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Entropy-Undercooling Regime Criterion for Metastable Phase Formation in Oxide Material

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Abstract

Undercooling a melt often facilitates a metastable phase to preferentially nucleate. In the present study, the formation of a metastable phase from undercooled melts was investigated from the point of the competitive nucleation criterion. The classical nucleation theory shows that the most critical factor for forming a critical nucleus is the interface free energy γ . In fact, on the simple liquid such as the melt of a mono-atomic metal, Spaepen's negentropic model regarding γ suggested the scaling factor α between γ and the entropy of fusion to be the decisive factor for forming the critical nucleus. However, recent numerical simulations such as the molecular dynamics or density functional theory show ambiguous relations between α and the crystal structures. Furthermore, in compound materials such as oxides, in which polyhedrons of oxygen are the structural units both in the solid and liquid phases, it is suggested that the decisive factor for forming the critical nucleus isn't α but the entropy of fusion. According to this idea, we proposed the entropy-undercooling regime criterion for metastable phase formation and, using REFeO₃ (RE: Rare-earth element) as the model material, experimentally verified the validity of the criterion.

1. Introduction

A metastable phase is a phase that does not exist in thermal equilibrium state and, although thermodynamically unstable, can temporarily exist when some conditions are fulfilled. Research into the metastable phase began with Ostwald's prediction that a phase formed first from supersaturated liquid is not always thermodynamically stable but is close to liquid in energy¹. This prediction is called "step rule". Later on, Stranski and Totomanov² suggested that the step rule is a consequence of preferential formation of a critical nucleus of the metastable phase. That is, the activation energy required to form a critical nucleus, ΔG_n^* , controls the nature of the process. Regarding this point, the classical nucleation theory³ states that ΔG_n^* can be understood in terms of the interfacial free energy γ between the liquid and solid phases. Turnbull⁴ and Spaepen⁵, assuming that γ of a simple material such as metal is related not to the enthalpy change but to the entropy change at the solid-liquid interface, formulated γ as

$$\gamma = \alpha \frac{\Delta S_f T}{(N_A V_m^2)^{\frac{1}{3}}} \quad (1)$$

where ΔS_f , T , N_A and V_m are the heat of fusion, the temperature of material, Avogadro number and the molar volume, respectively. Furthermore, Spaepen and Meyer⁶ derived α , dimensionless solid-liquid interfacial energy, as 0.86 for fcc or hcp crystals and 0.71 for bcc structures, respectively. The

α -factors, which strongly depend on the structure of both solid and liquid phase, are to be a critical parameter to determine ΔG_n^* . However, the recent numerical calculations of α by means of the molecular dynamics or density functional theory show less dependence on the structure, being scattered around 0.5, irrespective of the structure⁷. Authors, on the basis of this fact, proposed that in ionic crystals such as oxides, where the polyhedrons of anions are the structural units both in the solid and liquid phases, ΔS_f itself, rather than α , can be expected to become dominant in the determination of γ ^{8,9}. In accordance with this idea, using REFeO₃ as the model material, where RE means rare-earth elements, the entropy-undercooling regime criterion for phase selection between stable and metastable phases was proposed from the standpoint of the nucleation-controlled growth kinetics.

2. Entropy-undercooling regime criterion for phase selection

Before taking up the main subject of this chapter, we mention again the hypothesis that, in ionic crystals, ΔS_f is to be a dominant factor in the determination of γ .

Spaepen¹⁰ and Granasy¹¹, almost at the same time, developed rather similar models that γ at equilibrium state is given by

$$\gamma = \int_V (H(r) - TS(r)) dr \quad (2)$$

where $H(r)$ and $S(r)$ are cross-interfacial entalpy and entropy.

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This model can qualitatively infer the temperature dependence of the solid-liquid interface. However, we need analytical or numerical forms of $H(r)$ and $S(r)$ in order to evaluate the interface thickness that is the key parameter of the model.

On the other hand, in a material having faceted interface, the order parameter representing the regularity of the atomic arrangement rapidly changes as the interface is crossed. In this case, as shown in **Fig. 1(b)**, $H(r)$ can be approximated by the near-step function. Consequently, the interfacial energy is approximated with a triangle if we assume $S(r)$ as a linear function of r at the cross-interface region. This result means that α is a dimensionless interface thickness rather than a dimensionless interfacial energy. The recent numerical calculation of α suggests

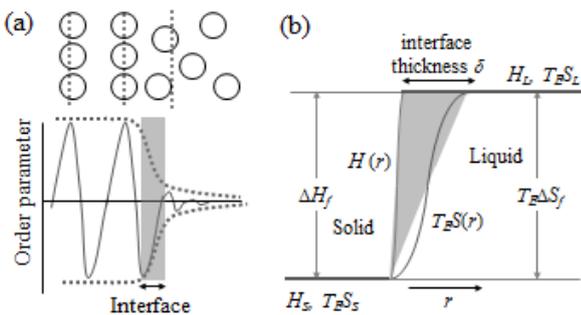


Fig. 1 Schematic representation of the faceted interface between solid and liquid. (a) Change of the atomic order and of the order parameter in solid and liquid. (b) Schematic representation of the change in the enthalpy $H(r)$ and the product $T_E S(r)$ of melting temperature and entropy at the solid-liquid interface. The colored area corresponds to the approximate value of the interfacial energy, showing that α is not a dimensionless interfacial energy but a dimensionless interface thickness.

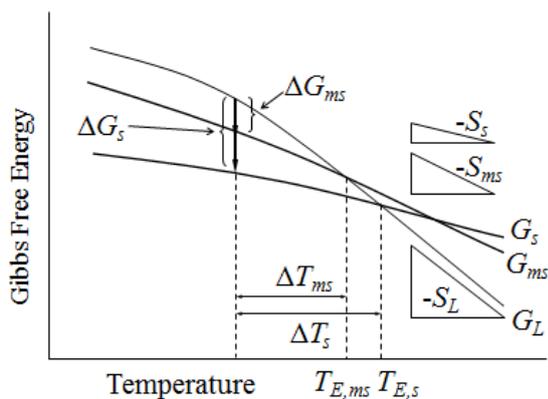


Fig. 2 Conceptual image of temperature dependency of free energy in liquid and solid phases (stable and metastable phases). The entropies of three phase are related $S_L > S_{ms} > S_s$. Therefore, as for entropy of fusion ΔS_f caused by solidification, the relation $\Delta S_{f,s} > \Delta S_{f,ms}$ becomes valid.

the interface thickness is approximately half of the atomic layer spacing.

Figure 2 is a conceptual image showing the thermodynamic relation considering the step rule. The figure depicts temperature and free energy of both liquid and solid phases (stable and metastable phases). The reason why liquid phase changes to solid phase is that the free energy of the liquid phase becomes larger than that of solid phase. The energy-balance point of both phases is the melting point. Comparing the metastable phase to the stable solid phase in terms of free energy, the free energy of the metastable phase (G_{ms}) is larger than that of stable phase (G_s) (the subscripts s and ms mean stable phase and metastable phase, respectively). Therefore, the melting point of the metastable phase ($T_{E,ms}$) becomes lower than that of stable phase ($T_{E,s}$). Meanwhile, the absolute value of the gradient of each curve (temperature coefficient of Gibbs free energy) in **Fig. 2** corresponds to the entropy when pressure is constant. From the figure, we can see the relation $S_L > S_{ms} > S_s$ between entropies of liquid phase S_L , stable phase S_s and metastable phase S_{ms} . Therefore, for the change of entropy (ΔS_f) caused by melting, we can find a relation $\Delta S_{f,s} > \Delta S_{f,ms}$ (i.e., the change of the entropy is smaller when the liquid phase changes to metastable phase). From the relative relations of the three phases above, we can see that the metastable phase is to be a higher entropy phase than the stable phase.

Factors determining the entropy of material are first, density of material and secondly, symmetry of arrangement of atoms and/or molecules making up the material. Therefore, high entropy phase is liquid rather than solid, and gas rather than liquid. Among solid phases, it is guessed that the low-density phase becomes higher-entropy phase. In conclusion, we can say that the metastable phase is lower density, higher symmetric material than the stable state.

The classical nucleation theory leads us to ΔG_n^* given by

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

where $f(\theta)$ is the contact angle function showing the catalytic potency for heterogeneous nucleation, and ΔG is the difference in G between the liquid and solid phases. Here if we use the simplest approximation of ΔG , such as $\Delta G = \Delta S_f \Delta T$, and Eq. (1), Eq. (3) is rewritten as:

$$\Delta G_n^* = \frac{16\pi\alpha^3 \Delta S_f T^3}{3N_A V_m^2 \Delta T^2} \quad (4)$$

where ΔT is undercooling given by $T_E - T$. If we assume that α , $f(\theta)$, and V_m are equivalent in stable and metastable phases, the criterion for the metastable phase to preferentially nucleate, $\Delta G_{n,ms}^* \leq \Delta G_{n,s}^*$, is expressed by:

$$\frac{\Delta S_{f,ms}}{\Delta S_{f,s}} \leq \frac{\Delta T_{ms}^2}{\Delta T_s^2} \quad (5)$$

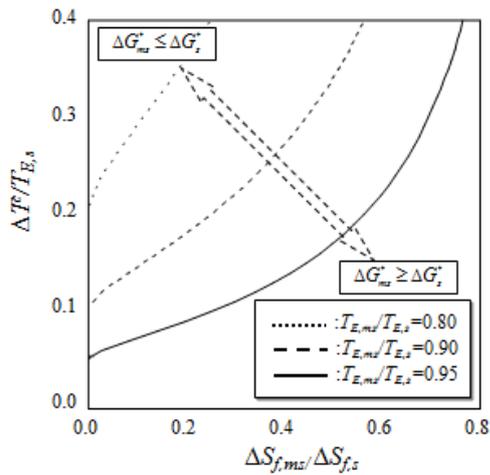


Fig. 3 Relationship between critical undercooling ΔT^c , and entropy of fusion of metastable phase $\Delta S_{f,ms}$, above which activation energy required for formation of critical nucleus of metastable phase exceeds that of stable phase.

Figure 3 shows the critical undercooling ΔT^c , at which $\Delta G_{n,ms}^* \approx \Delta G_{n,s}^*$, as a function of $\Delta S_{f,ms}$. In this figure, three cases are shown: each is the ratios between $T_{E,ms}$ and $T_{E,s}$ are 0.95, 0.90 and 0.80, respectively. As shown in this figure, the metastable phase nucleates dominantly on the upper and left-hand sides of the curves, where $\Delta G_{n,ms}^* < \Delta G_{n,s}^*$, while the stable phase is dominant on the lower and right-hand sides of the curves, where $\Delta G_{n,ms}^* > \Delta G_{n,s}^*$. It is clear that the smaller entropy of fusion facilitates the metastable phase to nucleate more preferentially.

3. Formation of metastable phase in oxide material by containerless process

Figure 4 shows SEM micrographs of samples of REFeO_3 solidified in containerless conditions. Stable phase of REFeO_3 is a dense, robust oxide called perovskite (ABO_3). As shown in the photographs, their surface profiles vary according to the type of rare-earth elements. The surface of LaFeO_3 is smooth and spherical while that of LuFeO_3 is rugged and polyhedral¹²⁾. Note that the different surface features result from differences in crystal structure, not differences in rare-earth element. Specifically, LaFeO_3 is a cubic-symmetric (though considerably distorted) perovskite while LuFeO_3 is a hexagonal symmetric structure similar to hexagonal paving tiles (although a little rugged). As the hexagonal phase has a 10%~20% smaller density than that of perovskite¹³⁾, it is estimated that the hexagonal crystal is a higher entropy phase than perovskite. In other words, the hexagonal crystal should have intrinsically become stable perovskite. However, having been largely undercooled to below $T_{E,ms}$ indicated in **Fig. 2** by the

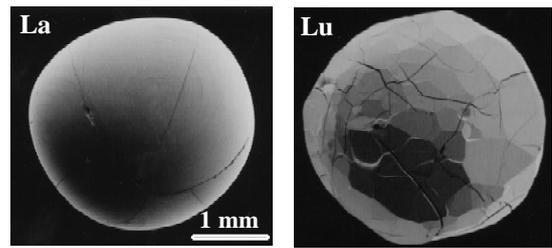


Fig. 4 Surface profiles of REFeO_3 (RE=La, Lu) formed by containerless process. LaFeO_3 with large ionic radius has a smooth and spherical surface while LuFeO_3 with small radius has a rugged and polyhedral surface.

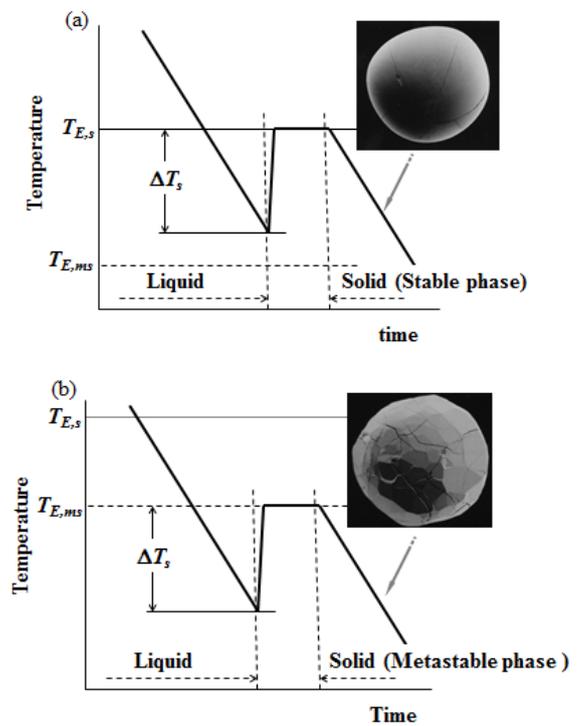


Fig. 5 Relation between temperature/time curve and solidified phase while being undercooled by containerless process. (a) Perovskite is formed when undercooled to $T_{E,s}$ to $T_{E,ms}$. (b) Meanwhile, metastable phase of hexagonal crystal is formed when supercooled largely to below $T_{E,ms}$.

containerless process, hexagonal crystals of high-entropy phase grew as metastable phase (**Fig. 5**). In fact, when we forced it to solidify at a temperature of around $T_{E,s}$ even by the same containerless process, stable-phase perovskite appears.

Perovskite ABO_3 becomes unstable as the radius of A ion decreases. In case of RE^{3+} , its radius is largest for La and smallest for Lu. This means that in REFeO_3 the perovskite structure becomes unstable as it moves to the right of the periodic table, although the equilibrium phases are perovskite for all RE^{3+} ¹⁴⁾. For REMnO_3 , however, the situation is quite

different although the ionic radius of Mn^{3+} is similar to that of Fe^{3+} . In $REMnO_3$, all elements from La to Dy in the periodic table form perovskite structure¹⁵⁾. Meanwhile elements from Ho, with a smaller ionic radius, form hexagonal structures in the same way as the metastable phase of $LuFeO_3$. The hexagonal $REMnO_3$ has multiferroic properties of (anti) ferromagnetism and ferroelectricity caused by breakage of space-inversion symmetry. Thus, the crystal is greatly anticipated as a new concept in memory media. The problem with the material is, however, that the transition temperature between (anti) ferromagnetism and paramagnetism is extremely low at approximately 100 K, because the spin structure is frustrated by the triangular array of magnetic ions. The transition temperature must be raised for the practical use of the material. The best way to raise the temperature is to clear the frustration. If this method is too difficult, a second solution is to use magnetic ions with a larger magnetic moment. One candidate is Fe (i.e., $REFeO_3$) but it has not been obtained in bulk sample in the past. This becomes possible for the first time with the containerless process. It is attracting a lot of attention now, and its future development and applications are anticipated.

4. Use of microgravity environment

Let me focus on the use of the space environment, particularly the microgravity environment. The significance of this environment in material-processing fields such as crystal growth and solidification can be expressed in two key phrases: "convection-free" and "containerless." Convection-free means literally no occurrence of convection induced by density differences because no gravity exists. A number of experiments including growth of defect-free crystals have been planned and conducted.

On the other hand, regarding containerless experiments, even plans are limited so far. Containerless here means that no container to retain liquid is required in a microgravity environment. When a container (crucible) is not required, the inclusion of impurities from the crucible wall, which is unfortunately inevitable for crystal growth of semiconductors such as silicon, could be avoided. In addition, a variety of uses could be provided, for example, the processing of chemically active materials and high melting-point materials (e.g. over 2,000 deg. C).

5. Concluding remarks

As discussed above, since the containerless process makes it possible to perform nonequilibrium process of solidification from undercooled liquids, it could pave the way for the creation of many new materials including not only the oxide mentioned above but also semiconductors and functional metals. At present, however, actual results are largely dependent on serendipity. The guiding principle, or the systematic approach, is still insufficient. The main reason is the experimental environment, since containerless experiments are difficult to perform on the earth. We strongly hope for more opportunities to use microgravity environments including the International Space Station.

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