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Application of Solidification Theory to Rapid Solidification Processing.

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The objective of this work is to develop guidelines based on kinetic and thermodynamic solidification theory for prediction and control of rapid solidification processes. In particular, segregation effects and rules governing the formation of equilibrium and non-equilibrium phases, including metallic glasses, will be investigated. Areas where significant improvements in alloy properties can be produced by rapid solidification will be emphasized.

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Table of Contents

Application of Solidification Theory to
Rapid Solidification Processing

1. Technical Report Summary

This semi-annual technical report for ARPA Order 3751 covers the period
April 1, 1980 to September 30, 1980.

Task Objective

The objective of this work is to develop guidelines based on kinetic and
thermodynamic solidification theory for prediction and control of rapid
solidification processes. In particular, segregation effects and rules governing
the formation of equilibrium and non-equilibrium phases, including metallic
glasses, will be investigated. Areas where significant improvements in alloy
properties can be produced by rapid solidification will be emphasized.

Technical Problem and General Methodology

Rapid solidification techniques make it possible to produce new types of
materials having significantly better properties than conventionally processed
materials. However, improved predictive techniques and control of rapid
solidification processes are needed. The current studies are focussed on the
science underlying areas where improved materials can be obtained. This work
is both theoretical and experimental. It addresses questions in rapid
solidification in the following areas:

1. Thermodynamics:

    (a) What is the bound on maximum extended solid solubility possible
         by rapid solidification?

    (b) What are the metastable reaction sequences in rapid solidification?

2. Microsegregation and Solid-Liquid Interface Stability:

    (a) Under what conditions is a liquid-solid interface stable during
         rapid solidification so that the solid formed is homogeneous?

1

(b) What segregation effects are produced when the interface is
unstable?

3. Glass Formation:

(a) Is formation of metallic glasses primarily nucleation or
growth controlled?

(b) If it can be a growth controlled process, then what is the
range of interface velocities and compositions where transitions
from crystalline to amorphous structures occur?

The approach taken in this work is to develop rules based on kinetic and
thermodynamic solidification theory to provide understanding of equilibrium
and non-equilibrium processes occurring during rapid solidification. This
information provides a framework which producers of RSR materials can use to
predict effects expected in rapidly solidified alloys. Thus, producers will
be able to make rational choices of materials, for example, choosing more
nearly optimal compositions and avoiding purely empirical trial-and-error
methods, which in the absence of scientific guidelines would otherwise need
to be employed. Work to date has resulted in important theoretical understanding
in each of the three areas described above. Experimental confirmation of
some predicted theoretical results also has been obtained.

Summary of Technical Results, Important Findings and Conclusions

Effects from accelerating the solidification velocity during directional
solidification of near-eutectic Pd-Cu-Si alloys were examined. A strikingly
sharp transition from crystalline solidification to metallic glass formation
was consistently found at a critical velocity of about 2 mm/s. This work
indicates the importance of crystal growth rate models for formation of
metallic glasses by rapid solidification. These measurements and associated
alloy characterization work provide quantitative data needed to test theories

predicting such maximum crystallization velocities. Application of these theories then can permit prediction of glass-forming compositions and critical interface velocities for other alloys.

Since microstructure and compositional variations in rapidly solidified alloys depend to a major extent on cell size and the presence or absence of dendritic or cellular solidification, the question of interface stability at rapid solidification velocities also is of major importance. In addition to previous calculations on critical velocities for the transition between planar and dendritic solidification, directional effects in the initial stages of cell growth in binary alloys have now been calculated. It was found that while cells will follow crystallographic directions at moderate growth velocities, they instead will follow temperature gradient directions when velocities are sufficiently high. The alloy segregation between cells which accompanies cellular growth has a strong effect on alloy properties. To help determine segregation effects, the solute segregation resulting from a curved solid-liquid interface of specified shape in a binary alloy undergoing directional solidification has been calculated numerically.

To test these theories of morphological stability, electron beam surface melting equipment has been modified to provide known heat flow conditions for rapid solidification experiments in Al-Ag alloys. This equipment also will be capable of providing tests of extended solubility resulting from rapid solidification in Cu-Ag alloys.

Plans and Implications for Future Research

Morphological stability results obtained in this work indicate that it is possible not only to calculate the rapid solidification velocity ranges in which planar solidification will be obtained but also to predict the

interdendritic spacing at the onset of interface instability and resulting
solute segregation in velocity ranges where planar solidification is not
obtained. In this latter range, the segregation that occurs between cells
plays a important role in determining the second phases that may form and
hence the properties of the material. During the current period, initial
calculations of the effect of curved solid-liquid interfaces in producing
segregation between cells have been made. In the coming six months, these
calculations will be extended, with particular attention being paid to the
dependence on solidification velocity; and additional factors, such as the
effect of thermal gradients on solute segregation due to curved solid-liquid
interfaces, will be investigated. To test results from this theory, electron
beam surface melting experiments will be performed on Al-Ag alloys. For these
experiments, the necessary equipment has been modified to produce heat flow
patterns comparable for present purposes to those from unidirectional rapid
solidification.

In the study of the range of alloy phases and compositions obtainable by
rapid solidification techniques, current work has shown the importance of
growth rate control on the formation of metallic glasses during unidirectional
rapid solidification of Pd-Cu-Si alloys. This work will be made more
quantitative. In addition, it is planned to use the effectively unidirectional
capability of the electron beam surface melting system to study quantitatively
the effect of solidification velocity on microstructure and composition in
rapidly solidified crystalline Cu-Ag alloys. Here, the possible production of
extended solid solubility and critical conditions for the onset of massive
(partitionless) solidification are of major interest. Theories of phase
reactions and thermodynamic relations derived earlier in the current work will
be applied to predict and explain the compositions and microstructures that

may be obtained. Since intermediate phases are absent in the phase diagram for this alloy system and the separate Cu and Ag terminal phases have the same crystal structure (fcc), this system provides good possibilities for straight forward theoretical explanations of results. After the necessary principles concerning stability and phase reactions are established in simple systems, such as Cu-Ag, it should be possible to extend these essential ideas to more complex systems.

2. Report of Technical Progress and Results

Theory

During the freezing of alloys, a planar solid-liquid interface can become unstable; this leads to a cellular or dendritic interface and causes solute microsegregation. In previous work on this contract, the transition between planar and non-planar growth during the directional solidification of binary alloys was investigated using morphological stability theory and regimes where cellular growth would be expected were defined. The practical implication of this result is that segregation of solute can be expected into the region between the growing cells. Solidification with a planar solidification inter-face will allow intercellular segregation to be avoided. Thus, it is significant to define the limits of this planar regime. In addition, in the unstable regime, a prediction of the wave length (cell size) at the onset of interface instability, such as given by the present theory, provides guidelines for controlling microstructure in these rapidly solidified alloys.

During the past six months, the emphasis in the current work has been put on investigations of the cellular solidification regimes. This work has included derivation of conditions for directional growth of the cells and calculation of the lateral segregation of solute occurring at a curved solid-liquid interface, such as found during cellular growth.

5

Directional effects in the initial stages of cell growth in binary alloys were investigated theoretically. It was assumed that the local solidification rate and composition of solid formed would only depend on the local interface conditions, the temperature, limiting liquid composition, interface orientations and individual components of interface curvature; and a theory was developed which includes all possible directional effects consistent with this assumption. The size of the cells is given by this theory, as well as their directional geometry, their lateral velocity and the compositional segregation, in terms of empirical parameters such as segregation coefficients whose behavior under rapid solidification conditions can be estimated. It was found that, while cells would follow crystallographic directions at moderate growth velocities, they should at high enough velocities follow temperature gradients and not crystal axes.

The lateral solute microsegregation at non-planar solid-liquid interfaces can lead to the formation of second phases in the cellular boundaries and interdendritic regions, with the phases and reaction sequences depending on the degree of segregation. In collaboration with R. F. Boisvert and R. G. Rehm of the Center for Applied Mathematics and R. F. Sekerka of Carnegie-Mellon University the solute segregation that results from a curved solid-liquid interface of specified shape during steady state unidirectional solidification of a binary alloy has been calculated by analytical and numerical methods. Numerical results have been obtained for a sinusoidally shaped interface for various values of the distribution coefficient k and the parameter $\beta = VL/D$ where V is the (constant) velocity of solidification, L is the wavelength of the sinusoidal perturbation, and D is the diffusivity of solute in the liquid. For both very large and very small values of β, the segregation is small and

6

proportional to the amplitude of the sinusoidally shaped interface. For intermediate values of β, dependent on k, the segregation is maximum and no longer proportional to the interface amplitude; the segregation profiles along the interface are distorted such as to be flat near projections of solid into the liquid and rapidly varying near projections of liquid into the solid.

In the calculations, we solve the two dimensional steady state diffusion equation $\nabla^2 C + \beta(\partial C/\partial y) = 0$ for the solute concentration C and evaluate this concentration at the solid-liquid interface whose position is given by $y = W(x) = \delta \cos(2\pi x/L)$. Numerical results have been obtained for amplitudes δ/L in the range 0.05 to 1.0, for k = 0.1, 0.5, 2.0, and 10.0 and for $\beta = 4\pi$, 0.4π, and 0.04π. Both finite difference and finite element methods were used to determine the concentration field.

For β small the cell size, L, is small compared to the diffusion boundary layer thickness, D/V, and the segregation is small and is in excellent agreement with a previously derived analytical expression [S. R. Coriell and R. F. Sekerka, J. Crystal Growth 46, 479 (1979)]. In the opposite extreme of large β, the solute boundary layer is small compared to the cell size; this thin boundary layer essentially bends to conform to the shape of the interface and the segregation is again small. At intermediate values of β, the segregation profiles are such that for a cellular structure one would expect little variation of concentration near the cell tip but pronounced segregation at the grooves. This segregation can strongly affect the alloy compositions and phases that are produced.

Segregation also is necessary to produce two-phase composite alloy structures during solidification at near-eutectic alloy compositions. Theoretical calculations are being done to compare the experimental results on eutectic

7

solidification discussed below with results expected from theory. In other alloys, extended solid solubility may result if the solidification rate is too fast to allow proper phase separation to take place but still slow enough so that crystallization occurs. It is planned to look at this extended solid solubility effect experimentally in Cu-Ag alloys.

Experimental Research

Research has continued on the relationship between eutectic solidification and the formation of metallic glass. The theory of how rapidly one needs to solidify to obtain a glassy structure has usually focussed on the nucleation of the solid phase as the difficult step in crystallization. In the present work, the focus instead has been on the growth process. Diffusional sorting of alloy components is necessary to form a two-phase eutectic composite structure. Theoretical predictions made of the limitation this imposes on eutectic spacing predict that at sufficiently rapid solidification rates this diffusional sorting would no longer be possible. In that case one could expect amorphous solids to be formed. Experiments performed during the first year of this contract under conditions where the solidification velocity was increased during the solidification process showed an abrupt change from crystalline to metallic glass microstructure in Pd-Cu-Si alloys at a critical velocity. Since the amorphous material was formed while in direct contact with the crystalline material, nucleation would not be a limiting factor here. Thus, the observed transition from crystal to metallic glass caused by accelerating the solidification rate indicates the importance of growth rate in producing these amorphous microstructures.

These initial results are being published in the Proceedings of the Second Reston Conference - Rapid Solidification Processing: Principles and

8

Technologies.   In that paper the evolution of solidification microstructure
with increasing interface velocity was documented for Pd-6 at % Cu-17 at % Si
and interpreted with eutectic solidification theory.   These samples were
obtained by quenching thin (1/2 mm ID) alloy filled quartz tubes into molten
gallium at controlled rates.   Experiment and theory point to a maximum velocity
above which crystallization cannot occur.   More recent work provides further
confirmation of this result.   Attempts to crystallize more rapidly than this
maximum velocity lead to glass formation.   A strikingly sharp transition from
crystalline to metallic glass solidification consistently is found.

Work during the current reporting period also was directed toward char-
acterizing and quantifying these results by investigations in the following
three areas:

1)   Characterization of the interface between glass and crystalline
alloys obtained when the alloy passes through the critical velocity.   Figure 1
shows a TEM micrograph of this interface.   The preparation of a thin foil
containing this interface was quite difficult and extensive characterization
of the composition of the crystalline phases present at the interface will be
performed using the NBS STEM.   Other work to characterize the crystal structure
of the phases present in Pd-Cu-Si alloys in the glass forming composition
range is under way.   Samples with compositions close to the nominal single
phase compositions determined by electron microprobe are being given long term
heat treatment and will be characterized by electron diffraction.

2)   The effect of composition on the critical velocity for glass formation.
Alloys with composition Pd-9 % Cu-15 % Si and Pd-15 % Cu-12 % Si have been
prepared for directional quenching experiments.

3)   Measurement of interface temperature during crystallization of Pd-
Cu-Si alloys.   According to eutectic solidification theory a relationship

9

exists between eutectic spacing, interface temperature and interface velocity. A determination of materials parameters involved in these relationships through experiment will permit a quantitative theoretical estimate of the maximum crystallization velocity of the alloy. So far measurement of the interface temperature has been elusive. The method employed uses a fine 0.25 mm sheathed thermocouple immersed in the alloy contained in the thin quartz tubes used to contain the alloy during directional quenching. Because of the directional heat flow and difference in thermal conductivity of liquid and crystalline alloy, a change in slope is normally observed in the temperature-time curve at the interface temperature. To date no such change in slope has been observed. New experiments are being attempted using large diameter alloy samples.

Other experimental work has involved the modification of an electron beam surface melting device to allow greatly improved control of rapid surface melting and solidification experiments. Using deflection coils, this instrument will melt thin surface layers over an area of 1 cm x 1 cm. In this area, heat flow will be essentially unidirectional and can be modelled accurately with heat flow calculations. Here the device will provide for solidification under known velocities and temperature gradients. Using this device, the results of morphological stability theory can be tested using Al-Ag alloys. This theory predicts the solidification of segregation free crystalline solids at high interface velocity. In addition, the essentially unidirectional nature of the heat flow in this apparatus makes it capable of providing tests of theories of extended solid solubility in experiments planned for Cu-Ag alloys.
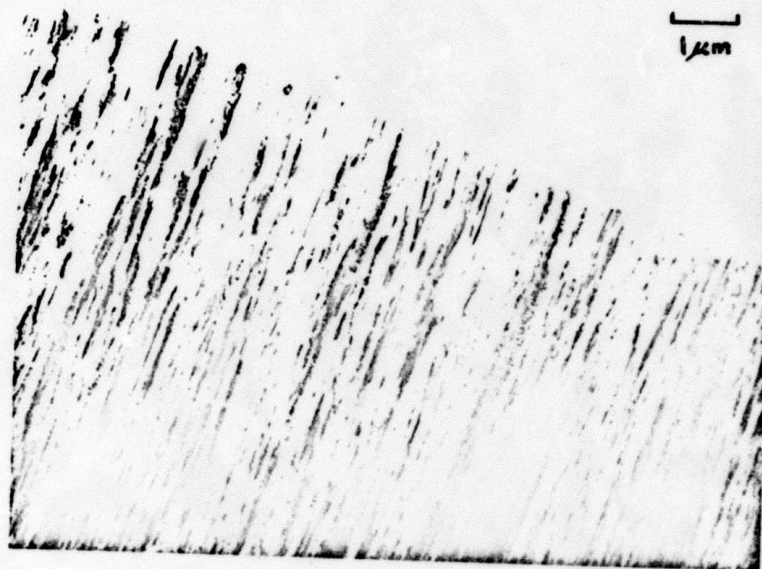
Fig. 1.   TEM micrograph of the interface between fine multiphase crystalline alloy and glassy alloy. This interface is obtained during directional quenching experiments and represents the position in the sample where the maximum eutectic crystallization velocity is achieved.