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SUBJECT: FACTORS INFLUENCING THE SIZES AND SHAPES OF CRYSTALS
FORMED DURING THERMAL GRADIENT MASS TRANSFER

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FROM: J. W. Prados and J. L. Scott

ABSTRACT

The differences in the sizes and shapes of crystals formed during four common types of thermal gradient mass transfer experiment are discussed. These differences are illustrated with photographs for each case considered. A mechanism is advanced to account for the variations in size of crystals between the various types of mass transfer experiment. Based on an idealized crystal model, equations are developed for predicting the limiting sizes and shapes of crystals which would be stable under various experimental conditions. Numerical computations for a specific system are presented in graphical form.

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Introduction

The shapes and sizes of the crystalline deposits formed during thermal gradient mass transfer have been the subjects of speculation for a considerable time. It has been observed that crystal sizes and shapes are markedly dependent on the nature of the mass transfer experiment, but apparently no attempts to explain this dependence have been reported. The present report describes the type of dependence observed and suggests a possible explanation.

Four of the most common experimental methods for studying thermal gradient mass transfer are the static capsule test, the seesaw furnace test, the thermal convection loop test and the forced convection loop test. These experiments have been adequately described by Hoffman¹ and others. It suffices to note here that the feature which most distinguishes these tests from each other is the degree of agitation in the liquid phase. This increases, in the order named, from approximate quiescence in the static capsule tests to a high degree of turbulence in the forced convection loops. With this increase in agitation, the deposits change in form from long individual crystals to masses of small crystals of approximately equal dimensions.

Observed Behavior

The variety of crystal sizes and shapes encountered in these experiments is shown strikingly in Figures 1 through 11. It is seen that not only size and general shape, but also the detailed structure of the crystals themselves vary from test to test. However, with samples obtained from a given type of test, certain noteworthy similarities are apparent.

In the static tests (Figures 1-5) the crystals formed have almost perfect crystalline facets and length to diameter ratios near ten. (Here the crystal "diameter" is taken as the average dimension perpendicular to the longest dimension.) The maximum length appears to be near 0.2 inch. The crystals grow in random directions from the wall to which they are attached, and, as can be seen in Figures 1 and 2, some of them are hollow.

The crystals grown in the seesaw tests also have maximum lengths near 0.2 inch and length to diameter ratios about 10. An interesting christmas tree type crystal which was observed in the seesaw test is shown in Figure 6.

Crystals formed during thermal convection loop tests appear to fall into two distinct categories. Those formed in short-time tests or close to the walls (and hence during the early stages) for long time tests are quite small (maximum dimension about 0.02 inch) with length to diameter ratios of order unity. Those formed during the later stages of long-time tests may be up to ten times as long and have complex shapes, similar to those observed in the seesaw tests. An illustration of the first class of crystal is shown in Figure 7; the second class appears in Figure 8. Both classes of crystal can be seen in Figure 9, with the finer crystals from the early stages of the run appearing near the walls, and the larger crystals from the later stages near the center of the test section.

The forced convection loop tests produce crystals which are uniformly small, with maximum dimensions near 0.02 inch and length to diameter ratios near unity. If crystallization is allowed to continue in such a system to any appreciable degree, the crystals will completely cover the tube wall in the region of deposition with a continuous granular mass. In forced convection loops, the larger sizes of crystals do not appear, even when the crystalline deposit is allowed to grow until it almost fills the tube. Figure 10 shows such a massive deposit, while a single crystal is shown in Figure 11.

Factors Influencing Crystal Size

Examination of the preceeding figures should convince one that the process of crystallization in liquid metal systems is a complex phenomenon, involving the interaction of many individual effects, some of which are but poorly understood. A complete mathematical description of the process would require a simultaneous application of the principles of fluid dynamics, heat transfer, diffusion in liquids and solids, the kinetics of liquid-solid transformations and many facets of theoretical metallurgy and solid state physics. With the uncertainty that exists in many aspects of the problem it appears that chances are not favorable for a successful mathematical description at this time.

In the present report, no attempt is made to attack the complete problem of liquid metal crystallization. However, a few qualitative and semi-quantitative considerations are presented, which are believed to provide a logical explanation for the dependence of crystal size and shape on the state of agitation in the liquid phase.

Fig. 1 - Crystals from static tests of austenitic stainless steels exposed to lithium 400 hr at 1000°C.

Fig. 2 - Crystals deposited in a static test of type 446 stainless steel exposed to lithium 100 hr. at 1038°C.

Fig. 3 - The crystals shown in Figure 2 at a higher magnification.

Fig. 4 - Crystals from static test of Monel exposed to lithium 100 hr.
at 815°C.

Fig. 5 - Crystals from static test of Type 347 stainless steel exposed to lithium 400 hr. at 1000°C.

Fig. 6 - Crystals from seesaw test of Type 304 stainless steel exposed to lithium for 100 hr., hot zone 815°C, cold zone 730°C.

Fig. 7 - Crystals from thermal convection loop.

Fig. 8 - Crystals from thermal convection loop.

Fig. 9 - Crystals from thermal convection loop of Type 316 stainless steel exposed to lithium-hot zone 815°C - cold zone 580°C. Loop plugged in 293 hr.

Fig. 10 - Crystal mass from Inconel heat exchanger exposed to sodium for 993 hr. Maximum circuit temperature variable between 815-870°C. Minimum temperature 650°C.

Fig. 11 - Single crystal from cold leg of forced convection loop of Hastelloy B exposed to sodium for 1000 hr. Hot leg temperature 815°C. Cold leg temperature 650°C.

The driving force for crystal growth in any of these systems is the degree of supersaturation in the liquid phase, i.e., the difference between the actual liquid composition and that composition which would be in equilibrium with the crystal at the crystal temperature. This driving force may not be the same at all points in the crystal surface due to local concentration and temperature gradients in the liquid phase. For example, in a pipe through which supersaturated liquid flows in turbulent motion with crystallization occurring near the wall, one would expect the degree of supersaturation to be almost constant in the bulk of the flowing liquid and to decrease rapidly near the wall. The result would be that crystals formed at the wall would tend to grow more rapidly in a direction away from the wall, i.e., toward a region of higher supersaturation. Such conditions might be expected to obtain in forced convection loops, and in the higher velocity thermal convection loops. In the static and seesaw tests, however, the liquid flow, temperature and concentration profiles are poorly defined, and it would be difficult to predict any preferred growth direction based on driving force alone.

As a matter of interest, it might be noted that the driving force mentioned above must be quite small in the static capsule tests. The test specimen is maintained in an "isothermal" furnace with no efforts made to cool any portion of it. Temperature variations in the experimental system are probably less than 10°F, corresponding to a very small solubility difference. However, as shown in Figure 1, the mass transfer obtained can be significant, indicating that only a slight degree of supersaturation is required before crystals will begin to form.

The maximum size of crystal formed in a static or seesaw test may well be limited simply by the length of time the test is allowed to proceed, or by the size of the test container. However, the absence of large crystals from forced convection and high velocity thermal convection loop tests indicates the existence of some other limiting mechanism in these situations. Since the sizes of crystals apparently decrease with increasing liquid agitation, the possibility arises that dynamic stresses produced by the fluid motion may be in part responsible for this behavior. If normal stresses at the base of a crystal should exceed the ultimate strength of the bond between crystal and container wall, the crystal would break away from the wall and perhaps be swept into the hot portions of the system where all or part of it could redissolve. If these

stresses should increase with increasing crystal size, then for given flow conditions and crystal shape and orientation there would be a critical size beyond which that crystal could not grow without being swept away. Since the fluid stresses increase with increasing degree of agitation, it would be expected that this critical size would correspondingly decrease as the fluid agitation increases. This could explain the observation of large crystals in static and slowly agitated systems, and small crystals in systems with a high degree of agitation.

In order to place the above considerations on a sounder basis, some computations have been made on an idealized crystal model in an attempt to determine the effect of the various crystal and hydrodynamic parameters on the induced stresses in the crystal. The model chosen is a cylindrical rod of uniform circular cross section attached rigidly its base to the container wall and growing out perpendicular to the wall.

A glance at the photographs previously presented will indicate the highly idealized nature of this model. However, its use leads to results which can be presented in simple form to show clearly the effects of various system variables. The circular cross section is a fair approximation to some of the shapes observed and is one for which the stress and hydrodynamic drag quantities can be calculated. Many of the crystals observed have a rod-like shape, and, except in cases of extremely large numbers of crystals, growth is in a direction generally away from the walls.

Forces on a Solid Rod Immersed in a Fluid

In developing a quantitative relationship between stable crystal size and system parameters, it is assumed that the crystal will adhere to the wall until the maximum tensile stress at its point of adherence exceeds some critical value. It is desired to express this stress in terms of crystal size, geometry, and physical properties, and the system fluid flow behavior. The desired expressions are developed in the Appendix and only the results are presented here.

From mechanical considerations, the maximum tensile stress acting on any cross section of the crystal a distance y from the wall is given by the expression

$$S(y) = \frac{32}{\pi d^3} \int_y^L y F(y) dy \quad (1)$$

where $S(y)$ = maximum tensile stress exerted on reference cross section

y = distance from wall to reference section

L = total length of crystal rod

d = diameter of crystal rod

$F(y)$ = force per unit length acting on crystal rod in a direction perpendicular to the axis of the rod.

It is assumed that the force, F , acts in the same direction along the rod so that the stress will attain its maximum value at the point where the rod joins the wall ($y = 0$). (It should be noted that this will not necessarily be the case for a rod of non-uniform cross-section.) Hence the logical value of stress to use as a criterion of failure is $S(0)$, hereafter simply called S , given by

$$S = \frac{32}{\pi d^3} \int_0^L y F(y) dy \quad (1a)$$

For a crystal suspended in a static system the only force will be that of gravity, which for a horizontal crystal will be:

$$F = \frac{\pi d^2}{4} (\rho_s - \rho) \frac{g}{g_c} \quad (2)$$

where ρ_s = density of crystal

ρ = density of liquid phase

g = acceleration of gravity

g_c = Newton's law proportionality constant

When this expression is substituted in Equation (1a) and the indicated integration performed, the result is

$$S = 4 \frac{g}{g_c} (\rho_s - \rho) d \left(\frac{L}{d}\right)^2 \quad (3)$$

Equation (3) determines the relationship between crystal size and shape, maximum tensile stress and system properties for a static test. It can be seen that for a fixed diameter the stress at the base will increase as the square of the length to diameter ratio, $\frac{L}{d}$, and for fixed $\frac{L}{d}$, the stress increases as the first power of the diameter. Within the limitations of the forgoing assumptions, Equation (3) may be used to predict the maximum size of crystal which would be stable in a given static system subject to a given strength of the bond between the crystal and the wall. Some numerical results calculated from Equation (3) are presented graphically in Figure 12 for the case of iron crystals forming in liquid sodium at 800°C.

In a system where the liquid metal is flowing the force produced on the crystal rod by hydrodynamic drag can be represented in terms of the drag coefficient, C_D , defined by the following expression for a circular cylinder whose axis is perpendicular to the direction of flow²:

$$F = \frac{C_D \rho d u^2}{2 g_c} \quad (4)$$

where C_D = drag coefficient for a circular cylinder immersed in a flowing liquid
 u = velocity of fluid approaching the immersed cylinder

The circular cylinder drag coefficient can be correlated in terms of the cylinder Reynolds number defined by

$$N_{R_c} = \frac{d u \rho}{\mu} \quad (5)$$

where N_{R_c} = cylinder Reynolds number
 μ = fluid viscosity

Such correlations are presented graphically by Knudsen and Katz².

For a cylinder attached to the wall of a pipe perpendicular to the direction of fluid flow, the local fluid velocity will vary from zero at the base of the cylinder to a maximum at its tip. This will lead to a non-uniformity of force along the length of the cylinder. However, if the flow of fluid in the pipe is turbulent (as it is in forced convection loops and many thermal convection loops) an error in S of less than 20% will normally be introduced by assuming the velocity

FIGURE 12. MAXIMUM TENSILE STRESS IN CRYSTAL
AS A FUNCTION OF CRYSTAL DIAMETER
AND LENGTH TO DIAMETER RATIO
SYSTEM: IRON CRYSTAL IN STATIC
LIQUID SODIUM AT 800°C

constant at the mean flow velocity through the pipe. This is probably well within the uncertainty introduced by the idealized crystal geometry. For a given system under the assumption of constant velocity, C_D will be constant and

$$S = \frac{8C_D \rho V^2}{\pi g_c} \left(\frac{L}{d}\right)^2 \quad (6)$$

where V = average velocity of fluid along length of crystal, here taken as the mean flow velocity through the containing pipe.

For a complete analysis, the forces due to hydrodynamic drag and gravity should be added vectorially at each crystal cross section prior to integration of Equation (1a). However, numerical calculations for systems of interest indicate that the hydrodynamic forces are usually one of three orders of magnitude greater than the gravitational forces, so that for agitated systems, only slight error should be introduced by neglect of the latter for all but very large crystals.

Numerical results from Equation (5) are presented graphically in Figure 13. The system chosen is the same as that for Figure 12, i.e., iron crystals in liquid sodium at 800°C. Hence, some idea of the relative magnitudes of hydrodynamic and gravitational forces may be obtained by comparison of the two figures. For example, consider an iron crystal 0.01 inch in diameter and 0.1 inch long, immersed in liquid sodium at 800°C flowing at 5 ft/sec. For this system Figure 12 predicts a stress due to gravity of 1.2 psi. The hydrodynamic drag-induced stress read from Figure 13 is 65 psi. Lest the reader be concerned about the small values of stress predicted by Equation (3) and (5), it should be emphasized that considerably larger stresses will be induced in regions where the cross section of the crystal is markedly reduced. That such cross section reduction frequently occurs can be seen from Figures 1, 5, 6, 9 and 10. Often the smallest cross section occurs at the point of attachment to the wall, forming a particularly susceptible spot for breakage to occur.

Equation (6) predicts that the maximum tensile stress due to hydrodynamic drag should be independent of the absolute size of the crystal, but is proportional to the squares of the length to diameter ratio, L/d and the flow velocity, V . (C_D is independent of N_{Re} , and hence V , over a wide range of turbulent flow conditions.) This prediction is supported by the fact that in the high-velocity, forced convection loops, the crystals formed are approximately

FIGURE 13. MAXIMUM TENSILE STRESS IN IDEALIZED CRYSTAL AS A FUNCTION OF FLUID VELOCITY AND CRYSTAL LENGTH TO DIAMETER RATIO SYSTEM; IRON CRYSTAL IN FLOWING LIQUID SODIUM AT 800°C.

equidimensional. Similar crystals are formed during the early stages of thermal convection loop runs when the channels are unrestricted and the flow velocities are high. However, as deposits build up in such loops, the flow channel becomes constricted, the fluid frictional losses increase rapidly, and the velocity of flow decreases. Hence, during the later stages of the thermal convection loop tests, the longer crystals are stable. The longer crystals do not have the opportunity of forming in the forced convection loops, since here the flow velocity does not decrease appreciably until the deposit has almost completely plugged the tube.

A question arises here from the fact that Equation (6) does not set a limit on the size of a crystal grown in a dynamic system, provided the length to diameter ratio does not increase. However, as previously pointed out, the preferred direction of crystal growth in such systems is away from the wall so that the length will tend to increase faster than the diameter. Larger crystals will eventually exceed the critical length to diameter ratio and be swept away. It is quite possible that when a crystal becomes detached, that it leaves behind an excellent nucleus for future growth, thus maintaining continuity of the deposit.

Conclusions

On the basis of the preceding considerations it is concluded that the size of individual crystals in dynamic thermal gradient mass transfer tests is limited by stresses induced in the crystal by hydrodynamic drag. An estimate of the magnitude of the maximum stress induced in an individual crystal is given by

$$S = \frac{8C_D \rho V^2}{\pi g_c} \quad (6)$$

which is based on an idealized crystal model.

In static and slightly agitated systems, the maximum crystal size is probably determined by the length of the test, or the geometry of the test section. However, stress induced by gravitational forces may also provide a limiting factor in certain systems. This stress is given by

$$S = 4 \left(\rho_s - \rho \right) \left(\frac{g}{g_c} \right) (d) \left(\frac{L}{d} \right)^2 \quad (3)$$

based on the same model as (6).

The testing of these equations would require the examination of crystals formed under controlled flow conditions over a range of fluid velocities and system physical properties. A series of controlled thermal gradient mass transfer experiments is now being initiated in the Liquid Metals Research group, and it is hoped that data may be obtained from these studies to test the validity of the concepts presented herein.

Appendix

Development of Working Equations for Computing Maximum Tensile Stress at the Base of a Cylindrical Rod

Consider a rod of circular cross section, attached rigidly to a supporting plane at one end in such a way that its axis is perpendicular to the support. The bending moment M_B on any reference plane perpendicular to the axis of the rod at a distance y from the base is given by³.

$$M_B (y) = \int_y^L y F (y) dy \quad (6)$$

where:

$M_B (y)$ = bending moment in rod at reference plane. To preserve the rod in equilibrium, this bending moment must be balanced by a restraining moment, M_R , given by

$$M_R (y) = \int_{-\frac{d}{2}}^{\frac{d}{2}} x s (x,y) b (x) dx \quad (7)$$

where:

$M_R (y)$ = restraining moment at reference plane

x = distance measured from center line of rod perpendicular to the rod axis and parallel to the applied load

$s(x,y)$ = normal stress parallel to axis of rod acting on the reference plane at a distance x from the center

$b(x)$ = area increment in reference plane per unit increment in x

Assuming that the rod behaves elastically, the maximum tensile stress, $S(y)$, will occur at the outer edge of the rod ($x = d/2$) and $s(x,y)$ will be directly proportional to the distance from the center of the rod, x . Hence:

$$M_R (y) = \frac{2 S (y)}{d} \int_{-\frac{d}{2}}^{\frac{d}{2}} x^2 b(x) dx \quad (8)$$

The integral in Equation (8) is the moment of inertia, I , of the rod about a horizontal diameter in the reference plane. For a circular cross section this integral is evaluated as

$$I = \frac{\pi d^4}{64} \quad (9)$$

Then

$$M_R(y) = \frac{S(y) \pi d^3}{32} \quad (10)$$

Since for equilibrium of moments one must have $M_R = M_B$, one may combine Equations (6) and (10) to yield the desired expression

$$S(y) = \frac{32}{\pi d^3} \int_y^L y F(y) dy \quad (1)$$

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Notations

<u>Symbol</u>	<u>Meaning</u>
$b(x)$	Area increment in reference plane per unit increment in x
C_D	Drag coefficient for a circular cylinder
d	Diameter of idealized crystal rod
$F(y)$	Normal force acting on a crystal rod at a distance y from its base
g	Gravitational acceleration
g_c	Newton's law force-mass conversion constant
I	Moment of inertia of cylindrical rod about a horizontal diameter
L	Length of idealized crystal rod
$M_B(y)$	Bending moment at a reference plane in a cylindrical rod
$M_R(y)$	Moment opposing bending at a reference plane in a cylindrical rod
N_{Rc}	Reynolds number for flow about a circular cylinder
$s(x,y)$	Normal stress at a point in a reference plane in a circular cylinder
$S(y)$	Maximum normal stress in a reference plane in a circular cylinder
S	Maximum normal stress at base of idealized crystal rod
u	Local velocity of fluid approaching an immersed circular cylinder
V	Mean flow velocity of fluid through a conduit
x,y	Distance coordinates
μ	Fluid viscosity
π	Ratio of circumference to diameter of a circle
ρ	Fluid density
ρ_s	Density of solid crystal

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