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1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE STRUCTURAL FEATURES OF LIQUID ALLOYS OF SOME BINARY SYSTEMS

(Presented by Academician G. V. Kurdyumov, 25 IV 1957)

In this work an attempt has been made to measure and compare various physical properties of liquid alloys of several binary systems and to determine the most probable characteristic features of short-range order in the corresponding liquids. We have established certain regularities concerning the influence of electron concentration on the properties of liquid alloys, the relation between their thermodynamic and kinetic properties, and the relationship between the structures of alloys in the liquid and solid states.

As "structure-sensitive" properties of a liquid, viscosity and electrical resistivity were chosen. The scheme of the apparatus on which measurements of these properties were carried out is shown in Fig. 1.

The method used by us is a combination of the method of measuring kinematic viscosity from the damping of torsional oscillations of a cylindrical crucible with liquid, suspended on an elastic thread (^{1}), and the method of measuring electrical conductivity from the magnitude of the angle of twisting of a specimen in a rotating magnetic field (^{2}). The apparatus makes it possible to determine viscosity and electrical resistivity in the course of a single experiment. The rotating magnetic field is produced by three pairs of coils located on the inner surface of the housing of the apparatus. The heating element is a graphite tube surrounded by a layer of thermal insulation (soot). Electrical resistivity is determined from the twisting angle α, which is recorded with the aid of a light beam reflected by a small spherical mirror fixed to the suspension. The kinematic viscosity is determined from the logarithmic decrement of the damping of free torsional oscillations of the crucible with the metal. The random error of the viscosity measurements was $\sim 2\%$.

The binary systems were selected in accordance with the type of their phase diagram. In this connection, liquid alloys of the systems Sb–Sn (the liquidus curve rises monotonically from Sn to Sb), Cd–Sb (the presence in the phase diagram of the stable intermetallic compound CdSb and of the metastable compound Cd_3Sb_2, which crystallizes on cooling the melt), Cd–Cu (the presence of an electronic compound with the structure of γ-brass and of the corresponding maximum on the liquidus curve), Pb–Tl (a diagram with a very flat maximum on the liquidus curve), Bi–Tl (a liquidus curve with two maxima), and Fe–Ni

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

(complete solubility in the solid state at high temperatures) were investigated.

The following were used in the work: spectrally pure tin; antimony with traces of iron; cadmium with traces of copper; spectrally pure lead; thallium with traces of copper and silver; bismuth with traces of copper; electrolytic copper, iron, and nickel. All experiments were carried out in an atmosphere of hydrogen. Pure metals, except for nickel, copper, antimony, and iron, and alloys, except for iron-nickel alloys, were prepared by joint melting in hydrogen followed by filtration through porous glass filters.

filters (under pressure). Filtration was used to remove from the liquid various insoluble impurities that strongly affect the viscosity.

Figure 2 shows the isotherms of the kinematic viscosity ν and of the electrical resistivity ρ' (in relative units) as a function of concentration for liquid alloys of the Cd—Sb system, crystallizing according to the metastable phase diagram. The viscosity isotherms have, in the concentration range 40-50 at.% Sb, a maximum that is sharply expressed at 450-550° C and gradually becomes smoothed out as the temperature is raised. When the temperature is lowered, the maximum of ν shifts from 50 at.% Sb toward lower Sb contents, i.e., toward the composition Cd_3Sb_2. At 50-80% Sb, liquid Cd—Sb alloys possess an anomalous temperature coefficient of electrical resistivity.

These data make it possible to consider that, after melting of alloys close to CdSb, an arrangement of atoms close to the structure of the compound CdSb continues to be preserved in the liquid phase,

Fig. 1. Diagram of the apparatus for measuring the viscosity and electrical conductivity of liquid metals.
1 —stator coil, 2 —thermal insulation, 3, 4 —graphite screens, 5 —heating tube (graphite), 6 —weight, 7 —suspension, 8 —tungsten wire, 9 —glass ground joint with a sealed-in molybdenum rod, 10 —crucible, 11 —spherical mirror, 12 — current leads.

Fig. 2. Isotherms of the kinematic viscosity ν (solid lines) and of the specific resistivity ρ' (dashed line) of liquid alloys of the Cd—Sb system.

an arrangement that progressively dissociates with increasing temperature.

From the data presented it may also be concluded that the state of liquid Cd—Sb alloys upon cooling differs from their state upon···

during the preceding heating. The shift of the maximum ν from 50% to 40% Sb upon cooling of the melt indicates that already in the liquid state mutual rearrangements of particles occur, leading to crystallization of the compound

Fig. 3

Figure 2: Fig. 3

Cd_3Sb_2. This assertion is consistent with the noticeable hysteresis of the viscosity of the alloy with 50 at. % Cd and, to a lesser degree, of the alloy with 60 at. % Cd (Fig. 3a, b): upon cooling, the viscosity runs somewhat higher than upon heating. This phenomenon may in principle be similar to the phenomenon of branching in the dependence of the viscosity of pure tin on temperature (^{3}).

Fig. 3. Kinematic viscosity of liquid alloys of the Cd—Sb system:
a—60 at. % Cd, *b*—50 at. % Cd; *c*—kinematic viscosity of pure thallium; *d*—kinematic viscosity ν and angle of twist in a rotating magnetic field α (relative units) of a Bi alloy with 72% Tl.

Hysteresis phenomena were also found in liquid alloys of the Pb—Tl and Bi—Tl systems. All these alloys crystallize with supercooling. The viscosity curve of Pb alloys with 20, 40, and 80 at. % Tl upon cooling lies lower than upon heating (the alloy with 60% Tl showed no hysteresis). Pure thallium behaves in a very distinctive way (see Fig. 3c); the viscosity curve of Tl has a small maximum in the region 350—450° (the electrical conductivity increases with temperature) and an inflection at 600—650° C. These features are reproduced upon reverse cooling of the sample. It may be assumed that in liquid thallium at 350—400° C there occurs a process of change in short-range order, associated with a relative increase in viscosity and electrical conductivity upon heating and with reverse phenomena upon cooling. This process affects the properties of thallium alloys. In particular, Tl alloys with Bi show an anomalous course of viscosity and electrical resistivity near 350—400°, as in the case of pure thallium; moreover, as the Tl content decreases, these anomalies become smoothed out. The second anomaly, in the region 500—600°, is not noticeable

already in alloys with 55.5% and with a lower Tl content. In alloys with 72% and 89% Tl it assumes a curious form: upon heating above 500° and subsequent cooling, the plot of $\nu(T)$ forms a "loop" (Fig. 3, d); the electrical conductivity during cooling is higher than during heating (Fig. 3, e). The dependence of the properties of liquid Bi—Tl alloys on time is found only in the region of the "loop." When an alloy with 72% Tl was held at a temperature of 650—670°, a decrease in viscosity and electrical resistance was observed; the process has an asymptotic character (the relaxation time is of the order of 1 hour). In subsequent slow coolings and heatings the anomalies are no longer noticeable.

The results presented make it possible to consider that, in a number of cases, there may exist states of a liquid which are metastable with respect to other states of the given liquid and stable for a more or less prolonged time. It should be noted that in all the cases investigated, hysteresis phenomena in liquid alloys were accompanied by tendencies toward supercooling.

The viscosity and electrical resistance of liquid alloys of the Cd—Cu system vary

Fig. 4. Isotherms of kinematic viscosity ν (solid lines) and specific resistivity ρ' (dashed lines) of liquid alloys of the Cd—Cu system.

Figure 3: Fig. 4. Isotherms of kinematic viscosity ν (solid lines) and specific resistivity ρ' (dashed lines) of liquid alloys of the Cd—Cu system.

nonmonotonically as a function of concentration; monotonicity is violated at 30—40 at. % Cu, i.e., above the electronic compound Cd_8Cu_5 (the δ-phase) (see Fig. 4, dashed line—relative electrical resistance). These phenomena are associated with the comparatively weak dissociation of the structure of γ-brass upon melting (in contrast to electronic compounds of another type).

Fig. 4. Isotherms of kinematic viscosity ν (solid lines) and specific resistivity ρ' (dashed lines) of liquid alloys of the Cd—Cu system.

In the Pb—Tl, Bi—Tl, and Cd—Sb systems, the form of the viscosity isotherms very much resembles the form of the curves for the onset of solidification. In the Sb—Sn and Fe—Ni systems the situation is, in general, the same; however, at the equiatomic concentration a tendency appears for the viscosity of the alloy to approach the mean value of the viscosities of the components. Therefore the viscosity isotherms of Sb—Sn alloys have two maxima with a minimum in the middle, while the viscosity isotherms of Fe—Ni alloys have two minima. The tendency mentioned is also observed in the Bi—Tl system.

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Received
25 IV 1957

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