NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ANNUAL SUMMARY

Under Contract Number NAS8-32691

June 1979

CRYSTAL NUCLEATION IN GLASS-FORMING ALLOY AND PURE METAL MELTS UNDER CONTAINERLESS AND VIBRATIONLESS CONDITIONS

Prepared For

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The objectives of our research are:

(1) to characterize crystal nucleation behavior in metallic alloys known to form glasses in melt quenching and to assess from this characterization the possibility that massive amounts of certain alloys may be slow cooled to the glass state;

(2) to reexamine the crystal nucleation behavior of pure liquid metals experimentally, under containerless conditions, and theoretically.

A. Experimental Studies

1. $Au_{82}Si_{18}$ Alloy - (Experiments by Carl Thompson)

This alloy has a glass temperature around 25°C. Because of its very low liquidus, about 360°C, it seemed well suited for studies of nucleation kinetics by the droplet dispersion technique. We have made droplet dispersions by two methods:

(a) grinding specimens of the crystalline alloy and, after remelting, sizing to obtain particles with diameters less than 38 microns,

b) shearing the molten alloy under a molten oxide mixture (in wt%: 43 P_2O_5, 25 B_2O_3, 18 LiF, 14 ZnO) in a blender at 650 to 700°C.

This produces a dispersion of alloy particles with diameters in the range 10-20 microns in a matrix of low melting glass. For some experiments we isolated the particles by dissolving away the glass in aqueous alkali. The crystallization and melting behavior of these dispersions were investigated calorimetrically with the Perkin-Elmer DSCII scanning calorimeter. In most of our experiments the particles were isolated from each other by thin SiO_2

coatings formed by oxidation of some of the silicon from the alloys. We presume, but haven't proved, that the coating is amorphous. We have found that after preheating to temperatures above 600°C the major fraction of all the dispersions crystallize at an undercooling of 80°, relative to the eutectic temperature. We have some as yet inconclusive evidence that a minor component of one dispersion crystallized at an undercooling of 155°C. It seems unlikely that the nucleation at 80° undercooling was homogeneous. We plan further exploratory experiments on dispersions in which the particle diameters are smaller (in the range of 2 - 10 microns) and on the effects of different coating techniques, before undertaking more quantitative kinetic studies.

2. $Au_{77-y}Cu_yGe_{14}Si_9$ Alloys - (Experiments by Carl Thompson)

We judged that the kinetic studies of the nucleation might be simplified if made on alloys with glass temperatures well above room temperature but still below 100°C. It seemed that the glass temperature of the Au_4Si based alloys ought to increase with substitution of Cu for some of the Au. Therefore we disc-quenched molten alloys of the type listed above with y = 19 1/4, 38 1/2 or 57 3/4. The alloys containing 19 1/4 and 38 1/2 % Cu were mostly amorphous after melt quenching. Upon reheating the kinetic crystallization temperature, T_{kc}, of the y = 38 1/2 % alloy was about 130°C higher than for the y = 0 alloy. This large effect of Cu substitution on T_{kc}, and apparently on T_g as well, is striking and was unexpected. It seems that we should be able to produce glassy alloys with T_g in the desired range, 50 to 80°C, by substituting the proper amount of Cu. Therefore we will plan to form and characterize glasses with copper substitutions ranging from 5 to 25 atom %.

3. Drop Tube Experiments - (Alvin Drehman)

Dr. Lewis Lacy has offered to make the Huntsville drop tube available for some of our experiments on the crystallization of pure metal and alloy droplets. However before utilizing this facility we are undertaking some smaller scale drop tube experiments in our Laboratories. We are now constructing a short drop tube. We hope to determine, by the recalescence phenomenon, the solidification temperature of molten droplets of Ni and Pd falling down this tube in a $He-H_2$ atmosphere. We are now testing the operation of the tube.

B. Theoretical Studies - (Spaepen, Thompson, Turnbull)

We are investigating some aspects of the theory for the measurement of the kinetics of crystal nucleation frequency by the droplet technique.

In one investigation Thompson and Spaepen examined critically the validity of various extrapolation methods used to evaluate the free energy of crystallization of undercooled liquids. They showed[1] (and see Quarterly Progress Report March, 1979) that the Hoffman extrapolation often used for polymers is much less appropriate for pure metals and metal alloys than are the simpler approximations.

Spaepen and Turnbull[2] (and see Quarterly Progress Report December, 1978) have made an analysis of the stresses which can develop in small metal droplets owing to the differential thermal contraction of the coating film and the molten metal. It was shown that the resulting displacement of the equilibrium crystallization temperature, T_m, can be quite large - enough in some instances to increase the apparent undercooling, relative to the zero stress T_m, at nucleation by as much as 10%. Other possible mechanisms whereby the apparent undercooling might become appreciably larger than the actual undercooling at

crystallization in droplet experiments are discussed in a paper,[3] "On Amomalous Prefactors from Analyses of Nucleation Rates", being prepared by Turnbull. Whether or not these or the tension mechanisms are operative might be tested by precise measurements of the coefficient of thermal expansion and of the heat capacity of the droplets with undercooling. The course of these coefficients with temperature should extrapolate in a reasonable way from those for the bulk liquids at $T > T_m$.

Thompson plans to check this extrapolation for dispersions of Hg or Ga droplets by high precision dilatometric measurements. The dilatometer and temperature bath are being constructed.

REFERENCES

1. On the Approximation of the Free Energy Change on Crystallization, Carl V. Thompson and F. Spaepen, in press, Acta. Met.

2. Negative Pressures and Melting Point Depression in Oxide-Coated Liquid Metal Droplets, F. Spaepen and D. Turnbull, Scripta Met. 13, 149 (1979).

3. On Anomalous Prefactors from Analyses of Nucleation Rates, D. Turnbull, in preparation.