THERMODYNAMIC CHARACTERISTICS OF REFRACTORY CARBIDES IN THEIR HOMOGENEITY REGIONS

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In their previous investigations [1-3], the authors experimentally determined the enthalpy of niobium, zirconium, and titanium carbides of various compositions in their homogeneity regions at temperatures ranging from 1300 to 2500°C and derived equations expressing the effect of temperature on the enthalpy and heat capacity of these compounds. The carbide compositions studied corresponded to the formulas: NbC₀.₉₉, NbC₀.₈₁, NbC₀.₇₅, ZrC₀.₉₉, ZrC₀.₇₆, ZrC₀.₆₉, TiC₀.₉₉, TiC₀.₈₂, TiC₀.₇₁, and TiC₀.₆₄.

An attempt will be made in the present work to interpret the results obtained in the light of theories explaining the character of the chemical bond in carbides and their crystallochemical-structure characteristics.

When the experimental heat-capacity data are compared with those established on the basis of Neumann-Kopp's rule, the following observations can be made. The experimental heat capacities of titanium and zirconium carbides for the region of relatively low temperatures are smaller than the additive values. With rise in temperature, the difference between the experimental and additive values of heat capacity gradually diminishes. As the carbon content of a carbide is lowered, the difference between the experimental and additive heat-capacity values also decreases. Thus, for the titanium carbides TiC₀.₉₉, TiC₀.₈₂, TiC₀.₇₁, and TiC₀.₆₄ at 1300°C, the difference is 7.9, 5.2, 4.9, and 4.3%, respectively. At the same temperature, for the carbides ZrC₀.₉₉, ZrC₀.₇₆, and ZrC₀.₆₉ the difference is 6.5, 3.3, and 2.0%, respectively (to calculate the additive heat capacities of these carbides, use was made of the heat-capacity data for the corresponding metals and carbon reported by Stull and Sinke [4]).

For all the niobium carbides investigated, in contrast to titanium and zirconium carbides, the experimental values of heat capacity at relatively low temperatures exceeded the additive values by about 5%.

Negative deviations from the rule of additivity can be explained by comparing the heating processes of chemico-compound crystals and a mechanical mixture of components of the same stoichiometric composition. Since, during the heating of any crystal, the bulk of the energy is expended on increasing the amplitude of vibrations of the atoms or ions at the crystalline-lattice points, a crystal of a chemical compound in which the atoms or ions are bonded more strongly can store up less energy compared with a mechanical mixture of components of the same composition, in which interatomic bonds are less strong.

In view of this, ignoring the contribution of electronic heat capacity and the anharmonicity of atomic vibrations at high temperatures, for substances of the same kind one can probably postulate the existence of the following qualitative correlation between heat capacity and total chemical-bond strength: the stronger the bonds in a chemical compound, the lower must be its heat capacity. Thus, according to Fesenko [5], total bond strength increases in the triple groups TiC, ZrC, HfC, and VC, NbC, TaC. Accordingly, as follows from our [1-3] and literature [6-8] data, heat capacity in these series decreases. It may be noted that the values of high-temperature elastic moduli of the first kind and mean-square atomic displacements [9], which directly characterize the strength of the chemical bond in a crystal, are also in (qualitative) agreement with the heat-capacity variation in these carbide series.

For niobium carbides, as already noted, positive deviations from Neumann-Kopp's rule were observed. This fact is probably caused firstly by the anharmonicity of atomic vibrations at high temperatures and secondly (and more importantly) by the contribution of electronic heat capacity to the over-all heat capacity of these carbides.


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Indeed, as can be seen from literature data [10, 11], the value of coefficient $\gamma$ in the electronic heat-capacity equation $C_e = \gamma \cdot T$ for niobium carbides is five times that for titanium carbide ($\gamma_{NbC} = 6.3 \cdot 10^{-4}$ and $\gamma_{TiC} = 1.2 \cdot 10^{-4}$ cal/mole/(deg C)). If one assumes that $\gamma = f(T)$ over a wide temperature range, then the contribution of electronic heat capacity to the total heat capacity of niobium carbide at 2000 K will be 9.2%, whereas for titanium carbide the extent of this contribution at the same temperature is 1.7%.

The total strength of the chemical bond in carbides decreases with increasing degree of their carbon deficiency [5]. A heat-capacity calculation with the aid of equations derived earlier [1-3] shows that, at the same time, its gram-formula magnitude also decreases. Heat capacity calculated per 1 g-at, however, increases with increasing number of structural vacancies in a carbide, which is in accord with the starting assumption that heat capacity is related to chemical-bond strength.

Figure 1 shows heat-capacity isotherms plotted for titanium, zirconium, and niobium carbides on the basis of data reported earlier [1-3] for the temperatures of 1200, 1400, and 1600 K. The choice of these temperatures was dictated by the fact that, at higher temperatures, the character of the isotherms becomes disturbed by a more rapid growth in the heat capacity of nonstoichiometric carbides [1-3]. The composition dependence of the heat capacity may be linked with the character of the Me-Me bonds in the carbide lattices.

Cubic carbides of the transition metals of groups IV and V of the periodic system have a NaCl type crystalline structure. The formation of the compounds under investigation is essentially the result of formation of predominantly localized Me-C and Me-Me bonds. Under these conditions, a small number of valence electrons of the metal and carbon atoms are collectivized and form a Fermi fluid of conduction electrons. However, the contribution to the total bond energy from these electrons is small and may be neglected. The C-C bond may also be ignored owing to the structural characteristics of these carbides. In fact, the carbon atoms are neutral because they participate in saturated covalent bonds. In addition, being located in the octahedral pores of the lattice, they are at a considerable distance from one another and are totally shielded by the metal atoms.

In this model of the chemical bond, as developed by Gel'd and Tskhai [12-16], one of the principal premises is that the energy of a single Me-C bond is independent of the number and mutual arrangement of structural C-vacancies. Under these conditions, the nature of the dependence of total bond energy on composition will be governed by the character of Me-Me bond variation with composition. Bearing in mind the above-mentioned qualitative correlation between total bond energy and heat capacity, let us now examine on the basis of the foregoing considerations how the latter varies with composition.

In titanium and zirconium carbides, all four valence electrons of the metal atoms effect (within the framework of the model described) directional bonds with four valence electrons of carbon. As a result, the Me-Me bonds in the lattice of these carbides are weak. The formation of structural vacancies in the carbon sublattice (decreased shielding of the Me-Me bonds) does not substantially alter the energy of this bond. Consequently, the heat-capacity isotherms of titanium and zirconium carbides are virtually linear.

In niobium carbide, because of the presence of the fifth valence electron of the metal atom, the Me-Me bonds are stronger than they are in the carbides of group IV. In the case of the stoichiometric niobium carbide, four electrons of the metal atoms form localized bonds with the carbon atoms, while the fifth reacts with the twelve metal atoms located in the second coordination sphere. The appearance of vacancies in the carbon sublattice results in an increase in the number of Me-Me bond electrons. When the number of vacancies increases, this affects not only the number of Me-Me bond electrons, but also the number of energetically nonequivalent Me-Me bonds passing, respectively, between two carbon atoms and in the vicinity of one or two vacancies. For this reason, when the number of structural vacancies in the carbide increases, the Me-Me reaction changes in a complex manner. Accordingly, the composition dependence of the heat capacity of niobium also has a complex character.