THE THERMAL CONDUCTIVITY OF THE SILICIDES OF TRANSITION METALS

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Inzhenerno-Fizicheskii Zhurnal, Vol. 15, No. 2, pp. 321–325, 1968

UDC 536.212

We present the results obtained from the measurement of the thermal conductivity exhibited by the silicides of various metals.

Earlier we investigated some of the quantitative relationships governing the electrophysical properties [1–6] and the thermal expansion [7] of the silicides of transition metals in connection with their crystal structure and chemical composition. The data available in the literature on the thermal conductivity of silicides are extremely limited and deal only with a few individual silicide phases [8]. Earlier, we measured the thermal conductivity of molybdenum silicides [9] and the alloys of isomorphic disilicides of molybdenum and rhenium [10] as a function of structure and composition.

In this study we have measured the thermal conductivities for a number of the silicides of transition metals by means of a steady-state heat flow, which is a particular variant of the method [11]. The test specimen is clamped between a copper cooling device and a cylinder—also made of copper—with a heater winding; excellent thermal contact is assured by a low-melting indium-gallium alloy. The temperature difference across the specimen was measured by means of chromel-copel thermocouples stamped into thin copper disks in contact with the specimen. The magnitude of the heat flow was measured by means of indium-antimonide plates whose thermal conductivity was known precisely, and for which the thermal emf and the temperature difference was measured by means of chromel-copel thermocouples. The convection heat losses were reduced by housing the system in a vacuum jar evacuated to a residual pressure of 10^{-2} mm. The average specimen temperature during the measurements was ~40° C, as a result of which we were able to neglect the radiation heat losses from the side surfaces of the specimens. It was established experimentally that with a specimen height of 8 mm or less, this has little effect on the results. Control measurements on materials with known thermal conductivity demonstrated that the error in the measurement of the thermal conductivity over the interval of magnitudes established in this study did not exceed 5–7%.

The silicides were prepared in the form of powders by direct synthesis from powders of the metals and silicon [12], and the compacted specimens were prepared for the measurement by hot pressing [13, 14]. It was revealed through x-ray phase analysis that all of the test specimens were of the single-phase variety; their structures and lattice periods corresponded to the known silicide structures of the given chemical composition. Chemical analysis revealed that the specimens produced here corresponded in composition to that predicted by calculation. The effect of the residual porosity on the thermal conductivity was taken into consideration with the familiar relationship

$$\varkappa_0 = \varkappa_p (1 - P),$$

where $\varkappa_0$ and $\varkappa_p$ are, respectively, the thermal conductivities of the specimens without and with pores and P is the porosity (in fractions of unity) [15].

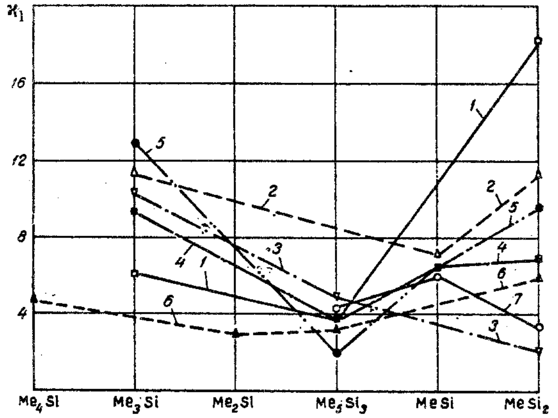
These results are presented in the table. Using the data on the electrical conductivity of the silicides [1, 4, 5, 16, 17] derived earlier with these same specimens, we calculated the contribution of the conductivity electrons to the electrical conductivity ($\varkappa_{el}$) on the basis of the Wiedemann-Franz law

$$\varkappa_{el} = L\sigma T$$

(where σ is the electrical conductivity), with consideration of the elastic scattering of the current carriers which corresponds to a Lorentz number of $L = 2.45 \cdot 10^{-8}$ W · Ω/deg^2 [18]. The lattice contribution to the thermal conductivity $\varkappa_l$ was evaluated as the difference between the measured values of the thermal conductivity and the electron contribution:

$$\varkappa_l = \varkappa_0 - \varkappa_{el}.$$

Earlier we considered [1, 2, 4] the quantitative relationships governing the change in the electrical conductivity and, consequently, in the electron contribution to the thermal conductivity of the silicides as a function of their composition and crystalline structure, as well as in connection with the electron structure. The theory of the lattice thermal conductivity of solids has not been sufficiently developed, and the existing quantitative relationships between the lattice thermal conductivity and the parameters associated with the nature and strength of the interatomic interaction pertain primarily to crystals with cubic symmetry and a comparatively simple structure. It therefore becomes difficult to undertake a detailed consideration—no matter how slight—of the data on the lattice contribution to the thermal conductivity of the silicides which, with rare exceptions, exhibit rather complex heterodesmic structures with a symmetry lower than the cubic [3, 19]. However, it should be noted that among the various successive phases in the metal-



Lattice thermal conductivity of silicides of transition metals versus their formula composition: 1) molybdenum silicides; 2) iron silicides; 3) vanadium silicides; 4) manganese silicides; 5) chrome silicides; 6) tantalum silicides; 7) titanium silicides.

silicon systems it is the phases within the average range of compositions (see figure) with relatively similar contents of metal and silicon that exhibit the smallest lattice thermal conductivity. One might suppose that this is due to the effect of the crystalline structure, since it is precisely the silicides of transition metals of such composition that are characterized by the most clearly defined heterodesmic structure in which we find chains of metal-metal and silicon-silicon bonds in addition to metal-silicon bonds, each with different force constants and, consequently, with different oscillation frequencies. We can therefore anticipate the most substantial contribution for these phases from the phonon-phonon scattering and, consequently, a reduction in the lattice thermal conducitivity.

We know that the lattice thermal conducitivity is reduced for many elements and compounds when the average atomic weight is increased ([11], page 347). However, the results (see table) show that this rule is not followed in the case of silicides. Thus, for example, for a comparatively large number of disilicides ($MeSi_2$) of the metals from group IV–VI—which, although of diverse structures, are similar in the way the metal and silicon atoms are packed [19]—we note a tendency toward an increase in the lattice thermal conductivity with an increase in the atomic number of the metal component in the period and in the group. If we bear in mind that in substances with a covalen-metal bond the contribution of the lattice oscillations to the thermal conductivity should be greater with an increase in the relative fraction of the localized electrons in the directed bonds relative to the collective electrons, the observed change in the lattice thermal conductivitity of the disilicides as a function of the position of the metals in the periodic system can be explained if we proceed from the hypothesis proposed by Samsonov [20] to the effect that the statistical weight of the stable localized d^5-electron configurations participating in the chemical bond increases with an increase in the total number of d-electrons and in the main quantum number of the d-shell.

Table

Measured Electron and Lattice Thermal Conductivity for the Silicides of Transition Metals (at a temperature of ~40° C)

Silicide phase	Thermal conductivity, W/m · deg.		
	$\varkappa_{0.meas}$	$\varkappa_{el}$	$\varkappa_l$
Ti_5Si_3	26.8	21.8	5.0
TiSi	16.8	10.7	6.1
$TiSi_2$	45.9	42.5	3.4
V_3Si	13.0	3.5	10.5
V_5Si_3	11.4	6.3	5.1
VSi_2	11.9	9.9	2.0
Cr_3Si	33.6	20.5	13.1
Cr_5Si_3	10.9	9.0	1.9
CrSi	11.9	5.3	6.6
$CrSi_2$	10.6	0.8	9.8
Mn_3Si	14.0	4.5	9.5
Mn_5Si_3	6.7	2.8	3.9
MnSi	9.4	3.8	6.6
$MnSi_{1.8}$	8.5	1.5	7.0
Fe_3Si	17.0	5.5	11.5
FeSi	10.2	2.7	7.5
$FeSi_2$	11.6	0.2	11.4
Co_3Si	13.0	5.6	7.4
CoSi	20.7	8.4	12.3
$CoSi_2$	15.1	10.3	4.8
Ni_3Si	18.2	7.7	10.5
$NiSi_2$	10.3	6.5	3.8
Zr_5Si_3	8.7	5.1	3.6
$ZrSi_2$	15.6	9.5	6.1
$NbSi_2$	19.1	15.6	3.5
Ta_4Si	9.0	4.1	4.9
Ta_2Si	8.3	5.3	3.0
Ta_5Si_3	9.9	6.7	3.2
$TaSi_2$	21.9	15.6	6.3
Mo_3Si	39.6	33.4	6.2
Mo_5Si_3	19.5	15.7	3.8
$MoSi_2$	51.8	33.3	18.5
WSi_2	46.6	28.3*	18.3
ReSi	23.4	1.0	22.4
$ReSi_2$	19.2	0	19.2
$LaSi_2$	13.7	3.1	10.6
$CeSi_2$	16.4	3.6	12.8
$PrSi_2$	17.6	1.8	15.8
$GdSi_{1.6}$	6.0	—	—
$BaSi_2$	10.0	~0	10.0

*Taken from $\sigma = 3.77 \cdot 10^4 \cdot \Omega^{-1} \cdot cm^{-1}$, measured in this study.

An analogous trend (toward a change in the lattice thermal conductivity) is shown by the isomorphous disilicides of the rare-earth metals.

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15 December 1967

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