Materials Science-Poland, 30(2), 2012, pp. 92-97
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-012-0013-4

VERSITA

Superconductivity at 9.5 K in the Ti_2GeC compound

A.D. BORTOLOZO[1,2*], O.H. SANT'ANNA[1], C.A.M. DOS SANTOS[1], A.J.S. MACHADO[2]

[1] Departamento de Engenharia de Materiais, Escola de Engenharia de Lorena – USP, P.O. BOX 116, Lorena – SP, 12600-970 Brazil

[2] Universidade Federal de Itajubá, Campus de Itabira, 35903-087 Itabira – MG, Brazil

We report on the investigation of the Ti_2GeC properties by X-ray diffraction, magnetic and electrical resistivity measurements. Polycrystalline samples of Ti_2GeC with nominal compositions were prepared by solid state reaction. X-ray powder patterns suggest that all peaks can be indexed with the hexagonal phase of Cr_2AlC prototype. The temperature dependence of both electrical resistivity and magnetization indicate a bulk type-II superconductivity at 9.5 K. Magnetoresistive data suggest an upper critical field of $B_{c2} \sim 8.1$ T and coherence length ~ 61 Å. Furthermore, the results highlight the highest critical temperature reported up to now for an H-phase.

Keywords: *superconductivity, carbide, nanolaminates, MAX phase*

1. Introduction

The $M_{n+1}AX_n$ (MAX) phases, where $n = 1 - 3$, are layered hexagonal compounds, in which near close-packed layers of *M* early transition metals are interleaved with the layers of group A element, mostly IIIA and IVA, with the *X*-atoms C and/or N, filling the octahedral sites between the *M* layers. Most of these phases were synthesized in powder form in the 1960s by Nowotny [1]. Nowadays, it is fairly well established that these phases have an unusual and sometimes unique combination of properties. [2–16] They are elastically stiff, have relatively low thermal expansion coefficients, and have good thermal and electrical conductivities [2, 17]. They are relatively soft, with Vickers hardness values of 2–8 GPa, easily machinable, thermal shock and damage tolerant. Some are fatigue, creep, and oxidation resistant [18]. At higher temperatures, they can undergo a brittle-to-plastic transition [12]. Some of them, such as Ti_2AlC, are exceptionally oxidation resistant and are candidate materials for high temperature structural applications [19]. Current interest in the fabrication of MAX compounds has been driven by initial reports, which indicate that the properties are quite unusual and these materials may have a wide range of potential uses. In 1963, Jeitschko *et al.* determined that Ti_2GeC has a hexagonal crystal structure with a = 3.079 Å and c = 12.93 Å [20] and is a member of MAX family. Indeed, Ti_2GeC phase is a natural nanollaminate, constituted of layered metal carbide [21]. The electronic structure and the bonding properties of the layered ternary carbide Ti_2GeC have been investigated by means of ab-initial linear combination of atomic orbital calculation [22]. The authors determined in that calculus that the electrical conductivity of Ti_2GeC is metallic and anisotropic. The electronic structure calculus suggests that the major factor governing the electronic properties is the pd hybridization from Ti 3d and C 2p states. Furthermore, the calculations suggest that Ge addition changes the C−Ti−C−Ti covalent bond chain into a C−Ti−Ge−Ti−C bond chain through its reaction with Ti. Within Ge layers the atoms are bonded through sp hybridization. Thus the structure of Ti_2GeC can be considered as two-dimensional close-packed Ge layer intercalated between the layers of Ti_6C octahedral [22].

So far, little work has been done regarding to the superconducting properties of this family of compounds, in particular the M_2AX compounds. Indeed, in the last years Bortolozo *et al.* have shown that it is possible to induce superconductivity in this family [23–25]. So, the principal goal of this paper is to

*E-mail: bortolozo@demar.eel.usp.br

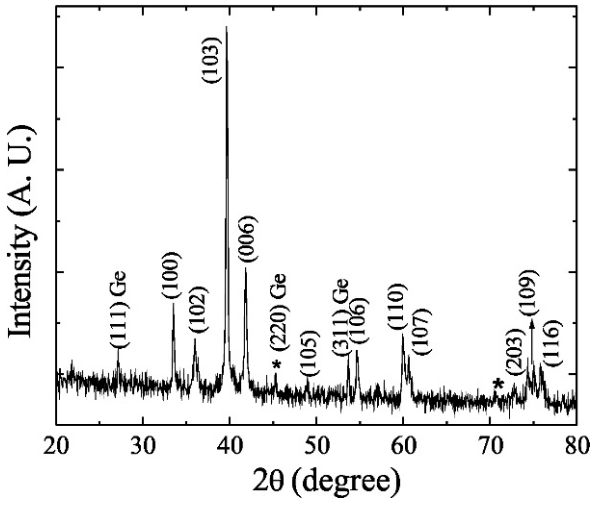

Fig. 1. X-ray diffractogram for the Ti_2GeC sample heat treated at 1200 °C for 120 h. the peaks are indexed by using a hexagonal symmetry Cr_2AlC prototype. Traces of metallic Ge can be found.

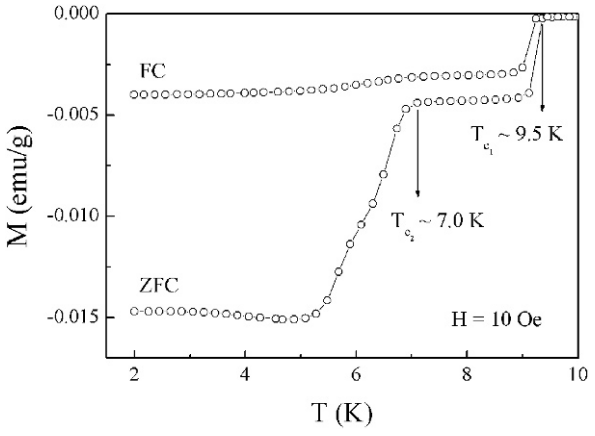

Fig. 2. Magnetization as a function of temperature for the sample presented in Fig. 1. The ZFC and FC regimes suggest superconducting behavior with the onset critical temperature close to 9.5 K.

report on the superconducting behavior observed in the Ti_2GeC compound. The results obtained through the electrical resistivity, magnetization and x-ray diffraction measurements indicate that Ti_2GeC is another superconducting material belonging to the large family of M_2AX compounds.

2. Experimental procedure

Ti_2GeC compounds were prepared using the mixtures composed of appropriate amounts of high purity graphite, Ti, and Ge powders. The mixture was compacted into a hexagonal structure of 8×8 mm^2 and 2 mm in thickness, sealed in quartz ampoules, and placed in a tubular furnace at 1000 °C for 24 h under ambient pressure. After this heat treatment, the samples were ground and homogenized in agate mortar, compacted again into the same dimensions as before, and heat treated at 1200 °C for 120 h. Some samples were heat treated at a higher temperature (1500 °C) in high vacuum for 30 minutes, in order to study the effect of the temperature on the formation of the Ti_2GeC phase.

All the samples were characterized by x-ray diffraction with a Shimadzu diffractometer (model XRD 6000) using CuKα radiation and Ni filter. The simulation of the structure and refinement of the lattice parameters were carried out using Powder Cell software [26]. The simulation of the crystal structure was based on the literature data and the results were compared with experimental diffractograms [27].

The measurements of electrical resistance as a function of temperature, R(T), were performed in the temperature interval between 2.0 and 30 K, by conventional four-point probe method with an equipment of the Oxford Instruments (MagLab EXA-9 T). Some R(T) curves were also determined under applied magnetic field in order to determine the field dependence of the superconducting critical temperature. The measurements of magnetization as a function of temperature, M(T), were carried out with a 5 T SQUID magnetometer of the Quantum Design using Field Cooling (FC) and Zero Field Cooling (ZFC) procedures.

3. Results and discussion

Ti_2GeC sample with a hexagonal structure, heat-treated at 1200 °C for 120 h was examined using XRD. Fig. 1 shows the diffraction pattern of the Ti_2GeC sample. The majority phase can be well indexed in the structure with Cr_2AlC prototype within the experimental resolution of the diffractometer. Some peaks can be also indexed as metallic germanium. The Rietveld refinement results agree with a

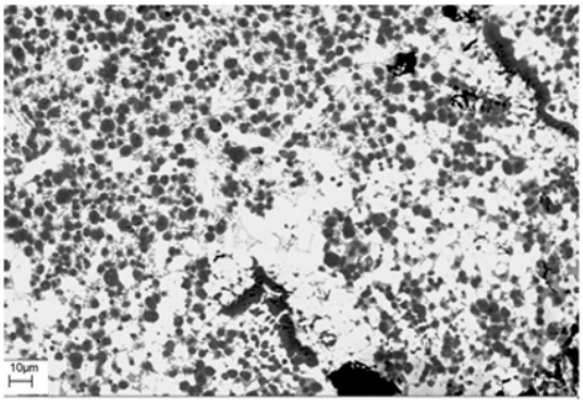

Fig. 3. SEM images for the sample annealed at 1500 °C for 30 minutes. Two phases in equilibrium can be clearly seen in the microstructure. The EDS analysis reveals Ti_2GeC (matrix phase) and Ti_2C (dark lobes).

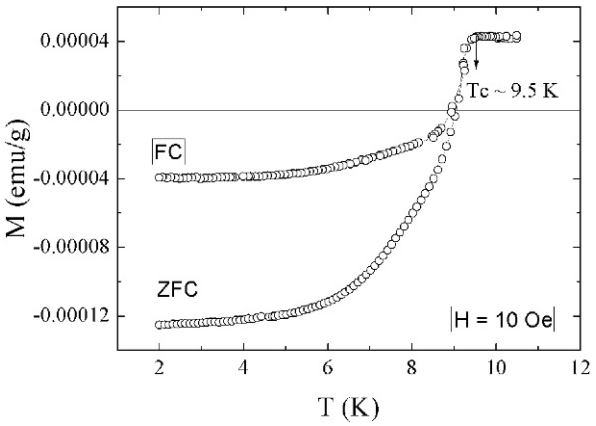

Fig. 4. Magnetization measurements in zero-field (ZFC) and field cooling (FC) procedures of the Ti_2GeC compound. A clear diamagnetic behavior below 9.5 K is in agreement with the electrical resistance measurement. The critical temperature close to 9.5 K can be attributed to the ternary phase and the second transition at 7.0 K – to the contamination by Ti_2C doped with Ge.

hexagonal lattice, space group $P6_3/mmc$ with the lattice parameters of a = 3.078 Å and c = 12.92 Å. These results are in good agreement with the data reported by Jeitschko *et al.* [20]. The magnetization measurement of this sample showed a diamagnetic signal below 9.5 K, as displayed in Fig. 2. This result strongly suggests superconductivity with the onset temperature close to 9.5 K. However, the magnitude of the diamagnetic signal is small, which indicates that the superconductivity is not the bulk effect. Indeed, the resistive behavior does not show any superconducting signal down to 2.0 K. In order to improve the superconducting volume fraction, the sample was annealed at 1500 °C. The diffractogram shows that the hexagonal phase is in equilibrium with Ti_2C (not shown). These results suggest a decomposition of the hexagonal phase, but it is difficult to identify which transformation occurs at this temperature. The Ti_2C compound is a superconducting material which displays the superconducting critical temperature close to 3.1 K [23]. The phase equilibrium can be easily observed in the microstructure analysis. Fig. 3 shows the thermodynamic equilibrium in the SEM micrograph where two phases can be recognized as dark and white grains. The white grains represent the matrix phase in which the dark grains are distributed. The EDS analysis of each grain revealed Ti_2GeC (matrix phase) and dark phase of Ti_2C doped with Ge. These results suggest that the Ti_2C doped with Ge could represent an intermediate phase between the precursors and the ternary phase of interest.

In order to determine the superconducting behavior of this material the measurement of magnetization as a function of temperature was performed. A plot of M(T) curve is shown in Fig. 4. It is possible to observe a clear superconducting behavior due to the diamagnetism signal in the Zero Field Cooled (ZFC) and Field Cooled (FC) procedures. The superconducting critical temperature of the material is close to 9.5 K. Furthermore, a second magnetic transition close to 7 K is observed. The plateau region of magnetic measurement between 7 K and 9 K corresponds to the flux penetration into the grains. The intragranular peak is subtle (FC regime), probably because the magnetic penetration (near the critical temperature) is comparable to the grain size (< 5 μm). Based on the SEM results (Fig. 3) we can attribute the first superconducting transition to the ternary phase (majority phase) in accordance to the results shown in the Fig. 2 and the second transition to the contamination by Ti_2C doped with Ge.

The sample annealed at 1500 °Cwas characterized by the electrical resistivity measurement as a

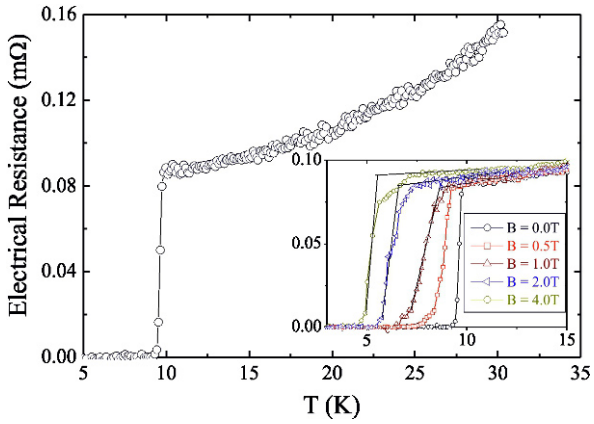

Fig. 5. Electrical resistance as a function of temperature from 2.0 up to 30 K for Ti_2GeC sample. Superconducting behavior can be observed below 9.5 K.

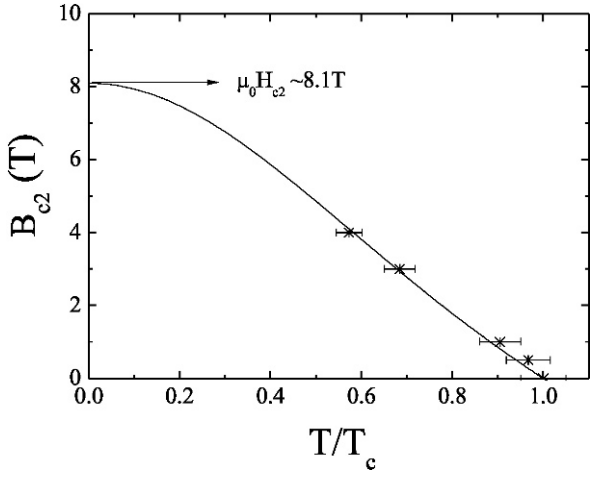

Fig. 6. B_{c2} vs T/T_c behavior built from the points extracted from the inset in Fig. 3. The upper critical field $B_{c2} \sim 8.1$ T is estimated by GL relation revealing $\xi \sim 61$ Å at zero temperature.

function of temperature. The results shown in Fig. 5 indicate that the onset of critical superconducting temperature is close to 9.5 K. The normal state reveals a typical metallic behavior between 10 and 30 K. The magnetoresistance behavior as a function of temperature [R(T,B)] is displayed in the inset of Fig. 5. In this inset one can see a progressive shift of T_c to lower temperatures with increasing B. The superconducting critical temperature can be defined as the normal state and transition extrapolations in the R(T,B) curve as indicated in the inset of Fig. 5. In order to build the B × T phase diagram, we have used the data from R(T,B). The B × T phase diagram, shown in Fig. 6, was plotted according to the criteria explained above. Due to the anisotropic behavior of the Ti_2GeC grains we had expected that the WHH theory is invalid [28]. Therefore we estimated the upper critical field using the Ginzburg-Landau (GL) theory [29, 30] (solid line), where

$$H_{c2}(T) = \frac{\phi_0}{2\pi\xi^2(T)} = H_{c2}(0)\left(\frac{1-t^2}{1+t^2}\right) \qquad (1)$$

In equation (1), $t \equiv T/T_c$ is the reduced temperature. Using this equation one can determine $B_{c2}(0)$ as approximately 8.1 T. This upper critical field value yields a coherence length of $\xi \sim 64$ Å at zero temperature.

The band structure calculations and several physical properties show strong anisotropic characteristics. So, these materials can be considered as two-dimensional.

Recently Bortolozo *et al.* [23] reported that Ti_2InC is also a superconducting material with a critical temperature close to 3.1 K. The band structure calculations also revealed 2D – like behavior with quasi-flat electronic bands along the *c* axis [22]. The near-Fermi bands involved in the formation of superconducting state are formed mainly by Ti 3d states. On the other hand, in 1964, Jeitschko *et al.* discovered the Ti_2InN compound [31], which crystallizes in the same prototype structure of carbide (Cr_2AlC). In this structure, the basic structural component is an octahedron composed of six Ti atoms with an N atom instead of carbon residing in the center [31]. The electronic band structure of this compound shows that the interactions in the TiN octahedra are weaker than those in the Ti_6N octahedral, which is in agreement with the general trend known for binary carbides and nitrides [32]. The electronic structure calculations show that Ti_2InC has 3.67 states/(eV cell) at Fermi level (E_F), while the Ti_2InN has 4.02 states/(eV cell) at E_F [32]. It is clear that the nitrogen atoms change the electronic structure of this compound and increase the state density at Fermi level. This characteristic band structure could probably affect the transport properties of Ti_2InN similar to its close relative – Ti_2InC. Indeed, in our previous work [25] on the electrical transport

in the Ti_2InN compound we found the superconducting critical temperature close to 7.3 K. This result represents the first evidence of superconductivity in the nitride of this family. In comparison with Ti_2InC, the superconducting critical temperature of the nitride compound is more than twice as high. This represents a clear evidence for 2D, characteristic in this class of materials. The nature of the covalent bond in these two materials (Ti_2InC and Ti_2InN) is unambiguously different, such as shown in the electronic band calculations for both materials; therefore superconductivity appears to occur in the M_2X layer. Another important aspect is the nature of the A element in the M_2AX compounds. The M_2X layers in Ti_2InC and Ti_2GeC (this paper) are the same. However, the A element is very important for superconductivity. The In and Ge belong to different groups in the periodic table (In – to 3A group and Ge – to the 4A group). Since Ge is more electronegative, the number of electrons in the outer shell is increased. Due to this fact it is plausible to conclude that there is an increase in the density of states at the Fermi level. This means that much more states are available for occupation, which affects directly the superconducting critical temperature. The results reported in this paper show unambiguously that the element A can work as acceptor or donor of electrons in this new superconducting family.

Perhaps a synthesis under high pressure could produce a single phase sample due the complicated phase equilibrium in this system. Finally, the superconductivity observed in Ti_2GeC represents the highest critical temperature reported so far for a compound of the nanolaminates family.

4. Conclusions

This work reports on a systematic study concerning the electrical and magnetic behavior of the Ti_2GeC compound. The Ti_2GeC compound with the layered structure exhibits zero resistivity and diamagnetism below 9.5 K. The A element is fundamental to the superconducting critical temperature. The synthesis of a single phase sample is very complicated but we speculate that synthesis under pressure may produce a higher quality compounds than the ambient pressure synthesis [2]. Furthermore, the results revealed the highest critical temperature reported so far for the nanolaminate compounds.

Acknowledgements

The work is supported by the FAPESP (grants no. 2009/00610-8, 2004/13267-6 and 2005/1257-9). We are grateful for the magnetization measurements done by Dr. Robson R. da Silva.

References

[1] NOWOTNY H., *Prog. Solid State Chem.*, 2 (1970), 27.
[2] BARSOUM M.W., *Prog. Solid State Chem.*, 28 (2000), 201.
[3] BARSOUM M.W., BRODKIN D., EL-RAGHY T., *Scr. Mater.*, 36 (1997), 535.
[4] BARSOUM M.W., EL-RAGHY T., *J. Am. Ceram. Soc.*, 79 (1996), 1953.
[5] BARSOUM M.W., EL-RAGHY T., *J. Mater. Synth. Process.*, 5 (1997), 197.
[6] BARSOUM M.W., EL-RAGHY T., *Metall. Mater. Trans. A*, 30 (1999), 363.
[7] BARSOUM M.W., EL-RAGHY T., RAWN C.J, PORTER W.D., WANG H., PAYZANT A., HUBBARD C., *J. Phys. Chem. Solids*, 60 (1999), 429.
[8] BARSOUM M.W., FARBER L., EL-RAGHY T., LEVIN I., *Metall. Mater. Trans. A*, 30, (1999), 1727.
[9] BARSOUM M.W., YAROSCHUCK G., TYAGI S., *Scr. Mater.* , 37, (1997), 1583.
[10] EL-RAGHY T., BARSOUM M.W., *J. Am. Ceram. Soc.*, 82, (1999), 2849.
[11] BARSOUM M.W., EL-RAGHY T., OGBUJI L., *J. Electrochem. Soc.*, 144, (1997), 2508.
[12] EL-RAGHY T., BARSOUM M.W., ZAVALIANGOS A., KALIDINDI S.R., *J. Am. Ceram. Soc.*, 82 (1999), 2855.
[13] EL-RAGHY T., ZAVALIANGOS A., BARSOUM M.W., KALIDINDI S.R., *J. Am. Ceram. Soc.*, 80 (1997), 513.
[14] FARBER L., BARSOUM M.W., ZAVALIANGOS A., EL-RAGHY T., LEVIN I., *J. Am. Ceram. Soc.*, 81 (1998), 1677.
[15] LOW I.M., LEE S.K., LAWN B., BARSOUM M.W., *J. Am. Ceram. Soc.*, 81 (1998), 225.
[16] MANOUN B., GULVE R.P., SAXENA S.K., GUPTA S., BARSOUM M.W., ZHA C.S., *Phys. Rev. B*, 73 (2006), 024110.
[17] HETTINGER J.D., LOFLAND S.E., FINKEL P., MEEHAN T., PALMA J., HARRELL K., GUPTA S., GANGULY A., EL-RAGHY T., BARSOUM M.W., *Phys. Rev. B*, 72 (2005), 115120.
[18] BARSOUM M. W. RADOVIC M., *Encyclopedia of Materials: Science and Technology*, edited by K.H.J. Buschow. Elsevier, Amsterdam, 2004.
[19] BARSOUM M.W., TZENOV N., PROCOPIO A., EL-RAGHY T., ALI M., *J. Electrochem. Soc.*, 148 (2001), C551.
[20] JEITSCHKO W., NOWOTNY H., BENESOVSKY F., *Monatsch. Chem.*, 94 (1963), 1201.

[21] BARSOUM M.W., EL-RAGHY T., *Am. Sci.*, 89 (2001), 334.

[22] ZHOU Y.C., DONG H.Y., WANG X.H. CHEN S.Q., *J. Phys. Condens. Matter*, 12 (2000), 9617.

[23] BORTOLOZO A.D., SANT'ANNA O.H., DOS SANTOS C.A.M., MACHADO A.J.S., *Solid. State. Commun.*, 144, 10 (2007), 419.

[24] BORTOLOZO A.D., SANT'ANNA O.H., DA LUZ M.S., DOS SANTOS C.A.M., PEREIRA A.S., TRENTIN K.S., MACHADO A.J.S., *Solid. State. Commun.*, 139 (2006), 57.

[25] BORTOLOZO A.D., SERRANO G., SERQUIS A., RODRIGUES JR D., DOS SANTOS C.A.M., FISK Z., MACHADO A.J.S., *Solid State Commun.*, 150 (2010), 1364.

[26] VILLARS P., CALVERT L.D., *Materials Park: ASM International*, 3 (1991).

[27] KRAUSS W., NOLSE G., *J. Appl. Crystallogr.*, 29 (1996), 301.

[28] WERTHAMER N.R., HELFAND E., HOHENBERG P.C., *Phys. Rev.*, 147 (1966), 295.

[29] MURAKAMI T., XU C.N., KITAHARA A., KAWAHARA M., TAKAHASHI Y., INUI H., YAMAGUCHI M., *Intermetallics*, 7 (1999), 1043.

[30] ISHIDA T., GOLDFARB R.B., KOS A.B., CROSS R.W., *Physical Review B*, 46 (1992), 18.

[31] JEITSCHKO W., NOWOTNY H., BENESOVSKY F., *Monatsh. Chem.*, 95, 1 (1964).

[32] LOUGHRAN R.J., GOLDFARB R.B., *Physica C*, 181 (1991), 138.

Received 18.01.2012
Accepted 14.05.2012