Journal of Alloys and Compounds 509 (2011) 9451–9455

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

HIP synthesis of η-carbide-type nitrides Fe_3W_3N and Fe_6W_6N and their magnetic properties

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ARTICLE INFO

Article history:
Received 9 May 2011
Received in revised form 7 July 2011
Accepted 8 July 2011
Available online 20 July 2011

Keywords:
Nitride materials
Gas–solid reactions
Sintering
Magnetisation
High magnetic field
Mössbauer spectroscopy

ABSTRACT

We have succeeded in synthesising iron–tungsten nitrides using the hot isostatic pressing (HIP) method and have measured their magnetic properties. Two η-carbide-type iron–tungsten nitrides with lattice constants $a = 11.043(1)$ and $10.937(2)$ Å were synthesised directly from metal elements under high-pressure nitrogen gas. Their compositions are expected to be Fe_3W_3N and Fe_6W_6N in analogy with other η-carbide-type compounds. Fe_3W_3N is a ferromagnet with a Curie temperature $T_C = 110$ K and a saturation moment $P_S = 0.78\mu_B$/Fe, whereas Fe_6W_6N is an antiferromagnet with a Néel temperature $T_N = 75$ K and shows a metamagnetic transition at around 25 T.

1. Introduction

The magnetism of iron-based and iron-alloy-based nitrides has been studied extensively because iron tends to have a large moment and is an earth-abundant element. Several iron nitrides (α-FeN, α′-FeN, α″-$Fe_{16}N_2$, γ′-Fe_4N, ε-Fe_3N, etc.) are known to exist [1]. Among them, α″-$Fe_{16}N_2$ has attracted much attention owing to its giant moment exceeding the value expected from the Slater-Pauling curve (for example, [2]), although several controversial reports are present [1,2]. $Sm_2Fe_{17}N_3$ is one of the most important iron-based nitrides because its Curie temperature, uniaxial anisotropy, and saturation moment are higher than those of $Nd_2Fe_{14}B$ (for example, [3]). In materials such as iron nitrides mentioned above and $Sm_2Fe_{17}N_3$, nitrogen atoms occupy interstitial sites and expand the lattice, stabilising the magnetic moment and improving the magnetic properties of these materials. However, although these materials are magnetically interesting, they cannot be used for industrial applications; this is because, these materials have low decomposition temperatures, and hence, they cannot be sintered in bulk, an important requirement for industrial use. On the other hand, iron-based nitrides containing other *d*-block elements, such as those of the η-carbide-type (Fe_3Mo_3N [4], Fe_3Nb_3N [5], Fe_3W_3N [6], and Fe_4W_2N [7]) and of the filled β-Mn-type ($Fe_{2-x}M_xMo_3N$ (M = Ni, Pd, Pt) [8]), are obtained by heat treatments at relatively high temperatures (~1000 °C). In order to sinter nitrides in bulk, a high-temperature reaction is likely to be more suitable. If these materials are found to be ferromagnetic at room temperature, they would be promising for industrial application. Recently, ferromagnetism has been reported in filled β-Mn-type nitrides [8]. Although their Curie temperatures are lower than room temperature (the highest Curie temperature of 225 K was obtained for $Fe_{1.25}Pt_{0.75}Mo_3N$), it is expected that some related compounds will exhibit room-temperature ferromagnetism.

The general formula of η-carbide-type compounds with the cubic Fe_3W_3C-type crystal structure (space group $Fd\bar{3}m$) is $M_6^fT_4^eT_2^dX_m^cX_n^a$, where M = Nb, Mo, W, Ta,. . .; T = Cr, Mn, Fe, Co, Ni; X = C, N, O; $m = 0, 2$; and $n = 0, 1$. The superscripts *f*, *e*, *d*, *c*, and *a* represent Wyckoff positions. In the case of $m = 2$ and $n = 0$, that is, T_3M_3X, the structure is referred to as η-6 (the number represents the number of metal atoms per X atom). Similarly, the case of $m = 0$ and $n = 1$, that is, T_6M_6X, is called η-12. The short T–T distances of 2.5–2.6 Å suggest that these η-carbide-type compounds will exhibit itinerant

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doi:10.1016/j.jallcom.2011.07.025

electron magnetism. However, few physical properties of these η-carbide-type iron-based nitrides have been reported.

Recently, we conducted a detailed study on Fe_3Mo_3N and found that this material does not order magnetically down to 0.5 K but shows a non-Fermi liquid behaviour in a low temperature region [9]. This material is located in the vicinity of the ferromagnetic quantum critical point. Ferromagnetism is easily induced by external perturbations. A very sharp itinerant electron metamagnetic transition was observed at 14 T at low temperatures. The substitution of a small amount of Co induces ferromagnetism with Curie temperatures lower than 20 K [10]. Hence, the magnetism of related iron nitrides is also expected to be interesting.

In general, the difficult synthesis of nitrides prevents us from studying the physical properties of these materials. Fe_3Mo_3N, Fe_3W_3N, and Fe_4W_2N were first synthesised by the ammonolysis of precursors $FeMoO_4$ for Fe_3Mo_3N [4] and metal-organic compounds for Fe_3W_3N [6] and Fe_4W_2N [7]. The handling of hazardous ammonia gas and air-sensitive metal-organic compounds requires special equipment. Prior and Battle developed an easy method for synthesising Fe_3Mo_3N in a single step by heating a mixture of Fe_2O_3 and MoO_3 in the proper molar ratio in a N_2(90%)-H_2(10%) gas stream [11]. We adopted this method to synthesise Fe_3Mo_3N in our studies on its physical properties [9,10]. This method also appeared to be promising for the synthesis of tungsten systems, but it was later found to be unsuitable.

A serious problem in synthesising nitrides is the desorption of nitrogen at high temperatures, resulting in the decomposition of the compound. To overcome this difficulty, we select the hot isostatic pressing (HIP) technique, which is often used to sinter nitrides such as Si_3N_4 at high temperatures. High-pressure nitrogen gas possibly suppresses the decomposition. We found that the iron–tungsten nitrides, Fe_3W_3N and Fe_6W_6N, can be synthesised directly from metal elements under high temperature and pressure. Magnetisation measurements revealed that Fe_3W_3N is a ferromagnet with a Curie temperature T_C = 110 K and that Fe_6W_6N is possibly an antiferromagnet with a Néel temperature T_N = 75 K.

2. Experiments

The HIP system (Kobe Steel, Ltd.) at Doshisha University was used in this experiment. A cold-pressed specimen, that is, a mixture of powdered iron and tungsten weighted in a proper molar ratio, was placed in a high-pressure vessel equipped with a carbon heater. The sample was capped with an alumina crucible to prevent carbon contamination. The vessel was purged several times and finally filled with nitrogen gas. The initial gas pressure was adjusted to attain the target pressure at the final temperature. The maximum temperature and pressure were 1500 °C and 200 MPa, respectively. The temperature was raised gradually and was maintained at the target temperature for 1–2 h. Then, the heater was turned off to cool the sample in the furnace. After the cooling, the pressure was released.

The synthesised samples were examined by X-ray diffraction (XRD) analysis (Rigaku MiniFlex) using Cu Kα radiation. Electron probe microanalysis (EPMA) was performed for some samples to determine chemical compositions. The temperature dependence of the magnetisation in the range of 5–300 K and up to 7 T was measured using a superconducting quantum interference device (SQUID) magnetometer, MPMS (Quantum Design) at the Research Center for Low Temperature and Materials Sciences, Kyoto University. ^{57}Fe-Mössbauer spectra of Fe_3W_3N were recorded at University of Hyogo using a constant acceleration method at several temperatures. The high-field magnetisation measurement was performed using a pulse magnet at ISSP, The University of Tokyo, up to 54 T at 4.2 K.

3. Results and discussion

3.1. Synthesis and phase analysis

Fig. 1 summarises the heat treatment conditions, namely, temperature and pressure, and the results of XRD characterisation. The numbers in parenthesis indicate the order in which the experiments were conducted. Case 1 (1500 °C, 200 MPa) was studied first. Although no liquid phase exists below 1500 °C in the Fe–W phase diagram [12], the surface of the specimen was found to be melted.

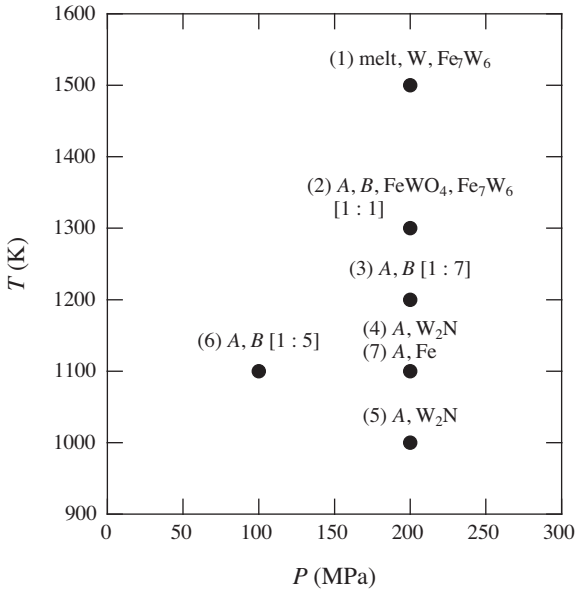

Fig. 1. HIP temperature and pressure conditions and obtained phases. The numbers in parenthesis indicate the order in which the experiments were conducted. The numbers in brackets represent the ratio of *A* to *B* estimated from XRD main peaks. The phases *A* and *B* are identified as Fe_3W_3N and Fe_6W_6N, respectively.

XRD showed that the sample consists of W and Fe_7W_6. No nitride phase was observed.

Fig. 2 shows the XRD pattern of sample 2 (1300 °C, 200 MPa) with the calculated pattern of Fe_3W_3N [6]. We found two sets of peaks, which were characteristic for the η-carbide-type structure. These η-carbide-type iron–tungsten nitrides were synthesised from pure elements for the first time. We name the phase with the larger lattice constant *A* (corresponding to the reflections indicated by solid triangles) and that with the smaller lattice constant *B*

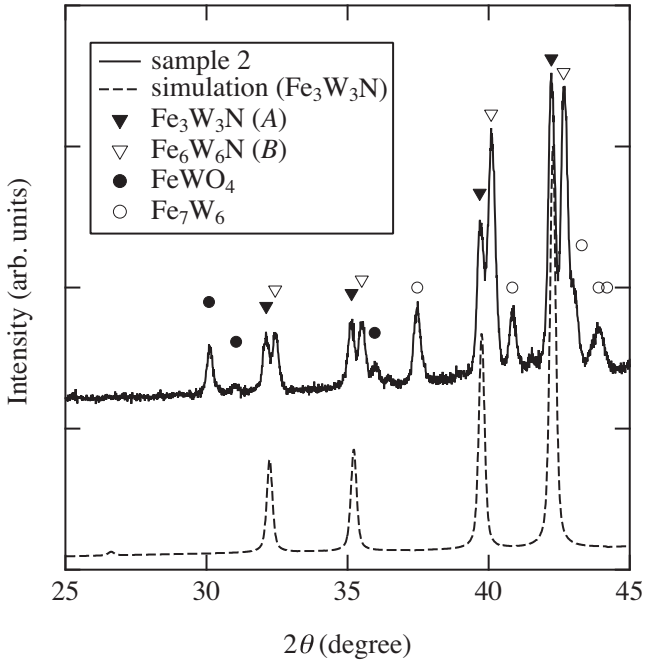

Fig. 2. The XRD pattern of sample 2 (solid curve). The simulated pattern of Fe_3W_3N [6] is represented by the dashed curve. Solid triangles, open triangles, solid circles, and open circles indicate reflections of Fe_3W_3N (*A* in the text), Fe_6W_6N (*B*), $FeWO_4$, and Fe_7W_6, respectively.