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Abstract

Full Text

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INVESTIGATION OF THE PHYSICOCHEMICAL PROPERTIES OF MELTS OF ZINC AND CADMIUM TELLURIDES

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Phase equilibrium in the binary systems Zn—Te and Cd—Te is described by a phase diagram with one congruently melting compound (^{1}). The compounds ZnTe and CdTe have, in the solid state, a structure of the ZnS type (^{2}) and melt without decomposition at temperatures of 1239 and 1045°, respectively (^{1}). The structure and physicochemical properties of zinc and cadmium tellurides in the solid state have been studied quite fully. However, the question of the behavior of zinc and cadmium tellurides in the liquid state has not yet been examined. The purpose of the present work was to investigate the chemical interaction between zinc (cadmium) and tellurium in the molten state at various temperatures. In doing so, the method of physicochemical analysis, developed in the works of N. S. Kurnakov (^{3}), associated with the construction of chemical composition-property diagrams, was employed. Viscosity and electrical conductivity were taken as structurally sensitive properties.

Fig. 1. Dependence of the electrical conductivity of zinc and cadmium tellurides on temperature

For the investigation, alloys of zinc with tellurium and cadmium with tellurium were prepared with tellurium contents of 30; 40; 45; 50; 55; 60; 70 at. %. Zinc, cadmium, and tellurium of a high degree of purity, containing no more than 10^{-4}% impurities, were used as starting materials. The synthesis was carried out in graphitized quartz ampoules evacuated to 10^{-3} mm Hg, or in corundum crucibles, previously calcined in vacuum and sealed in quartz jackets. The charge was subjected to stepwise heating with two- to three-hour holds at 600-800-1000° (in the case of the Zn—Te system) and 500-700-900° (in the case of the Cd—Te system). At these temperatures a reaction takes place between

Fig. 2 and Fig. 3: isotherms of viscosity and electrical conductivity of melts in the Zn—Te and Cd—Te systems.

Figure 2: Fig. 2 and Fig. 3: isotherms of viscosity and electrical conductivity of melts in the Zn—Te and Cd—Te systems.

the components. The partially reacted substances were crushed, thoroughly mixed, sealed again, and heated to a temperature 50-60° above the corresponding liquidus temperature; they were held for $1^1/_2$ hours with vigorous periodic stirring and slowly cooled with the furnace. From the resulting ingots, specimens 12 mm in diameter and 20 mm high were prepared for viscosity measurements, and specimens 15 mm in diameter and 15 mm high for electrical-conductivity measurements.

Specimens for measuring the viscosity of alloys of the Cd—Te system and the electrical conductivity of all alloys were placed in cylindrical corundum···

crucibles of the appropriate size, sealed in quartz ampoules. Samples for measuring the viscosity of alloys of the Zn—Te system were sealed in graphitized quartz ampoules, which, in turn, were placed in cylindrical graphite crucibles with a screw-on lid. Such an arrangement prevented deformation of the sample, which can occur under the influence of the vapor pressure of the alloy on quartz softened at high temperatures. Measurements of viscosity and electrical conductivity were carried out on the high-temperature vacuum apparatus described in [4].

Fig. 2. Isotherms of viscosity and electrical conductivity of melts in the Zn—Te system.
a —1280°, *b* —1300°, *v* —1350°, *g* —1400°

Fig. 3. Isotherms of viscosity and electrical conductivity of melts in the Cd—Te system.
a —1050°, *b* —1100°, *v* —1150°, *g* —1250°,
a′ —1100°, *b′* —1150°, *v′* —1200°, *g′* —1250°

The results of measurements of the temperature dependence of the electrical conductivity of zinc and cadmium tellurides are shown in Fig. 1. It is evident from the graphs that the electrical conductivity of the solid compounds before melting is very low—on the order of several $\Omega^{-1}\cdot\text{cm}^{-1}$. Upon melting it increases by approximately an order of magnitude. With further heating, the electrical conductivity continues to increase: at first sharply, within a narrow temperature interval above the melting point, and then more slowly. At superheatings of 120° for cadmium telluride and 60° for zinc telluride, the coefficient of the temperature dependence of the electrical conductivity increases noticeably, as a result of which the σ—t curve rises steeply upward.

The investigation of the electrical conductivity of alloys of the Zn—Te and Cd—Te systems

Fig. 4. Electron-valence scheme of the bonds between atoms in compounds of the type A^IITe in the liquid state

Figure 3: Fig. 4. Electron-valence scheme of the bonds between atoms in compounds of the type A^IITe in the liquid state

showed that a deviation of the composition from stoichiometric by $±$5 at.% has only a very slight effect on the absolute values of the electrical conductivity. With more significant deviations (by $±$10–20 at.%) the electrical conductivity increases noticeably with an excess of zinc and cadmium and, to a lesser extent, with an excess of tellurium. In Figs. 2 and 3 the results of measurements of the electrical conductivity and viscosity of alloys of the systems under consideration are presented in the form of isotherms, in comparison with the corresponding equilibrium phase diagrams.

It follows from these graphs that on the electrical-conductivity isotherms the compositions of the compounds ZnTe and CdTe correspond to clearly pronounced minima, while on the viscosity isotherms they correspond to maxima. As the temperature is raised, the extrema lose their singular character and become smoothed out. This phenomenon is observed, in the case of the Zn—Te system, already on the 1300° isotherm (60° above the melting point of the compound), and in the case of the Cd—Te system on the 1150–1250° isotherms.

Fig. 4. Electron-valence scheme of the bonds between atoms in compounds of the type AIITe in the liquid state

On the basis of the experimental data obtained, one can draw certain conclusions about changes in the structure and the nature of the chemical bond during melting and subsequent heating of melts of the compounds ZnTe and CdTe. The character of the temperature dependence of the electrical conductivity of zinc and cadmium tellurides makes it possible, according to the classification of A. R. Regel' 5,6, to assign them to compounds with a transition from the solid to the liquid state of the "semiconductor—semiconductor" type. In principle, the observed character of the transition and of the temperature dependence of the electrical conductivity in the liquid state is also possible in the formation of ionic liquids. However, melts of ionic liquids, as a rule, have a conductivity two orders of magnitude lower than that obtained for zinc and cadmium tellurides7. It therefore remains to assume that in zinc and cadmium tellurides homopolar bonds are preserved upon melting.

In the works of J. D. Bernal8 and A. R. Regel' 5 it was noted that, under conditions of high mobility of particles in a liquid, preservation of homopolar bonds is possible only in the presence of a one-dimensional structure of the chain or molecular type.

From an analysis of the electronic structure of the atoms forming compounds AIITe, it follows that destruction of the spatial system of *sp*3-hybrid bonds upon melting of these compounds may lead to the emergence either of molecules formed according to the valence rule, or of chains (Fig. 4).

In the first case, two covalent bonds may appear between a zinc (cadmium) atom and a tellurium atom, involving two unpaired *p*-electrons of tellurium and two *s*-electrons of zinc (cadmium). In the second case, each zinc (cadmium) atom forms one bond with two neighboring tellurium atoms, and each tellurium atom forms one bond with two neighboring zinc (cadmium) atoms, as a result of which a chain structure of the type A—B—A—B—A is obtained.

The formation of a chain structure seems to us more probable than a molecular one, since in the latter case all electrons would be bound and the electrical conductivity of the melt near the melting point would be very low, which contradicts the experimental results.

The relatively high values of electrical conductivity cannot be attributed to dissociation of the compounds during melting, since the character of the viscosity and electrical-conductivity isotherms indicates the manifestation of strong chemical interaction between zinc (cadmium) and tellurium in the liquid state and the preservation, upon melting, of individual features in alloys of stoichiometric composition corresponding to the compounds ZnTe and

CdTe. In the case of a chain structure, free charge carriers can form at the ends of the chains. The smearing of the extrema on the property isotherms at higher temperatures indicates a weakening of the interaction between the components.

Apparently, it is precisely with the onset of appreciable dissociation of the compounds that the sharp increase in the temperature coefficient of the electrical conductivity of the compounds is associated (Fig. 1).

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REFERENCES

1. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, N. Y.—Toronto—London, 1958.
2. G. B. Bokii, *Introduction to Crystal Chemistry*, Moscow, 1954.
3. N. S. Kurnakov, *Selected Works*, 1, Publishing House of the Academy of Sciences of the USSR, 1960.
4. D. V. Petrov, V. M. Glazov, *Zav. lab.*, No. 1, 34 (1958).
5. A. R. Regel, *Collection: The Structure and Physical Properties of Matter in the Liquid State*, Conference Proceedings, Kiev, 1954.
6. A. R. Regel, *Scientific Notes of the Leningrad State Pedagogical Institute named after A. I. Herzen*, 197, 187 (1958).

7. A. I. Belyaev, E. A. Zhemchuzhina, L. A. Firsanova, *Physical Chemistry of Molten Salts*, Moscow, 1957.

8. J. Bernal, *Trans. Farad. Soc.*, 33, No. 1, 27 (1937).

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