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Q Jiang[1,2], Z Wen[1] and T Wang[1]

[1] Department of Materials Science and Engineering, Jilin University at Nanling Campus, Changchun 130025, China
[2] Forschungszentrum Karlsruhe(GmbH), Institute of Nanotechnology, PO Box 3640, D-76021 Karlsruhe, Germany

E-mail: jiangq@jlu.edu.cn

Abstract
A lower limit for the grain size of nanocrystalline solids obtained by crystallization of the glass and its dependency on the crystallization temperature are thermodynamically considered. It is found that the nanocrystalline materials have the smallest grain size when the crystallization temperature is roughly half of the melting temperature. At this temperature, the Gibbs free energy difference between the undercooled liquid and the crystal reaches the maximum. It is found that for polymorphous crystallization the lower bound of grain size is essentially dependent on melting entropy. The results are consistent with available experimental evidence.

It is well known that nanocrystalline materials can be prepared by crystallization of glasses [1–3]. Experimentally it is found that the smallest grain size is obtained when the glasses are annealed at a crystallization temperature T_x near $T_m/2$ where T_m is the bulk melting temperature [1–3]. This has been interpreted in terms of transition kinetics, namely at $T_m/2$ the nucleation rate I is the largest while the growth rate u is relatively low [2]. Of course, besides the kinetic criteria, the crystallization process also needs to satisfy the energetic criterion that the total free energy diminishes upon crystallization. It is conceivable that such an energetic criterion can be of help in rationalizing experimentally observed grain size and its dependency on the materials parameters and on the temperature of crystallization. In this paper, we will consider a simple thermodynamic relation that suggests a general thermodynamic lower limit of the grain size of the metallic nanocrystalline materials at T_x.

Obtaining nanocrystalline materials by crystallization generally requires that T_x is above or close to the galss transition temperature, T_g [2]. Except for a small difference due to the discontinuity in heat capacities at T_g, the free energy of the amorphous state is therefore that of the undercooled liquid. Thus, what we discuss below is the transition between the undercooled liquid and the nanocrystalline state. We shall first discuss the case of polymorphous crystallization, where the nanocrystalline product phase is uniform in composition. The consequence of decomposition into two phases during crystallization will be commented on at the end of the paper.

Denoting by $-g(T)$ the change in Gibbs free energy when 1 mol of amorphous material is crystallized, and approximating the grain boundary area A created when the entire material (total volume V) crystallizes to the nanocrystalline state with grain size D by $A \approx 3V/D$ (which is suggested by reference [4] and is valid for a specific arrangement of grain boundaries as discussed therein), the free energy balance for the transition of the glass to the nanocrystalline state is

$$\Delta g(T_x) = -g(T_x) + 3v_g \gamma_{GB}/D \tag{1}$$

with γ_{GB} being the specific excess free energy of grain boundary and v_g the molar volume.

Because spontaneous processes require $\Delta g < 0$, we have for the temperature-dependent lower limit of the grain size $D_{min}(T_x)$ at $\Delta g = 0$, or

$$D_{min}(T_x) = 3v_g \gamma_{GB}/g(T_x). \tag{2}$$

While other parameters in equation (2) are weak functions of the temperature, it is clear that $D_{min}(T_x)$ reaches the minimum at a temperature where $g(T)$ takes its maximum. In the following, we use the symbol T_x^* to refer to the temperature which gives the lower limit for the grain size, and D_{min}^* to refer to this particular value. Several expressions for the temperature variation of $g(T)$ between T_m and T_g have been proposed in the literature [5–7]. In general, they predict the steepest variation near T_m, and a much weaker temperature-dependence near T_g. In fact, these treatments [5–7] suggest a maximum in $g(T)$ at or lower $T_m/2$. As examples, consider the expressions suggested by Hoffman [5] and by Thompson and Spaepen [6] under the condition that the specific heat difference between the crystal and the liquid is not equal to zero:

$$g(T) = s_m T(T_m - T)/T_m \tag{3}$$

and

$$g(T) = 2s_m T(T_m - T)/(T_m + T) \tag{4}$$

respectively, where s_m is the bulk melting entropy. Equation (3) takes its maximum at $T = T_m/2$ while equation (4) does so at $T = (2^{1/2}-1)T_m \approx 0.41\, T_m$. Since $T_m s_m = h_m$ where h_m is the bulk melting enthalpy,

$$g(T_x^*) = c\, h_m \tag{5}$$

with values for the constant $c = 1/4$ and $c = 0.34$ for equations (3) and (4), respectively.

The result for T_x^* corresponds indeed to the annealing temperature where the smallest grain size of the nanocrystalline material is obtained in experiments [2]. Note that $dg(T)/dT$ vanishes at T_x^*, and that consequently $g(T)$ has only little variation in a finite temperature-interval around its maximum. In fact, both equations (3) and (4) have c in the interval 0.27 ± 0.06 when the crystallization temperature is between $0.5\, T_m$ and $0.7\, T_m$. Since we aim at an estimate of D_{min}^*, and since in experiments usually $0.5\, T_m < T_x < 0.7\, T_m$ ($T_x > T_x^*$ due to the kinetic reason) [2], we may consider equation (5) with $c \approx 0.27$ as the basis for our discussion.

To predict D_{min}^*, we need to know γ_{GB} in equation (2). It is known that $\gamma_{GB} \approx 2\gamma_{sl}$ [8] where γ_{sl} denotes the specific excess Gibbs free energy of solid–liquid interface energy. γ_{sl} has been deduced according to the Gibbs–Thomson equation [9] as $\gamma_{sl} = 2h s_{vib} h_m/(3v_g R)$ with R being the ideal gas constant, h the atomic diameter, s_{vib} the vibrational part of the overall melting entropy s_m. For metals and alloys, $s_{vib} \approx s_m$ [9]. Thus, an approximate relation for γ_{GB} is

$$\gamma_{GB} = 4h s_m h_m/(3v_g R). \tag{6}$$

The estimated value of γ_{GB} of equation (6) is consistent with the phenomenological equation of $\gamma_{GB} = 1.3hh_m/v_g$ for metallic alloys [3] when $s_m/R \approx 1$ and $1.3 \approx 4/3$. Substituting equations (5) and (6) into equation (2), we have

$$D_{min}^*(T_x^*) \approx 4hs_m/(cR). \tag{7}$$

Equation (7) suggests that the minimal grain size is proportional to h and s_m. Keep in mind of $c \approx 0.27$, with a typical value for metals, $h \approx 1/4$ nm, D_{min}^* is of the order of 4 nm for metals where $s_m/R \approx 1$. For alloys, usually s_m/R is located between 1.5 and 2.5 [2], D_{min}^* is thus between 6 and 10 nm. Thus, the increase of component number of alloys leads to increase of s_m and thus that of D_{min}^* [2]. The experimental results compiled in reference [2] and listed in table 1 cite grain sizes of all elements in excess of 4 nm while the grain sizes of alloys with fewer and larger number of components are more than 6 and 10 nm, in agreement with our conclusion.

Table 1. Experimental results (according to reference [2]) on crystallized grain sizes of elements, compounds and alloys obtained by annealing glasses at the given T_a/T_m. The subscript for compounds is the atomic number of elements while that for alloys is the atomic percentage. D_{min} denotes the experimental results of the minimum grain size of nanostructured crystals in nanometers.

	Compositions	T_a/T_m	D_{min}
Elements and compounds	Si	0.50	7–8
	Se	0.76	7–8
	$CoZr_2$	0.50	8
	$NiZr_2$	0.49	8–10
Eutectic alloys	$Ni_{80}P_{20}$	0.50	6–7
	$Fe_{80}B_{20}$	0.46	8
	$Fe_{40}Ni_{40}P_{14}B_6$	0.55	9
Alloys without eutectic composition	$Fe_{60}B_{13}Si_9$	0.51	21–25
	$Fe_{60}Co_{30}Zr_{10}$	0.51	15
	$(Fe_{99}Mo_1)_{78}B_{13}Si_9$	0.52	17–20
	$(Fe_{99}Cu_1)_{78}B_{13}Si_9$	0.50	27
	$Pd_{78.1}Cu_{5.5}Si_{16.4}$	0.62	19
	$Fe_{73.5}Cu_1B_9Si_{13.5}$	0.53	18

Several data without values of T_a/T_m are not cited from reference [2].

The above consideration is based on crystal nucleation theory alone without invoking the kinetics of crystal growth. This is the reason why all experimental results on D_{min}^* are larger than our estimation. It is well known that the actual grain size of materials D_{act} is shown as [2]

$$D_{act} \propto (u/I)^{1/2}. \tag{8}$$

Since I reaches its maximum at about $0.5\ T_m$ while u increases steadily with temperature, it is plausible that D_{act} takes its minimal grain size at this temperature [2]. In terms of table 1, $D_{act} - D_{min}$ for alloys with larger number of components is larger than that with fewer numbers of components. This could be expected because although the multi-component alloys have lower u value, its value of I could be still lower for a given degree of reduced undercooling. Thus, the growth times of multi-component alloys will be longer than that of the alloys with fewer components.

On the other hand, nanocrystalline alloys have been reported to take on grain sizes as small as 2 nm, considerably below our lower limit [10]. This may be understood by the fact,

neglected in the simple analysis above, that the interaction of segregating solute with the grain boundary may reduce the grain boundary energy considerably [3] and, therefore, decrease the lower limit of grain size. Moreover, this reduction of γ_{GB} leads to a thermodynamic upper limit for the grain size [3]. Finally, we emphasize that our considerations above are based on the assumption that γ_{GB} is size-independent. This assumption is in question since it has been suggested that γ_{sl} vanishes when all atoms of a crystalline particle in a liquid matrix are located on its surface, so that the solid–liquid interface is quite diffuse [9]. It is therefore conceivable that γ_{GB} is also an increasing function of the grain size. Recent computer simulation results [4] and experimental data [11] qualitatively support this suggestion. In the framework of the considerations of the present paper, a diminishing of γ_{GB} with decreasing grain size would decrease D_{min}.

Our consideration so far has related to enthalpy and entropy changes due to melting, ignoring changes of composition. Therefore, they apply exclusively to polymorphous transitions. When crystallization involves a change of composition, or the crystalline product consists of multi-phases, additional terms in the free energy balance arise. The change in molar Gibbs free energy upon crystallization can then formally be written as

$$\Delta g(T) = 3v_g \gamma_{GB}/D - [g(T) + \Delta h^{mix} - T\Delta s^{mix}] \tag{9}$$

where Δh^{mix} and Δs^{mix} denote the difference in the enthalpy and the entropy, respectively, between the (metastable) homogeneous solid solution and the mixture of multi-phases, and $g(T)$ shows the free energy of (polymorphous) melting of the homogeneous solid solution. When the equilibrium state is the multi-phase mixture, the quantity $\Delta g^{mix} = \Delta h^{mix} - T\Delta s^{mix}$ is positive, and consequently the lower bound for the grain size is reduced relative to equation (7). Also, Δs^{mix} contributes a linear term in the temperature to Δg, thus, the minimum of grain size is no longer decided by $g(T)$ alone.

In summary, when a metallic glass undergoes polymorphous crystallization at temperatures near half of the melting temperature, the lower bound for the grain size is only weakly dependent on the temperature. This bound is proportional to the atomic diameter and the melting entropy.

Acknowledgment

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