Super Cooling

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VONNEGUT[1] has shown that an aggregate of very small droplets (1 to 10 microns) of liquid tin, separated by the oxide skin surrounding each particle, must be cooled 110 to 120°C below the thermodynamic liquid-solid transformation temperature before solidification proceeds rapidly.

We have made some observations on the rate of solidification of aggregates of mercury and gallium droplets. Collections of mercury droplets were prepared by dispersing mercury in solutions of sodium oleate in alcohol and in solutions of iodine in alcohol. In the latter, each mercury particle was coated with an iodide film. The particles averaged about 200 microns in diameter in the sodium oleate solution and about 50 microns in the iodine solution. The transformation was followed dilatometrically using alcohol as an indicator.

Starting about 20° above the melting point, T_m, samples were cooled about 10° an hour. After the transformation was completed the aggregate was slowly warmed through the melting temperature. Dilatometer readings were taken at close intervals in both the cooling and heating cycles. Mercury aggregates prepared by the first procedure did not show any measurable transformation until a temperature 33° below T_m had been reached. At this temperature the transformation was sluggish and probably confined to the larger particles. The rate of solidification became rapid at a temperature 39° below T_m. Aggregates held 22 degrees below did not transform after two hours.

Aggregates separated by the iodide film did not transform at a rapid rate until a temperature 46° below T_m had been attained. At 43° below T_m there was no appreciable transformation during a 1-hour holding period, except for 10 percent of the sample (probably the larger droplets) that transformed immediately.

Aggregates of gallium droplets were dispersed in alcoholic sodium oleate and the particles were about the same size as those of mercury in the same solution. The rate of solidification of gallium did not become appreciable until the gallium had been supercooled 70°C.

In Table I the maximum subcooling that has been obtained in bulk and in aggregates of small droplets are compared for tin, gallium, and mercury. It is interesting to note that the ratio T/T_m listed in the table, where T is the lowest absolute temperature to which the liquid has been subcooled, is roughly constant. Also shown in the table are liquid-solid interfacial energies σ calculated by the method of Fisher, Hollomon, and Turnbull.[2]

Calculations based on the theory of homogeneous nucleation[2] indicate that the increased subcooling attained by dispersing bulk samples into droplets cannot be accounted for by the decreased nucleation probability occasioned by decreasing the droplet size. Rather there is evidence that nucleation in bulk liquid samples is generally "catalyzed" at the surface of heterogeneties. In pure liquids these "nucleation catalysts" may be limited in number so that they are segregated on a small portion of the droplets when the sample is dispersed. These promote transformation only on the droplets in which they are localized. Transformation of particles containing no catalysts may occur by homogeneous nucleation which proceeds at measurable speeds at much lower temperatures.

TABLE I.

Metal	Maximum subcooling °C Bulk	Aggregates of small droplets	T/T_m	σ
Tin	31*	110**	0.78	65
Mercury	14*	46	0.80	23
Gallium	55	70	0.75	55

* Danilov and Neumark, Physik Zeits. Sowjet, union **12**, 313 (1937).
** See reference 1.

[1] Vonnegut, J. Colloid Science 3, 563 (1948).
[2] Fisher, Hollomon, and Turnbull, Science **109**, 168 (1949).

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