Non-Equilibrium Solidification, Modeling for Microstructure Engineering of Industrial Alloys (NEQUISOL)

Dieter M. HERLACH¹, Roman LENGSDFRD,², Sven REUTZEL¹,², Peter GALENKO¹, Helena Hartmann¹,²
Charles-André Gandin³, Salem Mosbah³, Asuncion Garcia-Escorial⁴, Hani Henein⁵

¹Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR) Köln,
Germany, dieter.herlach@dlr.de
²Institut für Festkörperphysik, Ruhr-Universität Bochum, Germany
³Ecole des Mines de Paris, CEMEF UMR CNRS 7635, Sophia Antipolis, France
⁴Dept. Metalurgia Fisica, CENIM-CSIC, Madrid, Spain
⁵University of Alberta, Edmonton, Canada

Abstract

Solidification is initiated by nucleation and completed by subsequent growth. In particular the growth conditions control the microstructure evolution. If the melt is undercooled prior to solidification a system of enhanced free energy is created that enables various solidification pathways into different metastable solids. Containerless processing is one of the most efficient methods to undercool metallic melts. In the present project electromagnetic levitation is applied both under terrestrial conditions and in reduced gravity. The non-equilibrium solidification during recalescence and segregation during post-recalescence phase is investigated and modelled. To solidify a spray of droplets a drop tube of 8m is used. A dedicated impulse Atomization facility and a closed coupled gas atomizer are employed to produce powders, which are solidifying in containerless state during free fall. Levitation experiments enable the measurement of undercooling and the corresponding dendrite growth velocity as a function of undercooling. Non-equilibrium effects during rapid solidification as solute trapping in alloys are investigated and analysed within current theories of dendrite growth. The comparison of experimental investigations on Earth and in reduced gravity allows for the determination of the effect of forced convection to the growth dynamics. Also, the evolution of grain refined microstructures upon undercooling is demonstrated and the influence of convection on the critical undercooling for the microstructural transitions from dendritic coarse grained to equiaxed grain refined microstructures is assessed within a model of dendrite break up.

1. Introduction

Solidification of alloys is a complex phenomenon arising in many modern industrial technologies related to casting and surface processing. The present work concentrates on industrially relevant materials such as Ni- and Al-based alloys. Ni-based multicomponent superalloys are important for the production of turbine blades and Al-based alloys are of high relevance for aerospace and automotive industries.

Presently, efforts are directed at optimizing industrial production routes through the use of computer assisted modelling and simulation of casting processes for the foundry industry. In order to develop physically relevant models of solidification, experimental validation is critical.

In the present project solidification is studied under the conditions of containerless processing on Earth and in reduced gravity. Atomization is widely used to produce powders often of metastable microstructures in masses of several kg. Similar conditions are given in drop tube processing in which a spray of droplets solidifies in containerless state under reduced gravity conditions during free fall. Atomization and drop tube experiments are very suitable to investigate the statistics of the formation of various structures and microstructures as a function of droplet size and cooling rate. However, these techniques do not allow for the diagnostics of individual droplets. For this purpose, we apply electromagnetic levitation on Earth and in reduced gravity. The freely suspended drop offers the advantage to directly measure undercooling prior to solidification and the velocity of the crystallization front. By comparing results obtained under terrestrial and reduced gravity conditions allows for investigation of fluid flow effects in the dendrite growth dynamics and in the microstructure evolution of solidification. Fluid flow and heat transfer by forced convection provide predictive tools for microstructure engineering from the melt. They are integrated into models of dendrite growth and dendrite fragmentation to develop a predictive capability of growth kinetics and its influence on the formation of grain refined microstructures.

2. Gas Atomization

Gas atomization is an industrial containerless process where a liquid stream of a molten alloy is disintegrated by high velocity gas, giving rise to powder particles in the range 10-100 microns using a close couple
gas nozzle. The size distribution of the atomized powder particles depends on processing parameters as gas pressure, metal/gas flow rate, melt superheat, diameter and the geometry of the nozzle; on the heat capacity and thermal conductivity of the atomizing gas used; and on the composition, surface tension, density and viscosity of the material to be atomized. This is schematically shown in Fig. 1.

Ni$_3$Al (at %) was melted under vacuum in a magnesia crucible of 2-litre capacity. The liquid was heated at 1650°C, poured into a tundish with a confined nozzle of 4 mm in diameter. At the nozzle exit the liquid stream was disintegrated by argon at a pressure of 2.4 MPa. The powder particles were sieved and classified into four size fractions: -25, 25-50, 50-100 and + 100 $\mu$m, respectively.

Investigations of as processed particles in the scanning electron microscope show that they are mainly spherical in shape as is exhibited in Fig. 2, for the – 25 $\mu$m powder size fraction. The dendrite structure of the powder particle can be observed on its surface as well as on powder particle cross section. As the particle size increases the interdendritic spacing increases, as well as the grain size.

X-ray diffraction patterns show that Ni$_3$Al is the principal phase present in all the powder particles. A small signal of NiAl phase is also detected, increasing with decreasing particle size.

Fig. 1 Schematic sketch of close coupled gas atomization process.

3. Impulse Atomization

Also a drop tube impulse system is used to vary droplet size and solidification modes in broader range. It is shown in Fig. 3. A mono-size or a controlled and narrow size distribution of droplets is generated. The droplets are either allowed to fall through a stagnant gas atmosphere and solidify or are deposited onto a substrate. Using conventional refractory materials, impulses are mechanically applied to a melt with low frequency and high amplitude. These impulses feed the melt through orifices located at the bottom of a crucible and provide the melt stream with the required instability for break up. Thus, discrete lengths of streams generated from an orifice, break up into droplets. Since the droplets accelerate under gravity, no droplet collisions occur despite a narrow spray angle (~5°).

Fig. 2 Surface morphology of Ni$_3$Al atomized 25 $\mu$m particle (left) and SEM micrograph of a cross section of the same powder particle fraction.

Fig. 3 Schematic diagram of Impulse Atomization.

A model was developed to study the solidification behaviour of droplets produced from Impulse Atomization. The model solves the heat balance equation as the droplet loses heat to the atomization gas and phase transformation occurs during solidification. Starting with an off-center nucleation site and an initial user-defined undercooling for the nucleation of the primary phase, the model predicts the thermal history, fraction solidification and microsegregation in the droplet as a function of time.

Fig. 4 shows a comparison of the weight percent of eutectic as measured from neutron beam results as well as SEM stereology for different Cu contents in Al-Cu alloys. The multiple points indicate the results for different powder sizes. It is clear that the effect of chemistry is more pronounced than powder size. Also plotted on Fig. 4 is the microsegregation that would be predicted assuming that solidification occurred under equilibrium conditions as well as Scheil-Gulliver conditions. Finally the model results are shown for two conditions. The first is the model as described by Prasad et al. assuming no undercooling of eutectic. The second is
using the same model by introducing eutectic undercooling. The values of undercooling that were assumed were the same as those measured in levitation experiments. For the eutectic undercooling used in the model, only the thermal component of the undercooling was accounted for at this stage.

4. 3D X-ray topography

3D X-ray tomography was conducted on Al-Cu samples produced by electromagnetic levitation, at the ESRF (European Synchrotron Radiation Facility, Grenoble, F). Stacks of images were recorded with a 0.3 μm voxel resolution, offering the possibility to reconstruct the primary dendritic solidification microstructure. Using a representative elementary volume (REV) moved in the 3D image of the microstructure, a distribution map was also deduced for the interdendritic area consisting of a Cu rich lamellar eutectic microstructure. Using the same REV, a distribution map of the average Cu content was deduced from EDS analyses conducted under a scanning electron microscope. A direct correlation was found between areas with high Cu content and areas with high eutectic fraction.

The average volume fractions of phases were compared with predictions using microsegregation models. The role of the nucleation undercooling and recalescence were identified for both the primary dendritic and the secondary eutectic microstructures. This information was predicted and compared with in-situ measurements of the temperature during processing of the samples. It was concluded that both eutectic undercooling and recalescence must be predicted together in order to predict the measured fraction of phases.

5. Temperature-Time-Profile of solidifying drops

Levitation experiments allow for measurements of temperature-time-profiles during an entire undercooling and solidification experiment, an example of which is shown in Fig. 5.

Solidification after undercooling ΔT of the melt proceeds in two steps. As soon as nucleation occurs, dendrites are formed and propagate rapidly through the volume of the undercooled melt. They release of the heat of crystallization leads to a rapid increase of the droplet temperature termed recalescence. The undercooled melt acts as a heat sink and due to rapid crystallization the heat transferred to the environment can be neglected (quasi-adiabatic solidification). The fraction solidified during recalescence is estimated as $f_R = \Delta T / \Delta T_{hyp}$ with the hypercooling $\Delta T_{hyp} = \Delta H_f / C_p$ ($\Delta H_f$: heat of crystallization, $C_p$: specific heat of liquid). Rapid dendrite growth during recalescence is subject of various non-equilibrium processes as kinetic undercooling of the interface, solute and disorder trapping and the formation of metastable solids. If $\Delta T = \Delta T_{hyp}$ the entire melt solidifies under non-equilibrium solidification. But normally, $\Delta T < \Delta T_{hyp}$ and the remaining part of the liquid $f_{pl} = 1 - f_R$ solidifies under near-equilibrium solidification conditions. While the recalescence time is very short due to rapid solidification, the post-recalescence time depends on heat transfer to the environment. During this period segregation, eutectic solidification of interdendritic liquid, fragmentation of dendrites and coarsening of dendrites can take place. At small cooling rates as present in levitation experiments the primary formed solid can undergo changes during cooling of the as-solidified sample such as disorder-order transition of superlattice structures, solid state transformations of crystalline structures and diffusion less martensitic transformations. For a full description of solidification of undercooled alloys all processes have to be considered.

6. Measurements of dendrite growth velocity

High speed camera technique is utilized to measure the velocity $V$ with which the solidification front propagates through the melt undercooled by electromagnetic levitation technique. Fig. 6 shows a sequence of recorded pictures at various time intervals for an AlNi sample undercooled by 259 K.
The high speed camera is applied both in electromagnetic levitation experiments on Earth and during equivalent experiments using the TEMPUS facility for containerless processing in reduced gravity during parabolic flight campaigns. The dendrite growth velocities of dilute Ni$_{99}$Zr$_1$ and congruently melting Al$_{50}$Ni$_{50}$ were measured, the latter one both in 1g and in reduced gravity.

7. Modelling of dendrite growth

An extended model of sharp interface theory is applied to describe the growth dynamics of dendrites as a function of undercooling. Accordingly, the total undercooling measured in the experiment is expressed as the sum of various contributions:

\[ \Delta T = \Delta T_T + \Delta T_r + \Delta T_k + \Delta T_c \]  

with \( \Delta T_T \) the thermal undercooling, \( \Delta T_r \) the curvature undercooling, \( \Delta T_k \) the kinetic undercooling and \( \Delta T_c \) the constitutional undercooling, respectively. The thermal undercooling \( \Delta T_T = T_L - T \) with \( T \) the temperature at the tip of the dendrite and \( T_L \) the liquidus temperature. Due to the strong curvature of the dendrite tip a depression of the melting temperature due to the Gibbs Thomson effect has to be taken into account by the curvature undercooling \( \Delta T_c = \frac{\sigma}{\rho c} \frac{d}{R} \) with \( \sigma \) the interfacial energy, \( \rho \) the density, \( c \) the thermal capacity and \( R \) the tip radius. For large velocities as given by

\[ \Delta T_c = V/\mu; \quad \mu = \mu_0 (1 - \alpha \cos 4\theta) \]  

where \( \mu \) is the kinetic coefficient for growth of the dendrite tip, \( \alpha \) is the parameter of anisotropy for the growth kinetics. In alloys also mass transport has to be considered. The constitutional undercooling in alloys is given by

\[ \Delta T_c = k \Delta T_f \frac{Iv(Pe_c)/(1-(1-k)Iv(Pe_c))}{\alpha + V/V_D} \]  

with \( k \) the Peclet number of chemical diffusion \( Pe_c = (VR)/2D \), \( D \) the diffusion coefficient, \( \Delta T_f = mC_p(k-1)/k_0 \) the non-equilibrium solidification interval, \( k \) the velocity dependent partition coefficient and \( k_0 \) the equilibrium partition coefficient. Under the conditions of rapid solidification the partition coefficient becomes dependent on the growth velocity. For the range of growth velocity \( V < V_D \) (\( V_D \): atomic diffusive speed) it yields

\[ k(V) = \frac{1 - V^2 / V_D^2}{1 - (V/V_D)^2} \]  

with \( V_D \) the interface diffusion coefficient. Eq.(1) describes the relation of undercooling in terms of the Peclet numbers, i.e. as a function of the product \( V \cdot R \). For unique determination of the growth velocity and tip radius as a function of undercooling one needs a second equation for the tip radius, which comes from stability analysis

\[ \frac{2d_\alpha}{VR^2} = \sigma \left( \frac{1}{2} \xi_f(Pe_f) + \frac{\alpha}{D^2 T_w} \frac{2 k_p}{(1-k)Iv(Pe_c)} \right) \]  

with \( \xi_f \) and \( \xi_c \) are the stability functions depending on thermal and chemical Peclet numbers.

8. Experimental results and discussion

Fig. 7 shows the growth velocity of dilute Ni$_{99}$Zr$_1$ alloy as a function of undercooling as measured (symbols) and the prediction of dendrite growth theory (solid lines). For comparison equivalent results are given for pure Ni.
Fig. 7 Dendrite growth velocity $V$ as a function of undercooling $\Delta T$ for pure Ni and dilute Ni$_{99}$Zr$_1$ alloy, as measured in levitation experiments (closed dots) and prediction of dendrite growth theory (solid lines).

In case of pure Ni very high velocities up to 80 m/s at $\Delta T = 300$K (not shown in Fig.7) are measured. The addition of a small amount of strongly partitioning element Zr leads to a drastic reduction of the velocity in the undercooling range $\Delta T < \Delta T^*$. In this range growth is controlled by chemical diffusion. If undercooling exceeds the critical undercooling $\Delta T^*$ solute trapping sets in and the partitioning coefficient becomes dependent on the growth velocity, $k(V)$. The growth velocity rises very rapidly and behaves as in the pure metal case because the concentration gradient vanishes and growth is only thermally controlled.

Effects of convection are expected if the growth velocity is comparable or less than the fluid flow motion in the melt. Hydrodynamic investigations of forced convection in electromagnetically processed liquid metals suggest values of fluid flow velocity up to 0.5 m/s. We have selected Al$_{50}$Ni$_{50}$ alloy to investigate effects of forced convection on growth dynamics since it forms a congruently melting (no constitutional contributions to undercooling and stability) intermetallic solid phase. Also the concentration effects on growth dynamics are investigated in detail. It is well known that growth of intermetallic phases are short-range diffusion controlled and therefore much more sluggish than in case of pure metals and solid solutions. Fig. 8 gives the results of measurements on electromagnetically levitated alloys Al$_{50}$Ni$_{50}$ both under 1g conditions (open symbols) and in reduced gravity measured during a parabolic flight campaign of DLR and ESA. Results in reduced gravity were obtained in the undercooling range $\Delta T < 100$K. In this range the growth velocity is less than the estimated fluid flow velocity and much reduced compared to measurements on Earth. The results are well described by sharp interface theory without taking into account convection. The deviations of results measured in 1g from the predictions of theory disappear if the growth velocity exceeds the fluid flow velocity. These findings clearly demonstrate that high accuracy measurements in reduced gravity are mandatory to experimentally verify theoretical models without disturbing effects due to convection.

9. Grain refinement by undercooling

Fig. 9 shows the grain size as a function of undercooling for Ni$_{99}$Zr$_1$ alloy. The dots represent measurements of microstructure on samples undercooled by electromagnetic levitation on Earth. It is evident that two microstructural transitions occur. At a critical lower undercooling $\Delta T^*(1)$ a coarse-grained dendritic microstructure changes to a grain refined equiaxed microstructure and at a higher critical undercooling $\Delta T^*(2)$ the coarse-grained dendritic microstructure reappears again. The grain diameter changes by two orders of magnitude at both transitions. Such microstructural evolution during solidification is described by a model of dendrite fragmentation, which was experimentally verified. The concept of the model is basing upon the assumption that narrow dendrites fragment in spherelike elements. A Platteau-Rayleigh instability acts as a driving force for this process. The fragmentation of dendrites requires a characteristic time $\Delta t_{bu}$, which is needed to break up the dendrites.

Assuming that side branches of dendrites perturb the trunk with an initial amplitude which scales with the dendrite tip radius $R$ and the main driving force for the perturbation is the concentration gradient in the dendrite trunk that counteracts the stabilizing effect of minimum interface area (energy), the break up time is calculated...
with $R_T$ the dendrite trunk radius. It is correlated to the dendrite tip radius $R(\Delta T)$ via an empirical relation as $z = R/T \approx 20^{(8)}$. From recently extended dendrite growth theory the dependence of $R$ from forced convection is estimated. The change of the critical undercoolings for microstructural transitions by fluid flow is determined$^{(5)}$. Since dendrite break up needs diffusion in liquid fragmentation appears if the break up time $\Delta t_{bu}$ is smaller than the plateau time $\Delta t_{pl}$ (cf. Fig. 5). The critical undercoolings for microstructural transitions are defined by the condition $\Delta t_{bu} = \Delta t_{pl}$. The shadowed regions represent the transition range if convection is switched off.

10. Summary and conclusion

It was shown that containerless processing by electromagnetic levitation on Earth and in reduced gravity is a powerful tool to study growth kinetics and microstructure evolution with new processing parameters as undercooling and convection in production routes of metals and alloys. If in such a way physical models of solidification are developed and experimentally verified capable to quantitatively predict microstructure evolution industrial production routes benefit by circumventing post solidification treatment. The upcoming period of the use of the International Space Station opens up a new area of research in which continuous and long duration series of experimental investigations in reduced gravity become possible.

Fig. 9 Grain size as a function of undercooling for Ni$_{99}$Zr$_1$ alloy. The microstructure changes from coarse grained dendritic (left) at a lower critical undercooling to grain refined equiaxed (middle) and at an upper critical undercooling to a coarse grained dendritic microstructure (right). The dots represent results of microstructure investigations of levitation processed samples. The shadowed regions represent the span of critical undercoolings for dendrite fragmentation calculated within the Karma model with and without convection$^{(3)}$. 

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References