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Abstract

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ON THE RELATION OF THE THERMOELECTRIC FIGURES OF MERIT OF MONOCARBIDES AND MONONITRIDES OF TRANSITION METALS TO THEIR ATOMIC CHARACTERISTICS

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In work ([1]) preliminary characteristics were given for the thermoelectric figures of merit of several refractory compounds.

The thermoelectric figure of merit Z, which determines the efficiency of a thermoelement material, is related to the thermoelectromotive force α of the material, its specific resistance ρ, and thermal conductivity λ by the known relation ([1]):

$$Z = \alpha^2/\rho\lambda. \tag{1}$$

Table 1 gives the values of Z, calculated by formula (1), for refractory monocarbides and mononitrides of transition metals of groups III–VI of the periodic system at room temperature. For comparison, values of Z are also given for several carbides of other formula composition. The data needed for the calculation were taken from works ([3-10]) and refer to the same specimens, with the exception of tungsten monocarbide, for which the data on α, ρ, and λ were used from different sources ([3]).

Table 1

Thermoelectric figures of merit of refractory carbides and nitrides

Phase	Z, deg^{-1}	Phase	Z, deg^{-1}
TiC	$2.1 \cdot 10^{-5}$	WC	$0.9 \cdot 10^{-4}$
ZrC	$1.1 \cdot 10^{-5}$	W_2C	$3.0 \cdot 10^{-6}$
HfC	$1.0 \cdot 10^{-5}$	$ScN_{0.98}$	$0.8 \cdot 10^{-4}$
$VC_{0.88}$	$0.9 \cdot 10^{-6}$	$TiN_{0.98}$	$1.2 \cdot 10^{-5}$
$NbC_{0.99}$	$2.1 \cdot 10^{-6}$	$ZrN_{0.98}$	$4.0 \cdot 10^{-6}$
TaC	$5.0 \cdot 10^{-6}$	$HfN_{0.86}$	$1.2 \cdot 10^{-6}$
Cr_3C_2	$2.2 \cdot 10^{-6}$	$VN_{0.93}$	$2.2 \cdot 10^{-6}$
Cr_7C_3	$3.1 \cdot 10^{-6}$	$NbN_{1.00}$	$3.1 \cdot 10^{-7}$

Phase	Z, deg^{-1}	Phase	Z, deg^{-1}
$Cr_{23}C_6$	$3.0 \cdot 10^{-7}$	$TaN_{1.01}$	$2.3 \cdot 10^{-7}$
Mo_2C	$7.6 \cdot 10^{-6}$	$CrN_{0.93}$	$1.4 \cdot 10^{-4}$

From the data of Table 1 it is seen that the thermoelectric figure of merit for most of the compounds considered is small and is of the order of 10^{-7}–10^{-5} deg^{-1}, which is consistent with the metallic character of their electrical conductivity ([11]). A higher value of Z ($1.4 \cdot 10^{-4}$ deg^{-1}) is observed for chromium nitride, which is due to its semiconducting character, and also for two metallic phases –scandium nitride ($0.8 \cdot 10^{-4}$ deg^{-1}) and tungsten carbide ($0.9 \cdot 10^{-4}$ deg^{-1}). The latter value cannot be regarded as fully reliable, because in its calculation parameter values obtained under different conditions were used; however, it indicates that tungsten monocarbide deserves more detailed study as a promising high-temperature thermoelectric material, especially in connection with its good technological properties ([12]).

Of all the monocarbides considered, vanadium carbide has the lowest value of Z. It should be noted that this is the only monocarbide that at room temperature has a positive sign of thermo-emf ([2]). It is possible that this anomaly is associated with the influence of electroactive oxygen impurities or with features of the defect structures of vanadium carbide, which in equilibrium with graphite has the limiting composition $VC_{0.86}$ ([13]). In contrast to the thermo-emf, the Hall coefficient for vanadium monocarbide has a negative sign, as for the monocarbides of the other transition metals. A study, carried out by one of the authors jointly with S. V. Airapetyan, of the temperature dependence of the thermo-emf of vanadium monocarbide showed that the thermo-emf of vanadium monocarbide, largest and positive at room temperature, already at 100° changes sign and, with further increase in temperature, grows toward negative values. It is known ([2]) that the thermal conductivity of metals and semiconductors is
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determined by the contribution both of the thermal conductivity of the electron gas λ_e and of the lattice λ_p, and can be represented in the form

$$\lambda = \lambda_e + \lambda_p. \tag{2}$$

The electronic thermal conductivity is related to the specific electrical resistance by the Wiedemann-Franz relation $\lambda_e = LT/\rho$, where L is the Lorenz number and T is the absolute temperature. On the other hand, the lattice thermal conductivity is inversely proportional to T ([14]). Taking these relations into account, formula (1) at constant temperature can approximately be represented in the form

$$Z \approx \alpha^2(A\rho + B), \tag{3}$$

Fig. 1

Figure 1: Fig. 1

if λ_e and λ_p are comparable in magnitude, or

$$Z \approx \alpha^2/B, \tag{4}$$

if $\lambda_e \gg \lambda_p$ (here A and B are certain constants).

Fig. 1. Dependence of the thermoelectric figure of merit Z of carbides and nitrides of transition metals on the acceptor-capacity criterion of the metals $\xi = 1/Nn$. a –carbides MeC, b –nitrides MeN, v –W_2C, g –Mo_2C, d –Cr_7C_3, e –Cr_3C_2

It was shown earlier ([15,16]) that the thermoelectric emf of metal-like refractory compounds of the type considered here increases, while the specific electrical resistance tends to decrease, as the acceptor-capacity criterion of the atoms entering the corresponding compound of transition metals increases; this criterion is characterized by the ratio $\xi = 1/Nn$, where N is the principal quantum number of the partially filled d-shell of the metal atom, and n is the number of electrons in it in the free atom ([17]). On the other hand, as we showed earlier ([10]), in passing from metal-like compounds formed by metals with low acceptor capacity to compounds of metals with high acceptor capacity, the role of the electronic contribution to the thermal conductivity increases in comparison with the lattice contribution; i.e., in this case there should be a tendency toward transition from describing the figure of merit Z by formula (3) to describing it by formula (4).

The reason for these phenomena is that, with an increase in the acceptor capacity of the metal, the tendency is strengthened for the valence electrons of the nonmetal to pass into the electronic collective of the compound lattice and, as a result, the number of collectivized electrons responsible for conduction and for the thermoelectric emf of metal-like compounds increases.

Taking the above considerations into account, one may expect that for a given class of metal-like compounds (for example, carbides or nitrides) with a homodesmic structure, an increase in the acceptor capacity of the atoms of the metallic component should increase the thermoelectric figure of merit of the compound. This is indeed observed experimentally, as can be seen from Fig. 1.

It is interesting to note that scandium nitride, whose d-shell is almost vacant and which therefore has a very high acceptor capacity, exhibits a figure of merit comparatively large for metallic substances $\left(0.8 \cdot 10^{-4}\ \text{deg}^{-1}\right)$, approaching that for the semiconducting chromium nitride. An exception to this regularity (for compounds of identical formula composition) is tungsten monocarbide; however,

as was already indicated earlier, the experimental data for this compound require careful verification. We note that the lower tungsten carbide W_2C (like Mo_2C) has a significantly smaller value of Z and on the graph falls on the common dependence of Z on the acceptor capacity of the metallic component shared with the monocarbides. The same is true

for chromium carbides of composition Cr_3C_2 and Cr_7C_3 (a stable chromium monocarbide does not exist). The lower chromium carbide $Cr_{23}C_6$, with a complex lattice and a very low carbon content ($\widehat{}12$), has a very low value of Z ($3 \cdot 10^{-7}$ deg^{-1}).

It is noteworthy that the figure of merit of carbides of metals with comparatively low acceptor capacity ($\xi \leq 0.15$) is higher than that for the corresponding nitrides, whereas at a higher acceptor capacity of the metals the values for their carbides and nitrides converge. Moreover, judging also from their dependence $Z = f(\xi)$, metallic monocarbides of metals with high acceptor capacity ($\xi > 0.2$), if they existed,* would have lower Z than the corresponding nitrides.

The observed regularity can be explained by comparing the acceptor capacity of the atoms of the metallic components and the ionization potentials of the nonmetal atoms. Since nitrogen has a higher ionization potential than carbon (respectively 14.5 and 11.2 eV), then, at a comparatively low acceptor capacity of the metal atoms, in their carbides there is a more complete collectivization of the valence electrons of the metalloid and a more uniform distribution of the collectivized electrons between the cores of the metal and nonmetal atoms than in the nitrides ($\widehat{}20$), which, as already indicated, should promote higher values of the figure-of-merit coefficients of metal-like compounds with a metallic character of conduction. In the case of metals with high acceptor capacity, however, the collectivized electrons in carbides are displaced to a considerable degree toward the cores of the metal atoms, and the distribution of electron density becomes more asymmetric. A more symmetric distribution of the electron collective should be achieved in this case in the nitrides of the corresponding metals, where the comparatively high ionization potential of nitrogen to one degree or another compensates the high acceptor capacity of the metal.

Hence one may conclude that, for example, in order to raise the thermoelectric figure-of-merit coefficients of metallic refractory compounds of the type considered here by alloying, the latter must be carried out in such a way that the alloying component causes a more complete transfer of the valence electrons of the metalloid constituent of the compound into the electron collective, with the most symmetric distribution of the latter in the space between the sites of the crystal lattice occupied by metal and nonmetal atoms.

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* Metal-like scandium monocarbide probably exists (^18,19); however, its electrophysical properties, with the exception of electrical resistivity, have not been studied.

Note: Figure translations are in progress. See original paper for figures.