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Abstract

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PHYSICAL PROPERTIES OF TRANSITION-METAL NITRIDES

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The study of the physical properties of nitrides of metals of the transition groups is of interest both because of the ever expanding use of these refractory and corrosion-resistant compounds in technology, and in connection with the heterodesmic nature of these phases, which simultaneously exhibit the properties of metallic compounds and ionic phases ([1,2]). The systematic study that we began of the electrical properties ([3]) and hardness ([4]) of transition-metal nitrides has been continued in the present work; in addition to electrical resistivity, thermo-emf, the Hall effect, and microhardness, the values of the thermal conductivity and melting temperature of nitrides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, and molybdenum were also measured. Nitride specimens were prepared by the method of nitriding metals, which excludes the possibility of their contamination by oxygen ([5]), with simultaneous or subsequent sintering in a nitrogen atmosphere. Measurements were made on specimens of various porosity, with subsequent extrapolation, in the case of the electrical properties, by Odelevskii' s formula ([6]), and in the case of thermal conductivity, by the formula of work ([7]), to zero porosity. The data obtained in the measurements are given in Table 1.

Table 1

Physical properties of transition-metal nitrides

Nitride	Nitrogen content, wt. %	Nitrogen content, at. %	Thermo-emf coefficient (abs.), α, μV/deg	Specific electrical resistance, ρ, $\mu\Omega\cdot$cm	Hall coefficient R, cm^3/C	Thermal conductivity, χ, cal/cm $\cdot$ sec $\cdot$ deg	Microhardness, H_m, kg/mm^2
$TiN_{0.98}$	22.4	49.8	-7.78 ± 1.1	26 ± 2	-0.67 ± 0	0.046 ± 0.003	1994 ± 137
$ZrN_{0.98}$	13.2	49.8	-4.78 ± 0.5	28 ± 3	-1.3 ± 0.2	0.049 ± 0.002	1520 ± 85

Nitride	Nitrogen content, wt. %	Nitrogen content, at. %	Thermo-emf coefficient (abs.), α, μV/deg	Specific electrical resistance, ρ, $\mu\Omega\cdot$cm	Hall coefficient R, cm^3/C	Thermal conductivity, χ, cal/cm·sec·deg	Microhardness, H_m, kg/mm^2
$HfN_{0.86}$	6.4	46.5	−2.96±0.6	33 ± 5	−4.2 ± 0.5	0.0517±0.006	1640 ± 161
$VN_{0.338}$	8.5	25.3	−5.3 ± 1.2	123±10	−0.9 ± 0.1	–	1900 ± 102
$VN_{0.74}$	16.8	42.4	–	–	–	–	1520 ± 115
$VN_{0.93}$	20.5	48.3	−4.6 ± 0.8	85 ± 4	−0.45±0.16	0.0270±0.007	–
$NbN_{0.46}$	6.6	31.7	–	–	–	–	1720 ± 100
$NbN_{0.5}$	7.1	33.5	−4.57±0.7	142 ± 6	−4.9 ± 0.4	0.0200±0.008	–
$NbN_{0.96}$	12.7	49.1	−1.65±0.1	85 ± 2	−0.47±0.2	–	1396 ± 26
$NbN_{1.00}$	13.1	50.0	−2.24	78 ± 4	−0.52±0.19	0.009 ± 0.002	–
$TaN_{0.45}$	3.4	31.2	−2.17±0.4	263±22	−0.46±0.1	0.0240±0.005	–
$TaN_{0.58}$	4.3	36.6	–	–	–	–	1220 ± 120
$TaN_{1.01}$	7.3	50.3	−1.6 ± 0.3	128±15	−3.61±0.9	0.0205±0.009	1060 ± 72
$CrN_{0.47}$	11.2	32.0	–	–	–	–	1571 ± 49
$CrN_{0.497}$	11.8	33.2	−2.3 ± 0.2	79 ± 5	−0.72±0.1	0.519 ± 0.004	–
$CrN_{0.926}$	20.0	48.1	−92 ± 4	640±40	−264 ± 25	0.0300±0.003	–
$CrN_{0.99}$	21.0	49.8	–	–	–	–	1093 ± 93
$MoN_{0.5}$	6.8	33.3	−2.18±0.5	19.8 ± 7	+2.83±1.2	0.0427±0.007	630±86

Unlike transition metals, which are hole conductors, all the nitrides studied, except for the nitrides of vanadium, niobium, and molybdenum, have predominantly electron conductivity, as is indicated by the signs of the Hall coefficient.

All nitride phases, except $MoN_{0.5}$ (Mo_2N), have negative values of the thermo-

Fig. 1. Dependence of the thermoelectric-power coefficient and specific electrical resistivity of nitrides on the criterion of the degree of unfilledness of the *d*-electron shells of atoms of transition metals

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emf coefficient; moreover, with increasing acceptor ability of the incomplete *d*-electron shells (estimated in accordance—

in agreement with the relation $1/Nn$, where N is the principal quantum number of the unfilled *d*-shell and n is the number of electrons in it) the thermoelectric-power coefficients increase almost linearly (Fig. 1). It should also be noted that there is a tendency toward an increase in the negative thermoelectric-power coefficient with decreasing nitrogen content in the V—N, Nb—N, and Ta—N systems; this tendency is not observed only in the Cr—N system, apparently because of the semiconducting character of the higher chromium nitride CrN (9).

The electrical resistivity of the nitrides of the metals considered decreases with increasing degree of unfilledness of the *d*-shells (Fig. 1), which, in combination with the character of the change in the thermoelectric-power coefficient, indicates an increase in the number of transitions of nitrogen valence electrons to the *d*-shells of the metal atoms with the formation of hybrid *spd*-states and a decrease in the degree of polarization of the metal—nitrogen bond. The decrease in the electrical resistivity of alloys in the V—N, Nb—N, and Ta—N systems with increasing nitrogen content corresponds to a decrease in the fraction of ionic bonding, similarly to what was noted for the homogeneity ranges of titanium (10) and zirconium (11) nitrides.

Fig. 1. Dependence of the thermoelectric-power coefficient and specific electrical resistivity of nitrides on the criterion of the degree of unfilledness of the *d*-electron shells of atoms of transition metals

It is noteworthy that the sign of the thermoelectric power does not everywhere coincide with the sign of the current carriers, determined from the sign of the Hall coefficient. Since the absolute values of the thermoelectric-power coefficients of these substances are small, it seems possible to assume that this discrepancy is caused by scattering of carriers by impurities, as was proposed earlier in works (12,13).

It is interesting that, as in the metal—silicon systems (14), with increasing nitrogen content the resistance decreases in metal—nitrogen systems where the higher nitride has a metallic type of conductivity, and increases in those systems where the higher nitride is a semiconductor (chromium—nitrogen).

Table 2

Fig. 2

Figure 2: Fig. 2

Calculated and measured thermal conductivity of nitrides
(cal/cm · sec · deg)

Nitride	χ_p	χ_{meas}	$\chi_p/\chi_{\text{meas}}$	Nitride	χ_p	χ_{meas}	$\chi_p/\chi_{\text{meas}}$
TiN	0.062	0.046	1.34	NbN	0.026	0.009	2.9?
ZrN	0.056	0.049	1.14	Ta_2N	0.006	0.024	0.25
HfN	0.047	0.051	0.93	TaN	0.008	0.020	0.40
VN	0.019	0.027	0.71	Cr_2N	0.021	0.051	0.41
Nb_2N	0.011	0.020	0.55	CrN	0.003	0.028	0.11

Examination of the data on thermal conductivity also shows a general tendency for the thermal conductivity to decrease with decreasing acceptor capacity of the *d*-shells (Fig. 2) and with increasing nitrogen content in nitride phases; it may be considered that with an increase in the fraction of the ionic component of the bond, the thermal conductivity decreases.

Comparison of the experimental data on thermal conductivity with the calculated values of the electronic thermal conductivity (Table 2) shows more or less satisfactory agreement for all nitrides except tantalum and chromium nitrides, for which the calculated electronic thermal conductivity is considerably smaller than the measured one, indicating the predominant role in the crystals of these nitrides of lattice thermal conductivity. This is in good agreement with the semiconducting character of CrN established in work (^{9}).

Fig. 2. Dependence of the thermal conductivity and Hall coefficient of transition-metal nitrides on the criterion of the degree of incompleteness of the *d*-electron shells of the metals. (The square marks the values for phases of the MeN type)

As follows from the data in Table 1, the microhardness of mononitrides is lower than the hardness of phases of composition Me_2N, which confirms the suggestion of A. M. Belikov and Ya. S. Umanskii (^{15}) concerning the weakening of the Me—Me bond forces upon incorporation of nonmetal atoms into the crystal lattices of metals, since the Me—Me distances in interstitial phases are 8-12% greater than in the metal. For nitride phases Me_2N the Me—Me bond remains predominant, whereas in MeN phases the weaker Me—N bond predominates. This is also confirmed by the higher melting temperatures of phases of composition Me_2N (for example, Nb_2N melts at 2420°, NbN at 2300°).

In conclusion, it should be noted that transition metals of group IV, having a *d*-shell with a high degree of unfilledness, in compounds with nitrogen that is difficult to ionize form nitrides with a predominantly metallic character of bonding between the cores of the metal and nitrogen atoms; moreover, as the nitrogen content decreases within the homogeneity regions of these phases, an energy gap arises and broadens between the *sd*-states of the metals and the *p*-states of nitrogen, which is manifested in the appearance of semiconducting properties.

On passing to nitrides of transition metals of groups V and VI, where the degree of incompleteness of the *d*-electron shells decreases, the fraction of the ionic component of the bond in nitride phases increases, the homogeneity regions decrease, and a tendency is observed toward reduced stability of the cubic NaCl-type lattice; the hexagonal structure of mononitrides is stabilized and stable nitrides of composition Me_2N are formed, while mononitrides, with increasing degree of filling of the *d*-shell, acquire an increasingly pronounced semiconducting character.

With regard to the nature of the chemical bond in nitride lattices, it should be noted that the present experimental results confirm the conclusion of work ([1]) concerning the predominantly metallic character of the nitrides of titanium, zirconium, hafnium, and vanadium; the predominantly ionic character of the bond in the lattices of the nitrides of molybdenum and, apparently, tungsten; and also the combination of metallic and ionic bonding, with some predominance of the latter, in the lattices of the nitrides of niobium, tantalum, and chromium.

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