [15] whereby Ge served as an internal standard (a_{Ge}= 0.5657906 nm). Nano-indentation measurements were performed by a nano-indenter TTX NHT at room temperature at a maximum load of 50 mN. Loading and unloading rates were 100 mN/min with 10 s pause before unloading. Twenty indents were performed to verify the accuracy of the indentation data.

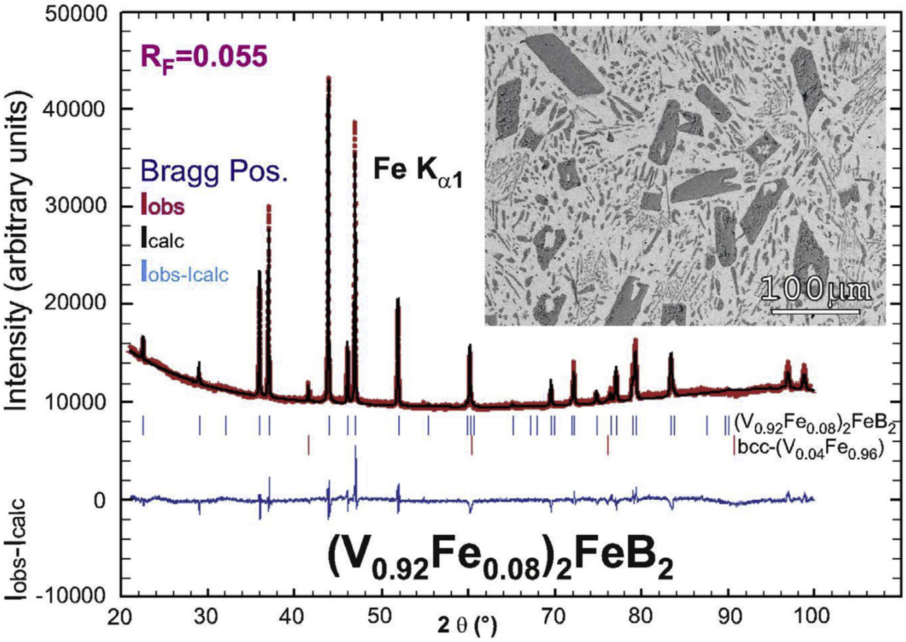

Fig. 1. Results of Rietveld refinement for the acid solution residue of alloy V42Fe40B18 (EPMA, at. %), confirming the presence of $V_{1.84}Fe_{1.16}B_2$ (U_3Si_2-type) + (Fe,V)-matrix (W-type). Vertical bars represent the location of indexed peaks. A SEM backscatter micrograph of V42Fe40B18 is shown as insert with edged dark crystals of $V_{1.84}Fe_{1.16}B_2$.