Summary

In this work, the dendrite growth velocity of tetragonal Ni$_2$B was measured as a function of undercooling under different convective flow conditions to critically assess the effect of fluid flow on the growth dynamics and microstructure evolution in undercooled metallic melts as well as to investigate the influence of a non–cubic crystal structure on the anisotropic properties and the resulting pattern formation mechanism.

The undercooled state of a liquid is accessible by containerless processing and melt–fluxing techniques where heterogeneous nucleation on container walls is completely avoided. An undercooled melt is in a metastable state that provides a strong driving force for rapid solidification. The propagation of the solid–liquid interface visible on the surface of solidifying droplets during non–equilibrium solidification was observed by a high–speed video camera whereas the non–contact measurement of the undercooling was accomplished by an IR pyrometer. Different experimental methods were applied to obtain varying fluid flow velocities in the liquid samples. In ground–based electromagnetic levitation (1g EML), samples are levitated and heated by alternating electromagnetic fields where forced convective cooling is used to adjust the sample temperature. In this case, fluid flow is driven directly by the positioning forces that lead to a strong inductive stirring of the melt and solidification takes place under the condition of forced convection. Unfortunately, the flow velocity cannot be measured directly and has thus been evaluated by magnetohydrodynamic (MHD) modeling [11,154–156] to be of the order of 0.3 m/s. The importance of Marangoni convection and natural convection was evaluated, but these flows have been demonstrated to be orders of magnitude smaller than the electromagnetically driven flow [11]. Since, in general, melt convection depends crucially on various experimental parameters, the flow velocity in 1g EML was estimated experimentally by observing the non–equilibrium solidification process in undercooled Co–84at%Cu. This alloy is characterized by a metastable miscibility gap in the regime of the undercooled
melt. If the undercooling is large enough, the melt separates into a Co–rich and a Cu–rich liquid and solidification starts with a sequence of bright spots which are due to small coagulated Co droplets solidifying close to the surface of the surrounding Cu matrix. These Co droplets are driven by fluid flow and can be observed over extended periods of time to estimate the velocity. It is expected that this method is far more reliable than the observation of surface tracking particles which tend to collect in stagnation points where the local velocity of the flow vanishes and, moreover, are likely to act as sites for heterogeneous nucleation. The results are in close agreement with the values given in the literature. Forced convection due to positioning forces as well as natural convection were reduced by performing undercooling experiments in reduced gravity during a parabolic flight using the TEMPUS electromagnetic levitation facility (\( \mu g \) EML) aboard the A300 Zero–G aircraft. The positioning forces necessary to compensate disturbing accelerations and to stabilize the sample position during the reduced gravity phase are about three orders of magnitude smaller than the levitation forces to counteract gravity under terrestrial conditions. The respective fluid flow velocities are calculated to be of the order of 0.02 m/s \([155]\). In addition, melt–fluxing experiments (MF) were conducted in which the sample is heated by thermal radiation and is embedded in a fluxing agent, e.g. a liquid or glassy slag, in order to avoid direct contact of the melt with crucible walls and to protect the liquid surface against contaminations. In this case, external positioning forces are absent and one has to consider only natural convection due to buoyancy forces as well as Marangoni flows caused by non–uniform cooling conditions. The maximum fluid flow velocity is expected to be of the order of about 0.01 m/s as confirmed by an investigation on Co–84at\%Cu similar to that performed in 1g EML. Moreover, a new experimental facility was constructed that allows to perform melt–fluxing experiments in the presence of external static magnetic fields up to 1.12 T to study the stabilizing influence on the melt flow. Electrostatic levitation (ESL) under ultrahigh vacuum conditions was performed where the levitation force does not drive convection. The samples are heated locally by an IR laser which causes Marangoni flows due to large temperature and surface tension gradients. As soon as the heating laser is switched off, the sample freely cools and the flow quickly damps so the minimum velocity is expected to be near zero \([155]\).

Among various compounds tested against numerous experimental requirements, \( \text{Ni}_2\text{B} \) was demonstrated to be ideally suited for this investigation. Due to its low melting temperature of 1392 K and low reactivity, samples can be easily processed in melt–fluxing experiments where chemical reactions with the fluxing agent have to be avoided. It forms a chemically ordered intermetallic phase with growth dynamics controlled by atomic diffusion and thus exhibits rather sluggish solidification rates comparable to the fluid flow velocities present in 1g EML. This is important as the influence of convection is expected to be particularly pronounced in this case. In addition, \( \text{Ni}_2\text{B} \) is characterized by an underlying
body–centered tetragonal (bct) symmetry with lattice parameters $a' = b'$ and $c' \approx 0.85 a'$, which provides a good starting point to investigate the influence of a non–cubic crystal structure on the pattern formation mechanism. In this work, the composition was slightly shifted about 0.5 at% to Ni–32.83at%B in order to avoid varying conditions because it is almost impossible to produce samples that are exactly stoichiometric. As revealed by electron backscatter diffraction (EBSD), the solidified samples consist of a primary phase of Ni$_2$B and a small fraction of a secondary eutectic two–phase mixture of Ni$_2$B and Ni$_3$B. Rapid solidification was observed up to a maximum undercooling of $\Delta T = 272$ K. In undercooling experiments, nucleation can occur either spontaneously from the melt or through the use of a nucleation stimulation device. The investigation was limited to the case of spontaneous nucleation as triggering solidification was demonstrated to yield non–repeatable and inconsistent results.

The high–speed video data obtained under different convective flow conditions were analyzed by means of the ray–tracing software POV–Ray [198]. The propagating phase boundary is visible only on the surface of the droplets and, consequently, a precise determination of the growth velocities starts with analyzing the macroscopic geometry of the solidification front in the bulk liquid. A spatial analysis was performed, in which the overall shape of the growing crystal is approximated by an envelope that links to the outermost points of the solid–liquid interface, i.e. the dendrite tips. After specifying a suitable geometry, the intersection of this envelope with the spherical sample surface can be fitted to the experimental data to reproduce the entire solidification process and to evaluate the velocities. For systems with a cubic lattice symmetry, dendrites are commonly found to grow along the crystallographic $<100>$ directions which are supposed to be the axes of a regular octahedron with the six vertices corresponding to the primary dendrite tips and the edges corresponding to the secondary tips [195–197]. A code was developed that allows to simulate experimental high–speed video data by using an arbitrary polyhedral envelope to represent the overall shape of the growing crystal. In the case of tetragonal Ni$_2$B, the situation was found to differ significantly from the cubic case. For a wide range of undercoolings, the crystal is bounded by a rectangular prism in which two opposite faces are squares of side length $a$ at a distance $c = 1.1755 a$. In contrast, for $\Delta T > 230$ K, the high–speed video data was reproduced by using a spherical envelope.

In order to determine the growth velocities with respect to particular dendrite growth directions, a detailed microstructure analysis was performed to specify the underlying inner dendritic structure that spans the volume of the prism–shaped envelope and thereby to completely resolve the pattern formation mechanism. The evolution of a microstructure can be reconstructed from a sample cross section only if the sample is cut and prepared in a well–defined orientation with respect to the growth direction. Samples solidified in ESL and MF were found to exhibit pronounced texture patterns consisting of well–marked
lines across the surface that provide a suitable sample alignment procedure to preserve the sample axes orientation after solidification. The surface line texture becomes less pronounced with increasing fluid flow in the liquid sample which reflects directly the order and magnitude of the flow velocities present in the comparative experimental methods as determined by MHD and investigations on Co–84at%Cu. As revealed by scanning electron microscopy (SEM) and EBSD, the prism–shaped envelope was confirmed to originate from the growth of single crystals. It is spanned by dendrite arms growing perpendicular to the crystallographic \{111\} planes at a constant and uniform velocity. The axis ratio of the prism, \(c/a = 1.1755 = (c'/a')^{-1}\) is uniquely determined by the lattice parameters of the Ni$_2$B tetragonal crystal structure and explains its highly anisotropic growth behavior. In fact, this may set the stage for further studies, e.g. by systematically investigating systems with varying \(c'/a'\) ratios. This finding led to a complete three–dimensional reconstruction of the Ni$_2$B microstructure as obtained under weak convective flow conditions. The surface line patterns observed in electrostatically levitated samples as well as melt–fluxing samples were identified with the dendrite tips intersecting the sample surface where well–marked lines are due to primary and secondary dendrites and narrow lines originate from dendrites of higher generations.

Interestingly, according to the Jackson rule, Ni$_2$B (\(\Delta S_f/R_G \approx 2\)) is predicted to fall into the intermediate region between dendritic and faceted growth, governed by a competition between the respective interface structures. During the solidification process, samples processed under the condition of forced convection (1g EML) show a sudden transition to faceted rod–like structures growing along the \(<001>\) direction where the internal structure of each rod exhibits a pronounced hopper–shaped morphology. This transition cannot be resolved in the POV–Ray simulations. Surprisingly, the crystal growth velocity along the \(<001>\) direction is unchanged during the transition and the prism–shaped envelope is preserved. The underlying reason remains unclear but is probably due to a common physical origin of both growth modes. In fact, the internal structure of a rod was found to be composed of adjacent \{111\} planes. The transition to a spherical envelope was clearly identified to originate from the onset of polycrystal growth. The samples were found to be composed of grains growing perpendicular to the \{111\} planes in a bouquet–like symmetric fashion. This explains both the increased variance as well as the continuous behavior of the growth velocity in this region.

In addition, the growth velocity was found to be greatly affected by convective flow in the liquid sample. In general, \(v(\Delta T)\) was found to be a monotonically increasing function. The growth velocities are well below 1 m/s and are thus comparable to the expected fluid flow velocity present in 1g EML. The lowest growth velocities are obtained by ESL and, for a fixed undercooling, gradually increase with the flow present in MF and \(\mu\)g EML. Accordingly, the highest velocities are obtained by 1g EML with a maximum increase of roughly 60%
at $\Delta T \approx 100$ K as compared to the ESL results. As revealed by melt–fluxing measurements in the presence of an external static magnetic field of 1.12 T, the growth velocities are reduced and, within the limits of accuracy, overlap with the data obtained by ESL. It is found that such a field can be used to stabilize melt flow in conductive materials and should thus provide an efficient tool to control the evolution of solidification structures. Further investigations are needed to determine whether high static magnetic fields can be applied to stabilize even forced convective flow as present in 1g EML.

The experimental growth velocity data measured under different convective flow conditions were analyzed within the sharp–interface model. In order to reproduce the experimental data, it was necessary to include both constitutional effects as well as trapping of solute at the moving solid–liquid interface. It was confirmed that fluid flow has a substantial influence on the growth kinetics. It is thus not sufficient to consider only purely diffusive transport mechanisms. However, the effect was found to be only partly due to an enhanced heat and mass transfer at the propagating phase boundary but can be mainly attributed to a drastic change in growth kinetics caused by a convection–induced transition from dendritic to more faceted solidification structures as observed in 1g EML. In general, the diffusion–limited growth in Ni$_2$B was clearly demonstrated to be predominantly affected by kinetic effects at the solid–liquid interface. Accordingly, the influence of capillarity was shown to play a minor role and an inclusion of anisotropy of the interfacial free energy led to rather small corrections. A lower limit for the Ni$_2$B interfacial free energy anisotropy parameters was estimated numerically by applying the three–dimensional minimum stiffness criterion taking into account the bct symmetry. For this purpose, data for pure Ni determined by molecular dynamics simulations [1] were used as a reference. Further research is needed to precisely determine the respective anisotropy parameters as well as the magnitude of kinetic anisotropy which may have a large effect on the growth kinetics.