5.6 Thermodynamics and Kinetics of Transformations

A. Context and state of the art

In metallic alloys, microstructures are the result of phase separations. Their kinetics of formation is generally controlled by diffusional processes, considerations on thermodynamic equilibrium and interfacial phenomena. Processing of metallic materials usually starts from a melt of chosen composition. Upon cooling, solidification proceeds with the nucleation of crystalline or amorphous phases, concomitantly or successively, with coupled or divorced growth, giving rise to a wide variety of structures, most often revealing multiple phases formed when observed at room temperature. The experience also shows that it would be presumptuous to claim a solidification sequence from a simple visualization of a metallographic cross section. A thorough analysis requiring experimental and numerical studies is required for almost all systems if one aims to reach quantitative understanding of the formation of the structures. This is particularly true for multicomponent melts where the simplest phase equilibrium consideration is never met.

Solidification studies of metallic alloys are part of physical metallurgy and, more generally, materials science. They rely on the development of kinetics models coupled with computation of phase equilibria. Hence, thermodynamic databases are commonly used to determine phase diagrams and system state in term of coexisting phases, providing with information on their nature, composition and fraction. While full equilibrium of a system is not met during solidification studies, interfacial equilibrium is generally a good approximation for moderate interfacial velocities (< 0.1 m/s in metallic alloys). It can be directly extracted from thermodynamic equilibrium. The use of thermodynamic databases thus constitutes a starting point to compute phase change kinetics during cooling from the liquid state of a close system. The effects of boundary conditions, cooling rate or average compositions on fraction and composition of phases are typical output of such models. Coupling with the processing scale is then possible, mainly offering a description of the kinetics for an open system with respect to heat and mass exchanges in the presence of phase convection, and thus producing a multi-scale and multi-physics approach.

B. Current activity

Mean-field approach. Current activities aim to study and model solidification microstructures. A chosen example is given in the below Figures 1-3 [1, 2]. Atomization is an industrial process from which a liquid melt is distributed in small particles, with range between few to hundreds of micrometers. As the system is limited in size, a model sample of few millimeters can be processed containerless using electromagnetic levitation. Thus, cooling of the liquid is controlled using a pyrometer (colors curves in Figure 1) and the final distribution of the phases is accessible by standard metallography (open symbols at 42 s in Figure 2). Modeling using a volume averaging method is then developed and applied, considering the growth kinetics of dendritic (labelled Al_3Ni_2 phase), peritectic (labelled Al_3Ni_2 and Al_3Ni phases) and eutectic (labelled Al_3Ni and Al phases) microstructures successively formed from the melt, mass transfer between phases due to segregation of chemical species, heat transfer with the surrounding gas, and thermodynamic equilibrium at phase interfaces. The model study on a levitated sample permits calibration of unknown material and model parameters and application to atomized melt. The pertinence of the methodology is demonstrated in Figure 3 where the variation of the phase fraction as a function of droplet size (i.e. cooling rate) is well reproduced by the model, here mainly controlled by the diffusion in the solid phase.

Phase-field approach. Direct simulation of microstructure development is also possible and permit direct access to the morphology of the solid phases formed from the melt. An example is given in Figure 4. This method offers direct access to the phase field, the temperature field and the composition field. However, it requires heavy computational resources and, for this reason, is often limited to

binary alloys and single phase solidification from the melt. Its first comparisons with a mean-field approach yet demonstrate the pertinence of the previous methodologies, despite its limitation to provide with morphological information. It is also worth mentioning that simulations using phase field can only be reliable if one knows properties such as interfacial energy and its anisotropy, the latter being responsible for the preferred growth directions of the dendritic microstructures. These properties are usually not available and are known to vary with temperature and composition. Their access remains difficult and limited.

Mesoscopic approaches. Intermediate length scales approaches are developed for the modeling of dendritic structures, going from the cellular automaton method to the dendritic needle network. While their objective is to reach direct modeling of microstructures, as phase field, they are based on approximations made in order to permit application at larger domain size or faster computations.

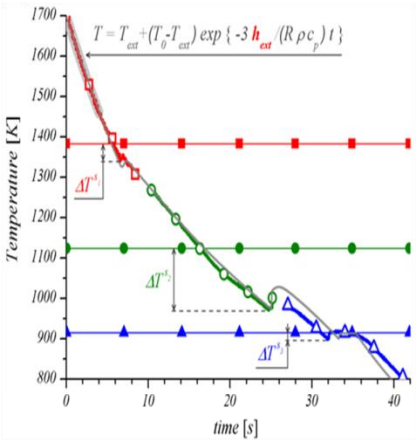

Figure 1. Cooling history of a levitated Ni-75at.%Al 6 mm diameter droplet (colored curve) measured and (grey) calculated (DLR, Köln, DE) [1].

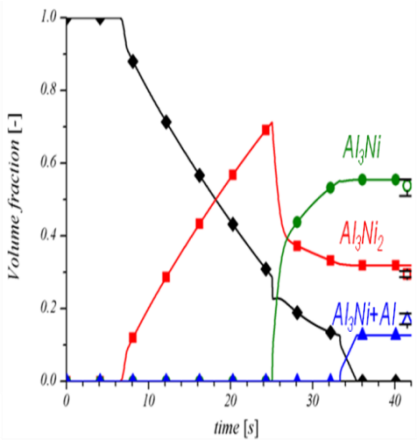

Figure 2. Time evolution of the fraction of phases (full symbols) predicted and (open symbols at 42 s) measured for the same sample as in Figure 1 [1].

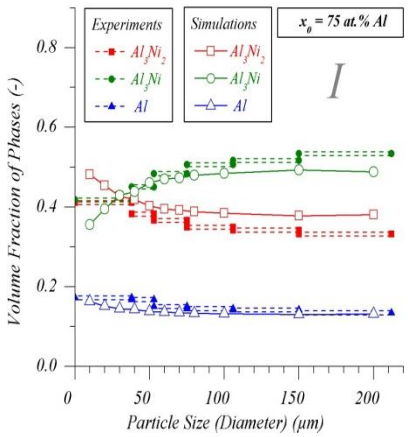

Figure 3. Fraction of phases (plain lines) predicted and (dashed lines) measured using neutron diffraction (Aix-Marseille University) in atomized particles [2].

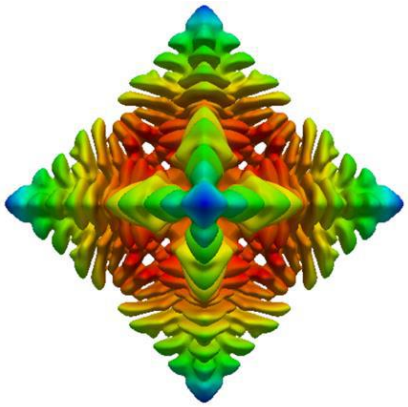

Figure 4. Phase field simulation of dendritic growth in an undercooled melt revealing the overal morphology of the primary solid phase formed from the melt [3].

[1] *Multiple non-equilibrium phase transformations: Modeling versus electro-magnetic levitation experiment* D. Tourret, Ch.-A. Gandin, Th. Volkmann, D. M. Herlach, Acta Materialia 59, 4665 (2011)

[2] *Gas atomization of Al-Ni powders: solidification modeling and neutron diffraction analysis* D. Tourret, G. Reinhart, Ch. A. Gandin, G. N. Iles, U. Dahlborg, M. Calvo-Dahlborg, C. M. Bao, Acta materialia 59, 6658-6669 (2011)

[3] *Phase-field modeling of dendritic solidification for an Al-4.5wt%Cu atomized droplet using an anisotropic adaptive mesh* C. Sarkis, MINES ParisTech, PhD thesis, under preparation.

C. Future steps

Several projects with the European Space Agency have the objective to access microgravity solidification experiments in the International Space Station. Several directional solidification experiments have already been conducted and analyzed. However, containerless experiments are only planned in the current phase of the projects, within the next 1 to 2 years. Meanwhile, parabolic flight campaigns, sounding rockets and ground studies are organized.
The latter also includes modeling following the methodologies previously described. It is worth mentioning that the stabilization of physical metallurgy tools coupled with thermodynamic equilibrium calculations is under progress in a dedicated library. The tools include growth kinetics of interfaces, mean field solidification modeling for multicomponent melt, solidification paths using various thermodynamic approximations, and solid state precipitation and diffusion simulations considering cross diffusion terms.

D. International collaborations

- Dieter Herlach, Thomas Volkmann, *German Space Agency, Köln, DE*
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E. List of people involved in the project

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- Gildas Guillemot, Mines ParisTech, Assistant Professor

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F. Most significant publications of the team

- *Analytical model for equiaxed globular solidification in multicomponent alloys*
  G. Guillemot, Ch.-A. Gandin, Acta Materialia, 97, 419–434 (2015)
- *Structures in directionally solidified Al - 7 wt% Si alloys – Benchmark experiments under microgravity –*
  D.R. Liu, N. Mangelinck-Noel, Ch.-A. Gandin, G. Zimmermann, L. Sturz, H. Nguyen-Thi, B. Billia, Acta Materialia, 64, 253-265 (2014)
- *3D CAFE modeling for solidification grain structures in GTAW*
  S. Chen, G. Guillemot, Ch.-A. Gandin, ISIJ International, 54 (2), 402-408 (2014)
- *Numerical simulation of precipitation in multicomponent Ni-base alloys*
  L. Rougier, A. Jacot, Ch.-A. Gandin, P. Di Napoli, P.-Y. Théry, D. Ponsen, V. Jaquet, Acta materialia 61, 6396-6405 (2013)
- *Multiple non-equilibrium phase transformations: Modeling versus electro-magnetic levitation experiment*
  D. Tourret, Ch.-A. Gandin, Th. Volkmann, D. M. Herlach, Acta Materialia 59, 4665 (2011)

I. Short CV of participants

Charles-André GANDIN, Research Director with CNRS in physical metallurgy. Head of research group "Structures and Properties in Solidification Processing". Modelling of multiple phase transformations and kinetics of microstructure developments coupled with thermodynamic equilibrium calculations. 72 publications in international journals, 25 PhDs supervised or co-supervised.

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coupled with thermodynamic computations. 21 publications in international journals, 7 PhD co-supervised.