The Ag-Rich Side of the Binary Phase Diagrams Ag/Au and Ag/Cu as Studied by Zone Refining

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The Ag-rich side of the system Ag/Au and Ag/Cu has been investigated by the zone refining method. The opening angle of the liquidus-solidus gap of the system Ag/Au is in disagreement with older data, but is indistinguishable from the recent reinvestigation of the system. The system Ag/Cu also deviates from the commonly accepted phase diagram in that the opening angle is greater than that commonly accepted. Determinations of the segregation coefficients as a function of concentration of solute in the concentration range investigated show that the ratio of the activities departs markedly from the ratio of concentrations for Cu in Ag for concentrations above 0.5 atomic %. No such departure was found in the system Ag/Au in the concentration range investigated. The obvious usefulness of the zone refining method in the determination of the opening angle of the liquidus/solidus gap in binary systems is shown.

Since the invention of the zone refining method by Pfann [1], several practical consequences of the invention have been evaluated and have been used in many laboratories. Much work has also been done on the evaluation of concentration profiles, based on either the simple or the more complicated equations describing this process.

It is usual to define the distribution coefficient as the ratio between the solubilities in the solid and the liquid states:

$$k_0 = \frac{c_s}{c_1}$$

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If k_0 can be found by experiment, the opening angle between the liquidus- and the solidus-curve can be determined to the same degree of accuracy as the liquidus-curve. It is well known that the accuracy in determining the liquidus-curve is much higher than that of the solidus-curve. The accuracy of the opening angle in the binary phase-diagrams so far published is probably low.

Since most binary phase-diagrams have few or no experimental data for very low concentrations of the components, the beginning of the curves are more artistic than real. The steadily growing interest in pure and ultrapure materials requires more exact data. Determination of k_0 by zone refining experiments is one way of obtaining more exact information.

Following Burton and Schlichter [3] one can define an effective distribution coefficient

$$k = \frac{k_0}{k_0 + (1 - k_0)\exp - v\delta/D}$$

where δ is the extension of the diffusion layer, v the velocity of the zone and D the diffusivity in the liquid. It is customary to rearrange this equation in the forms

$$\ln\left(\frac{1}{k} - 1\right) = \ln\left(\frac{1}{k_0} - 1\right) - v\delta/D \text{ for } k_0 < 1$$

and

$$\ln\left(1 - \frac{1}{k}\right) = \ln\left(1 - \frac{1}{k_0}\right) - v\delta/D \text{ for } k_0 > 1$$

D is usually known and δ is usually unknown. δ/D can be calculated or esti- mated. As δ/D is nearly independent of the zone velocity it can also be found or eliminated by zone refining experiments at different zone velocities. If D for the solute in question is unknown, but known for another solute, it can be determined by zone refining of the two systems in question.

EXPERIMENTAL

The specimens were contained in a graphite crucible and heated by induction. The silver did not stick to the graphite and the zone was thoroughly stirred. Purified nitrogen was used as inert atmosphere and the zone velocity was quite low, 1.51×10^{-2} mm/sec. The geometry of the melted zone was determined by quenching experiments. We tried to achieve nearly optimum conditions for zone refining.

The concentration profiles were determined from different methods:
1) neutron activation analysis,
2) radioactive tracer technique,
3) chemical analysis,
4) direct spectrographic analysis.

All of these methods were used to evaluate the usefulness of the different methods for this and other similar problems [4].

The amount of solute used for analysis by neutron activation, was determined from calculations of the neutron flux available, the time of irradiation and the type of solute to be determined. In the cases where neutron activation and radioactive tracers were used, the registration of the concentration profiles after the zone refining experiments was done by picking out the characteristic radiation in a β spectrometer. In the cases where radioactive tracers were used, the concentration profiles were also determined by a direct photographic method.

An estimate of the error for the different methods was made.

Direct spectrographic methods gave the poorest results and in our case the radio-active tracer technique seemed to be the most useful method for determining small amounts of solute.

THE SYSTEM Ag—Au

By comparing the experimental concentration profiles and the deduced k-values with the concentration profiles and the effective k-values given by Pfann [5], the k-value was found to differ only slightly from the k_0-value. The comparison of the experimental and theoretical concentration profiles for 10 passes of the zone showed $1.08 < k < 1.10$. Assuming a maximum (the least favourable) value of $\delta/D = 100$ sec/cm the result is $1.08 < k_0 < 1.12$.

Fig. 1 gives the opening angle for the phase diagram ($k_0 = 1.11$) as found by the experiments and that taken from Metals Reference Book [2]. The dis-agreement is evident.

In 1954, Wagner [6] calculated the width of the gap between the liquidus and the solidus to be $1.3°K$ at 50 atomic % Au. The system was more recently reinvestigated by White et al.[7] based on the measured thermodynamic pro-perties of the solid and liquid alloys. They determined the gap between the liquidus and solidus to be $1.5°K$ at 50 atomic % Au. In a recent paper White [8] has confirmed the results also by thermal analysis. The opening angle taken from the work of White et al.[7] cannot be distinguished from that of the present investigation. This does not only confirm the usefulness of the zone refining method in determining the opening angle of binary phase diagrams, but it also shows that for the concentrations used (starting concentration = 1 %), there is apparently no deviation from ideality. Therefore $a_1/a_2 = c_1/c_2$, where a_1 and a_2 are the activities of the two components and c_1 and c_2 the corresponding concentrations.

THE SYSTEM Ag—Cu

The concentration profils after zone refining for specimens with Cu as solute did not correspond with concentration profiles calculated for a number of k-values and zone passes. The reason for this may be found in the invalidity
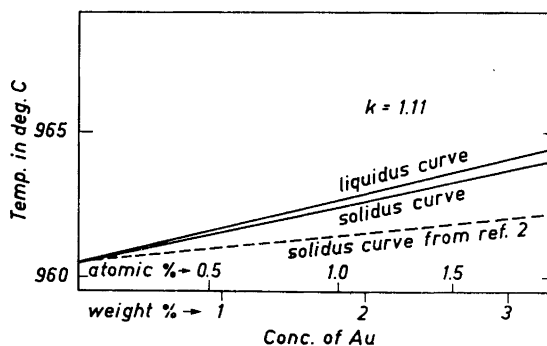

Fig. 1. The Ag-rich side of the phase diagram Ag/Au.

of the assumptions made in the evaluation of the zone refining formulae, *i.e.*
at the solute concentrations used, the solution deviated from ideality. At too
high solute concentrations this will cause a variation of k with concentration
in part of the specimen. From the experimental concentration profiles it was
possible to calculate the k-value continuously from 0.05 % — 2.5 % Cu.
The calculation was based on the concentration profiles from the purest part
of the rod. The values of these for 1, 3, 5 and 10 zone passes were compared
with those from theory. The amount of copper in the distance from the starting
end of the rod was calculated $(c_1(x))$, and the calculations were compared
with the amount of copper in the solidified rod $(c_s(x))$.

The equation:

$$k(x) = k(c_1(x)) = \frac{c_s(x)}{c_1(x)}$$

gives the k-value as a function of the concentration in the liquid zone. The
solidus' curve in the phase diagram could then be calculated, based on the liqui-
dus curve. The results are given in Fig. 2, where the opening angle is greater than
that found in Ref.[2]. At about 0.5 % Cu, the numerical value of the gradient
begins to decrease, owing to departure from ideality $(a_1/a_2 \neq c_1/c_2)$. The first
part of the curve represents the correct gradient based on a k_0-value of 0.41
and a k-value of 0.45. This allows not only a determination of k- and k_0-values
which determines the opening angle of the phase diagram (equilibrium dia-
gram), but also gives measure for the departure from ideality, $(a_1/a_2$ compared
with $c_1/c_2)$.

CONCLUSION

It may be expected that the deviation from ideality starts at lower con-
centrations of copper in silver than of gold in silver.

It is shown that opening angles in binary diagrams can be determined
with a high degree of accuracy by use of the zone refining method, provided
that the concentration profiles can be exactly determined.

It is also shown that the method can give informations regarding devia-
tions from ideality as a function of concentration of solute.
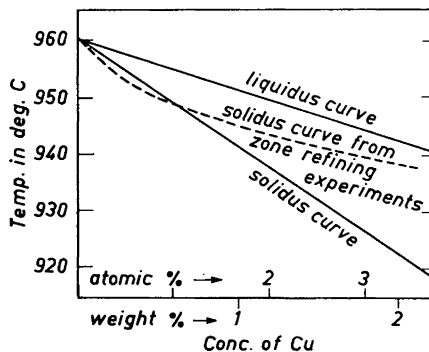

Fig. 2. The Ag-rich side of the phase dia-
gram Ag/Cu.

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