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Corresponding Member of the Academy of Sciences of the USSR D. M. Chizhikov, M. E. Volkova, Yu. V. Tsvetkov

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Abstract

Full Text

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Determination of the Activity of Tin Monoxide in Melts of the SnO–SiO_2 System by the E.M.F. Method

The study of the thermodynamics of SnO–SiO_2 melts is of practical importance for the pyrometallurgy of tin. The properties of this silicate system largely determine the losses of tin with the slag and the possibilities of reducing them. However, the thermodynamic characteristics of the SnO–SiO_2 system, both in the solid and in the liquid state, have been little studied. Investigation of the phase diagram ([1,2]) showed that the tin monoxide–silica system is a simple eutectic one. Information on the existence of chemical compounds, such as, for example, $2SnO \cdot SiO_2$ ([3]), was not confirmed.

In the present study, the activity of tin monoxide in silicate melts was determined by the e.m.f. method. For the measurements a galvanic cell was assembled, constituting a concentration cell without transference, which eliminated distortions introduced by the diffusion potential and thermoe.m.f.:

$$\mathrm{Sn} \mid \mathrm{SnO} + \mathrm{SiO_2} \mid \mathrm{Al_2O_3} \mid \mathrm{SnO} \mid \mathrm{Sn}.$$

Tin monoxide served as the standard. Since contradictory data are available in the literature ([4,5]) concerning the possibility of the existence of liquid SnO, we first carried out thermographic and X-ray structural investigations, which confirmed the stability of SnO in the liquid state.

The e.m.f. of the cell is determined by the activity of SnO in the silicate melt

$$E = \frac{RT}{2F} \ln \frac{1}{a_{\mathrm{SnO}}}.$$

Fig. 2. Activity of SnO in melts of the SnO—SiO_2 system at temperatures: 1—1000°; 2—1050°; 3—1100°; 4—1150°

Figure 2: Fig. 2. Activity of SnO in melts of the SnO—SiO_2 system at temperatures: 1—1000°; 2—1050°; 3—1100°; 4—1150°

Fig. 1. Schematic of the electrolytic cell. 1 —tin electrodes; 2 —electrolytes; 3 —molybdenum current leads.

As the initial version of the cell for measuring the e.m.f. in the concentration cell, two corundum crucibles placed one inside the other were used (^{6}). However, because of wetting by the silicate melts of the corundum capillaries protecting the molybdenum current leads, it was not possible to prevent their contact with the silicates; this led to dissolution of molybdenum and a change in the sign of the e.m.f. This difficulty was eliminated with the aid of tin seals formed by two additional crucibles.

The schematic of the electrolytic cell is shown in Fig. 1. The silicate melts were prepared by melting tin dioxide and silica of chemically pure grade in the presence of carbon in a Tammann furnace flushed with nitrogen. The results of phase analysis (^{2}) were in good agreement with the calculated charge data. The experiments were carried out in an atmosphere of purified nitrogen at temperatures of 1000, 1050, 1100, and 1150°. The e.m.f. was measured by the compensation method with

with an accuracy of ±1 mV. To check the concentration cell, silicates of identical composition were loaded into both compartments of the cell. The absence of millivoltmeter readings confirmed that the e.m.f. measured by us was indeed a consequence of the difference in concentration in the silicate melts.

Measurements were made 10-15 min after melting of the silicates, over 1-2 min. For each composition at one temperature, up to 10 measurements were carried out. Fluctuations of the e.m.f. usually did not exceed 2-5%. The activity of SnO was calculated from the mean e.m.f. values using the formula

$$\ln a = -\frac{2F}{RT}E.$$

Fig. 2. Activity of SnO in melts of the SnO—SiO_2 system at temperatures: 1 —1000°; 2—1050°; 3—1100°; 4—1150°.

Figure 2 shows the dependence of the activity of tin monoxide on the composition of the melt for the temperatures studied. As can be seen, in the tin monoxide—silica system there are sign-changing deviations from the laws of ideal solutions. Thus, for example, at a temperature of 1100° in the composition interval from 0.35 to 0.65 mole fractions of SnO there are considerable negative deviations from Raoult' s law; further, a sharp bend is observed, and above 0.7 N SnO there are positive deviations.

Thus, in melts of the SnO—SiO_2 system there is a region in which comparatively strong ordered groupings of atoms of the Sn—O—Si type exist. The stability of these groupings decreases with increasing temperature and concentration of tin monoxide. At 1150° positive deviations are observed practically over the entire concentration interval studied. The transition to positive deviations from Raoult' s law is accompanied by stratification of the system. After high-temperature centrifugation, two layers were clearly distinguished (Fig. 3, see inset, p. 401). Chemical analysis showed that the upper layer corresponded to the composition $2SnO \cdot SiO_2$ (83%) and the lower to a composition of 95.2% SnO. Analysis for SiO_2 gave, respectively, 17.2 and 5.04%.

The inhomogeneity of silicate melts rich in SnO is also indicated by the results of measurements of electrical conductivity at different electrode immersion depths. Thus, for example, for a composition of 90% SnO and a temperature of 1050°, the value of the specific electrical conductivity at an immersion depth of 5 mm was 0.2 $\Omega^{-1}cm^{-1}$, and at a depth of 15 mm, 0.37 $\Omega^{-1}cm^{-1}$. In comparative experiments with non-stratifying silicates (63.3% SnO), the specific electrical conductivity practically did not change with electrode immersion depth. It should be noted that the presence of a stratification region at low silica concentrations is a peculiarity of the system studied. For MeO—SiO_2 systems having sign-changing deviations, stratification at high SiO_2 contents is characteristic, i.e., in regions adjacent to the less polar component (7).

The cause of the anomaly apparently should be sought in comparing the magnitudes of the Me—O bond energy for different oxides with the Si—O bond energy. The Si—O bond energy in the silico-oxygen tetrahedron at $N_{SiO2} = 1/3$, when all SiO_4 tetrahedra are surrounded by metal atoms, may be taken as equal to 104 kcal/mol (8). For an approximate estimate of the Me—O bond energy in the oxides SnO, PbO, FeO, use was made of

values calculated from spectroscopic data and, respectively, equal to 131.99 and 92 kcal/mole. Here a certain regularity is already apparent: in the system MeO —SiO_2, separation in the region adjoining MeO is observed only in a system in which the bond energy of Me—O is greater than that of Si—O. Conversely, stable silicates are formed in those systems where the Me—O bonds are weaker than the Si—O bond.

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