

THE SUPERCOOLING OF AGGREGATES OF SMALL METAL PARTICLES

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Aggregates of small metal droplets of mercury, bismuth, gallium, and lead have been supercooled to a much greater extent than have large continuous liquid masses of the same metals. These results are interpreted on the basis that breaking a large liquid mass into small droplets isolates inclusions that usually catalyze nucleation in a small fraction of the droplets so that most must nucleate homogeneously.

R ECENTLY it has been shown that aggregates of small liquid droplets of tin,¹ mercury² or gallium² kept from intercommunicating by suitable films do not solidify at an appreciable rate unless the supercooling is very much greater than that usually necessary to cause a large continuous mass of the metal to solidify. For example oxide-coated tin droplets¹ (1 to 10 micron diam) must be supercooled 100° to 110°C before their rate of solidification becomes rapid, although large continuous masses of liquid tin usually begin to solidify when supercooled 30° or less.³

These experiments have been interpreted² on the hypothesis that nucleation of crystals in large continuous metal samples is almost always catalyzed by accidental inclusions. Therefore, if the metal is dispersed into a number of isolated droplets large in comparison with the number of inclusions, most of the droplets should not crystallize until a temperature sufficiently below the thermodynamic melt-



Fig. 1—Low (a) and high (b) temperature dilatometers.

ing point, T_{o} , has been reached to permit an appreciable rate of homogeneous (noncatalyzed) nucleation. In general this temperature is very much less than the temperature at which the rate of heterogeneous (catalyzed) nucleation is appreciable. If this interpretation is correct then investigation of the kinetics of crystallization of small droplet aggregates should be one of the most fruitful methods of obtaining information about the homogeneous formation of crystal nuclei in liquids.

In this paper the results obtained on gallium and mercury are reported more fully. In addition, results on the supercooling of aggregates of liquid bismuth and lead droplets are included.

Experimental Procedure

Some care must be exercised in the choice of a barrier to prevent the liquid droplets from coalescing lest the barrier itself catalyze the formation of crystal nuclei. From this standpoint, the most desirable barrier is vacuum or inert gas, but, because of the difficulty of experimental arrangement, solid compounds and adsorbed films have been selected. There are two guiding principles in the selection of compounds as barriers in addition to the requirement that they prevent coalescence of liquid droplets. First, the compound should be almost insoluble in the liquid metal and second, its lattice structure should be quite unlike that of the forming metal crystal. Even so, there is no a priori assurance that the solid compound film will not catalyze to some extent the formation of metal crystal nuclei. An adsorbed protective monolayer is less likely to be catalytic than a crystal compound film, but it is not often possible to find a monolayer that is stable under the experimental conditions. Also, it is desirable, though not generally essential, that the aggregate of droplets be prepared by breaking up the massive metal rather than from a powdered compound of the metal.

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The sources and purity of the metals used in this investigation are given in table I. Aggregates of gallium or mercury droplets were prepared by manually shaking the molten metal in the appropriate solution. To form the droplet aggregates coated with sodium oleate, the solution used was 95 pct ethyl alcohol saturated with sodium oleate. A solution of $\frac{1}{2}$ g of iodine per 100 cc of 95 pct ethyl alcohol served to disperse mercury droplets and coat them with an iodide film. The resulting droplet sizes are given in table I.

A film of bismuth oxide was formed on bismuth particles by heating the powder in air for 1 hr at 125°C.

Lead "chloride" or "sulphate" coatings were formed by treating the powder with one half normal solutions of the corresponding acids. The particles were then filtered, washed with alcohol, and heated in an oven at 125°C to drive off moisture. Lead iodide coatings were formed similarly excepting that an alcoholic solution of iodine and acetic acid was used instead of the aqueous acid solution. It seems likely that the lead surface coatings were basic salts rather than the normal salts.

Dilatometry, Low Temperature

A typical dilatometer employed in the lowtemperature work on gallium and mercury is shown in fig. 1*a*. The dilatometer fluid used was 95 pct ethyl alcohol. The liquid level in the capillary was read to ± 0.02 cm by means of a cathetometer. The dimensions of the dilatometer and size of the samples were chosen so that the liquid level changed 3 to 6 cm upon solidification and so that readings could be taken from temperatures well above the melting point to well below the solidification temperature.

Temperatures were determined from measurements with a G.E. thermocouple potentiometer of the potentials developed by a copper-constantan thermocouple. Above dry-ice temperature, a constant temperature bath containing trichlorethylene and controlled by a bimetallic thermoregulator was used. The coolant, acetone at dry-ice temperature, was pumped through a copper coil immersed in the bath. For below dry-ice temperature, the bath arrangement that proved most satisfactory consisted



Fig. 2—Bath used in low temperature experiments.

of a well insulated can containing freon 11 entirely surrounded (except for outlets) by a controlled bath of the same fluid, as shown in fig. 2. The external bath was cooled by liquid nitrogen circulated in copper coils.

Dilatometer readings were taken as a function of temperature through a cooling-heating cycle that began and terminated above the thermodynamic melting point and that extended to the temperatures of complete solidification. In cooling, the bath was held at a given temperature until the dilatometer reading remained constant for an appreciable period before the temperature was again lowered. After solidification, the sample was warmed at a constant rate of approximately 1°C per min. With this heating rate the temperature of the sample differed from that of the bath by only a fraction of a degree excepting while melting took place.

High Temperature

Fig. 1b is a sketch of the high-temperature dilatometer. Para (mp 212°C, bp 376°C) or meta (mp 86°C, bp 363°C) diphenyl-benzene proved satisfactory as dilatometer fluids for the lead and bismuth

Table I. Source, Purity, and Droplet Size of Metals Investigated

| Metal | Source | Purity, Wt Pet | Initial Form | Pro- tective Film | Particle Size Range, (Micron) | Diam of Particle Having Mean Volume, (Micron) |
|-----------|---------------------|-------------------|-----------------|---|--|--|
| Mercury | Triple distilled | 99.9999 + | Liquid | Adsorbed sodium oleate | 50-500 | 200 |
| Land Star | | | | Mercuric iodide | 2-100 | 50 |
| Gallium | Eagle- Picher | 99.94 | As cast | Sodium oleate adsorbed on gallium oxide | 50-300 | 200 |
| Bismuth | Eimer & Amend | 99.999 | Powder | Bismuth, oxide | 4-12 | 10 |
| Lead | Eimer & Amend | 99.95 | Powder | Lead { iodide, chloride, or sulphate | 2-20 | 17 |



Fig. 3—Fraction of iodide-coated mercury particles solidified as a function of amount of supercooling (ΔT_{-}) .

respectively. During the measurements, 1½ atm pressure of nitrogen or helium was maintained in the dilatometer in order to prevent cavitation. An electrically heated, 32 mil nichrome wire wound around the fluid reservoir and capillary caused the diphenyl-benzene to remain liquid.

Temperatures were obtained by a Woods metal bath heated in a vertical nichrome wound furnace, and a chromel-alumel couple was used in temperature measurement. Dilatometer readings were taken as a function of temperature in a cooling-heating cycle during which the temperature was changed continuously (1° to $\frac{1}{2}$ °C per min) both in cooling and heating. Close agreement between bath and sample temperatures, excepting during melting and rapid solidification, was confirmed by the fact that cooling and heating curves coincided within the experimental error when the metal was completely melted or solid.

Thermal Method

For measuring the temperature at which the major part of the transformation took place, the thermal method proved more convenient, though as applied, less accurate than the dilatometric method. One junction of a copper-constantan thermocouple was placed in a thermocouple well embedded in the sample that was contained in an evacuated pyrex tube, and the other was placed in a well in the



Fig. 4—Dilatometer readings vs. temperature on aggregate of mercury particles coated with sodium oleate.

Woods metal bath. The ends of the copper wires were connected to a G.E. portable high sensitivity (10^{-9} amp/mm) galvanometer that thus registered deflections proportional to the temperature difference between the sample and the bath.

Galvanometer readings were taken as a function of temperature during a heating-cooling cycle that was scheduled in the same way as in the dilatometric experiments.

Results, Mercury

Fig. 3 shows the percent of iodide-coated mercury particles transformed, calculated from dilatometric data, as a function of the supercooling, ΔT_{-} . Appreciable solidification begins at $\Delta T_{-} = 43$ but most takes place at $\Delta T_{-} = 46$ (-85°C). These results were reproducible for a given sample and for others prepared in the same way.

Quantitative measurements of the isothermal rate of solidification are being made now. However qualitative experiments have indicated that the fre-





quency of solidification of iodide-coated droplets changes by a factor of at least 10 per 1°C in the range -82° to -85° C. For example, in one experiment no transformation was perceptible in a sample for a period of 1 hr at -82° , but it solidified completely within 1 min at -85° .

Fig. 4 shows dilatometer reading as a function of temperature during a cooling-heating cycle for an aggregate of droplets dispersed in alcoholic sodium oleate. Most of the transformation takes place at $\Delta T_{-} = 39$, but it is interesting that the rate at ΔT_{-} = 33 is much more rapid upon quenching from ΔT_{\perp} = 39 than upon cooling from the melting temperature. In view of the results with iodide-coated particles, these phenomena cannot be accounted for in terms of slow growth of mercury crystals at ΔT_{\perp} = 39. Rather, since the droplets often agglomerated upon melting, a reaction in which the film becomes no longer protective (possibly due to precipitation or discharge of adsorbed ions) is indicated. If the film no longer prevents welding at $\Delta T_{-} = 39$, the sample could be completely solidified by nuclei formed heterogeneously.

Gallium

Fig. 5 shows the fraction of an aggregate of gallium droplets solidified as a function of ΔT_{-} . Transformation begins at $\Delta T_{-} = 70$ (-40°C) and is completed at $\Delta T_{-} = 82^{\circ}$ (-52°).

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Fig. 6—(a) Dilatometer reading vs. temperature in cooling heating cycle of oxide-coated bismuth powder (b) fraction of bismuth solidified as a function of supercooling (ΔT_{-}).

Solidification of some continuous 1-g samples of gallium sealed in evacuated quartz tubes was followed by the thermal method. When the maximum temperature, T_m , attained in the liquid state after melting was only a few degrees above the melting point, T_o , ΔT_- was a function of thermal history (i.e., ΔT_- proportional to $T_m - T_o = \Delta T_+$). However, ΔT_- was independent of ΔT_+ for values of the latter ranging between 50° and 1000°C. Values of ΔT_- corresponding to solidification of various 1-g samples for which $\Delta T_+ = 50$ are indicated in fig. 5 by asterisks. The values were characteristic of each sample and ranged between 30° and 56°. The supercooling of these specimens was very sensitive to mechanical vibrations. Vigorous manual shaking sometimes decreased the characteristic ΔT_- by about 15°.

Bismuth

Dilatometer readings obtained in an experiment on the solidification of bismuth powder are plotted against temperature in fig. 6a. The fraction of the sample solidified, calculated from these data, is shown as a function of the supercooling in fig. 6b. Although there is perceptible solidification at ΔT_{-} as small as 65°, the major part of the sample (more than 70 pct) transforms at $\Delta T_{-} = 90$.

For the experiment just described $\Delta T_{+} = 9^{\circ}$. In a second experiment for which $\Delta T_{+} = 2.5$ the major part of the sample again solidified at $\Delta T_{-} = 90^{\circ}$ and observations' confirmed this for values of ΔT_{+} as large as 100°.





These experiments show that the marked thermal history dependence of solidification temperature observed by Webster⁵ on large continuous bismuth samples is entirely absent in small particles that solidify at the maximum supercooling. From this result it may be concluded that the thermal history phenomenon in solidification generally is not inherent in the properties of the substance itself but is connected with extraneous influences.

It was established that the temperature coefficient of the solidification frequency of bismuth droplets is also very large. For example one sample of bismuth droplets was cooled slowly to $\Delta T_{-} = 86^{\circ}$ then heated slowly to $\Delta T_{-} = 46^{\circ}$ and held there for 12 hr. Upon subsequent slow cooling no perceptible solidification took place until $\Delta T_{-} = 90^{\circ}$.

Lead

Fig. 7 shows the fraction of "iodide" coated lead particles solidified as a function of ΔT_{-} as calculated from dilatometric data. Essentially the same curve was obtained from two experiments. The major part of the sample crystallized in the range $\Delta T_{-} = 55^{\circ}$



Fig. 8—Supercooling (ΔT_{-}) of lead particles with different surface coatings.

to 65° but a small significant fraction does not crystallize until the sample is quenched to $\Delta T_{-} > 80^{\circ}$.

The course of solidification of chloride-coated lead powder was followed by the thermal method. In fig. 8 the galvanometer deflection (proportional to amount of solidification) is plotted against ΔT_{-} . The major fraction of the sample solidified in the same range as the iodide-coated powder in the dilatometric experiments (i.e. $\Delta T_{-} = 55^{\circ}$ to 65° C). A small fraction appears to solidify in the range $\Delta T_{-} = 80^{\circ}$ to 90° C although the evidence is less definite than in the dilatometric experiments. This curve was very reproducible and independent of ΔT , values ranging from 15° to 55°.

Although most of the particles crystallized around $\Delta T_{-} = 60$ in the two sets of experiments, the temperature of appreciable homogeneous nucleation is believed to be in excess of 80° supercooling because of the dilatometric evidence. If this be so, then the crystallization that took place at $\Delta T_{-} = 60^{\circ}$ must have been catalyzed either by some heterogeneities within the particle or by surface films. In order to impart the property to the films of preventing the particles from coalescing when liquid, it was necessary to heat the aggregates at 100°C in air before

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the experiments. Therefore it seems reasonable to suppose that the films consisted of basic lead halide.

Definite evidence of nucleation catalysis by surface films was found in the thermal experiments on "sulphate"-coated lead powder. Fig. 8 shows galvanometer deflections as a function of supercooling in one of these experiments. Two definite peaks were observed and their presence and location checked in several experiments. One of them centers at $\Delta T_{-} = 20^{\circ}$ and the other at $\Delta T_{-} = 47^{\circ}$ and both are well above the temperature range at which the major part of the "chloride" and "iodide" coated samples crystallized. Essentially the same results were obtained for $\Delta T_{+} = 15^{\circ}$ or 55° .

Since the particle size distribution was identical in the several sets of experiments, the most reasonable interpretation of the results seems to be that the products of a reaction between lead and the sulphate coating (possibly PbO or Pb₂O and PbS) catalyze the formation of lead crystals. Apparently nucleation was catalyzed by two major substances in the film. The most effective of these could have been in contact with the metal in only a fraction of the particles else the entire sample would have crystallized around $\Delta T_{-} = 20^{\circ}$.

These results are reminiscent of those obtained by Wang and Smith⁶ on the solidification of tin particles in an aluminum matrix and suggest that the solidification behavior of an aggregate of droplets may be described conveniently in terms of a number distribution curve with respect to solidification temperature. It is evident that the particles dc not distribute themselves uniformly with respect to solidification temperature but tend to fall within certain discrete narrow bands of temperature each of which is perhaps associated with the catalytic action of a particular impurity.⁷

Discussion of Results

Table II summarizes the data on supercooling that were obtained in this investigation. In this table, the maximum supercooling observed on small particles is compared with the maximum reported on large continuous samples by various investigators. Generally, the amount of supercooling of small particles is very much greater than that of the large continuous samples. However, it is an important fact that in gallium, which has the most complex crystal structure of the metals studied, the disparity is not so great (76° to 55°).

| Table II. Summ | ary of | Supercooling | Data |
|----------------|--------|--------------|------|
|----------------|--------|--------------|------|

| Metal | | Diam of | Msximum Supercooling °C(∆T_) | | |
|---------|---|--|------------------------------------|-------------------------------------|----------------|
| | Protective Film on Small Particles | Particles Having Mean Volume, (Micron) | Small Par- ticles | Large Con- tinuous Samples | <u>∆T_/T</u> ₀ |
| Mercury | Sodium oleate 400 39 | | 4 | 0.20 | |
| | Mercuric iodide | 50 | 46 | - | 0.20 |
| Gallium | Sodium oleate+ gallium oxide | 200 | 76 | 55 | 0.25 |
| Bismuth | Bismuth oxide | 10 | 90 | 30* | 0.165 |
| Lead | ead Lead iodide+ Lead oxide | | 80 | 3* | 0.13 |

There is good evidence that the rate determining step in the solidification of small particles is not the growth but the nucleation of crystals. For example, in continuous 1-g samples of gallium supercooled to $\Delta T_{-} = 35^{\circ}$ to 55° , the crystal growth rate after the nucleation period was too rapid to measure and was certainly greater than 1 cm per sec. It might be expected that metal crystals having more simple structures than gallium would grow into their melts with even greater rapidity at comparable supercooling.

Also, it is an important fact that mild mechanical vibrations that have such a marked effect in promoting the crystallization of the larger continuous gallium samples have no observable effect upon the course of small particle solidification.

Summary

Aggregates of small particles of liquid mercury, gallium, bismuth, and lead were supercooled to temperatures that are respectively 0.80, 0.75, 0.84, and 0.87 of the absolute melting temperature before the rate of crystal nucleation became appreciable. This amount of supercooling is much greater than usually observed on large continuous samples.

The rate determining step in the solidification of small particle aggregates is not the rate of crystal growth but the rate of crystal nucleation.

These results can be interpreted satisfactorily if it is supposed that the effective crystal nucleation catalysts usually present in large continuous specimens are isolated on a small fraction of the resulting particles when the specimen is broken up.

There is no thermal history effect upon the solidification behavior of the major fraction of liquid bismuth small particle aggregates.

It has been demonstrated that lead sulphate films are more effective in catalyzing the formation of lead crystals than are the lead halide films. Two welldefined temperature ranges of solidification were found in the sulphate-coated lead powder. It is believed that each of these ranges is associated with the catalytic action of a specific product of the reaction between liquid lead and lead sulphate.

Although the solidification of large continuous gallium samples is promoted by mild mechanical vibrations, these have no observed effect upon the solidification behavior of small particle aggregates.

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