

Determination of Solid Solubility by Means of Diffusion Measurements

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The solubility of Ag in solid Sn has been determined by measuring the diffusion of the radioactive isotopes Ag-110, Sn-123 and Tl-204 in Sn-Ag alloys.

The concentration dependence of the diffusion constant changes if a new phase appears. By the help of the break points the phase boundary of the solid solution can be drawn on the Sn-side of the Sn-Ag phase diagram.

DÉTERMINATION DE LA SOLUBILITÉ EN PHASE SOLIDE PAR LE MESURAGE DE LA DIFFUSION

La solubilité de Ag dans Sn était déterminée par le mesurage de la diffusion des isotopes radioactifs de Ag-110, Sn-123 et Tl-204 dans des alliages de Sn-Ag.

La dépendance de concentration de la constante de diffusion change en cas de l'apparition d'une nouvelle phase. A l'aide des points d'angle la limite de phase de la solution solide peut être dessinée sur la partie Sn du diagramme de phase.

ОПРЕДЕЛЕНИЕ РАСТВОРИМОСТИ ТВЕРДЫХ ТЕЛ ПОСРЕДСТВОМ ДИФФУЗИОННЫХ ИЗМЕРЕНИЙ

Определили растворимость серебра в твёрдом олове с помощью измерения диффузии радиоактивных изотопов Ag-110, Sn-123 и Tl-204 в сплавах Sn-Ag.

Зависимость коэффициента диффузии от концентрации, изменяется при появлении новой фазы. С помощью точек излома на кривых можно было нарисовать границу твёрдого раствора на фазовом диаграмме Sn-Ag со стороны Sn.

LÖSLICHKEITSBESTIMMUNG IN FESTER PHASE DURCH DIFFUSIONSMESSUNGEN

Die Löslichkeit von Ag im festen Sn wurde durch die Diffusionsmessung der radioaktiven Isotope Ag-110, Sn-123 und Tl-204 in Sn-Ag Legierungen bestimmt.

Die Konzentrationsabhängigkeit der Diffusionskonstante ändert sich bei dem Auftreten einer neuen Phase. Mittels der Knickpunkte konnte die Phasengrenze der festen Lösung auf der Sn-Seite des Sn-Ag Phasendiagrammes angegeben werden.

THERE is not too much information in the literature about the determination of solid solubility by means of diffusion measurements though SEITH and KEL⁽¹⁾ had completed the conductivity data for the solubility of Ag in solid Pb with results of diffusion measurements as early as 1933. Probably the first reason for this is the high man power requirement of such experiments compared with other methods and also the relatively high experimental errors.

The data in the literature about the solubility of Ag in solid Sn⁽²⁾ are insufficient and contradictory. Therefore, and also because of the small solubility values, the phase-boundary of the terminal solid solution is not given in the

Sn-side of the Sn-Ag phase diagram. Earlier, we investigated the conditions of the homogenization of Sn-Ag alloys of Ag contents between 10⁻⁷ and 10⁻¹ per cent^(3,4) and now we determined the solubility of Ag.

The determination was based on the assumption that the concentration dependence of the diffusion coefficients changes if a new phase develops.

For the solubility measurements we investigated the diffusion of Sn, Ag and Tl in Sn-Ag alloys using the radioactive isotopes Sn-123, Ag-110 and Tl-204. In such cases the phase equilibrium is not supposed to be disturbed by the diffusing atoms.

EXPERIMENTAL

Alloys were prepared by melting high purity (JOHNSON and METTHEY) Sn and Ag in quartz vessel in 10^{-4} Torr vacuum. The alloys were homogenized by heating them also in vacuum at 220°C . The homogeneity of the samples was controlled by analyzing different parts of them. Samples of low Ag concentration were made diluting stock-alloys with Sn by vacuum-melting. The samples had the following Ag concentration values:

| |
|-----------------------------|
| 3.3×10^{-4} atm % |
| 1.10×10^{-3} atm % |
| 5.45×10^{-3} atm % |
| 8.72×10^{-3} atm % |
| 1.09×10^{-2} atm % |
| 5.45×10^{-2} atm % |
| 5.45×10^{-1} atm % |
| 1.09 atm % |

A homogeneous Ag distribution could be

supposed only in the bulk of crystals even after a heat-treatment of the 10 mm thick samples which were discs of 9 mm diameter. We have found earlier⁽⁵⁾ that the Ag concentration of the grains differs from that in the grain-boundaries, which also depends on the relative orientation difference.

The average grain-size of our samples in the one phase state was about 3 mm, therefore the volume of the boundary-zone was only a small fraction of that of the grains and the error caused in the mean concentration value by the grain-boundaries was negligible.

A radioactive layer of a thickness between $0.1\text{--}0.5 \mu\text{m}$ containing one of the Ag-110, Sn-123 or Tl-204 isotopes was electrodeposited on the base of the samples, which were then annealed in vacuum with an accuracy of $\pm 1^{\circ}\text{C}$ on a temperature between $137\text{--}200^{\circ}\text{C}$.

Diffusion measurements were made by autoradiography⁽⁶⁾ using Kodak AR-10 stripping films. The density of the autoradiograms was

TABLE I. Volume diffusion constants of Ag, Sn and Tl in different Sn-Ag alloys

| C_{Ag} atm% | $D \text{ cm}^2\text{-S}^{-1}$ | | | |
|-----------------------|--------------------------------|------------------------|------------------------|------------------------|
| | 137 | Ag 165 | 186 | 200 |
| 3.3×10^{-4} | 4.28×10^{-11} | | 2.73×10^{-10} | |
| 1.10×10^{-3} | 4.24×10^{-11} | | 2.46×10^{-10} | 4.24×10^{-10} |
| 5.45×10^{-3} | 2.58×10^{-11} | | 1.67×10^{-10} | |
| 8.72×10^{-3} | 2.58×10^{-11} | | 1.32×10^{-10} | |
| 1.09×10^{-2} | 2.61×10^{-11} | | 1.05×10^{-10} | 2.29×10^{-10} |
| 5.45×10^{-2} | 2.74×10^{-11} | | 1.13×10^{-10} | |
| 5.45×10^{-1} | 5.07×10^{-11} | | 2.06×10^{-10} | 2.93×10^{-10} |
| 1.09 | 10.5×10^{-11} | | 4.26×10^{-10} | 5.84×10^{-10} |
| | | Sn | | |
| 3.3×10^{-4} | 0.45×10^{-11} | 1.96×10^{-11} | 5.52×10^{-11} | 1.02×10^{-10} |
| 1.10×10^{-3} | 0.45×10^{-11} | 2.00×10^{-11} | 5.86×10^{-11} | 1.07×10^{-10} |
| 5.45×10^{-3} | 0.49×10^{-11} | 2.67×10^{-11} | 5.69×10^{-11} | 1.26×10^{-10} |
| 8.72×10^{-3} | 0.50×10^{-11} | — | 7.69×10^{-11} | 1.46×10^{-10} |
| 1.09×10^{-2} | 0.51×10^{-11} | 2.73×10^{-11} | — | 1.55×10^{-10} |
| 5.45×10^{-2} | 0.53×10^{-11} | 2.81×10^{-11} | 8.32×10^{-11} | 1.96×10^{-10} |
| 5.45×10^{-1} | 0.86×10^{-11} | 4.06×10^{-11} | 11.8×10^{-11} | 2.32×10^{-10} |
| 1.09 | 1.6×10^{-11} | 5.89×10^{-11} | 15.8×10^{-11} | 2.76×10^{-10} |
| | | Tl | | |
| 3.3×10^{-4} | 2.54×10^{-11} | 7.85×10^{-11} | 1.45×10^{-10} | 2.36×10^{-10} |
| 1.10×10^{-3} | 2.48×10^{-11} | 7.33×10^{-11} | 1.43×10^{-10} | 2.26×10^{-10} |
| 5.45×10^{-3} | 2.24×10^{-11} | 6.95×10^{-11} | 1.34×10^{-10} | 2.17×10^{-10} |
| 8.72×10^{-3} | 2.34×10^{-11} | 6.64×10^{-11} | 1.26×10^{-10} | 2.00×10^{-10} |
| 1.09×10^{-2} | 2.40×10^{-11} | 6.28×10^{-11} | 1.23×10^{-10} | — |
| 5.45×10^{-2} | 2.54×10^{-11} | 6.35×10^{-11} | 1.25×10^{-10} | 1.85×10^{-10} |
| 5.45×10^{-1} | 2.82×10^{-11} | 7.18×10^{-11} | 1.39×10^{-10} | 2.16×10^{-10} |
| 1.09 | 3.30×10^{-11} | 8.31×10^{-11} | 1.63×10^{-10} | 2.49×10^{-10} |

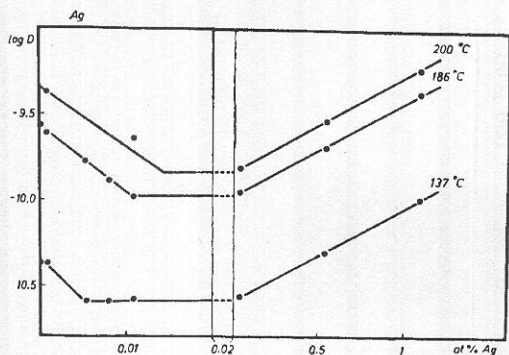


Fig. 1a. Diffusion of Ag-110 in Sn-Ag alloys of different composition.

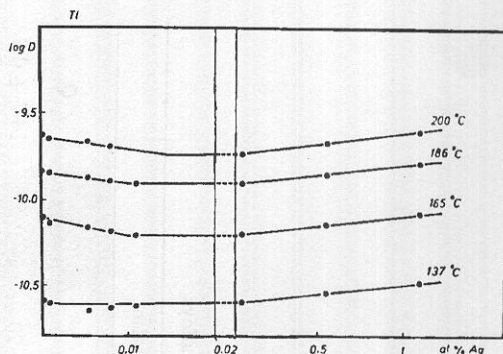


Fig. 1c. Diffusion of Tl-204 in Sn-Ag alloys of different composition.

measured with a Zeiss recording microphotometer on places free of grain boundaries. In case of two-phase samples an effective diffusion coefficient was measured.

RESULTS AND DISCUSSION

The measured diffusion coefficients were summarized in Table I, and were plotted against the Ag concentration.

The diffusion-isothermes have two linear parts. The concentration-value at the break point was considered as the solubility limit for the Ag. Below that concentration a single phase system exists characterized by the tin-lattice containing dissolved Ag atoms. Above this concentration a new phase appears which increases with the increasing mean-concentration of Ag but the composition of the phases remains constant. The rate of diffusion in the new phase differs from that in the solid solution

phase and the whole system can be characterized with a mean value. This mean value will differ from the diffusion in the concentrated solid solution only if the new phase is sufficient for causing an effect higher than the experimental error. The mean value has also a third component, the grain-boundary diffusion, which

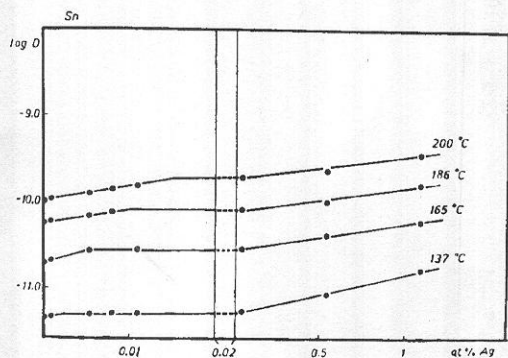


Fig. 1b. Diffusion of Sn-123 in Sn-Ag alloys of different composition.

▲ (9)
■ (10)
x, o, ● present work

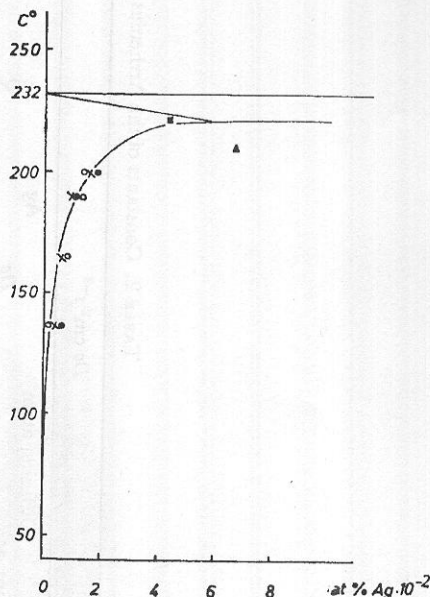


Fig. 2. The phase-boundary of the Sn-Ag solid solution.

may have a role because of the big specific surface of the small new-phase particles. But the role of it decreases with increasing Ag concentration. Thus, the mean value of the diffusion coefficient in a two phase system could be described schematically as follows:

$$D = mD_{v_1} + nD_{v_2} + s \cdot D_{1-2}$$

where m , n and s are relative figures for the participation of the three events in the whole process, D_{v_1} and D_{v_2} are the volume-diffusion coefficients in the two phases, and D_{1-2} is the diffusion-coefficient on the boundaries between the two phases.

For the reasons mentioned above, the measurements are not well defined experimentally in the two phase system close to the solubility-limit, therefore the break-point can be determined by extrapolation using points relatively far from it. For emphasizing this fact we made a break on the abscissa of our Fig. 1(a, b and c) and we also changed the scale of it.

The temperature dependence of the diffusion-coefficients can be described by Arrhenius equations which are valid—as an approach—to a certain concentration-region. Table 2 shows the constants of such equations. The data are

in agreement with those found earlier for the diffusion of the same radioactive atoms in high-purity tin.⁽⁶⁻⁸⁾

The solid-solution boundary line of the phase diagram—drawn on the basis of the break-points of the diffusion-isothermes is shown in Fig. 2, which contains also results of other authors.

The experiments proved the applicability of diffusion measurements for determination of solid-solubility.

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