

Single crystal growth of $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$ from Al-rich solutions by the Czochralski method

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Czochralski growth of large metallic alloy single crystals of $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$ from Al-rich solutions has been demonstrated for the first time. A detailed description of all decisive steps of the growth procedure is given with particular emphasis to seeding from a native phase as well as spontaneous nucleation if no seed crystal from a preceding experiment is available. Czochralski growth in a high-temperature solution system requires much lower pulling rates compared to typical growth experiments from the melt and a time-dependent temperature program to compensate the change of the liquidus temperature that results from the permanently increasing Al content of the liquid phase. With a given amount of the initial melt, the size of the $\text{Al}_{13}\text{Co}_4$ crystals is limited by the rather narrow temperature range of the $\text{Al}_{13}\text{Co}_4$ primary crystallization window, followed by Al_9Co_2 phase crystallization. In the Al-Fe system, despite the huge temperature range of equilibrium between $\text{Al}_{13}\text{Fe}_4$ and its Al-rich melt, Czochralski growth of $\text{Al}_{13}\text{Fe}_4$ is restricted to higher temperatures due to the limited solubility that leads to mother liquid inclusions even at extremely low pulling rates.

Dedicated to Prof. Ladislav Bohatý on the occasion of his 60th birthday

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1 Introduction

Complex metallic alloys (CMA) often consist of clusters that can be found in quasicrystalline structures, too. For this reason, periodic CMA crystals are called approximants of the corresponding quasicrystalline phase. They may help in the structural analysis of quasicrystals by allowing the application of usual 3D-structure determination and finding a starting model for the quasicrystal structure solution. On the other hand, comparative studies on physical properties of such CMAs can contribute to the open question whether a specific feature of similar quasicrystals originates from their cluster structure or from the absence of 3D-periodicity. Such kind of investigations make single crystal growth of complex metallic alloys an interesting challenge.

After the discovery of stable decagonal quasicrystals in the Al-Co-Ni system [1], extensive studies on the subject of the structural relationships between the decagonal quasicrystals and related crystalline phases have been done. In these studies, a strong resemblance between the local structures of the decagonal phase and those of the various so-called Al_3Co phases has been found [2–7], the latter nowadays more precisely named $\text{Al}_{13}\text{Co}_4$. However, the preparation of large single crystals (e.g. at least approximately cm^3 in size) of these phases did not succeed. Thus, a systematic comparison between the physical properties of quasicrystals and their periodic approximants is an interesting task still to be done as soon as suitable samples will be available for a variety of different basic studies. Due to several advantages that have been demonstrated in the growth of decagonal AlCoNi [8,9] and AlCoCu quasicrystals [10], the Czochralski method may be regarded as the most versatile technique to meet the various conditions necessary for growing a series of different complex metallic alloys. It has been applied to the single crystal growth of the orthorhombic $\text{Al}_{13}\text{Co}_4$ and the monoclinic $\text{Al}_{13}\text{Fe}_4$ phase.

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The structural data of these two phases were determined long time ago by Grin et al. resulting in space group $Pmn2_1$ (Pearson symbol $oP102$) for $\text{Al}_{13}\text{Co}_4$ [3] and space group $C2/m$ (Pearson symbol $mC102$) for $\text{Al}_{13}\text{Fe}_4$ [11].

2 Growth strategy

Phase diagrams According to the published phase diagrams, $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$ are incongruently melting intermetallic compounds. This is a common feature of most of the complex metallic alloys and does not allow crystal growth from a stoichiometric melt. Instead, primary crystal growth of these phases can only occur from incongruent melts at a temperature below their peritectic transformations. For all Al-based intermetallics this incongruent melt is in fact an Al-rich solution and crystal growth problems to be solved are more typical of crystallization from a high-temperature solution than from a melt.

Various binary phase diagrams [12-14] with differences mainly in the vicinity of the high-temperature part of the $\text{Al}_{13}\text{Co}_4$ phase have been published. These differences do not affect the growth of orthorhombic $\text{Al}_{13}\text{Co}_4$ since the maximum growth temperature is limited by its peritectic reaction at 1092°C according to the phase diagram published by Gödecke and Ellner [14] that is shown in figure 1.

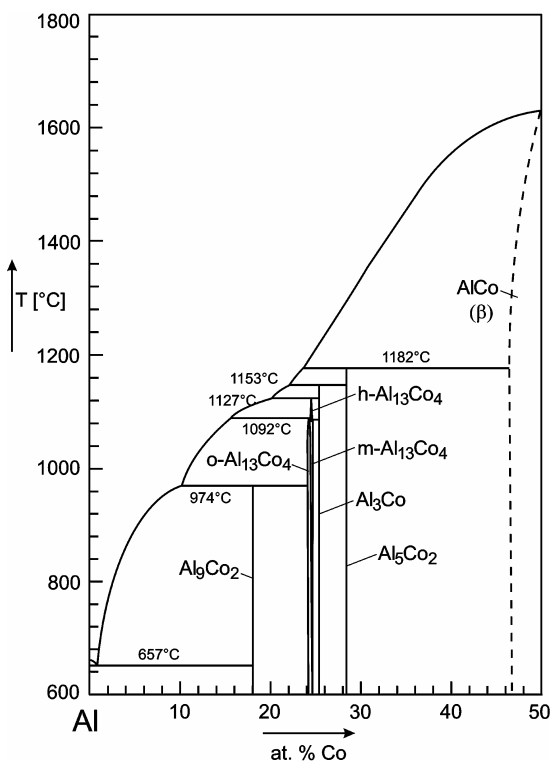


Fig 1 Al-rich part of the Al - Co phase diagram according to Gödecke and Ellner [14]. Phase relations between hexagonal (h), orthorhombic (o) and monoclinic (m) $\text{Al}_{13}\text{Co}_4$ in the high-temperature region that have been matter of some controversy do not affect the growth of o- $\text{Al}_{13}\text{Co}_4$ from an Al-rich solution.

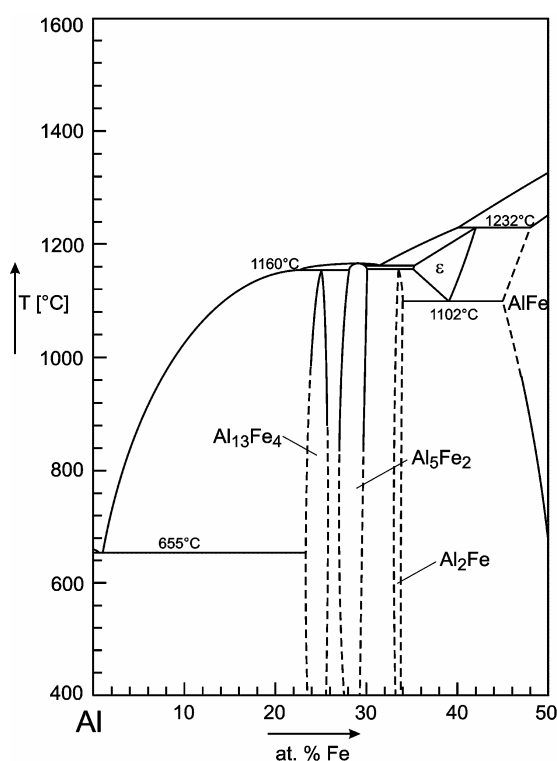


Fig 2 Al-rich part of the Al - Fe phase diagram according to [16].

According to Gödecke's results, a high-temperature hexagonal $\text{Al}_{13}\text{Co}_4$ phase exists that decomposes via a eutectoid reaction at 1083°C into orthorhombic $\text{Al}_{13}\text{Co}_4$ and monoclinic $\text{Al}_{13}\text{Co}_4$ the latter having a slightly higher Co content. Monoclinic $\text{Al}_{13}\text{Co}_4$ cannot be grown as a primary phase from a melt or binary solution. Thus, in the temperature range 974°C < T < 1092°C orthorhombic $\text{Al}_{13}\text{Co}_4$ is the only solid phase in equilibrium with an Al-rich solution followed at lower temperatures by Al_9Co_2 which structure is monoclinic (space group $P2_1/c$, Pearson symbol $mP22$) [15].

The Al-rich part of the assessed Al-Fe binary phase diagram (Fig. 2) [16] seems to be less sophisticated with respect to $\text{Al}_{13}\text{Fe}_4$ being the primarily crystallizing phase in the temperature range $655^\circ\text{C} < T < 1160^\circ\text{C}$.

Regarding the too high Al excess of low-temperature solutions, single crystal growth of monoclinic $\text{Al}_{13}\text{Fe}_4$ should be carried out at temperatures not much lower than 1000°C .

Czochralski growth from a solution Crystal growth from a melt using the Czochralski method is widely used and may be regarded as the best studied solidification technique for single crystal production. This is mainly due to its successful application in semiconductor and oxide single crystal growth. Regardless the huge variety of special demands arising from the requirements of the specific material to grow, there are some features that are common to all Czochralski growth apparatus: slowly pulling the rotating crystal from the melt that is kept in a (in most cases) counter-rotating crucible. In principle, there is no decisive difference whether crystal pulling occurs from a congruent melt, from a slightly off-stoichiometric melt or even from a solution. Therefore, in the case of growing a complex metallic alloy from an Al-rich solution of a strongly deviating composition we call the technique Czochralski method as well. Nevertheless, some special prerequisites have to be considered that are mainly driven by the principles of solution growth:

- 1) Starting crystal growth from a native seed may be easier than in melt growth, since the seed material is stable up to temperatures higher than that of the seeding procedure, and partially dissolving of the seed is much slower than melting it.
- 2) Compared to melt growth, much lower pulling rates have to be chosen as to meet the needs of the materials transport to carry the excess component away from the growing phase boundary.
- 3) Diameter control by influencing the meniscus shape via heat supply or pulling rate change is regarded as one of the advantages of the Czochralski technique. This remains true, if in meniscus shape calculations for pulling from a solution, the liquidus temperature is taken instead of the fixed melting point in solidification from a melt.
- 4) In crystal growth from a defined amount of solution, the liquidus temperature is not fixed over the whole process but is depending on the fraction of material that has already been crystallized. It changes the composition of the rest of the liquid. Thus, the change of the liquidus temperature vs. time is the result of the pulling rate, of the ratio of crystal to crucible diameter, and of the slope of the liquidus line in the phase diagram.
- 5) Diameter control in the same sense like in pulling from a congruent melt now means stabilizing the meniscus shape by compensating the reduced liquidus temperature by a progressively decreasing heat supply.

To date, rather little efforts have been done to study these influences in detail, but empirical approaches may be good enough to influence the diameter of the growing crystal to some extent.

Pulling a single crystal of a new phase that has not been grown before, usually lacks a suitable seed crystal. Instead of taking some polycrystalline material that can easily be obtained in a simple normal freezing experiment, spontaneous nucleation at some dummy seed, as shall be shown below, may be a better choice.

3 Experimental approach

Synthesis The initial compositions of the Al-rich solutions (overall compositions $\text{Al}_{86.5}\text{Co}_{13.5}$ or $\text{Al}_{89.5}\text{Fe}_{10.5}$) were chosen from the existing phase diagrams (Figs. 1 and 2) trying to meet a compromise between a high enough solubility and not too high temperatures that would increase Al loss by evaporation. Pieces of the metallic components (CrysTec Berlin, Germany) Al (4N grade) and Co (3N grade) or Fe (3N grade) of about 17 g total mass were carefully etched to remove some surface contamination and precisely adjust the calculated composition. Prior to pulling the complex metallic alloy phases from an Al-rich solution a homogeneous solution has to be prepared from the binary components. This was done ex-situ in an alumina crucible under Ar atmosphere using a RF heating facility. Co and Fe have much higher melting points (1495°C and 1535°C) compared to Al. Instead of melting the two constituting elements at temperatures higher than 1500°C we did the syntheses by dissolving the high-melting point component at rather moderate temperatures lower than 1300°C . The homogenized melt usually did not wet the alumina crucibles and could easily be removed after quenching it and cooling down to room temperature.

Czochralski pulling The most obvious difference to pulling from a melt is the very low pulling rate in crystal growth from a solution. This is necessary to meet the needs of excess component transport and thus to avoid liquid inclusion incorporation. Therefore, Czochralski growth from a solution requires weeks instead of

days or hours for an individual growth run. Having the strong affinity of Al to oxygen in mind, the growth chamber has to be as tight as possible to avoid any oxidation. Therefore, the crystal growth chamber has been constructed from metal-sealed parts only. A sketch of the apparatus used in the growth experiments is shown in figure 3.

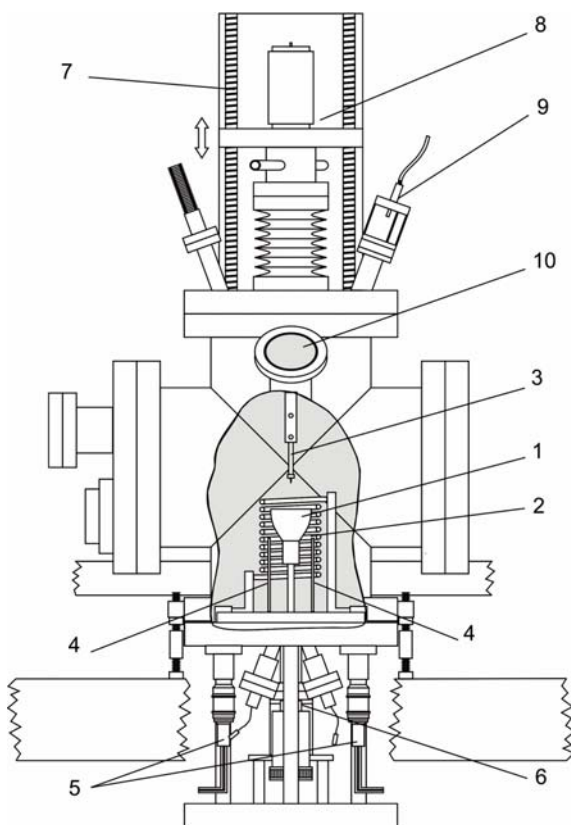


Fig 3 Schematic sketch of the fully metal-sealed Czochralski growth apparatus. (1: Ni support containing a 10 ml alumina crucible; 2: Kanthal resistance heater; 3: ceramic seed holder; 4: thermocouples; 5: water-cooled electrical feedthroughs for power supply; 6: motor and rotary feedthrough for crucible rotation; 7: step motor-driven linear translation unit; 8: motor and rotary feedthrough for crystal rotation; 9: illumination; 10: viewport).

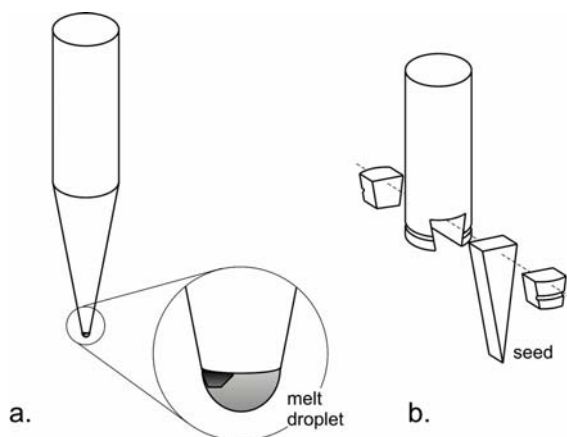


Fig 4 Different types of crystal holders to be mounted at the end of the pulling rod. a) Tapered alumina rod allowing spontaneous nucleation in a solution droplet that is attached to the truncated tip. b) Ceramic seed holder to fix a wedge-shaped oriented seed of $\text{Al}_{13}\text{Co}_4$ or $\text{Al}_{13}\text{Fe}_4$. All parts to be in contact with the metallic alloy are made from alumina and are bound by a thin wire.

The pre-synthesized source was placed in an alumina crucible. Due to the lack of single-crystalline material large enough for the preparation of native seeds, we used spontaneous nucleation on a tapered alumina rod in the first growth runs (see Fig. 4a). Later on, single-crystalline seeds of well defined orientation were wedge-shaped cut from crystals of preceding growth experiments. These seeds were kept in an all-ceramic seed holder (see Fig. 4b). After having evacuated and heated-out the growth chamber for several days to remove traces of oxygen, it was filled with 520 mbar Ar (5.0 grade) reaching ambient pressure after heating to growth conditions.

The molten source material was kept at least 12 hours at temperatures 100 K higher than the respective liquidus temperature to ensure homogenisation of the initial solution. Since the thermocouples for temperature control are located next to the heating element and no measurement in the melt is attempted, the accurate seeding temperature has to be found by direct observation. For this purpose, the melt was undercooled to allow spontaneous nucleation of crystals at the surface. These Al-rich solutions can easily be supercooled by about 20 K until long $\text{Al}_{13}\text{Co}_4$ or $\text{Al}_{13}\text{Fe}_4$ needles form spontaneously. Using a moderate temperature ramp, these needles can be slowly re-dissolved under permanent observation. The last temperature at which traces of the

needles have been found is regarded the liquidus temperature T_L suitable for the seeding procedure. Then, a short overheating was followed to make sure that all crystallites were dissolved.

In case of using a pre-grown seed from a preceding growth run it was brought into contact with the solution at temperature T_L . After wetting the seed by the solution, the seed was lowered by additional 1 – 2 mm and the pulling process was started using translation rates as low as 100 – 150 $\mu\text{m/h}$. In the very first experiments without having any material suitable to serve as a seed crystal, a slightly truncated alumina tip (see Fig. 4a) was submerged into the solution and then slowly withdrawn. By this, a single droplet of the solution was taken from the melt hanging at the tip of the alumina rod. Slowly pulling the rod to lower temperatures according to a larger distance to the melt surface makes the solution droplet to become partially crystallized. This is nothing else than solution growth by cooling-down, but is restricted to the tiny volume of the droplet. Usually, only one single crystal forms that is still embedded in the remaining Al-rich solution. This can be brought into contact with the molten source in the crucible and the following growth procedure was not different from that with the large seed crystal. After this spontaneous nucleation process the growing crystal was simply sticking at the ceramic tip.

As explained above, crystal diameter control, i.e. the diameter increase to get the shoulder of the Czochralski-grown crystal can be obtained by slightly decreasing the temperature. This was done very carefully using typical temperature ramps less than 0.1 K/h. The diameter increase in this stage of the growth has been found to be a self-amplifying process because of the increased heat loss occurring with the increasing crystal surface. That is, why this is the most critical part in shaping the crystal. After having obtained the desired diameter of the crystal, the temperature set point was permanently further decreased while pulling the crystal with a constant rate of about 100 $\mu\text{m/h}$. As to compensate the changing composition and therefore the decreasing liquidus temperature of the solution that becomes enriched with Al proportional to the total amount of crystallized material, a progressively higher temperature ramp was needed up to 0.5 K/h at the last third of the grown ingot. Thus, an overall decrease of the growth temperature by about 100 K during a typical 2 - 3 weeks growth run was necessary to obtain a more or less well-shaped $\text{Al}_{13}\text{Co}_4$ or $\text{Al}_{13}\text{Fe}_4$ crystal. Crystal growth was completed by a very fast pulling of the crystal combined with a slightly increasing melt temperature. Cooling down to room temperature was done at a constant rate of several 100 K/h.



Fig. 5 $\text{Al}_{13}\text{Co}_4$ single crystal grown by the Czochralski method from an Al-rich solution of initial composition $\text{Al}_{86.5}\text{Co}_{13.5}$ using a [001] oriented single-crystalline native seed. (Online color for figures 5 and 6 at www.crt-journal.org)



Fig. 6 $\text{Al}_{13}\text{Fe}_4$ single crystal grown by the Czochralski method from an Al-rich solution of initial composition $\text{Al}_{89.5}\text{Fe}_{10.5}$ using a [010] oriented single-crystalline native seed.

4 Results and discussion

Morphology Photographs of typical $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$ single crystals grown by the Czochralski technique are shown in figure 5 and 6. In both cases the wedge-shaped native seeds indicate the position of the beginning growth. In these low-symmetry materials, the anisotropy of growth rates leads to cross sections that remarkably deviate from a circular shape. Occurring facets in the region of the crystals' shoulder reflect the symmetry of the growing phases and allow in the early stage of the experiment to judge whether or not single crystal growth has been achieved. As mentioned above, the transition from the shoulder to the constant diameter region of the growing ingot has always been the most critical situation in the diameter control. From the photographs it can be seen that completing the diameter increase at the end of the shoulder usually led to

some degree of overcompensation, i.e. to a slightly decreasing diameter. This is regarded as a result of the strongly influenced temperature field when the crystal's shape changes.

Usually, single crystal growth was completed after having crystallized less than half the mass of the initial melt. In the Al-Co system (see phase diagram, Fig. 1) as in many other complex metallic alloys, there exists a cascade of peritectic transformations and $\text{Al}_{13}\text{Co}_4$ growth is followed by the next peritectic phase, Al_9Co_2 , at a transition temperature of 974°C . Therefore, the growth of $\text{Al}_{13}\text{Co}_4$ should be completed by separating the grown crystal from the rest of the solution before the temperature of the phase boundary has been reached the peritectic transition. Figure 7 shows a longitudinal section of the end of an $\text{Al}_{13}\text{Co}_4$ single crystal grown in an experiment when the right moment to stop the growth run was missed. Al_9Co_2 being the next phase in equilibrium with the Al-rich solution at lower temperatures was crystallized onto the primary grown $\text{Al}_{13}\text{Co}_4$ single crystal resulting in a lot of thermomechanical stress and even cracks during cooling down to room temperature.



Fig. 7 Longitudinal section through the very rare part of an $\text{Al}_{13}\text{Co}_4$ single crystal grown parallel to $[001]$ from an Al-rich solution of initial composition $\text{Al}_{86.5}\text{Co}_{13.5}$. With the growth temperature at the phase boundary falling below the peritectic temperature of 974°C , polycrystalline growth of monoclinic Al_9Co_2 onto the orthorhombic $\text{Al}_{13}\text{Co}_4$ single crystal occurred resulting in stress-induced cracks. Bright spots are eutectic structures of practically pure Al resulting from fast cooling down at the end of the experiment.

What is interesting in this example, is the sudden diameter increase accompanying the change of the crystallized material. This simply reflects the influence of the different slopes of the liquidus curve above and below the 974°C transition (see Fig. 1). Bright spots at the polished and etched surface are inclusions of the Al-rich solution due to a much higher growth rate at the very end of the experiment.

In the Al-Fe system, $\text{Al}_{13}\text{Fe}_4$ is the Al-richest stable phase and, in principle, primary growth of $\text{Al}_{13}\text{Fe}_4$ occurs till the eutectic composition of the melt is reached and no second phase crystallization has to be feared.

Structure The single crystals of $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$ grown in this study were used to re-determine the crystal structure by Grin [17] and to analyse chemical bonding. The earlier structure determination by the same author [3, 11] could be confirmed, but a number of new details were revealed. The lattice parameters of orthorhombic $\text{Al}_{13}\text{Co}_4$ (space group $Pmn2_1$) were determined to be $a = 0.8158(1)$ nm, $b = 1.2342(1)$ nm and $c = 1.4452(2)$ nm. The density of $\text{Al}_{13}\text{Co}_4$ calculated from X-ray data amounts to $\rho_{\text{calc}} = 3.966(1)$ g/cm³, whereas the experimental density is $\rho_{\text{exp}} = 3.962(1)$ g/cm³ measured using a buoyancy balance immersing specimen weighing system with a cm³-size $\text{Al}_{13}\text{Co}_4$ single crystal.

The re-determined lattice constants of monoclinic $\text{Al}_{13}\text{Fe}_4$ (space group $C2/m$) are $a = 1.5488(1)$ nm, $b = 0.80866(5)$ nm, $c = 1.24769(8)$ nm and $\beta = 107.669(4)^\circ$. The calculated density of $\text{Al}_{13}\text{Fe}_4$ amounts to $\rho_{\text{calc}} = 3.8415(8)$ g/cm³, and the experimental density was measured to be $\rho_{\text{exp}} = 3.847(3)$ g/cm³.

Second-phase inclusions Mother liquid inclusions are regarded the main problem arising from the incongruent growth conditions in single crystal growth from solutions. The excess component not incorporated into the crystal has to be removed from the growing phase. Since adjacent to the phase boundary of the growing crystal diffusion is the only transport mechanism, the continuity equation of matter transport can be written as

$$v(C_L - C_S) = -D \text{grad} C_L,$$

wherein v is the crystal growth rate, C_S and C_L are the concentrations of the solid and the liquid at the interface,

D is the diffusion coefficient, and $\text{grad}C_L$ is the concentration gradient in the liquid next to the phase boundary. Thus, it is the difference ($C_L - C_S$) that makes the difficulty and the crystal growth rate proportionally amplifies the materials transport problem. Comparing the two binary phase diagrams (Figs. 1 and 2) it becomes obvious that with the lower solubility of $\text{Al}_{13}\text{Fe}_4$ in the Al-rich solution in the Al-Fe system the inclusion formation becomes more severe than in the Co-containing crystals. With growth temperatures that decrease during the growth run and therefore with a changing liquidus composition, liquid inclusions become more likely with increasing axial position of the growing crystal. Actually, $\text{Al}_{13}\text{Fe}_4$ single crystals frequently have large Al-rich inclusions incorporated in the second part of the ingot even with a pulling rate as low as $50 \mu\text{m/h}$ whereas it has not been observed in $\text{Al}_{13}\text{Co}_4$ crystal growth with a doubled rate. Therefore, a higher Fe content of the initial solution and accordingly a higher growth temperature to start with, should avoid solvent inclusion formation.

High-temperature stability From the phase diagrams it can be seen that both alloys, $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$, are incongruently melting phases that decompose at their peritectic temperatures of 1092°C and 1160°C , respectively. Additional to these phase transitions, in differential thermal analyses (DTA) of $\text{Al}_{13}\text{Co}_4$ and $\text{Al}_{13}\text{Fe}_4$ single-crystalline samples a weak but continuous decomposition can be measured even at lower temperatures. The onset of the weak endothermal signal roughly coincides with the growth temperature that can be assigned to the axial position of the crystal where the sample was taken from.

5 Conclusion

Single crystal growth of complex metallic alloys in the Al - Co and Al - Fe systems has been achieved. The Czochralski technique has proved to be by no means restricted to the growth from the melt, but makes special conditions necessary when applied to high-temperature solutions. Orthorhombic $\text{Al}_{13}\text{Co}_4$ and monoclinic $\text{Al}_{13}\text{Fe}_4$ can be grown from strongly Al-rich solutions if pulling rates are limited to the range of $100 \mu\text{m/h}$ or less. A special technique for spontaneous seeding has been suggested that was successfully used in case of lacking material for a preparation of suitably native seeds which is the typical situation if a single crystal of a really new material has to be grown.

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