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Abstract

Full Text

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CONTACT POTENTIAL DIFFERENCES BETWEEN CERTAIN LIQUID METALS AND THEIR ALLOYS

(Presented by Academician A. N. Frumkin, December 10, 1960)

In work ([1]) it was noted that contact potential differences between liquid metals have still been insufficiently studied, and that in some cases the reliability of the results obtained is not great. Continuing investigations in this direction, we carried out measurements of contact potential differences between certain liquid metals and their alloys.

Unfortunately, the choice of objects for investigation is not as broad as it might seem at first glance. For determining contact potential differences we use the thermoelectronic method, the essence of which consists in recording the current-voltage characteristics of a diode in which first a pure metal and then its alloy is used as the anode. In this case the magnitude of the contact potential difference can be judged from the shift of the current-voltage curves along the potential axis. In order to increase the reliability of the results, it would have been desirable to use such metals and their alloys for which the contact differences would be as large as possible. It is known ([1]) that, in terms of the magnitudes of the potentials of zero charge (p.z.c.), Zn, Cd, Tl, and Bi, on the one hand, and Te, on the other, differ most substantially. Since the contact potential differences are assumed to be close to the differences in the p.z.c. ([3]), it is expedient to determine them between the above-mentioned metals (Zn, Cd, Tl, Bi) and their alloys with Te. However, during preparation of the experiment the liquid metals are subjected to prolonged evacuation in vacuum. Therefore the use of Zn and Cd is difficult, since they have a high vapor pressure. In addition, many metals, including Bi, form chemical compounds with Te with fairly high melting points, which makes it difficult to obtain alloys concentrated in Te.

Fig. 1. Current-voltage curves:

Fig. 2. Volt-ampere curves A: 1 –Tl, 2 –Tl–Sn alloy (49.8% Sn); B: 1 –Tl, 2 –Tl–Te alloy (50.5% Te)

Figure 2: Fig. 2. Volt-ampere curves A: 1 –Tl, 2 –Tl–Sn alloy (49.8% Sn); B: 1 –Tl, 2 –Tl–Te alloy (50.5% Te)

Fig. 3. Dependence of the PZC of Sn–Tl alloys on composition

Figure 3: Fig. 3. Dependence of the PZC of Sn–Tl alloys on composition

1 –Sn, 2 –Sn-Tl alloy (23.8% Tl)

Below are given the results of measuring the contact differences between Sn and the Sn-Tl alloy (23.8% Tl), Tl and the Tl-Sn alloy (49.8% Sn), Tl and the Tl-Te alloy (50.5% Te), and also Bi and the Bi-Te alloys (3.6% and 9% Te). All concentrations are given in atomic percent. The results of these measurements are compared with the difference in the p.z.c. of the metals and the corresponding alloys. Such a comparison, as is known ([3]), is of great interest.

in connection with the development of the theory of the electromotive forces of galvanic cells.

The Bi and Sn used in the work had purity class B-3; Tl contained Fe, Pb, and Cd impurities in an amount of about 0.02%.* Te was obtained by double sublimation in vacuum of chemically pure Te. The measurement procedure is described in detail in ([1]). All measurements were carried out at a temperature of 450°.

The volt-ampere curves for Sn and the Sn–Tl alloy (23.8% Tl) are shown in Fig. 1, and for Tl and the Tl–Sn alloy (49.8% Sn) in Fig. 2A. The contact potential difference is equal in the first case to 0.17 V, and in the second to 0.25 V.

In order to compare the contact potential differences with the difference in PZC, we determined the PZC from electrocapillary measurements. The results of these determinations are presented in Fig. 3 as the dependence of the PZC on the composition of the alloys. As can be seen from Fig. 3, the PZC of the indicated alloys are shifted, respectively, by 0.14 and 0.22 V relative to the PZC of Sn and Tl, in the first case in the negative direction and in the second in the positive direction.

The volt-ampere curves for Tl and the Tl–Te alloy (50.5% Te) are shown in Fig. 2. The contact potential difference in this case is 0.65 V. Data on the PZC of Te–Tl alloys are given in ([4]). As follows from that work, the PZC of the Tl–Te alloy containing 50.5% Te is shifted by 0.67 V in the positive direction relative to the potential of zero charge of Tl.

Fig. 2. Volt-ampere curves A: 1 –Tl, 2 –Tl–Sn alloy (49.8% Sn); B: 1 –Tl, 2 –Tl–Te alloy (50.5% Te)

Fig. 3. Dependence of the PZC of Sn–Tl alloys on composition

Figure 4. Volt-ampere curves A: 1 –Bi, 2 –Bi–Te alloy (3.6% Te); : 1 –Bi, 2 –Bi–Te alloy (9% Te)

Figure 4: Figure 4. Volt-ampere curves A: 1 –Bi, 2 –Bi–Te alloy (3.6% Te); : 1 –Bi, 2 –Bi–Te alloy (9% Te)

The volt-ampere curves for Bi and Bi–Te alloys containing 3.6 and 9% Te are shown in Fig. 4. As can be seen from these figures, the contact potential differences between Bi and the Bi–Te alloys of the given compositions are respectively 0.3 and 0.35 V. The electrocapillary measurements carried out by us showed that the PZC of the Bi–Te alloys are shifted in the positive direction relative to the PZC of pure Bi by 0.25 and 0.33 V, respectively.

From the results obtained it follows that the contact potential differences between the metals studied by us and their alloys are indeed close to the difference in the potentials of zero charge of the corresponding metals and their alloys. Thus, the assumption of the approximate coincidence of these quantities, expressed by A. N. Frumkin ([3]), receives additional confirmation here.

The following circumstance is noteworthy. The volt-ampere curves of the Tl–Sn, Tl–Te, and Bi–Ti alloys are shifted toward more positive potentials in comparison with the volt-ampere curves of Tl and Bi (Figs. 2, 4)). This evidently means that the electron work function from the indicated alloys is higher than from the corresponding pure metals. In this case

* The spectral analysis of Tl was carried out by R. Gutkina, to whom the authors express their gratitude.

of the c.p.d. of the alloys prove to be shifted in the positive direction by an amount approximately equal to the contact potential difference. On the contrary, the volt-ampere curve of the Sn–Tl alloy is shifted toward less positive potentials (Fig. 1), which indicates a decrease in the electron work function from the alloy as compared with the work function for Sn. At the same time, the c.p.d. of the alloy proves to be shifted in the negative direction. This confirms the existence of a parallelism between the c.p.d. of metals and the work function of electrons from them, established in work ([5]).

Fig. 4. Volt-ampere curves **A**: 1 –Bi, 2 –Bi–Te alloy (3.6% Te); **B**: 1 –Bi, 2 –Bi–Te alloy (9% Te)

In conclusion, we express our deep gratitude to Academician A. N. Frumkin for his exceptional attention to our work and for valuable advice.

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