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ABSTRACT

We have quenched 10-20 mm drops of molten 75 w/o Si-25 w/o Fe alloy at about 1350 °C with catchers of steel, graphite, ice and in 1 m-deep water at four temperatures between 7 °C and 90 °C. The luminous drops in free fall were imaged by photographic and video techniques and, after cooling, were examined visually and gravimetrically. Chemical and physical reactions of the hot drops with the catchers were negligible.

The drops seemed to be immediately coated with a skin of solid when they contacted the water. Spontaneous steam explosions never occurred in the meter-deep liquid water at any temperature or in small water-filled cavities in ice. Recalescence could not be detected as an intensification of either the photographic or video records, suggesting little or no supercooling of the melt during quenching. The smaller particles seem to burn in hot water, possibly explaining the absence of smaller particles in the debris recovered from quenches in hot water.

The drops cool 4- or 5-times faster in cold water than in hot water. But in ice, they cool a bit more slowly than in our coldest water; thus, motion of the globules through the water is an important component of the heat transfer during the quenching.

If ice is used as a quencher, the penetration depth of a molten globule is only a few centimeters, facilitating video and photographic imaging and optical pyrometry. If the globule melts through a moderate thickness of ice before falling into water, its fall path will be “compressed.” Although quenching of the drops in ice does not exactly simulate the quenching in deep water, it might provide important differential information when varying, e.g., drop composition, temperature or diameter. Also, drop releases into water-filled cavities in ice would provide the subcooled water and confinement that favor initiation of spontaneous or triggered steam explosions.

INTRODUCTION

In certain industrial operations, it is desirable to release 10-20 mm-diameter drops of molten ferrosilicon (75 w/o Si, 25 w/o Fe, liquidus temperature approximately 1350 °C) into liquid water. Because drops of some molten metals (e.g., Sn and Pb) produce spontaneous steam explosions under conditions such as these, a research program was initiated to determine whether drops of molten ferrosilicon would explode similarly when released into water. This program was sponsored by SINTEF Materials Technology of Trondheim, Norway, and was performed at the University of Wisconsin-Madison.

From discussions with persons familiar with the industrial operations, it has been learned that in the production processes the drops of molten ferrosilicon are brightly luminous when released at or somewhat above the liquidus temperature. The drops fall a short distance in air and then enter quenching water, which is usually in rapid, turbulent motion. During several seconds and several meters of fall through the water, the luminosity decays as the drops cool and solidify. Apparently, the temperature of the water is quite important, affecting both the quality and texture of the solidified drops as well as the amount of smaller particles (fines) that remain after the quenching process. Also, it is not known whether spontaneous steam explosions can occur with any of the drops as they are quenched in the cooling water.

In the experimental program described in this report, we have learned how to produce 10-20 mm-diameter drops of the molten alloy in an inert atmosphere by a pendant drop technique, using a small, lightweight and inexpensive resistively heated furnace. The drops were released and allowed to fall into either solid catchers or into one meter-deep liquid water. Video and photographic imaging followed the progress of the incandescent drops as they cooled and the luminosity extinguished. Then the debris was collected from the solid or liquid quenchers for further examination. We also produced careful photographic records of the materials used and the debris generated in each experiment, as well as of the experimental setups. Thirty drop release experiments were performed: five with steel or graphite catchers, five with ice catchers and twenty with liquid water as the quenchant.

EXPERIMENTAL

Tower

The experiments described here were performed with the apparatus mounted in a 3 m-tall framework shown in Figure 1; it was assembled from commercial Unistrut beams and components. The tower was divided into three approximately one meter-tall segments: the furnace and the solenoid-operated drop release apparatus were mounted in the upper meter, the catcher in the central meter and the spill control container in the lower meter.

The furnace and drop release apparatus were mounted in a welded steel framework that was suspended on a trolley system from the top cross beams of the tower as shown in the schematic diagram in Figure 2 (photgraphs of this assembly are shown in Figures 3 and 4a, while the drop release solenoid is shown in

Figure 1. Photograph of the 3 m-tall tower in which the ferrosilicon drop release experiments were performed. The upper meter contains the trolley-mounted furnace and drop release apparatus. The center section contains the 1 m-deep water chamber. The lower meter is devoted to the spill control system. At the upper left of the tower is the optical pyrometer. Below it is the 60 A variable transformer, the power supply for the silicon carbide furnace element. On the floor at the left is the constant temperature water circulation bath. Above, at the far left, is the digital thermocouple readout for the meter-long Type E thermocouple that estimates water temperatures in the chamber. (C-57-1)

Figure 4b). The trolley system allowed us to start with the furnace and drop release apparatus at the right side of the tower before an experiment while we prepared the catcher and brought the furnace to the desired temperature, to move them to the left side, over the catcher, during an experiment and then to return them to the right side again after the experiment to allow us to retrieve the quenched drop and debris and remove or otherwise service the catcher.

Silicon Carbide Furnace

The central component of the apparatus is the simple and inexpensive resistively heated tube furnace that uses a helical silicon carbide heating element. This element operates in air with a maximum usable temperature of about 1675 °C. This maximum operating temperature is adequate to produce the molten ferrosilicon alloy with liquidus temperature of about 1350°C, and probably could be used to produce drops of both molten iron (melting temperature = 1535 °C) and molten silicon (melting temperature = 1410 °C) as well.

In addition to its simplicity and low cost, several other significant advantages of this furnace are its light weight and portability, its modest power supply and connectors, and its ability to operate at high temperatures for long periods without gas or water cooling. These features allow the furnace to be moved easily and mounted at various heights as desired. (These features should be compared to an induction furnace of similar capabilities.)

The furnace and the procedures for preparing the molten alloy drops have been briefly described by Nelson et al. (1996). Only a few minor modifications were made in the original unit, namely, the replacement of the silicon carbide element that fractured during testing for other applications, and the replacement of one of the firebricks that had cracked during the original experiments. (Cracking of firebricks did not occur in this round of experiments.)

(The replacement silicon carbide element, obtained from I Squared R Element Company, Akron, New York, has the “amps” designation of 25 marked on its side. This may be used in the empirical relationship supplied by the manufacturer, hot resistance = 52 volts / “amps” = 2.1 ohms. This empirical value is important to use in determining the current requirements for each element, which would have been significantly underestimated if the cold resistance of this element, 4.5 ohms, had been used.)

A ceramic tube is centered within the helical heating element to provide a controlled internal atmosphere in which to melt the alloy while allowing the element to operate in air and thus achieve the maximum operating temperature. (The maximum operating temperature is reduced sharply if the element is operated in either an inert or a reducing atmosphere.) The axes of both the element and the tube are vertical.

The temperature of the furnace is estimated by sighting on the silicon carbide element through a horizontal hole in the firebrick with a disappearing filament optical pyrometer. The optical pyrometer is designated as a Pyro Microoptical Pyrometer, Serial No. 7189.

Details of the construction of the furnace are shown in Figures A-5 through A-8 in Nelson et al. (1996) .

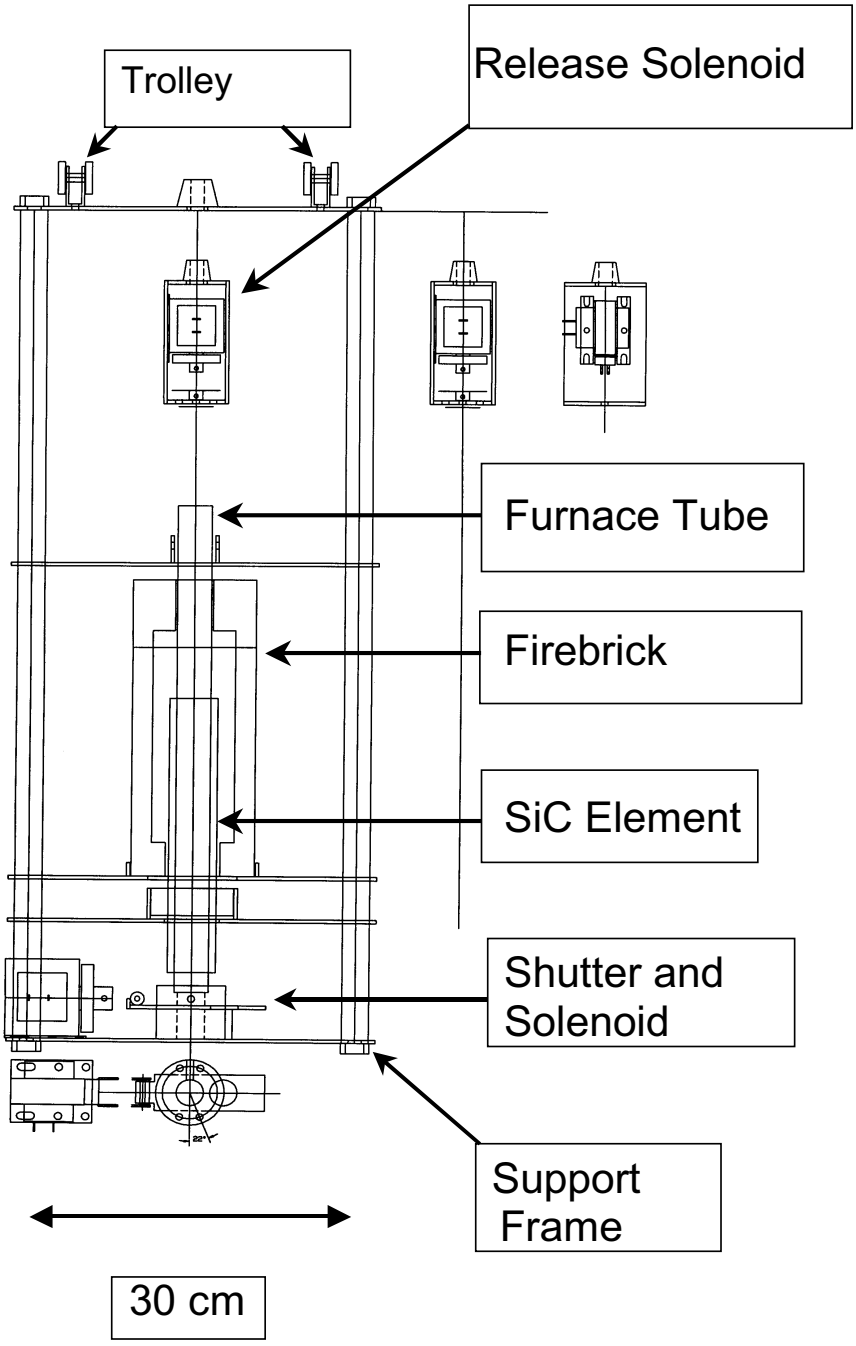

Figure 2. Schematic drawing of the furnace, drop release apparatus and trolley system used for generating single drops of molten materials.

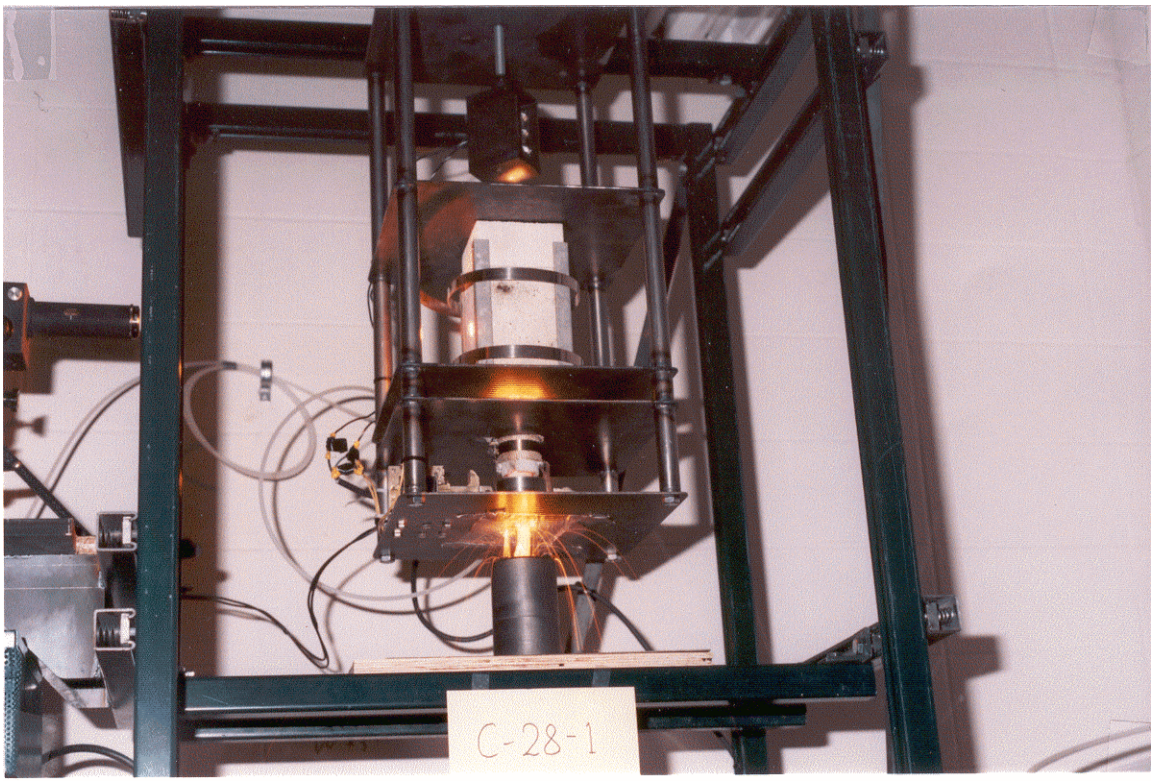

Figure 3. The furnace and drop release apparatus mounted in the welded steel framework that is suspended on a trolley system from the top cross beams of the tower. The photograph is a self-luminous time exposure that shows a molten ferrosilicon drop being released into a graphite catcher. Flash backup illumination was added after the experiment to show details of the experimental rig. (C-28-1)

Preparation of Drops of the Molten Alloy

The drops of molten alloy were prepared by lowering the bottom end of a 10 mm-diameter, nominally 100 mm-long ferrosilicon rod (details are given below) into the heated zone of the furnace. The atmosphere within the furnace consisted of upward flowing commercial cylinder argon, used without further purification. The argon was introduced into the apparatus through a hole drilled horizontally through the block that holds the mechanical shutter (see Figure 2). The upward flow of gas was maintained prior to the experiment by taping a thin polyvinyl chloride foil (Glad Cling Wrap, 0.13 mm-thick) over the lower end of the furnace tube; as the hot drop fell, the foil melted through and opened quickly, acting as a "fast-opening valve" to allow the hot drop to fall into the atmosphere of air below. The distance from the lower tip of the rod to the lower end of the furnace rig was about 22 cm.

A groove about 2 mm wide was made around the upper circumference of each rod with a tungsten carbide hacksaw blade. In this groove, Type 316 stainless steel wire was wound and twisted to produce a pair of "ears" from which the rod could be hung. The rod was then suspended from these "ears" on a length of Type 316 stainless steel wire, the upper end of which was attached to a vertically operating solenoid; the armature of the solenoid was usually activated from the "up" position when the wire was attached. The temperature of the heated zone was then adjusted to about 1525 °C before the rod was lowered into the furnace. The lower end of the rod was held in the heated zone for 15 minutes, during which time a pendant

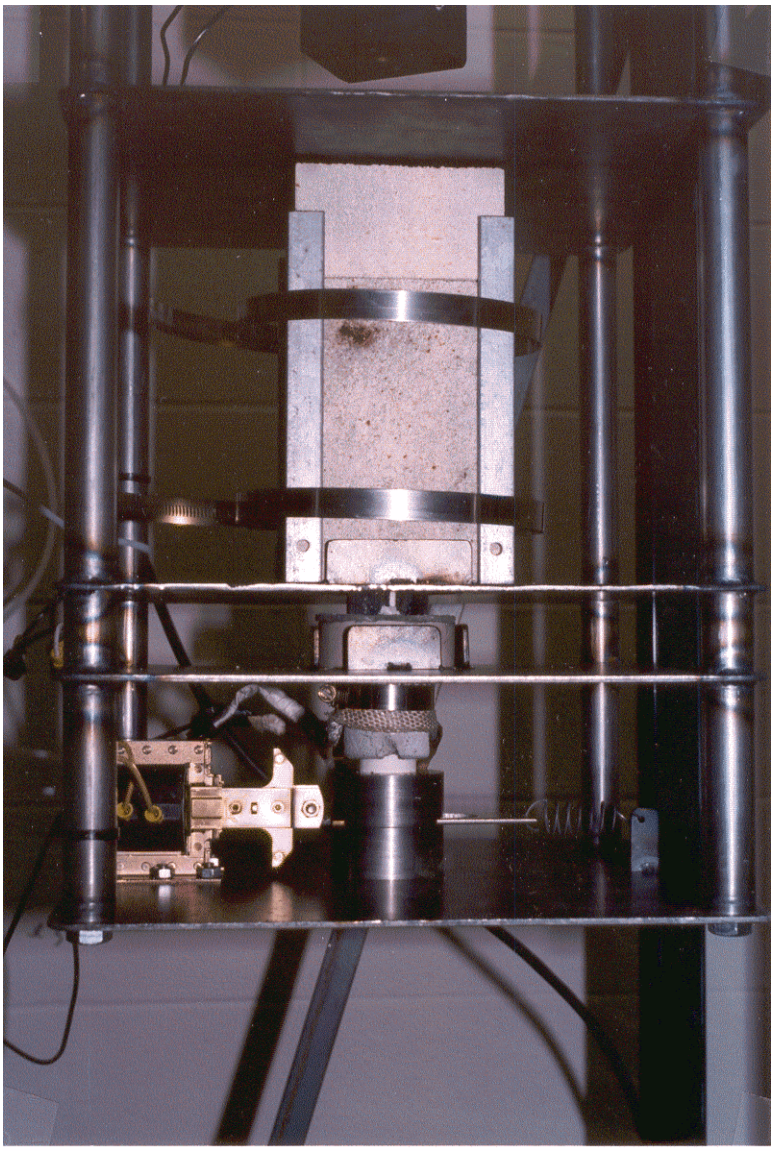

Figure 4a. Closer view of the furnace and drop release apparatus. The solenoid-operated mechanical shutter and the lower ends of the furnace tube and silicon carbide heating element are seen in the lowest section. The collar that supports the heating element is visible in the next to lowest section. The firebrick insulation can be seen in the upper section. The solenoid was very noisy and was replaced by a gas-driven piston in later experiments to avoid mechanically disturbing the molten ferrosilicon inside the furnace. (C-22-1a)

drop of molten alloy formed on the bottom end of the rod. At the desired release time, the solenoid was deactivated, allowing the armature and the rod to drop suddenly. This action usually caused a molten drop to detach reproducibly from the rod and fall downward through the furnace tube into the catcher below.

The ferrosilicon rods were taken from two batches—B-62-1 and C-34-1. Batch B-62-1 was received from Dr. Karl Forwald of Elkem Metals in September, 1995, while batch C-34-1 was received from Dr. Trond Bergstrøm of SINTEF Materials Technology in September, 1996. The approximate compositions supplied with these rods are given in Table 1.

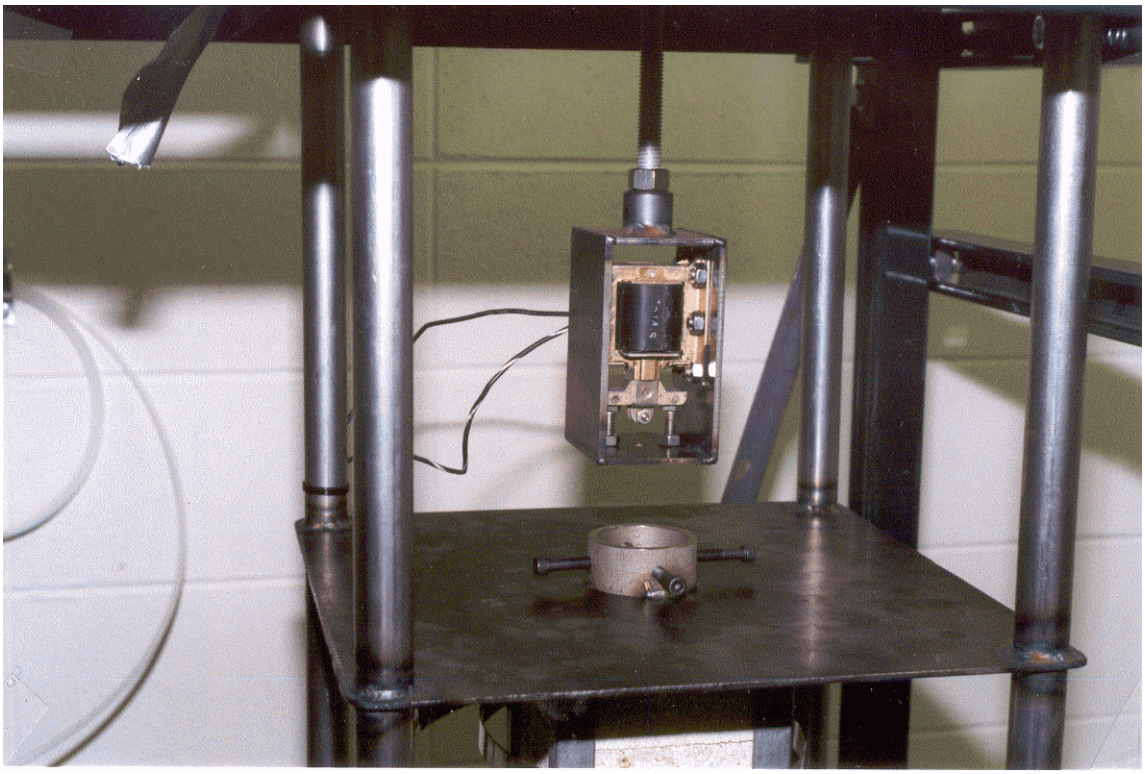

Figure 4b. Solenoid that raises and lowers the ferrosilicon rod inside the furnace. A Type 316 stainless steel wire is attached to the lower end of the armature and supports the rod. The stroke of the solenoid is adjusted with the two cap screws visible beneath the armature, which is in the "down" position. The four set screws in the collar below the solenoid are used to position the upper end of the furnace tube. (C-22-1b)

Table 1. Composition of Ferrosilicon Rods (Weight Percent)

Batch No.	B-62-1	C-34-1
Si	75.1	75.4
Fe	24.0	24.0
Al	0.76	0.37
Ca	0.025	0.014
Mn	NR	0.175
C	NR	0.0525
Ti	NR	0.0275

NR = not reported

Figure 5. Ferrosilicon rod that had been heated to about 1550 °C in a high alumina furnace tube before cooling to room temperature. The rod was kept in flowing cylinder argon at all times. Notice the powdery white deposit on the sides of the rod. Notice also the rosette of solidified melt near the right end of the rod. The scale immediately above the rod is divided in millimeters. (C-23-1)

Furnace Tubes

In the first three experiments, we attempted to use a 36 cm-long, 3.8 cm-OD high alumina ceramic tube as the furnace liner. These experiments, performed with the furnace nominally at 1525 °C, were disappointing because no drops seemed to form or detach. Instead, after they had cooled, we observed only a white powdery coating on the rods and no sign of melting (e.g., experiment C-23-1; see Figure 5). We had anticipated the furnace to perform better with the more costly alumina tube than with the relatively inexpensive mullite tube used in the preliminary testing (Nelson et. al., 1996, Appendix A).

Reluctantly, we returned to a mullite tube and, surprisingly, the drops formed and released with little difficulty as in the earlier work. Moreover, the black coatings observed on the rods after cooling to room temperature in argon were greatly reduced when the mullite tube was substituted for the alumina furnace tube. Although we did not study this further, we attributed the difference to an evolution of oxygen from the alumina tube at 1525 °C that was diminished or eliminated when the mullite tube was used.

Catchers

In this work, we used three solid catchers, graphite, steel and ice, and one liquid, water.

Solids

The graphite catcher was a cylindrical block with a cavity on the top surface; its axis was positioned vertically. The cylinder was 13 cm tall and 8.4 cm OD; the cavity was 4.5 cm ID and 7 cm deep with a flat bottom. A photograph of a molten ferrosilicon drop falling into the graphite catcher is shown in Figure 3.

The steel catchers were made from 3.2 mm-thick Type 1018 sheet. These catchers were used with either a flowing gaseous argon atmosphere or liquid water above their upper surface.

Ice

The ice was used in the form of blocks approximately 11 x 15 x 25 cm that weighed about 5 kg. The ice was of high optical clarity, of the sort used for restaurant ice sculpture. These ice blocks were obtained from the Hometown Ice Co., Madison, WI, as "party blocks." One, two or three blocks were stacked one on top of the other to produce the catcher. Holes a few centimeters in diameter and depth were drilled vertically downward in the upper surface of the uppermost block to catch the falling drops. These holes were usually filled with liquid water during the quenching experiments.

Liquid Water

In most of the experiments reported here, the molten materials were quenched in liquid water. Except for the situations just described where ice was used to hold the water, the water was contained in a chamber constructed from 12.7 mm-thick transparent polycarbonate sheet (Tuffak bisphenol A polycarbonate sheet from Autohaas North America, Philadelphia, PA; although of high optical clarity, this material has a distinct gray coloration). The inner dimensions of the chamber were 1 m-tall by 30.5 cm-square. The chamber was assembled by appropriately cementing together sheets of the plastic. The chamber was fabricated by Laird Plastics, Madison, WI. The chamber holds approximately 90 liters of water during an experiment.

The water used in these experiments was obtained from three sources at the University of Wisconsin-Madison: the Engineering Building (purified but of unknown treatment), the Nuclear Reactor (distilled) and from the tap in the Engineering Research Building (with a definite brown coloration). We also used water obtained from the Lindsay Water Company, Madison, WI (deionized). Unless visibly contaminated, several experiments were performed with the same filling of water. No attempt was made here to determine the effect of water purity on the quenching experiments.

The primary parameter varied in these experiments was the temperature of the water. We used four water temperatures, nominally 8, 22 (room temperature), 50 and 90 °C. When cold water was desired, three or four 5 kg blocks of ice were normally used to reduce the temperature of the water in a mostly filled chamber to about 5 °C. The cooling was accomplished by moving the blocks of ice up and down which vigorously stirred the water in the chamber as it reduced the temperature. Final adjustment of the temperature was achieved by alternately adding water or moving the blocks of ice. The temperature of the water was measured with a 1.3 m-long, 3.2 mm-diameter Type E thermocouple with a digital readout system.

When the desired temperature of the water was above room temperature, immersion heaters were used. Several units were tested initially, but we settled ultimately on two 51 cm-long Heetomatic 1.1 kW stainless steel bayonet-type pail heaters boosted if necessary with two 0.5 kW rod-type quartz immersion heaters. To minimize temperature gradients in the chamber, the water was circulated from bottom to top with a Haake constant temperature water circulation unit (this unit is visible at the lower left of Figure 1). This unit has an output of about 0.6 kW that could be added to the 3.2 kW supplied by the combined immersion heaters. When high water temperatures were used, the vertical walls of the chamber were covered with rock wool sheet insulation to reduce heat loss during heatup. The insulation was removed a few minutes before an

experiment to permit video and photographic imaging. If the water was to be used again for a hot water experiment, the insulation was replaced to reduce heatup time for the next experiment.

Spill Control

The lower meter of the tower apparatus is devoted to spill control. This is accomplished simply with a 150 liter plastic container on casters that is placed beneath the water chamber during an experiment. The water chamber is supported on Unistrut beams positioned in such a way that if the chamber should somehow be damaged during an experiment (for example, by the action of a vigorous steam explosion), all water and debris would be collected and contained in the plastic container below. Moreover, this container is made of white plastic and has smoothly rounded internal corners that would assist in the quantitative retrieval of the debris produced during the damaging event. (The need for spill control in an experiment in which the chamber might fail became apparent in a very vigorous steam explosion of 10 g of molten aluminum in which partial ignition of the melt occurred (Nelson et al., 1994, 1995; Nelson, 1995). Not only were there the annoyance and hazards associated with the flood but also the loss of the debris which could have provided important information about the manner in which the explosion took place. It was particularly disappointing to lose this valuable information because this experiment never could be repeated within the time available.)

Diagnostics

Three types of diagnostics were used in this work: photographic imaging, both time-exposed and motion picture, recorded during an experiment; video imaging, also recorded during an experiment; and examination of the debris recovered after an experiment, both visually and with photographs, and by weighing.

Photography

Most of the photographic records made during the experiments were taken in a room darkened just before the drops were released. We used a Minolta X-370n 35 mm camera with a 50 mm f/1.7 lens and mounted on a sturdy tripod. We used Kodak Gold ISO 200 film, an open shutter ("bulb" setting on the camera) and a lens aperture of f/16. In some of the early experiments, we added a background flash during the several seconds while the shutter was open to record the experimental setup and surroundings along with the luminous trace. We soon found, however, that the flash was not needed because the luminosity of the falling globules was adequate to provide a usable record of the setup and surroundings even at apertures as small as f/16.

In the last few experiments, we used a Hycam I high-speed camera to record the falling drops. We used a 12-120 mm zoom lens with aperture wide open (the effective aperture is unknown), Kodak Type 7250 color reversal film on 30.5 meter rolls, and framing rates of 400 or 1000 per second, depending on the length of time the drop was expected to spend in the field of view of the camera. (Our Hycam I camera does not have an internal system for marking times along the edge of the film. Therefore, our timing was accomplished with the dial settings on the camera that select framing rates. The timing obtained with these settings is not always accurate during the early portions of a film because the camera has a variable framing rate during its initial acceleration. To minimize timing inaccuracies, our films were sequenced to place the events of interest 5 or 10 meters into the roll, after the camera speed had stabilized near that indicated by the settings.) One or two 1 kW quartz-halogen photoflood lamps at 30-50 cm distances were used, but as in the time-exposed photography, the luminosity of the falling drops usually provided good imaging even at these framing rates. The high-speed films were obtained from and, after exposure, processed by BPS Photo Services, Batavia, IL.

Various other photographs were taken with the 35 mm camera, e.g., images of the rods before and after the experiments, of the recovered debris, and of the apparatus used in each experiment. To avoid setting up

photographic lights, we usually took the 35 mm photographs with existing room light and the "automatic" shutter setting on the camera. By exposing for several seconds at an aperture of f/16, we were able to achieve reasonable quality and good depth of field. The photographs of the rods and debris were usually taken with a +4 diopter close-up lens added to the normal 50 mm lens on the camera, although a +7 lens was used occasionally when some feature of unusual interest was found. In each photograph, a millimeter or meter scale was included in the image.

Video

A standard speed (30 fps) video camcorder was used to record the fall of the luminous drops. This camcorder uses standard 12.7 mm-wide VHS video tape with U. S. recording format. This camera operates with automatic shutter aperture control. In the darkened room, this control could not set the exposure of the luminous drop properly, usually yielding overexposed images. Better video exposures were obtained when the photographic floodlights were used.

Examination of the Debris

The solidified globules and the accompanying smaller particles were retrieved from the solid catchers (graphite, steel or ice) with tweezers and allowed to dry in air. The debris from the quenching experiments in water was removed from the chamber by slowly lifting the debris catcher plate upward with 1.5 meter-long Type 316 stainless steel wires attached to the four corners. The slow motion of the plate, held horizontally, allowed the globules and other debris particles to be removed through the column of water without disturbing the positions in which they originally landed on the plate. This permitted correlation of individual particles with their photographic and video images when desired. After removal from the chamber, the catcher plate was tilted slightly, allowing the water to drain away; the particles were then allowed to dry in air.

After drying, the debris particles were photographed as described above. Then they were weighed with an Ohaus Dial-O-Gram Balance (a hanging pan beam balance with 310 g capacity and a sensitivity of 0.01 g). Usually, the major particle, the frozen globule, was weighed individually while the smaller debris particles, the "fines," were weighed together. The ferrosilicon rods used in these experiments also were weighed both pre- and post-test with the same balance.

Other than the weighings and careful visual examination, little further investigation of the debris was attempted. All granules and particles are archived at the University of Wisconsin-Madison, however, in case further exploration or analyses are desired at a later time.

RESULTS

The thirty experiments and the salient findings are summarized in Tables 2 and 3. Due to unavoidable delays in contractual arrangements, the total time available for the experimental work during 1996 was only about ten weeks. As a result, certain practices to minimize uncertainties, such as performing the experiments in random order, could not be utilized properly. Moreover, many procedures, in particular materials procurement and photographic processing, had to be expedited, adding to the costs of the program.

Experiments with Solid Catchers

Graphite

After several unsuccessful attempts to produce drops with the alumina furnace tube, the first good drop in this program was generated in experiment C-28-1 when the mullite furnace tube was used. The catcher used here was the graphite cylinder. A time-exposure photograph (with flash backup) of the drop as it fell into the catcher is shown in Figure 3**.** A few tiny "sparks" were ejected as the drop struck the graphite. A picturesque "splat" solidified in the bottom of the catcher, showing that the melt had moved into the circumference of the 4.5 cm-diameter hole. A photograph of the "splat" is shown in Figure 6. The flat material in the center of the "splat" suggests that a solid material, e.g., a surface slag, may have been present on the drop when it hit the surface of the graphite. There was no sign of adherence or reaction between the molten ferrosilicon and the graphite surface.

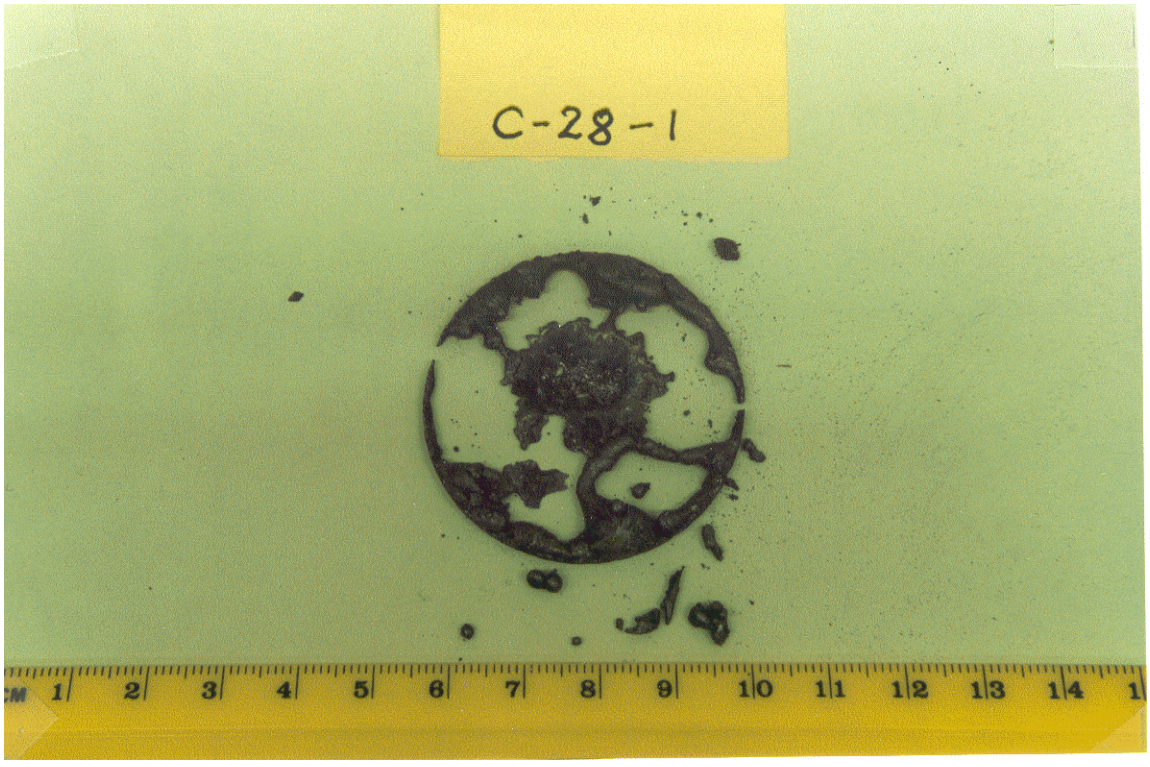

Figure 6. A "splat" solidified in the bottom of the graphite catcher, showing that the melt had moved radially outward into the circumference of the 4.5 cm-diameter cavity. The flat material in the center of the "splat" suggests that a solid material, e.g., a surface slag, may have been present on the drop when it hit the surface of the graphite. The scale is divided into millimeters. (C-28-1)

Table 2. Summary of Releases of Drops of Molten Ferrosilicon into Solid Catchers[a]

Expt. No.	Catcher	T_{melt} Max. (°C)	Rod Loss I (mm)	Rod Loss Wt. (g)	Main Drop Wt. (g)	Main Drop d (mm)[b]	Fines Wt. (g)	Imaging	Fall Time (s)	Luminous Time (s)	Remarks
C-22-1,2	Graphite	1570	9	NM	-	-	-	35,F	NM	NM	Alumina furnace tube
C-23-1	Graphite	1550	-	NM	9.21	5.00	-	35,F	NM	NM	Same
C-26-1	Graphite	1550	?	NM	-	-	-	35,F	NM	NM	Same
C-28-1	Graphite/ steel	1550	8	NM	4.68	14.1	-	35,F	NM	NM	Mullite furnace tube; 2 drops, second fell spontaneously
C-30-1	Steel	1560	-	NM	-	-	-	35,F	NM	NM	Rod fell; no drops
C-32-1	Ice	1540	Bag[c]	NM	3.40	12.7	0.20	35,F,V	~0.1	5,6,4	Splattering; 2 drops + 1 spontaneous
C-34-2	Ice	1520	~6	NM	-	-	-	35,F,V	~0.2	4	Poor alignment, splattering
C-36-1	Ice	1520	26	NM	6.18	15.5	None	35, V	~0.1	7	Excellent quench
C-38-1	Ice (2 blks)	1560	21	NM	2.39	11.3	-	35,V	~0.1	5+1	Drop broke through upper block
C-40-1	Ice (2 blks)	1535	19	NM	4.79	14.2	0.05[d]	35,V	~0.1	7	Small drops broke through; main did not

NM = not measured; 35 = Time-exposed 35 mm photography; F = flash booster; V = video.
[a] A ll drops were formed from B-62-1 FeSi rods (see Table 1).
[b] d = equivalent diameter calculated from weight of main drop with equation (1).
[c] After experiment, frozen rod had elongated "bag" shape.
[d] Material in lower block of ice.

Table 3. Summary of Releases of Drops of Molten Ferrosilicon into One-Meter-Deep Water[a]

Expt. No.	T_{water} (^oC)	T_{melt} Max. (^oC)	Rod Loss l (mm)	Rod Loss Wt. (g)	Main Drop Wt. (g)	Main Drop d (mm)[b]	Fines Wt. (g)	Imaging	Fall Time (s)	Luminous Time (s)	Remarks
C-44-1	21.1	1540	20	5.18	4.52	13.9	0.20	35, V	2	c	V-shaped drop swerves in the water
C-46-1	21.7	1500	NM	0.72	-	-	-	V	2	7	Rod fell spontaneously
C-47-1	21.7	1530	13	3.90	3.26	12.5	0.25	35, V	2	5	Good release
C-49-1	22	1540	22	4.87	2.84	11.9	1.99	35, V	3	5	Drop blew out, hole through it
C-52-1	8	1540	28	7.00	6.17	15.4	0.34	35, V	2	6	Some solid from rod on globule
C-54-1	8	1550	31	7.68	6.05	15.3	1.50	35, V	2	6	
C-55-1	8	1530	28	8.99	8.00	16.8	0.62	35, V	2	7	Drop undulates, flash at end; spearpoint
C-57-1	52	1525	20	5.74	5.33	14.7	0.34	35, V	2	11	Good release
C-59-1	50.4	1520	28	6.60	6.54	15.7	0.06	35, V	2	11	Tap water, brownish
C-61-1	49.9	1520	18	4.73	3.49	12.8	1.20	35, V	2	9	Drop swerved strongly @ 0.58 m
C-63-1	85	1525	17	3.81	3.76	13.1	0.04	35, V	3	21	Good release
C-65-1	90	1530	8	2.50	2.00	10.6	0.34	35, V	5,3	8,18	2 drops: 1st, ~6 mm; 2nd, average diam.
C-67-1	90	1530	10-30[d]	5.25	6.88?	16.0?	0.29	35, V	3	27	Drop froze @ wall; weights questionable
C-69-1	8	1530	22	6.10[e]	4.53	13.9	0.41	H3/3, V	2	NM	Lights on. Both drop and rod fell.
C-72-1	20.8	1525	19	6.95	6.77	15.9	0.17	35, V	2	6	Bubbled 5% N_2-H_2 through water.
C-74-1	7.5	1520	26	6.43	5.74	15.1	0.20	H,U/3,V	2	4?	Video confused by movie lights.
C-76-1	78	1540	27	6.80	5.32	14.7	0.68	H,U/3,V	2	23	Main globule + 5 tiny drops.
C-79-1	89	1530	11	3.52	2.40	11.3	0.39	H,L/3,V	3	22[f]	Main globule + 4 tiny drops; 1 rose.
C-81-1	7.0	1525	18	3.87	3.56	12.9	0.25	H,L/3,V	2	NM	Video confused by movie lights.
C-85-1	18.8	1540	28	6.57	5.22	14.6	1.37	35, V	2	7	Demonstration experiment.

NM = not measured; 35 = Time exposed 35 mm photography; H = High speed motion picture photography (3/3 = view of entire water chamber, U/3 = view of upper 1/3 of chamber, L/3 = view of lower 1/3 of chamber).

[a]All drops were formed from C-34-1 FeSi rods except for C-44-1 and C-46-1, which were formed from B-62-1 rods (see Table 1).

[b]d = equivalent diameter calculated from weight of main drop with equation (1).

[c]Drop froze out of view of the video.

[d]Very tapered rod after the experiment.

[e]Some of support wire was lost during melting.

[f]Bubbling stopped after 42 seconds.

Figure 7. A drop that fell spontaneously and "splatted" on the steel shutter in a flowing argon atmosphere. Notice that, unlike the "splat" on graphite shown in Figure 6, this frozen globule shows no thin solid at the center of the pattern. The scale is divided into millimeters. (C-28-1)

Steel

Immediately after the drop fell in experiment C-28-1, the steel mechanical shutter was closed beneath the furnace tube to retain the flow of argon and minimize entry of air into the hot furnace in which the partially molten rod remained. Some time after the closure, a second drop fell spontaneously onto the surface of the steel, unknown to the experimenters. Only after the furnace had cooled to room temperature with continued argon flow was the "splatted" and frozen drop discovered. A photograph of the frozen melt still in place on the steel shutter is shown in Figure 7. Notice that, unlike the "splat" on graphite shown in Figure 6, this frozen globule shows no thin solid at the center of the pattern, suggesting that no solid had been present on the drop when it struck the steel plate. The solidified drop did not adhere to or react with the steel plate; only a slight discoloration of the steel beneath the frozen material could be detected. From this second drop release in experiment C-28-1, it seems reasonable to conclude that, at least in an argon atmosphere, cold Type 1018 steel at least 3.2 mm thick provides a usable quencher for 10-20 mm drops of molten ferrosilicon.

This same steel was used to fabricate the debris catcher placed in the bottom of the chamber during the quenching experiments in 1 meter-deep water. A photograph of the steel debris catcher is shown in Figure 8. In none of these tests was there any sign of interaction, either chemical or physical, between the underwater steel surface and the ferrosilicon particles, large or small, luminous or nonluminous, molten or solidified.

Figure 8. A photograph of the steel debris catcher used at the bottom of the water chamber. It is approximately 30 cm square. (C-52-1b)

Ice

There were three objectives in investigating ice as a catcher:

- Provide a nonreactive impact surface at the end of the drops' fall through water;
- Provide a small volume of water at ice temperature with some degree of confinement to look for spontaneous vapor explosions of the drops in water of maximum possible subcooling; and
- Slow or stop the fall of the hot drops to permit photography, pyrometry and other instrumental measurements to estimate cooling rates and luminous extinction times and to observe unusual behaviors of the drops during cooling and solidification, e.g., fragmentation, evolution of gases or void formation. This objective should be applicable to understanding industrial processes in which quenching of the molten globules may take tens of seconds and involve many meters of fall through the cooling water.

Several attempts were made early on to place a block of ice underwater at the bottom of the chamber to catch the drops and smaller debris as they fell through the water. Quickly, we discovered that the drops did not fall in a straight path and their landing places could not be predicted. Since the blocks of ice were smaller than the bottom of the chamber and melted away quickly, it was not possible to be sure the drops would impact ice and not land elsewhere. And, after it was learned that the steel debris catcher also provided a good nonreactive impact surface, ice was not considered further as an underwater catcher.

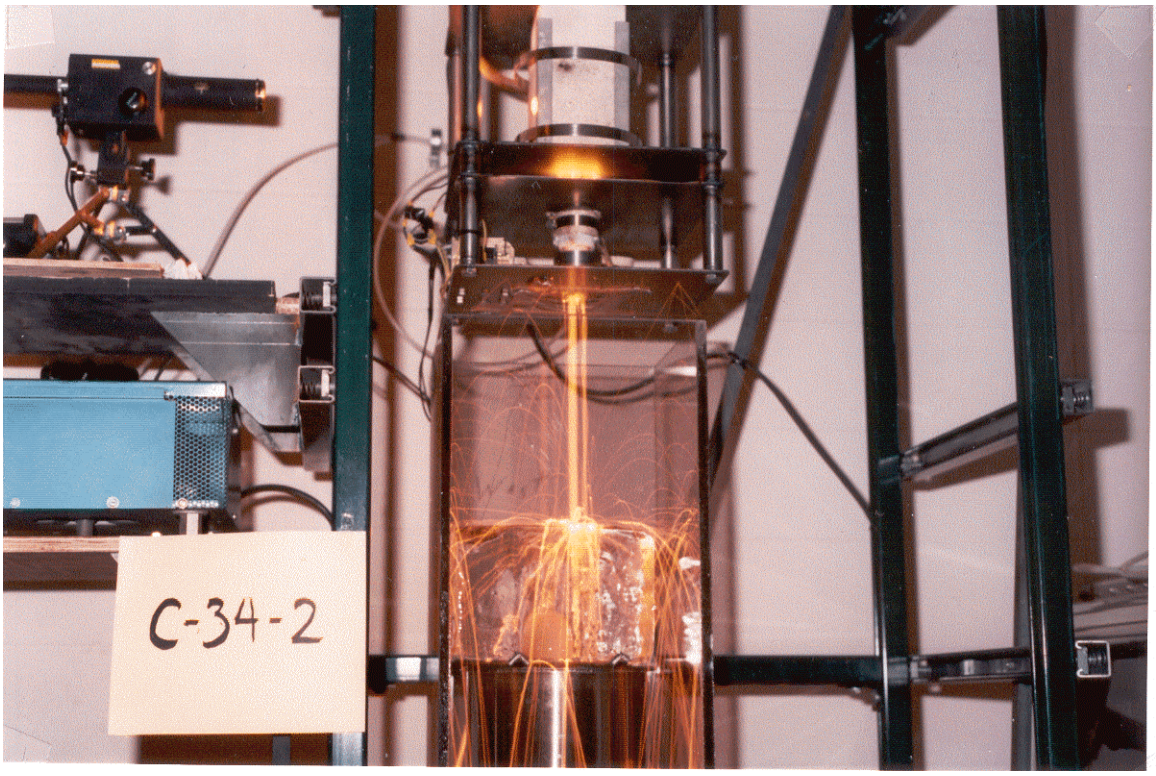

Figure 9. A time-exposed photograph of a drop of molten ferrosilicon released into a cavity in a block of ice, showing the effects of slight misalignment of the fall path. Backup flash illumination was also used here. (C-34-2)

Using the ice to provide small volumes of very cold water and to slow the fall of the drops seemed more promising. Because the ice may be placed at various heights including very close to the bottom of the furnace, various fall distances in gaseous atmospheres can be realized. And by forming cavities of different shapes and sizes in the upper surface of the ice, the volumes of cold water and confinements for vapor explosion investigations can be chosen as desired.

We did not study ice as a catcher very extensively. As indicated in Table 2, five experiments were attempted with one or more blocks of ice in several configurations as intended catchers. In the earliest experiment, C-32-1, we used three blocks of ice, one on top the other, as the catcher; the total thickness of ice in the fall path was about 25 cm. The thickness was chosen to make sure melt-through did not occur. (Because the literature for predicting the penetration depth of a hot body, solid or liquid, into ice is not extensive, we included a large margin of safety.) We discovered empirically that the penetration was only a few centimeters; therefore, in the next experiments, we used only one block. We also discovered that it was important to form a cavity in the ice, and to align it carefully beneath the furnace to avoid splattering from the flat top of the block or even from the edge of the cavity. This splattering produces a shower of "sparks" and dramatic, but unwanted, photographic images (see Figure 9 for the effects of slight misalignment of the fall path of a drop).

In ice, our best single drop quenching experiment was C-36-1. Here, after it left the furnace tube, the molten globule fell about 6 cm in air into a cavity in the ice, where it solidified as a single roughly hemispherical body. A time-exposed photograph of the drop as it fell into the ice (without flash backup) is shown in Figure 10. The solidified globule is shown imbedded in the ice in Figure 11 and after retrieval in Figure 12.

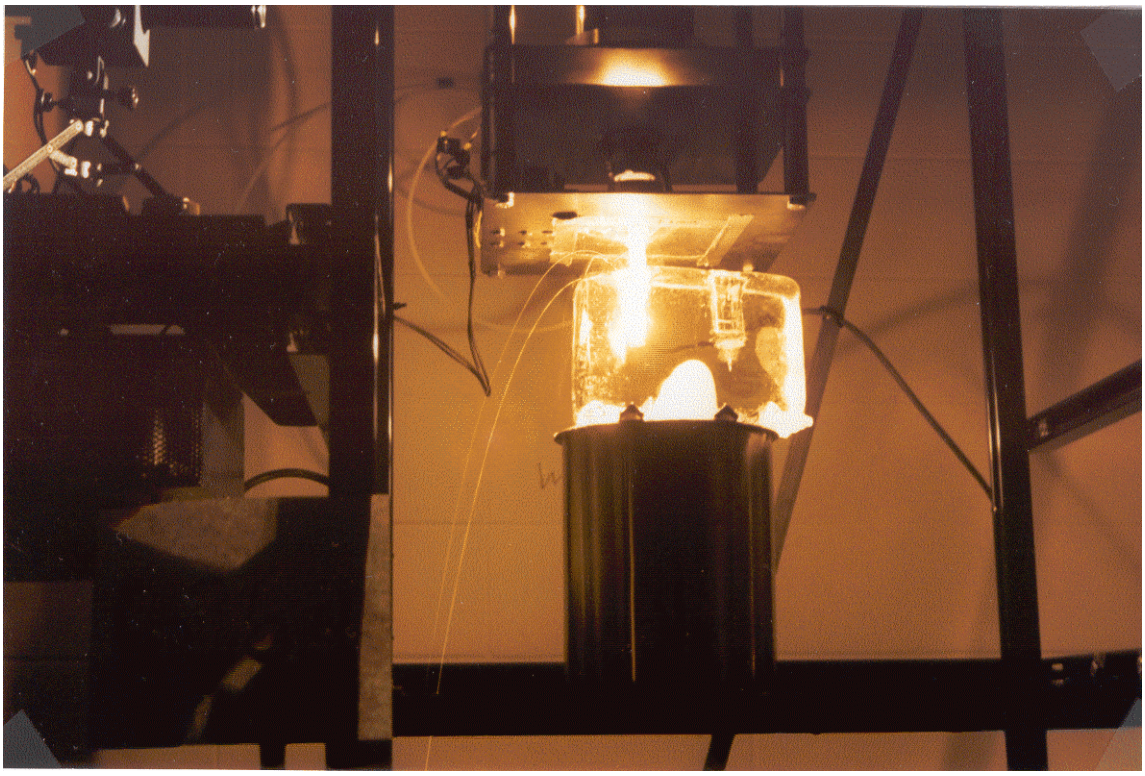

Figure 10. A time-exposed photograph (without flash backup) of a molten ferrosilicon drop as it fell about 6 cm in air into a cavity in a block of ice. (C-36-1e)

The last two experiments using ice as catchers were C-38-1 and C-40-1. In these experiments, we attempted to allow the drop to fall into a cavity with a thin bottom, melt through and drop through air into a cavity in a second block of ice below the first. In this way, the drop would start its cooling in the first cavity and then complete its cooling and solidification in the lower cavity. The idea behind this effort was to shorten the fall distance to solidification by interposing a known thickness of ice that the drop had to penetrate partway through its fall.

After we demonstrated in experiments C-38-1 and C-40-1 that this procedure is feasible, we did not attempt to investigate ice quenching farther.

In the experiments in which ice was used as the catcher, there was never any indication that a spontaneous vapor explosion had occurred. In most of these experiments, the cavities contained liquid water, presumably at 0 °C.

Experiments with Liquid Water as Catcher

As indicated in Table 3, twenty experiments were performed in which the molten drops were released into liquid water 1 meter deep. Four water temperatures were used: cold (about 8 °C), room temperature (about 20 °C), intermediate (about 50 °C) and hot (about 90 °C). In fifteen of the experiments, images of the falling drops were recorded during fall with time-exposed open-shutter 35 mm photography and with the video camcorder. In the five remaining experiments, drop images were recorded with both the Hycam 16 mm camera and the camcorder. In all experiments, the drops fell 30 cm through gaseous atmospheres (argon and then air) from the lower tip of the heated ferrosilicon rod to the surface of the water.

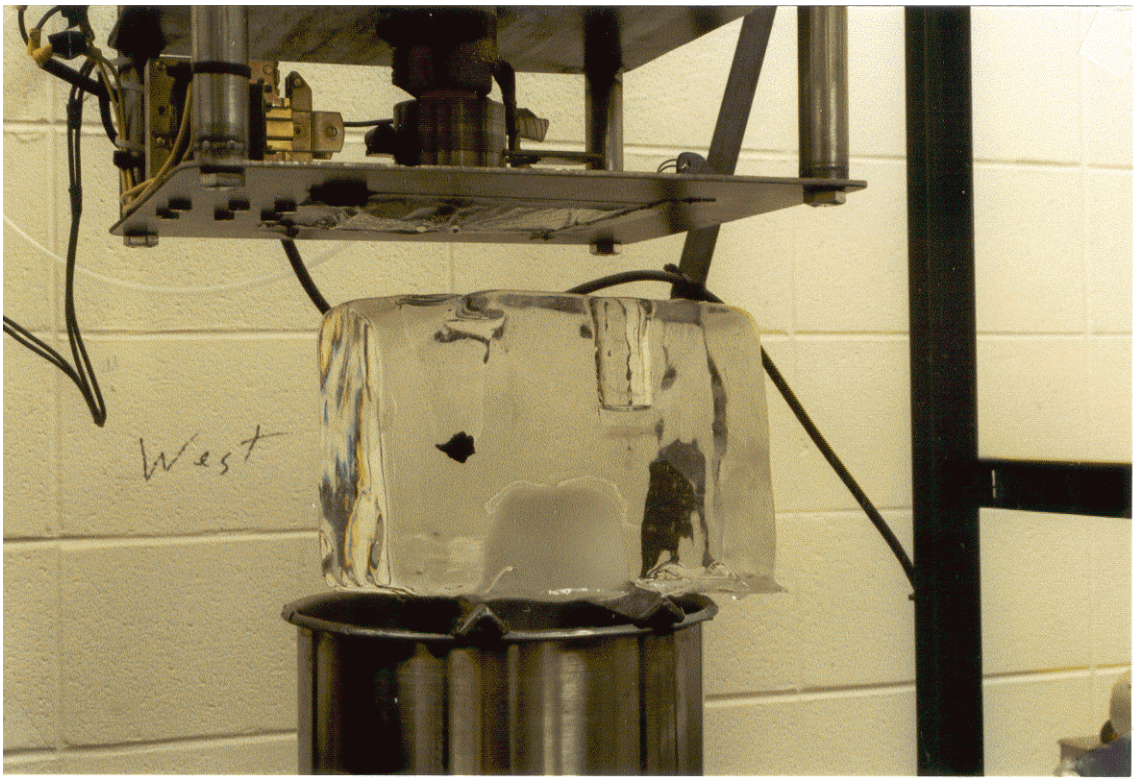

Figure 11. The solidified globule from Figure 10 is shown imbedded in the ice. (C-36-1f)

At all water temperatures, the drops initially fell along a short, straight vertical path about 8 cm long as they first entered the water. In all cases, this path was followed by an erratic, swerving downward path for the remainder of the fall. The drops remained intensely luminous during the entire fall and also for a time after they landed on the debris catcher at the bottom of the chamber. Occasionally, the path might swerve more abruptly than usual, and sometimes even fork into two or more tracks. In many of the images, one or more smaller, less erratic traces paralleled the path of the main drop.

A typical time-exposed photograph of a falling drop is shown in Figure 13. This image was formed entirely with the drop's own luminosity (no backup flash). During their fall, the drops never showed tracks that terminated abruptly with a radial burst of short luminous traces, the behavior that indicates a spontaneous vapor explosion. (In this round of experiments, we did not attempt to trigger steam explosions of the drops.) Moreover, there never were detectable intensifications of the tracks, either abrupt or gradual, to indicate recalescence (release of heat of crystallization due to solidification from the supercooled state; see Nelson (1965, 1966)).

We interpret these traces as follows:

The short, straight, initial portion of the trace is produced by the entrainment of air as the hot drop passes into the water. The entrainment of the ambient atmosphere as a projectile or falling body enters water has been studied for nearly a century (Worthington and Cole, 1900; May, 1951). It has been shown that the amount of gas drawn in above the body before the cavity that forms above it closes is a function of the dimensions of the body, its velocity and the wettability of the body by the water. Cavities that form and pinch off above small (2.9 mm diameter) drops of laser-melted iron oxide as they fall into water have been observed by Nelson and Duda (1981, 1982). These authors showed that a small entrained air bubble stays

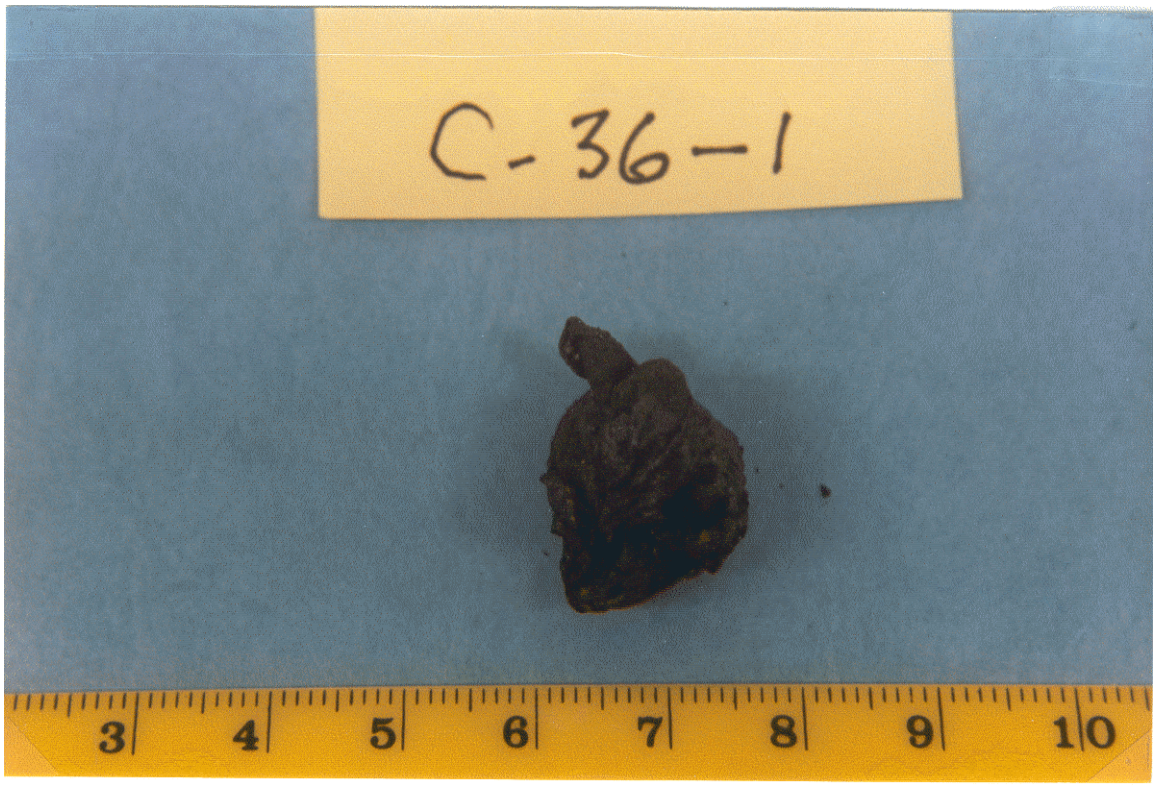

Figure 12. The solidified globule from Figure 10 is shown after retrieval. The scale is divided into millimeters. (C-36-1k)

with each drop as it descends in the water. This air stabilizes the boiling film around the drop and reduces the tendency to produce a spontaneous steam explosion. (A steam explosion can still be triggered with a localized pressure transient in the water, however.)

We attribute the onset of the swerving traces to the solidification of the drops almost immediately upon entering the water. We believe that the swerving or fluttering will be possible only if the globules have a fixed and somewhat flattened geometry, e.g., with a solid shell on the outside. Otherwise straight or smoothly curved traces will result (Konuray et al., 1975). The immediate swerving was unexpected, because we fully anticipated deep supercooling of the molten drops in the film boiling situation where heterogeneous nucleation seems unlikely.

The occasional sudden swerve of the drop as it falls seems related to a change in the geometry of the globule as it falls. This can occur, for example, when melt is ejected from the interior of the drop as it solidifies. The forking of the traces indicates complete ejection and separation of some of the melt from the parent drop as it falls, producing one or more new luminous drops. Note that the abrupt swerve does not produce a new luminous particle, suggesting that if the ejected material is still luminous, it does not separate from the drop to produce a forked trace and a new luminous trace. It is also possible that an abrupt swerve can be produced by the ejection or other movement of non-luminous material, for example, the breaking off of a piece of solid associated with the falling drop.

The smaller tracks that parallel the main drop, e.g., those shown in Figure 13, are presumed to be produced by tiny satellite drops (fines) generated during the initial release of the pendant drop from the ferrosilicon rod, or from luminous material ejected from the main drop during its fall. In many cases, the smaller tracks

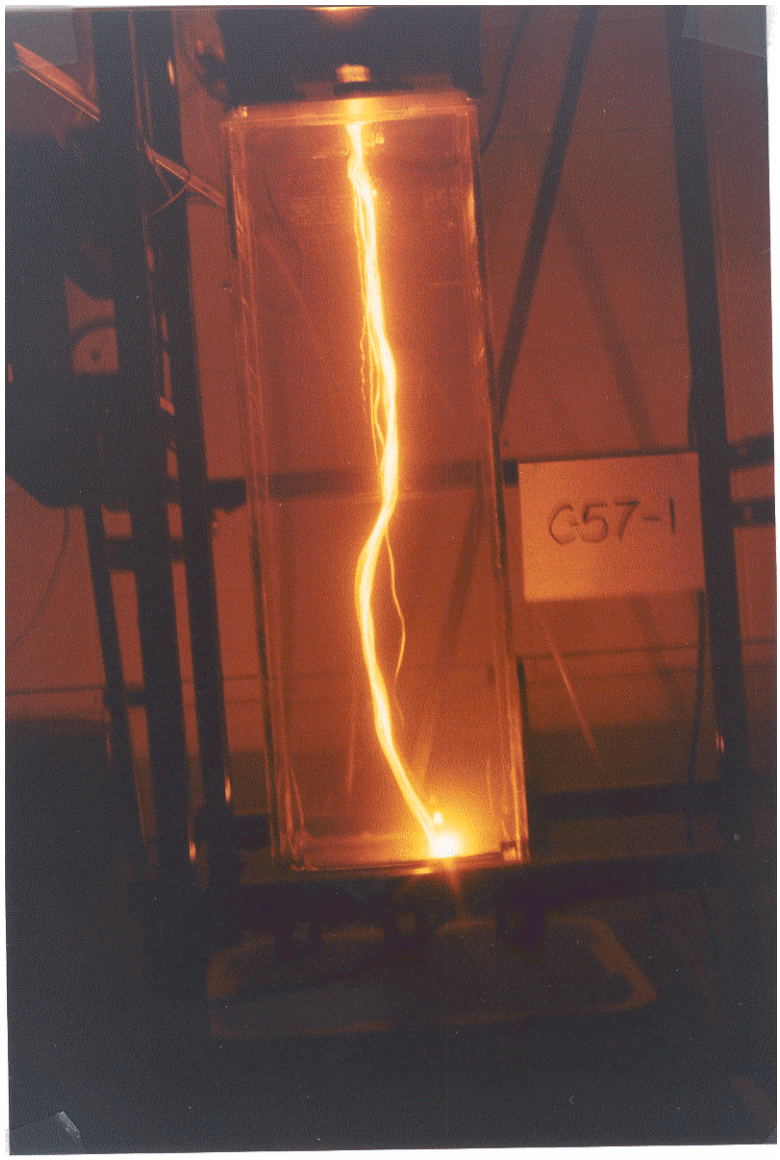

Figure 13. A typical time-exposed photograph of a falling drop without backup flash. Notice fainter parallel images of smaller luminous particles. (C-57-1)

on the open-shutter photographs can be directly related to small particles found on the debris catcher after the experiment.

After the main drops land on the debris catcher plate, they remain luminous for some time. This usually causes an overexposure on the open-shutter photographs, as may be seen in Figure 13. The duration of the luminosity of the drop on the catcher plate depends on the temperature of the water. This will be discussed in the next section.

Dependence of the Duration of Luminosity on Water Temperature

The length of time the drops remain luminous may be estimated from the video images. These images were usually overexposed when the room was darkened for the open-shutter 35 mm photography. Nevertheless,

these images provided a good indicator of when the drop was released, its time of fall to the catcher surface (ice or the steel debris catcher at the bottom of the water chamber) and the time at which the luminosity extinguishes. The video images were harder to interpret when the drop's fall path was illuminated, either by room lights or photographic lights. It was also possible to observe the luminous behavior of the drops on several of the 16 mm high speed films; because of the small number of films and possible uncertainties in framing rates, however, we did not attempt to use them for estimating durations of drop luminosities.

As indicated in Table 3, twenty experiments were performed with drops released into water at four temperatures (nominal): cold, 8 °C, 6 experiments; room temperature, 21 °C, 6 experiments (in one of these, gaseous 5% hydrogen-95% nitrogen was bubbled through the water); moderate, 50 °C, 3 experiments; and hot, 78-90 °C, 5 experiments. The duration of luminosity as determined from the video records increased from 5 seconds to 27 seconds as the water temperatures increased from cold to hot. The luminous durations are plotted against water temperature in Figure 14.

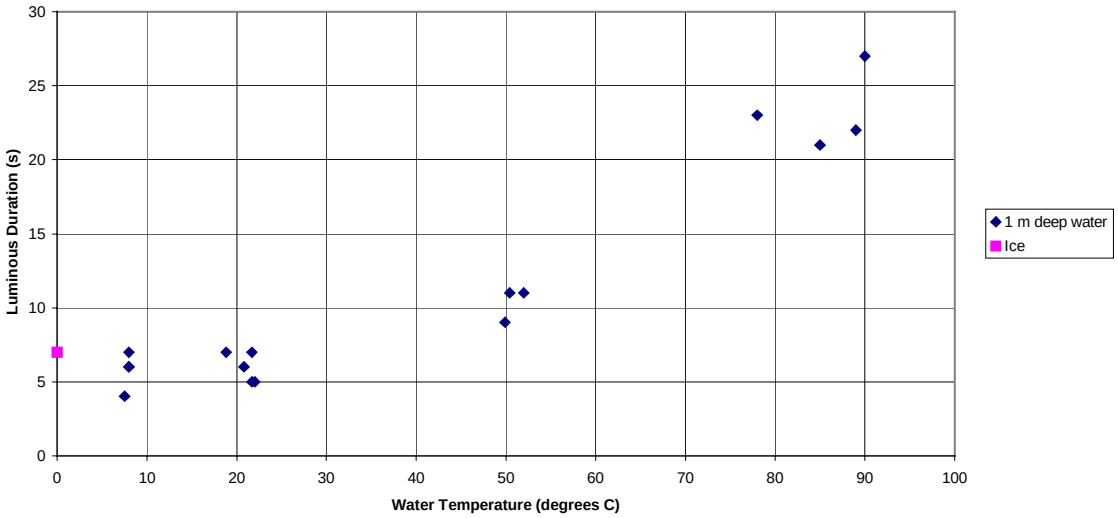

Figure 14. Luminous durations plotted against water temperature for the quenching of 10-20 mm-diameter molten ferrosilicon drops in 1 meter of water. Note that the drops cooled in free fall for approximately 2 s; the rest of the cooling occurred while the drops were lying on an underwater steel surface. (Exceptions are the drops that quenched in a block of ice; these cooled for the entire time adjacent to the ice surface.)

From the video records, we were also able to estimate luminous durations of the drops released into ice catchers. These times, about 7 seconds, may have been slightly longer than the luminous durations of the drops released into the meter-deep cold water. It is apparent that motion of the drops through cold water cools them more efficiently than keeping them statically in an environment of water initially at 0 °C. Heat transfer from a hot body in film boiling as a function of the temperature of the water will be discussed in a later section.

We performed one experiment, C-72-1, in which we bubbled a gaseous mixture of 5% hydrogen-95% nitrogen upward through a column of water at room temperature. This experiment was intended to simulate an industrial situation where many molten globules are reacting chemically during the quenching to produce hydrogen bubbles dispersed throughout the water. In this experiment, we could not detect differences in the durations of luminosity or in the open-shutter photographic images that could be attributed to the presence of the bubbling hydrogen mixture. However, the solidified main globule appeared somewhat more metallic (shinier) than the globules produced in water without the bubbling hydrogen mixture.

Quenched Material

The material recovered from these experiments usually consisted of a single main drop accompanied by smaller material. The weights of the main globules and of the combined finer material produced in each experiment are shown in Tables 2 and 3.

Main Globules

The weights of the solidified main globules recovered in these experiments ranged from 2 g to 8 g. Using a density of 3.2 g per cc for the molten ferrosilicon alloy and assuming spherical shapes, the corresponding equivalent diameters of the globules would be given by the equation

$$d(cm) = [0.5968\ W(g)]^{1/3} \quad (1)$$

or 10.6 mm to 16.8 mm. These diameters clearly fall within the range of interest to the sponsor.

The solidified globules were usually black, flattened bodies, sometimes with patches of darker black, slag-like material on the surface. Often, the globules also had small, nodular growths on the surface. We attribute these nodular growths to ejection from already solidified material of small amounts of more dense liquid as it solidifies. (Nodular growths of this sort also were frequently produced on the surface of the rods after a drop had been released and the rod had cooled slowly in argon to room temperature.) Typical debris recovered from experiments performed with cold water (Figure 15, experiment C-55-1, water temperature = 8 °C) and hot water (Figure 16, experiment C-63-1, water temperature = 85 °C) as the quenchants. Notice the larger number of finer particles produced in cold water compared to the hot water. This will be discussed further in the next section.

On several occasions, drops with blown-out cavities were recovered. A photograph of the debris recovered from experiment C-74-1, in which a blown-out main globule was produced, is shown in Figure 17. (This experiment was performed with water at 7.5 °C; again, note the large number of smaller particles, similar to experiment C-55-1, Figure 15.)

Fines

The smaller particles produced in these experiments were essentially spherical, with diameters of a few millimeters. Most of these particles are thought to have formed as satellite drops during the shaking that causes the main drop to detach from the heated ferrosilicon rod. Some small particles, however, may have been produced during the mild fragmentations that sometimes occurred during the fall of the drops through the water. The forked self-luminous images probably are the result of these fragmentations. Others may have been produced during the blowing-out of the globules that occurred, for example, in experiment C-74-1, Figure 17. Both forked traces and blown-out globules were relatively rare in these experiments, leading us to believe that most small particles were formed as satellite drops during the mechanical release of the main drop.

The observation noted in the previous section that the debris formed in hot water has fewer smaller particles than that formed in cold water (compare Figures 15 and 17 with Figure 16) may perhaps be explained by the high speed photographs taken of the upper one-third of the water chamber (experiments C-74-1, 7.5 °C water, and C-76-1, 78 °C water). While these films were taken primarily to examine the entrainment of air by the molten globules as they entered the water, we noticed that in the hot water, a number of the small

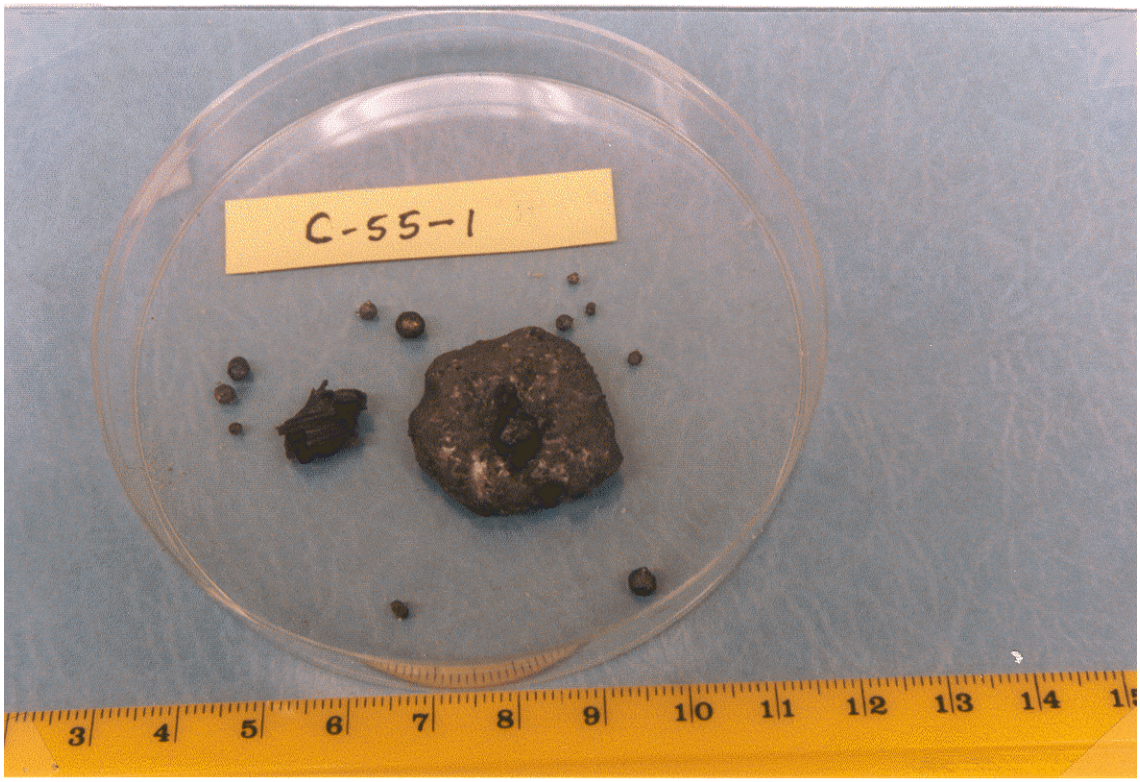

Figure 15. Typical debris recovered from an experiment performed with cold water; water temperature was 8 °C. Note the large number of smaller particles. The scale is divided into millimeters. (C-55-1)

particles were caught in the bag-like region where the air had been entrained and lingered there for many seconds after the main globule had descended from the frame. In addition to remaining near the surface of the water, the luminosity of the particles remained high and sometimes brightened or oscillated during this period. Often, the luminosity of the particles ended abruptly. This behavior was greatly reduced or entirely absent in the cold water.

We suggest that the extended residence and luminous behavior near the surface of hot but not cold water may be explained by the combustion of the smaller particles to produce hydrogen and very fine (colloidal) oxide particles. The steam and hydrogen may form bubbles around the burning particles that provide buoyancy and cause them to remain near the surface. As the particles burn, their diameters may decrease, causing greater surface area and more intense combustion, hence the increased luminosity. And the comment of a person familiar with the industrial process that colloidal materials sometimes form during quenching of ferrosilicon drops in water may indicate that perhaps the reason fines are less plentiful in material quenched in hot water is that the smaller particles burn away as the larger globules cool and solidify. It should be noted that this hypothesis is based on the examination of only a very few films; more extensive investigation seems warranted, however.

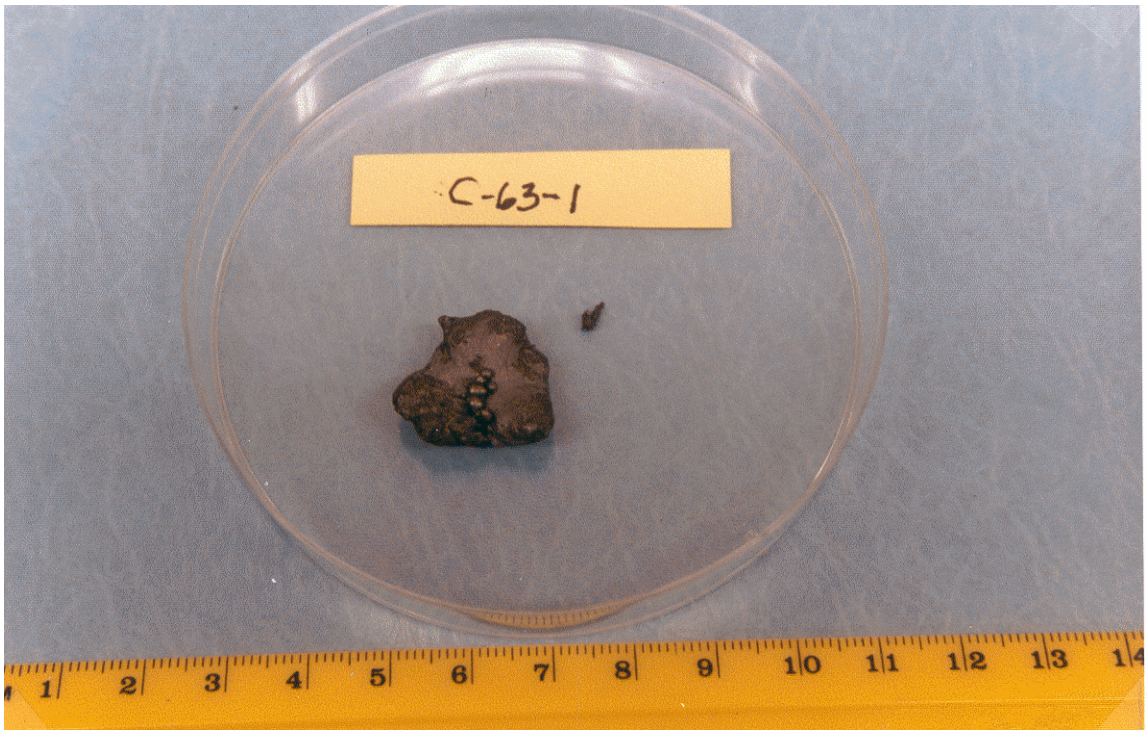

Figure 16. Typical debris recovered from an experiment performed with hot water; water temperature was 85 °C. Note the absence of smaller particles. The scale is divided into millimeters. (C-63-1)

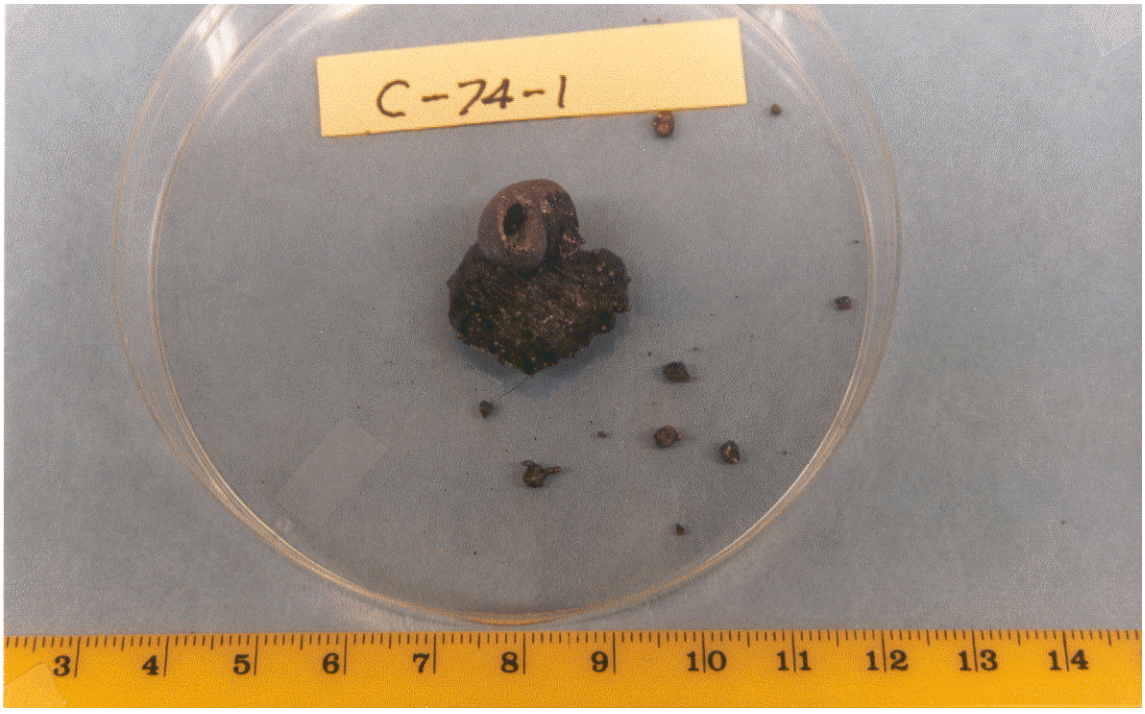

Figure 17. Debris recovered from an experiment in which a blown-out main globule was produced. This experiment was performed with water at 7.5 °C; note the large number of smaller particles, similar to Figure 15. The scale is divided into millimeters. (C-74-1)

DISCUSSION

Absence of Spontaneous Steam Explosions

The primary objective of this work was to investigate steam explosion phenomena associated with drops of molten 75 w/o Si 25 w/o Fe alloy when released into an environment of liquid water. In none of the 25 releases into water contained in the 1 m-deep chamber or in cavities in ice was there any indication of a spontaneous steam explosion when the water temperatures were: that of melting ice (0 °C), cold (about 8 °C), at room temperature (about 20 °C), moderate (about 50 °C) or hot (78 to 90 °C). Instead, the drops that fell into meter-deep water seemed to exhibit a fixed geometry as soon as they entered the water, fluttering and swerving as they descended in the chamber. It was more difficult to observe the contact behavior of the drops that fell into the more confined shallow cavities in ice, in which the initial volume of water was only a small fraction of a liter; but again there was no fine fragmentation or vigorous ejection of water that would indicate a steam explosion had occurred. We believe that a solid exterior skin forms quickly around the molten globules and protects them from the action of the repeated collapses of the boiling film that can initiate spontaneous steam explosions.

The apparent instantaneous generation of a solid exterior when the drop of alloy contacted water was not anticipated. We had expected the molten globule, which we believe was released at its liquidus temperature, to supercool in the molten condition for at least a short time after it entered the liquid water because the steam atmosphere that would blanket the drop probably would not present active heterogeneous nucleation sites to initiate solidification. It seems likely that some solid present on the surface of the drop nucleated crystallization and prevented supercooling. There are several possible sources of this nucleating solid:

(1) Solid may form when the molten alloy first encounters an oxidant—air or water. We may have some evidence for this explanation, namely, examination of two "splats," both from experiment C-28-1. One formed from a drop that fell through about 22 cm of argon and quenched on a steel surface; it is shown in Figure 7. The other fell first through about 22 cm of argon and then continued through approximately 8 cm of air before quenching on a graphite surface; it is shown in Figure 6. The drop apparently did not have solid on its surface when it quenched from the argon atmosphere, as indicated by the absence of solid material in the ring-like "splat" recovered after the drop had fallen onto the steel catcher. But after a short additional fall through air, some solid may have formed, as suggested by the rough textured center inside the ring-like "splat" that was quenched in graphite, shown in Figure 6. It is possible that a solid of very high melting temperature forms on the melt as soon as the drop enters an oxidizing environment–the short fall through air or the water. Perhaps upon encountering the oxidizer the small amounts of metals in the melt that form oxides with high melting temperatures, e.g., Al and Ca, may quickly form nucleating oxide crystals that prevent supercooling of the globule. As indicated in Table 1, the alloys used in these experiments contained 0.76% Al and 0.025% Ca (Batch B-62-1, used in experiments C-22-1 through C-46-1) and 0.37% Al and 0.014% Ca (Batch C-34-1, used in experiments C-47-1 through C-85-1).

(2) The pendant drop may have detached from the rod with some solid attached. It may be that melting in an atmosphere of commercial purity argon flushing through a mullite tube at about 1525 °C cannot provide an oxygen potential low enough to prevent the formation of patches of oxide or slag on the surface of the pendant drop as it forms. This comment is based on the observations of Krishnan et al. (1996) that when attempting to produce small, levitated drops of molten iron in flowing argon, the surface of the drops always showed patches of solid floating on the surface, presumably oxide. It was necessary to add hydrogen to the argon flow to remove the patches of oxide. We suggest for future experiments similar treatment with hydrogen while melting the ferrosilicon alloy. The addition of small amounts of hydrogen to our argon stream would not be difficult. Also, prepurified argon and non-oxidic furnace tubes, e.g., boron nitride, might be used to reduce the oxygen potential in the furnace.

(3) The thermal perforation of the thin polyvinyl chloride sheet that seals the lower end of the furnace rig and acts as a "fast-opening" shutter may not be as inert a process as assumed. It may leave a deposit of some sort on the surface of the drop as it passes through that can cause nucleation of the melt. The substitution of a fast-operating mechanical valve for the plastic sheet would eliminate this possibility.

There may be other explanations for the rapid formation of a solid skin on the outside of the globule. Clearly, this is a worthy target for more extensive investigation.

It should be noted that the absence of spontaneous steam explosions of the ferrosilicon drops in water of any temperature eliminated one simple and inexpensive technique for deliberate triggering of the explosions of the ferrosilicon drops—the introduction of sharp negative temperature gradients in the column of water. Arakeri et al. (1978) used this scheme to trigger explosions of molten tin drops. Because tin exhibits a "temperature interaction zone" (the TIZ, a series of water temperature thresholds above which spontaneous explosions do not occur as melt temperature is increased; see Dullforce et al., 1976), it is possible to construct a water chamber in which hot water (non-exploding) lies above colder water (spontaneously exploding). As the molten tin drop falls from hot into cold water, a steam explosion is triggered. Because the ferrosilicon drops in our experiments never exploded spontaneously in water of any temperature, hot or cold, this triggering scheme had to be abandoned. But simply because the drops have a thin shell of solid that prevents spontaneous explosions does not mean that explosions cannot occur when these drops are properly triggered, for example, by exposure of the drop to an appropriate pressure transient as it falls through the water. In this way, Nelson et al. (1988) were able to induce explosions of 3 mm drops of molten iron oxide that had partially frozen before the pressure transient trigger was applied. They were able to photograph the explosion and observe the formation of and later retrieve fragments of the thin shell that was broken open when the explosion was triggered. Because of the industrial safety implications, pressure transient triggering of both completely molten and partially frozen globules of the ferrosilicon alloy should be studied. (We had intended to include pressure transient triggering in this program, but time constraints did not permit it.)

The Quenched Globules

Once it became apparent that spontaneous steam explosions would not occur with the alloy and procedures used here, we turned our attention to the nature of the quenched materials—both the main globule and the "fines." Because of the severe time limitations of the program, we were not able to study the retrieved materials very extensively. Our only quantitative technique involved two weighings to determine: (a) the total weight of all materials recovered, and (b) the weight of all materials with the globule removed. The difference is the weight of the main globule. Our other procedure was semiquantitative, to measure the dimensions of the globule. Because the geometries of the globules were uncertain, the measurements were only approximate. We also weighed and measured the rods before and after each experiment. And finally, we recorded the appearance and other aspects of all recovered materials and the rods. We were not able to do any sectioning, metallography or chemical analyses during this work, but all samples have been archived at the University of Wisconsin-Madison for further study if desired.

The globules quenched in water are black, mostly round and flat, with thicknesses about one-third of the diameter (see Figures 15 and 16). These thicknesses are not necessarily an indication of the true thicknesses that would have resulted if the drops had fallen freely for several meters more and had not struck a solid and possibly deformed after just a meter of fall. We are quite certain the drops were still partially molten at the end of the two-second fall through the meter of water (see, for example, the blown out globule in Figure 17), but also quite uncertain of the thickness and rigidity of the solid shell that surrounds the melt. Sectioning of globules might give an indication of their shell thicknesses.

The frozen globules that deviated from this simple lozenge form usually produced very swervy, self-luminous traces on the time-exposed photographs. An example is the strange-looking globule and its photograph produced in experiment C-44-1 and shown in Figures 18 and 19, respectively. In experiment C-

Figure 18. Strange-looking globule produced in experiment C-44-1. Water temperature was 21.1 °C. The scale is divided into millimeters.

67-1, another very swervy trace was generated as a piece of solid broke from the parent. The resulting globule and the broken piece are shown in Figure 20; the corresponding time-exposed photograph is shown in Figure 21.

A fork in the trace accompanied the inflation and blowing out of the globule in experiment C-49-1. The solidified globule and its self-luminous trace are shown in Figures 22 and 23. (To indicate its openness, a 0.5 mm-diameter pencil lead has been passed through the cavity in the parent globule in Figure 22.)

Not all globules were completely black. The globule retrieved from experiment C-72-1 had a somewhat metallic appearance, as shown in Figure 24. This experiment was performed with the 5% hydrogen in nitrogen mixture bubbling upward through the water column. Apparently, the reducing environment in the water prevented the formation of at least some of the black coating.

Common features observed on many of the globules as well as on the rods after cooling to room temperature were small nodules or rosettes of solidified melt that seemed to have been forced as a liquid from a pore in the larger ferrosilicon body as it cooled. This phenomenon perhaps results from the expansion of the melt as it cools, similar to that of molten elemental silicon. A good example of these nodules is shown in Figure 25, where nodules formed on both the solidified globule and on the sides and tip of the rod from which the molten globule had been detached. In several experiments, these nodules froze as a beautiful cluster of crystals that we call rosettes.

A final comment has to do with the dark slag-like material on the surface of the solidified globules. This material can be seen on all but one of the globules shown in the figures. There appears to have been a solid skin floating on the surface of the molten body that fractured as the body froze (and expanded?). There is

one exception to this—the globule that quenched in ice, experiment C-36-1, shown in Figure 12. It seems to have a continuous dark black coating that did not fracture. It should be noted, incidentally, that samples of Elkem production granules supplied by Dr. Karl Forwald did not have this slag-like outer skin either. We do not know whether the absence of the slag on these granules is due to the specifics of the production quenching process or to a melt composition difference, or both. Unfortunately, the details of the industrial process and the composition of these granules are unknown to us at this time.

The Smaller Particles

The smaller particles are usually roughly spherical and metallic-looking, with diameters of a few millimeters. Their total weights are several tenths of a gram, compared to the main globule that weighs a few grams (see Table 3). (Although we probably have the information needed for calculating particle diameter and weight distributions, we have postponed these determinations due to time constraints.) And, as mentioned above, there were fewer fine particles recovered in the experiments performed with hot water than with cold water.

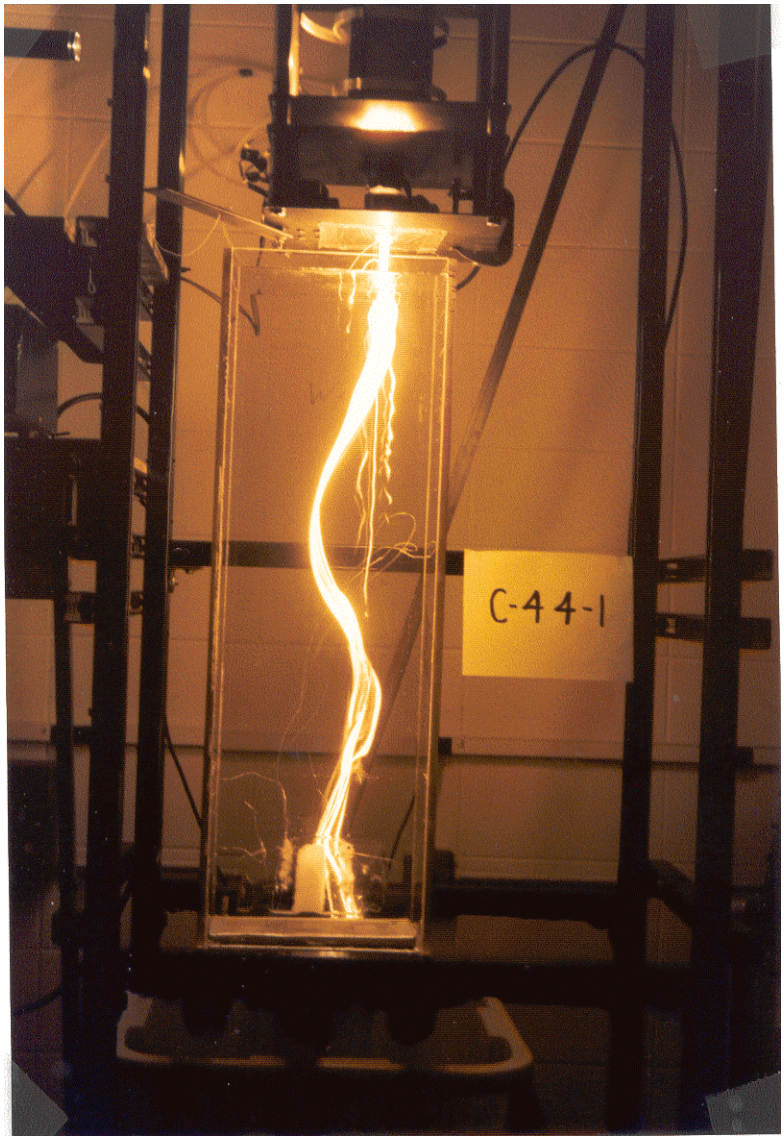

Figure 19. Very swervy self-luminous trace on the time-exposed photograph produced in experiment C-44-1. Water temperature was 21.1 °C.

Figure 20. In experiment C-67-1, a piece of solid broke from the parent. The resulting globule and the broken piece are shown here. The scale is divided into millimeters.

We believe that many characteristics of the fine particles can be attributed to their partial combustion in water before quenching. (In the Results section, we described high-speed motion picture evidence for the separation and ignition of some of the small drops from the large globule as the assemblage of drops entered the water. Apparently the smaller drops, because of their greater drag and buoyancy, stayed behind and were able to escalate in temperature to a self-sustained, highly luminous combustion in the water. This ignition and combustion may have been aided by the air entrained with the assemblage of drops. The hydrogen produced in the combustion probably collected around the tiny drops and enveloped them in bubbles that caused them to rise to the surface as they burned.) Clearly the diameters of the resulting drops will be smaller or even diminished to zero diameter (that is, the particles disappear) after a period of underwater combustion.

The surface textures of the small drops should also be affected by the combustion. If the ideas suggested above are correct, there should be a constant outward purging of ferrosilicon as vapor or colloidal particles as the combustion proceeds. Thus, little or no dark black material can collect on the small particles as they cool in water, compared to the significant deposits observed on the large frozen globules. Thus the small particles that remain after the combustion should have clean, metallic appearances, as seen in Figures 15, 17, 24 and 25.

It should be emphasized that the comments here on small particle combustion are based on the examination of only a few high-speed films that were intended for recording the entrainment of air by the falling globule and were not optimized for the study of the unanticipated small particle combustion. Clearly the ability of the small hot ferrosilicon alloy drops to ignite and burn in water has important implications for the amounts of fines and colloidal materials generated but also from the standpoint of steam explosions. These observations open the possibility that if a fragmentation is initiated by a steam explosion, the finely divided

metal might ignite and burn in the accompanying steam and liquid water; this process could add significant energy to what might normally be mainly a transfer of thermal energy to the surroundings. Steam explosions accompanied by chemical reaction have been shown to be extremely energetic in the case of molten aluminum on both the 10 g scale by Nelson et al. (1994, 1995) and on the 10 kg scale by Rightley et al. (1993). In the larger scale experiments, Rightley et al. measured energy releases that approached those expected from similar weights of high explosives, e.g., TNT. Recently, Cho et al. (1995) described a moderate scale technique to determine whether a molten metal can produce these devastating explosions and to estimate their energetics.

It is evident that further study should be devoted to the ignition and combustion of the small, hot ferrosilicon drops in water and to learning whether chemical-type steam explosions can occur with the molten alloy.

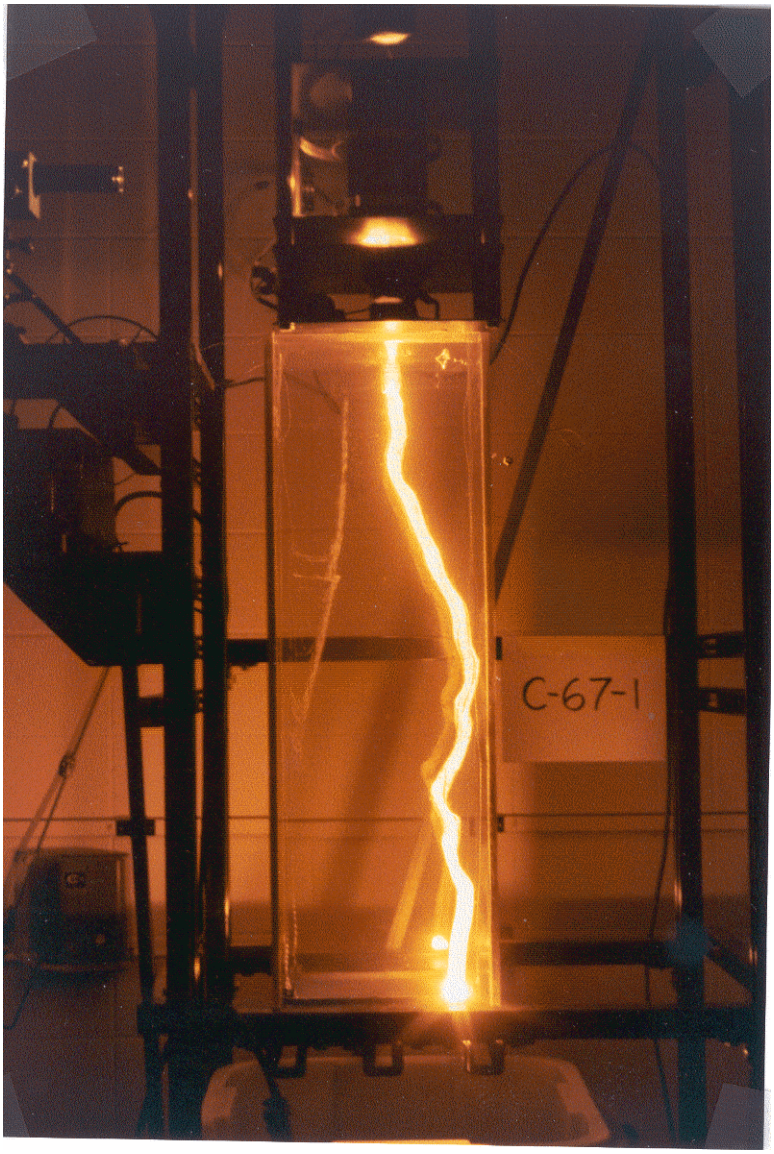

Figure 21. A very swervy trace was generated as a piece of solid broke from the parent in experiment C-67-1. The apparent "trace" at the left side of the chamber is an artifact, caused by a broad mark on the inside of the chamber wall.

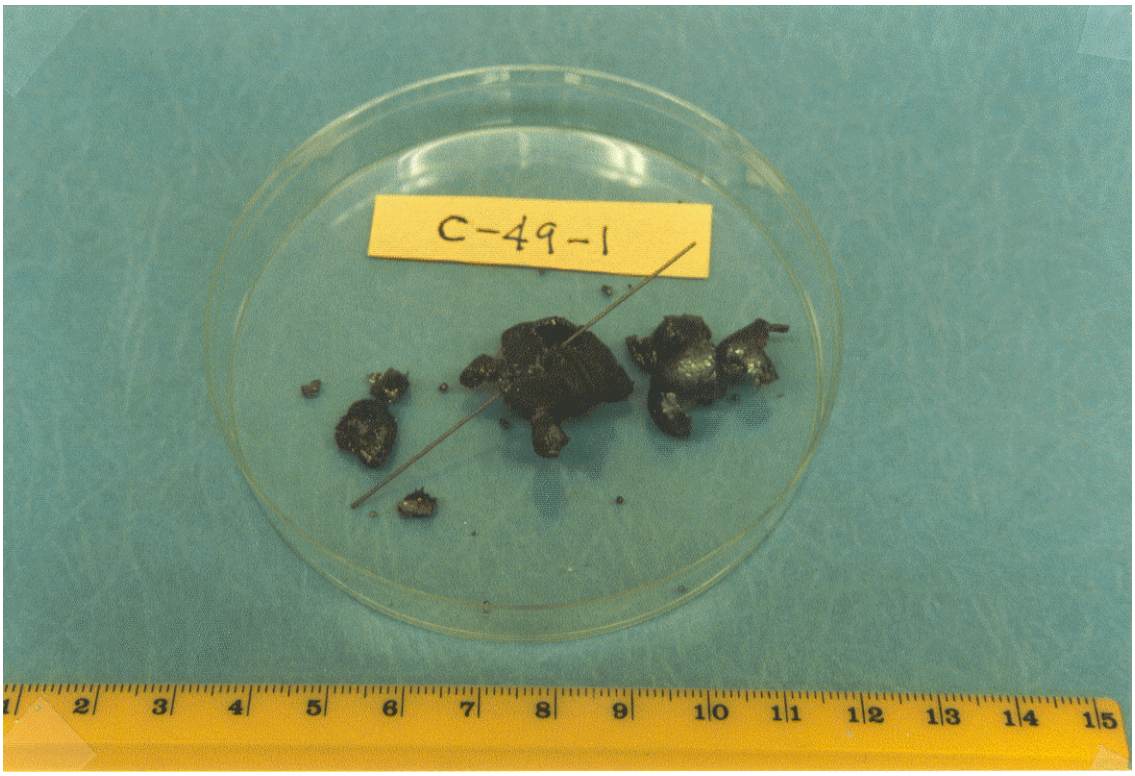

Figure 22. A fork in the self-luminous trace accompanied the inflation and blowing out of the globule in experiment C-49-1. The solidified globule is shown here. (To indicate its openness, a 0.5 mm-diameter pencil lead has been passed through the cavity in the parent globule.) The scale is divided into millimeters.

Duration of the Luminosity

The length of time a hot globule glowed after release into water was plotted as a function of quenching water temperature, as shown in Figure 14. The times shown there increase about four-fold over the temperature range from about 8 to 90 °C—from about 5 seconds at the lowest water temperatures to about 20 seconds at the highest. When the drops were released into a cavity in ice, as in experiment C-36-1, the luminous duration seemed to be somewhat longer, about 7 seconds, than for the drops released into

8 °C water. Apparently, the fall through water removes heat from the drops more effectively than does the non-flowing water in the cavity in the ice, even though the water temperature may be lower. Heat transfer between the drops and the melting ice will be discussed later.

Several comments should be made about the data in Figure 14. First, it should be pointed out that the drop-to-water heat transfer regime was changed substantially where the drops in free fall (in both the meter-deep water and the ice) by being stopped by a solid. In ice, the impact occurred very soon, while in the meter-deep water, the drops impacted the steel debris catcher after about 2 seconds. Thus in both situations, the drops spent most of their luminous time underwater next to a solid.

Had they been allowed to continue their free fall through deeper water, the heat transfer would have been greater due to the water flow past the drop, and the luminous durations would have been shorter than shown in Figure 14. Thus in the coldest water, 8 °C, the luminous durations might be 1 or 2 seconds shorter. To translate this into depth, it might require falls through about 3 meters of 8 °C water for luminosity to extinguish completely before it impacts a solid surface. A water chamber this deep could still fit in a normal laboratory.

A second comment is that our video recording scheme does not provide very precise measurements of time intervals, certainly no better than about 1 second. This uncertainty should be borne in mind when viewing Figure 14. Moreover, the video camcorder used for the time measurements has an automatic exposure setting which has difficulty recording a small luminous object against a dark background. The camcorder is usually operating at maximum sensitivity during our experiments, causing the images of the drops and any unusual events, such as fragmentation, to be grossly overexposed. This causes much detail to be uncertain during the recording. But a definite extinguishment is observed on the video records; its exact interpretation becomes difficult, however. Clearly, additional and better photosensing of the luminosity, both photographic and photoelectric, is necessary.

There is another question to ask about the termination of the luminosity: just what does it coincide with? There are several possibilities. One is that it marks the end of solidification, namely, the point at which

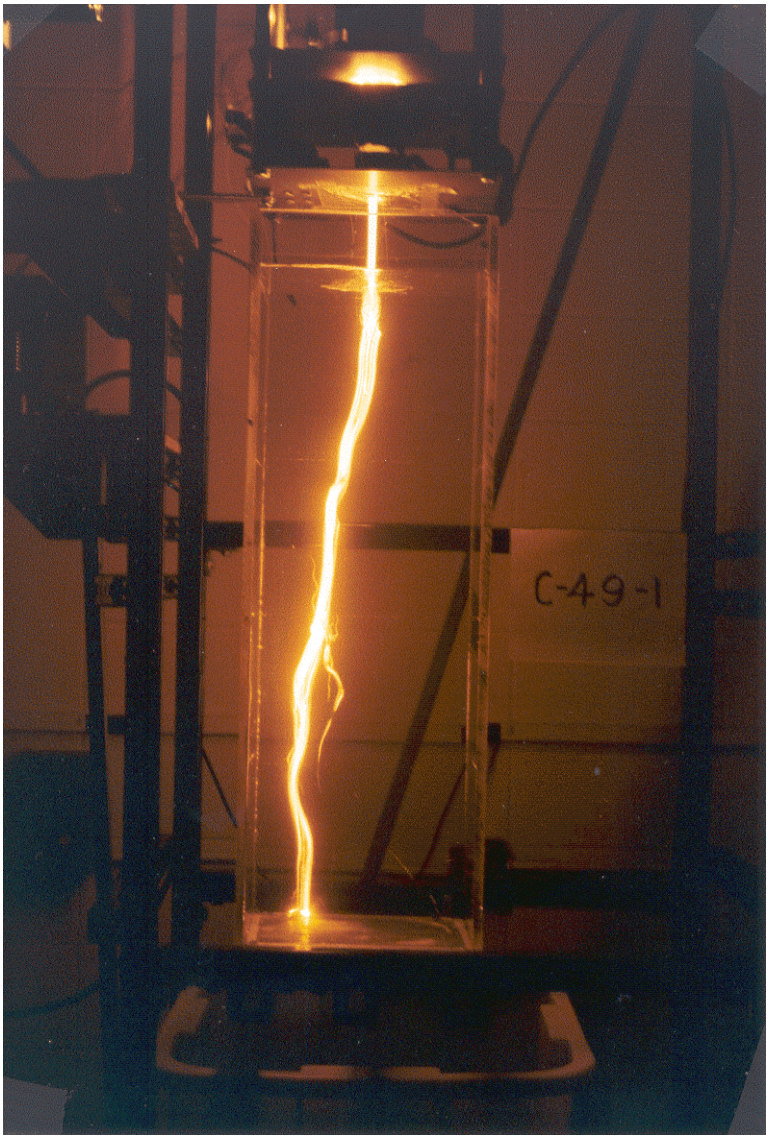

Figure 23. The time-exposed self-luminous photograph that corresponds to Figure 22. Notice the fork in the trace after about 2/3 of the total fall. (C-49-1)

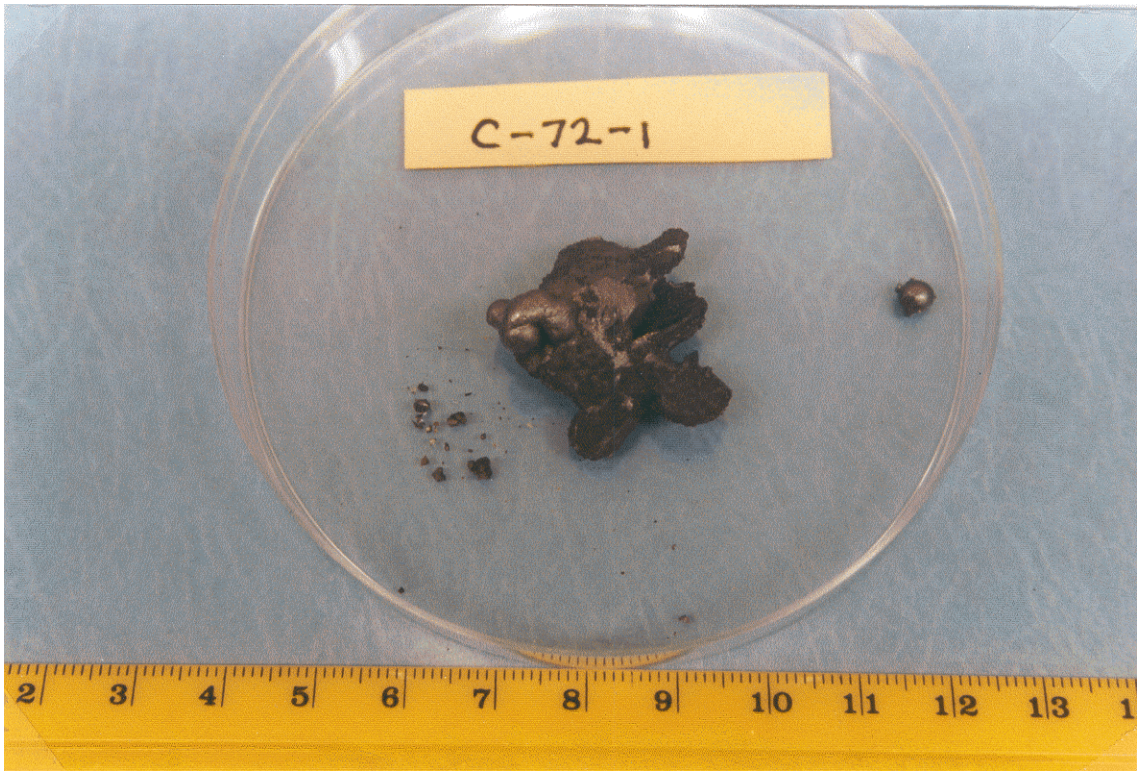

Figure 24. The globule retrieved from experiment C-72-1 had a somewhat metallic appearance. This experiment was performed with a 5% hydrogen in nitrogen mixture bubbling upward through the water column. The water temperature was 20.8° °C. The scale is divided into millimeters.

there no longer is liquid to supply heat of crystallization. Another is that somehow there is an abrupt decrease in the emissivity of the globule that makes it appear that the luminosity has terminated. This might occur when a surface coating forms, or is altered chemically or physically. Another is that it is simply an artifact of the video recording system, for example, a cutoff in the ccd output at some intensity threshold. More studies must be performed to identify the process(es) associated with the cutoff.

The longer luminosity in hot water than in cold shown in Figure 14 was expected from discussions with persons familiar with the industrial processes. It is also predicted from the theory of multiphase heat transfer during film boiling (see, for example, Collier (1972)).

Quenching in Ice

While quenching drops of molten ferrosilicon in ice was not a primary goal of this program, its use provides several interesting possibilities associated mainly with shortening the fall path for the quench. As discussed in the previous section and described in Table 3, a 10-20 mm-diameter drop of molten ferrosilicon requires about 5 seconds for the extinguishment of luminosity in 8 °C water. The time to fall 1 meter in water is about 2 seconds, so the free fall distance for complete luminous decay, then, would probably be about 3 meters in 8 °C water and somewhat longer in water near room temperature.

While quenching in ice does not precisely simulate quenching in cold water, it does provide a simple, compact and inexpensive approximation with the important advantages that:

Figure 25. On many of the globules and the rods after cooling to room temperature were small nodules or rosettes of solidified melt that seemed to have been forced as a liquid from pores in the larger ferrosilicon bodies as they cooled.

(a) as the drop cools off, it is reasonably fixed in space for photographic and video imaging and for pyrometric and other instrumental measurements;

(b) if spontaneous steam explosions are possible with drops of any molten material, a small water-filled cavity in ice would probably provide the most favorable conditions for initiating the explosions, namely, the most subcooled water possible, 0 °C, along with a strong degree of the confinement that often leads to efficient triggering; and

(c) if the globule is first allowed to melt through a thin slab of ice early on before continuing its fall, its travel in water to a given point in the quemching process can be substantially shortened. For example, if it is desired to study the final extinguishment of the globule while still in free fall, the distance might be shortened from a normal 3 meters to 1 meter in 8 °C water. This type of "path compression" might be valuable if quenching in water at elevated temperatures is of interest. For example, if one wanted to study the drop at its point of extinction before it strikes the bottom of the chamber in moderate to high temperature water, where luminous durations are 10 to 27 seconds (see Table 3), the free fall path to extinguishment would be essentially unattainable in a normal laboratory. If the drop were first allowed to melt through, say, 1 or 2 cm of ice, however, the final fall path might be shortened from tens of meters to a few meters, a distance that could be accommodated in a typical laboratory.

Before we started the ice quenching experiments, we attempted to estimate the penetration depths for a hot molten drop released into a shallow cavity in ice. The studies of this phenomenon reported in the literature are very limited, being confined largely to the penetration of heated cylinders into paraffin wax (Moallemi and Viskanta, 1986) and to the penetration of molten material into the earth after a nuclear reactor core

meltdown (the "China syndrome," see Emerman and Turcotte, 1983). A recent review by Bejan (1994) discusses these topics and treats the sinking velocity of heated spheres and cylinders in phase change materials, but does not present information about the maximum penetration depths unheated bodies at a given initial temperature will achieve.

We estimated the maximum penetration depth of a 5 g (14.4 mm-diameter, using equation (1)) molten ferrosilicon sphere into ice by determining the amount of ice that must melt to remove the heat liberated as the drop freezes and is cooled to ice temperature. Because good values of the thermodynamic properties are not available to us, we used some approximations: that the heat capacity of the melt and solid are both the same at 0.2 cal/g/K; that the heat of fusion of the alloy is 200 cal/g; and that the temperature of the drop would be reduced from the liquidus, 1350 °C, to 0 °C. Thus, nominally the heat of fusion of 1000 calories and heat content of the solid of 1350 calories must be removed from the 5 g globule by melting of the ice. Using a heat of fusion for ice of 80 cal/g, the weight of ice melted would be 2350/80 = 29.4 g. If we assume the globule is spherical and would melt only an area in the ice equal to its own cross section, 1.63 square centimeters, then a column of ice 17.7 cm tall would be required. Thus, we conclude that, to a first approximation, the globule would penetrate no further than 18 cm into the ice. This, of course, is a very conservative estimate because it does not take into account the very considerable (and difficult to calculate) heat removal by film boiling of the liquid water in the cavity made by the globule as it cools. Nevertheless, this rough estimate provided a valuable upper limit for the penetration when we were setting up the initial experiments.

We also made an estimate of the descent rate of the same globule as it melts through ice, using more sophisticated flow equations taken from Bejan (1994). The descent rate was estimated to be about 1 cm/s, again disregarding film boiling and the cooling of the drop. If we use the measured luminous duration of 8 s (unknown, of course, before we began the experiments), this would give a maximum penetration of about 8 cm into the ice, of the same order of magnitude as the penetration depth estimated in the previous paragraph.

Unfortunately, we never made a precise experimental determination of the penetration of a globule, but it always was roughly a few centimeters, consistent with the above estimates.

Entrainment of Air

The entrainment of air as a falling drop enters water was observed on our high speed photographs in both cold water (7.5 °C, experiment C-74-1) and hot water (78 °C, experiment C-76-1). A cylindrical bag of air was pulled down around the globules for about 8 cm before it pinched off, allowing the drop to pass downward with little or no air moving along with it. Associated with this bag, however, were small luminous particles that remained near the surface of the water. These particles continued to emit light for several seconds after the main drop had left the photographic frame. As mentioned earlier, these small particles are believed to burn in the water near the entry point. It is not known whether the small particles were traveling with the large drop as it fell, or were torn from the drop by hydrodynamic stripping as it entered the water.

The importance of the entrainment of air in the industrial quenching processes is not known. It is likely, however, that if significant amounts of hydrogen are generated by the metal-water reaction, these air-filled cylindrical cavities would provide an excellent site for producing rich hydrogen-air mixtures that would ignite because of the high temperature of the hydrogen (the self-ignition temperature of hydrogen in air is about 500 °C (Conti and Hertzberg (1988)). This action should cause essentially continuous ignition and burn off the hydrogen as it forms, preventing it from collecting elsewhere and becoming an explosion hazard.

Our observations should be compared with the work of May (1951), who used high-speed motion picture photography to study the splashes formed when steel spheres with diameters between 3 and 76 mm were

released into water with entry velocities between 0.91 and 7.6 m/s. May found that a sphere with low velocity would produce a "smooth" splash consisting of an upward jet unaccompanied by a cavity. But when this sphere's entry velocity increased, the splash became "rough", a cavity was formed and the splash assumed a "basket-shape." (May's cavities are the same as our entrained air bags.) May also found that the entry velocity at which the transition from smooth to rough splash occurs is strongly dependent on the wettability of the sphere's surface, because the smooth splash requires that the water cling to the rear of the sphere as it moves downward through the surface of the water. May found threshold velocities for cavity formation (air entrainment) several times greater for clean, wettable spheres (washed with alcohol) than for dirty spheres (coated with grease). He also observed that the threshold velocity for a nonwetting sphere is predicted by its Froude number, given by equation (2):

$$F = v^2/gd \qquad (2)$$

where v is the velocity of the sphere, d is its diameter and g is the acceleration due to gravity. This relationship seems valid for cold metal spheres up to diameters of about 19 mm.

We look at May's data for 12.7 mm spheres, the diameter of his spheres that falls in the diameter range of interest to our sponsors. He reported that clean spheres of this diameter had a threshold velocity of about 6.1 m/s, while the dirty ones had a threshold velocity of about 1.5 m/s. That is, at velocities above this threshold, the spheres pull a bag of air down below the surface of the water; below the threshold, the water closes quickly behind the sphere and no air is taken beneath the surface of the water. The quick closure is produced by the water clinging to the upper surface of the sphere due to adhesion, which is high with clean spheres and low with dirty ones. Our globules, which enter the water after 30 cm of free fall in argon plus air, have an entry velocity of about 1 m/s, yet still produce cavities. This velocity is lower than May's critical velocity for the dirty spheres.

Our explanation for this low velocity is that our hot globules, above the film boiling temperature in water, are very "dirty" or nonwettable; that is, the water cannot possibly cling to the upper surface of the hot drop and cause the cavity to close smoothly. Thus it probably never will be possible to eliminate the air-filled bags drawn into the water above the hot drops, at even the slowest entry velocities. Although the implications of this statement are unknown at this time, it is important to realize that this phenomenon exists in order to understand all aspects of the industrial quenching processes.

One final comment: As the diameter of the hot spheres decreases, the air bags that are pulled down into the water do not detach. Nelson and Duda (1981, 1982) observed that when 3 mm-diameter drops of molten iron oxide were released into water at velocities above the threshold, the air bags traveled downward with the drops for at least 10 cm. The presence of oxygen and nitrogen in these air-filled bags might be important in the combustion of the tiny ferrosilicon drops described earlier.

Suggestions for Improving the Experiments

In this section, we will suggest ways to improve our present apparatus and procedures. We will not attempt to propose new experiments or strategies, topics best discussed in other documents.

Furnace, Drop Formation and Release

Perhaps the most important improvement we can suggest is to drill one or two small holes in the furnace tube for viewing the positioning of the tip of the rod and the formation of the pendant drop. By proper placement of the helical heating element around the furnace tube, it will be possible to sight the heated tip or, later, the drop through the hole with the pyrometer telescope in order to assure the correct placement of the metal. We feel this simple modification will greatly improve drop quality and the reproducibility of drop weights (see Tables 2 and 3). It would also allow us to sight the optical pyrometer directly onto the

pendant drop, rather than onto the silicon carbide heating element. This would provide good blackbody conditions and, hopefully, confirm our assumption that the drop must be at the liquidus temperature at the time of release.

A second improvement, also relatively simple and inexpensive, would be to eliminate the need for the polyvinyl chloride "fast-acting valve" to close the lower end of the furnace tube by reversing the direction of flow of argon or other atmosphere control gas(es) to downward instead of upward. This would require moving the pipe tee from the bottom to the top of the furnace tube and closing or strongly constricting the top of the tee to cause the gas to flush downward through the heated zone of the furnace and then out through the bottom end of the furnace tube. If desired, the atmosphere control gas can be continued to the water surface below by placing a tube of larger diameter beneath the furnace tube; it would extend to the surface of the water or other catcher. With this arrangement, the drop would not pass through air on its way to the catcher.

The quality of the molten drops might be improved by using either a reducing or more inert atmosphere for heating and melting the alloy. The reducing atmosphere could easily be achieved by flowing a very dilute hydrogen-in-argon mixture over the metal as it melts, while the more inert atmosphere could be achieved by passing the argon flow over heated titanium chips at 500 °C before it enters the furnace. The latter procedure has been used often in our laboratories for experiments with metallic lithium.

A final suggested improvement is the addition of electrical meters to measure both the current and voltage applied to the variable transformer that powers the silicon carbide heating element. These would prevent overloading of either the transformer or the element. A temperature controller for the furnace would be a valuable addition, but not absolutely necessary.

Water Chamber

There are several practical changes that would improve the water chamber. One would be to install a dark background behind the chamber to improve both video and photographic imaging of the luminous globules. In this round of experiments, we used no background. The combination of white walls, struts from the tower and wiring that appears in the images makes for confusion and poor quality. A simple black drape or board behind the chamber would be very helpful. Even better would be the addition of a black matte surface to the inside of the reflective polycarbonate plastic sheet used to construct the water chamber.

Another modification for future chamber construction would be to use non-tinted polycarbonate plastic sheet in its construction. The chamber used here was made from a gray-tinted material. It tends to attenuate the luminosity of the drops, although this is not a serious handicap.

Installation of a small electric winch above the chamber to remove the debris catcher from the chamber with a steady controllable motion would be a great convenience. Our current method for manually removing the horizontal plate from beneath a meter of water uses four wires, one attached to each corner of the plate. Raising the plate with these wires can allow the plate to tilt and drop debris to the bottom of the chamber. The winch would be especially convenient when the experiments are performed with hot water.

A final suggested improvement would be to use a semi-plumbed constant temperature water circulation system in the chamber, along with firmly mounted auxiliary heaters and perhaps a crushed ice bath to remove much of the manual setup and attention as the temperature of the water in the chamber is adjusted either upward or downward.

Ice Catchers

Our few exploratory experiments with ice catchers indicated several needs: the ability to work with the ice physically by slicing and cutting, and by making cavities of desired shapes and depths; the ability to

photograph and otherwise record the boundaries of these cavities and positions and behavior of the drops when within them, for example, by proper lighting; and the ability to work with ice that is considerably subcooled, perhaps with a mechanical freezer or with dry ice, to prevent rapid melting as it is handled. It is also important to be able to clamp and position the blocks of ice rigidly and reproducibly. There seems to be little need for placing the blocks of ice beneath the surface of the water because of the efficient underwater quenching offered by the underwater steel plate.

Diagnostics

Although our time-exposed, open-shutter 35 mm photographs are visually attractive, we believe the images easily can be made to yield quantitative information about the fall of the drops. We suggest: (1) the addition of a motor-driven shutter wheel in front of the camera lens to superimpose time markers on the images of the fall path; (2) placement of fiducial marks on the front and one side of the chamber to provide vertical and horizontal spatial information about the fall paths; and (3) positioning of a meter-tall mirror at 45 degrees along the side of the chamber with fiducial marks to allow the fall path to be photographed simultaneously from two directions perpendicular to each other. By appropriate measurements from the time markers and the fiducials, the velocities and the three-dimensional fall paths taken by the drops can be determined. A further sophistication could be added if desired, namely, recording the photographic images of the fall paths on high resolution black and white film, along with images of standard lamps and an appropriate gray scale. The resulting images can then be converted into temperature-time plots via densitometry. This is not a simple process, but has the potential for adding temperature to the distance and position information obtained above.

Several improvements should be made before further high-speed photography is attempted. These include: (1) placement of timing markers along the edge of each film by addition of a simple time-mark generator to the Hycam camera (these units usually generate flashes of focused light to produce spot images 1 millisecond apart with every tenth spot highlighted); (2) use of a lens on the camera better suited to moderate closeup photography (we used a very wide range zoom lens, 12 to 130 mm, that does not favor sharp closeup focusing); (3) improve our photographic lighting to achieve better uniformity of illumination; (4) obtain a better support stand for the camera (because we did not have access to an appropriate tripod for the camera, we used a stepladder as a makeshift support; we actually favor a drill press stand over the bulkier and more costly heavy duty tripods); and (5) improve our capability for projecting and analyzing our films after processing (the projectors available to us are aged and tend to damage the films).

Our treatment of the debris can be improved by determining the size distributions of the smaller particles (there are optical instruments that operate on photographic images of the debris to generate size distributions automatically) and by determining the densities of the main globules by the Archimedian scheme of weighing them in and out of water.

CONCLUSIONS

From the analyses of the results of thirty experiments related to the quenching of drops of molten 75 w/o Si-25 w/o Fe (with 0.37-0.76 w/o Al and 0.014-0.025 w/o Ca), we conclude the following:

We have been able to reliably produce 10-20 mm drops of the molten alloy and release them into several catchers. Because they are formed as pendant drops at the lower ends of 10 mm-diameter rods of the alloy, we believe their temperatures are at or near the liquidus temperature of about 1350 °C as they are detached. The high temperature system we used is simple, trustworthy and inexpensive; it consists of a mullite tube furnace flushed with argon and heated with a helical silicon carbide resistive element. Its operating temperature is usually 1525 °C. The drops in free fall have high luminosities that provide excellent imaging by photographic and video techniques.

Several catchers can be used to quench the drops. We have used three solids, steel, graphite and ice, and a meter-deep column of liquid water at four different temperatures that range from 8 to 90 °C. The hot drops did not appear to react chemically or physically with the steel or graphite, while there was only a mild chemical reaction with the water indicated by release of hydrogen bubbles.

From examination of the photographic records and the quench patterns on the solid catchers, the drops seemed to be completely liquid as they entered the water, but immediately were coated with a skin of solid when they contacted the water. Spontaneous steam explosions never occurred in the meter-deep liquid water at any temperature. Neither did they occur in small water-filled cavities in ice where the water temperature was assumed to be 0 °C, the maximum subcooling possible. Deeply subcooled water is normally regarded to provide the most favorable condition for initiating spontaneous steam explosions. In no experiment could recalescence be detected as an intensification of either the photographic or video records of the luminous emissions from the drops; this suggests that little or no supercooling of the metal occurs during the quenching.

Each drop, as it enters the water, drags a bag of air down with it. Each bag pinches off after it has grown about 8 cm long. After this occurs, the main globule continues its descent through the water, but smaller particles that may accompany the main globule seem to separate from the parent and remain near the surface of the water.

The smaller particles seem to burn in hot water, near the surface, after separating from the parent drop. This may explain the significant absence of smaller particles in the debris recovered from releases of ferrosilicon drops into hot water.

As anticipated from both anecdotal experiences and heat transfer theory, the drops cool faster in cold water than in hot water. Examination of the video records indicates that in meter-deep water the duration of the luminosity of the drops increases 4- or 5-fold, from about 5 seconds to about 25 seconds as the water temperature is increased from 8 to 90 °C. (These durations arise from cooling of the drops for about 2 seconds in free fall through the water, with the balance of the time spent on a steel catcher plate at the bottom of the chamber.) Related to this, molten alloy globules that fall into shallow cavities in ice exhibit luminous durations of about 7 seconds, possibly somewhat longer than those in 8 °C liquid water. This observation suggests that motion of the globules through even the coldest water provides an important component of the overall heat transfer during the quenching processes.

Ice has interesting characteristics as a quencher for laboratory studies. The penetration depth of a 10-20 mm-diameter molten globule is only a few centimeters, providing a reasonably fixed target for video and photographic imaging, and possibly for high-speed optical pyrometry. If the globule is allowed to melt through a moderate thickness of ice before falling into water, there will be a “compression” of the fall path. This would allow studies of the final seconds of the quenching that might normally require many meters of fall through water; these studies, then, could be performed in laboratories with normal ceiling heights. We

realize that quenching of molten alloy drops completely in ice, or "compressing" the fall by a short period of melting through ice would not provide perfect simulations of the quenching of drops actually in free fall through deep water of a given temperature. Nevertheless it could provide a simple way to obtain important differential information when varying one parameter at a time, for example, drop composition, temperature or diameter. Another possible application of ice quenching would be to use cavities with larger volumes (e.g., several liters) filled with water at ice temperature to look for either spontaneous or triggered steam explosions. The ice would provide not only the highly subcooled water but also the confinement that favors initiation of steam explosions.

ACKNOWLEDGEMENTS

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FINAL NOTE

This document originally was submitted to the sponsor, SINTEF Materials Technology, Trondheim, Norway, on March 15, 1997, as the draft final report that describes the research performed at the University of Wisconsin-Madison during 1996.

Related research has been performed at NTNU, the Norwegian Technological University, Trondheim, Norway, under the direction of Professor Johan Kr. Tuset, and has been described in the thesis "Steam explosions during granulation of Si-rich alloys: Effect of Ca- and Al-additions" by Kjetil Hildal, dated 25 March, 2002. It may be accessed via the Internet link http://www.ub.ntnu.no/dravh/000057.pdf.

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Appendix A

Formation of 10–20 mm Drops of Molten Ferrosilicon

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