ELECTRODIFFUSION AND RELATIVE DENSITY OF ENERGY STATES AT THE FERMI LEVEL IN THE SYSTEM Al–Zn AT 700°C

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The effective charge of zinc in the system Al–Zn was determined, using the electrodiffusion method, at 700°C. On the basis of the relation of electrodiffusion to the electric conductivity and using the experimentally determined values of the effective charge in the mentioned system the relative density of energy states at the Fermi level over the whole concentration region as well as the factor g for pure Al were calculated.

The aim of this communication is to determine the effective charge of zinc in the system Al–Zn at 700°C and with its help to investigate the electron characteristics over the entire concentration region of this system.

The effective charge of zinc in the system under study was determined earlier at 580°C. According to this study[1], an inversion of the effective charge occurs at this temperature. In addition, in the determination of the effective charge at 700°C the task was to check the experimental method for higher temperatures[2,3]. This method differs from that one used in ref.[1], where the effective charge was determined by the non-stationary method. In this method the velocity of migration of a component in the electric field, *i.e.* the relative electric mobility, is determined. The coefficient of mutual diffusion must be known in order to determine the effective charge. As in ref.[1] the temperature was 580°C, the effective charge for highly diluted Al solutions could not be determined.

A detailed theoretical treatment as well as experimental results on electrodiffusion in melted metals and semiconductors have been reported in the literature[4-6].

EXPERIMENTAL

Method

A modification of the high-temperature stationary method[2,3] was employed in the measurements of electrodiffusion in the system Al–Zn at 700°C. Straight vertical graphite capillaries were used: graphite bars of O. D. 6 mm, 60 mm long, were bored axially to obtain circular holes of I. D. 1·2 mm, 45 to 50 mm deep. The capillaries were heated up to 1100°C under the vacuum of 10^{-3} Torr before being filled up. The filled capillary was exposed to the electrodiffusion annealing for a time necessary to achieve a stationary state of the components in the sample. The current density was kept with each sample at 1·0–1·5 A/mm^2. The current polarity was chosen so that the heavier component migrated downwards in the vertical capillary (Zn, in this case). In the opposite case, convection in the melt can take place. For the same reason, the temperature gradient along the capillary was chosen in such a way that the temperature of the alloy in the upper part of the capillary was by 10—12°C higher than in the lower part. After the period of time necessary to reach the stationary state (24—30 hours), the samples were suddenly cooled in water from 700°C so that the stationary distribution of the components along the capillary was fixed. The graphite envelope of the solidfied sample was then broken, the metal surface was mechanically cleaned, cut to 6—7 mm long pieces, and subjected to chemical analysis. Zinc was analyzed by vacuum distillation at 700°C and 10^{-3} Torr for 60 minutes. These conditions were satisfactory to quantitatively remove zinc from the samples. Small amounts of aluminium were determined by complexometric titrations.

Calculations

The effective charge was calculated from the relation[2]

$$\mathrm{d}\ln a/\mathrm{d}x = EeZ^*/kT \qquad (1)$$

in which a is the activity of one of the components, x the capillary-length parameter, E the intensity of the electric field, e the elementary charge, k the Boltzmann constant, T the absolute temperature, Z^* the effective charge in units of electron charge. The differential quotient on the left side of equation (*1*) can be rewritten as $\mathrm{d}\ln a/\mathrm{d}x = \mathrm{d}\ln a/\mathrm{d}\ln N \, . \, \mathrm{d}\ln N/\mathrm{d}x$, where N is the mole fraction of the component studied. The thermodynamic coefficient $\mathrm{d}\ln a/\mathrm{d}\ln N$ for the required temperature is obtained from the published data[7]. Values of the coefficient $\mathrm{d}\ln N/\mathrm{d}x$ were evaluated from the chemical analysis by the least-square method. The coefficient $\mathrm{d}\ln N/\mathrm{d}x$ represents the slope of the straight line of the dependence $\ln N = \mathrm{f}(x)$.

According to the Mott–Faber theory[8,9] the specific electrical conductivity of a liquid metal is given by

$$\varkappa = g^2 e^2 Sl/12\,\pi^3\,h\,, \qquad (2)$$

where l is the Fermi electron free path, h the Planck constant, S the Fermi surface area in the k space assuming free electrons, g is the factor given by $g = N(\varepsilon_F)/N(\varepsilon_F)_{\mathrm{Fem}}$, where the numerator is the actual density of energy states at the Fermi level of real metals and the denominator is the energy states density for the free electron model (Fem).

Starting from the Mott–Faber theory and employing the relation between electrodiffusion and electrical conductivity in molten metals, Belaščenko[10] pointed out that an important characteristics of the electron gas can be obtained — the relative density of energy states at the Fermi level. For a binary system and a constant temperature the following expression was derived by him

$$\ln\left[\frac{Z_2\varrho V(k_F^2g^2)}{Z\varrho_2V_2(k_F^2g^2)_2}\right] = \int_0^{N_1}\left(\frac{Z_2^*}{ZN_1}\right)\mathrm{d}N_1\,. \qquad (3)$$

Here, ϱ is the specific electrical resistance of the melt, V the molar volume of the melt, Z_2^* the effective charge of the second component, N_1 the mole fraction of the first component, $Z = Z_1N_1 + Z_2N_2$ is the mean charge of ions in the solution, where Z_1 and Z_2 are actual charges of the ions, according to the group number of the periodic system, k_F is the absolute value of the wave-vector of an electron at the Fermi level. Symbols indexed "2" refer to properties of the pure second component (Zn, in our case), and symbols without indices refer to properties of the solution. Equation (*3*) makes it possible to determine ($k_F^2g^2$) for any solution of a binary system with respect to a pure component, assuming the dependence of effective and actual charges on the concentration is known.

RESULTS AND DISCUSSION

The dependence of the effective charge of zinc, Z_{Zn}^*, on the concentration at 700°C is shown in Fig. 1. A change of the effective charge sign occurs at ≈0·52 and ≈0·67N_{Zn} with a minimum of the function at ≈0·6N_{Zn}. The value of Z_{Zn}^* decreases steeply

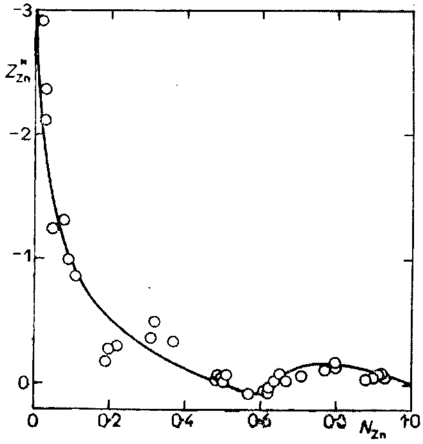

FIG. 1

Dependence of the Effective Charge of Zn on Concentration at 700°C

TABLE I

Dependence of Electron Characteristics on Concentration

N_1	V cm^3/mol	$\varrho \cdot 10^6$ Ω . cm	$\bar{Z}$	$\frac{k_F^2}{(k_F^2)_2}$	$\frac{g}{g_2}$
0·0	10·440	36·85	2·0	1·0	1·0
0·1	10·525	36·80	2·1	1·028	1·0
0·2	10·630	36·50	2·2	1·053	0·998
0·3	10·750	33·20	2·3	1·077	1·047
0·4	10·869	34·90	2·4	1·100	1·026
0·5	10·980	33·20	2·5	1·123	1·057
0·6	11·075	32·20	2·6	1·146	1·076
0·7	11·155	30·70	2·7	1·169	1·102
0·8	11·235	29·10	2·8	1·192	1·129
0·9	11·328	27·80	2·9	1·214	1·145
1·0	11·450	24·70	3·0	1·233	1·180

with the concentration. Z^*_{Zn} in this system was measured at 580°C by the non-stationary method[1]: it was found that over the region 60 – 68 mol% of zinc Z^*_{Zn} was positive, outside of this region it was negative. The differing results in the values of the effective charge of zinc may be explained by the different experimental methods and partially also by different temperatures. The change of sign of the effective charge at a certain composition of the solution may be caused by a change in the short-range structure of the melt, *i.e.* by a change of short-range order.

From equation (*3*) values of $k_F^2 g^2/(k_F^2 g^2)_2$ and g/g_2 were calculated for the entire concentration region of the system Al–Zn at 700°C (Table I). Values of the specific electrical resistance and the molar volume V were taken from the literature[11,12]. Numerical values of the integral in equation (*3*) were obtained by graphical integration of the function $Z_2^*/\bar{Z}N_1 = f(N_1)$. Values corresponding to $k_F^2/(k_F^2)_2$ were calculated for the free electron model using the relation[13]: $k_F^2/(k_F^2)_2 = (\bar{Z}V_2/Z_2V)^{2/3}$. It follows from Table I for g/g_2 that the irregularity in the course of the functional dependence $g/g_2 = f(N_1)$ occurs between 0·3 and $0{\cdot}4N_1$ in comparison with the course of the dependence $k_F^2/(k_F^2)_2 = f(N_1)$ for the free electron model. This indicates that in the region $0{\cdot}3 - 0{\cdot}4N_1$ a change in the short-range structural arrangement of the melt occurs. According to ref.[2], in the system Ag–Sn at 1 100°C a minimum of the function g/g_{Sn} agrees with the position of a maximum on the isotherm of the specific electrical resistance. This maximum is due to peculiarities in the short-range structural arrangement of the melt, as it was confirmed by theoretical calculations of the electrical resistance, too[14]. Similarly, in the system Al–Zn the position of the maximum on the specific electrical resistance[11] at $0{\cdot}6N_1$ agrees well with the minimum of the function $g/g_2 = f(N_1)$ (Table I).

If one knows the g-factor of one component of the binary mixture, the unknown g-factor of the other component can be calculated with the help of the function g/g_2 for $N_1 = 1$. According to ref.[15], $g_{Zn} = 1{\cdot}19$. From Table I for $N_1 = 1$, $g/g_2 = 1{\cdot}18$, which leads to $g = g_{Al} = 1{\cdot}18 \,.\, 1{\cdot}19 = 1{\cdot}40$. The relative density of energy states is in case of Al by 40% higher in comparison with the free electron model.

The experimental data obtained show that the electrodiffusion method can be successfully applied to the studies of properties of molten metal systems. Electrodiffusion appears to be – in comparison with other methods (*e.g.*, viscosity or electrical conductivity) a method more sensitive to the structure of melts. From studies carried out up to now as well as from the experimental data obtained one may conclude that the factor g introduced by Mott characterizes not only the relative density of energy states at the Fermi level, but probably indicates also changes in the structural arrangement of the melt.

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