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FORMATION OF CRYSTAL NUCLEI IN LIQUID METALS

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Formation of Crystal Nuclei in Liquid Metals

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The known facts about nucleation phenomena in liquid metals are interpreted satisfactorily on the basis of the critical size and interfacial energy concepts. In large continuous masses nucleation is almost always catalyzed by extraneous interfaces. However, in very small droplets the probability that a catalytic inclusion is present is so much less that their minimum nucleation frequencies are reproducible and form a consistent set of values.

Interfacial energies, σ, between crystal nuclei and the corresponding liquids have been calculated from nucleation frequencies of small droplets on the basis of the theory of homogeneous nucleation. Energies of interfaces, σ_g, one atom thick and containing N atoms were calculated from the σ's. The ratio of σ_g to the gram atomic heat of fusion, ΔH_f, was approximately 0.45 for most metals but ~0.32 for H_2O, Bi, Sb, and Ge.

The effect of relative complexity of crystal structure upon the supercooling behavior of pure metals apparently is a reflection of its effect upon ΔH_f.

The solidification of pure metals may be thought of as a sequence of two steps: nucleation of crystals and their subsequent growth. It is known that the growth of large metal crystals into their supercooled melts is very rapid and usually limited only by the rate at which the heat of solidification can diffuse from the interface. On the other hand the time preceding the appearance of "macroscopic" crystals may be very long relative to the duration of rapid growth and often controls the solidification rate. This time delay is known as the "nucleation" period. The reciprocal of the average nucleation period is the nucleation frequency or rate and is proportional to the volume of liquid or to the area of interfaces in the system that catalyze nucleation.

Nucleation rates measured on large continuous liquid metal masses are not reproducible. However, recent experiments[1, 2] on the supercooling of small metal droplets have shown that the temperatures at which the rate of crystal nucleation becomes appreciable in them are consistent and reproducible to within about ±5 percent.

Generalizations about the solidification behavior of small droplets have been made in a preceding paper.[2] By combining these generalizations with the known facts of the supercooling behavior of large masses, a theory of nucleation can be constructed that accounts qualitatively for the nucleation behavior of liquid metal masses of all sizes and surface conditions.

CRYSTAL NUCLEATION AND ITS CATALYSIS

In nearly all theories of homogeneous (non-catalyzed) nucleation of crystals in liquids it is supposed that the nucleation period is the time necessary for a crystal of a certain critical size to form by thermal fluctuations. The radius of a critical size nucleus is directly proportional to the interfacial energy between the liquid and crystal and inversely proportional to the difference in free energy between liquid and crystal phases of infinite volume. The free energy of a crystal of critical size is decreased by fluctuations that either add or subtract atoms to it; consequently, any crystal that is smaller than the critical size will usually disappear and any that becomes larger will usually grow.

On the basis of these concepts and absolute rate theory, the following expression has been derived[3] for the homogeneous nucleation frequency of crystals in supercooled liquids:

$$I = A \exp[-K\sigma^3/(\Delta F_V)^2 kT], \qquad (1)$$

where $A = n(kT/h)\exp[-\Delta F_A/kT]$ and the other symbols are defined as follows: I = number of nuclei/sec. ×cm^3, n = number of atoms in the mass of liquid, K = a factor determined by the shape of the nucleus, σ = interfacial energy/cm^2 between liquid and crystal, ΔF_V = difference in free energy/cm^3 between crystal and liquid phases of infinite volume, and ΔF_A = free energy of activation for transporting an atom across the liquid-crystal interface.

In Eq. (1) three parameters σ, K, and ΔF_A are not known. However, experience indicates that ΔF_A is very small, at least for large crystals, and there is reason to believe that it is of the same magnitude as the activation energy for viscous flow, $\Delta F_A'$. If $\Delta F_A \approx \Delta F_A'$ then $\exp(-\Delta F_A/kT)$ is of the order of 10^{-2} at the solidification temperature for most metals. Therefore, it is expected that $A \approx 10^{33\pm1}$ sec.$^{-1}$ cm^{-3}. A can be evaluated from measurements of the homogeneous nucleation frequency as a function of temperature and its value compared with the predictions of theory. If the theory is thus approximately verified, Eq. (1) can be used to calculate σ (assuming some shape for the nucleus) from the nucleation frequency measured at a single temperature.

There is convincing evidence that nucleation of crystals in large continuous masses of liquid metals is almost always catalyzed by accidental inclusions and container walls.[4–6] The theory of nucleation catalysis is

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[1] D. Turnbull, J. Metals **188**, 1144 (1950).

[2] D. Turnbull and R. E. Cech, J. App. Phys. **21**, 804 (1950).

[3] D. Turnbull and J. C. Fisher, J. Chem. Phys. **17**, 71 (1949).

[4] W. T. Richards, J. Am. Chem. Soc. **54**, 479 (1932).

[5] D. Turnbull, J. Chem. Phys. **18**, 198 (1950).

[6] J. H. Hollomon, A.S.M. Symposium on Thermodynamics, Cleveland (1949).

also based upon the critical size concept. When crystals form on the surfaces of catalytic interfaces the total increase in free energy due to forming the crystal surfaces is less than the increase that would accompany the formation of the same mass of crystal without the aid of extraneous interfaces. Catalysis requires that interfaces be present such that the equilibrium contact angle, θ, made by the crystal and the interface in the presence of liquid be less than 180°. An expression can be written for the frequency of heterogeneous (catalyzed) nucleation analogous to the expression for homogeneous nucleation as follows:[7]

$$I_s = A' \exp[-K\sigma^3\{f(\theta)\}/(\Delta F_V)^2 kT], \tag{2}$$

where $A' = n_s(kT/h)\exp[-\Delta F_A/kT]$, $f(\theta) = (2+\cos\theta) \times (1-\cos\theta)^2/4$, I_s = nuclei/sec. cm^2, n_s = number of atoms in the interface/cm^2, and A' is estimated to be $\approx 10^{25\pm1}$ sec.$^{-1}$ cm^{-2}. Thus a clear distinction can be made between homogeneous and heterogeneous nucleation on the basis of the coefficient A evaluated from data on the nucleation frequency as a function of temperature. However, in large masses of liquid the nucleation frequency usually follows no regular relation such as (2) because accidental catalysts of varying degrees of effectiveness (i.e. different θ values) are liable to be present in different samples. Due to these difficulties adequate testing of the nucleation theory with data on large masses of liquid metals is almost impossible.

One approach to the problem of measuring the rate of homogeneous nucleation is to pass the liquid through fine filters prior to the rate studies in order to remove catalytic particles. It is known that the frequency of nucleation in filtered samples often is much smaller than in unfiltered ones.[8, 9] However, the method is not promising for the investigation of nucleation in metal samples. Because of the relatively rapid growth rate of metal crystals, a nucleus originating at a single catalytic site can quickly transform a very large mass of liquid.

A method of eliminating the effects of nucleation catalysis that appears more promising for liquid metals is to break the sample into a number of non-communicating droplets that is large in comparison with the number of catalytic sites. This technique has recently been used to study the solidification behavior of a large number of pure metals.[1, 2]

Data on the isothermal rates of solidification of small droplet aggregates of tin[10] and mercury[11] at several temperatures are now available. The temperature dependence of the nucleation frequency is so great that it was easily measurable only in narrow ranges of temperature corresponding to 59 to 63° supercooling for mercury and 100 to 115° for tin. Analysis of the data showed that $A = 10^{30.4}$ for tin and $10^{30.9}$ for mercury. Considering the theoretical and experimental uncertainties these numbers are in good agreement with the value for $A \approx 10^{33}$ calculated from the theory of homogeneous nucleation but considerably larger than the value 10^{25} to be expected if nucleation were catalyzed by a film coating the entire surface of all the droplets. Thus it appears that the conditions for homogeneous nucleation were closely approached in these experiments.

Because of the sharp temperature dependence of the nucleation frequency shown in these experiments (for mercury, I changed by a factor of 10 in $1\frac{1}{2}$°C), it is possible to specify a narrow range, δ, of supercooling ΔT_- such that the nucleation frequency is practically zero when $\Delta T_- < \delta$ and immeasurably fast when $\Delta T_- > \delta$. On the basis of these results it is expected that crystals would be formed at a measurable rate in small droplets of other metals within a comparatively narrow temperature band characteristic of the metal. Microscopic observations of the solidification of small droplets (10 to 100 micron diameter) of many other metals confirmed this expectation.[2]

A maximum supercooling $(\Delta T_-)_{\max}$ was found for each pure metal corresponding to a temperature at which the nucleation frequency becomes appreciable. Not all droplets supercool as much as $(\Delta T_-)_{\max}$ but under suitable conditions a large fraction do. For most metals $(\Delta T_-)_{\max}$ is of the order of 0.18 times the absolute melting temperature, T_0. Also, it is found that $(\Delta T_-)_{\max}$ is reproducible (±5 percent) and not dependent upon the source of the metal in cases where this factor was varied.

SIZE EFFECT IN NUCLEATION

According to the critical size concept, the frequency of homogeneous nucleation of crystals, I_v, in droplets of volume v is

$$I_v = Iv, \tag{3}$$

where I is given by Eq. (1). From the results on mercury and tin I_v may be calculated for any volume of liquid metal or alternatively the amount of supercooling (ΔT_-) at which the rate of nucleation becomes appreciable in droplets of a given size can be calculated as a function of the volume. For example, mercury droplets 4 microns in diameter were found to solidify[11] with a frequency of about 10^{-5} sec.$^{-1}$ at $\Delta T_- = 60$. From the rate equation it was calculated that nuclei should form with the same frequency in a mercury droplet 1 cm^3 in volume at a supercooling $\Delta T_- \sim 49°$. Since similar relations for the rate of nucleation are expected to be valid for other substances it is inferred that large continuous masses of liquid metals (of the order of 1 cm^3 in volume) *completely free of catalytic inclusions* and *not subjected to mechanical vibration* should supercool about

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[7] D. Turnbull, A.S.M. Symposium on Thermodynamics, Cleveland (1949).

[8] J. Meyer and W. Pfaff, Zeits. f. Anorg. Chemie **217**, 257 (1934).

[9] V. I. Danilov and V. Neumark, J. Exp. Theor. Phys. (U.S.S.R.) **10**, 942 (1940).

[10] B. Vonnegut, J. Colloid Sci. **3**, 563 (1948).

[11] D. Turnbull, J. Chem. Phys. **18**, 768 (1950).

0.8 of the maximum supercooling observed in small droplets $(\Delta T_-)_{\max}$, before solidification.

In agreement with this view, large continuous masses of liquid have been supercooled occasionally almost as much as small droplets. For example, comparatively large masses of gallium,[1] water,[12] and iron[13] have been supercooled more than 0.73 $(\Delta T_-)_{\max}$.

The fact that continuous liquid masses 1 cm^3 or more in volume rarely supercool more than $\sim 0.05\ (\Delta T_-)_{\max}$ is consistent with the viewpoint that the probability of finding accidental inclusions effective in promoting crystal nucleation is much greater in large than in small masses. This probability should increase either as the volume or surface area of the droplet so that, for example, the chances of finding one accidental inclusion in a 1 cc mass of mercury is about 10^{11} times greater than the chance of finding an inclusion in a 4 micron droplet separated from it. Thus, it appears that the known facts about the supercooling of small droplets and large masses of liquid metals are adequately accounted for on the basis of the critical size concept.

THERMAL HISTORY EFFECT IN SOLIDIFICATION

It has been fairly well established that the thermal history dependence of the nucleation frequency usually observed in the solidification of large continuous liquid masses is due to catalytic inclusions and container walls.[4,5] It follows that the nucleation frequency of small droplets should not be thermal history dependent provided that the catalysts responsible for the effect are in fact segregated in a small proportion of the droplets. This prediction has been verified by experiments on bismuth.[1] The nucleation frequency in large continuous masses of bismuth has been shown to be very dependent upon thermal history[14] but in small droplet aggregates it is independent of thermal history.[1]

From the facts that the nucleation frequency of lead crystals in sulfate-coated droplets, though increased by the catalytic effect of the film, is apparently not dependent on thermal history, it may be inferred that the presence of nucleation catalysts is a necessary but not a sufficient condition for thermal history dependence. On the basis of the micro-cavity theory of the effect,[5] the following conditions should be fulfilled in order for a thermal history effect to be observed:

1. Suitable microcavities be present in the catalytic surface. These microcavities retain small crystals above the melting temperature, but in order to be effective their diameter has to be very small (*ca.* 10^{-6} cm).
2. The substance must penetrate and fill the microcavities.
3. The contact angle θ made by the crystal with the catalytic surface when immersed in liquid should be less than 90°.

ALTERNATIVE INTERPRETATIONS OF THE SUPERCOOLING OF SMALL DROPLETS

In the foregoing it has been established that the known facts about nucleation of crystals in liquids can be explained satisfactorily on the basis of the "critical size theory." It remains to be considered whether any alternative hypotheses might explain the phenomena as well.

The basic fact to be accounted for is the long waiting period prior to the rapid growth of large crystals. Apart from the critical size hypothesis such a result might be explained if very small crystals, assumed to be stable, grow into supercooled melts at a rate many orders of magnitude less than do large crystals.

Two hypotheses that could lead to such an effect are thought worthy of serious consideration. First, it might be assumed that crystals need to have some type of imperfections in their surface in order to grow rapidly. Conceivably the probability that small crystals contain such imperfections might be much smaller than for

TABLE I. Summary of data on supercooling of small droplets.

Metal	T_0	Entropy of fusion $(\Delta H_f/T_0)$	$(\Delta T_-)_{\max}$	Reference	$(\Delta T_-)_{\max}/T_0$	$[(\Delta T_-)_{\max}/T_0]^{\frac{2}{3}} \times [(T_0-\{\Delta T_-\}_{\max}/\Delta H_f]^{\frac{1}{3}}$
Mercury	234.3	2.38	58	11	0.247	0.268
Gallium	303	4.42	76	1	0.250	0.218
Tin	505.7	3.41	105	10	0.208	0.216
Bismuth	544	4.60	90	1, 2	0.166	0.154
Lead	600.7	2.04	80	1	0.133	0.196
Antimony	903	5.28	135	2	0.150	0.154
Aluminum	931.7	2.74	130	2	0.140	0.183
Germanium	1231.7	4.94	227	2	0.184	0.177
Silver	1233.7	2.19	227	2	0.184	0.232
Gold	1336	2.27	230	2	0.172	0.222
Copper	1356	2.29	236	2	0.174	0.222
Manganese	1493	2.31	308	2	0.206	0.243
Nickel	1725	2.43	319	2	0.185	0.224
Cobalt	1763	2.08	330	2	0.187	0.239
Iron	1803	1.97	295	2	0.164	0.224
Palladium	1828	2.25	332	2	0.182	0.223
Platinum	2043	2.30	370	15	0.181	0.226
Water	273.2	5.28	39	25	0.143	0.149

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[12] R. Smith-Johannsen, Science **108**, 652 (1948).

[13] Bardenheur and Bleckman, Stahl u. Eisen **61**, 49 (1941).

[14] W. L. Webster, Proc. Roy. Soc. **140A**, 653 (1933).

TABLE II.* Interfacial energies between various crystal nuclei and the corresponding liquid calculated from frequency of nucleation in small droplets.

Metal	Crystal structure	Interfacial energy σ ergs/cm^2	σ_g Cal./g atom	$\sigma_g/\Delta H_f$	σ_g/T_0
Mercury	Hexagonal	24.4	296	0.53	1.32
Water	Hexagonal	32.1	461	0.32	1.69
Gallium	Orthorhombic	55.9	581	0.436	1.91
Tin	Tetragonal	54.5	720	0.418	1.47
Bismuth	Rhombohedral	54.4	825	0.33	1.52
Lead	Face centered cubic	33.3	479	0.386	0.80
Antimony	Rhombohedral	101	1430	0.302	1.59
Aluminum	Face centered cubic	93	932	0.364	1.00
Germanium	Diamond	181	2120	0.348	1.71
Silver	Face centered cubic	126	1240	0.457	1.00
Gold	Face centered cubic	132	1320	0.436	0.99
Copper	Face centered cubic	177	1360	0.439	1.01
Manganese	Tetragonal	206	1660	0.480	1.11
Nickel	Face centered cubic	255	1860	0.444	1.08
Cobalt	Face centered cubic	234	1800	0.490	1.02
Iron	Body centered cubic	204	1580	0.445	0.88
Palladium	Face centered cubic	209	1850	0.450	1.01
Platinum	Face centered cubic	240	2140	0.455	1.05

* Heats of fusion and absolute melting points used in the computations summarized in Tables I and II are those recommended by K. K. Kelley ["Contributions to the Data on Theoretical Metallurgy. V. Heats of Fusion of Inorganic Substances," Bureau of Mines Bulletin No. 393 (1936)] with the exception of the heat of fusion of germanium (6100 cals/g atom) that was calculated by R. A. Oriani of this Laboratory from equilibrium data on the binary systems Ge-Au, Ge-Pb, Ge-Ag.

large crystals so that ΔF_A would be larger for the former. However, it is not easy to construct a model that would account for such a marked effect of imperfections upon growth rate unless the interfacial energy between liquid and crystal is quite large. Thus, dissociation of the imperfection and critical size hypotheses is difficult. A further difficulty with the imperfection hypothesis is that it does not account for the effect of specimen volume upon nucleation frequency.

The other hypothesis considered is that minute amounts of soluble impurities inhibit nucleation in some way. In the experiments on the solidification of small droplets[1,2] impurity concentrations were usually of the order of 0.001 to 0.1 atomic percent. It does not seem likely that such small concentrations of impurity could inhibit nucleation by causing the liquid-crystal interfacial energy to be increased. However, it is well known that minute quantities of impurity sometimes profoundly affect the macroscopic growth rate of crystals so it is conceivable that the growth of very small metal crystals in supercooled melts is practically stopped by such impurities.

Nevertheless, there are convincing arguments against this interpretation of nucleation during solidification. A mechanism whereby impurities effectively inhibit the growth of microcrystals but not macrocrystals is possible but complicated. In the small droplet experiments $(\Delta T_-)_{\max}$ was found to be independent, within experimental error, of the source and purity (within limits) of particular metals. Also it is important that the $(\Delta T_-)_{\max}$ values obtained by Turnbull and Cech[2] and Mendenhall and Ingersoll[15] on the metals common to both investigations are in close agreement. This consistency in the experimental data would not be expected if the rate controlling factor were inhibition by soluble impurities. Finally it appears that the wide difference in nucleation frequency for large and small masses of liquids cannot be explained on the basis of the inhibition hypothesis unless the critical size theory is also used. There is no reason why minor amounts of soluble impurities should be more effective in inhibiting crystal growth in small droplets than in large continuous liquid masses unless it is supposed that in the latter crystals are formed by a different mechanism such that their continued growth is not inhibited. It appears that the only other reasonable mechanism involves the catalytic action of insoluble impurities.

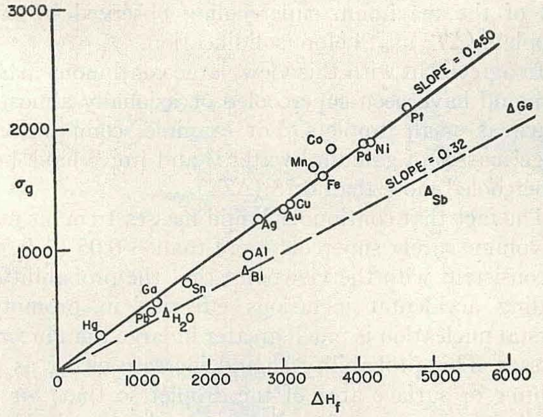

FIG. 1. Gram-atomic interfacial energy as a function of the gram-atomic heat of fusion for various substances.

In view of these arguments it seems that the known facts about nucleation of crystals in liquids can be interpreted much more satisfactorily on the basis of the critical size theory than in terms of either of the slow-growth hypotheses examined. The excellent correlations of the small droplet supercooling data to be presented in the following sections constitute a further decisive argument in favor of the critical size interpretation.

CORRELATIONS OF DATA ON SUPERCOOLING OF SMALL DROPLETS

The ratio of the maximum supercooling observed in small droplets to the absolute melting temperature, $(\Delta T_-)_{\max}/T_0$, is nearly a constant for many metals. These ratios for 50 micron diameter droplets of various metals are given in Table I. In calculating $(\Delta T_-)_{\max}/T_0$ for iron and manganese there is the problem that the metals solidify in temperature ranges in which the most stable crystal phase is different from that in equilibrium with the liquid at the normal melting point. It is not known which phase nucleates most rapidly in the liquid at the solidification temperature but it was assumed arbitrarily that the solid phase stable at the normal melting point nucleates first. The assumption can cause little error in the iron calculation since the difference in free energy between the face centered and body centered cubic phases is very small.

For all but six of the substances $(\Delta T_-)_{\max}/T_0$ is

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[15] C. E. Mendenhall and L. R. Ingersoll, Phil. Mag. **15**, 205 (1908).

≈ 0.185 with maximum deviations of ± 0.02. Considering all the data, the ratio ranges from 0.133 for lead to 0.250 for gallium.

When the implications of the approximate constancy of $(\Delta T_{-})_{\max}/T_0$ are examined in terms of the theory of homogeneous nucleation (see Eq. (1)) it is found that the ratio would be constant if σ were proportional to the gram atomic heat of fusion, ΔH_f, and if the entropy of fusion $(\Delta H_f/T_0)$ were constant. Entropies of fusion of metals are approximately 2.3 cal./deg.×g atom but there are some marked deviations from this value (e.g. 4.4 for Ga). These considerations suggested that a deeper insight into the phenomena might be gained by comparing σ directly with ΔH_f.

Values of σ were calculated from the nucleation frequency at one temperature and Eq. (1) with the aid of the following assumptions:

1. Crystal nuclei are spherical in shape so that $K=16\pi/3$.
2. $\mathrm{Exp}(-\Delta F_A/kT)=10^{-2}$.
3. The entropy of fusion is independent of temperature.

The validity of these assumptions has been discussed elsewhere.[7] It follows from 3 that

$$\Delta F_V=\lambda\Delta T/T_0, \tag{4}$$

where λ = heat of fusion/cm^3 and $\Delta T = T - T_0$. It is believed that the available data are in general not sufficiently accurate to justify the use of a more precise free energy function. From the assumptions and Eq. (1)

$$\sigma=[\{3\times 2.303\lambda^2(\Delta T)^2kT/16\pi T_0{}^2\} \times\log(nkT\exp\{-\Delta F_A/kT\}/Ih)]^{\frac{1}{2}}. \tag{5}$$

I is estimated to be $10^{-(1\pm 1)}$ sec.$^{-1}$ per 50-micron particle at the maximum supercooling. Although the uncertainty in I is very large, a factor of 10 error in its value introduces an error of only 1 percent in the calculated σ.

Since ΔH_f is a gram-atomic quantity it should be compared with a gram-atomic surface energy σ_g, which may be defined as the free energy of an interface containing Avogadro's number, N, atoms. If the area of such an interface is A,

$$\sigma_g=\sigma A. \tag{6}$$

Let it be assumed arbitrarily that the interface is one atom thick and let V be the gram-atomic volume; then,

$$A=N^{\frac{1}{3}}V^{\frac{2}{3}}, \tag{7}$$

where a structure factor of the order of unity is neglected. This treatment is analogous to that of Skapski[16] on liquid-vapor interfaces. Substitution of (7) into (6) gives:

$$\sigma_g=N^{\frac{1}{3}}V^{\frac{2}{3}}\sigma. \tag{8}$$

σ_g has been calculated for all of the substances whose solidification was studied by the small particle technique and the resulting values expressed in calories/gm atom are given in Table II.

Calculated ratios of σ_g to ΔH_f (see Table II) are fairly constant, ranging from about 0.31 for antimony to 0.53 for mercury. It is interesting that $\sigma_g\approx\frac{1}{2}\Delta H_f$ for one class of substances and $\approx\frac{1}{3}\Delta H_f$ for a smaller class. This difference is shown in Fig. 1 where σ_g is plotted against ΔH_f. The points for the more metallic substances (Class I) fall (within the experimental error) on a straight line of slope 0.45. Points corresponding to water and the semimetallic elements (antimony, bismuth, and germanium) (Class II) fall on a second line of slope 0.32.

Correct evaluation of σ_g depends upon the validity of the theory of homogeneous nucleation. There is an empirical correlation upon which the success of the correlation of σ_g with ΔH_f is based. This relation is:

$$[(\Delta T_{-})_{\max}/T_0]^{\frac{2}{3}}[\{T_0-(\Delta T_{-})_{\max}\}/\Delta H_f]^{\frac{1}{3}}=M, \tag{9}$$

where M is constant for a class. M is equal to (see Table I) 0.222 ± 0.01 for Class I and 0.158 ± 0.01 for Class II.

The greater success of the $\sigma_g/\Delta H_f$ correlation relative to that of $(\Delta T_{-})_{\max}/T_0$ is in part illusory since the most important empirical factor (see Eq. (9)) leading to the success of the former is $[(\Delta T_{-})_{\max}/T_0]^{\frac{2}{3}}$. However, when this is corrected for, the $\sigma_g/\Delta H_f$ correlation is still the better of the two and in addition it appears to be more promising from a theoretical standpoint.

It is noted that the point for aluminum (see Fig. 1) on the σ_g *vs.* ΔH_f curve falls considerably below the Class I line on which it would seem to belong. Probably the most reasonable explanation of this disagreement is that surface films that may have catalyzed nucleation of aluminum crystals were not completely eliminated in the experiments.[2]

INTERPRETATION OF GRAM-ATOMIC INTERFACIAL ENERGIES

It is not surprising that mercury, tin, and the metals having cubical crystal structures fall into a distinct class with respect to solidification behavior. The four substances in Class II have the property of expanding upon solidification. In addition, their crystal structures are relatively more complex than the substances of *I* and excepting water over certain ranges of temperature they are all semiconductors. However, gallium exhibits all these properties yet it certainly falls in Class I. It is, of course, possible that the separation into two classes is more apparent than real. Perhaps the elements of Class II did not supercool the maximum amount for some unknown reason (in order to belong to Class I bismuth droplets should supercool 130° compared to the 90° observed) or approximations necessary in calculating σ_g may have caused misleading results. Nevertheless, the separation may be intrinsic for reasons not now apparent.

The parameter σ can be identified with the interfacial

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[16] A. S. Skapski, J. Chem. Phys. 16, 386 (1948).

energy between small crystal nuclei and liquid but it is important to know whether or not it corresponds to the interfacial energy between large crystals and their melts. Any such correspondence or lack of it can only be established by measurement of σ for large crystals. However, there is some indirect evidence that σ may not be markedly dependent on crystal size. The interfacial energies between liquid nuclei and vapor calculated from the nucleation rates[17, 18] measured by Volmer and Flood[19] are in good agreement with the values measured directly on extensive liquid surfaces. Apparently decreasing the size of liquid droplets to the dimensions of nuclei has little effect upon vapor-liquid interfacial energies.

Consider now the interfacial energy between adjacent crystals of widely different orientation σ_B (i.e., grain-boundary free energy). It follows that at equilibrium $\sigma_B \leqslant 2\sigma$ at the melting point of the substance. Fisher[20] has found σ_B between adjacent copper crystals of very different orientation to be about 535 ergs/cm^2 at 800°C. σ for copper solid-liquid is calculated from nucleation data to be 177 ergs/cm^2. Considering the experimental and theoretical uncertainties the numbers are not inconsistent with the condition that $\sigma_B \leqslant 2\sigma$.

It has been assumed in making the calculations that the nuclei are spherical i.e., that σ is independent of crystal orientation. There is some experimental justification of an indirect nature supporting this assumption. It has been found[21] that the microstructures of two phase lead-copper alloys equilibrated at relatively high temperatures can be interpreted satisfactorily by assuming that the liquid lead-solid copper interfacial energy is independent of the orientation of copper crystals. A number of other microstructures in two-phase alloys have been explained on the basis of analogous assumptions.

Recently it has been shown[22] that the interfacial energy between differently oriented adjacent crystals of silicon ferrite is practically independent of the orientation difference providing it is not very small or not of such magnitude that the orientations approach a twin relationship. When the orientations are very different it appears that the grain boundary should be highly disorganized so that the transition region between the grain boundary and adjacent crystal should be somewhat similar in nature to a liquid-crystal boundary. Thus, independence of grain boundary energy upon the orientation of the abutting crystals is a point in favor of the hypothesis that liquid-crystal interfacial energies for metals are isotropic.

Although the facts that have been presented do not prove that σ or σ_g values calculated from nucleation rates can be identified positively with the free energy of extended liquid-crystal interfaces it is believed that they afford substantial credibility for this identification.

EFFECT OF CRYSTAL STRUCTURE

It is well known that large masses of liquid metals that crystallize to close packed structures rarely can be supercooled more than 3 to 10 degrees while large masses that crystallize to more complex structures often can be supercooled much more. These facts have led to the concept[9] that the failure of large masses of the former class to supercool is an inherent property that is explained by the similarity in structure between close-packed crystals and their melts.

However, in view of the evidence that crystallization in large masses of all liquid metals is catalyzed by impurities, the facts are accounted for as well when it is assumed that effective catalysts for the nucleation of close-packed crystals occur much more frequently than those effective in the nucleation of crystals having more complicated structures.

Experiments on the supercooling of small droplets seem to have verified the latter theory. Small droplets of metals such as cobalt, silver, or nickel that crystallize to a cubical close-packed structure have been supercooled about as much relative to their melting points as have droplets of substances such as bismuth or tin that crystallize to more complex structures.

The arguments in favor of the concept that liquids crystallizing to close-packed structures should supercool much less than those crystallizing to more complicated structures hinge upon the idea that because of the structural similarity between the liquid and crystal[23] the interfacial energy between them should be small. This idea is quite reasonable, but by the same argument the heat of fusion, and therefore the free energy decrease in forming close-packed crystals should be and is small relative to that accompanying the formation of non-close-packed crystals.

Since it appears that σ_g is directly proportional to ΔH_f for most metals the effect of crystal structure upon supercooling behavior is but a reflection of its effect upon ΔH_f within one class of substances. However, additional insight into the effect of crystal structure upon σ_g can be gained by comparison of the σ_g/T_0 values listed in Table II. These ratios are roughly in the order of complexity of crystal structure and range from 1.91 for gallium to 0.80 for lead.

FURTHER IMPLICATIONS OF SMALL DROPLET RESULTS

The relation between σ_g and ΔH_f that has been found is analogous to similar relations between liquid-vapor

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interfacial energies and heats of vaporization.[16] It suggests that analogous relations exist for liquid-crystal interfacial energies of classes of substances other than those studied in these investigations and in other types of phase transformations. For example, the interfacial energy between two solid phases in solid-state transformations of a certain class might turn out to be proportional to the heat of transformation. Unfortunately, not much effort has been made to minimize possible nucleation catalysis in solid-solid reactions so it is not known to what extent the results now available have been affected by this factor. It may be possible in some instances to minimize this factor by applying the small particle technique to solid-state reactions.

Finally, it appears that one of the most promising fields of further research in phase transformations will be that of seeking what generalizations can be made about the chemical and structure relations between nucleation catalysts and the phase that is nucleated. Already considerable progress has been made in this direction by Vonnegut[24] and Schaefer[25] on the catalysis of ice nucleation.

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