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MICROSCOPIC OBSERVATION OF THE SOLIDIFICATION OF SMALL METAL DROPLETS

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Microscopic Observation of the Solidification of Small Metal Droplets

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The solidification behavior of small metal (10 to 100 micron diameter) droplets has been observed on a high temperature microscope stage. An abrupt change in surface appearance and in the case of high melting metals a sudden brightening ("blick") accompanies solidification. The solidification temperatures observed for a collection of droplets may be widely distributed, but a significant, usually the major, fraction of the droplets supercool some maximum amount $(\Delta T_-)_{max}$ that is reproducible and characteristic of the metal. For many metals $(\Delta T_-)_{max} \approx 0.18$ times the absolute melting temperature. $(\Delta T_-)_{max}$ is not much changed by wide variations in the cooling rate and droplet size. The growth rate of metal crystals is very great so that the solidification rate of the droplets is controlled by the nucleation frequency.

INTRODUCTION

IN another article[1] it was pointed out that if a metal specimen is broken up into a large number of isolated parts catalysts for crystal nucleation may be localized in a small fraction of the particles. Thus, in most of the particles crystal nucleation must take place homogeneously. In that investigation the solidification behavior of entire aggregates of particles was followed. An alternative procedure that is often advantageous is to remove a small number of particles from an aggregate and observe their solidification behavior microscopically. This is done by placing them in a stage recently designed by one of us[2] for microscopic observation at elevated temperatures. If only a small fraction of the particles contain nucleation catalysts there is a high probability that most of the ones selected for microscopic observation will be free of them. This principle has guided the present investigation.

A distinct advantage of the microscopic method of observation is its adaptability to the study of metals which melt at very high temperatures as well as medium and low melting point metals. Thus, it becomes possible by the use of one experimental technique to compare the solidification behavior of many metals.

For a long time[3] it has been known that small particles of liquid gold supercool significantly before solidification. A sudden brightening or "blick" occasioned by the liberation of the heat of fusion (recalescence) is known to accompany the solidification of the supercooled particle. This phenomenon is observed in the assaying of gold.

Mendenhall and Ingersoll[4] have observed this phenomenon in a number of other high melting metals including platinum, palladium, silicon, rhodium and iridium.

In their experiments metal particles 50 to 100 microns in diameter were supported on a Nernst glower in air or a CO_2 atmosphere, the solidification being observed microscopically. Particles of the same metal often solidified at widely different temperatures but the amount of supercooling, ΔT_-, was considerable and appeared to be roughly proportional to the melting point of the metal. However, the actual numbers for the maximum ΔT_- were given for only two of the metals, platinum and rhodium—370°C for both. These results of Mendenhall and Ingersoll were incidental to an investigation of another topic and their significance does not seem to have been realized.

In the current investigation the supercooling of many metals has been observed directly and the phenomenon studied in detail.

EXPERIMENTAL

In addition to its ease of adaptation to observation of metals having wide variety in melting temperature the microscopic method has the further advantage that particles isolated from one another on the hot stage do not require a film on their surface to prevent coalescence. It has been pointed out that[1] any crystalline protective film on the surface of a metal particle is undesirable in these experiments since it may catalyze crystal nucleation. On the other hand there are certain definite disadvantages of the method that must be recognized.

[1] D. Turnbull (to be published).
[2] R. E. Cech (to be published).
[3] A. D. Van Riemsdyk, Ann. Chim. Phys. **20**, 66 (1880).

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

In producing aggregates of particles or in transferring them to the stage it is possible for nucleation catalysts to be picked up. Also, the particles, though free of crystalline films, must be supported on the stage and the possibility exists that the supporting surface or certain areas of it might catalyze crystal nucleation. In order to minimize this possibility, flakes of freshly blown quartz or pyrex glass were used as the supporting surface. These glass flakes, being amorphous, would not be likely to catalyze crystal nucleation. Another disadvantage of the microscopic method is that vibrations probably are more likely to promote solidification of small particles on a rigid supporting surface than particles in the interior of an aggregate. Sometimes these vibrations can be minimized by floating the particle in a suitable liquid flux.

MATERIALS

The source, purity, form, and method of preparation of particles are summarized in Table I. When the metal was supplied in the form of rod or wire small particles were made either by crushing with a mortar and pestle if brittle or by chipping with a sharp fragment of pyrex if ductile. Nickel particles and one sample of copper particles were formed from wire (fabricated from form listed in Table I) by means of a metallizing spray gun and the particles collected on a clean surface. These particles and those of other metals particularly susceptible to oxidation probably contained considerably more oxide than would be inferred from the purity listed. These metals were always given an *in situ* treatment with pure hydrogen in order to remove oxygen prior to observations of solidification. Different lots of some metals were obtained from two or three independent sources and the source designation used in the presentation of results is indicated in the table.

MICROSCOPE STAGE

Full details in the design of the microscope stage used in this investigation will be published in another paper.[2] A rough sketch is given in Fig. 1. The sample to be investigated was supported on a $\frac{1}{4}$-in. wide and 10 mil thick strip of molybdenum or platinum that was heated electrically.

Temperature was controlled by the amount of current passing through the ribbon heater and was varied by means of a variac transformer operated from a constant voltage source. By maintaining a constant power input
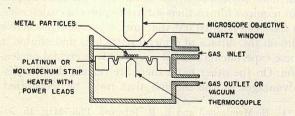
TABLE I. Source and purity of metals used in this investigation.

Metal	Source designation	Company	Purity (percent)	Form
Selenium		Johnson-Matthey	99.92	Shot
Bismuth	A	Eimer and Amend	99.999	Powder
	B	Johnson-Matthey	99.999	Rod
Lead	A	National Lead Co.	99.995	Ingot
	B	Eimer and Amend	99.95	Powder
Antimony		Johnson-Matthey	99.92	Ingot
Aluminum		Eimer and Amend	99.97	Powder
Germanium		Eagle-Picher Co.	99.99	Pellets
Silver		Handy and Harmon	99.97	Powder
Gold	A	Eimer and Amend	99.98	Powder
	B	Handy and Harmon	99.96	Wire
Copper		Amer. Smelting and Refining Co.	99.999	Rod
Manganese		Johnson-Matthey	99.99	Electrolytic sheet
Nickel		Int. Nickel Co.	99.98	Pellets
Cobalt		Johnson-Matthey	99.99	Powder
Iron		Nat'l Radiator Co.	99.99	Powder
Palladium		Amer. Platinum Works	99.95	Wire

into the heater it was possible to keep the temperature constant to $\pm 5°$ for long periods of time. The maximum temperature attainable was limited by the melting point of the heater metal. The stage is vacuum tight and its atmosphere (hydrogen, helium, or vacuum) is controlled by the indicated gas inlet. Temperature was calculated from the e.m.f. developed in an 0.005-in. diameter thermocouple welded to the underside of the heater. This e.m.f. was measured with a General Electric thermocouple potentiometer. The thermocouple was calibrated to read the temperature of the particles by accepting the known melting point of the metal as the standard. Deviation from the nominal temperature determined from standard calibration charts was usually +2 percent at the melting point. Solidification temperatures were corrected by assuming the deviation to be a linear function of temperature. A chromel-alumel thermocouple was used for temperatures below 1200°C and a platinum-platinum 10 percent rhodium thermocouple for temperatures greater than this. A new thermocouple was used for each specimen placed in the stage in order to prevent cumulative contamination from evaporation and condensation of the metals investigated. The error in the measured supercooling due to uncertainties in thermocouple and potentiometer calibrations and potentiometer readings is estimated to be ± 5 percent at most.

PROCEDURE

Figure 2 shows the two types of experimental arrangements that proved most satisfactory. In (a) the heater has two bends or stirrups that were introduced to

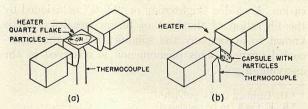FIG. 1. Microscope stage with flat strip heater.

FIG. 2. Experimental arrangements used in investigation.

increase the effective length so that the temperature of the center horizontal section would be more uniform. This section supported a quartz flake on which a number of metal particles were placed for observation. In (b) a few metal particles were placed in the quartz capsule $\frac{1}{32}$-in. diameter by $\frac{1}{4}$-in. long which in turn was placed inside the single stirrup. A much larger number of particles could be observed at one time in arrangement (a) than in (b) in which the number was limited to 3–5. On the other hand, in (b) the temperature was very uniform along the length of the capsule and the calibration of the thermocouple more closely approximated that of the standard calibration charts. Also, (b) was much more satisfactory than (a) for observing volatile melts since in the latter arrangement the quartz window became fogged due to condensation of metal vapors on it. A new heater was used for each metal investigated in order to prevent contamination of the particles from condensation of metals accumulated in the heater during previous experiments.

An atmosphere of pure hydrogen, helium, or argon was maintained in the stage (excepting in the few instances that it was evacuated) during observations. Tank hydrogen was purified by passing it over a train consisting of a sulfuric acid bubbling tower and ascarite predryer, a copper chip furnace deoxidizer and a final dryer having dryerite and a liquid air trap. Tank helium or argon was forced through a purification train of two calcium chip furnaces in series operated at 550°C and 350°C.

In some of the experiments with metals melting at high temperatures Pyrex glass powder was mixed initially with the particles to provide a liquid coating during the solidification observations. It was thought that a liquid flux would cushion the particles against vibration and carry away or react with accidental crystal nucleation catalysts that might be present on the particle. However, it was demonstrated that the
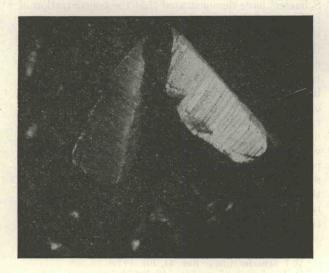

FIG. 3. Gold particles chipped from ingot. 25°C. 75×.

presence of a flux is not essential to the behavior to be described.

Melting and solidification of metals having melting points below 1000°C were inferred from the abrupt change of the surface condition of the particles that accompanied the processes. Upon initial melting, the particle lost its irregular shape and became spherical. Oblique illumination caused a bright spot or ribbon of light to be reflected from its mirror-like surface. When solidification occurred the rapid crystal growth in the particle caused a disruption of the smooth surface to one apparently having many sharp ridges and protrusions. These surface changes are illustrated in photomicrographs showing gold particles originally chipped from the ingot (Fig. 3), melted (Fig. 4), and solidified (Fig. 5). Melting and solidification temperatures were determined by association with the corresponding surface changes.

Solidification of metals having melting points greater than 1000°C was detected by the blick accompanying it. The initial melting of the particle permitted a thermocouple calibration as the particle became spherical. A further calibration was obtained by finding the maximum thermocouple e.m.f. that could be reached such that the particle did not blick upon cooling from the corresponding temperature. This e.m.f., which agreed within experimental error with that accompanying the initial shape change, was assumed to be that characteristic of the thermodynamic melting temperature. It was necessary to use filters for visual observations above 1100°C.

The melting and solidification temperatures of copper, gold, and germanium were measured by both the surface change and blick and the comparative results of the two methods are in complete agreement. Also, the maximum supercooling of bismuth particles (90°C) measured by observation of the surface changes is in close agreement with the value (90°C) determined dilatometrically by Turnbull.[1] In view of these facts there can be little doubt that the observed surface changes are caused by melting and solidification and that the blick observed in high temperature experiments is caused by solidification.

Particle diameters of the metals observed ranged from 10 to 100 microns excepting that some germanium particles were 400 microns in diameter. With the highest magnification that could be used, 240 diameters, it was not possible to detect the solidification temperature of particles smaller than 10 to 15 microns with certainty.

To determine the solidification temperature, the particles on the stage were cooled by decreasing the current through the strip heater. At intervals the cooling was interrupted and the thermocouple potentiometer exactly balanced and the e.m.f. recorded. The solidification temperature was taken to be that corresponding to the lowest exactly measured e.m.f. at which the particle was still liquid. Of the order of five minutes time usually elapsed in cooling from the melting point to the solidifi-
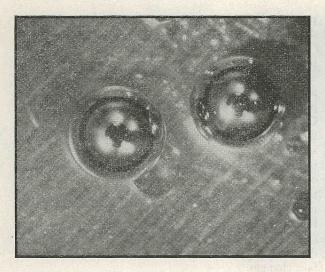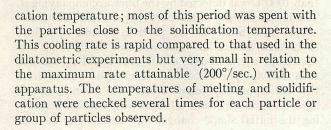
Fig. 4. Gold particles molten. 1070°C. 75×.

Fig. 5. Gold particles after solidification. 830°C. 75×.

cation temperature; most of this period was spent with the particles close to the solidification temperature. This cooling rate is rapid compared to that used in the dilatometric experiments but very small in relation to the maximum rate attainable (200°/sec.) with the apparatus. The temperatures of melting and solidification were checked several times for each particle or group of particles observed.

RESULTS

In general, the solidification temperatures of pure metal particles observed in a group ranged between the melting temperature, T_0, and some minimum temperature, T_{min}. The results could be represented in terms of a number distribution curve relative to solidification temperatures or degrees of supercooling ΔT_-, where $(\Delta T_-)_{max} = (T_0 - T_{min})$.

Depending upon the metal and circumstances (e.g., surface films) the number distribution of solidification temperatures sometimes had a maximum at $\Delta T_- \to 0$ (this is not certain for metals studied by the blick procedure since a blick cannot be certainly detected for $\Delta T_- < 25$), or at $\Delta T_- \to (\Delta T_-)_{max}$ or at some intermediate value of ΔT_-, and occasionally was fairly uniform so that no maximum was apparent.

It is an important fact that the solidification temperatures of a particular particle were not randomly distributed between $\Delta T_- = 0$ and $(\Delta T_-) = (\Delta T_-)_{max}$ throughout successive melting-solidification cycles but remained fixed for at least several and usually all such cycles. Occasionally the solidification temperature, after remaining nearly constant for several cycles, did shift abruptly to some other value and remained there in a series of succeeding cycles. This behavior is analogous to that of the one g continuous gallium samples described in a preceding paper.[1]

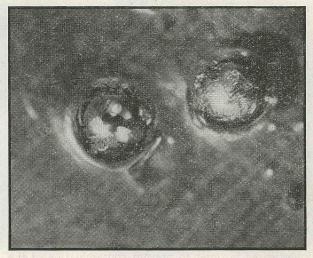As noted before the sizes of the particles observed generally were between 10 and 100 microns. From a statistical standpoint the solidification temperature of smaller particles tended to be less than that of larger ones. However, it is significant that the solidification behavior of particular particles often deviated consistently from this generalization. Thus, 10-micron particles were occasionally observed to solidify at the melting temperature while 50-micron particles solidified at $\Delta T_- \approx (\Delta T_-)_{max}$ throughout several melting-solidification cycles.

It appears reasonable to attribute the great differences in the solidification behavior of individual particles to the influence of minute quantities of accidental impurity particles. It is quite probable that colloidal particles suspended in the atmosphere and capable of serving as crystal nucleation catalysts become lodged in the quartz surface or on the surface of the metal particles during the assembly and operation of the microscope stage. (The experiments of Vonnegut[5] and Schaefer[6] have demonstrated that the concentration of colloidal material that can be effective in promoting the formation of snow is fantastically small.) Further, the abrupt change sometimes observed in the solidification behavior of particular particles can be attributed to the capture or dislodgement of a minute amount of impurity. A priori these impurities could either promote or inhibit solidification. However, there is much justification for the belief that such impurities promote crystal nucleation. This evidence has been summarized elsewhere[7] and will be discussed more fully in a following paper.[8] For the present purpose it will be assumed that minute impurities catalyze solidification. It follows that the only solidification temperature that could be characteristic of uncatalyzed solidification is $(\Delta T_-)_{max}$. For this reason only the maximum supercooling $(\Delta T_-)_{max}$

[5] B. Vonnegut, J. App. Phys. 18, 593 (1947).
[6] V. J. Schaefer, Chem. Rev. 44, 291 (1949).
[7] D. Turnbull, J. Chem. Phys. 18, 198 (1950).
[8] D. Turnbull (to be published).

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TABLE II. Summary of results of microscopic observations on supercooling of small droplets.

Metal	Source	Melting point °K (T_0)	Method of observation	Atmosphere	Flux	Particle size (microns)	Maximum super-cooling $(\Delta T_-)_{max}$	$(\Delta T_-)_{max}/T_0$
Selenium		493	Surface change	Hydrogen	None	75	25[a]	0.051
Bismuth	A	544	Surface change	Hydrogen	None	10–15	90	0.166
	B	544	Surface change	Hydrogen	None	20–50	90	
Lead	A	600.7	Surface change	Hydrogen or vacuum	None	15–50	67	0.151
	B	600.7	Surface change	Hydrogen	NaOH+KOH	10–20	69	
Antimony		903	Surface change	Hydrogen	None	15–30	135	0.150
Aluminum		931.7	Surface change	Hydrogen	None	50–100	48	
			Surface change	Hydrogen	NaOH	50–100	130	0.140
Germanium		1231.7	Surface change+blick	Helium	None	15	235	0.184
					Pyrex	400	219	
Silver		1233.7	Surface change	Helium	Pyrex	20–40	227	0.184
Gold	A	1336	Surface change+blick	Helium or vacuum	Pyrex	20–50	221	0.172
	B	1336	Surface change+blick	Helium or vacuum	None	40–50	230	
Copper		1356	Surface change+blick	Hydrogen or helium	None	15–50	236	0.174
Manganese		1493	Blick	Hydrogen	Pyrex	50	308	0.206
Nickel		1725	Blick	Helium	Pyrex	50–100	319	0.185
Cobalt		1763	Blick	Helium	None	20–50	330	0.187
Iron		1803	Blick	Helium	None	30–100	295	0.164
Palladium		1828	Blick	Helium	None	30–100	332	0.182

[a] Corresponds to maximum supercooling that could be reached such that crystallization did not occur on re-heating.

that could be reproduced under various conditions will be listed in the results.

The results are summarized in Table II. Values of $(\Delta T_-)_{max}$ determined in different atmospheres or in vacuum agreed within experimental error. The $(\Delta T_-)_{max}$ listed is the average value. Absolute melting temperatures of the metals listed in column 3 are from Kelley's[9] compilation.

FRACTION OF PARTICLES SUPERCOOLING MAXIMUM AMOUNT

In general the major fraction of metal particles melting at temperatures more than 950°C (Ge through Pd) did not solidify until supercooled to or nearly to $(\Delta T_-)_{max}$. Particles of source (A) gold constituted an interesting exception to this behavior. Without any Pyrex flux none of the particles were observed to supercool more than about 40°C. In the presence of the flux the supercooling was larger and a significant fraction supercooled to $(\Delta T_-)_{max}$. On the other hand the major fraction of gold particles chipped off gold wire (source B) supercooled to $(\Delta T_-)_{max}$ either with or without flux. The difference in the behavior of these two samples appears to confirm the principle set forth in an earlier publication[1] that crystal nucleation catalysts are more likely to be absent in metal particles freshly formed by breaking up a massive piece of metal than in particles formed "separately" or that have been permitted to

[9] K. K. Kelley, Bureau of Mines, Bulletin No. 393 (1936).

accumulate catalytic dust on their surfaces for long periods. Another factor that might account for the difference is that the particles of source A gold actually observed were coalesced from several of the original particles which by themselves were too small for their solidification to be detected by the microscopic method. Thus, in effect more surface having the possibility of holding catalytic dust went into source A particles than into source B particles.

The distribution of particles of low melting metals with respect to solidification temperature had some interesting aspects and will be considered separately.

EFFECT OF ATMOSPHERE

Whenever a high melting metal having an oxide stable at the melting point was studied pure hydrogen was passed over the heated particles for some time and the melting and solidification temperatures were observed concurrently. After this the stage was flushed with pure helium and solidification observations were made in this atmosphere. When results were obtained for both atmospheres those for helium have been put in the table for the reasons that (1) hydrogen is significantly soluble in some of the metals and (2) e.m.f.'s of the platinum platinum-rhodium couple are not reproducible when the junction is in a hydrogen atmosphere. However, the maximum supercooling in the two atmospheres did not differ by as much as the uncertainty of the measurements.

It is significant that the supercooling of copper par-

ticles fabricated with a metallizing spray gun increased by about 100° after having been treated in hydrogen at 1000–1100°C for about 15 min. This may indicate that Cu_2O that formed in the fabrication process catalyzes the formation of copper crystals. Further evidence in favor of this view is that copper particles chipped from the original rod that supercooled the maximum amount in hydrogen or helium did not supercool significantly when the atmosphere was changed to air at low pressure.

The solidification of iron particles that had been hydrogen treated, evacuated, and sealed off in a quartz capsule also took place at the same temperature as in a helium atmosphere.

ALUMINUM

As received, the aluminum particles had a rod-like form that persisted in the liquid state due to the rigidity of the oxide skin. When placed on a quartz leaf with no flux practically all of these particles supercooled $48 \pm 2°C$. The solidification range was so narrow that there was some temptation to assert that aluminum crystals nucleate spontaneously at $\Delta T_- = 48$. However, in order to test the possibility that solidification was catalyzed by the oxide film, observations were made on solidification in a molten sodium hydroxide "flux." Under these conditions the particles spheroidized but a surface film (possibly sodium aluminate) remained. However, after heating 200° in excess of T_0, the particles supercooled 120° to 130°. This result appears to demonstrate that aluminum oxide does in fact catalyze the nucleation of aluminum crystals possibly by the mechanism suggested by C. S. Smith.[10] Of course there is no assurance that the film remaining in molten sodium hydroxide does not also catalyze solidification.

LEAD

Particles of lead placed on a Pyrex leaf in a hydrogen atmosphere solidified at temperatures ranging from the melting point to 60–65° below it at which only a minor fraction crystallized. As already noted, however, the behavior of particular particles was constant throughout successive melting solidification cycles. When sodium hydroxide was used as a flux the fraction of particles solidifying at lower temperatures was greatly increased and a maximum supercooling of 69° was observed. On the other hand, in a flux consisting of a nitrate-nitrite mixture (56 percent KNO_3 and 44 percent $NaNO_2$) practically all the particles solidified at only 20–30° supercooling. A yellow film presumed to be lead oxide was present on the surface of the particles in the latter experiments. Thus, it seems likely that either lead oxide (PbO) or lead suboxide (Pb_2O) is a very effective catalyst for the crystallization of lead. Also it is interesting that the major fraction of source A particles supercooled to or nearly to $(\Delta T_-)_{max}$ with no

[10] C. S. Smith, J. of Metals **1**, 204 (1949).

flux when the stage was evacuated to a pressure of 0.01 mm of mercury.

The maximum supercooling obtained in these experiments is about the same order as the supercooling of the major portion of lead in dilatometric and thermal experiments described in a preceding paper but is more than 10° less than the maximum measured in dilatometric experiments. Also, excepting when a sodium hydroxide flux was used, the fraction of source B particles that supercooled to 55–65° was much smaller in the microscopic experiments than in the thermal and dilatometric ones. These results perhaps may be accounted for by the fact that the particles observed in the microscopic experiments were considerably larger on the average than those used in the dilatometric and thermal experiments and so had more opportunity to contain or pick up nucleation catalysts.

BISMUTH

Although a major fraction of source A oxide coated bismuth particles supercooled 90° in dilatometric experiments only a minor fraction (presumed not to be oxide coated) supercooled the maximum of 90° on the microscope stage. However, it is significant that more than one-half of the particles made by breaking up source B bismuth rod in a mortar and pestle did not solidify unless supercooled about 90°. This difference in behavior of source A and B particles observed microscopically cannot be accounted for on the basis of different particle sizes for the B particles were significantly larger than the A. On the other hand, it seems probable that the difference in behavior of A particles in the dilatometric and microscopic experiments can be accounted for by the fact that many of the A particles observed on the stage had formed by coalescence of several small particles. As a result of this process, the proportion of particles containing nucleation catalysts was larger.

It is also significant that the temperature of solidification of bismuth particles that supercooled the maximum amount was not a function of the maximum temperature reached in the range of liquid stability when this was 10 to 100° greater than the melting point. This fact coupled with the lack of thermal history dependence in the dilatometric experiments proves that the thermal history effect observed in the solidification of large continuous bismuth samples is not an intrinsic property of bismuth and must be due to some extraneous effect.

The most important result of these experiments on bismuth is that the same maximum supercooling, 90°C, was obtained by two independent methods and with bismuth particles from two sources.

CRYSTAL GROWTH RATES

With the exception of selenium all of the droplets that had supercooled considerably solidified in a time too short to estimate, even to an order of magnitude,

after a nucleus had formed. From these observations it can only be maintained that the linear growth rates were greater than 1 mm/sec. It seems likely that crystals with relatively more complex structures such as bismuth and germanium would grow into their melts much more slowly than cubic crystals but this could not be proved or disproved by these experiments.

The extremely short period of growth relative to the total time required for solidification of a particle proves that "nucleation" is the rate-determining step in the reaction. Here the term nucleation is used in the broad sense as referring to a period of very slow growth of small crystals relative to large for whatever reason.

In no case excepting selenium was it possible to form a "glass" from the metal particles by quenching directly from the melt. Liquid selenium particles cooled to room temperature without crystallization. However, the glass particles so obtained crystallized upon reheating to temperatures 100°C or greater.* By cooling rapidly to some given temperature below the melting point and reheating, it was established that selenium nuclei were formed when the supercooling was greater than 25–30°C.

KINETICS OF ISOTHERMAL SOLIDIFICATION

Up until now it has been tacitly assumed that it is possible to assign "solidification temperatures" to particular particles. Since solidification is a rate process some justification of this assumption is necessary. As has been pointed out already, qualitative observations of Turnbull[1] have indicated that the temperature coefficient of the solidification rate of small metal particles is so very great that the rate changes by several orders of magnitudes within a narrow temperature range. Thus, solidification will be observed to take place only within this narrow range for widely different rates of cooling from the melting temperature.

This was confirmed by some observations on gold and copper particles. Liquid gold particles were on several occasions held at temperatures 180 to 190° below their melting point for one to three hour periods

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* This agrees with prior observations of Apker and Dickey (private communication) on the crystallization of amorphous selenium films.

without solidification. They did not then solidify until cooled 230° below the melting point that corresponds to $(\Delta T_-)_{max}$ reported in Table II. Similar results were obtained with copper particles chipped from the rod.

DISCUSSION

The basic phenomena involved in the solidification of small metal particles now seem clear. In general, particles 100 microns or less in size can be supercooled to an extent far in excess of that ever attained on large continuous samples. Only for iron has a ΔT_- been reported[11] for a large continuous sample that is of the same order of magnitude (258°) as $(\Delta T_-)_{max}$ (295°) measured for small particles. For other metals having cubic crystal structures it has rarely been possible to supercool large continuous samples of the liquid more than 5–10°.

In an aggregate of metal particles the solidification behavior of individuals is quite specific and persistent but a significant fraction supercools some maximum amount $(\Delta T_-)_{max}$ that is reproducible and characteristic of the particular metal. The ratio of $(\Delta T_-)_{max}$ to the absolute melting temperature T_0 is 0.18 ± 0.02 (see Table II) for the metals studied having cubic crystal structures excepting lead and aluminum. (In making this calculation for iron and manganese, it was assumed that the crystal modification in equilibrium with the liquid at atmospheric pressure was nucleated although solidification in both instances takes place in a temperature range where a different crystalline modification is stable.) The lowest temperature of solidification of small particles is varied only a small extent with widely different rates of cooling from the melt and with changes in the particle volumes amounting to factors of 10^3.

The interpretation of these phenomena is to be given in a succeeding paper by one of us.[8]

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

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