THERMAL DIFFUSIVITY AND CONDUCTIVITY OF PYROLYTIC TITANIUM CARBIDE, COLUMBIUM CARBIDE, AND TITANIUM NITRIDE AT HIGH TEMPERATURES

B. A. Fridlender, V. S. Neshpor,
B. G. Ermakov, and V. V. Sokolov

UDC 536.212

Results are shown of thermal diffusivity measurements and of thermal conductivity calculations pertaining to monolithic specimens of $TiC_{0.94}$, $CbC_{0.77}$, and $TiN_{0.94}$ produced by chemical precipitation from a gas phase, and covering the temperature range from 1500 to 2200-2400°C.

Titanium carbide, columbium carbide, and titanium nitride crystallize into the NaCl-form lattice [1] and become solid refractory compounds with melting points 3150, 3480, and 2950°C respectively. Their high melting points make them suitable as heat-resistant materials for special applications. It would be of interest, therefore, to examine their thermophysical properties, especially their thermal diffusivity and conductivity, at high temperatures. Published test data on the thermal conductivity of TiC, CbC, and TiN [2, 3, 4] refer to materials produced by powder-metallurgy processes and having some residual porosity. In this study we were concerned with the thermal diffusivity and conductivity of titanium monocarbide, columbium monocarbide, and titanium nitride which had been produced by the method of chemical precipitation from a gas phase [5].

The results of chemical and x-ray analysis are given in Table 1.

No change in the chemical composition during thermal diffusivity measurements was noted in TiC and CbC specimens up to 2400° and in TiN specimens up to 2200°C.

An intensity analysis of diffraction peaks on diffractograms of specimens has revealed the existence of a definite growth texture with the predominant orientation parallel to the precipitation surface (normal to the direction of heat flow during thermal diffusivity measurements) in the crystallographic (100) plane. The specimen density measured by hydrostatic weighing was 4.87 g/cm^3 for TiC, 7.15 g/cm^3 for NbC, and 5.37 g/cm^3 for TiN — close to their theoretical densities [1] — and indicated an almost zero porosity of the specimens.

In order to stress relieve the specimens, TiC and CbC were annealed under vacuum at 2200°C and TiN at 1500°C for 1 h.

TABLE 1. Physicochemical Characteristics of TiC, CbC, and TiN

Material	Chemical composition, % (weight)				Formula composition	Lattice period, Å
	metal	total carbon	nitrogen	oxygen		
TiC	79,52	18,84	0,10	0,46	$TiC_{0,945}N_{0,004}$	4,327 ± 0,001
NbC	90,97	9,02	0,05	—	$NbC_{0,77}$	4,446 ± 0,002
TiN	76,14	0,15	20,88	—	$TiN_{0.938}C_{0,008}$	4,237 ± 0,001

State Institute of Applied Chemistry, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 24, No. 2, pp. 294-296, February, 1973. Original article submitted April 18, 1972.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

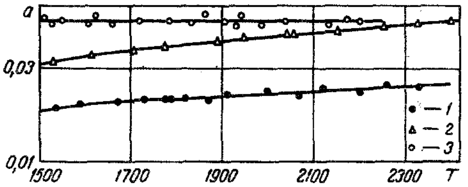

Fig. 1

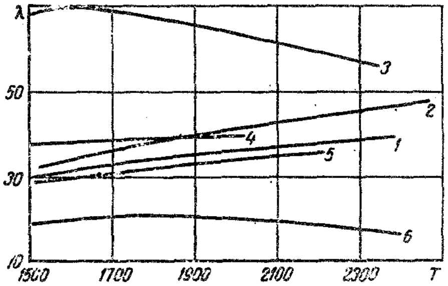

Fig. 2

Fig. 1. Thermal diffusivity a (m^2/sec) as a function of the temperature T (°C) for specimens of pyrolytic TiC (1), CbC (2), TiN (3).

Fig. 2. Thermal conductivity λ (W/m · °C) as a function of the temperature T (°C) for pyrolytic TiC (test) (1), CbC (test) (2), TiN (test) (3), TiC according to [2] (4), CbC according to [4] (5), TiN according to [3] (6).

The TiC and CbC specimens had a coarse-crystalline columnar dendritic microstructure, with the axes of the columnar crystals oriented normally to the precipitation surface. The TiN specimens had a similar microstructure, but without dendrites. The electrical resistivity of the TiC, CbC, and TiN test specimens at room temperature was 220, 130, and 20 $\mu\Omega \cdot$ cm respectively.

The thermal diffusivity was measured by the phase-angle method [6], namely by the phase difference between a periodically varying thermal flux and resulting temperature fluctuations at the opposite surface of a flat specimen (0.25-0.30 mm thick). A specimen was heated under a vacuum of about 10^{-5} mm Hg by electron bombardment from a flat and spiral tungsten cathode 4-6 mm away from that specimen serving as the anode. An alternating component of power was produced by modulation of the anode voltage with a model ZG-10 audio oscillator. The phase shift between the alternating components of power and temperature respectively was measured with a model F2-1 phase meter. The anode voltage was modulated at a 112 Hz frequency. The specimen temperature was measured with a model OMP-043 optical micropyrometer. The emissivity of the specimens was found to be approximately ε_λ = 0.70 for TiC, 0.75 for CbC, and 0.60 for TiN at the wavelength λ = 0.65 μm.

The test apparatus used for these measurements differed only slightly from that described in [6]. The error of thermal diffusivity measurements did not exceed 5%.

The thermal diffusivity a as a function of the temperature is shown in Fig. 1. Using the published data in [3] on the specific heat c of TiC, CbC, and TiN at high temperatures, and assuming that this property does not depend on the specimen structure, we have calculated the thermal conductivity λ of pyrolytic TiC, CbC, and TiN according to the well known relation $\lambda = ac\gamma$ and as a function of the temperature (Fig. 2). For comparison, in Fig. 2 are also shown earlier published ([2-4]) values of thermal conductivity of metal-ceramic specimens.

The thermal diffusivity and conductivity of TiC and CbC are much lower than those of TiN, largely because the electrical conductivity of carbides is lower than that of nitrides and, correspondingly, the electron thermal conductivity of carbides is lower than that of nitrides, while their lattice thermal conductivitities are comparable [7]. The differences between the temperature characteristics of pyrolytic TiC, CbC, and TiN with approximately equal lattice components of thermal conductivity can be explained phenomenologically by an appreciable difference in their residual electrical resistance, the lattice affecting the temperature dependence of the electron thermal conductivity [8]. It has been shown earlier that the thermal conductivity of pyrolytic zirconium carbide increases with rising temperature [9], as in the case of TiC and CbC, while the thermal conductivity of pyrolytic zirconium nitride decreases with rising temperature above 1500°C [10], as in the case of TiN.

LITERATURE CITED

1. G. V. Samsonov, Solid Compounds of Refractory Metals [in Russian], Metallurgizdat, Moscow (1963).
2. R. E. Taylor, J. Amer. Ceram. Soc., <u>44</u>, No. 10, (1961).
3. D. S. Neel and C. D. Pears, Progress in Internatl. Res. on Thermodynamic and Transport Properties, Academic Press, New York (1962).

4. D. S. Neel, C. D. Pears, and S. Oglesby Jr., Thermal Properties of Thirteen Solid Materials up to 5000°F or Their Destruction Temperatures, Southern Res. Inst., WADD-TR-60-924, Contract AF-33(616)-6312, (1962).
5. V. S. Davydov, B. G. Ermakov, and V. S. Sokolov, in: Refractory Carbides [in Russian], Izd. Naukova Dumka, Kiev (1970).
6. O. A. Kraev and A. S. Stel'makh, in: Testing at High Temperatures [in Russian], Izd. Nauka, Novosibirsk (1966).
7. V. S. Neshpor, Neorgan. Materialy, 4, 2200 (1968).
8. W. Williams, J. Amer. Ceram. Soc., 49, 156 (1966).
9. B. A. Fridlender and V. S. Neshpor, Teplofiz. Vys. Temp., 8, 795 (1970).
10. B. A. Fridlender and V. S. Neshpor, Teplofiz. Vys. Temp., 6, 1004 (1970).