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Superconductivity in the hexagonal-layered nanolaminates Ti_2InC compound

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Abstract

The hexagonal-layered Ti_2InC compound is a member of the large family of lamellar materials that crystallize in the hexagonal structure with space group $P6_3/mmc$, which are isomorphs with the Cr_2AlC compound, and known as H-phase. In this work the Ti_2InC phase is investigated by X-ray diffraction, magnetization and resistivity measurements. Susceptibility and resistivity measurements display superconducting critical temperature close to 3.1 K. In spite of the great number of compounds which belong to this family, superconductivity has been reported only for four cases: Mo_2GaC, Nb_2SC, Nb_2AsC and Nb_2SnC. This work supports the existence of a new class of superconducting materials that crystallize in an H-phase.

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Keywords: A. Superconductivity; C. H-phase; C. Nanolaminates; E. Carbides

1. Introduction

Recently a new family of layered ternary carbides, referred to as "MAX" or "H-phase", has attracted the attention of material scientists as well as physicists and chemists [1–3]. The H-phase materials exhibit a number of interesting properties such as high strength and modulus, damage tolerance at room temperature, high thermal and electrical conductivities, and being readily machinable by high speed steel tools [4,5]. The unique combination of these properties makes H-phase materials candidates for various applications. The MAX-phase consists of one transition metal M with A being an A-group element (mostly III A and IV A) and X being either carbon or nitrogen. These compounds have the general formula $M_{n+1}AX_n$, with $n = 1$, 2 or 3, which are composed of molecular layers of the d-metal carbide separated by atomic networks of p-elements. Due to this structure, the nanolaminate compounds combine the elastic and thermomechanical properties inherent to d-metal carbides and some other interesting thermal, electrophysical, and tribological properties [1–5]. Among those phases is Ti_2InC which was first reported by Jeitschko et al. [6] and recently synthesized in bulk form [7]. The presence of covalent-bonded TiC octahedral, built in 2D oriented packets connected by In metallic layers which promote an untypical set of properties, has not been reported for any metallic or ceramic materials.

Although Nowotny synthesized several phases with M_2AX stoichiometry, only four articles have reported superconductivity in this type of structure, which are Mo_2GaC, Nb_2SC, Nb_2SnC, and Nb_2AsC [8–11]. However, the Nb_2SnC has only been obtained in single phase when synthesized under high pressure**.** Theoretical arguments suggest that the superconductivity in the Nb_2SC compound arises from pairing of electrons of the sulfur atoms [12]. This suggests that a decisive role in the superconductivity of nanolaminates is played by electron–phonon coupling involving niobium carbide layers. Differences in the superconducting behavior of the nanolaminates Nb_2SnC and Nb_2SC have shown that their critical transition temperatures are correlated with the orbital contributions of the carbon atoms [12]. These results indicate that the superconducting behavior should not be a particularity of these four compositions.

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Within this scenario we report in this work the observation of superconductivity in the Ti_2InC compound which was prepared under ambient pressure. The results revealed that the compound superconducts below 3.1 K. Sharp superconducting transitions in both transport and magnetization measurements are observed. The results suggest that the so-called nanolaminates M_2AX compound may represent a new class of superconducting material.

2. Experimental procedure

The samples were prepared using mixtures of graphite (<325 mesh), Ti (<325 mesh), and In powders of high purity in the Ti_2InC stoichiometry. The mixture of powders were compacted in square shape of 10×10 mm^2 and 2 mm in thickness, sealed in quartz ampoules, and placed in a tubular furnace at 800 °C for 24 h under ambient pressure. After this heat treatment, the samples were ground and homogenized in agate mortar, compacted again in the same dimensions mentioned before, and heat treated at the same temperature additionally for 96 h. Some samples were heat treated at higher temperatures in order to study the effect of the temperature on the formation of the Ti_2InC phase. The samples were characterized by X-ray diffraction in a Shimadzu diffractometer (model XRD 6000) using Ni filter Cu Kα radiation. The microstructures of the samples were observed by Scanning Electron Microscopy (Leo Zeiss equipment). Electrical resistance as a function of temperature were performed by using the conventional four-point probe method in the interval between 2.0 and 300 K in an Oxford Instruments (MagLab EXA-9 T). Magnetization measurements (magnetization versus temperature and versus applied magnetic field) were carried out in a 5 T SQUID magnetometer from Quantum Design.

3. Results and discussion

Typical X-ray diffractograms, displayed in the upper part of Fig. 1, for the samples heat treated at 800 °C show that they are single phase. The simulated diffractogram (bottom of Fig. 1) agrees with the experimental results and demonstrates that the single phase samples have hexagonal structure in the space group $P6_3/mmc$ with lattice parameters $a = 3.132$ Å and $c = 14.06$ Å. The lattice parameters are in good agreement with those reported previously by Jeitschko et al. [6]. For the $P6_3/mmc$ structure, Ti, In, and C atoms occupy the 4f, 2d, and 2a positions, respectively. The layered structure consists of three types of slabs, two Ti–In–Ti and one Ti–C–Ti, which obey the sequence C–Ti–In–Ti–C. Furthermore, it is important to emphasize that there are no Ti and In atoms placed below or above the carbon atoms along the c-axis.

For samples heat treated above 800 °C, the following phases are observed under thermodynamic equilibrium: In, Ti_2C and Ti_2InC, which suggests that the Ti_2InC compound decomposes by a peritectic or peritectoid reaction at higher temperatures under ambient pressure (see Fig. 2).

Based on the microstructure analysis performed in a sample heat treated at 800 °C, it is possible to observe a homogeneous

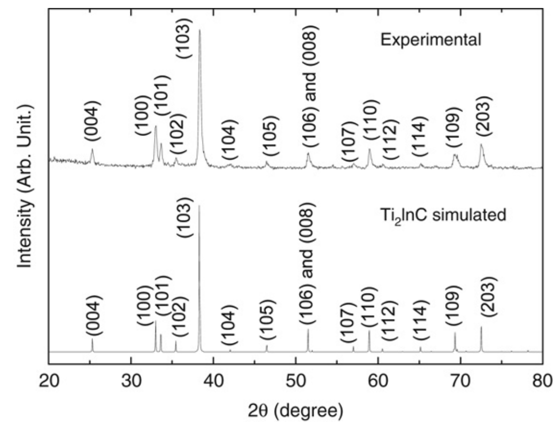

Fig. 1. Experimental (top) and simulated (bottom) X-ray diffractograms for a sample prepared at 800 °C. The results show only peaks of the Ti_2InC phase in agreement with the hexagonal structure.

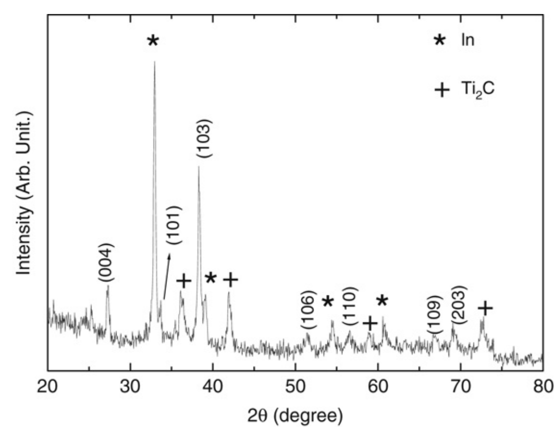

Fig. 2. X-ray diffraction for the sample prepared at 900 °C. The results show a decomposition of the sample in In, Ti_2C and Ti_2InC.

morphology with high porosity due to low heat treatment temperature and consequently poor densification (Fig. 3). The Energy Dispersive Spectroscopy (EDS) analysis reveals that the stoichiometric ratio is in agreement with the nominal composition without traces of segregated phases. The X-ray and microstructure results allow us to say unambiguously that this sample is single phase.

The electrical resistance as a function of temperature measured between 2.0 K and 9.0 K on the same sample is shown in Fig. 4(a). The sharp transition at 3.1 K with transition broadening of ∼0.2 K can be observed in the measurement. In the inset of this figure is displayed the same measurement between 2.0 K and 30.0 K. In Fig. 4(b) is shown the magnetization versus temperature measured in the Field Cooled (FC) procedure. Essentially it is observed that the same transition temperature is displayed in the electrical resistance measurement.

The $M(H)$ curve performed at 2.0 K is displayed in Fig. 5 which clearly reveals the signature of type-II superconductivity. These results reveal bulk superconductivity of the Ti_2InC compound which supports the idea of the existence of a new class of layered superconducting materials with M_2AX composition.

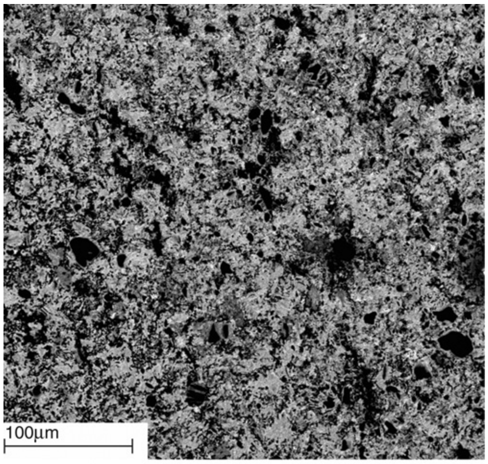

Fig. 3. Micrograph of the Ti_2InC sample related to Fig. 1 revealing single phase microstructure. The spots with different contrast are due to the difference in topography.

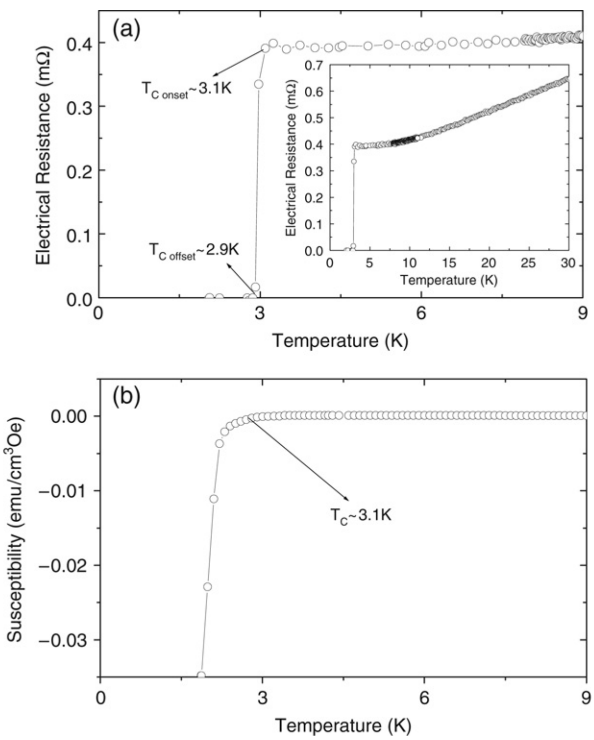

Fig. 4. (a) Electrical resistance as a function of temperature displaying superconducting transition at 3.1 K. In the inset is displayed the same kind of measurement between the 2.0 and 30.0 K interval. (b) displays the susceptibility measurement which shows a diamagnetic transition essentially at the same critical temperature.

4. Conclusion

The compound Ti_2InC with layered structure exhibits zero resistivity and diamagnetism below 3.1 K with bulk type-II superconductivity. The superconducting behavior is extremely dependent on the synthesis method. These characteristics are due to the difficulty in preparing dense samples in this family of materials under ambient pressure. Along with Mo_2GaC, Nb_2SC, Nb_2SnC and Nb_2AsC compounds [8–11] the results reported here suggest a new class of superconducting materials which crystallize in an H-phase with Cr_2AlC structure.

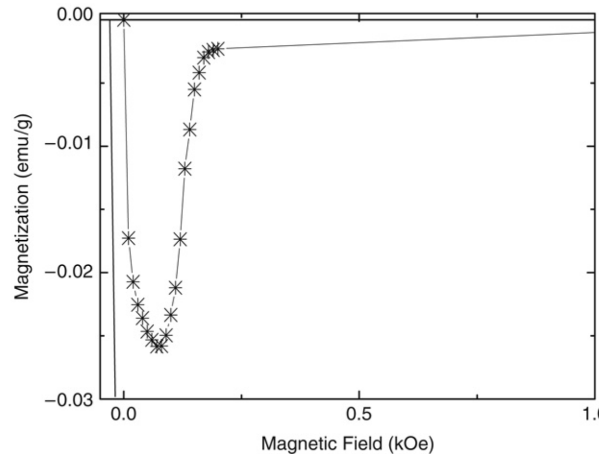

Fig. 5. Magnetization as a function of applied magnetic field at 2.0 K for a Ti_2InC single phase. The result clearly demonstrates the existence of mixed state or type-II superconductivity.

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