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Principles of solidification

In earlier studies, we learned how materials are classified based on their atomic, ionic, or molecular order. During the solidification of materials that crystallize, the atomic arrangement changes from a short-range order (SRO) to a long-range order (LRO). The solidification of crystalline materials requires two steps. In the first step, ultra-fine crystallites, known as the nuclei of a solid phase, form from the liquid. In the second step, which can overlap with the first, the ultra-fine solid crystallites begin to grow as atoms from the liquid are attached to the nuclei until no liquid remains. Some materials, such as inorganic silicate glasses, will become solid without developing a long-range order (i.e., they remain amorphous).

Many polymeric materials may develop partial crystallinity during solidification or processing. The solidification of metallic, polymeric, and ceramic materials is an important process to study because of its effect on the properties of the materials involved.

Industry also uses the solidification process as a **primary processing** step to produce metallic slabs or ingots (a simple, and often large casting that later is processed into useful shapes). The ingots or slabs are then hot and cold worked through **secondary processing** steps into more useful shapes (i.e., sheets, wires, rods, plates, etc.). Solidification also is applied when joining metallic materials using techniques such as welding, brazing, and soldering.

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College of science   *2018 - 2019*   *Dr. Mohammed Ghazi*
Dept. Of physic   *MATERIALS SCIENCE*   *Chapter (5)*

5-1- Nucleation

In the context of solidification, the term **nucleation** refers to the formation of the first nanocrystallites from molten material. For example, as water begins to freeze, nanocrystals, known as **nuclei**, form first. In a broader sense, the term nucleation refers to the initial stage of formation of one phase from another phase. When a vapor condenses into liquid, the nanoscale sized drops of liquid that appear when the condensation begins are referred to as nuclei. Later, we will also see that there are many systems in which the nuclei of a solid (β) will form from a second solid material (α) (i.e., β- to α-phase transformation). What is interesting about these transformations is that, in most engineered materials, many of them occur while the material is in the solid state (i.e., there is no melting involved). Therefore, although we discuss nucleation from a solidification perspective, it is important to note that the phenomenon of nucleation is general and is associated with phase transformations.

There are two types of nucleation: ***homogeneous*** and ***heterogeneous***. The distinction between them is made according to the site at which nucleating events occur. For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, whereas for the heterogeneous type, nuclei form preferentially at structural in homogeneities, such as container surfaces, insoluble impurities, grain boundaries, dislocations, and so on. We begin by discussing homogeneous nucleation because its description and theory are simpler to treat. These principles are then extended to a discussion of the heterogeneous type.

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College of science   **2018 - 2019** **Dr. Mohammed Ghazi**
Dept. Of physic   **MATERIALS SCIENCE** *Chapter (5)*

-   *Homogeneous Nucleation*

A discussion of the theory of nucleation involves a thermodynamic parameter called **free energy** (or *Gibbs free energy*), *G*. In brief, free energy is a function of other thermodynamic parameters, of which one is the internal energy of the system (i.e., the *enthalpy, H*), and another is a measurement of the randomness or disorder of the atoms or molecules (i.e., the *entropy, S*). It is not our purpose here to provide a detailed discussion of the principles of thermodynamics as they apply to materials systems. However, relative to phase transformations, an important thermodynamic parameter is the change in free energy(ΔG_v), a transformation will occur spontaneously only when (ΔG) has a negative value.

For the sake of simplicity, let us first consider the solidification of a pure material, assuming that nuclei of the solid phase form in the interior of the liquid as atoms cluster together so as to form a packing arrangement similar to that found in the solid phase. Furthermore, it will be assumed that each nucleus is spherical in geometry and has a radius *r*. This situation is represented schematically in Figure (1). There are two contributions to the total free energy change that accompany a solidification transformation. The first is the free energy difference between the solid and liquid phases, or the volume free energy(ΔG_v). Its value will be negative if the temperature is below the equilibrium solidification temperature, and the magnitude of its contribution is the product of (ΔG_v) and the volume of the spherical nucleus (i.e. $\frac{4}{3}\pi r^3$).

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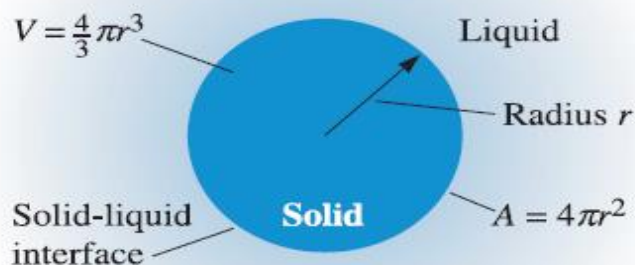
Figure (1) Schematic diagram showing the nucleation of a sphere-ical solid particle in a liquid.

The second energy contribution results from the formation of the solid–liquid phase boundary during the solidification transformation. Associated with this boundary is a surface free energy, γ, which is positive; furthermore, the magnitude of this contribution is the product of γ and the surface area of the nucleus (i.e., $4\pi r^2$). Finally, the total free energy change is equal to the sum of these two contributions that is,

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \dots\dots\dots\dots..(1)$$

These volume, surface, and total free energy contributions are plotted schematically as a function of nucleus radius in Figures (2). Here (Figure 2) it will be noted that for the curve corresponding to the first term on the right-hand side of Equation (1), the free energy (which is negative) decreases with the third power of *r*. Furthermore, for the curve resulting from the second term in Equation (1), energy values are positive and increase with the square of the radius. Consequently, the curve associated with the sum of both terms (Figure 2) first increases, passes through a maximum, and finally decreases. In a physical sense, this means that as a solid particle begins to form as atoms in the liquid cluster together, its free

4

University of Anbar
College of science
Dept. Of physic

2018 - 2019
MATERIALS SCIENCE

Assist prof.
Dr. Mohammed Ghazi
Chapter (5)

energy first increases. If this cluster reaches a size corresponding to the critical radius r^*, then growth will continue with the accompaniment of a decrease in free energy.
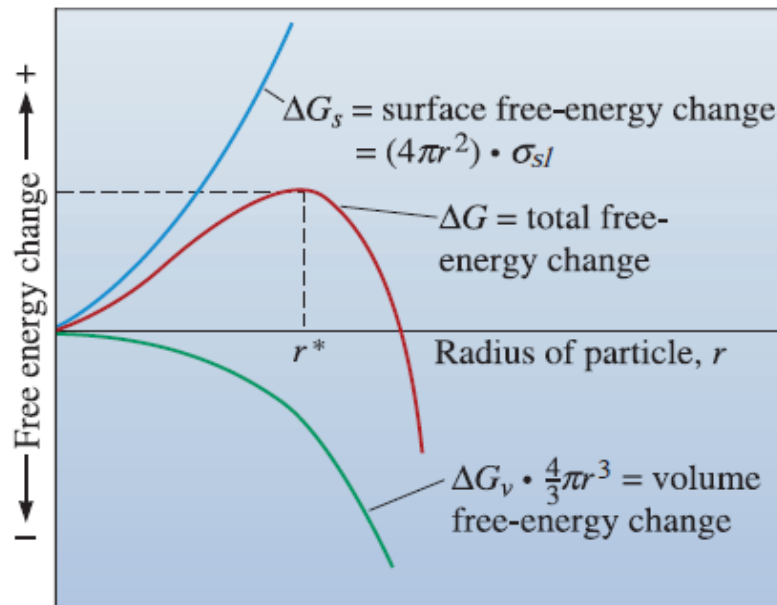

Figure 2 The total free energy of the solid-liquid system changes   with the size of the solid. The solid is an embryo if its radius is less than the critical radius and is a nucleus if its radius is greater than the critical radius.

On the other hand, a cluster of radius less than the critical will shrink and redissolve. This subcritical particle is an *embryo,* whereas the particle of radius greater than r^* is termed a *nucleus*. A critical free energy ΔG^*, occurs at the critical radius and, consequently, at the maximum of the curve in Figure (2). This ΔG^* corresponds to an *activation free energy,* which is the free energy required for the formation of a stable nucleus. Equivalently, it may be considered an energy barrier to the nucleation process.

Since r^* and ΔG^* appear at the maximum on the free energy-versus-radius curve of Figure (2), derivation of expressions for these two parameters is a simple matter. For r^*, we differentiate the ΔG equation

5

University of Anbar
College of science
Dept. Of physic

2018 - 2019
MATERIALS SCIENCE

Assist prof.
Dr. Mohammed Ghazi
Chapter (5)

(Equation 1) with respect to r, set the resulting expression equal to zero, and then solve for $r = (r*)$. That is,

$$\frac{d(\Delta G)}{dr} = \frac{4}{3}\pi \Delta G_v (3r^2) + 4\pi\gamma(2r) = 0 \ldots\ldots\ldots (2)$$

This leads to the result:

$$r^* = -\frac{2\gamma}{\Delta G_v} \ldots\ldots\ldots\ldots (3)$$

Now, substitution of this expression for $r*$ into Equation (1) yields the following expression for $\Delta G*$:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \ldots\ldots\ldots\ldots\ldots (4)$$

This volume free energy change ΔG_v is the driving force for the solidification transformation, and its magnitude is a function of temperature. At the equilibrium solidification temperature T_m, the value of ΔG_v is zero, and with diminishing temperature its value becomes increasingly more negative. It can be shown that ΔG_v is a function of temperature as:

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m} \ldots\ldots\ldots\ldots (5)$$

Where ΔH_f is the latent heat of fusion (i.e., the heat given up during solidification), and T_m and the temperature T are in Kelvin. Substitution of this expression for ΔG_v into Equations (3 and 4) yields:

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)\ldots\ldots\ldots\ldots (6)$$

University of Anbar   *Assist prof.*
College of science   *2018 - 2019*   *Dr. Mohammed Ghazi*
Dept. Of physic   **MATERIALS SCIENCE**   *Chapter (5)*

And

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2} \quad \ldots\ldots\ldots\ldots (7)$$

Thus, from these two equations, both the critical radius r^* and the activation free energy ΔG^* decrease as temperature T decreases. (The γ and ΔH_f parameters in these expressions are relatively insensitive to temperature changes.) Figure (3), a schematic ΔG-versus-r plot that shows curves for two different temperatures, illustrates these relationships. Physically, this means that with a lowering of temperature at temperatures below the equilibrium solidification temperature (T_m), nucleation occurs more readily.
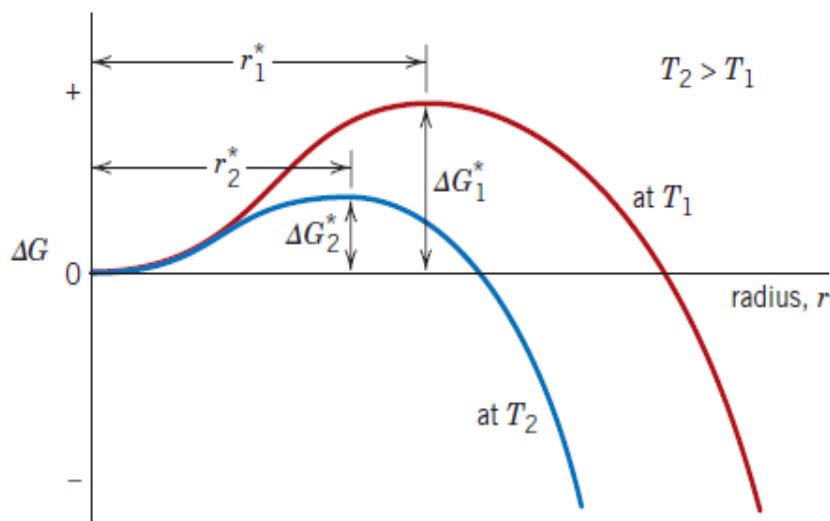

Figure (3) Schematic free energy- versus-embryo/nucleus radius curves for two different temperatures. The critical free energy change ΔG^* and critical nucleus radius r^* are indicated for each temperature.

Furthermore, the number of stable nuclei n^* (having radii greater than r^*) is a function of temperature as:

$$n^* = K_1 exp\left(-\frac{\Delta G^*}{kT}\right) \ldots\ldots\ldots\ldots (8)$$

University of Anbar   *Assist prof.*
College of science   *2018 - 2019*   *Dr. Mohammed Ghazi*
Dept. Of physic   *MATERIALS SCIENCE*   *Chapter (5)*

Where the constant K_1 is related to the total number of nuclei of the solid phase. For the exponential term of this expression, changes in temperature have a greater effect on the magnitude of the ΔG^* term in the numerator than the T term in the denominator. Consequently, as the temperature is lowered below T_m the exponential term in Equation (8) also decreases such that the magnitude of n^* increases. This temperature dependence (n^* versus T) is represented in the schematic plot of figure (4a).

There is another important temperature-dependent step that is involved in and also influences nucleation: the clustering of atoms by short-range diffusion during the formation of nuclei. The influence of temperature on the rate of diffusion (i.e., magnitude of the diffusion coefficient, D) is given in Equation (9).

$$D = D_0 exp\left(-\frac{Q_d}{RT}\right) \dots\dots\dots\dots\ (9)$$

where

D_0 = a temperature-independent preexponential (m²/s)
Q_d = the **activation energy** for diffusion (J/mol or eV/atom)
R = the gas constant, 8.31 J/mol-K or 8.62×10^{-5} eV/atom-K
T = absolute temperature (K)

Furthermore, this diffusion effect is related to the frequency at which atoms from the liquid attach themselves to the solid nucleus, v_d. Or, the dependence of v_d on temperature is the same as for the diffusion coefficient—namely,

$$v_d = K_2 exp\left(-\frac{Q_d}{kT}\right)\dots\dots\dots\dots\ (10)$$

8

University of Anbar   *Assist prof.*
College of science   ***2018 - 2019***   *Dr. Mohammed Ghazi*
Dept. Of physic   ***MATERIALS SCIENCE***   *Chapter (5)*

Where Q_d is a temperature-independent parameter—the activation energy for diffusion and K_2 is a temperature-independent constant. Thus, from Equation (10) a diminishment of temperature results in a reduction in. This effect, represented by the curve shown in Figure (4*b*), is just the reverse of that for n^* as discussed above.
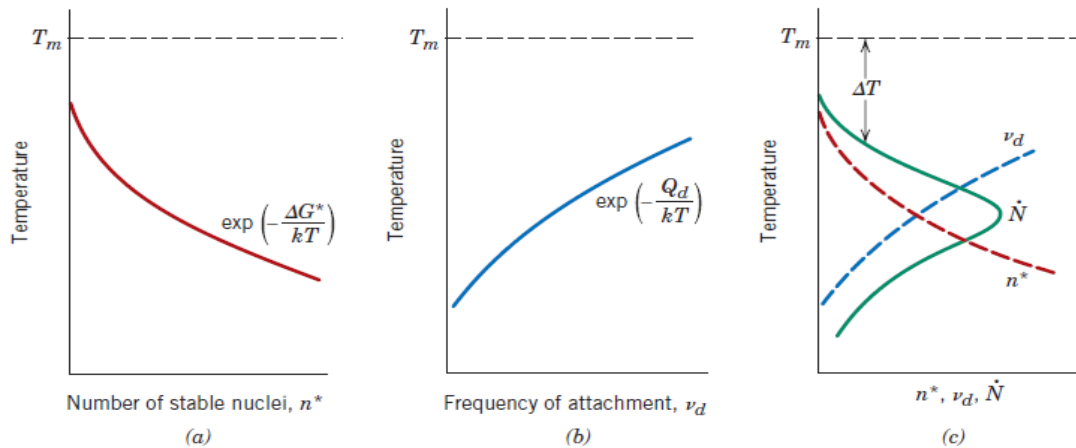

Figure (4) For solidification, schematic plots of (*a*) number of stable nuclei versus temperature, (*b*) frequency of atomic attachment versus temperature, and (*c*) nucleation rate versus temperature (also shown are curves for parts *a* and *b*).

The principles and concepts just developed are now extended to a discussion of another important nucleation parameter, the nucleation rate $\dot{N}$ (which has units of nuclei per unit volume per second). This rate is simply proportional to the product of n^* (Equation 8) and v_d (Equation 10); that is,

$$\dot{N} = K_3 n^* v_d = K_1 K_2 K_3 \left[exp\left(-\frac{\Delta G^*}{kT}\right) exp\left(-\frac{Q_d}{kT}\right) \right] \dots \dots \dots \dots \dots (11)$$

Here K_3 is the number of atoms on a nucleus surface. Figure (4*c*) schematically plots nucleation rate as a function of temperature and, in addition, the curves of Figures (4*a*) and (4*b*) from which the $\dot{N}$ curve is derived. Note (Figure 4*c*) that, with a lowering of temperature from below

9

University of Anbar   *Assist prof.*
College of science   *2018 - 2019*   *Dr. Mohammed Ghazi*
Dept. Of physic   *MATERIALS SCIENCE*   *Chapter (5)*

T_m, the nucleation rate first increases, achieves a maximum, and subsequently diminishes.

The shape of this $\dot{N}$ curve is explained as follows: for the upper region of the curve (a sudden and dramatic increase in $\dot{N}$ with decreasing T), ΔG^* is greater than Q_d, which means that, the exp $(-\Delta G^*/kT)$ term of Equation (11) is much smaller than $\exp(-Q_d/kT)$. In other words, the nucleation rate is suppressed at high temperatures due to a small activation driving force. With continued diminishment of temperature, there comes a point at which ΔG^* becomes smaller than the temperature-independent Q_d with the result that $\exp(-Q_d/kT) < \exp(-\Delta G^*/kT)$, or that, at lower temperatures, a low atomic mobility suppresses the nucleation rate. This accounts for the shape of the lower curve segment (a precipitous reduction of $\dot{N}$ with a continued diminishment of temperature). Furthermore, the $\dot{N}$ curve of Figure 10.4c necessarily passes through a maximum over the intermediate temperature range where values for ΔG^* and Q_d are of approximately the same magnitude.

Several qualifying comments are in order regarding the above discussion. First, although we assumed a spherical shape for nuclei, this method may be applied to any shape with the same final result. Furthermore, this treatment may be utilized for types of transformations other than solidification (i.e., liquid–solid)- for example, solid–vapor and solid–solid. However, magnitudes of ΔG_v and γ, in addition to diffusion rates of the atomic species, will undoubtedly differ among the various transformation types. In addition, for solid–solid transformations, there may be volume changes attendant to the formation of new phases. These changes may lead to the introduction of microscopic strains, which must

University of Anbar   *Assist prof.*
College of science   **2018 - 2019**   **Dr. Mohammed Ghazi**
Dept. Of physic   **MATERIALS SCIENCE**   *Chapter (5)*

be taken into account in the ΔG expression of equation (1), and, consequently, will affect the magnitudes of r^* and ΔG^*.

From Figure $4c$ it is apparent that during the cooling of a liquid, an appreciable nucleation rate (i.e., solidification) will begin only after the temperature has been lowered to below the equilibrium solidification (or melting) temperature (T_m). This phenomenon is termed **supercooling** (or **undercooling**), and the degree of supercooling for homogeneous nucleation may be significant (on the order of several hundred degrees Kelvin) for some systems. In Table (1) is tabulated, for several materials, typical degrees of supercooling for homogeneous nucleation.

Table 1 Values for freezing temperature, latent heat of fusion, surface energy, and maximum undercooling for selected materials

Material	Freezing Temperature (T_m) (°C)	Heat of Fusion (ΔH_f) (J/cm³)	Solid-Liquid Interfacial Energy (σ_{sl}) (J/cm²)	Typical Undercooling for Homogeneous Nucleation (ΔT) (°C)
Ga	30	488	56×10^{-7}	76
Bi	271	543	54×10^{-7}	90
Pb	327	237	33×10^{-7}	80
Ag	962	965	126×10^{-7}	250
Cu	1085	1628	177×10^{-7}	236
Ni	1453	2756	255×10^{-7}	480
Fe	1538	1737	204×10^{-7}	420
NaCl	801			169
CsCl	645			152
H_2O	0			40

EXAMPLE PROBLEM :

Example (1)
Computation of Critical Nucleus Radius and Activation Free Energy
(a) For the solidification of pure gold, calculate the critical radius r^* and the activation free energy ΔG^* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are -1.16×10^9 J/m³ and 0.132 J/m², respectively. Use the supercooling value found in Table (1).

University of Anbar　　　　　　　　　　　　　　　　　　　　*Assist prof.*
College of science　　　　　　*2018 - 2019*　　　　*Dr. Mohammed Ghazi*
Dept. Of physic　　　　　　*MATERIALS SCIENCE*　　　　*Chapter (5)*

(b) Now calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.413 nm for solid gold at its melting temperature.

Solution

(a)　　In order to compute the critical radius, we employ Equation (6), using the melting temperature of $1064^{\circ}C$ for gold, assuming a supercooling value of $230^{\circ}C$ (Table 1), and realizing that $\varDelta H_f$ is negative. Hence

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)(0.132 \ \text{J/m}^2)(1064 + 273 \ \text{K})}{-1.16 \times 10^9 \ \text{J/m}^3}\right]\left(\frac{1}{230 \ \text{K}}\right)$$

$$= 1.32 \times 10^{-9} \ \text{m} = 1.32 \ \text{nm}$$

For computation of the activation free energy, Equation (7) is employed. Thus

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

$$= \left[\frac{(16)(\pi)(0.132 \ \text{J/m}^2)^3(1064 + 273 \ \text{K})^2}{(3)(-1.16 \times 10^9 \ \text{J/m}^3)^2}\right]\left[\frac{1}{(230 \ \text{K})^2}\right]$$

$$= 9.64 \times 10^{-19} \ \text{J}$$

(b)　　In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius r^*), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as gold has the FCC crystal structure (and a cubic unit cell), its unit cell volume is just, where a is the lattice parameter (i.e., unit cell edge length); its value is 0.413 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

University of Anbar
College of science
Dept. Of physic

2018 - 2019
MATERIALS SCIENCE

Assist prof.
Dr. Mohammed Ghazi
Chapter (5)

$$\text{\# unit cells/particle} = \frac{\text{critical nucleus volume}}{\text{unit cell volume}} = \frac{\frac{4}{3}\pi r^{*3}}{a^3}$$

$$= \frac{\left(\frac{4}{3}\right)(\pi)(1.32 \text{ nm})^3}{(0.413 \text{ nm})^3} = 137 \text{ unit cells}$$

In as much as there is the equivalence of four atoms per FCC unit cell, the total number of atoms per critical nucleus is just

(137 unit cells/critical nucleus)(4 atoms/unit cell) = 548 atoms/critical nucleus

Example (2): Calculation of Critical Radius for the Solidification of Copper

Calculate the size of the critical radius and the number of atoms in the critical nucleus when solid copper forms by homogeneous nucleation. Comment on the size of the nucleus and assumptions we made while deriving the equation for the radius of the nucleus.

SOLUTION

From Table 1 for Cu:

$$\Delta T = 236°C \qquad T_m = 1085 + 273 = 1358 \text{ K}$$
$$\Delta H_f = 1628 \text{ J/cm}^3$$
$$\sigma_{sl} = 177 \times 10^{-7} \text{ J/cm}^2$$

Thus, r^* is given by

$$r^* = \frac{2\sigma_{sl}T_m}{\Delta H_f \Delta T} = \frac{(2)(177 \times 10^{-7})(1358)}{(1628)(236)} = 12.51 \times 10^{-8} \text{ cm}$$

Note that a temperature difference of 1°C is equal to a temperature change of 1 K, or $\Delta T = 236°C = 236$ K.

The lattice parameter for FCC copper is $a_0 = 0.3615$ nm $= 3.615 \times 10^{-8}$ cm. Thus, the unit cell volume is given by

$$V_{\text{unit cell}} = (a_0)^3 = (3.615 \times 10^{-8})^3 = 47.24 \times 10^{-24} \text{ cm}^3$$

The volume of the critical radius is given by

$$V_{r*} = \frac{4}{3}\pi r^3 = \left(\frac{4}{3}\pi\right)(12.51 \times 10^{-8})^3 = 8200 \times 10^{-24} \text{ cm}^3$$

The number of unit cells in the critical nucleus is

$$\frac{V_{\text{unit cell}}}{V_{r*}} = \frac{8200 \times 10^{-24}}{47.24 \times 10^{-24}} = 174 \text{ unit cells}$$

University of Anbar   *Assist prof.*
College of science   ***2018 - 2019***   *Dr. Mohammed Ghazi*
Dept. Of physic   ***MATERIALS SCIENCE***   *Chapter (5)*

Since there are four atoms in each FCC unit cell, the number of atoms in the critical nucleus must be

(4 atoms/cell)(174 cells/nucleus)= 696 atoms/nucleus

In these types of calculations, we assume that a nucleus that is made from only a few hundred atoms still exhibits properties similar to those of bulk materials. This is not strictly correct and as such is a weakness of the classical theory of nucleation.

-    *Heterogeneous Nucleation*

From Table 1, we can see that water will not solidify into ice via homogeneous nucleation until we reach a temperature of -40°C (undercooling of 40°C)! Except in controlled laboratory experiments, homogeneous nucleation never occurs in liquids. Instead, impurities in contact with the liquid, either suspended in the liquid or on the walls of the container that holds the liquid, provide a surface on which the solid can form (Figure 5). Now, a radius of curvature greater than the critical radius is achieved with very little total surface between the solid and liquid. Relatively few atoms must cluster together to produce a solid particle that has the required radius of curvature. Much less undercooling is required to achieve the critical size, so nucleation occurs more readily. Nucleation on preexisting surfaces is known as **heterogeneous nucleation**. This process is dependent on the contact angle (θ) for the nucleating phase and the surface on which nucleation occurs. The same type of phenomenon occurs in solid-state transformations.

In order to understand this phenomenon, let us consider the nucleation, on a flat surface, of a solid particle from a liquid phase. It is assumed that both the liquid and solid phases "wet" this flat surface, that is, both of these phases spread out and cover the surface; this

University of Anbar   *Assist prof.*
College of science   **2018 - 2019**   **Dr. Mohammed Ghazi**
Dept. Of physic   *MATERIALS SCIENCE*   *Chapter (5)*

configuration is depicted schematically in Figure (5). Also noted in the figure are three interfacial energies (represented as vectors) that exist at two-phase boundaries γ_{SL}, γ_{SI} and γ_{IL} as well as the wetting angle Θ (the angle between the γ_{SI} and γ_{SL} vectors). Taking a surface tension force balance in the plane of the flat surface leads to the following expression:

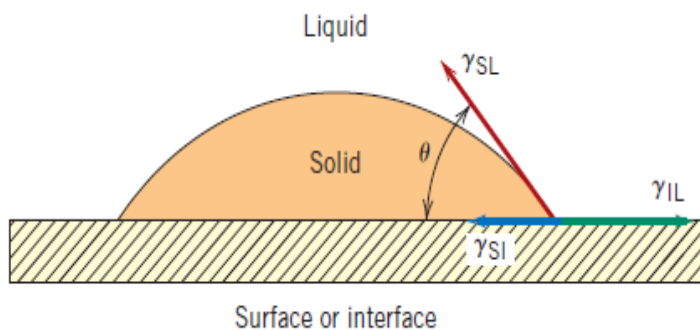$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta \ \dots\dots\dots\dots..(12)$$

Figure (5) Heterogeneous nucleation of a solid from a liquid. The solid–surface (γ_{SI}), solid–liquid (γ_{SL}), and liquid–surface (γ_{IL}) interfacial energies are represented by vectors. The wetting angle (θ) is also shown.
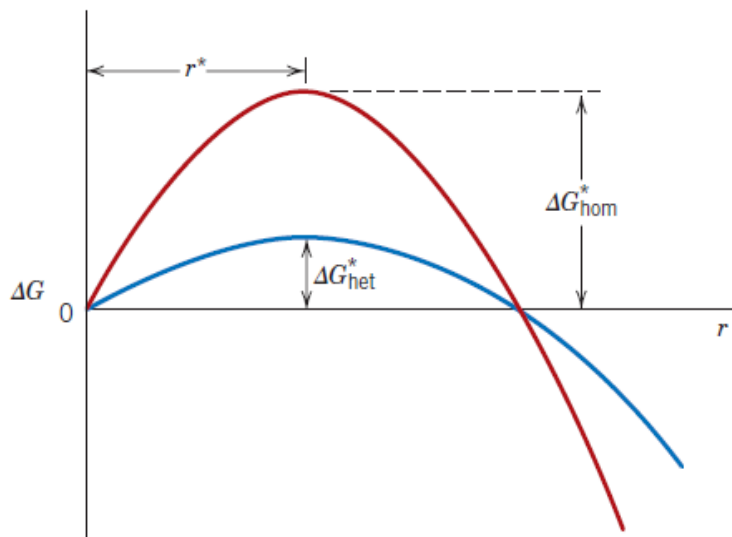

Figure (6) Schematic free-energy-versus-embryo/nucleus-radius plot on which are presented curves for both homogeneous and heterogeneous nucleation. Critical free energies and the critical radius are also shown.

Now, using a somewhat involved procedure similar to the one presented above for homogeneous nucleation (which we have chosen to

University of Anbar   *Assist prof.*
College of science   **2018 - 2019**   **Dr. Mohammed Ghazi**
Dept. Of physic   **MATERIALS SCIENCE**   **Chapter (5)**

omit), it is possible to derive equations for $r*$ and ΔG^*; these are as follows:

$$r^* = \left(-\frac{2\gamma_{SL}}{\Delta G_v}\right) \ldots \ldots \ldots \ldots (13)$$

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right) S(\theta) \ldots \ldots \ldots \ldots .. (14)$$

The term of this last equation is a function only of (i.e., the shape of the nucleus), which will have a numerical value between zero and unity (For example, for Θ angles of 30° and 90°, values of $S(\Theta)$ are approximately 0.01 and 0.5, respectively).

From Equation (13), it is important to note that the critical radius $r*$ for heterogeneous nucleation is the same as for homogeneous, inasmuch as γ_{SL} is the same surface energy as γ in Equation (3). It is also evident that the activation energy barrier for heterogeneous nucleation (Equation 14) is smaller than the homogeneous barrier (Equation 4) by an amount corresponding to the value of this $S(\Theta)$ function, or

$$\Delta G_{het}^* = \Delta G_{hom}^* S(\theta) \ldots \ldots \ldots \ldots .. (15)$$

Figure (6), a schematic graph of ΔG versus nucleus radius, plots curves for both types of nucleation, and indicates the difference in the magnitudes of ΔG_{het}^* and ΔG_{hom}^* in addition to the constancy of $r*$. This lower ΔG^* for heterogeneous means that a smaller energy must be overcome during the nucleation process (than for homogeneous), and, therefore, heterogeneous nucleation occurs more readily (Equation 11). In terms of the nucleation rate, the $\dot{N}$ versus T curve (Figure 4c) is shifted to higher temperatures for heterogeneous. This effect is represented in

University of Anbar
College of science   **2018 - 2019**
Dept. Of physic   **MATERIALS SCIENCE**

Assist prof.
Dr. Mohammed Ghazi
Chapter (5)

Figure (7), which also shows that a much smaller degree of supercooling (ΔT) is required for heterogeneous nucleation.
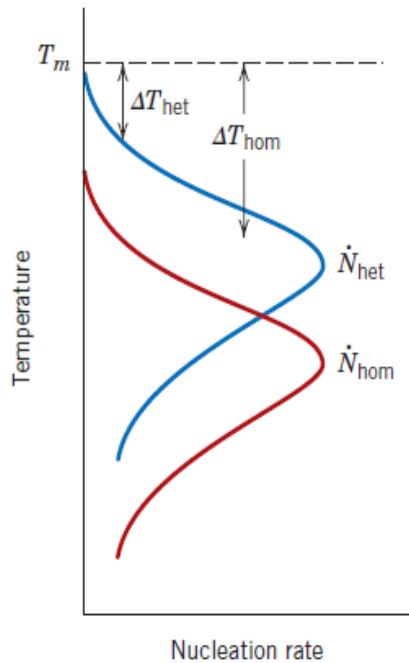
Figure (7) Nucleation rate versus temperature for both homogeneous and heterogeneous nucleation. Degree of supercooling (ΔT) for each is also shown.

5-2- Rate of Nucleation

The *rate of nucleation* (the number of nuclei formed per unit time) is a function of temperature. Prior to solidification, of course, there is no nucleation and, at temperatures above the freezing point, the rate of nucleation is zero. As the temperature drops, the driving force for nucleation increases; however, as the temperature decreases, atomic diffusion becomes slower, hence slowing the nucleation process.

Thus, a typical rate of nucleation reaches a maximum at some temperature below the transformation temperature. In heterogeneous nucleation, the rate of nucleation is dictated by the concentration of the nucleating agents. By considering the rates of nucleation and growth, we can predict the overall rate of a phase transformation.

University of Anbar   **Assist prof.**
College of science   **2018 - 2019**   **Dr. Mohammed Ghazi**
Dept. Of physic   **MATERIALS SCIENCE**   **Chapter (5)**

5-3- *Growth*

The growth step in a phase transformation begins once an embryo has exceeded the critical size *r**, and becomes a stable nucleus. Note that nucleation will continue to occur simultaneously with growth of the new phase particles; of course, nucleation cannot occur in regions that have already transformed to the new phase. Furthermore, the growth process will cease in any region where particles of the new phase meet, since here the transformation will have reached completion.

Particle growth occurs by long-range atomic diffusion, which normally involves several steps—for example, diffusion through the parent phase, across a phase boundary, and then into the nucleus. Consequently, the growth rate $\dot{G}$ is determined by the rate of diffusion, and its temperature dependence is the same as for the diffusion coefficient namely,

$$\dot{G} = C \, exp\left(-\frac{Q}{kT}\right) \ldots \ldots \ldots \ldots (16)$$

Where Q (the activation energy) and C (a preexponential) are independent of temperature. The temperature dependence of $\dot{G}$ is represented by one of the curves in Figure (8); also shown is a curve for the nucleation rate, $\dot{N}$ (again, almost always the rate for heterogeneous nucleation). Now, at a specific temperature, the overall transformation rate is equal to some product of $\dot{N}$ and $\dot{G}$. The third curve of figure (8), which is for the total rate, represents this combined effect. The general shape of this curve is the same as for the nucleation rate, in that it has a peak or maximum that has been shifted upward relative to the $\dot{N}$ curve.
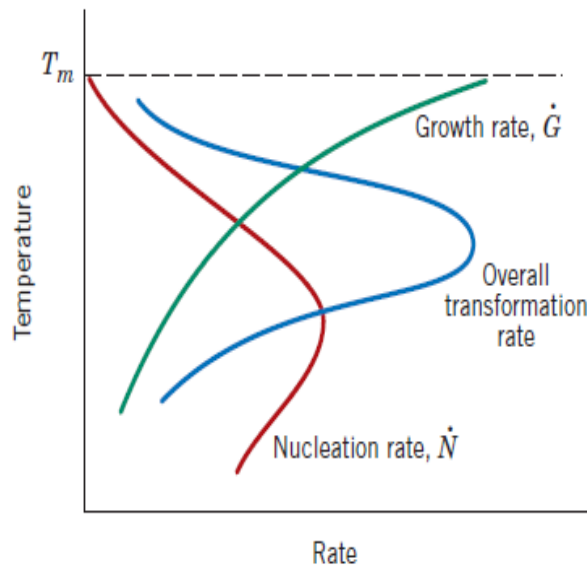
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College of science
Dept. Of physic

2018 - 2019
MATERIALS SCIENCE

Assist prof.
Dr. Mohammed Ghazi
Chapter (5)

Figure (8) Schematic plot showing curves for nucleation rate ($\dot{N}$), growth rate ($\dot{G}$), and overall transformation rate versus temperature.

Several physical phenomena may be explained in terms of the transformation rate- versus- temperature curve of figure (8). First, the size of the product phase particles will depend on transformation temperature. For example, for transformations that occurs at temperatures near to T_m corresponding to low nucleation and high growth rates, few nuclei form that grow rapidly. Thus, the resulting microstructure will consist of few and relatively large phase particles (e.g., coarse grains). Conversely, for transformations at lower temperatures, nucleation rates are high and growth rates low, which results in many small particles (e.g., fine grains). Also, from figure (8), when a material is cooled very rapidly through the temperature range encompassed by the transformation rate curve to a relatively low temperature where the rate is extremely low, it is possible to produce nonequilibrium phase structures.

5-4- Kinetic Considerations of Solid-State Transformations

The previous discussion of this section has centered on the temperature dependences of nucleation, growth, and transformation rates.

University of Anbar
College of science
Dept. Of physic
2018 - 2019
MATERIALS SCIENCE
Assist prof.
Dr. Mohammed Ghazi
Chapter (5)

The *time* dependence of rate (which is often termed the **kinetics** of a transformation) is also an important consideration, often in the heat treatment of materials. Also, since many transformations of interest to materials scientists and engineers involve only solid phases, we have decided to devote the following discussion to the kinetics of solid-state transformations.

With many kinetic investigations, the fraction of reaction that has occurred is measured as a function of time while the temperature is maintained constant. Transformation progress is usually ascertained by either microscopic examination or measurement of some physical property (such as electrical conductivity) the magnitude of which is distinctive of the new phase. Data are plotted as the fraction of transformed material versus the logarithm of time; an S-shaped curve similar to that in figure (9) represents the typical kinetic behavior for most solid-state reactions. Nucleation and growth stages are also indicated in the figure.
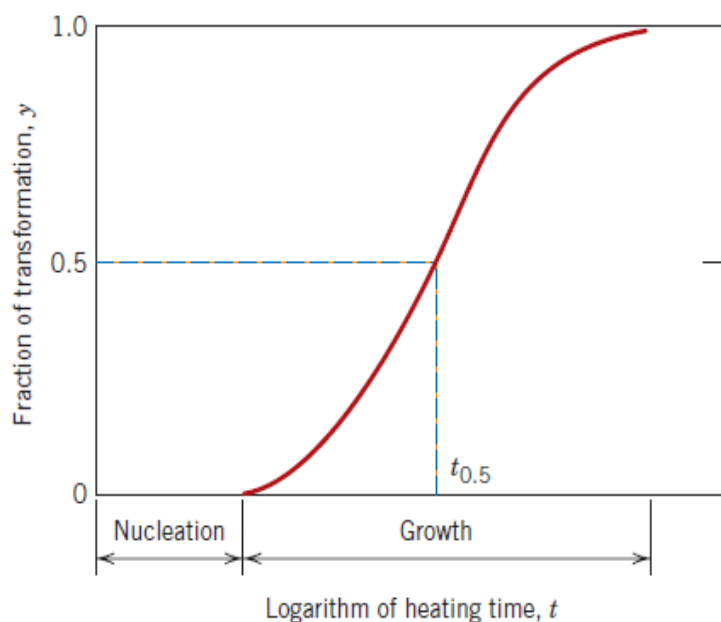

Figure (9) Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

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2018 - 2019
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Chapter (5)

For solid-state transformations displaying the kinetic behavior in figure (9), the fraction of transformation *y* is a function of time *t* as follows:

$$y = 1 - \exp(-kt^n) \dots \dots \dots \dots \dots (17)$$

Where *k* and *n* are time-independent constants for the particular reaction. The above expression is often referred to as the *Avrami equation*. By convention, the rate of a transformation is taken as the reciprocal of time required for the transformation to proceed halfway to completion, $t_{0.5}$, or

$$rate = \frac{1}{t_{0.5}} \dots \dots \dots \dots \dots \dots (18)$$

Temperature will have a profound influence on the kinetics and thus on the rate of a transformation. This is demonstrated in Figure (10), where *y* -versus- log *t*
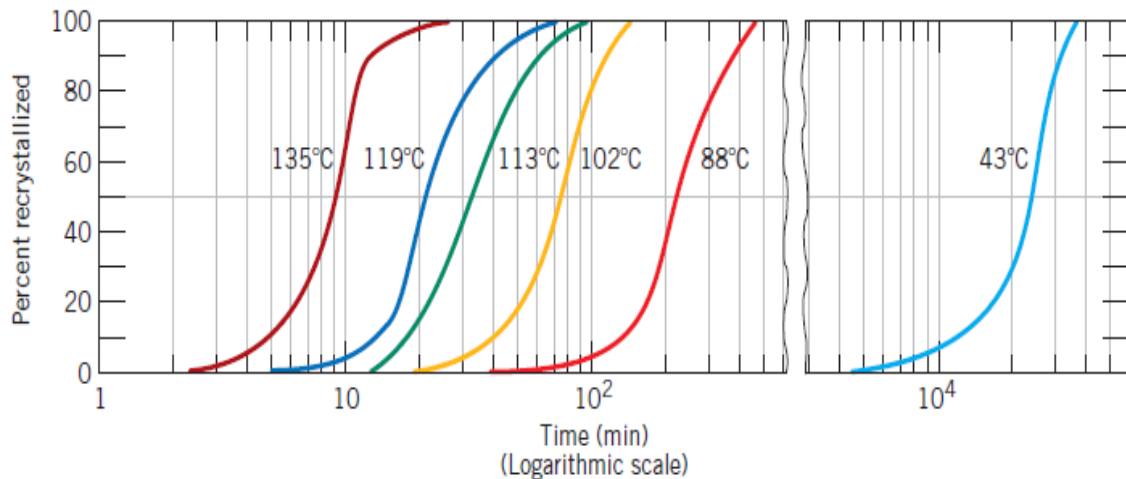

Figure (10) Percent recrystallization as a function of time and at constant temperature for pure copper. S-shaped curves at several temperatures for the recrystallization of copper are shown.

21

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QUESTIONS AND PROBLEMS

1- Name the two stages involved in the formation of particles of a new phase. Briefly describe each.

2- It is known that the kinetics of recrystallization for some alloy obeys the Avrami equation and that the value of *n* in the exponential is 2.5. If, at some temperature, the fraction recrystallized is 0.40 after 200 min, determine the rate of recrystallization at this temperature.

Solution

This problem gives us the value of **y** (0.40) at some time **t** (200 min), and also the value of **n** (2.5) for the recrystallization of an alloy at some temperature, and then asks that we determine the rate of recrystallization at this same temperature. It is first necessary to calculate the value of **k** in Equation (17) as

$$k = -\frac{\ln(1-y)}{t^n}$$

$$= -\frac{\ln(1-0.4)}{(200 \text{ min})^{2.5}} = 9.0 \times 10^{-7}$$

At this point we want to compute **t₀.₅** $t_{0.5}$, the value of **t** for **y** = 0.5, also using Equation (17). Thus

$$t_{0.5} = \left[-\frac{\ln(1-0.5)}{k}\right]^{1/n}$$

$$= \left[-\frac{\ln(1-0.5)}{9.0 \times 10^{-7}}\right]^{1/2.5} = 226.3 \text{ min}$$

And, therefore, from Equation (11.2), the rate is just

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{226.3 \text{ min}} = 4.42 \times 10^{-3} \text{ (min)}^{-1}$$

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Dept. Of physic   *MATERIALS SCIENCE*   *Chapter (5)*

3-   For some transformation having kinetics that obey the Avrami equation (Equation **(18)**), the parameter n is known to have a value of 1.7. If, after 100 s, the reaction is 50% complete, how long (total time) will it take the transformation to go to 99% completion?

<u>Solution:</u>

This problem calls for us to compute the length of time required for a reaction to go to 99% completion. It first becomes necessary to solve for the parameter **k** in the Avrami equation. Rearrangement of the Avrami equation and substitution of the stated values for 50% completion (i.e., y = 0.50) leads to

$$k = -\frac{\ln(1-y)}{t^n} = -\frac{\ln(1-0.5)}{(100 \text{ s})^{1.7}} = 2.76 \times 10^{-4}$$

Now, solving for the time to go to 99% completion

$$t = \left[-\frac{\ln(1-y)}{k} \right]^{1/n}$$

$$\text{or, } t = \left[-\frac{\ln(1-0.99)}{2.76 \times 10^{-4}} \right]^{1/1.7} = 305 \text{ s}$$