

STRUCTURAL DESIGN AND PROPERTIES OF LAYERED NANOCOMPOSITE TITANIUM CARBIDE-SILICIDE MATERIALS *

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Abstract. The titanium carbide-silicide Ti_3SiC_2 phase with crystal lattice formed by alternative structural blocks with the block thickness in the order of 1 nm, for the first time, is fabricated by the method based on the carbo-thermal reduction of titanium and silicon oxides and high temperature processing of titanium carbide in SiO vapors. It is experimentally revealed that the Ti_3SiC_2 compound (treated as a layered nanocomposite) exhibits the unique combination of properties which are non-typical for conventional ceramic materials. In particular, the crystal structure and chemical transformations showed an increase in the paramagnetic component of magnetic susceptibility, which can be attributed to titanium (III). It is found that the titanium carbide-silicide phase with layered structure has antiferromagnetic properties.

The well-known method of magnetochemical control over the state of paramagnetic atoms in oxygen lattices is applied, for the first time, to titanium carbide-silicide phase. The obtained data can be used as the basis of a new method to control either the formation of layered titanium carbide-silicide phase or the gaseous silicon monoxide content in various physical and chemical processes.

1. INTRODUCTION

Crystal structure design provides the basis for the engineering of solid materials with unique characteristics. Thus, prominent technical parameters of layered superconductors, high strength construction composites and nanocrystalline ceramics allow one to suggest new directions in fabrication of composite materials.

For example, phases with lattices formed by alternative structural blocks with the block thickness sizes in the order of 1 nm can be treated as layered composites. Anisotropic properties revealed in macrocharacteristics are distinctly exhibited by such composites.

The crystal structure of a wide class of complex carbide-nitride is described as a sequence of carbide

(nitride) blocks, separated from each other by hexagonal atomic layers of IIIA and IVA elements. The general formula of layered compound can be expressed as $M_n A_m X_k$, where M is a transition element (Ti, Zr, Hf, V and others) which can form NaCl-type carbide lattices; A denotes IIIA and IVA elements (Si, Ge or Al); X denotes intercalation atoms (C, N or O) capable of occupying octahedral positions created by atoms of transition metals (Fig. 1). Nowadays the most well known compounds of this type are titanium carbide-silicide Ti_3SiC_2 and such compounds as Ti_3GeC_2 , Ti_2GeC , $Ti_3Al_{1.1}C_{1.8}$, Ti_2AlN , $Ti_2AlC_{0.5}N_{0.5}$, Ti_4AlN_3 , etc [1-3]. Layered carbides of 312-type are interesting objects for examining the chemical structure of carbide compounds and the investigation of politypism of complex compounds. Also, they are promising materials for applications.

The interest in the titanium carbide-silicide [4-6] (Fig. 2) has been growing up from the beginning of 90-s. Layered Ti_3SiC_2 possesses the unique combination of the following properties which are non-typical for conventional ceramic materials:

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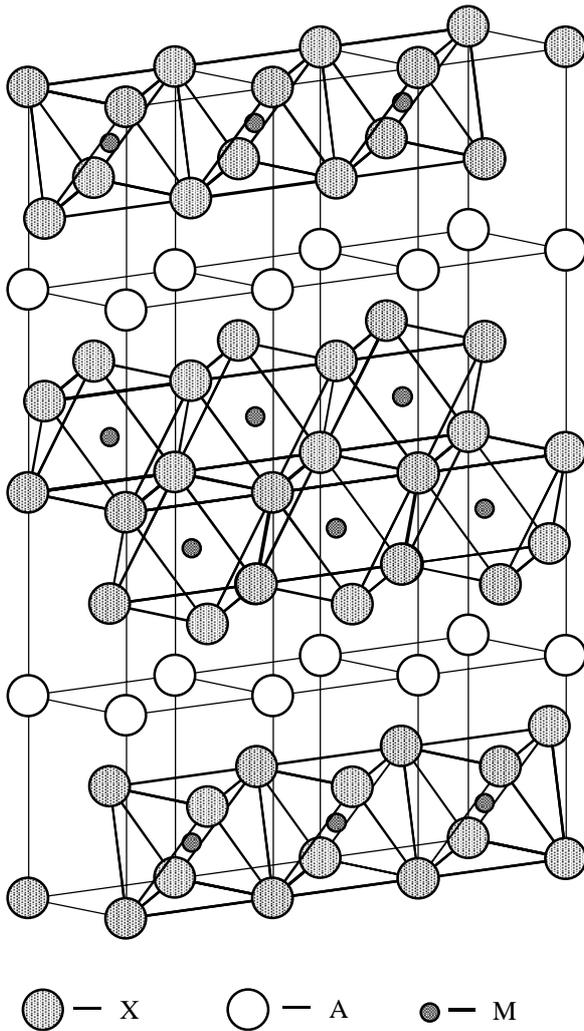


Fig. 1. A-atom layers distributed among MX structural blocks (with distance between the layers (for example A-A) being about 1 nm).

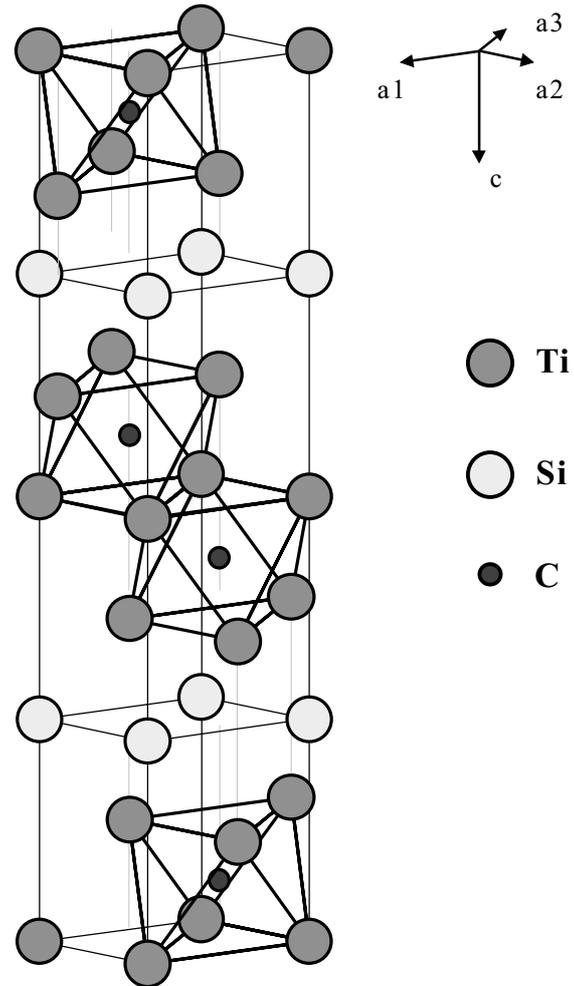


Fig. 2. The Ti_3SiC_2 unit cell.

insensitivity to thermal shock treatment, high resistance to crack formation (attaining 7-9 MPa $\text{m}^{1/2}$) and mechanical hardness are preserved after the temperature abruptly has changed from 1700K to 300K; comparatively high thermo- and electroconductivity; the microhardness changes along the direction of the force action from 4 to 13 GPa; the plasticity at temperatures higher than 1473K; low friction, etc. [7-12] (Table 1). It is important to emphasize that this material (without disintegration) is able to absorb locally considerable amounts of mechanical energy, in which case it is stable relative to various destructive influences.

The above properties are generally stipulated by the layered type of crystal lattice. Hence a similar behavior is expected to be exhibited by layered carbides. Taking into account high functional

characteristics of layered carbides, new ceramic materials are developed on their basis, namely, micro- and nanocomposite ceramics, composites with ceramic matrix, etc.

In this paper we will consider the special features of the crystal structure and some properties of the structural components of Ti_3SiC_2 conceiving it as a layered nanocomposite.

2. COMPARATIVE DESCRIPTION OF TITANIUM CARBIDE TiC AND TITANIUM CARBIDE-SILICIDE Ti_3SiC_2 CRYSTAL STRUCTURES

Titanium carbide TiC has the NaCl-type crystal structure with the cubic cell lattice parameter $a=0.433$ nm (for stoichiometric phase). The distances be-

Table 1. Comparative properties of titanium carbide TiC, silicon Si and titanium carbide-silicide Ti_3SiC_2 .

Properties	TiC	Si	Ti_3SiC_2	
Density, gm/cc	4.92-4.93	2.33	4.53	[1]
Space group	Fm3m	Fd3m	$P6_3/mmc$	[1]
Cell parameter, nm				
A	0.430-0.433	0.543	0.3062	[1]
C			1.7637	[1]
Interatomic distances, nm				
Ti - C	0.2165		0.2135	
Ti - Si			0.2696	
Si - Si		0.384	0.3062	
Ti - Ti	0.3061		0.3062	
Heat capacity C_p at 298K, 34.23 J/mol·K		20.16	110	[7]
Thermal conductivity at 298K, W/m·K	33	95.5	37	[7]
Thermal expansion coefficient, (at 300-1400K), $grad^{-1}$	7.0-7.9	2.3-4.8	9.1	[7]
Brittle-to-ductile transition temperature, K		1100	~1500	[2]
Hardness Hv, GPa	30		4-13	
Fracture toughness K_{1C} , MPa $m^{1/2}$	Less than 4		7 [5], 7-9 [15]	
Shear modulus, GPa			133	[21]
Young modulus, GPa	460-494		325	[21]
Air oxidation resistance (temperature, K)	Till 1100-1300	Till 400-1500	Till 1300-1400	
Activation energy for oxidation, kJ/mol	270		370	[25]
Magnetic susceptibility, 10^6 emu/g	13	- 3.9	83, present work	

tween neighbouring titanium atoms and neighbouring titanium and carbon atoms are $R_{Ti-Ti} = 0.3061$ nm and $R_{Ti-C} = 0.2165$ nm, respectively. This structure can be represented as a sequence of alternated hexagonal (trigonal) layers of titanium and carbon, which are located in the [111] plane. The neighbouring titanium and carbon layers distant by $R_{[Ti-C]} = 0.1250$ nm. The layers are located in the A B C A B C ... sequence, where underlined letters correspond to titanium layers, while non-underlined letters denote carbon layers.

Titanium carbide-silicide Ti_3SiC_2 (Fig. 2) has a hexagonal lattice with the parameters $a=0.3062$ nm and $c=1.7637$ nm. The distances between neighbouring titanium atoms, neighbouring titanium and carbon atoms, and neighbouring titanium and silicon atoms are $R_{Ti-Ti}=0.3062$ nm, $R_{Ti-C}=0.2135$ nm, and $R_{Ti-Si}=0.2696$ nm, respectively. The crystal

structure can be represented as a sequence of hexagonal layers of titanium, silicon and carbon, which are arranged in a plane perpendicular to the *c*-axis. The distances between the atoms in each layer are equal to R_{Ti-Ti} . The distances between neighbouring titanium and carbon layers, and neighbouring titanium and silicon layers are $R_{[Ti-C]}=0.1197$ nm, and $R_{[Ti-Si]}=0.2035$ nm, respectively. The layers are arranged in the A B C **Si** C B A C B **Si** B C ... sequence with underlined, non-underlined and bold letters corresponding to titanium, carbon and silicon layers, respectively.

Titanium carbide-silicide structure Ti_3SiC_2 can be obtained by the substitution of every third carbon layer in titanium carbide TiC by a silicon layer. In this case structural blocks, located between silicon layers and consisting of three titanium and two carbon atomic layers are shifted in such a way as

to provide coincidence of titanium layer orientations. Silicon layers are located between titanium layers.

In the situation discussed, silicon forms atomic planes with the period 0.89 nm between $[\text{Ti}_6\text{C}]$ octahedra blocks, the basic structural elements of titanium-carbide-silicide lattice. Thus, the hexagonal structure is formed with regular alternate silicon- and titanium-carbide layers.

The well-known methods of Ti_3SiC_2 synthesis (CVD, SPS, solid-phase synthesis, reactionary hot isostatic pressing, arc fusion, synthesis from liquid-phase, etc.) [4, 13-20] have some drawbacks, preventing a wide use of Ti_3SiC_2 . The most essential drawbacks are a high cost of initial reagents, the presence of by-products in the final multiphase materials, the necessity of using complex technological equipment and the meeting of rigorous conditions of the synthesis.

In this work the heterophase method of Ti_3SiC_2 synthesis is suggested and studied for the first time. The method is based on high temperature processing of titanium carbide in SiO vapors [22]. To produce SiO, we used condensed silicon monoxide (synthesized by reaction $\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO}$ beforehand) or a $\text{SiO}_2 + \text{Si}$ reaction mixture, which provided $P_{\text{SiO}} \sim 10^2 - 10^3$ Pa at 1573K.

The X-ray analysis of solid products of reaction of gaseous SiO with TiC_x allows us to establish that the formation of Ti_3SiC_2 starts at 1473-1573K. In doing so, no other products have been observed.

Ti_3SiC_2 is resulted from the reaction:



It is necessary to note that the lattice parameters of TiC and Ti_3SiC_2 remain constant for a long time of processing (more than 3 hours) at the conditions of the experimental oxidizing of solid phases under the action of oxygen-containing components of gas phase (SiO and CO). Therefore, the methods of synthesis of monophase titanium carbide-silicide is principally new in comparison with other methods, in which case there is a possibility to control the process by regulating the gaseous component (SiO and CO) pressure. Moreover, this approach allows Ti_3SiC_2 to be produced by carbo-thermal reduction of titanium and silicon oxides, accessible and cheap initial reagents.

For the first time, we applied the well-known method of magnetic susceptibility to control the process of phase formation of layered titanium carbide-silicide. This method allows one to control the atom states of transition elements in the crystal lattices of complex compounds. The chemical structure of numerous solid solutions of oxide systems with

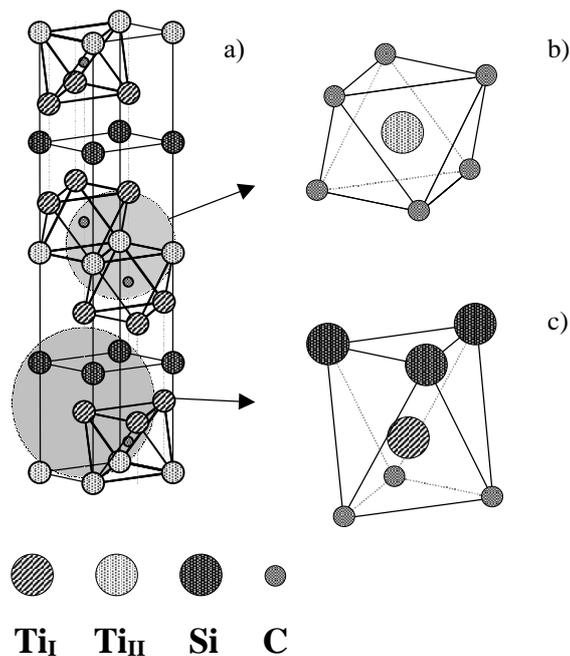


Fig. 3. (a) Ti-containing crystal structure blocks of Ti_3SiC_2 ; (b) $[\text{TiC}_6]$ octahedra; (c) distorted $[\text{TiC}_3\text{Si}_3]$ octahedra.

various structures (perovskite, corundum, layered K_2NiF_4 -type structures, etc. [23]) were studied with the help of the method discussed. However, the use of this method in studying the carbide structures is rather seldom.

We studied the products of high-temperature processes resulting in layered titanium carbide-silicide phase from low paramagnetic titanium carbide in the medium of silicon monoxide. The crystal structure and chemical transformations (in accordance with to the reaction 1) depend on the time of carbide-phase exposure in gaseous SiO. In this situation, control measurements of magnetic susceptibility of carbide-silicide compounds showed an increase in the paramagnetic component of magnetic susceptibility, which can be attributed to titanium (III). Examination of the specific structural features of layered titanium carbide-silicide phase, carried out before, showed that titanium atoms, joining to silicon layers, are surrounded mixed carbon-silicon octahedra (Fig. 3).

The transition of titanium atoms into the 2T_2 -state is confirmed by the results of X-ray-photoelectron research which indicate about the presence of titanium atoms in two reliably distinctive degrees of oxidation (Ti^{IV} and Ti^{III}) [24].

To study the distribution of paramagnetic titanium atoms in the $(1-x)\text{TiC}-x\text{Ti}_3\text{SiC}_2$ composition

Table 2. Conditions of the formation of layered titanium carbide-silicide during exposition of TiC in gaseous SiO.

No of samples	Conditions			Phase contents in the products, %		Magnetic susceptibility, 10^6emu/g (at R. T.)	Effective magnetic moment, BM (at R.T.)
	P_{SiO} , Pa	Exposition h	T °C	TiC	Ti_3SiC_2		
	0	0	–	100	0	13	0.18
1	10^2 - 10^3	1	1300	84	16	35	0.28
2	10^2 - 10^3	2	1300	78	22	40	0.31
3	10^2 - 10^3	3	1300	66	34	51	0.34

by the above-mentioned scheme, model samples were synthesized (with x from 0 to 0,34). Their magnetic susceptibility was measured (see Table 2).

3. DISCUSSION OF MAGNETIC SUSCEPTIBILITY RESULTS

Magnetic susceptibility of samples 1, 2 and 3 was measured in the temperature range from 77 to 400K. The paramagnetic component of magnetic susceptibility per 1 mole of titanium contained in the material was calculated.

Effective magnetic moments were calculated in accordance with the formula $\mu_{\text{eff}} = \frac{3k}{N\beta^2} \sqrt{\chi T}$ and plotted vs. T (Fig. 4). The effective magnetic moments (0,15-0,40 BM), on the one hand, indicate about the presence of paramagnetic centers in the samples, which must be $\text{Ti}^{+3}(d^1)$, and, on the other hand, allow one to estimate their fraction in carbide-silicide compound (for a single titanium atom with d^1 electronic configuration, the spin-only value of μ_{eff} is 1,73 BM).

A similar character of temperature dependencies of effective magnetic moments, for all the compositions, allows one to conclude the following:

- (i) The nature of paramagnetic centers is of the same origin. Their generation causes the special features of the layered structure of titanium carbide-silicide.
- (ii) The character of the temperature dependences indicate on the antiferromagnetic type of interactions between paramagnetic centers.

An increase in isothermal values of μ_{eff} with the increase in the content of Ti_3SiC_2 in the sample points to the fact that paramagnetic titanium atoms $\text{Ti}^{+3}(d^1)$ are contained in this phase. To prove this supposition, it is necessary to determine the additivity of the variation of the fraction of Ti_3SiC_2 phase and of

the increase in the effective magnetic moment. It is important that the fraction of titanium atom with d^1 electronic configuration (Ti^{+3}) (a_i) must not change with temperature over the range of magnetic susceptibility measurements, for every composition.

The concentration of paramagnetic centers (a_i) in samples 2 and 3 was reduced to that in sample 1 (a_1) in accordance with the following formula:

$$K_j = \frac{a_i}{a_1} = \frac{\mu_i^2}{\mu_1^2}, \quad (2)$$

where K_j is the relative fraction of paramagnetic centers. The values of K_2 and K_3 are statistically distributed over their average value (K_2 1.14 ± 0.03 , K_3 1.43 ± 0.02) at different temperatures (Fig. 5). This shows that as far as a_i cannot depend on temperature, our calculations are quite adequate for all the compositions under study. The dependence of the relative fraction of paramagnetic centers (K) on the content of Ti_3SiC_2 is tentatively linear (coefficient of correlation is $r = 0.99988$). It gives the prerequisite

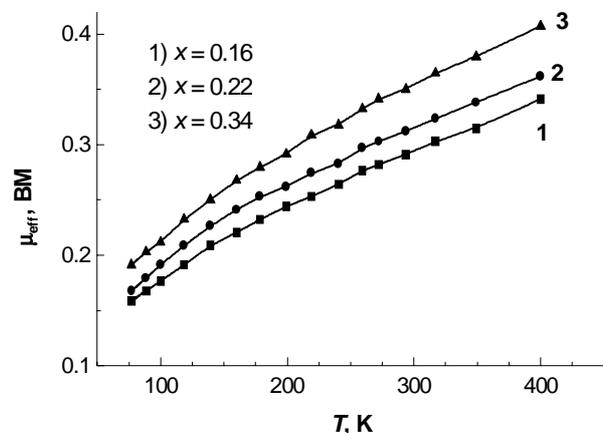


Fig. 4. Variation of effective moment μ_{eff} (BM) with temperature, for $(1-x)\text{TiC}-x\text{Ti}_3\text{SiC}_2$ samples.

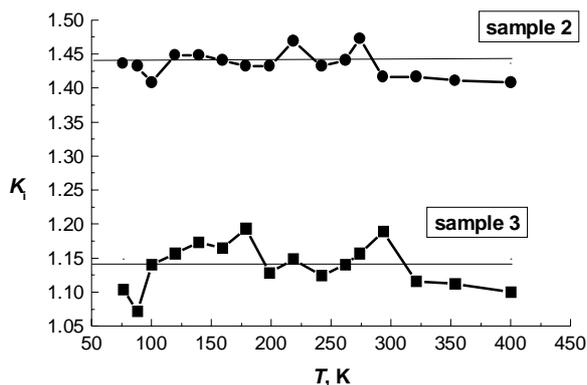


Fig. 5. Relative fraction of paramagnetic centers (K_i) in the samples 2 and 3, reduced to the fraction of paramagnetic centers in the sample 1 at test temperatures.

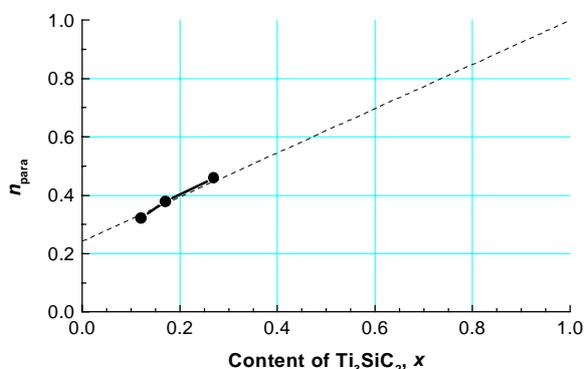


Fig. 6. Ti_3SiC_2 concentration dependence of the relative part of paramagnetic atoms Ti^{+3} (n_{para}) in the samples of the system $(1-x)\text{TiC}-x\text{Ti}_3\text{SiC}_2$, reduced to the fraction of paramagnetic centers in the pure Ti_3SiC_2 (dotted line is the extrapolation to pure Ti_3SiC_2 ($x=1$) and pure TiC ($x=0$)).

for extrapolating K_i (in general, it is incorrect) to pure TiC and Ti_3SiC_2 . The dependence of relative concentration of paramagnetic centers in the samples of the $\text{TiC} - \text{Ti}_3\text{SiC}_2$ system, reduced to the concentration of paramagnetic centers in Ti_3SiC_2 (extrapolated values) is shown in Fig. 6. Temperature dependence of μ_{eff}^2 , for the Ti_3SiC_2 phase was calculated using the extrapolated K_i values (Fig. 7).

4. CONCLUSIONS

In samples of the $(1-x)\text{TiC}-x\text{Ti}_3\text{SiC}_2$ system an increase in the fraction of titanium carbide-silicide results in an additive increase in the mole paramagnetic characteristics; the concentration of paramagnetic centers does not depend on temperature (effective magnetic moment of samples of the $\text{TiC} - \text{Ti}_3\text{SiC}_2$ system depends additively on the content

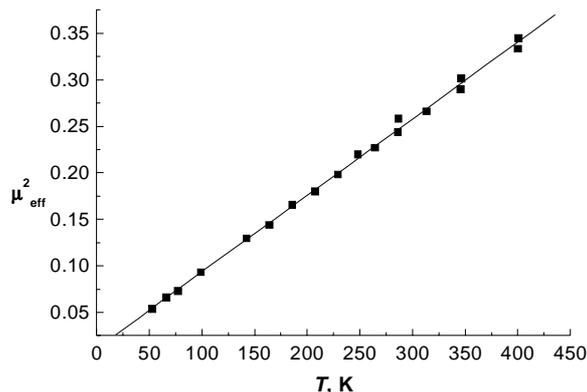


Fig. 7. Calculated temperature dependence of μ_{eff}^2 , for the Ti_3SiC_2 phase.

of Ti_3SiC_2). Therefore, the layered structure of a carbide-silicide composition, resulting from the synthesis, causes the variations in the magnetic properties of this material.

The estimating calculation of the effective magnetic moment of Ti_3SiC_2 in the range of temperatures under study gives the value nearly 5 times greater than μ_{eff} of TiC . The temperature dependence of the effective magnetic moment of the Ti_3SiC_2 phase in carbide-silicide composition was determined using the extrapolated data.

The experimental and calculated reduced temperature dependences of magnetic characteristics of the materials, containing titanium carbide-silicide phase Ti_3SiC_2 with layered structure, indicate on the antiferromagnetic exchange interactions between paramagnetic titanium atoms.

The well-known method of magnetochemical control over the state of paramagnetic atoms in oxygen lattices is applied, for the first time, to titanium carbide-silicide phase. The obtained data may form the basis of a new method to control either the formation of layered titanium carbide-silicide phase or monoxide silicon content in various physical and chemical processes.

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