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LIQUID TO SOLID NUCLEATION IN METAL-SEMICONDUCTOR EUTECTIC ALLOYS

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INTRODUCTION

Two steps appear during the nucleation of binary eutectic alloys. First, primary nucleation involves the creation of a crystal in the supercooled liquid, then below eutectic temperature the nucleation of the second phase takes place, either on the primary phase by heterogeneous nucleation or independently within the liquid. The resultant solidification structure will vary for those two different ways of eutectic nucleation. In this paper we will analyse the general nucleation behaviour of metal semiconductor eutectic alloys with more emphasis to the Ag-Ge and Al-Ge systems.

EXPERIMENTAL PROCEDURE AND RESULTS

We measured both primary and eutectic nucleation temperatures during continuous cooling with a differential thermal analyser (1). The experiments were performed with the following conditions: Alumina crucibles, mass of samples: 100 mg, cooling rate: 20K min⁻¹, protective atmosphere: Argon purified over Zirconium, superheating of the liquid: 300K above the liquidus. More details of the experimental procedure are given elsewhere (1,2).

Figure 1 shows the results concerning the maximum undercooling observed for primary nucleation in the whole composition range of the Ag-Ge system. For each composition we give mean and maximum values of the undercoolings obtained with 3 or 4 alloys at the same composition, each alloy having been undercooled 6 to 8 times.

Figure 2 gives the values of the undercoolings for the eutectic nucleation - i.e. for the nucleation of Ge with Ag already present in the melt (hypoeutectic alloys) and that of Ag with Ge crystals in the undercooled liquid (hypereutectic alloys). The eutectic nucleation phenomena were also studied by in-situ observation in a very high voltage electron microscope (1 MeV): small cells (10μ in diameter, 1μ in thickness) of Al-Ge alloys prepared by ultra high vacuum evaporation, were observed using a heating stage as described in detail elsewhere (3).
In both cases, crystal orientation analysis shows that there is an epitaxy between the Al crystal in the eutectic and the Ge crystal that acted as a substrate for nucleation.

**DISCUSSION**

**Nucleation of primary crystals**

Figure 1 shows a drastic decrease of primary nucleation undercoolings for both Ag and Ge crystals as the solute concentration is increased. In the classical theory of homogeneous nucleation\(^{(5)}\), the free enthalpy of formation of the critical nucleus, that is responsible for the undercooling, is given by:

\[
\Delta G_{\text{hom}}^{*} = \frac{16\pi \sigma_{\text{SL}}^3}{3\Delta G_{\text{SL}}}
\]

where \(\sigma_{\text{SL}}\) = solid-liquid interface tension,

\(\Delta G_{\text{SL}}\) = free enthalpy variation during the phase transformation.

We have calculated the ratio:

\[
\phi = \frac{\Delta G_{\text{Ge pure liq.}} - \Delta G_{\text{Ge solid}}}{\Delta G_{\text{Eut. liq.}} - \Delta G_{\text{Ge solid}}}\]

of the energy barrier for nucleation of pure Ge

**Fig. 2**: Eutectic nucleation undercooling for various Ag-Ge alloys.

Figure 3 presents typical observations: with hyper-eutectic alloys, the nucleation of the eutectic structure takes place at an undercooling of about 20K and the eutectic grows on the primary Ge crystal. But, on the Al-rich side, the existence of an Al crystal inside the undercooled liquid does not affect the nucleation scheme: at a higher undercooling (\(\approx 50\)K), an independent Ge crystal nucleates and it is on this crystal that the eutectic nucleates. In both cases, crystal orientation analysis\(^{(4)}\) shows that there is an epitaxy between the Al crystal in the eutectic and the Ge crystal that acted as a substrate for nucleation.

**Fig. 3**: In-situ observation of eutectic nucleation in Ge-rich (a,b) and Al-rich (c,d) Al-Ge alloys.
from an undercooled pure liquid to that obtained from a liquid at eutectic composition. $\Delta G_{SL}$ has been evaluated using thermodynamic data of Hultgren(6), while $\sigma_{SL}$ was obtained with a thermodynamic statistical model(7). We have found $\phi \sim 1$, while from the undercooling measurements, we would have expected a ratio at least one order of magnitude higher than the calculated value. Clearly the classical nucleation theory cannot explain the results obtained for these alloys. Actually the theory has been established for monoatomic liquids and alloys and it does not take into account structural particularities of the liquid phase. Now, from small angle neutron scattering experiments, Desré and Bellissent(8) have proposed a description of the liquid Ag-Ge alloys near the eutectic composition based on polyatomic chains Ag$_3$Ge. These chains could act as preferred centers for nucleation, leading to the Ge crystals through a metastable compound. Indeed hcp Ag$_3$Ge metastable compound have been obtained by splatcooling(9). Such a scheme is in good agreement with observations of crystallization behavior of amorphous alloys obtained by Köster(10) for metal-semiconductor systems.

**Eutectic Nucleation**

The comparison of the undercoolings necessary for the nucleation of Ag in the presence and in the absence of primary Ge crystals leads us to conclude that Ge crystals catalyze the nucleation of Ag while the reverse is not true. During in-situ experiments we observed also a marked difference in eutectic undercoolings and we have seen that Ge crystals always act as nucleation substrate for Al, but that Al crystals do not (Fig. 3). This seems to be a general behaviour for this type of alloys : on table I, one can see that eutectic undercoolings are always lower with Ge or Si crystals present in the melt, than with Al or Ag.

<table>
<thead>
<tr>
<th>A - B</th>
<th>$\Delta T_{A/B}(K)$</th>
<th>$\Delta T_{B/A}(K)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Ge</td>
<td>21</td>
<td>$\geq 37$</td>
<td>This work</td>
</tr>
<tr>
<td>Al-Ge</td>
<td>59</td>
<td>115</td>
<td>11</td>
</tr>
<tr>
<td>Al-Si</td>
<td>47</td>
<td>68</td>
<td>11</td>
</tr>
</tbody>
</table>

**TABLE I** : Undercooling results $\Delta T_{i/j}$ for the nucleation of $i$ in the presence of primary crystals of $j$.

This can be explained with surface tension considerations involved in heterogeneous nucleation:

During heterogeneous nucleation, the free energy of formation of the critical nucleus is lowered by a geometrical factor, the value of which depends upon the contact angle $\theta$ of the nucleus with the substrate on which it was nucleated(12) :

$$\Delta G_{het} = \Delta G_{hom} f(\theta); \quad f(\theta) = \frac{1}{4}(2-3\cos\theta + \cos^3\theta)$$

with $\cos\theta = \frac{\sigma_{CL} - \sigma_{CN}}{\sigma_{NL}}$

where $\sigma$ is the interfacial tension and the subscript $C, L, N$ refer to the crystalline substrate, the liquid and the nucleus.

During the two types of heterogeneous nucleation the different phases involved are the same and the interfaces tensions also but the substrate and the nucleus phases are exchanged. We then need to analyze the difference in interface tension for the metal-eutectic liquid and semiconductor-eutectic liquid interfaces.

Evaluation of solid-liquid interfacial tension(7) shows that there are two contributions in $\sigma_{SL}$ : a structural term $\sigma_{SL}^e$ due to change of physical state across the interface and a chemical term $Z$ which takes into account the composition difference $\Delta X$ between the two phases involved. For a given binary system, we obtain : $\sigma_{SL}^o = \sigma_{SL}^e + Z(T,\Delta X)$

In the case of semiconductors the values of $\sigma_{SL}^o$ are larger than in the case of simple metals(12). Moreover, usually $Z$ increases with $\Delta X$ and in the
systems considered, the eutectic points are on the metal rich side, leading to a higher $\Delta X$ for the semiconductor (SC) - eutectic liquid than for the metal (M) - eutectic liquid interface. As a consequence of it, we have:

$$\rho = \frac{\sigma(\text{solid SC - eutectic liquid})}{\sigma(\text{solid M - eutectic liquid})} > 1$$

this gives always:

$$\phi = \frac{f(\theta)_{SC}}{f(\theta)_{SC/M}} < 1$$

As an example, for SC = Ge and M = Ag, we have calculated $\rho \sim 2.3$ and $\phi \sim 0.12$.

This shows that the effect of semiconductor on the nucleation of metals would be always higher than the reverse effect.

CONCLUSIONS

For the nucleation of primary Ag and Ge crystals from Ag-Ge liquid alloys studied by D.T.A., a minimum undercooling has been observed for the eutectic composition. We have shown that the result is inconsistent with the classical nucleation theory for monoatomic liquids but that it can be interpreted taking into account heteroatomic associations existing in the liquid which would act as preferential centers of nucleation of metastable compounds. Moreover, we found that Ge crystals catalyze nucleation of Ag while the reverse is not true. This non reciprocal nucleation behaviour has been also shown for Al-Ge alloys by in-situ observations of nucleation processes in a 1 MeV electron microscope. This general behaviour can be explained by the relative values of the solid-liquid interfacial tensions in the metal-semiconductor systems.

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