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Abstract

Full Text

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PHYSICAL PROPERTIES OF TITANIUM CARBIDE IN THE REGION OF HOMOGENEITY

(Presented by Academician N. N. Semenov, March 6, 1964)

Determining the dependence of the properties of phases of variable composition on the content of their components is of scientific and practical interest. Among phases of variable composition, a large group consists of interstitial phases, which include most carbides of transition metals. Titanium monocarbide TiC, which has the widest region of homogeneity (18-50 at.% C) (^1) and a simple crystal structure, is a convenient object of study for the above-mentioned purpose. Of special interest is the investigation of the electrical properties, in particular the electrical conductivity and its temperature dependence, of titanium carbide, since the data on this question in different works show not only large quantitative but also qualitative discrepancies.

Fig. 1. Temperature dependence of the specific electrical resistance of titanium carbide:
1 –TiC = 0.59, 2 –TiC = 0.72, 3 –TiC = 0.81, 4 –TiC = 0.988

The first extensive measurements of the dependence of specific electrical resistance on temperature in the interval from the temperature of liquid air to room temperature on titanium carbide and other refractory carbides and nitrides were carried out by Arte and Moers (^2). For all the compounds they investigated, the specific electrical resistance increased with increasing temperature. Titanium carbide constituted an exception: for it they observed a clearly expressed decrease in electrical resistance with increasing temperature. On the other hand, according to works ($^{3\text{-}}$5), the electrical resistance of TiC increases linearly with increasing temperature up to 2000°. In work (^6), for titanium carbide deposited from the gas phase, depending on the substrate material, directly opposite forms of the temperature dependence of the specific electrical resistance were obtained: on a substrate of alumina or tungsten, TiC had a positive temperature coefficient of electrical resistance, while on quartz it had a negative one. The reasons for such contradictions in these works have not been established.

In view of the contradictory data, in the present work the temperature dependence of the specific electrical resistance and of the thermoelectric-power coefficient was investigated in the temperature interval from room temperature to 1200° for titanium carbide of limiting composition and for several compositions with a deficiency of carbon content from within its region of homogeneity. At room temperature the Hall coefficient and magnetic susceptibility were also measured.

Carbides with a deficiency of carbon were obtained by the interaction of a carbide close in composition to the limiting one with pure titanium. Mixtures of titanium carbide containing 19.6% bound and 0.4% free carbon with the corresponding–

with appropriate amounts of metallic titanium powder, were heated in a vacuum furnace at temperatures of 1600–1700°. The products obtained were ground, and specimens 8 mm in diameter and 10–12 mm high were prepared by hot pressing at temperatures of 2200–2300° and a load of 130–150 kg/mm^2.

The specimens obtained had the following composition:

Ti	Cbound	Cfree	Compound formula
87.3	12.47	not detected	TiC0.59
84.5	15.3	not detected	TiC0.72
82.4	17.1	not detected	TiC0.81
79.8	19.6	0.4	TiC0.988

The results obtained are given in Table 1, and also in Figs. 1 and 2.

Table 1

Specific electrical resistivity (ρ), Hall coefficients (R), and thermopower (α_T) of titanium carbide in its homogeneity range

Phase	α_T, μV/deg	$R \cdot 10^4$, cm^3/C	ρ, $\mu\Omega \cdot$ cm	U^*, cm^3/V $\cdot$ s	$\chi_m \cdot 10^6$*
TiC0.59	-7.7 ± 0.2	-4.0	174	2.3	3.22 ± 0.36
TiC0.72	-8.8 ± 0.3	-4.85	131	3.7	3.0 ± 0.1
TiC0.81	-10.4 ± 0.3	-6.5	104	6.2	3.0 ± 0.7
TiC0.988	-12.5 ± 0.2	6.7 ± 0.2	52.5 ± 0.5	12.8	3.2 ± 0.1

* For titanium $\chi_m = 3.2 \cdot 10^{-6}$.

Fig. 3

Figure 2: Fig. 3

As follows from these data, the specific electrical resistivity of titanium carbide at room temperature decreases linearly on approaching the stoichiometric composition, while the thermopower and Hall coefficients increase. It is characteristic that the Hall and thermopower coefficients coincide in sign and exhibit an analogous character of variation with increasing carbon content. Attention is also drawn to the fact that the magnetic susceptibility, referred to unit mass, is almost unchanged for all the compositions studied and is practically equal to the susceptibility of pure titanium.

For discussion of the results obtained within the framework of the two-zone model, we calculated the Hall mobility u^* of the current carriers; its values are given in Table 1 and graphically in Fig. 3, where the course of the change in the difference

$$\delta = n_- u_-^2 - n_+ u_+^2,$$

calculated from the data on the Hall coefficient and the specific electrical conductivity (7), is shown. Here n_-, n_+ are the concentrations, and u_-, u_+ the mobilities of electrons and holes, respectively.

Fig. 2. Temperature dependence of the thermopower coefficient of titanium and its carbides: 1-4—as in Fig. 1; 5 —TiC = 0.15, 6 —Ti

These data show that the Hall mobility increases rather sharply as the limiting composition TiC is approached.

Negative values of the Hall and thermopower coefficients indicate the predominantly electronic character of the electrical conductivity of the carbide under consideration throughout the investigated part of its homogeneity range.

ness. At the same time, the values of δ show that the relative contribution of electrons to the electrical conductivity increases on approaching the stoichiometric composition and rises especially sharply in the region of 46–50 at.% C.

The obvious increase in electrical conductivity observed with increasing carbon content may be explained by an increase in the mobility of conduction electrons. The latter is apparently due to two factors. First, with increasing carbon content within the homogeneity range of the phase, the degree of ordering of the lattice increases, as a result of which the intensity of scattering of electron waves by lattice inhomogeneities should decrease. Second, in carbides of transition metals, in particular in TiC,

Fig. 3. Dependence of the specific electrical resistivity (1), Hall coefficient R (2), thermoe.m.f. α_T (3), u^* mobility of current carriers (4), and the difference

Fig. 4

Figure 3: Fig. 4

$$\delta = -n\_u_-^2 - n_+u_+^2$$

(5) on the carbon content in titanium carbide.

Fig. 4. Dependence of the angular coefficients of slope of the curves: ρ—temperature and α_T—temperature on the carbon content in titanium carbide.

there is probably formed a collectivized electron ensemble that ensures its electrical conductivity through hybridization of the titanium $4s$-electrons and the $2p$-electrons of carbon atoms, which are distributed in the hybrid $4s$—$2p$ band. The displacement of $2p$-electrons from carbon atoms in transition metals is confirmed by their positive charge, the magnitude of which was determined from electronegativity ([8]). On the other hand, from the preservation of a constant value of the magnetic susceptibility for all unsaturated carbide phases, equal to the susceptibility of titanium itself, one may conclude that there is no transfer of carbon $2p$-electrons into vacant $3d$-states of titanium atoms. Thus, the $2p$-electrons of carbon apparently take an active part in the process of electrical conductivity of the carbide, since their bond with both carbon atoms and titanium atoms is weakened.

The absence of filling of vacancies in the $3d$-states during the formation of transition-metal carbides is also indicated by the results of X-ray spectral studies ([9]). If the latter assumptions are correct, then, with approach to stoichiometry, owing to the participation of the $2p$-electrons of carbon atoms in the conduction process, the concentration of conduction electrons and their mobility should increase, since overlap of the completely occupied titanium $4s$-band with the almost free carbon $2p$-band leads to the formation of a conduction band, the density of occupied states in which should decrease as the role of the $2p$-states of carbon atoms in it increases. The defective $3d$-band of titanium atoms is, in all probability, responsible for some fraction of hole conductivity. The role of this component must

decrease with increasing carbon content, since, with the formation of a hybrid $4s$—$2p$ band weakly filled with electrons, transitions of $3d$-electrons of titanium atoms into this band are possible. In connection with the relative, and possibly also absolute, decrease of the hole component of the electrical conductivity and the increase of its electronic part on approaching the limiting stoichiometric composition, the negative values of the Hall and thermoelectric-power coefficients increase, because in this case the compensating influence of the corresponding terms in the expressions for both coefficients is reduced.

The order of magnitude of the specific electrical resistivity and of the thermoelectric-power and Hall coefficients of the carbide phases in the homogeneity region and of the carbide of limiting composition is close to the values of the corresponding properties in metals. This indicates the metallic character of the electrical conductivity of titanium carbide not only of stoichiometric composition, but also when stoichiometry is violated. The metallic character of the electrical conductivity of the compounds investigated is retained also at elevated temperatures (up to 1200°). At the same time, a definite regularity is observed in the temperature dependence of electrical resistivity and thermoelectric power on composition: with increasing carbon content the slope of the ρ–temperature curves decreases linearly, while that of the α_T–temperature curves increases (Fig. 4). The weakening of the dependence of the specific electrical resistivity on temperature on approaching the stoichiometric composition can be explained by the strengthening of the role of covalent C—C bonds. With increasing intensity of the C—C bonds the rigidity of the lattice increases, as a result of which, with increasing temperature, the dependence of the intensity of the root-mean-square vibrations of the lattice atoms on temperature is weakened, and consequently the temperature dependence of the electrical resistivity is also weakened.

Figure 2 also gives the temperature dependence of the thermoelectric-power coefficient for pure titanium and the carbide phase $TiC_{0.15}$. For these two curves a characteristic kink is observed, the origin of which is evidently associated with the α—β transformation of titanium, which occurs at a temperature of 880—890°.

Thus, the results obtained give no indication of the possibility of the occurrence of semiconductor conductivity in titanium carbide of stoichiometric composition, or also upon deviation from it toward lower carbon contents. As was shown in works ([10,11]), semiconductor conductivity with increasing temperature is observed in unsaturated titanium nitride and in titanium monoxide TiO. Consequently, the semiconductor character of electrical conductivity attributed to titanium carbide and found in works ([2,6]) is apparently due to the presence of nitrogen or oxygen impurities, whose atoms occupy carbon sites when the latter is deficient relative to the stoichiometric composition of titanium carbide; this occurs readily owing to the isomorphism of TiC, TiN, and TiO.

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