Physical Chemistry

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1965

SovietRxiv

Abstract

Full Text

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Experimental proof of the absence of absolute electromigration in liquid Pb, Sn, In, Ga

(Presented by Academician G. V. Kurdyumov, 20 VII 1964)

In a number of works the phenomenon of absolute electromigration in solid pure metals and alloys was discovered ($^{1-8}$), having many features in common with the Kirkendall effect. The mechanism of absolute electromigration can be understood by using the concept of an activated state of the moving ion (^{1}). Since in a pure solid metal, when a direct current is passed through a specimen, a redistribution of matter relative to a certain fixed plane of the lattice should occur, the displacement of the ions is reckoned relative to an inert marker, the atoms of which do not participate in diffusion motion under the given conditions ($^{2-8}$). But the question of whether absolute electromigration exists in liquid metals has not been investigated by anyone.

When studying electromigration in liquid metals, the displacement of one of the components should be determined relative to another component ($^{9-12}$).

We studied this phenomenon for liquid Pb, Sn, In, Ga by the "capillary" method. For this purpose it was necessary to place, inside a capillary filled with metal (approximately in the middle), an inert marker, for which colloidal particles of Co^{60}, suspended in the liquid metal, served.

Table 1

Nos.	Object	τ, h	E, V/cm	T, °C	d, mm
1	Pb	9	0.150	480	0.50
2	Pb	20	0.090	430	0.80
3	Pb	15	0.100	380	0.63
4	Pb	27	0.070	360	0.86
5	Pb	27	0.075	360	0.76
6	2-4 at. % Co alloy in Sn	20	0.035	400	1.00
7	2-4 at. % Co alloy in Sn	23	0.085	400	0.55
8	2-4 at. % Co alloy in Sn	30	0.045	400	0.83
9	2-4 at. % Co alloy in Sn	30	0.060	300	0.72
10	2-4 at. % Co alloy in Sn	50	0.045	300	0.75
11	2-4 at. % Co alloy in Sn	12	0.030	270	0.47
12	2-4 at. % Co alloy in Sn	19	0.025	180	0.63

Fig. 1

Figure 1: Fig. 1

Nos.	Object	τ, h	E, V/cm	T, °C	d, mm
13	In	23	0.045	180	0.63
14	In	19	0.025	190	0.67
15	In	15	0.055	100	0.53
16	Ga	25	0.030	90	0.72
17	Ga	15	0.030	60	0.61

Note. 1. τ —duration of the experiment, E —field strength, T —temperature, d —capillary diameter, Δ —displacement of the inert marker of colloidal Co^{60} particles. Displacement of the inert marker $\Delta = 0.0 \pm 1$-3 mm. 2. The displacement of the inert marker from its initial position during electromigration (1-3 mm) is mainly due to thermal displacement: the transition from the solid state to the liquid state and from the liquid to the solid state, respectively, increases or decreases the linear dimensions of the metal being studied.

The inert marker was introduced in the following way: a) the quartz capillary filled with metal ($d = 0.5$-0.8 mm) was broken approximately into two equal parts; b) into the end of one of these capillaries, freed of metal (4-5 cm long), a piece of cobalt alloy (4 at. %) in tin, 0.5-1 mm long, was inserted above the flame of an alcohol lamp with the aid of a molybdenum wire, and then 5-10 mm of the metal under investigation was added in the same way; c) at the end of the other capillary, 1-2 mm of metal was bared from the quartz; d) a quartz tube of such an internal ···

diameter, so that both capillaries could enter it. In this case, 1-2 mm of metal not covered with quartz was brought close to the end of the second capillary into which the radioactive insert had been introduced; d) over the flame of an alcohol lamp both capillaries were brought into good mechanical and electrical contact, and copper wires were tightly inserted into the ends of the combined capillary.

Inside the copper block of the apparatus it was possible to place two capillary samples at once. First the copper block was heated to the melting temperature of the metal under study, and then a direct current was passed through the capillary samples for a definite time (Table 1). The temperature of the copper block was measured with a thermocouple, and the temperature increase in the capillary sample arising as a result of the passage of the direct current was determined from the change in the resistance of the liquid metal by the compensation method.

Fig. 1. Distribution curve of the concentration of Co^{60} in liquid Pb along the capillary sample, $\tau = 20$ h, $T = 430°$, $E = 0.09$ V/cm,

Fig. 2

Figure 2: Fig. 2

$d = 0.8$ mm

Fig. 2. Distribution curve of the concentration of Co^{60} in liquid In along the capillary sample, $\tau = 19$ h, $T = 190^\circ$, $E = 0.025$ V/cm,
$d = 0.67$ mm

After completion of the experiment the sample was freed from the quartz, and the remaining cylindrical wire of metal was cut into pieces, the γ-activity of which was measured on a PS -100 (“Volna”) counting apparatus, and the weight was determined on microanalytical balances. The distribution of the specific γ-activity along the sample for liquid lead is shown in Fig. 1, in which the origin of coordinates coincides with the place in the capillary sample where the Co^{60} particles were placed. Curves of the same type were also obtained for indium (Fig. 2), gallium, and a 2-3 at.% alloy of cobalt in tin, with the difference that the solubility “tails” in these metals and alloys were larger than for lead (Fig. 1).

In the case of the presence of absolute electromigration, the colloidal particles of Co^{60} serving as an inert label, being in suspension, should move together with the flow of liquid metal in the direction opposite to the direction of electromigration. This is due to the fact that the activated ions of the liquid metal will move in the direction of the resul-

of the acting force, and since the capillary is closed at both ends by electrodes, an impulse will be imparted to the entire liquid in it in the direction opposite to electromigration.

In experiments on electromigration in solid metals and alloys it was shown that the determining force of electromigration is the force of the “electron wind” (3–8), i.e., the transfer of matter occurs toward the anode. Applying Fiks’s calculation of the “electron-wind” force (1), the rate of electromigration in liquid metals may be taken as ~ 0.1 cm/hr. Thus one should have expected a displacement of the inert marker toward the cathode by 1-5 cm (for 10-50 hr of experiment).

However, in our experiments with liquid Pb, Sn, In, and Ga we did not observe such a displacement of the inert marker, to an accuracy of 1-3 mm, either toward the cathode or toward the anode (see Figs. 1 and 2, Table 1).

In order to verify the correctness of the problem posed, it was necessary to prove that: 1) the radioactive insert and the main mass of the metal were in the liquid state, 2) colloidal particles were present in the radioactive insert, and 3) the colloidal particles of Co^{60} were suspended in the liquid metal and did not settle to the bottom of the capillary during the experiment.

Fig. 3. Distribution of γ-activity over the diameter of the radioactive insert for

Figure 3

Figure 3: Figure 3

colloidal Co^{60} particles in liquid lead at $\tau = 9$ hr, $T = 400^\circ$, $E = 0.135$ V/cm, radius of the cylindrical insert $r = 0.265$ mm (a), and $\tau = 9.5$ hr, $T = 350^\circ$, $r = 0.275$ mm (without current) (b).

The "tails" of solubility in our experiments (Figs. 1, 2) indicate that the radioactive insert was in the liquid state during the experiment. The capillary specimen with the inert marker was placed in a vertical furnace, where it was held for 10-30 hr at the same temperature as in the experiments studying electromigration. By determining the distribution of γ-activity over height, we could estimate the size of the Co^{60} particles using Stokes' s formula and assuming that the particles had a spherical shape. By regulating the quenching rate of a 4% Co alloy in tin, we succeeded in finding a particle size such that, over 20-50 hr, the particles remained practically immobile, i.e., did not settle to the bottom of the horizontally lying capillary specimen. The radius of such colloidal particles, if they are spherical, should be less than $0.1\,\mu$.

By successive etching in aqua regia (after the end of the electromigration experiment), we determined the distribution of γ-activity over the diameter of the insert. Figure 3a shows the distribution of γ-activity over the diameter of the insert for Co^{60} particles in lead (direct current), and Fig. 3b shows the same for Co^{60} particles in lead in an experiment with the temperature of liquid lead but without current. The observed increase in γ-activity toward the axis of the insert in electromigration experiments, in comparison with the distribution of particles over the diameter of the insert in the experiment without current, can be explained by the different electrical conductivity of the colloidal particle and the liquid metal. When a direct current passes through the liquid metal, because of the presence of its own magnetic field, a Lorentz force directed toward the axis of the capillary will act on the particle. Therefore the effect of particle concentration near the capillary axis should be greater for liquid lead and smaller

for liquid indium. We were able to note such a regularity in studying the distribution of the γ-activity of colloidal particles of Co^{60} along the diameter of the insert in experiments on the phenomenon of absolute electrotransport in liquid Pb, Sn, In, Ga. A rough estimate of the magnitude of the displacement of a colloidal particle under the action of the Lorentz force agrees with the experimental data.

Thus, the problem was posed correctly: the colloidal particles, being suspended in the liquid metal, played the role of an inert marker in our experiments.

Analyzing the fact that the phenomenon of absolute electrotransport is absent in liquid Pb, Sn, In, Ga, together with experiments on isotope separation by direct current in these liquid metals (15-17), one may, in our opinion, draw the following conclusions:

1. The mechanism of diffusion in liquid Pb, Sn, In, Ga is not of an activation character, but of a viscous character; i.e., an atom (ion) does not pass into an activated state, but, by means of fluctuation-acquired energy, is displaced by some nonfixed distance, while as if pushing apart its neighbors. This process is similar to the diffusion motion of Brownian particles or to the diffusion motion of macromolecules in a solvent consisting of small molecules or atoms.
2. The effect of isotope separation by direct current in liquid Ga, In, Sn (15–17), from the standpoint of the absence of absolute electrotransport in these liquid metals, can be explained as follows. Forces differing in direction will act on the light and heavy isotopes, causing the light isotope to move toward the anode and the heavy one toward the cathode. Different electron-scattering cross sections of the heavy and light isotopes determine their motion in different directions, whereas, in the opinion of a number of authors (1, 13, 14, 18), light and heavy isotopes should move in one direction, but the light isotopic ion should overtake the heavy one.

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Received
10 VII 1964

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