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INFLUENCE OF THE SUPERFICIAL MASS MIGRATION PHENOMENON ON THE DETERMINATION OF THE METALLIC INTERFACIAL TENSIONS BY MULTI-PHASE EQUILIBRIUM METHOD

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Abstract

The prominent superficial mass migration (abbr. SMM below) phenomenon of Pb or Bi radially along the solid surface of Cu from the liquid drop has been observed during the measurement of interfacial tensions in the binary systems of Cu-Pb, Cu-Bi with multi-phase equilibrium (abbr. MPE below) method. In order to reflect the influence of such SMM effect on the measurement of interfacial tensions with MPE method, the \( \omega \) factor, which is called SMM factor and defined as \( \omega = \gamma_{SV} / \gamma_{ST} \) (where \( \gamma_{SV} \) represents the solid-vapor interfacial tension influenced by SMM effect), has been introduced. The initial analysis reveals that the \( \omega \) factor is related with surface diffusion coefficient of liquid phase, temperature, configuration of solid surface and mutual solubility between liquid and solid phase.

The interfacial tensions in the binary systems of Cu(solid)-Pb(liquid) and Cu(solid)-Bi(liquid) have recently been determined with the popular multi-phase equilibrium method /1/, /2/, /3/ (abbr. MPE below). In the process of the experiment a prominent superficial mass migration (abbr. SMM below) phenomenon has been observed. The authors considered that the traditional equations, on which the MPE measurement developed, must be improved. By an initial analysis, a new equation group, in which the SMM effect has been considered, is set up in this paper by introducing a special factor called SMM factor.

(1) The Experiment

A high purity and oxygen-free copper substrate, which had been completely annealed, carefully ground and polished, was horizontally placed on the stage of a vacuum furnace. A small cylindrical lead particle with high purity was
located on the surface centre of the substrate. The specimen was kept at 850 °C and 900 °C respectively for two hours after the whole system was evacuated and high purity argon was then introduced. The mass migration trace of lead atoms radially along the copper surface from the liquid drop could be observed obviously at room temperature under a microscope.

(2) Analysis of SMM Phenomenon

From the view of the surface diffusion theory, the mass migration on solid surface is substantially a transport process of alien atoms on the surface. It could be approximately considered that the migration observed in our experiment belongs to non-regional diffusion on solid surface. Based on this argument, the migration might be driven by two forces: one comes from the atomic mass gradient of lead existing radially along the copper surface from the lead drop. The migration driven by this force is characteristic of disordered transition. The other is a capillary force, by which the lead atoms moves along intergranular grooves of the copper surface and then results in thermal etching so that the surface free energy of copper could be minimized. Obviously these two forces are not limited only in Cu-Pb system, therefore, it could be assumed that SMM phenomena possibly exist on all kinds of solid surfaces, as long as they are partly touched by some liquid, although the degree of prominence may varies with temperature, the kinds of solid and liquid, surface state of solid and diffusion coefficient of liquid atoms on solid surface.

(3) Discussion of the Traditional MPE Equation Group

The traditional multi-phase equilibrium equation group is:

\[
\begin{align*}
\gamma_{SV} &= \gamma_{SL} + \gamma_{LV} \cos \theta \\
\gamma_{SS} &= 2 \cdot \gamma_{SL} \cos (\phi/2) \\
\gamma_{SS} &= 2 \cdot \gamma_{SV} \cos (\psi/2)
\end{align*}
\]

(1) (2) (3)

This group is directly originated from the balanced relationship of all tensions exerted on the interfaces of solid-vapor, solid-liquid as well as the junction of solid-liquid-vapor respectively (Fig. 1).

\[\text{Fig.1: Sketch Showing All Kinds of Tensions Exerted on Solid-Liquid, Solid-Vapor Interfaces and Solid-Liquid-Vapor Junction}\]

In the above equation group, the \(\gamma_{SL}, \gamma_{SV}\) and \(\gamma_{SS}\) could be simultaneously obtained in principle by the measurements of \(\theta, \phi, \psi\) and \(\gamma_{LV}\). However, when SMM phenomenon exists, the solid surface adjacent to the liquid drop, is no longer a clean surface. The originally ideal state, in
which the solid surface is exposed directly to the vapor phase, is spoiled. As the result of this effect, $\gamma_{SV}$ in equation (1) can not represent the real solid-vapor interface tension, that is, the traditional MPE equation group is not any longer applied to the systems in which such prominent SMM phenomena exist.

(4) Introduction of $\omega$ Factor and Improvement of the Traditional MPE Equation Group

In order to make MPE still applied to the determination of interfacial tensions in systems where SMM phenomena exist, influence of which could be called SMM effect, a $\omega$ factor, which is defined as $\omega = \gamma_{SV}^{1}/\gamma_{SV}$ (the superscript on the $\gamma_{SV}$ represents the solid-vapor interface tension which has been disturbed by SMM effect), could be introduced to embody SMM effect. The definition range of $\omega$ is: $1 \leq \omega \leq 1$. When $\omega = 1$, $\gamma_{SV} = \gamma_{SV}$, corresponding to the situation of no or negligible SMM effect. On the other hand, when $\omega = \gamma_{SL}/\gamma_{SV}$, $\gamma_{SV} = \gamma_{SL}$, corresponding to the situation of the complete spreading of the liquid on the solid surface, which means that the original solid-vapor interface has already become solid-liquid interface.

After the introduction of $\omega$ factor, the traditional MPE equation group could be improved on as follows:

$$\begin{align*}
\gamma_{SV} &= \gamma_{SL} + \gamma_{LV} \cdot \cos \theta \\
\gamma_{SS} &= 2 \cdot \gamma_{SL} \cos (\theta/2) \\
\gamma_{GS} &= 2 \cdot \gamma_{SV} \cdot \cos (\psi/2) \\
\gamma_{SV} &= \omega \cdot \gamma_{SV}
\end{align*}$$ (4-7)

When $\omega = 1$, e.g., there is no SMM effect existing, the new equation group returns to the original one.

The condition under which the equations (4)-(7) hold is that the experiment concerned with $\phi$, $\psi$ measurement should be carried out seperately under the same environment (including temperature, atmosphere etc.) so as to avoid the disturbance of SMM effect on this angle (Fig.2).

![Fig.2: Sketch for the $\psi$ Experiment with MPE Method](image)

The determination of $\omega$ factor, whether by theoretical or experimental method, is a complicated problem. The reason, which has been mentioned above in (2), is that the SMM phenomenon is subject to both interior and exterior conditions and factors which are not easily analysed quantitatively. Nevertheless, by the experimental determination of $\phi$, $\psi$ angles, the ratio of $\gamma_{SL}/\gamma_{SV}$ could be obtained, so that we could at least ascertain the upper
and lower limits of $\omega$. In our experiment, $\phi$, $\psi$ angles of Cu-Pb system are measured to be $\phi = 54^\circ$, $\psi = 150^\circ$ when $T = 850^\circ C$ and $\phi = 61^\circ$, $\psi = 158^\circ$ when $T = 900^\circ C$. By applying equations (5) and (6), the ratio $\tilde{\gamma}_{SL}/\tilde{\gamma}_{SV}$ is 0.29 at 850 °C and 0.22 at 900 °C. So the range of $\omega$ for Cu-Pb system is $0 \leq \omega \leq 1$ at 850 °C and $0 \leq \omega \leq 1$ at 900 °C respectively.

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