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Advanced Solidification Studies on Transparent Alloy Systems: A New European Solidification Insert for Material Science Glovebox on Board the International Space Station

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Investigations on solidifying transparent model alloys have served frequently to gain knowledge on physical phenomena occurring during solidification of metallic alloys. However, quantitative results were obtainable in thin samples where convection can successfully be suppressed. Quantitative studies on three-dimensional phenomena not being affected by natural convection are thus only possible under microgravity conditions. Therefore, the European Space Agency (ESA) is planning to launch a new insert for the material science glovebox on board of the International Space Station for studies on solidification phenomena in thick samples. Four different classes of transparent model alloys will be used to address the following scientific topics: (I) columnar to equiaxed transition in solidification processing, (II) novel peritectic structures and in situ composites; (III) solidification along an eutectic path in binary alloys; and (IV) solidification along an eutectic path in ternary alloys. In this article, we give details on the scientific objectives and the operational features ESA's new solidification device will offer.

INTRODUCTION

Transparent alloys are organic compounds that show a nonfacetted high-temperature phase. Molecules in this phase are more or less free to rotate around their center; therefore, the solidification is similar to metals. Studies on solidification of transparent model alloys have since long led to breakthrough findings that permitted deeper understanding of physical phenomena occurring during solidification of daily life alloy systems. With that knowledge, it was possible to set up advanced computer codes that nowadays help the metallurgical industry to optimize product quality and reduce production time.

Currently, four European research teams together with the European Space Agency (ESA) are involved in the planning, design and implementation of a new solidification related insert for the materials science glovebox (MSG) on board of the International Space Station (ISS). These four teams are as follows:

- CETSOL (Columnar to Equiaxed Transition in Solidification Processing)
- METCOMP (Metastable Solidification of Composites: Novel Peritectic Structures and In Situ Composites)
- SEBA (Solidification along an Eutectic Path in Binary Alloys)
- SETA (Solidification along an Eutectic Path in Ternary Alloys)

The aim of the planned experiments is to study the morphological instabilities of directionally solidified transparent alloys under purely diffusive conditions. Observations will be performed in real time, and the dynamics of the solidification structures will be followed with a micron-scale resolution, over a large (centimetric) space scale and over long (up to several 10 h) periods of time. Such observations would be strongly sensitive to convective motions in the liquid, which in ordinary conditions on Earth, entail a detrimental redistribution of the solute on a scale comparable to the container size. Such convective motions are suppressed in microgravity.

In the current publication, the research objectives of three from the aforementioned four research teams are described insofar as they are concerned with *in situ* observation of transparent model alloys. In addition, we present the main features of the new piece of hardware, which is termed the Transparent Alloys instrument.

PROJECT OBJECTIVES

In the following, the objectives and specific goals are given.

CETSOL (Columnar to Equiaxed Transition in Solidification Processing)

The grain structure in many castings is often a competition between columnar and equiaxed dendritic growth. The investigation of the transition between these grain structures is the objective of the CETSOL research program, both experimentally and numerically. From experimental point-of-view, transparent organic materials offer *in situ* and real-time observation with microscopic optics. The underlying phenomena and physics like columnar dendritic growth and grain selection, nucleation and equiaxed dendritic growth, as well as flow phenomena in the melt interacting with solidification can be assessed.[1] A significant contribution to the improvement of integrated modeling of grain (crystal) structure in industrially important castings is expected. In particular, this is aimed to give scientists and industries confidence on the reliability of the relationships and numerical tools introduced in the integrated numerical models of casting they are using for in-house optimizing of processes.

The major aim of solidification experiments of the CETSOL team in the Transparent Alloys instrument using transparent model alloys will be to identify growth regimes (columnar or equiaxed or mixed) and physical mechanisms in dependence of the experimental parameters (solidification velocity, temperature gradient) for diffusive heat and mass transport and without gravity effects. The critical parameters for the columnar-to-equiaxed transition will then be determined and compared to numerical predictions. Convective transport in the melt and sedimentation of equiaxed grains or inoculation particles will be avoided in the low-gravity regime and will enable modeling approaches a basis for sound comparison.

The CETSOL experiments focus on different aspects of the CET using the two binary alloys neopentylglycol-(D)camphor and the succinonitrile-(D)camphor. For the first system heterogeneous nucleation and subsequent equiaxed growth in the bulk melt ahead of the columnar front was already observed.[2] The Transparent facility shall enable a systematic investigation of the critical parameters under low-gravity conditions and for different alloy compositions (20–40 wt.% (D)camphor). Pulling rate jumps in the Bridgman-type solidification setup will be carried out at constant thermal gradient. The sequence shall be repeated at different thermal gradients and for different pulling rates to identify the influence of these solidification parameters on CET. Figure 1 shows an example for columnar and equiaxed dendritic growth obtained in the Transparent facility.

For succinonitrile-(D)camphor, a thermal gradient decrease will be performed. These experiments are closer to casting conditions and should give information on the fragmentation phenomenon (Fig. 2). The sequence shall be repeated using different cooling rates. The parameters gained by microgravity experiments will be determined and compared to ground-based experiments and numerical predictions.

METCOMP (Metastable Solidification of Composites: Novel Peritectic Structures and In Situ Composites)

Investigations on peritectic metallic systems show a wide range of possible microstructures. Bands, islands, tree-like microstructures, and coupled peritectic growth are appearing when the primary and peritectic phase solidify in a competitive manner. Postmortem analyses of quenched peritectic alloys were studied to estimate the process conditions necessary for the occurrence of the different microstructures.[4] However, the dynamic of morphological transitions can only be studied by *in situ* observations. Therefore, corresponding studies on transparent peritectic model systems are highly

Fig. 1. Typical situation of equiaxed dendrites made from neopentylglycol solid-solution, nucleation, and growing ahead of the columnar dendritic front.

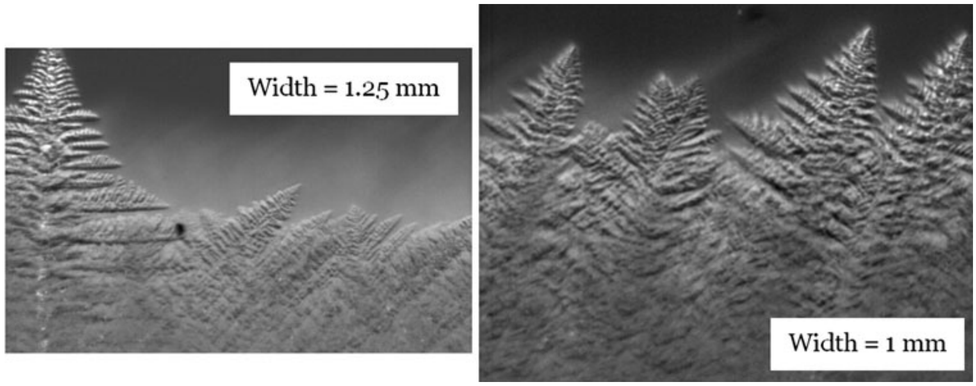

Fig. 2. Typical image of dendritic columnar growth (succinonitrile—8.4 wt.% camphor). The clear observation of secondary branches allows to study their growth dynamics and to reveal particular phenomena such as bending or detachment that may be involved in CET.[3]

wanted. In such a system, both the proeutectic and the peritectic phase must reveal a nonfacetted solid/liquid interface, so that their growth morphology is indeed comparable with metals, a condition that could not be full filled till a corresponding system was first described in literature in 1995.[5]

Today, a few more model systems have been reported to show a peritectic phase diagram and the required plastic phases needed for nonfacetted solid/liquid interfaces. For the investigations of the MET-COMP team, the peritectic system neopentylglycol tris-hydroxymethyl-aminomethane (NPG-TRIS) was selected as the temperature range necessary for *in situ* observations of peritectic solidification phenomena in a micro Bridgman-furnace setup is still accessible.[6] The most problematic fact with this system is the instable behavior of TRIS at elevated temperature.[7] It must strictly be ensured that corresponding NPG-TRIS alloys must never be heated above a given temperature limit. This condition restricts of course the use of larger temperature gradients and in consequence extends the duration of a single experiment to 10 h or more. During such long experiments, natural convection in the liquid ahead of the solid/liquid interface affects the stable growth conditions and thus alters the growth morphologies. It is thus necessary to reduce natural convection to a minimum. Long-time experiments and reduced natural convection makes corresponding studies on board of the ISS compulsory.

To prepare for corresponding experiments on the ISS, laboratory experiments on Earth were performed. We have tested a variety of cartridge geometries, temperature gradients, and alloy composition, and we worked out process conditions for the occurrence of a wide range of peritectic microstructures above, close to, and below the limit of constitutional undercooling.[8] For instance, oscillating behavior was found close to the peritectic concentration at pulling rates above the critical velocity.[9] Here, both phases grow in a competitive manner whereby the primary phase solidifies in form of dendrites/cells. The second phase solidifies

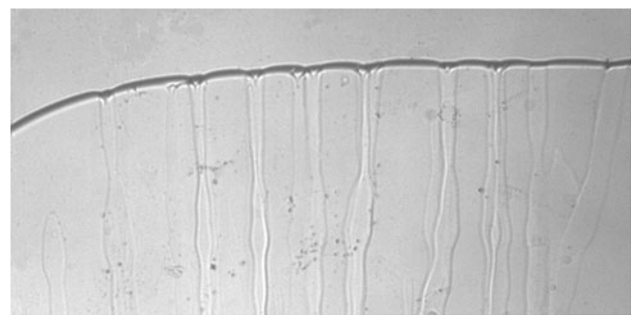

Fig. 3. Example of isothermal peritectic coupled growth in thin samples (NPG-0.46% mol fraction TRIS). Although the isotherms are horizontal, the left side of the picture shows a curved solid/liquid interface, which is a result of convection in the cartridge.[10]

within the interdendritic liquid and influences the solidification structure of the primary phase in a way that oscillating solidification occurs. At a solidification rate close to and below the critical velocity, only a planar solidification front is observed. In a few cases, the growth of bands is observed at the beginning of the solidification. In other cases, the formation of coupled peritectic growth and its destabilization was observed (Fig. 3).

SEBA (Solidification along an Eutectic Path in Binary Alloys)

The team will focus on the dynamics of formation of rod-like eutectic structures (a regular dispersion of thin fibers of one phase into a continuous matrix of the other eutectic solid). Such eutectic microstructures result from a coupled growth of the two eutectic phases. Ideally, the coupled-growth dynamics leads to the formation, in steady regime, of periodic patterns with a hexagonal symmetry along the solidification front.[11] Specific goals are as follows:

- To study the formation and the relaxation of topological defects in rod-like structures

- To study the rod-to-lamellar transition of eutectic growth patterns
- To study the forcing effects of the distortions of the thermal gradient

These topics can be detailed as follows:

(1) Hexagonal eutectic patterns most often exhibit a large density of topological defects (this is due to the rotational degeneracy of hexagonal patterns about the solidification axis).[12] To date, the dynamics of such defects is essentially unknown.
(2) A transition from hexagonal (rod-like microstructure) to banded (lamellar microstructure) can occur, which is known to depend primarily on the concentration of the alloy. However, some evidence in the literature suggests that hexagonal and banded patterns can coexist in a given experiment.[13] The conditions under which such coexistence is possible remain to be determined.
(3) Experimental systems can deviate slightly from the ideal case, defined as being isotropic (no crystallographic effect) and planar (axial thermal gradient). In particular, the difference of thermal conductivity of the liquid, the solid, and the container walls that are in contact with each other creates a distortion of the thermal field, which induces a continual forcing of the structure. This effect remains to be characterized in long-duration experiments.

The team proposes to perform real-time observations using the method described in Ref. [14] of a directional-solidification front in bulk samples of transparent eutectic alloys. The growth front is observed obliquely in dark field through the liquid and a glass wall of the container with a long-distance microscope. It is shown that a focused image of the whole growth front can be obtained at a certain tilt angle of the microscope. At this tilt angle, eutectic fibers of about 3–5 μm in diameter can be clearly seen over the whole growth front in 400-μm-thick samples (Fig. 4).[15,16] Samples of succinonitrile-(D)camphor alloys of near-eutectic composition are proposed. For minimizing crystallographic effects, the samples would comprise a crystal selector. Solidification will be performed at various pulling speed values. The misalignment of the thermal gradient will be tunable.

DIRECTIONAL SOLIDIFICATION DEVICE

ESA's transparent alloys instrument, designed by QinetiQ Space (McLean, VA), is a kind of classical Bridgman furnace, which is based on the famous thin-sample directional solidification method. It possesses three specific features. First, the thickness of the cartridge will be considerably larger (in the millimeter range) than that of the widely used thin samples (in the 10-μm range). Second, observation will be possible both in side view (optical axis perpendicular to the sample plane) and in oblique view. Third, a grain selector will allow one to study growth of large crystals or eutectic grains of given orientation.

The solidification bench is composed of a "hot zone" and a "cold zone," made of thermally regulated metallic blocks fixed at a defined distance from each other (the so-called adiabatic zone). The temperatures of the cold and hot zones will be tuned in such a way that the solid–liquid interface is located near the middle of the adiabatic zone. Solidification (melting) will be controlled by moving the sample along the thermal axis at a tunable velocity toward the cold (hot) zone.

Flat glass-wall cartridges will be used, with inner dimensions of 100 mm along the thermal gradient axis), 60 mm perpendicular to the optical axis (parallel to the isotherms), and 1 or 6 mm in the third direction (thickness). Inside the cartridge, special means will be applied to compensate for any volume changes (especially the around 5% density difference between solid and liquid).

The length of the adiabatic zone will be 7 mm. The thermal environment will be such that the solidification process will be controlled by the hot- and cold-zone temperatures and by the pulling rate of the sample. The hot-zone temperature will be adjustable between 323 K and 500 K, and the cold-zone temperature will be between 263 K and 400 K. Having set the temperature of the hot and the cool zone, the temperature gradient will range from about 5 K/cm to 100 K/cm. As the thermal gradient in the sample alloy cannot be measured directly, a dedicated reference cartridge containing at least one thermocouple within the melt will be used to verify the actually achieved gradients inside the sample alloy in a thermally representative setup during ground reference experiments.

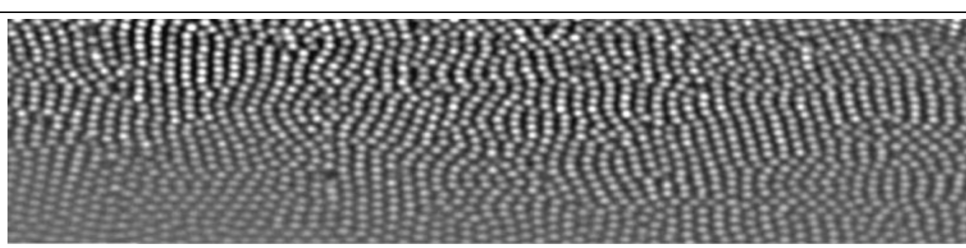

Fig. 4. Images of a eutectic solid/liquid interface resulting from scientific breadboard tests by SEBA team and confirmed to be of sufficient quality for analysis.

The cartridge will be translated in longitudinal Z-direction in a controlled way over the whole length of the samples. Translation speed of the cartridge will be 0.01 μm/s < v < 100 μm/s. The mechanism is programmable in order to perform various speeds in steps of ≤0.003 μm/s during one experiment. The mechanism will offer long-term stability of 1% over a time period > 12 h.

The experiment will run following a preprogrammed experiment procedure, but interaction from ground will also be possible. Heater and cooler temperatures, pulling velocity and optical parameters will be adjustable from ground with a reaction time compatible to the experiment objectives. The system will have the possibility to store images onboard and to send selected images to ground during the experiment runs.

The instrument will be equipped with two digital cameras with image resolution ≥1280 × 980 pixels and ≥8 bit. It will allow to select image recording frequency up to 15 Hz. The field of view will be 6 mm × 5 mm in Y–Z direction for side-view observation and not less than 2.4 mm × 2.1 mm in Y–Z direction in oblique view. It will be possible to scan through and focus over the whole depth of the sample (X-direction) with accuracy better than 25% of the depth of field in operation for both camera angles. Scanning through the whole depth of the sample will be completed in ≤5 s.

The illumination system (I) will support both bright- and dark-field illumination; (II) will be adjustable about the Y-axis for ensuring both side and oblique view; (III) allows switching the illumination without detectable thermal perturbation; and makes possible flashing of the illumination and synchronization with camera image taking.

In the MSG Utilization Manifest, which is agreed between ESA and NASA the TRANSPARENT ALLOYS instrument is scheduled for ISS's Increment 38 so that launching will happen between January and March 2014. At present, the TRANSPARENT ALLOYS instrument is passing Phase C/D.

SUMMARY

Microgravity conditions are still of great importance for performing solidification experiments on transparent model systems without the ambiguous effect of natural convection. With the installation of ESA's TRANSPARENT ALLOYS instrument onboard of the ISS, the scientific community will get access to a new Bridgman-type facility which alloy to process thick samples under controlled conditions. During the Breadboard tests, it was shown that the possibility of observing the solid/liquid interface not only from a side view but also from an oblique view will result in fascinating pictures/videos from three-dimensional (3-D) phenomena happening at the solid/liquid interface. It is thus understandable that four different European research teams are looking forward to use the new facility for studying different 3-D aspects of alloy solidification.

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