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Supercooling (ΔT) dependence of nano-nucleation of PE by SAXS and proposal of a new nucleation theory

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Abstract

Degree of supercooling (ΔT) dependence of nano-nucleation was studied by means of small angle X-ray scattering (SAXS) and a new nucleation theory was proposed. We obtained the ΔT dependence of size distribution $f(N,t)$ directly, where N is number of particle and t is time, which concluded that the "induction period" of crystallization is not controlled by so called "spinodal decomposition" but by nucleation one. It clarified that the critical nano-nucleation mainly controls not only the steady nano-nucleation but also macro-crystallization experimentally as the zero-th approximation by using the newly obtained ΔT dependence of $f(N,t)$ and nucleation rate (I) of macroscopic crystal obtained by means of optical microscope (OM). Time evolution of total free energy of nucleation of a huge closed system $\delta G(t)$ was obtained experimentally for the first time, which clearly confirmed that nano-nucleation is the process where $\delta G(t)$ passes through an activation barrier and reaches the most stable state by completion of melt-solid (crystal) phase transition due to well known "Ostwald ripening". We proposed a new nucleation theory by introducing a "mass distribution function $Q(N,t) \propto Nf(N,t)$". We proposed a new basic equation of the mass conservation law, $\partial Q(N,t)/\partial t = -\partial \boldsymbol{j}(N,t)/\partial N$, where $\boldsymbol{j}(N,t)$ is net flow. This solved the serious problem in classical nucleation theory (CNT), where so called "fundamental kinetic equation" does not satisfy the mass conservation law. The coupling of our "real image" and correct theory will enable us to realize the ultimate structure and physical properties of materials, which should be a very interesting "fruit".

Keywords: Nucleation; Supercooling; Free energy

1. Introduction

Goal of study of "nucleation" which is the early state of crystallization is to obtain size distribution $f(N,t)$ of nucleus in nm order (we will call "nano-nucleus"). $f(N,t)$ indicates how size, shape and number of nucleus evolve with increase of crystallization time (t), where N is number of atom, "particle" or "repeating unit" in a nucleus (hereafter we will simply call "particle"). "To obtain $f(N,t)$" means to observe $f(N,t)$ directly experimentally and to predict $f(N,t)$ theoretically. As it will be shown below, we have recently succeeded in obtaining the $f(N,t)$ "partly" in our previous study [1], i.e., we obtained $f(N,t)$ experimentally at only one degree of supercooling (ΔT). Therefore the next main purpose of our nucleation study is to obtain ΔT dependence of the $f(N,t)$ and to obtain the $f(N,t)$ theoretically. Since it is well known that "the driving force" of the nucleation and growth is free energy of melting (Δg) and that $\Delta g \propto \Delta T$, it is very important to obtain the ΔT dependence of $f(N,t)$ experimentally.

Although nucleus was assumed by classical nucleation theory (CNT) proposed by Becker and Döring [2], Turnbull and Fisher [3] and Frenkel [4] in the 1930s, nobody had succeeded

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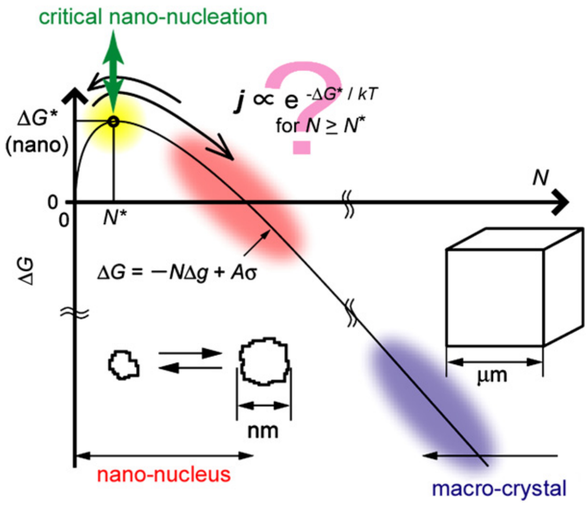

Fig. 1. Illustration of a sequential process of nucleation which shows ΔG against N. Δg is free energy of melting and A is surface area of nucleus. Nano-nucleus shows significant fluctuation with respect to its size and shape. ΔG^*(nano) corresponds to critical nano-nucleation, as shown in Ref. [1]. After Eyring's theory of absolute reaction rate, critical nano-nucleation should become activation barrier of nucleation. Macro-crystal has smooth and flat surface and has no disappearance.

in observing nano-nuclei directly. It is due to too low number density of nano-nuclei. Therefore macroscopic crystals in µm order (we will call ''macro-crystal'' in this study) have been observed by means of optical microscope (OM) for long years in classical nucleation study (CN study), which should be regarded as an ''alternative nucleation study''.

We succeeded in observing directly nano-nucleation by means of small angle X-ray scattering (SAXS) for the first time reported in our recent study [5,6], which we will name ''direct nucleation study''. We added ''nucleating agent (NA)'' to sample (polyethylene (PE)), because of which the scattering intensity $I_X(q,t)$ from nano-nuclei increased as high as 10^4 times [5,6], where q is scattering vector. We obtained $f(N,t)$ directly for the first time for one ΔT [1]. But ΔT dependence of nucleation has not been studied yet. Therefore the first purpose of this work is to obtain the ΔT dependence of $f(N,t)$ directly.

We showed at the same time that ''kinetic parameter'', such as free energy of end surface (σ_e) of nano-nucleus (σ_e(nano)), is 1/5 [1] as large as that of ''macro-crystals'' (σ_e(macro)) that is estimated from Gibbs−Thomson's plot of melting temperature (T_m) against lamellar thickness (l) [7]. Fig. 1 illustrates sequential process of nucleation which shows free energy of nucleation for a nucleus of size N ($\Delta G(N)$) against N. N^* and $\Delta G^*(N^*)$ are N and $\Delta G(N)$ of ''critical nucleus'' which corresponds to an activated state in nucleation process. $\Delta G^*(N^*)$ corresponds to critical nano-nucleation. We clarified in the previous paper [1] that nano-nucleus shows significant fluctuation with respect to size and shape and repeats frequent generation and disappearance, which is ''real image'' of nano-nucleation. On the other hand, we clarified that macro-crystal has smooth and flat surface and has no disappearance. Fig. 2 illustrates schematic nucleation and crystallization process. Here we consider a huge closed system including huge total number of particle (ν_0). Nano-nuclei generate from the supercooled melt and finally the system transforms into a single crystal. Details will be shown later in this study.

1.1. Relationship of ''direct and alternative nucleation studies'' on nano-nuclei and macro-crystals, respectively

Although the direct nucleation study on nano-nucleation is important for science to clarify real image of nano-nucleation exactly, the study by means of SAXS is not so easy. On the other hand, the alternative nucleation study by means of OM is very easy and useful for a routine work of nucleation study for practical purposes, such as industrial evaluation of solidification rate of polymers in processing of plastics. In CN study of these days, it has been assumed ''a priori'' (without any

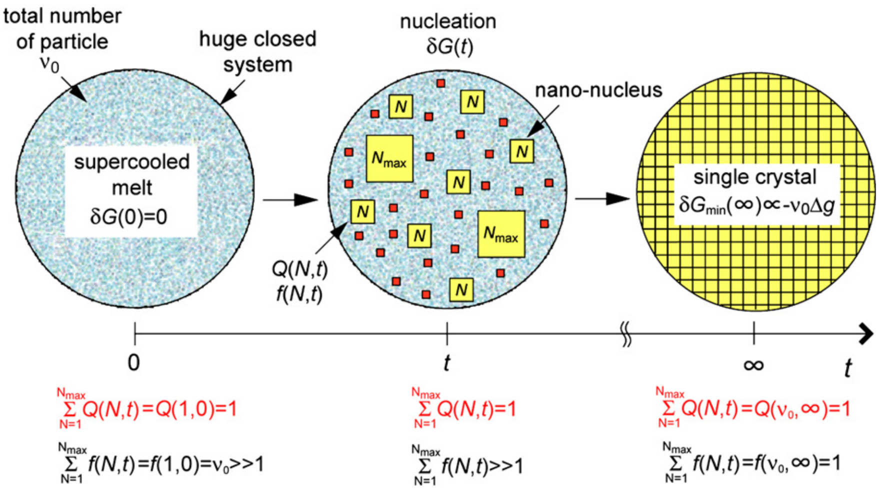

Fig. 2. Illustration of schematic nucleation and crystallization processes. We consider a huge closed system. Nano-nuclei generate from the supercooled melt and finally the system transforms into a single crystal. Total free energy of nucleation ($\delta G(t)$), mass distribution function ($Q(N,t)$) and $f(N,t)$ are also shown. $\delta G(t)$ changes from zero at the supercooled melt to minimum ($\delta G_{min}(t)$) at 100% crystal. Summation of $Q(N,t)$ satisfies unity for all t, however, $f(N,t)$ does not at all.

experimental evidence) that the alternative nucleation study can detect the most essential process in nucleation as the zero-th approximation. We will show in this study that the most essential process in nucleation should be ''critical nano-nucleation process'', by showing that both nano-nucleation and macro-crystallization are mainly controlled by the critical nano-nucleation. The assumption in CN study has been believed for long years as the observation of macro-crystallization which is an indirect observation of nano-nucleation, however, it has not been verified yet that the assumption is correct or not. The second purpose of this work is to clarify that the critical nano-nucleation mainly controls both steady nano-nucleation and macro-crystallization as the zero-th approximation by using the newly obtained ΔT dependence of $f(N,t)$. If we could verify that the assumption is correct, it will be shown that alternative nucleation study can be applicable as the zero-th approximation for practical routine work.

1.2. Total free energy of nucleation of a closed system

If ''total free energy of nucleation of a huge closed system ($\delta G(t)$)'' could be obtained, it should give us clear image of nucleation process, i.e., we will be able to understand why nucleation happens. We will show in this study that the $\delta G(t)$ could be obtained from $f(N,t)$. Although the $\delta G(t)$ is important to understand kinetic process of nucleation, $\delta G(t)$ has not been obtained, because $f(N,t)$ had not been observed directly for long years. Therefore the $\delta G(t)$ has not been studied explicitly in CN study of these days. The third purpose of this work is to obtain $\delta G(t)$ experimentally, which should give us clear image why nucleation happens. We will show that the phase transition process from the supercooled melt to crystal corresponds to $\delta G(t)$ changes from zero at the supercooled melt to minimum ($\delta G_{\min}(t)$) at 100% crystal as shown in Fig. 2 passing through an activation barrier.

1.3. Basic equation of nucleation

Since it is natural to regard the nucleation as a kind of a stochastic process, nucleation should be described by a ''basic equation'' of a stochastic one, which is the basic view point of this study. But it has not been made clear whether so called ''fundamental kinetic equation'' in CNT satisfies the necessary condition of the basic equation or not. It is well known that the necessary condition of the basic equation of the stochastic process is that it should satisfy the ''mass conservation law'' with respect to a ''distribution function $y(x,t)$'' that should satisfy a normalized condition, i.e.,

$$\sum_{x=1}^{x_{\max}} y(x,t) = 1 \quad \text{for any } t, \tag{1}$$

where x indicates a variable [8].

CNT assumed a linear sequential rate process [4], that is, one particle repeats attachment and detachment one by one on the surface of a nucleus. The fundamental kinetic equation as proposed in CNT is given by

$$\partial f(N,t)/\partial t \equiv I(N-1,t) - I(N,t), \tag{2}$$

where nucleation rate $I(N,t)$ is defined by

$$I(N,t) \equiv \alpha'_N f(N,t) - \beta'_{N+1} f(N+1,t). \tag{3}$$

Here α'_N and β'_{N+1} are transition probability of forward and backward flows between N-th and $N+1$-th stages, respectively. It has been long believed that a ''fundamental kinetic equation'' with respect to $f(N,t)$ proposed by CNT can describe the nucleation process correctly. But we will show in this study that $f(N,t)$ and the kinetic equation in CNT do not satisfy the normalized condition and the mass conservation law, respectively. Hence the $f(N,t)$ is not a distribution function.

The fourth purpose of this work is to propose a new nucleation theory formulating a new basic equation that satisfies the mass conservation law by using a ''mass distribution function $Q(N,t)$'' which satisfies the normalized condition. $Q(N,t)$ will be defined and explained later in Section 4.2.

1.4. Purpose

Purposes of this work are (1) to obtain the ΔT dependence of $f(N,t)$ directly, (2) to clarify that the critical nano-nucleation mainly controls the steady nano-nucleation and macro-crystallization as the zero-th approximation by using the newly obtained ΔT dependence of $f(N,t)$, (3) to obtain the total free energy of nucleation of a huge closed system $\delta G(t)$ experimentally and (4) to propose a new nucleation theory by formulating a new basic equation that satisfies the normalized condition using a mass distribution function $Q(N,t)$.

The coupling of our ''real image'' of nano-nucleation and new correct basic equation will enable us to realize the ultimate structure and physical properties of materials, which should be a very interesting ''fruit''.

2. Method

2.1. How to clarify the direct correspondence between nano-nucleation and macro-crystallization

In the nucleation theory so called ''net flow of nucleation ($\boldsymbol{j}$)'' takes an important role in nucleation process illustrated in Fig. 1, as will be shown later in Section 4.2. As the zero-th approximation, critical nano-nucleation should become main controlling process of activation barrier in nucleation after Eyring's kinetic theory of absolute reaction rate (theory of absolute reaction rate) [9]. Hence $\boldsymbol{j}$ can be given by

$$\boldsymbol{j} \propto \exp[-\Delta G^*(N^*)/kT], \tag{4}$$

where kT is thermal energy. $\Delta G^*(N^*)$ is given by

$$\Delta G^* \cong 4\sigma\sigma_e/\Delta g \quad \text{for } \Delta g \gg \Delta\sigma, \text{ two dimensional (2D) nucleus,} \tag{5}$$

[10] where σ is surface free energy, $\Delta\sigma$ is interface free energy between nucleus and NA and Δg is free energy of melting.

Table 1
Kinetic parameters

σ_e(nano) × 10^{-21} J rep. unit^{-1}	$\Delta\sigma \times 10^{-21}$ J rep. unit^{-1}	$\sigma \times 10^{-21}$ J rep. unit^{-1}	$\Delta h \times 10^{-21}$ J rep. unit^{-1}
3.5	0.06 (NA)	0.4	6.7[a]

[a] Ref. [10].

They are defined in this study per one particle. If critical nano-nucleation mainly controls not only nano-nucleation but also macro-crystallization, ***j*** is rewritten as

$$\boldsymbol{j} \propto \exp[-C/\Delta T], \tag{6}$$

where

$$C = (\Delta G^*/kT)\Delta T = 4T_m^0\sigma\sigma_e/kT\Delta h, \tag{7}$$

[10] where T_m^0 is equilibrium melting temperature and Δh is enthalpy of melting per one particle [10]. Here Δg given by

$$\Delta g = \Delta s\Delta T = \left(\Delta h/T_m^0\right)\Delta T \propto \Delta T \tag{8}$$

[10] is used, where Δs is entropy of melting. We show the kinetic parameters used in this study in Table 1.

It is impossible to observe ***j*** directly. But some observable quantities should correspond to it. Inverse of "induction time (τ_i)" in nano-nucleation should be directly related to ***j***, where τ_i is defined by Andres and Boudart [11] in CNT. "Nucleation rate (I)" in macro-crystallization observed should be also related to ***j*** [3]. I is defined by the rate of macro-crystallization per unit volume and time, as will be shown later. If critical nano-nucleation mainly controls nano-nucleation and macro-crystallization, both τ_i^{-1} and I should be proportional to ***j***, respectively, i.e.,

$$\tau_i^{-1} \propto I \propto \boldsymbol{j}. \tag{9}$$

Therefore the direct correspondence between nano-nucleation and macro-crystallization should be verified by obtaining Eq. (9) experimentally.

2.2. Experimental

The materials used in this study were of two kinds of fully fractionated PE such as NIST, SRM1483 ($M_n = 32 \times 10^3$, $M_w/M_n = 1.1$) for SAXS and Sunallomer, J-PE2 ($M_n = 30 \times 10^3$, $M_w/M_n = 1.15$) for OM [12]. As the condition $\Delta g \gg \Delta\sigma$ is satisfied from Eq. (5), the results in this work do not depend on $\Delta\sigma$ or materials. Hence there is no problem to use two different PE's. Further, I obtained by using J-PE2 by means of OM has been published in Ref. [12]. In this work, we added the observation of nano-nucleation.

The NA of sodium 2,2′-methylene-bis-(4,6-di-*t*-butylphenylene) phosphate (ADEKA Corp., NA-11SF) was used and lateral size of NA (a_{NA}) is 0.23 ± 0.12 μm. PE mixed with NA was prepared for SAXS to increase $I_X(q,t)$ from nano-nuclei [13], which is named as "PE + NA". We used samples of PE + NA to observe nano-nucleation. Concentration of NA in mixture of PE and NA (C_{NA}) was 3 wt%.

In the case of SAXS experiment, the sample was melted at 160 °C for 5 min within a thin evacuated capillary (ϕ 1 mm) and then isothermally crystallized at crystallization temperatures (T_cs), $T_c = 126.5–129.0$ °C. In the case of OM, the sample was melted at 160 °C for 5 min and isothermally crystallized at $T_c = 126.0–129.9$ °C [12]. As T_m^0 is 139.5 °C [14], $\Delta T = 10.5–13.0$ K for SAXS and $\Delta T = 9.6–13.5$ K for OM, where ΔT is defined as $\Delta T \equiv T_m^0 - T_c$.

The SAXS experiment was carried out by using synchrotron radiation at beam line, BL40B2 of SPring-8 at Japan Synchrotron Radiation Research Institute (JASRI), Harima and BL-10C of Photon Factory at High Energy Accelerator Research Organization (KEK) Tsukuba. The range of q was $(7–214) \times 10^{-3}$ Å^{-1} and wave length (λ) was 1.50 Å^{-1}. In the case of OM, 0.1 mm thick samples were put in hot stage (Linkam, LK-600). The nitrogen gas flow was at a rate of 50 mL/min. Number of isolated crystals near the center of the sample was counted using polarizing OM (Olympus, BX). We counted number density of nuclei whose size is $a \geq 1$ μm ($\nu(t)$) in this study. We observed I from the plot of $\nu(t)$ against t. I is defined by

$$I \equiv d\nu(t)/dt. \tag{10}$$

3. Results and discussion

3.1. ΔT dependence of *f*(*N*,*t*) and mainly controlling process of critical nano-nucleation

3.1.1. ΔT dependence of *f*(*N*,*t*) of nano-nucleus

We obtained *f*(*N*,*t*) by applying extended Guinier plot method [1]. Here we will explain briefly the method. The logarithmic excess scattering intensity ($\ln I_X(q,t)$) of small angle X-ray is plotted against q^2. The $\ln I_X(q,t)$ vs. q^2 is analyzed by applying $I_X(q,t) = \sum_{j=1}^{5} I_{Xj}(q,N_j,t)$, where j indicates the different nuclei of size (N_j) and $I_{Xj}(q,N_j,t)$ does $I_X(q,t)$ from the nuclei of N_j. From the $I_{Xj}(q,N_j,t)$, *f*(*N*,*t*) was obtained. *f*(*N*,*t*)s were plotted against t in Fig. 3a as a parameter of ΔT for $N = 2.2 \times 10^4$ [rep. unit] > $N^*(\Delta T = 10.5$ K) ≅ 450 [rep. unit] which is the maximum $N^*(\Delta T)$ in this study as shown in our previous paper [1]. *f*(*N*,*t*) started increasing after some time, increased linearly with increase of t and saturated. *f*(*N*,*t*) increased rapidly with increase of t at large ΔT, while *f*(*N*,*t*) increased slowly at small ΔT. It clarified that nano-nucleation becomes impossible for smaller ΔT. It was impossible to observe the saturation of *f*(*N*,*t*) for larger ΔT due to onset of lamellar stacking [5,6].

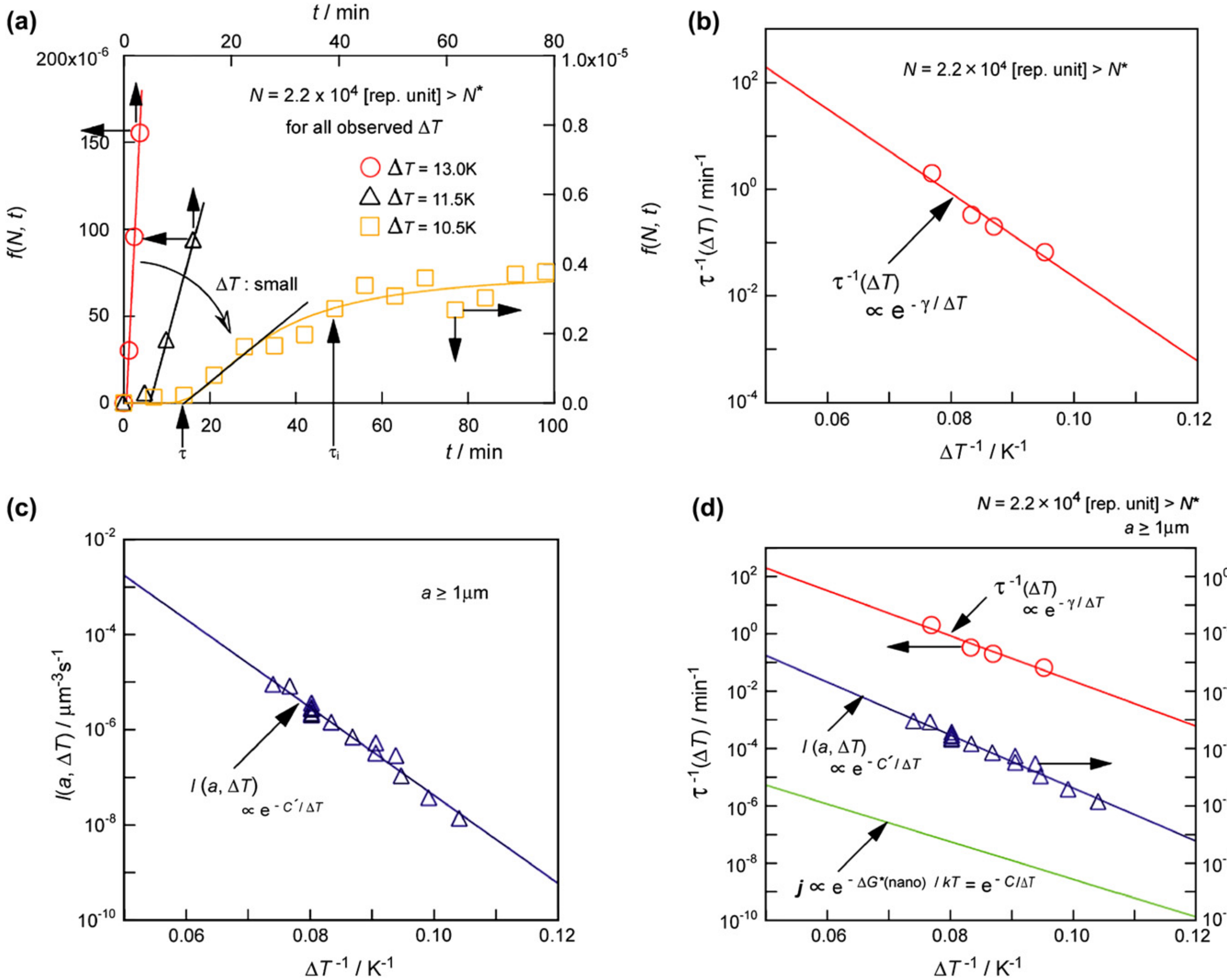

Fig. 3. ΔT dependence of nano-nucleation and macro-crystallization. (a) Plots of ΔT dependence of $f(N,t)$ against t for $N = 2.2 \times 10^4$ [rep. unit] $> N^*$. $N^*(\Delta T = 10.5\ \mathrm{K}) \cong 450$ [rep. unit] which is the maximum N^* in this study. $f(N,t)$ of $\Delta T = 13.0$ and 11.5 K are shown in left and top axes. $f(N,t)$ of $\Delta T = 10.5$ K are shown in right and bottom axes. $f(N,t)$ increased slowly with decrease of ΔT, which clarified that nano-nucleation becomes difficult with decrease of ΔT. It was impossible to observe the saturation of $f(N,t)$ for larger ΔT due to onset of lamellar stacking. τ_i of $\Delta T = 10.5$ K and onset times (τs) of $f(N,t)$ for each ΔT are shown. (b) Plots of τ^{-1} against ΔT^{-1} for $N = 2.2 \times 10^4$ [rep. unit] $> N^*$. τ^{-1} decreased exponentially with increase of ΔT^{-1}, which means that nano-nucleation is difficult significantly when ΔT becomes 0. Therefore it was concluded that induction period is not spinodal decomposition process but nucleation one. (c) Plots of I against ΔT^{-1} for $a \geq 1\ \mu\mathrm{m}$. I decreased exponentially with increase of ΔT^{-1}. Therefore it was concluded that nucleation is difficult significantly when ΔT becomes small. (d) Plots of τ^{-1}, I and theoretical $\boldsymbol{j}$ against ΔT^{-1} and comparison of these slopes. $\boldsymbol{j}$ was calculated as a function of ΔT by using Eqs. (6) and (7) and Table 1. The parallel lines show same ΔT dependence. Therefore it was verified that the critical nano-nucleation controls not only nano-nucleation but also macro-crystallization experimentally.

3.1.2. ΔT dependence of τ

From the $f(N,t)$ vs. t plot, τ_i is obtained by Andres and Boudart's method [11] as is shown in Fig. 3a. We can obtain $\tau_i \equiv \int_0^\infty \{f_{\mathrm{st}}(N) - f(N,t)\}\mathrm{d}t/f_{\mathrm{st}}(N)$ [11], where $f_{\mathrm{st}}(N)$ is $f(N,t)$ in the steady state. I in Ref. [11] was changed to $f(N,t)$. As the saturation of $f(N,t)$ against t could not be observed at large ΔT, observation of τ_i was impossible. Therefore we obtained alternatively "onset time $\tau(\Delta T)$" which is defined as extrapolated time of the linearly increasing $f(N,t)$. In this study, we assumed simply that the $\tau(\Delta T)$ is in proportion to the τ_i. We plotted $\tau^{-1}(\Delta T)$ against ΔT^{-1} in Fig. 3b for $N = 2.2 \times 10^4$ [rep. unit] $> N^*(\Delta T)$. $\tau^{-1}(\Delta T)$ decreased exponentially with increase of ΔT^{-1}. Experimental formula was

$$\tau^{-1}(\Delta T) \propto \exp[-\gamma/\Delta T], \tag{11}$$

where γ is a constant given by

$$\gamma = 1.8 \times 10^2\ \mathrm{K}. \tag{12}$$

Hence we obtained

$$\lim_{\Delta T \to 0} \tau = \infty. \tag{13}$$

This means that when ΔT approaches 0, nucleation becomes impossible.

3.1.3. ΔT dependence of macro-crystallization

We plotted $I(\Delta T)$ against ΔT^{-1} for $a \geq 1$ μm in Fig. 3c. $I(\Delta T)$ decreased exponentially with increase of ΔT^{-1}. Experimental formula was obtained by

$$I(\Delta T) \propto \exp[-C'/\Delta T], \tag{14}$$

where C' is a constant given by

$$C' = 2.1 \times 10^2\ \mathrm{K}. \tag{15}$$

Therefore it was shown again that nucleation becomes difficult significantly when ΔT becomes small.

3.1.4. Critical nano-nucleation controls both nano-nucleation and macro-crystallization

Fig. 3d shows obtained $\tau^{-1}(\Delta T)$, $I(\Delta T)$ and theoretical $\boldsymbol{j}$ against ΔT^{-1}, where $\boldsymbol{j}$ was calculated as a function of ΔT by using Eqs. (6) and (7). The slope C of Eq. (7) is given by

$$C = 1.5 \times 10^2\ \mathrm{K} \tag{16}$$

by using Table 1. It is to be noted that three straight lines in Fig. 3d were nearly parallel, i.e., their slopes are nearly the same. The slopes of γ, C' and C were given by

$$\mathrm{Slope} = \langle \mathrm{Slope} \rangle \pm \Delta\mathrm{Slope} = (1.8 \pm 0.3) \times 10^2\ \mathrm{K}, \tag{17}$$

where $\langle \mathrm{Slope} \rangle$ is mean of slope and $\Delta\mathrm{Slope}$ is scatter of the slopes. The relative error $\Delta\mathrm{Slope}/\langle \mathrm{Slope} \rangle$ was as small as 16%. Thus we obtained approximately

$$\gamma \cong C' \cong C. \tag{18}$$

That is,

$$\tau^{-1} \propto I \propto \boldsymbol{j}, \tag{19}$$

which verified Eq. (9). So they showed same ΔT dependence. Hence it was verified that critical nano-nucleation mainly controls not only nano-nucleation but also macro-crystallization experimentally. Therefore it is concluded that the nano-nucleation directly corresponds to macro-crystallization.

As Eqs. (11) and (19) are not expected for spinodal decomposition, it was concluded that the "induction period" of crystallization is not controlled by so called "spinodal decomposition" process proposed by Imai et al. [15] but by nucleation one.

3.2. Total free energy of nucleation of a huge closed system $\delta G(t)$

3.2.1. Theory of $\delta G(t)$

Total free energy of nucleation of a huge closed system $\delta G(t)$ is given by

$$\delta G(t) = \sum_{N=1}^{\nu_0} f(N,t)\Delta G(N), \tag{20}$$

where ν_0 is total number of particle of a closed system. We assumed $\nu_0 \cong 10^{12}$ [rep. unit] as a huge closed system, where lateral size of the system is several μm. Since nuclei are 2D in all observed ΔT, $\Delta G(N)$ is given by

$$\Delta G(N) = -(\Delta g - \Delta\sigma)N + 4(\sigma\sigma_e)^{1/2}N^{1/2} \quad \text{for 2D nucleus}. \tag{21}$$

[1] Eq. (20) is rewritten as

$$\delta G(t) = \sum_{N=1}^{1} f(N,t)\Delta G(N) + \sum_{N=2}^{N_{\max}} f(N,t)\Delta G(N) + \sum_{N=N_{\max}+1}^{\nu_0} f(N,t)\Delta G(N), \tag{22}$$

where $N_{\max}$ is maximum of N. Here first term of Eq. (22) becomes zero because $\Delta G(N) = 0$ for $N = 1$. And third term also becomes zero since $f(N,t) = 0$ for $N > N_{\max}$. Hence we can obtain

$$\delta G(t) = \sum_{N=2}^{N_{\max}} f(N,t)\Delta G(N). \tag{23}$$

Eq. (23) is decomposed into

$$\delta G(t) = \sum_{N=2}^{N_{\min}-1} f(N,t)\Delta G(N) + \sum_{N=N_{\min}}^{N_{\max}} f(N,t)\Delta G(N), \tag{24}$$

where $N_{\min}$ is observable minimum of N. As the first term of Eq. (24) can be neglected due to small $\Delta G(N)$, we have approximated formula,

$$\delta G(t) \cong \sum_{N=N_{\min}}^{N_{\max}} f(N,t)\Delta G(N). \tag{25}$$

$N_{\min}$ in this study was $\cong 10$ [rep. unit]. We used Eq. (25) in this paper.

3.2.2. N_{max} is a function of t

Since the $N_{\max}$ will increase with increase of t, $N_{\max}$ is function of t, $N_{\max} = N_{\max}(t)$. We obtained $N_{\max}$ for each t by extrapolating observed $f(N,t)$, as is shown typically in Fig. 4a. We plotted $N_{\max}$ against t for $\Delta T = 10.5$ K in Fig. 4b. Typical error is also shown by an error bar. $N_{\max}$ increased linearly with increase of t. Hence we have an experimental formula,

$$N_{\max}(t) \propto t^{2.3}. \tag{26}$$

3.2.3. Time evolution of $\delta G(t)$

We obtained time evolution of $\delta G(t)$ for the first time as shown in Fig. 4c by using Eq. (25), where we used σ, σ_e and $\Delta\sigma$ of nano-nucleus [1]. $\delta G(0) = 0$ at the starting point of 100% supercooled melt. $\delta G(t)$ increased with increase of t, passed through an activation barrier of a maximum ($\delta G_{\max}$) on $t \cong 60$ min, decreased significantly and finally saturated to a minimum, $\delta G_{\min}(t)$ ($\propto -\nu_0\Delta g$) for $t > 300$ min $\gg$ 60 min which corresponds to 100% solid. Thus it is shown that

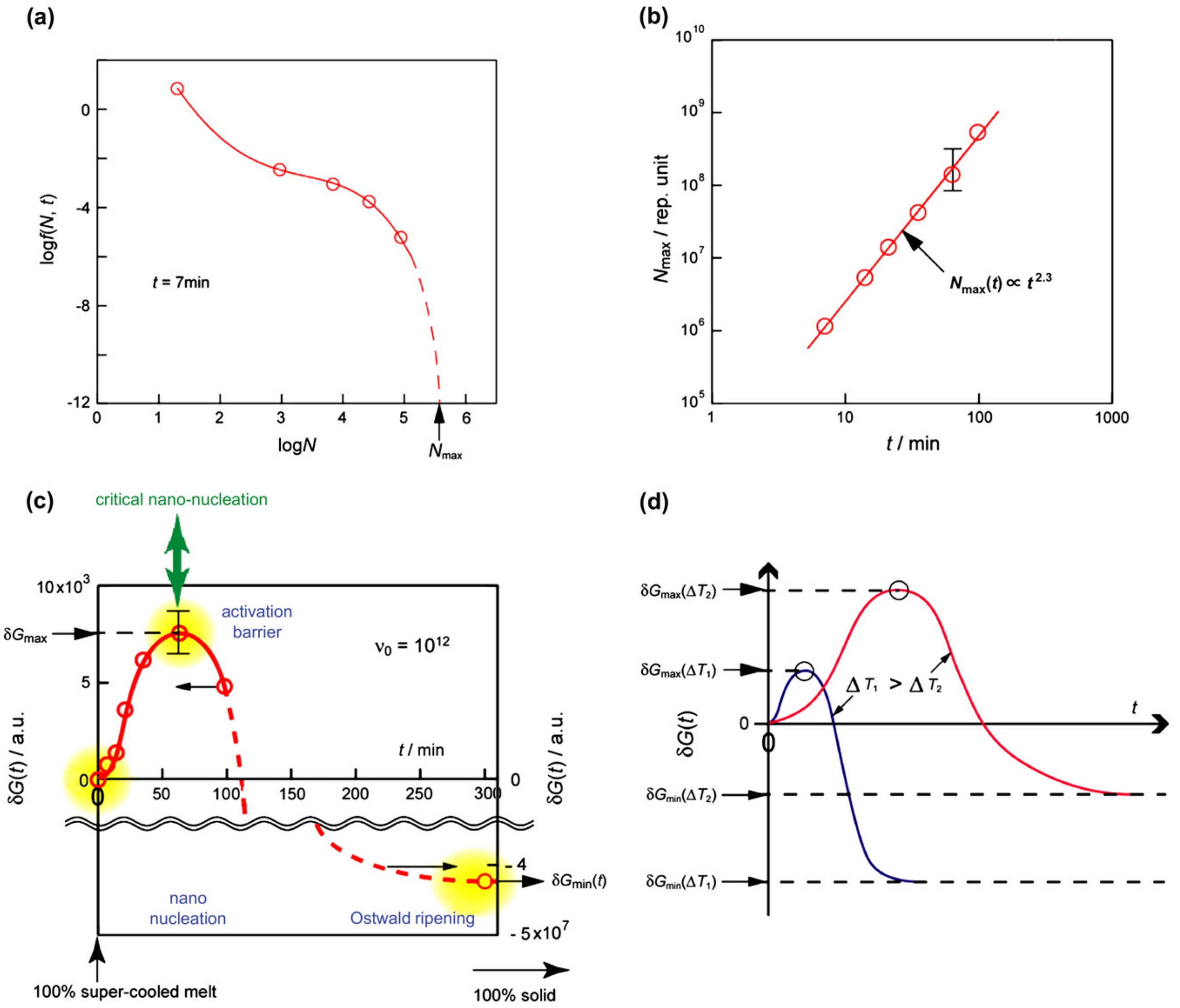

Fig. 4. (a) Typical example of how to obtain $N_{\max}$. Plots of $\log f(N,t)$ against $\log N$ for $t = 7$ min and $T_c = 129.0$ °C or $\Delta T = 10.5$ K. $N_{\max}$s were obtained for each t by extrapolating observed $f(N,t)$. $N_{\max}$ should have ambiguity, since $N_{\max}$ depends on how to obtain asymptotically N. (b) Plots of $N_{\max}$ against t for $T_c = 129.0$ °C and $\Delta T = 10.5$ K. $N_{\max}$ increased linearly with increase of t. Error bar indicates typical error. (c) Plots and illustration of $\delta G(t)$ against t for $T_c = 129.0$ °C and $\Delta T = 10.5$ K. We assumed $\nu_0 = 10^{12}$ [rep. unit] as a huge closed system. $t = 0$ indicates 100% supercooled melt. $\delta G(t)$ increased with increase of t, passed through an activation barrier of a maximum ($\delta G_{\max}$) on $t \cong 60$ min, decreased significantly and finally saturated to minimum ($\delta G_{\min}(t)$) for $t > 3 \times 10^2$ min which corresponds to the most stable state of the 100% solid. It clarified that nano-nucleation is the process where $\delta G(t)$ passes through $\delta G_{\max}$. (d) Schematic illustration of ΔT dependence of $\delta G(t)$ against t. When ΔT is large, $\Delta T = \Delta T_1$, $\delta G_{\max}(\Delta T_1)$ and $\delta G_{\min}(\Delta T_1)$ should be small because of large driving force of crystallization as obtained by Eq. (27). When ΔT is small, $\Delta T = \Delta T_2 < \Delta T_1$, $\delta G_{\max}(\Delta T_2)$ and $\delta G_{\min}(\Delta T_2)$ should be large due to difficulty of nucleation and crystallization. $\delta G_{\max}$ should correspond to critical nano-nucleation, since the critical nano-nucleation is the main controlling process in nucleation as is concluded in Section 3.1.

$$
\begin{aligned}
\delta G(t) &= 0 && \text{for } t = 0 \text{ min (supercooled melt)} \\
&= \delta G_{\max} && \text{for } t \cong 60 \text{ min (activation barrier)} \\
&= \delta G_{\min}(t) \propto -\nu_0 \Delta g && \text{for } t > 300 \text{ min} \gg 60 \text{ min} \\
& && \text{(completion of solidification)},
\end{aligned}
\tag{27}
$$

which is shown in Fig. 2. It clarified and confirmed that nano-nucleation is the process where $\delta G(t)$ passes through $\delta G_{\max}$ and reaches the most stable state of the solid by completion of melt-solid (crystal) phase transition, due to well known "Ostwald ripening". A typical error bar due to error in $N_{\max}$ is also shown in Fig. 4c. Since the critical nano-nucleation is the main controlling process in nucleation as is concluded in Section 3.1, the $\delta G_{\max}$ should correspond to critical nano-nucleation.

Since nano-nucleation depends on ΔT, $\delta G(t)$ should significantly depend on ΔT. Expected ΔT dependence of $\delta G(t)$ is schematically shown in Fig. 4d. $\delta G_{\max}$ should increase with decrease of ΔT, because $\Delta G^*(N^*)$ becomes large with decrease of ΔT. $\delta G_{\min}$ should increase with decrease of ΔT because of decrease of driving force of crystallization as is shown by Eq. (27).

4. New nucleation theory

We will propose a new basic equation in this section by regarding that nucleation is a kind of stochastic process as shown in Section 1.

4.1. Problems in fundamental kinetic equation of CNT

If we regard logically the "whole nucleation process" as the phase transition from the 100% supercooled melt to 100% crystal, i.e., formation of a single crystal or polycrystal, as is illustrated in Fig. 2, it is obvious that $f(N,t)$ should satisfy the following relationship,

$$\begin{aligned}\sum_{N=1}^{N_{\max}} f(N,t) &= f(1,0) = \nu_0 \gg 1 && \text{for } t=0 \text{ (i.e., 100\% melt)} \\ &= f(N_{\max},\infty) = 1 \text{ (or a finite small value)} && \text{for } t=\infty \text{ (i.e., 100\% crystal)}\end{aligned} \qquad (28)$$

As the $f(N,t)$ does not satisfy the requested normalized conditions of Eq. (1) for the distribution function of a stochastic process, the $f(N,t)$ cannot be a distribution function. Since the $f(N,t)$ and $f(N+1,t)$ do not mean any number of particles, the nucleation rate I defined by Eq. (2) cannot mean "net flow" in any stochastic process. This results in the fact that the fundamental kinetic equation of CNT given by Eq. (2) cannot satisfy the mass conservation law. Therefore the fundamental kinetic equation cannot be a basic equation of a stochastic process [8], which is a serious problem of CNT.

4.2. Proposal of a new basic equation of nucleation

Here we will propose a new "basic equation of nucleation" of a stochastic process described by a linear sequential process for simplicity shown in Fig. 5. The size N corresponds to N-th stage in the process. We will introduce a new "mass distribution function $Q(N,t)$" in this study defined by

$$Q(N,t) \equiv Nf(N,t)/\nu_0. \qquad (29)$$

As $\sum_{N=1}^{N_{\max}} Nf(N,t)$ means total number of particles within a closed system, i.e.,

$$\sum_{N=1}^{N_{\max}} Nf(N,t) = \nu_0, \qquad (30)$$

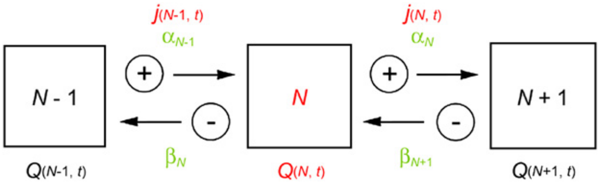

Fig. 5. Illustration of a linear sequential process. The size N corresponds to N-th stage in the stochastic process. ⊕ and ⊖ indicate attachment and detachment of a particle to a nucleus, respectively. α_N and β_{N+1} are forward transition probability from N-th to $N+1$-th stage and backward transition one from $N+1$-th to N-th stage per one particle, respectively.

Physical meaning of the $Q(N,t)$ is the "normalized total number of particle" included in nuclei of size N within a huge closed system. ⊕ or ⊖ in Fig. 5 indicate attachment or detachment of a particle to or from a nucleus, respectively. From the definition of Eq. (29), it is obvious that

$$\sum_{N=1}^{N_{\max}} Q(N,t) = 1 \quad \text{for all } t, \qquad (31)$$

as is illustrated in Fig. 2. Therefore $Q(N,t)$ can be a normalized conserved quantity, i.e., it can be a "distribution function" in the present stochastic process (Fig. 5). Normalized net flow $\boldsymbol{j}(N,t)$ with respect to $Q(N,t)$ from the N-th to $N+1$-th stage is given by

$$\boldsymbol{j}(N,t) \equiv \alpha_N Q(N,t) - \beta_{N+1} Q(N+1,t), \qquad (32)$$

where α_N and β_{N+1} are forward transition probability from N-th to $N+1$-th stage and backward transitions one from $N+1$-th to N-th stage per one particle, respectively (Fig. 5). As $Q(N,t)$ means normalized number of particles, we can propose a new basic equation of nucleation by a mass conservation law of $Q(N,t)$, i.e.,

$$\partial Q(N,t)/\partial t \equiv -\partial \boldsymbol{j}(N,t)/\partial N. \qquad (33)$$

If we assume after well known theory of diffusion that

$$\boldsymbol{j}(N,t) \equiv -\Gamma\, \partial Q(N,t)/\partial N, \qquad (34)$$

where Γ is a constant, we have

$$\partial Q(N,t)/\partial t - \Gamma \partial^2 Q(N,t)/\partial N^2 = 0. \qquad (35)$$

This is similar to well known "basic equation of diffusion process". It is interesting future problem to predict and explain the nucleation behavior applying the proposed new nucleation theory.

4.3. Direct observation of Q(N,t)

We plotted in Fig. 6a observed $\log Q(N,t)$ against $\log N$ as a parameter of t which is obtained for the first time. $f(N,t)$s obtained in our previous paper [1] were also plotted for comparison in Fig. 6a. Fig. 6b plotted $Q(N,t)$ in linear scale against N as a parameter of t.

With increase of N, $Q(N,t)$ decreased at first for $N \le N^*$, showed a minimum at $N \cong N^*$ and then increased. After that it passed a maximum at a $N > N^*$, then decreased and became zero at $N = N_{\max}(t)$. It is natural that $N_{\max}(t)$ increases with increase of t. The $Q(N,t)$ at a N increased with increase of t and attained a steady state (denoted as $Q_{\mathrm{st}}(N)$) for $t \ge 10^2$ min.

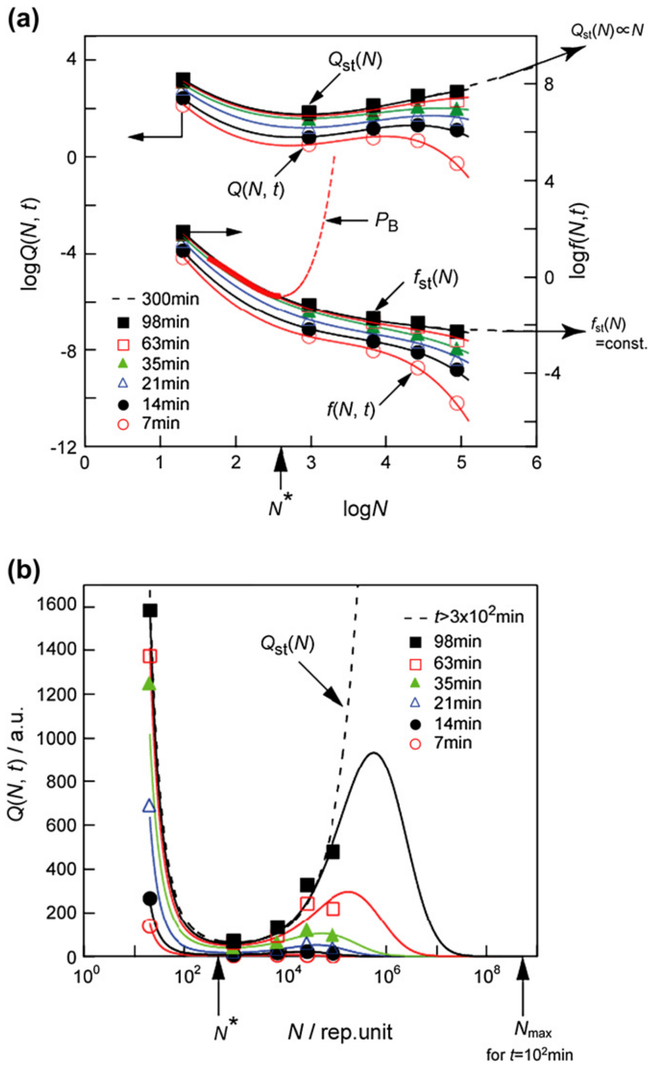

Fig. 6. (a) Plots of $\log Q(N,t)$ against $\log N$ as a parameter of t for $T_c = 129.0\,^\circ\mathrm{C}$ and $\Delta T = 10.5$ K. Log $Q(N,t)$ is shown on left axis. Log $f(N,t)$ obtained in our previous paper [1] against $\log N$ is shown on right axis. P_B is Boltzmann distribution. $Q(N,t)$ showed a minimum at $N \cong N^*$ and increased with increase of N for each t. $Q(N,t)$ reached steady state at $t \cong 10^2$ min. (b) Plots of $Q(N,t)$ against N as a parameter of t for $T_c = 129.0\,^\circ\mathrm{C}$ and $\Delta T = 10.5$ K. We plotted $Q(N,t)$ which has the range of $N \le N_{\max}$. Typical $N_{\max}$ at $t \cong 10^2$ min is shown. $Q_{st}(N)$ is a steady state of $Q(N,t)$ for $t \ge 10^2$ min. It is easily expected that the $Q_{st}(N)$ rapidly increases for $N > 10^4$ [rep. unit] and $t > 3 \times 10^2$ min, as shown by a broken curve.

The maximum $Q(N,t)$ was seen at $N \cong 10^6$ [rep. unit] for $t \cong 10^2$ min. It is easily expected that the $Q_{st}(N)$ rapidly increases for $N > 10^4$ [rep. unit] and $t \ge 3 \times 10^2$ min, as shown by a broken curve in Fig. 6b. It is interesting that the "U-shape" broken curve of $Q(N,t)$ is essentially similar pattern as predicted by Boltzmann distribution, as shown in Fig. 6a, although the increasing rate of the $Q(N,t)$ with increase of N is very much smaller than expected from Boltzmann distribution.

It is predicted from Eq. (29) that

$$Q_{st}(N) \propto N \quad \text{for large } t \text{ and } N. \tag{36}$$

This is experimentally confirmed in Fig. 6a by the fact that

$$Q_{st}(N) \propto N \quad \text{for large } t > 3 \times 10^2 \text{ min}, \; N \gg N^*. \tag{37}$$

The above novel results made clear the real image of nucleation for the first time as summarized below:

(1) When we focus on the time and N evolution of the observed $Q(N,t)$ in Fig. 6, it is confirmed that a lot of nano-nuclei generate and disappear frequently for $N < N^*$ and that the increase of mass of larger nuclei ($N > N^*$) will accelerate significantly with increase of time and N. This interesting new experimental fact of acceleration of nucleation gives us a natural real image of nucleation for the first time as an important "co-operative nature" of the phase transition from the supercooled melt into crystals, as has been theoretically long expected.
(2) When we focus on time and N evolution of the observed $f(N,t)$, it is also confirmed that a lot of nano-nuclei generate and disappear frequently for $N < N^*$. It shows that only a very little part of them can survive into larger nuclei and macro-crystals. After growing into larger nuclei and macro-crystals, they will not disappear, as everybody has imagined.

Physical meaning and reason of the above characteristic behaviors of $Q(N,t)$ are interesting open questions.

We obtained time evolution of $Q(N,t)$ as a parameter of N_k in Fig. 7, where k indicates different size of N. Only N_5 shows right axis and the others show left axis. $Q(N,t)$ increased significantly with increase of t with respect to smaller N. $Q(N,t)$ of $N_4 = 9.4 \times 10^2$ [rep. unit] $\cong N^*$ which is near to minimum increased slowly and its quantity of saturation was small. $Q(N,t)$ of $N_1 = 8.8 \times 10^4$ [rep. unit] had late onset time and increased slowly. The quantity of saturation of N_1 was larger than that of N_2, N_3 and N_4, which corresponds to Fig. 6a and b.

Thus we can illustrate a new elementary process of nucleation in Fig. 8a. It shows that increase of net flow $j(N,t)$ for $N \gg N^*$ comes from growth of smaller nuclei by adding particles from the melt by showing ⊕ in Fig. 8a. The nuclei grow

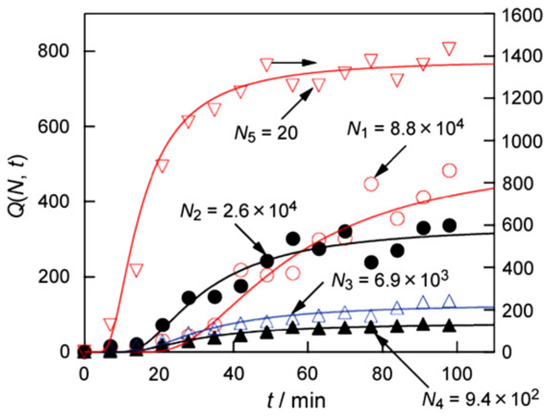

Fig. 7. Plots of $Q(N,t)$ against t as a parameter of N for $T_c = 129.0\,^\circ\mathrm{C}$ and $\Delta T = 10.5$ K. N_1 to N_5 correspond to five plots of Fig. 6a. $Q(N,t)$s for N_1, N_2, N_3 and N_4 correspond to left axis and that for N_5 does to right axis. $Q(N,t)$ of N_5 increased significantly with increase of t. $Q(N,t)$ of N_4 which is near minimum of $Q(N,t)$ increased slowly and its quantity of saturation was small. $Q(N,t)$ of N_1 showed late onset time and increased slowly.

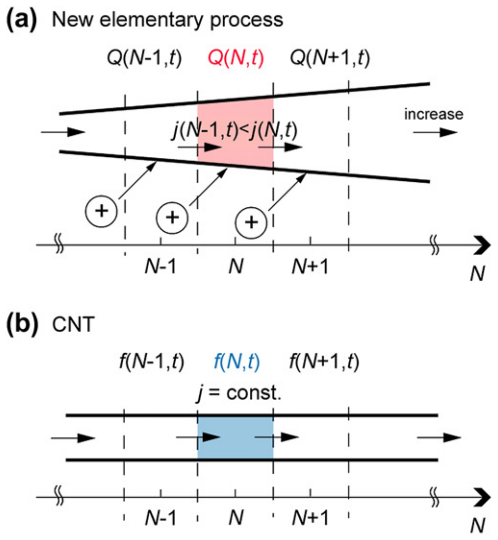

Fig. 8. Illustration of elementary process and net flow $\boldsymbol{j}(N,t)$ of nucleation in the steady state for $N \gg N^*$. (a) New elementary process. Direct observation of $Q(N,t)$ clarified that $\boldsymbol{j}(N,t)$ for $N \gg N^*$ increases with increase of N. ⊕ indicates absorbed particles from the melt. (b) The $\boldsymbol{j}(N,t)$ of CNT. CNT assumed that $\boldsymbol{j}(N,t)$ does not depend on N, i.e., it is constant for N.

up to much larger one by absorbing particles which comes not only from the melt but also from disappeared nucleus indirectly via melt. This corresponds to the "Ostwald ripening". Fig. 8a shows that $\boldsymbol{j}(N,t)$ for $N \gg N^*$ increases with increase of N in the steady state. On the other hand, CNT assumed that the $\boldsymbol{j}(\mathrm{N},t)$ in the steady state does not depend on N, i.e., it is constant for N, which is illustrated in Fig. 8b.

4.4. Overall crystallization $\chi_c(t)$ obtained from $Q(N,t)$

$Q(N,t)$ is useful to obtain time evolution of "overall crystallinity ($\chi_c(t)$)". It is reasonable to define it by

$$\chi_c(t) \equiv \frac{\int_{N'_{\min}}^{N_{\max}(t)} Q(N,t)\mathrm{d}N}{\int_{N'_{\min}}^{N_{\max}(\infty)} Q_{\mathrm{st}}(N)\mathrm{d}N} \propto \int_{N'_{\min}}^{N_{\max}(t)} Q(N,t)\mathrm{d}N, \tag{38}$$

where $N_{\max}(\infty)$ is the final size of nucleus or crystal after completion of solidification and $N'_{\min}$ is the lower limit of "crystal size" of N. As smaller nano-nucleus than critical nucleus ($N < N^*$) (so called "embryo" in CNT) generates and disappears too frequently, the embryo should be omitted from evaluating the $\chi_c(t)$. Therefore we will evaluate $\chi_c(t)$ for $N \geq N^*$, i.e.,

$$\chi_c(t) \equiv \frac{\int_{N^*}^{N_{\max}(t)} Q(N,t)\mathrm{d}N}{\int_{N^*}^{N_{\max}(\infty)} Q_{\mathrm{st}}(N)\mathrm{d}N} \propto \int_{N^*}^{N_{\max}(t)} Q(N,t)\mathrm{d}N. \tag{39}$$

In Fig. 9a, the range N of the integral is colored pink. Fig. 9b shows the $\chi_c(t)$ against t obtained for $T_c = 129.0\ ^\circ\mathrm{C}$ and

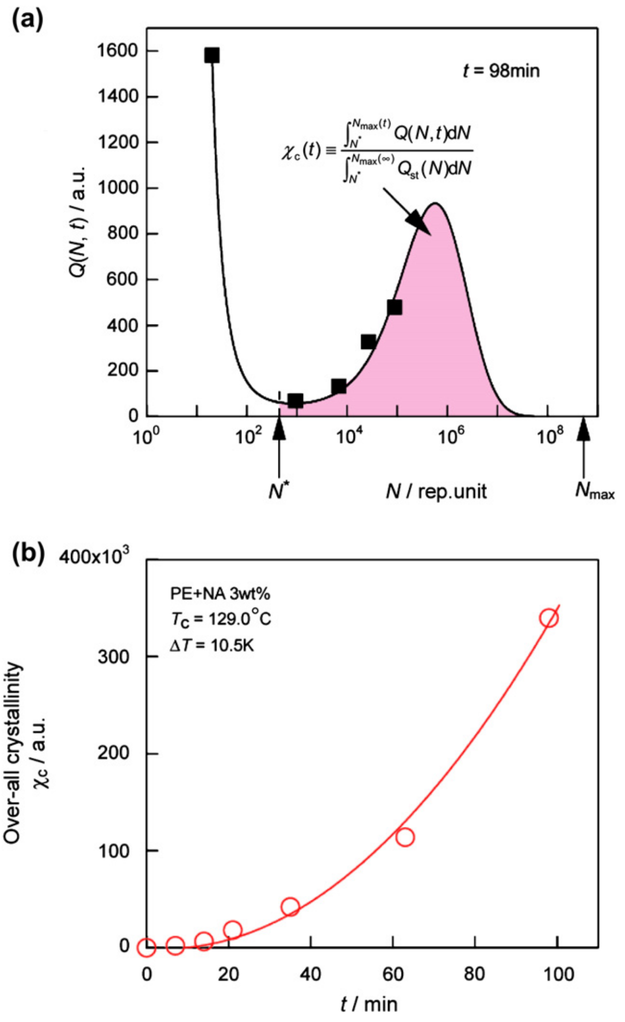

Fig. 9. (a) Plot of $Q(N,t)$ against N for $t = 98$ min and $T_c = 129.0\ ^\circ\mathrm{C}$ or $\Delta T = 10.5$ K. Overall crystallinity (χ_c) is obtained by integrating the pink colored range [For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.] of N in Eq. (39). (b) Plots of $\chi_c(t)$ against t for $T_c = 129.0\ ^\circ\mathrm{C}$ and $\Delta T = 10.5$ K. $\chi_c(t)$ started increasing after rather short time (only several min.) and increased slowly at first and then fast with increase of t. It is noted that the steady nucleation was observed for $t \geq 10^2$ min and any "depletion" of the melt was not observed in this study, as shown in Fig. 7.

$\Delta T = 10.5$ K by using Eq. (39). $\chi_c(t)$ started increasing after rather short time (only several minutes) and increased slowly at first and then fast with increase of t. It is noted that the steady nucleation was observed for $t \geq 10^2$ min and any "depletion" of the melt was not observed in this study, as shown in Fig. 7. Therefore it is concluded that the observed $\chi_c(t)$ in this work should be significantly small, that means

$$\chi_c(t) \ll 1. \tag{40}$$

It is expected logically that $\chi_c(t)$ should finally saturate to unity that corresponds to completion of the melt-solid phase transition from the supercooled melt into (assumed) single crystal. This result of $\chi_c(t)$ can be used as a test of nucleation theory, which is one of the future interesting problem.

5. Conclusion

(1) We obtained the degree of supercooling (ΔT) dependence of size distribution $f(N,t)$ directly by means of small angle X-ray scattering (SAXS). $f(N,t)$ increased rapidly with increase of t at large ΔT, while $f(N,t)$ did slowly at small ΔT. We also obtained ΔT dependence of "onset time $\tau(\Delta T)$" which is defined as extrapolated time of the linearly increasing $f(N,t)$ with t. Experimental formula was described by $\tau^{-1}(\Delta T) \propto \exp[-\gamma/\Delta T]$, where γ is a constant, which means that when ΔT approaches 0, nucleation becomes impossible. Therefore it is concluded that the "induction period" of crystallization is not controlled by so called "spinodal decomposition" process but by nucleation one.

(2) We obtained ΔT dependence of nucleation rate (I) of macroscopic crystal (we call "macro-crystal") whose size is more than 1 μm by means of optical microscope (OM). Experimental formula was described by $I(\Delta T) \propto \exp[-C'/\Delta T]$, where C' is a constant. τ^{-1} and I by using the newly obtained ΔT dependence of $f(N,\mathrm{t})$ were proportional to net flow of nucleation ($\boldsymbol{j}$), i.e., $\tau^{-1} \propto I \propto \boldsymbol{j}$, as the zero-th approximation. It clarified that the critical nano-nucleation mainly controls not only nano-nucleation but also macro-crystallization experimentally, i.e., it is concluded that the nano-nucleation directly corresponds to macro-crystallization. This showed that alternative nucleation study can be applicable as the zero-th approximation for practical routine work.

(3) Time evolution of total free energy of nucleation of a huge closed system $\delta G(t)$ was obtained experimentally for the first time. $\delta G(t)$ is given by $\delta G(t) = \sum_{N=2}^{N_{\max}} f(N,t)\Delta G(N)$, where $N_{\max}$ is maximum of N and $\Delta G(N)$ is free energy of nucleation for a nucleus of size N. $\delta G(t)$ increased with increase of t, passed through an activation barrier of a maximum ($\delta G_{\max}$), decreased significantly and finally saturated to a minimum, $\delta G_{\min}(t) \propto -\nu_0 \Delta g$ which corresponds to the most stable state of the solid by completion of melt-solid (crystal) phase transition, due to well known "Ostwald ripening".

(4) Although it has been long believed in CNT that a "fundamental kinetic equation" given by $\partial f(N,t)/\partial t \equiv I(N-1,t) - I(N,t)$ can describe the nucleation process correctly, we found it is not correct. We found that the $f(N,t)$ and the fundamental kinetic equation in CNT do not satisfy the normalized condition and the mass conservation law, respectively. Hence the $f(N,t)$ cannot be a correct distribution function and the kinetic equation cannot be a correct basic equation in so called "stochastic process". We proposed a new nucleation theory in this study. We introduced a mass distribution function $Q(N,t)$ defined by $Q(N,t) \equiv Nf(N,t)/\nu_0$, where ν_0 is total number of particle of a closed system. Here $Q(N,t)$ satisfies the normalized condition. We proposed a new basic equation, $\partial Q(N,t)/\partial t \equiv -\partial \boldsymbol{j}(N,t)/\partial N$ which satisfies the mass conservation law. With increase of N, observed $Q(N,t)$ decreased at first for $N \le N^*$, showed a minimum at $N \cong N^*$ and then increased. After that it passed a maximum at a $N > N^*$, then decreased and became zero at $N = N_{\max}(t)$. This confirms that a lot of nano-nuclei generate and disappear frequently for $N < N^*$ and that the increase of mass of larger nuclei ($N > N^*$) will accelerate significantly with increase of time and N. Nuclei grow up to much larger one by absorbing particles which comes not only from the melt but also from disappeared nucleus indirectly via melt. This corresponds to the "Ostwald ripening". We obtained overall crystallinity ($\chi_c(t)$) experimentally which is defined by $\chi_c(t) \equiv \int_{N^*}^{N_{\max}(t)} Q(N,t)\mathrm{d}N / \int_{N^*}^{N_{\max}(\infty)} Q_{\mathrm{st}}(N)\mathrm{d}N$. $\chi_c(t)$ started increasing after rather short time (only several minutes) and increased slowly at first and then fast with increase of t. Therefore it is concluded that the observed $\chi_c(t)$ in this work should be significantly small, that means $\chi_c(t) \ll 1$. It is expected logically that $\chi_c(t)$ should finally saturate to unity that corresponds to completion of the melt-solid phase transition from the supercooled melt into (assumed) single crystal.

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