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P07

Estimation of the supercooling limit of liquid Zr

液体 Zr の過冷却限界の推定

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1. Introduction

It is known that deep undercooling can be observed in the melting and solidification processes of metals by electrostatic levitation. The depth of the undercooling is limited and has a certain distribution. The distribution is expressed by the probability of nucleus growth using the nucleation frequency based on the classical nucleation theory by Herlach et al[1)]. In this study, we analyze how the distribution of the degree of undercooling changes with the purity of Zr by simulation using classical nucleation theory.

2. Experiment

In the electrostatic levitation method, the Coulomb force between the sample and the electrodes is balanced by gravity to levitate the sample. The position of the sample is detected optically, and the levitation is stabilized by feedback control using a PC.

After the sample was levitated by the electrostatic levitator, it was irradiated by CO2 laser and heated to melt it. The laser was then turned off simultaneously to observe the temperature change. This process was repeated 100 times to obtain the distribution of the degree of undercooling. A schematic diagram of the cooling curve during solidification and the degree of undercooling ΔT are shown in Figure 1.

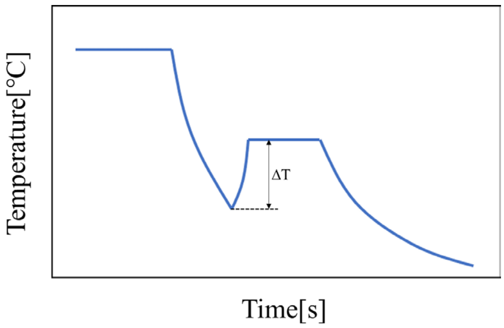

Figure 1 Schematic diagram of cooling curve and ΔT

We then analyzed the histogram[2)] of ΔT for metallic Zr using classical nucleation theory.

3. Results and Discussion

The probability of coagulation at ΔT is expressed by the equation

$$(Coagulation\ probability\ at\ \Delta T) = \Delta\tau \cdot f(\Delta T) \cdot \mathrm{P}(\Delta T) \tag{1}$$

where Δτ represents the residence time at ΔT and is proportional to the inverse of the cooling rate.

P(ΔT) is written as follows;

$$P(\Delta T) = exp\left(\frac{-\Delta g_C}{k_B T}\right) = exp\left(-\frac{16\pi\sigma^3}{3k_B \Delta G_v^2}\right) = exp\left(\frac{-B}{(T_m - \Delta T)\Delta T^2}\right) \tag{2}$$

where Δg_c is the free energy of the critical nucleus, T_m is the melting point, k_B is Boltzmann's constant, ΔT is the degree of undercooling, ΔGv is the free energy difference between the solid and liquid phase, and σ is the solid-liquid interface energy per unit area.

where B is

$$B = \left(\frac{16\pi\sigma^3}{3k_B E^2}\right) \tag{3}$$

E is a constant when the free energy difference ΔGv between the solid and liquid phases is assumed to be proportional to the degree of undercooling ΔT, ΔGv=EΔT.

f(ΔT) is assumed to increase exponentially with ΔT, and the following equation is used

$$f(\Delta T) = exp(D \cdot \Delta T) \tag{4}$$

where ΔT is the degree of undercooling.

At a certain ΔT, a number of random numbers proportional to the nucleation frequency are generated. If any of the random numbers exceeded P(ΔT), solidification was assumed to have occurred, otherwise, the same procedure was repeated with a slightly larger ΔT. The values of D and B were adjusted to simulate the half-width and degree of undercooling, and their distributions were obtained.

The constant B of P(ΔT) was fixed at $B=5.0\times10^8$, and the constant D of f(ΔT) was adjusted to express the measured value of 99.9%Zr at $D=5.95\times10^{-3}$ and the measured value of 99.5%Zr at $D=9.5\times10^{-3.3}$, which could be represented at $D=9.5\times10^{-3}$. (Solid line is the distribution obtained by simulation)

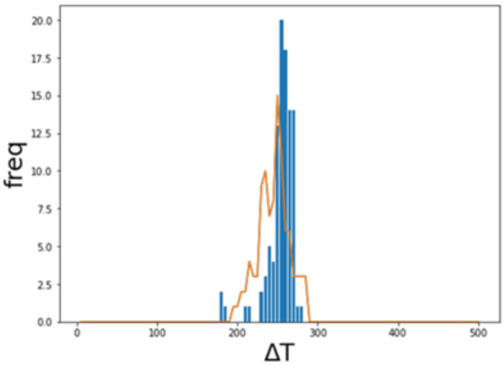

Figure 2 Simulated Results and Purity 99.9% Zr Histogram

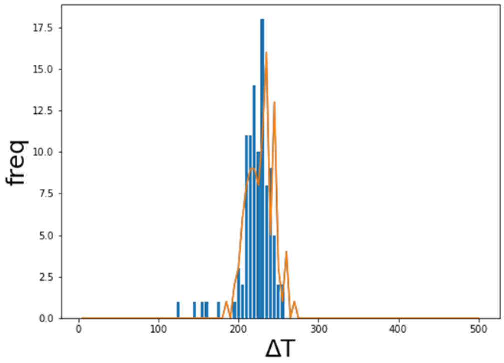

Figure 3 Simulated Results and Purity 99.5% Zr Histogram

f(ΔT) and P(ΔT) are shown in Figures 4 and 5.

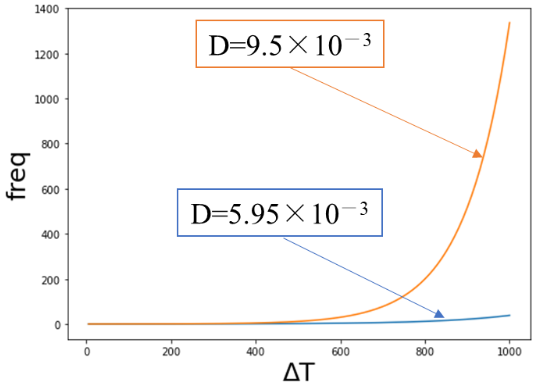

Figure4 Frequency of nucleation

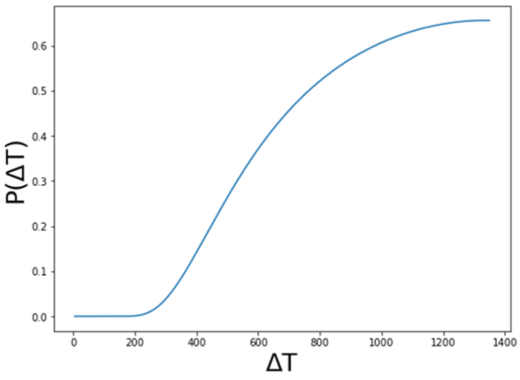

Figure5 Probability of nucleus growth

4. summary

Historical Zr undercooling temperature data could be reproduced by simulation analysis using classical nucleation theory

References

1)M.Herlach:Crystal nucleation in undercooled liquid zirconium,(2009)