Heterogeneous Nucleation of Au on Al2O3 Substrate under the Impact of Droplet Size and Cooling Rate

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Abstract. Investigating the heterogeneous nucleation is of high importance due to the fact that the nucleation is a sign of the occurrence of solidification. The present study presents the influence of droplet size and cooling rate on the undercooling of Au solidified on Al2O3 substrate. The results show that the undercooling is proportional to cooling rate and inversely proportional to droplet size. In addition, the influence of droplet size on undercooling can be enlarged if the higher cooling rate is employed, whereas the influence of cooling rate on undercooling can be enlarged if the smaller droplet size is selected. The underlying reasons are discussed by formulating the relationship between undercooling, cooling rate and droplet size.

1. Introduction
Nucleation is an important process in metal solidification and significantly influences mechanical properties of solidified materials. According to classical nucleation theory[1,2,3], the free energy barrier which heterogeneous nucleation needed to overcome during metal solidification is much lower than homogeneous nucleation. Since there are always impurities as the potential nucleation sites in the molten metal, heterogeneous nucleation occurs almost in every industry cases[4].

It is well known that the degree of undercooling is an important nucleation parameter[5]. Droplet size and cooling rate are two vital factors determining the melt undercooling during the process of nucleation of small droplet[6].Li et al.[7] achieved a deep undercooling of the metal Ge melt by means of a combination of DSC and flux (B2O3), and reported that the undercooling raised with the increasing of cooling rate. Moreover, our previous work [8] has evaluated the relationship between the melt undercooling and cooling rates of Au droplet. It is found that the undercooling is proportional to the cooling rate.

In 1950, Turnbull[9] proposed "the size effect in nucleation" and pointed that the probability of finding accidental inclusions effective in promoting crystal nucleation is much greater in large than in small masses. Recently, Guan et al.[10]established a mathematical model for microdroplets with infinitesimal size through the research of Al-4.5 wt% Cu alloy. Their investigation shown that the degree of undercooling are evidently influenced by the size of micro droplets D. When the size of droplets is larger than 20 µm, an approximative linear relation exists among them. Yang et al. [11]have studied the influence of cooling rate on single Sn droplet and proposed that the undercooling could be increased first significantly with increasing cooling rate going over to a stage of slow increase for high cooling rates. The “crossover” was at a cooling rate of about 1000 K/s. Hao He et al. [12]have studied the relationship between size and phase structure of gallium droplet with DSC
experiments. They found that the degree of undercooling have a relation with volumes of gallium particles.

However, previous researches focused on investigating the effect of droplet size and cooling rate on melt undercooling separately. Little attention has been paid on studying the combined effect of the two factors on metal solidification. This paper concentrates on investigating the influence of these two aspects comprehensively. It is considered by using DSC to measure the undercooling of Au droplets with different size solidified on single crystal substrates under different cooling rates.

2. Experimental materials and methods

2.1 Materials

In this experiment, Al₂O₃ single crystal foils (14mm*10mm*0.5mm) with an exposed surface of (11-20) are chosen as the substrate. As shown in Figure 1, the surface of the substrates used in this research is carefully inspected using an atomic force microscope (AFM) to confirm the roughness is less than 1 nm.

![Figure 1. Atomic force microscope images of Al₂O₃ (11-20)](image)

For sake of avoiding the occurrence of the melt Au droplet nucleated on the impurity particles inside the melt bulk, the high purity Au (>99.999wt%) is employed. Due to surface tension, the droplets can be assumed to be spherical. Assuming that the spherical radius of the droplet is r, the volume and size of the melt Au can be respectively expressed by the formulae (1) and (2)[13]:

\[
V = \frac{2\pi r^3}{3} (1 - \cos \theta) \tag{1}
\]

\[
D = 2r = 2 \times \sqrt[3]{\frac{3V}{2\pi(1-\cos \theta)}} \tag{2}
\]

where V represents the volume, D is the diameter of the nucleation phase, and \(\theta\) is the macroscopic wetting angle. As shown in Figure 2, the solidification process of every droplet were recorded, then the macroscopic wetting angle of Au droplet on substrate can be measured via the photo shooting by the high speed camera.

![Figure 2. Wetting angle measurement chart](image)

Since the droplet size is too small to measure directly, the size of the melt Au is controlled by the weight. The weight of Au droplets was measured by analytical balances, and the mass error is within ±1mg. With accurate weights and measured wetting angles, the droplet size can be calculated by the
formulae (1) and (2). The results are presented in Table 1. As can be seen, it is obvious that more weight means larger size.

| Weight /mg | Wetting angle/° | Size /mm |
|-----------|-----------------|----------|
| 40.3      | 108.16          | 1.825    |
| 20.5      | 107.35          | 1.462    |
| 10.8      | 103.65          | 1.199    |
| 5.4       | 105.28          | 0.945    |

2.2 Experimental apparatus and method

As shown in Figure 3a, a developed DSC-wetting angle measurement setup (Linseis Thermal Analysis Company, Selb Germany) is used for thermal analysis and specimen preparing. The weighted Au particles above Al₂O₃ substrate were horizontally placed on the temperature sensor. The furnace was first evacuated to about 5×10⁻³ Pa and then high-purity argon (oxygen content is less than 0.1 ppm) were filled until reaching the same pressure as the outside (1.013×10⁵ Pa). The process was repeated for twice to exclude the oxygen gas. Then the furnace was heated following the temperature routes shown in Figure 3b. As can be seen, the heating rate was raised from 10 K/min to 15 K/min as soon as the temperature achieved 873 K. Based on our previous research [8], the undercooling of Au droplet on Al₂O₃ single crystal substrate was significantly influenced by the cooling rates of sample. In this paper, the sample was cooled at three different cooling rates of 2 K/min⁻¹, 10 K/min⁻¹ and 20 K/min⁻¹. The temperature was recorded by a platinum–rhodium–platinum thermocouple with an accuracy of ±0.1°C. The experiments were repeated at least 10 times to ensure the repeatability of the experiments and the reliability of the results. The whole apparatus was described in detail in our previous work [8].

![Figure 3](image-url)  
Figure 3. (a) Schematic illustration of the improved DSC measurement (The upper right corner is the photograph of Au droplet on substrate); (b) Schematic diagram of the temperature curves employed in DSC experiments

3. Results

Figure 4(a–d) shows the measured endothermic peaks of Au droplet with different sizes melting on the Al₂O₃ substrates with (11-20) crystal planes at the heating rate of 15°C/min. As can be seen, the intensity of endothermic peaks decreases with reducing Au size. This is mainly because the smaller the
size of Au, the less heat is absorbed from outside by the melting process. Meanwhile, the smaller DSC endothermic peak area shown in the figure. Figure 5 (a-d) shows the corresponding exothermic peaks of Au droplet with different sizes solidified on the Al₂O₃ substrates with (11-20) crystal planes. Similarly, bigger size represents more heat released to outside during the solidification process. That means the larger DSC exothermic peak area is shown in Figure 5 when the droplet size is gradually increased.

![Figure 4. DSC melting curves of Au with different sizes of (a) D_{Au}=1.825mm (b) D_{Au}=1.462mm (c) D_{Au}=1.199mm (d) D_{Au}=0.945mm](image)

![Figure 5. DSC solidification curves of Au with different sizes of (a) D_{Au}=1.825mm (b) D_{Au}=1.462mm (c) D_{Au}=1.199mm (d) D_{Au}=0.945mm](image)

Based on the measured DSC curve above, the melting point of Au droplets are acquired by tangent method, the measured results presented on Table 2. It is clearly shown that the measured melting point
of Au is in the range of 1337.5~1337.9K, indicating that the melting point of Au is not influenced by droplet size and cooling rate.

The undercooling was defined as the temperature gap between the melting temperature $T_m$ and the solidification temperature $T_s$. The calculated undercooling ($\Delta T = T_m - T_s$) of Au droplet with different size solidified on $\text{Al}_2\text{O}_3$ (11-20) substrate at three kinds of cooling rates is shown in Figure 6. As can be seen, the undercooling is proportional to the cooling rate, whereas an inverse proportional relationship is achieved between the undercooling and droplet size.

Moreover, as shown in Figure 6a, when the small cooling rate of 2K/min is applied, the solidification undercooling of four different droplet size is relatively close, mainly concentrated in the value of 6-8K. As the cooling rate is increased to 10K/min, the undercooling of different size is in the range of 8~16K. When the maximum cooling rate of 20K/min is employed, the measured undercooling of four different size is in the range of 12~24K. It indicates the influence of droplet size on undercooling can be enlarged if the higher cooling rate is employed. As shown in Figure 6b, the variation amplitude of undercooling with the increasing of cooling rate is gradually reduced if the droplet size is larger. Similarly, it means that the influence of cooling rate on undercooling can be enlarged if the droplet size is smaller. The corresponding values of undercooling varied with cooling rate and droplet size are shown in Table 3 to clearly show this tendency.

### Table 2. Melting points $T_m$ of Au with different sizes and cooling rates

| Cooling Rate | Size  | 1.825mm | 1.462mm | 1.199mm | 0.945mm |
|--------------|-------|---------|---------|---------|---------|
| 2K/min       |       | 1337.7K | 1337.9K | 1337.8K | 1337.7K |
| 10K/min      |       | 1337.8K | 1337.8K | 1337.7K | 1337.5K |
| 20K/min      |       | 1337.7K | 1337.9K | 1337.9K | 1337.6K |

### Table 3. Undercooling $\Delta T$ of Au with different sizes and cooling rates

| Cooling Rate | Size  | 1.825mm | 1.462mm | 1.199mm | 0.945mm |
|--------------|-------|---------|---------|---------|---------|
| 2K/min       |       | 6.0K    | 5.9K    | 6.8K    | 7.6K    |
| 10K/min      |       | 8.9K    | 9.6K    | 14.3K   | 15.1K   |
| 20K/min      |       | 13.6K   | 14.8K   | 15.8K   | 22.5K   |

### Figure 6. Relationship between undercooling of Au droplet and (a) cooling rate, (b) droplet size

In order to further verify the tendency, the repeated DSC experiments with 10 times were performed on substrates of $\text{Al}_2\text{O}_3$ (11-20) according to the procedure displayed in Figure 3. Based on three different cooling rates of 2K/min, 10K/min and 20K/min, the results are divided into three groups as shown in Figure 7(a-c). As can be found, although the measured results have some
fluctuations, they still follow a clear rule that the undercooling of nucleation phase is proportional to the cooling rate and inverse proportional to the droplet size. Furthermore, in order to show the variation of undercooling caused by the interaction between cooling rate and droplet size, the corresponding average values of undercooling calculated from Figure 7 are presented as shown in Figure 8. As well, it can be found the same tendency that the influence of droplet size on undercooling can be enlarged if the higher cooling rate is employed, whereas the influence of cooling rate on undercooling can be enlarged if the smaller droplet size is selected.

Figure 7. Relationship between the undercooling and Au droplet size under different cooling rates of (a)2K/min, (b)10K/min, (c)20K/min achieved by repeating DSC experiment ten times

Figure 8. Relationship between the average undercooling of Au droplet (calculated from Figure 7) and (a) cooling rate, (b) droplet size

4. Discussion
According to the classical nucleation theory, it is assumed that at the beginning of solidification there is at least one nucleation particle. For volume nucleation, the following formula can be obtained:

\[ J_V V t = 1 \]  

where \( J_V \) is the nucleation rate per volume, \( V \) is the nucleation phase volume, and \( t \) is the nucleation time.

For the diameter \( D \), the volume \( V \) of droplet can be expressed by the following formula:
\[ V = \frac{\pi D^3}{12} (1 - \cos \theta) \]  

(4)

The nucleation rate can be expressed as:

\[ J_V = N_c \frac{kT_s}{3\pi a_0^3 \eta} \exp \left[ -\frac{16\pi \sigma_{SL}^3 f(\theta)}{3kT_s \Delta G_V} \right] \]  

(5)

where \( N_c \) is the number of nucleation particles per volume, \( a_0 \) is the atomic radius, \( k \) is the Boltzmann constant, \( \sigma_{SL} \) is the solid-liquid interface energy, \( f(\theta) \) is the nucleation contact angle factor, \( \eta \) is the viscosity and \( \Delta G_V \) represents the driving force for nucleating.

The melt viscosity varied with temperature is ignored. The nucleation time \( t \) can be expressed as \( \Delta T/R \). The relationship between undercooling and the nucleation driving force can be expressed as the following formula:

\[ \Delta G_V = \Delta H_V \frac{\Delta T}{T_m} \]  

(6)

Bring equations (4) - (6) into equation (3):

\[ \frac{D^3}{R} = A \frac{T_s}{\Delta T} \exp \left( \frac{B}{T_s \Delta T^2} \right) \]

(7)

\[ A = \frac{36a_0^3 \eta}{kN_c(1 - \cos \theta)} \]

\[ B = \frac{16\pi \sigma_{SL}^3 T_m^2 f(\theta)}{3k\Delta H_V^2} \]

From the above equation (7), it can be seen that \( \Delta T \) is a function of \( D \) and \( R \), which can be simplified to \( \Delta T \sim R/D^3 \). It shows that the undercooling is proportional to cooling rate and inversely proportional to droplet size, which is consistent with the experimental results. Moreover, it can be seen that the variation of undercooling is more sensitive to the droplet size. This may be the reason that the larger variation of undercooling is achieved when the droplet size is smaller.

5. Conclusion

The present research investigates the influence of droplet size and cooling rate on the undercooling of Au droplet which was nucleated on \( \text{Al}_2\text{O}_3 \) (11-20) single crystal substrate plate. The experimental results clearly show that the evolution of undercooling can be achieved by varying the droplet size and cooling rate. The undercooling is proportional to the cooling rate and inversely proportional to the droplet size. In addition, the contribution of droplet size variation to undercooling can be enlarged if the higher cooling rate is employed, whereas the influence of cooling rate on undercooling can be enlarged if the smaller droplet size is selected. These gained insights is due to the relationship \( \Delta T \sim R/D^3 \).

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7. References

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