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# Effect of primary phase structure on the undercoolability of quasicrystal-forming melt*

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**Abstract** The relationship between $\alpha$ and $\Delta T_{rel}$ is investigated, where $\alpha$ is a factor that depends on the structure of primary phase and $\Delta T_{rel}$, the relative undercooling of melt. A linear relationship between $\alpha$ and the relative undercooling $\Delta T_{rel}$ is observed, which is represented by $\Delta T_{rel} = A + B\alpha$.

**Keywords:** **primary phase, quasicrystals, short-range order (SRO).**

In the early 1950s, Frank[1] pointed out that an icosahedral short-range order (SRO) should exist in the undercooled melts. However, icosahedral SRO, characterized by the fivefold symmetry and incompatible with the translational symmetry of crystalline phase, will lead to an increase of barrier potential for the nucleation of crystalline phase, since crystal nucleation requires a breakup of the icosahedral SRO. On the other hand, icosahedral SRO is the basic unit cell of quasicrystal phase, which will reduce the nucleation potential of the quasicrystal phase. Consequently, the nucleation undercooling of quasicrystal phase should be decreased.

Later on, the inference of prevailing icosahedral SRO in the undercooled melts was confirmed by molecular dynamic calculations of Lenard-Jones liquids[2]. The structure of icosahedral SRO has attracted a lot of attention since Shechtman et al. discovered quasicrystal phase in the rapidly quenched Al-Mn alloys[3]. Subsequently, besides the icosahedral I-phase of quasicrystal, other phases which exhibit a more or less pronounced degree of polytetrahedral SRO were also found. The typical examples are the decagonal quasicrystal (D-phase)[4], which is quasiperiodic in two dimensions and periodic in the third dimension, and Frank-Kasper phase, which is a crystalline phase characterized by polytetrahedral symmetry elements constructing their large unit cell. These phases possess SRO structure similar to that in the undercooled melts.

In their study, Maret et al.[5] applied neutron diffraction to investigate the structural state of undercooled $Al_{80}Mn_{20}$ melts. The pair potentials determined in these experiments were used for molecular dynamic calculation. The calculation result indicate that the topological SRO structure exists indeed in the undercooled melts.

Based on the previous results of the studies on the undercooling of quasicrystal-forming melts, this study analyzes the effect of primary phase structure on the undercoolability of quasicrystal-forming melt.

## 1 Previous experimental results on the undercooling of quasicrystal-forming melt

The quasicrystal-forming alloy generally contains some highly reactive elements, such as Al, Ti, and Mg. These elements react with oxygen to form stable metal-oxide compounds, which act as the heterogeneous nucleation site of the undercooled melts. By means of electromagnet levitation melting under high-vacuum condition, the above-mentioned reaction can be avoided. This processing is very successful in high undercooling of alloy melts. In recent years, Moritz and Schroers et al. carried out separately several experiments on the undercooling of Al-Co, Al-Cu-Fe and Al-Cu-Co alloys using the methods of electromag-

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net levitation melting and cyclic superheating under high-vacuum condition[6,7]. Besides, Herlach et al. studied the undercooling of Al-Mn alloy by melt atomization[8] and Song et al. utilized glass denucleating and cyclic superheating to research the undercooling of Al-Mn-Si-B alloy[9]. These experimental results are listed in Table 1.

Table 1. Primary phases and their relative undercoolings in the quasicrystal-forming alloy melts[6~9]

| Alloy | Primary phase | Liquidus temperature $T_L$(K) | Undercooling $\Delta T$(K) | Relative undercooling ($\Delta T_{rel} = \Delta T / T_L$) |
|---|---|---|---|---|
| $Al_{60}Cu_{34}Fe_6$ | IQC | 1098 | 100 | 0.091 |
| $Al_{58}Cu_{34}Fe_8$ | IQC | 1130 | 100 | 0.088 |
| Al-Mn | IQC | 1081 | 100 | 0.093 |
| Al-Mn-Si-B | IQC | 1293 | 100 | 0.077 |
| $Al_{74}Co_{26}$ | DQC | 1440 | 210 | 0.146 |
| $Al_{67}Cu_{21}Co_{12}$ | DQC | 1293 | 200 | 0.155 |
| $Al_{65}Cu_{25}Co_{10}$ | DQC | 1259 | 204 | 0.162 |
| $Al_{64}Cu_{22}Co_{14}$ | DQC | 1273 | 189 | 0.148 |
| Al-Mn | DQC | 1136 | 170 | 0.150 |
| $Al_{13}Fe_4$ | $\lambda$ | 1420 | 170 | 0.120 |
| $Al_{62}Cu_{25.5}Fe_{12.5}$ | $\lambda$ | 1258 | 173 | 0.138 |
| $Al_5Fe_2$ | $\mu$ | 1430 | 205 | 0.143 |
| $Al_{72}Co_{28}$ | $\beta$ | 1605 | 390 | 0.243 |
| $Al_{65}Cu_{20}Co_{15}$ | $\beta$ | 1485 | 360 | 0.242 |

## 2 Analysis of the previous results and discussions

The results shown in Table 1 indicate that the relative undercooling of the quasicrystalline I-phase is the smallest, in the middle are the crystalline $\lambda$-phase and $\mu$-phase (Frank-Kasper phases) with polytetrahedral symmetry elements, as well as the two-dimensional quasicrystalline D-phase, and the crystalline $\beta$-phase with a CsCl-type crystal is the largest. This can be described by

$$\Delta T_{rel}^{I} < \Delta T_{rel}^{\lambda} < \Delta T_{rel}^{\mu} < \Delta T_{rel}^{D} < \Delta T_{rel}^{\beta}. \quad (1)$$

According to the classical nucleation theory, the nucleation work $\Delta G^*$ for the formation of a critical nucleus is given by

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G^2} f(\theta), \quad (2)$$

where $\sigma$ is the solid/liquid interfacial energy, $\Delta G = G_L - G_S$ is the Gibb's free energy difference between liquid and solid phase (unit volume), and $f(\theta)$ the catalytic potency factor for heterogeneous nucleation. It is found that $\Delta G^*$ consists of three parts which are $\Delta G$, $f(\theta)$, and $\sigma$. Since $\Delta G$ and $f(\theta)$ are determined by the physical properties of melts and are independent of the primary phase structure, $\Delta G^*$ is strongly related to the interfacial energy $\sigma$ between the solid nucleus and melt. The larger the value of $\sigma$, the higher the nucleation work $\Delta G^*$ is, which leads to an increase in the nucleation undercooling.

The interfacial energy $\sigma$ is determined by structural similarities of SRO between the solid nucleus and undercooled melt. The higher the degree of similarity between the SRO of undercooled melt and the solid nucleus, the smaller the interfacial energy $\sigma$ is. So far no experimental techniques can directly measure the interfacial energy between the solid nucleus and undercooled melt. Therefore, interfacial energies can only be determined by the undercooling experiment in which the maximum undercooling is calculated according to the limit of homogeneous nucleation. So we conduct the same procedure to evaluate the interfacial energy $\sigma$.

It is assumed that at least one nucleation event is necessary to initiate the solidification of the undercooled melt of volume $V$ during the experimental time $t_N$. This means the product of the steady-state nucleation rate $I_{SS}$, volume $V$ and time $t_N$ must be equal to or greater than unity, that is

$$I_{SS}(T_N) V t_N \geqslant 1. \quad (3)$$

The nucleation temperature $T_N$ and the experimental time $t_N$ are measured from the corresponding cooling curve of the undercooling experiment. The volume $V$ is estimated from the mass of the sample and its density. The steady nucleation rate is calculated according to[10]

$$I_{SS} = \frac{k_B T \xi N_A}{3\eta(T) a_0^3} \exp\left( - \frac{\Delta G^* f(\theta)}{k_B T} \right), \quad (4)$$

where $\eta(T)$ is viscosity of the melt, $T$ absolute temperature, $a_0$ atomic spacing, $k_B$ Boltzmann's constant, $N_A$ Avogadro number and $\xi$ fraction of atoms that act as a nucleation site. For homogeneous nucleation $\xi = 1$ and for heterogeneous nucleation $\xi \ll 1$. $\Delta G$ is estimated by

$$\Delta G = \Delta S_f \Delta T - \frac{\Delta S_f}{\ln(T_L / T_0)} \left[ \Delta T - T \ln\left( \frac{T_L}{T} \right) \right], \quad (5)$$

where $\Delta S_f$ is the entropy of fusion and $T_0$ the ideal glass-transition temperature. As a rough approximation, we suppose $T_0 \approx 0.5 T_L$ for the calculation. The temperature dependence of the viscosity $\eta(T)$ is given by the Vogel-Fulcher-Tammann expression[11]

$$\eta(T) = \eta_0 \exp\left( \frac{A}{T - T_0} \right), \quad (6)$$

where $A$ and $\eta_0$ are constants.

Employing Eqs. (2)~(6), the interfacial energy $\sigma$ at the nucleation temperature $T_N$ can be calculated using the data listed in Table 2. The calculated results can be arranged according to the values of $\sigma$ of different primary phases as follows

$$\sigma^{I} < \sigma^{D}_{Al-Mn} < \sigma^{D}_{Al_{64}Cu_{22}Co_{14}} < \sigma^{D}_{Al_{65}Cu_{25}Co_{10}} < \sigma^{D}_{Al_{67}Cu_{21}Co_{12}} < \sigma^{\lambda}_{Al_{62}Cu_{25.5}Co_{12.5}} < \sigma^{\lambda}_{Al_{13}Fe_4} \approx \sigma^{D}_{Al_{74}Co_{26}} < \sigma^{\beta}_{Al_{65}Cu_{20}Co_{15}} < \sigma^{\mu} < \sigma^{\beta}_{Al_{72}Co_{28}}. \quad (7)$$

Table 2. Interfacial energy $\sigma$ and structure dependent factor $\alpha$ of different primary phases calculated using the data of quasicrystal-forming melts[6~9]

| Alloy | Primary phase | $A$(K) | $\eta_0$(mPa·s) | $a_0$(nm) | $V_m$($10^{-6}$ m$^3$·mol$^{-1}$) | $\Delta S_f$(J·K$^{-1}$·mol$^{-1}$) | $\sigma(T_N)$(J·m$^{-2}$) | $\alpha$ |
|---|---|---|---|---|---|---|---|---|
| $Al_{60}Cu_{34}Fe_6$ | IQC | 2106 | 2.16 | 0.24 | 8.30 | 11.3 | 0.091 | 0.28 |
| $Al_{58}Cu_{34}Fe_8$ | IQC | 2106 | 2.41 | 0.24 | 8.30 | 11.3 | 0.094 | 0.27 |
| Al-Mn | IQC | 2106 | 0.69 | 0.24 | 9.48 | 8.42 | 0.070 | 0.32 |
| Al-Mn-Si-B | IQC | 2106 | 0.68 | 0.24 | 9.48 | 8.42 | 0.079 | 0.26 |
| $Al_{74}Co_{26}$ | DQC | 2106 | 5.20 | 0.24 | 8.30 | 11.6 | 0.160 | 0.40 |
| $Al_{67}Cu_{21}Co_{12}$ | DQC | 2106 | 3.85 | 0.24 | 8.30 | 7.6 | 0.116 | 0.45 |
| $Al_{65}Cu_{25}Co_{10}$ | DQC | 2106 | 3.52 | 0.24 | 8.30 | 7.6 | 0.112 | 0.46 |
| $Al_{64}Cu_{22}Co_{14}$ | DQC | 2106 | 3.66 | 0.24 | 8.30 | 7.6 | 0.109 | 0.42 |
| Al-Mn | DQC | 2106 | 1.22 | 0.24 | 9.48 | 8.45 | 0.096 | 0.44 |
| $Al_{13}Fe_4$ | $\lambda$ | 2106 | 5.15 | 0.24 | 8.30 | 13.7 | 0.160 | 0.33 |
| $Al_{62}Cu_{25.5}Fe_{12.5}$ | $\lambda$ | 2106 | 3.51 | 0.24 | 8.30 | 13.7 | 0.153 | 0.36 |
| $Al_5Fe_2$ | $\mu$ | 2106 | 5.26 | 0.24 | 8.30 | 13.6 | 0.182 | 0.37 |
| $Al_{72}Co_{28}$ | $\beta$ | 2106 | 7.19 | 0.24 | 8.30 | 8.3 | 0.190 | 0.61 |
| $Al_{65}Cu_{20}Co_{15}$ | $\beta$ | 2106 | 5.86 | 0.24 | 8.30 | 8.3 | 0.169 | 0.63 |

Eqs. (7) and (1) indicate that the maximum relative undercooling of melt and interfacial energy $\sigma$ are strongly dependent on the structure of primary phase, while the relation of the maximum relative undercooling of different primary phases is not corresponding to the relation of interfacial energy $\sigma$. However the interfacial energy $\sigma$ can be calculated by the negentropic model of Thompson and Spaepen[12]

$$\sigma = \alpha \frac{\Delta S_f T}{(N_A V_m^2)^{1/3}}, \quad (8)$$

where $V_m$ is the molar volume and $\alpha$ a factor that depends on the structure of solid nucleus.

Employing Eq. (8), the $\alpha$ values of different primary phases can be calculated using the interfacial energy data shown in Table 2, which have the following relation:

$$\alpha^{I} < \alpha^{\lambda} < \alpha^{\mu} < \alpha^{D} < \alpha^{\beta}. \quad (9)$$

Relation (9) reflects the same sequence as Relation (1) for the different primary phases, indicating that the $\alpha$ value can represent the undercoolability of melt. Fig. 1 shows a linear fitting of the structural dependent factor $\alpha$ versus the relative undercooling $\Delta T_{rel}$, which can also be expressed by

$$\Delta T_{rel} = A + B\alpha, \quad (10)$$

where $A$ and $B$ are constants, $A = -0.033$, $B = 0.44$.

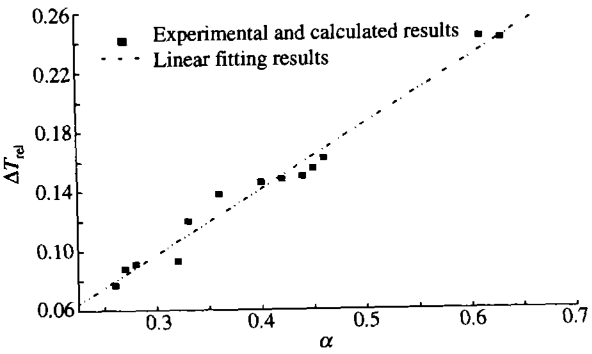

Fig. 1. The relation between the relative undercooling $\Delta T_{rel}$ and the structural dependent factor $\alpha$.

## 3 Conclusion

Based on the previous experimental results on the relative undercooling of quasicrystal-forming melts, we analyzed the effect of different primary phases on the undercoolability of melt. Results indicate that the undercoolability of melt is determined by the primary phase structure. The more similar SRO of the undercooled melt to the primary phase, the lower the interfacial energy and the relative undercooling are. A linear equation $\Delta T_{rel} = -0.033 + 0.44\alpha$ is obtained.

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