KED 0012

UAH8-38609 D.O 52

Final Report

submitted to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER, ALABAMA 35812

April 19, 1993

for Contract NAS8 - 38609

Delivery Order 52

entitled

Melt Spinning Study

by

Gary L. Workman Ph.D.
Principal Investigator
and
Thomas Rathz
Research Scientist

Materials Processing Laboratory
Center for Automation & Robotics
University of Alabama in Huntsville
Huntsville, Alabama 35899

N94-19423

Unclas

G3/31 0181598

(NASA-CR-193823) MELT SPINNING
STUDY Final Report (Alabama Univ.)
15 p

Final Report

submitted to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER, ALABAMA 35812

April 19, 1993

for Contract NAS8 - 38609

Delivery Order 52

entitled

Melt Spinning Study

by

Gary L. Workman Ph.D.
Principal Investigator
and
Thomas Rathz
Research Scientist

Materials Processing Laboratory
Center for Automation & Robotics
University of Alabama in Huntsville
Huntsville, Alabama 35899

TABLE OF CONTENTS

INTRODUCTION

Containerless processing of materials provides an excellent opportunity to study nucleation phenomena and produce unique materials, primarily through the formation of metastable phases and deep undercoolings. Deep undercoolings can be readily achieved in falling drops of molten material. Extended solute solubilities and greatly refined microstructures can also be obtained in containerless processing experiments. The Drop Tube Facility at Marshall Space Flight Center has played an important role in enhancing that area of research.

Previous experiments performed in the Drop Tube with refractory metals has shown very interesting microstructural changes associated with deep undercoolings. It is apparent also that the microstructure of the deep undercooled species may be changing due to the release of the latent heat of fusion during recalescence. For scientific purposes, it is important to be able to differentiate between the microstructures of the two types of metallic species.

A review of the literature shows that although significant advances have been made with respect to the engineering aspects of rapid solidification phenomena, there is still much to be learned in terms of understanding the basic phenomena. The two major ways in which rapid solidification processing provides improved structures and hence improved properties are:[1]

1. production of refined structures such as fine dendrites and eutectics

2. production of new alloy compositions, microstructures, and phases through extended solid solubility, new phase reaction sequences, and the formation of metallic-glass microstructures.

The objective of this work has been to determine the optimal methodology required to extract this excess energy without affecting the thermo-physical parameters of the under-cooled melt. In normal containerless processing experiments recalescence occurs as the melt returns toward the melting point in order to solidify. A new type of experiment is sought in which the resultant microstructure of the undercooled species is frozen in without going through the melting point regime and subsequent near equilibrium solidification of the remaining liquid. This experimental approach entails the design of an appropriate melt spinning system which is compatible with Drop Tube operations and processing constraints. That work is the goal of this study.

Rapid Solidification Techniques

A number of experimental techniques have been used to rapidly solidify materials in order to generate unique morphologies. One of the more successful techniques used in industry to provide such unique materials by rapid solidification is the melt spinner process.[2-10] The melt spinner provides for such rapid heat extraction ($\sim 10^6$ °/s) that the solidification front is always faced with a highly undercooled liquid in which to grow. There are a variety of techniques which use the melt spinner approach. The most general is where liquid metals are ejected directly onto a spinning copper drum or roller(s), etc. for extracting the heat in the liquid very rapidly. An added consideration for this work requires the degree of undercooling to be a high priority in order to obtain appropriate microstructures representative of undercooled species normally obtained in Drop Tube studies.

The use of a spinning disk has been around a considerable amount of time. Many references occur in the literature concerning this technology. A major concern in developing this type of experimentation is whether the dominant process is controlled by thermal transport or momentum transport.[17] Thermal transport controlling occurs when heat is extracted faster than the momentum is transferred. This occurs when the frozen layer is in motion with the velocity of the chill zone. Momentum transport controlling, on the other hand, occurs when drop momentum is faster than the chill surface and a liquid boundary layer is dragged out of the melt puddle by the moving substrate to solidfy downstream. Many experiments occur as a combination of both cases also.

Some simplifying equations describing the melt spinning process are presented now so that the process variables will be better understood. An average empirical heat transfer coefficient between a puddle of liquid metal and a substrate moving with relative velocity v_r is [10]

$$h = \frac{V_r t_m (C_p \Delta T + L_f)}{\ell (T - T_s)}$$

where C_p = specific heat, L_f = latent heat of fusion, t_m = measured ribbon thickness, T = temperature of the superheated melt, T_s = temperature of the substrate, l = distance from the backedge of the meltpuddle to the end of solidification through the ribbon thickness (see figure). Other equations exist which relate the surface roughness of the substrate, etc. if further non-empirical analysis is needed [11].

The ribbon thickness (t) is given by

$$\bar{t} = \frac{cQ^{1/4}}{V_r^{3/4}}$$

where Q is the volumetric flow rate onto the substrate and c is the constant of proportionality. The ribbon width is given by

$$w = \frac{1}{c} \frac{Q^{3/4}}{V_r^{1/4}}$$

The cooling rate, $\dot{T}$, and the solidification velocity, $\dot{x}$, are given by

$$\dot{T} = \frac{\alpha_0 h}{\bar{t}} \qquad \dot{x} = \alpha_0' h$$

$$\alpha_0 = (T - T_a) / \rho C_p \qquad \alpha_0' = (T_m - T_a) / \rho L_m$$

where T_a is the initial substrate temperature, ρ is the splat density, and L_m is the latent heat. With these equations, one can obtain approximate relationships to describe the outcome of spin melting experiments relative to the Drop Tube configuration.

Previous work at the Drop Tube using a copper plate oriented at 45 degrees provided some interesting results with TiAl system.[16]

One form of the twin substrate technique is a twin roller melt spinnning system reported by Wright, et. al. at the Idaho National Engineering Laboratory.[4] A small system which places the roller seam just below a levitation coil works very well. However the height in which the drop falls is only of the order of several centimeters and it's easy for the drops to hit the slotted region of the rollers most of the time. Ribbons produced from 0.3 grams of aluminum are typically 10 mm wide, 0.2 mm thick and 50 mm. long. Assuming a meter would be the maximum distance traveled then one would expect the maximum velocity of the drop to be around 4.4 m/sec when it impinged onto the rollers. The rollers can rotated to achieve a radial velocity of 5 to 15 m/s. It is estimated that a 80 μm thick ribbon produces a cooling rate of 10^4 to 10^5 °C/sec. A major difficulty arises when the drop does not hit the center of the roller slot. When that happens, then the solidified material comes off in different shapes.

The use of two copper plates attached to dc driven solenoids has also been shown to work nicely for rapid solidification of Nb-Si[6] and Ti-Ce[7]. This technique is known as the hammer and anvil or just anvil technique. A trigger signal is derived from the molten drop passing through an infra-red detector and after a pre-determined time, the solenoids are activated. The plates typically are moving at 4 m/sec upon impact. Comparison of the rapidly solidified products from reference 7 indicated that the hammer and anvil splats had a foil thickness of 0.2 mm, while the splats from a melt spinner rotating with a radial velocity of 50 m/sec varied up to 0.09 mm for normal splats and 0.1 to 1 mm for undercooled splats.

Another useful approach to achieving rapid solidification, called the self substrate technique, is by laser melting and resolidification experiments[12, 13]. Since the bulk metal in a surface laser melt can extract heat from the melt at the same rate as a splat cooled material, the morphologies can be quite similar. In the case of the Drop Tube experiments; however, this technology would not be applicable.

The simplest of these techniques is called the Single Substrate Technique. This uses only one surface upon which to rely for rapid heat extraction from the molten material. A subdivision of this technique called "Chilled" Block Casting makes use of a chilled substrate upon which a stream or droplet impinges with a relative velocity. It is this process that has been performed by past experiments in the Drop Tube using a motionless, (room temperature) copper plate.

All the experiments to date have reported finer microstructure and/or some metastable phase present upon splatting on the 45^{o} copper plate after deep undercooling [16, 6, 18, 7]. Kegley's study [7] of Ti-Ce describes details of the differences achieved using (a) melt-spinning of non-undercooled melts, (b) anvil splat-quenching of non-undercooled melts, and (c) chill block quenching of highly undercooled melts in the Drop Tube using a non-moving copper plate. The quenching conditions and results are listed in Table 1.

TABLE 1

CASE	Foil/Ribbon Thickness (μm)	Melt-to-substrate relative velocity (ms^{-1})	Results
(a)	~200	50	mainly columnar but non-uniform structure.
(b)	~90	4	combination of equiaxed and columnar structure.
(c)	100-1000	42	near-uniform equiaxed microstructure.

Table 1 strongly suggest that better microstructure characteristics can be obtained by highly undercooling the melt before a splat quench is performed. If the relative velocity of the drop-to-plate can be increased by the use of a spinning drum or disc, it can be argued via the heat transfer equation that greater amounts of heat can be extracted from the liquid and thinner ribbon thickness can be achieved. With thinner ribbons, the better the chances of extending the glass transition isotherm further into the melt than just at the surface as reported in the Nb-Si studies [6, 19].

Microstructure Considerations

Grain shapes occuring in splat cooled experiments normally vary from elongated to equiaxed.[15]. Grains elongated to the extent of several mm in the plane of thin foils have been observed for foils (<0.1 μm) near the foil edges. It has been suggested that the elongated grains grow in the liquid spreading out from the from the area where the solidification is already in progress. Otherwise the grains can be equiaxed in the plane of the foil. Impact conditions obviously affect the type of microstructures observed.

Thicker specimens often show columnar growth directed normally from the splat surface. This columnar-to-equiaxed transition is also observed in ingot formation. However, preferred orientations associated with grain structures in splat cooled specimens are rarely observed. This is not unexpected since the rapid cooling provides access to competitive solidification pathways not normally observed in equilibrium controlled processes.

Observations of decreased grain sizes has also been attributed to the onset of increased nucleation in rapidly solidified specimens. Grain sizes as small as μm have been identified in thin areas of splat cooled alloys for certain conditions.

A number of observations from splat cooling experiments have also shown that metals, which normally solidify in a dentritic manner, can solidify in elongated dendritic or rod-like structures in splat cooling experiments. Sufficiently rapid solidification can extend the composition range of the cooperative eutectic growth and lead ultimately to a change in eutectic growth to a degenerate form. Both effects can be attributed to increased cooling rate and subsequent undercoolings. Hence, the primary formation of the equilibrium phase is suppressed as well as producing sufficient disparity in growth rates between the eutectic phases to destroy the cooperative growth processes. For instance, regular cooperative growth of the $Al\text{-}Al_2Cu$ eutectic can be maintained at cooling rates up to 10^5 °K sec^{-1}.

Design Concepts

A melt spinner device placed at the bottom of the Drop Tube should provide the means of extracting an amount of heat equivalent to the heat of fusion before recalescence occurs, so that upon impacting the spinner, any "annealing" effects are prevented. These annealing effects, which are deleterious to maintaining any metastable or supersaturated phases that might have formed in an undercooled liquid, are undesirable if new alloys are to be produced. Obviously much thought will be required for development of drop cooling conditions such that the impact with the melt spinner occurs at the proper time.

Spinning Disk Approach

However, consideration must be given to the possibility that for angles less than 90^o the shear produced in the (Newtonian) liquid may be large enough to eliminate the formation of a continuous ribbon and produce an atomized powder. An atomized powder is a distinct possibility since the momentum of the sheared-off liquid is being thrown back into the melt at these lower angles.

An important consideration is insuring that the undercooled drop is rapidly cooled as it impinges onto the melt spinner. If the tangential velocity of the rotating splat surface is greater than the velocity of the drop, then heat extraction greater than that for a stationary plate will occur. The velocity of a drop at the base of the Drop Tube is around 42 m/sec. Assuming rotating structures of various radii, then one would obtain the following values for rpm of the melt spinner.

radius m	tangential velocity m/s	rpm

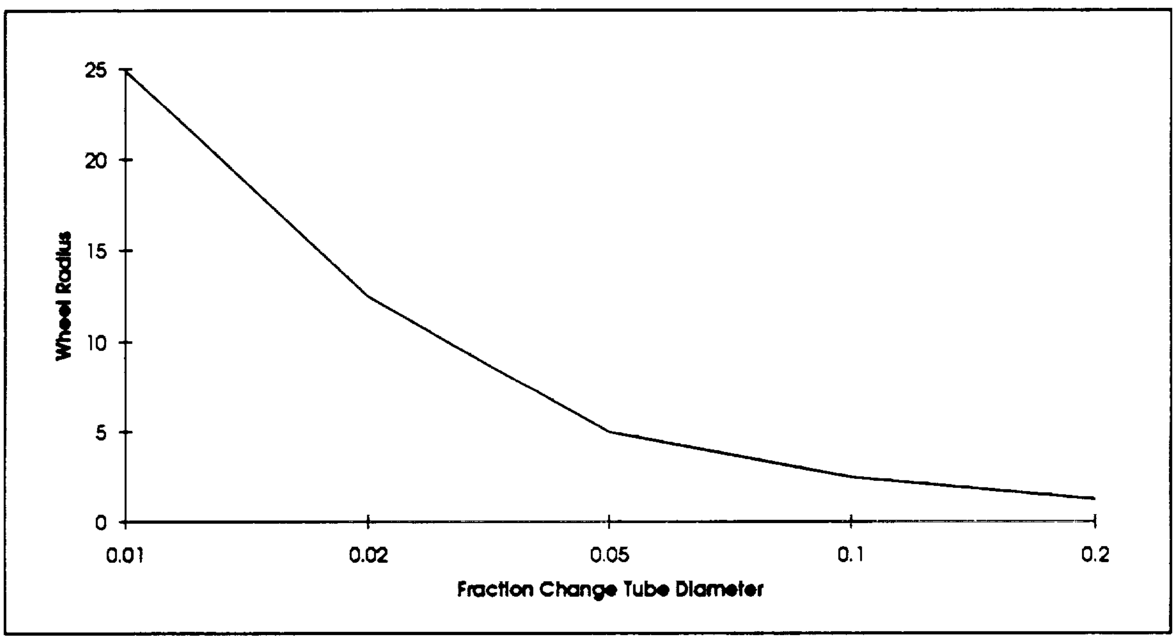
0.5	50	954.92
1	50	477.46
1.5	50	318.30
2	50	238.73

A sensivity analysis to determine the variation in velocity along the radius of the wheel shows that

Required Wheel radius = (Tube Diameter)/ (Fraction of Velocity Change)

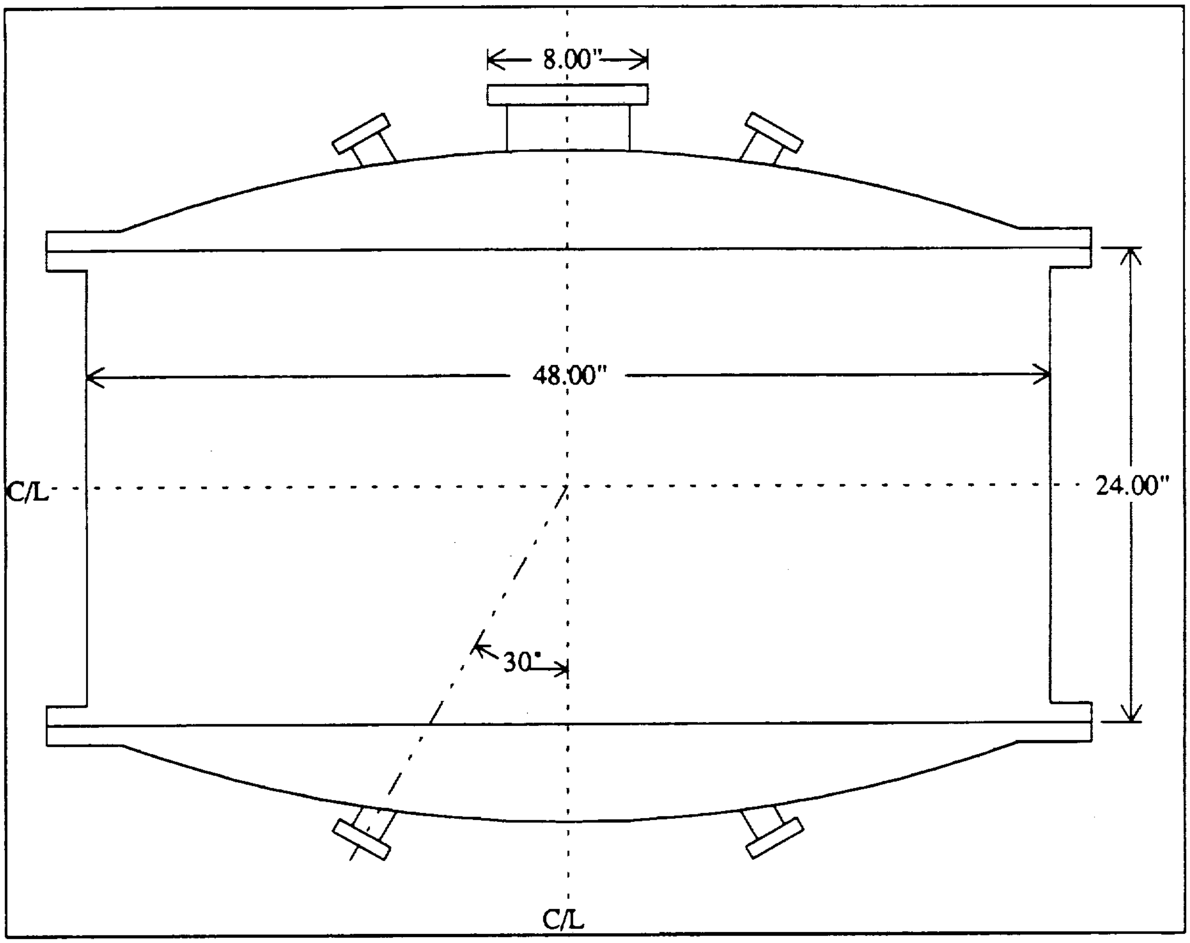
Hence plotting $r = t/(\Delta v/v)$ we get the following graph:

Figure 1. Plot of Radius versus Fraction of velocity across Section of Tube.



In order to implement such technology into the Drop Tube at Marshall space Flight, a very large vacuum containment will have to be constructed at the base of the tube. Figure 2. shows a preliminary design concept for the vacuum chamber as proposed:

Figure 2. Vacuum Chamber required for Melt Spinning Disk



Several discussions with vendors of motors which will operate in the vacuum have been positive. For instance the motors which would work for the proposed system are available from Empire Magnetics will handle both the necessary rpm and the vacuum environment. A major concern exists for an impinging angle other than 90° due to an asymmetric transient torque occuring along the axle of the disk. Using a two bearing mount, which some leverage running along the axle should make the installation robust enough for 45° or any other angle.

A general constraint for using any single substrate rotating spinner at the bottom of the Drop Tube is that the diameter will have to be at least the diameter of the Tube. A wheel configuration of this diameter would have a zero velocity point if centered directly under the Tube. An off-axis wheel would eliminate the zero point but add to the overall dimensions. A drum would have an angular dependent velocity contingent on which side of the drum the drop fell upon. A "conveyor belt" system consisting of a thin metal sheet or even a thin film metal substrate would work harden and fail very quickly due to the continual flexing of the metal as it rotated around the rollers.

To overcome these obstacles, several methods could be used; however, each method will have its own intrinsic problem. One method would be to place a drop "collimator" at the bottom of the Tube which would allow drops to fall only on that portion of a spinner with a known velocity. This would greatly reduce the productivity of useful drops since the drop trajectory is not know for each drop. Another method might be to allow the drop to fall randomly on a wheel but have a technique devised that would determine the impact location. Then knowing the location and the angular speed, the linear throw-off velocity of the ribbon could be found. Other methods are still being considered.

REFERENCES

1. Mehrabian, R., "Rapid Solidification", from *Rapid Solidfication Technology Source Book*, pp. 209,ASM, Metals Park, OH 1983

2. Vogt, E. and G. Prommeyer, "The Influence of Process Parameters on the Cooling Rate of the Meltspinning Process", Rapidly Solidified Metals, Ed. Steeb, Elsivier Science Publishers, 1985

3. Eckler, K., et. al., "Evidence for a transition from diffusion controlled to thermally controlled solidification in metallic alloys", Phys. Rev. 45B (1992) pp 5019 - 5022.

4. Wright, R.N., et. al., "A containerless-melting twin roller melt sppinning system", Rev. Sci. Instr. 61 (1990) pp. 3924 - 3926.

5. Buehler Inc. promotional literature

6. Bertero, G.A., et. al., "Splat Quenching of Undercooled Nb-Si Alloys from 20 to 27 At.% Si", Met. Trans. 22A, 2713(1991).

7. Kegly, D.R., Jr., et. al., "Effect of Undercooling on the Structure of Rapidly Solidified Titanium - 4 Wt. % Cerium", to be published

8. Huang, S.C., et al., "Rapid Solidification Characteristics in Melt Spinning a Ni-Base Superalloy", Met. Trans. 16A (1985) pp. 1773 - 1779.

9. Jech, R.W., et. al. , "Rapid Solidification via Melt Spinning: Equipment and Techniques", J. Met. (1984) pp. 41 - 45.

10. Tenwick, M.J. and H. A. Davies, "The Mechanism of Ribbon Formation in melt Spun Copper-Zirconium", Rapidly Quenched Metals, (eds. S. Steeb and H. Warlimont, Elsevier Science Pub., 1985), p. 67

11. Cremer, P. and J. Wadier, "Analysis of Casting Conditions of Amorphous Ribbons", Rapidly Quenched Metals, Elsevier , 1985, pp. 83 - 86.

12. David, S.A. and J. M. Vitek, "Microstructure of Rapidly Quenched Type 308 Stainless Steel Weld Filler Metal and its Implications on Rapid solidification Processes", Rapidly Quenched Metals, Elsevier , 1985, pp. 847 - 850

13. Baden, B., et. al. "Rapid Solidification of Surface Layers on Alloy Steels Melted by Laser.", Rapidly Quenched Metals, Elsevier , 1985, pp. 851 - 854.

14 Vogt, E. and G. Frommeyer, " The influence of process parameters on the cooling rate of the meltspinning process", Rapidly Quenched Metals, Elsevier , 1985

15. Gresock, L. R. and M. T. Clapp, "Effect of Melt-spinning on the Structure and Superconducting Transition Temperature of Nb_3Si Alloys.", Mat. Ltrs. 6A (1984) pp. 492 - 495.

16. Anderson, et. al. "A Microstructural Examination of Ti-50Al and other binary Ti-Al Alloys that have been Splat Quenched after Bult Undercooling:, Proceedings of the International Materials Conference, 1988

17. (a) Kavesh, S. in **Metallic Glasses** (eds. J.J. Gilman and H.J. Leamy, ASM, Metals Park, OH, 1978), p. 36.

18. Sharma, S.C. and Herlach, D.M., Microgravity Sci. Technol. 3, 145(1992).

19. Bendersky, L., et. al., Mat. Sci. Eng., 89, 151(1987).