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PS24

ガスジェット浮遊による過冷却液滴からの準安定 γ-Al_2O_3成長とその融解熱測定

Growth of metastable γ-Al_2O_3 from a supercooled droplet and its heat of fusion measurement using an aerodynamic levitation

兵頭慧 [1], 小畠秀和 [1], 後藤琢也 [1],
Kei HYODO[1], Hidekazu KOBATAKE[1], Takuya GOTO[1]
[1] 同志社大学，Doshisha University#1,

1. Introduction

The heat of fusions of oxides is one of the fundamental thermodynamic properties that govern the heat transport process during the solidification of functional materials[1)] or the crystallization of minerals from magma[2)]. Conventionally, the heat of fusion has been measured using drop calorimeters[3)] or differential scanning calorimeters. However, for the oxide with high melting temperature, it becomes difficult task to measure the heat of fusion due to chemical interactions with the contact materials. Additionally, heat loss through radiative heat transfer causes experimental uncertainty in the measurement using the drop calorimetry at elevated temperature[4)]. Furthermore, conventional measurements are limited to stable phases, despite the growing interest in the thermodynamic properties of metastable oxides for functional material processing[5)]. To overcome these difficulties, the heat of fusion of oxide materials has been measured based on hypercooling (ΔT_{hyp}) limit determination using an aerodynamic levitator. Al_2O_3 was used for the evaluation of the validity of this technique.

2. Experiment

A spherical α-Al_2O_3 sample (diameter: 2 mm) was levitated in an Ar gas flow using the aerodynamic levitator and then melted by CO_2 laser irradiation. The temperature of the samples was measured with a two-color radiation thermometer, which was calibrated based on Wien's law using the liquidus temperature. From the temperature profile during the solidification process, the hypercooling limit was determined. Using the hypercooling limit, the heat of fusion of the Al_2O_3 was determined. The phase of the obtained sample was evaluated by X-ray diffraction (XRD).

3. Measurement Principle

Our previous investigation[6,7] have shown that there is a linear relation between the degree of supercooling (ΔT) and the plateau duration (Δt).

$$\Delta H_{\mathrm{f}} = C_{\mathrm{p}}\Delta T + \alpha\Delta t \tag{1}$$

Here, ΔH_{f} denotes the heat of fusion, C_{p} is the heat capacity of liquid phase at constant pressure, and α represents the term accounting for heat loss caused by forced convection by gas flow and by radiation. The x-intercept of this line corresponds to the hypercooling limit. Using the hypercooling limit, the heat of fusion simply can be expressed as

$$\Delta H_{\mathrm{f}} = C_{\mathrm{p}}\Delta T. \tag{2}$$

4. Results and discussion

Figure 1 shows the temperature profile of the sample. From the recalescence process, the both plateau temperature duration (Δt) and degree of undercooling (ΔT) can be obtained. Figure 2 shows the correlation between thermal plateau time (Δt) and degree of undercooling (ΔT). From the fitting line, ΔT_{hyp} was determined to be 393 K.

Using the heat capacity of liquid Al_2O_3 (192.464 J mol^{-1} K^{-1}) in literature[8], the heat of fusion of Al_2O_3 was determined as 75.7 kJ mol^{-1}. This value is 23% smaller than the heat of fusion of α-Al_2O_3 in literature[8].

Meanwhile XRD analysis showed that the metastable phase γ-Al_2O_3 was formed during the solidification process. Further, it was found that γ-Al_2O_3 appeared at larger undercooling region; $\Delta T > 101$ K. Moreover, the intensity of γ-Al_2O_3 peak in XRD increased as increase of the degree of undercooling. These results inferred that metastable γ-Al_2O_3 can be formed at larger undercooling. The determined of heat of fusion of Al_2O_3 in this study was close to the that of γ-Al_2O_3 in the NIST-JANAF database (78.5 kJ mol^{-1}) indicating that the heat of fusion of metastable γ-Al_2O_3, was directly determined.

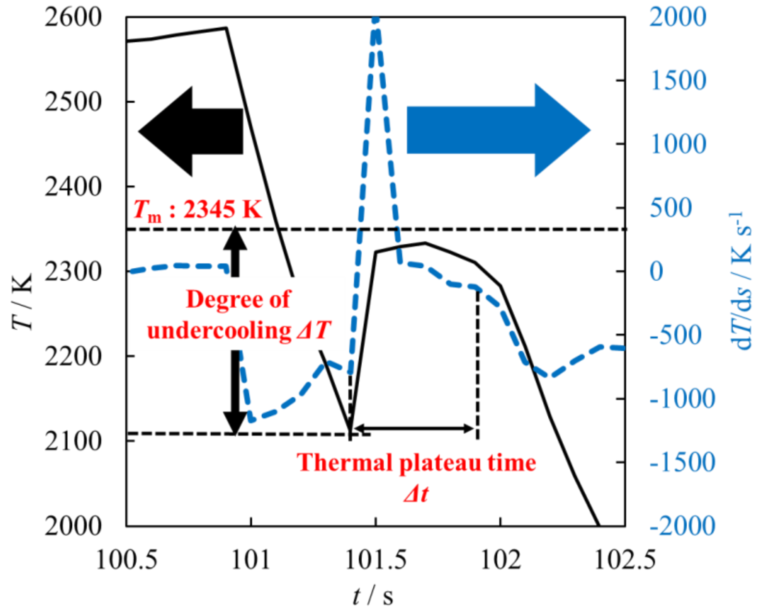

Figure 1. A typical temperature profile of the recalescence of Al_2O_3.

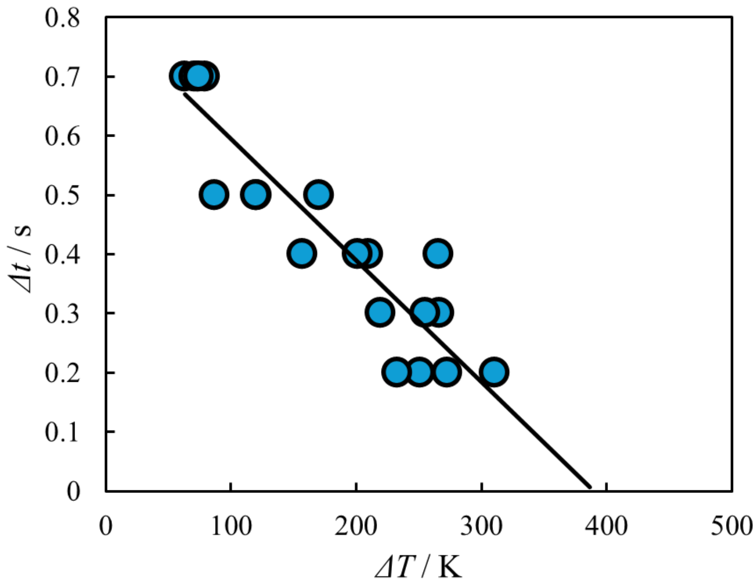

Figure 2. The correlation between thermal plateau time (Δt) and degree of undercooling (ΔT)

References

1) T. Kuroki, N. Mori and K. Ogi: Melt-Growth Joining of Superconductive YBCO Crystals with YBCO/Ag Insert. 日本金属学会誌, **66** (2002) 492.
   DOI: https://doi.org/10.2320/jinstmet1952.66.5_492
2) T. Sugawara: 落下型熱量計による酸化物融体の熱量測定, Materia Japan, **58** (2019) 616.
3) F. Wust, A. Meuthen and R. Durrer: Forsch. Gebiete Ingenieurw. VDI, **204** (1918).
4) K. Yamaguchi, K. Itagaki, 落下型熱量計による高温熱含量測定, Netsu Sokutei, **29** (2002) 173.
5) K. Kaneko, S. Fujita: Synthesis of Metastable or Non-Equilibrium Phased Oxides and Their Physical Properties. Journal of Society of Materials Science, **68** (2019) 733.
   DOI: https://doi.org/10.2472/jsms.68.733
6) S. Jeona, M.P. Sansoucieb and D.M. Matsona: Hypercooling limit, heat of fusion, and temperature-dependent specific heat of Fe-Cr-Ni melts. The Journal of chemical thermodynamics, **138** (2019) 51,
   DOI: 10.1016/j.jct.2019.06.001.
7) K. Kawamoto, T. Goto, H. Kobatake: Development of Heat-of-fusion Measurement for Metals Using a Closed-type Aerodynamic Levitator. ISIJ International, **64** (2024) 1155.
   DOI: https://doi.org/10.2355/isijinternational.ISIJINT-2024-053
8) M. W. Chase, Jr., ed.: NIST-JANAF Thermochemical Tables, 4th ed. Part1 Al_2O_3, American Chemical Society, (1998).

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