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Controlling the Morphology and Distribution of an Intermetallic Zn_{16}Ti Phase in Single Crystals of Zn-Ti-Cu

Grzegorz Boczekal

AGH-University of Science and Technology, Faculty of Non-Ferrous Metals, Cracow, Poland

1. Introduction

The work discusses the relatively poorly investigated area of various phenomena accompanying monocrystallization of hexagonal metal alloys, containing second phase inclusions in the structure. Metals of hcp structure form a, not very numerous but having a fundamental industrial importance, group.

Altogether about 27 metals of hcp structure are known, including 11 actinides [1,2,3]. The industrial applications of hexagonal metals cover many different sectors, from zinc sheets used for roofing up to light titanium-based alloys for parts of planes. Single crystal layers based on zinc are also used in electronics [4].

Hexagonal metals are characterised by features unprecedented for other metals. These include the value of c/a ratio (Table 1), which largely determines the metal properties [1,2], as well as very low mutual solubility observed in alloys composed of two metals with hexagonal structure each (Zn-Ti, Cd, Zn, Mg-Zn, Mg-Zr, Mg-Sc and others) [5,6].

The value of the c/a ratio and the related disorder in an ideal structural model are inherently related with the physics of interatomic bonds. In the case of metals with regular face centred lattice and regular body centred lattice, the bonding is of a purely metallic (non-directional) character and there is no phenomenon of interpenetration of the wave functions originating from lower orbitals. In hexagonal metals, the metallic bond predominates, but there is also a significant share of atomic bonds originating from an interaction that is said to exist between the wave functions of the neighbouring atoms [1,2,7,8].

Metals such as Zn, Cd, Tl were classified by Wyatt as a class of intermediate elements, i.e. the elements of a coordination number low enough to enable the occurrence of covalent interactions [1]. The directionality typical of an atomic bonding disturbs the perfect sequence of atomic layers and, consequently, the c/a ratio assumes values different than 1.633, which is perfect quantity when a rigid sphere model is used. Since the interatomic interaction in metals with $c/a \neq 1.633$ is a combination of metallic and atomic bonds, any change in temperature must significantly affect the properties of metals with a hexagonal structure. Lowering the temperature reduces the distance between the atomic cores and, consequently, increases penetration of the lower orbital wave functions, which leads to an increase in the share of atomic bonds. Additionally, the structure where the atoms do not fill in an ideal space is characterised by low energy required to produce and promote migration

of point defects (vacancies), and also by strong variation of diffusion coefficients for different crystallographic directions [7,8,9]. Both the temperature and the degree of deformation also strongly influence the number of vacancies in the material. These phenomena are responsible for the specific properties of hexagonal metals at low temperatures, such as the anomalies of a hardening coefficient and yield strength [9].

Metal	a [Å]	c [Å]	c/a
Na-α	3.767	6.154	1.6336
Be-α	2.287	3.583	1.5666
Mg	3.209	5.210	1.6235
Sc-α	3.309	5.273	1.5935
Y-α	3.647	5.731	1.5714
La-α	3.770	12.159	3.2251
Pr-α	3.673	11.835	3.2221
Nd-α	3.658	11.779	3.2200
Ti-α	2.951	4.684	1.5872
Zr-α	3.232	5.148	1.5928
Hf-α	3.195	5.051	1.5809
Tc	2.743	4.400	1.6040
Re	2.761	4.458	1.6146
Ru	2.706	4.281	1.5820
Os	2.735	4.319	1.5791
Zn	2.664	4.947	1.8569
Cd	2.979	5.619	1.8862
Tl-α	3.456	5.525	1.5986

Table 1. Some of the hexagonal metals and their c/a coefficients [2,3].

Hexagonal metals are characterised by large stress variations in the individual slip systems. With proper orientation respective of the stress applied, these metals can be deformed in one system, operating as a primary system, obtaining a wide range of the deformation values [10-14]. It is typical, in particular, of metals having the c/a ratio > 1.633, such as zinc and cadmium. Zinc single crystals of "soft" orientation are deformed to more than 100% (elongation) within the range of an easy slip in a (0001) <11-20> system. Only a very serious change of orientation caused by deformation and the strong strain hardening effect in the basal system of (0001) <11-20> are capable of activating a different slip arrangement [15]. Conducting research on the phenomena and processes occurring in metallic materials requires samples with clearly defined structure of both matrix and lattice obstacles in the form of phases precipitated or introduced from the outside. Metals and alloys in the polycrystalline form are not suitable for studies aiming at the identification of the mechanism of deformation because of the need to examine the phenomena which occur in different and separated areas characterised by different crystal orientations (grains). The use of materials with single crystal structure of the matrix eliminates this problem, as it becomes possible to analyse various phenomena within the whole sample volume, in a well-defined research environment. The ability to control the structure of the lattice obstacles while

maintaining the same single crystal matrix enables, moreover, designing of technological processes by means of which products of the desired structure can be made in a reduced number of the necessary technological steps.

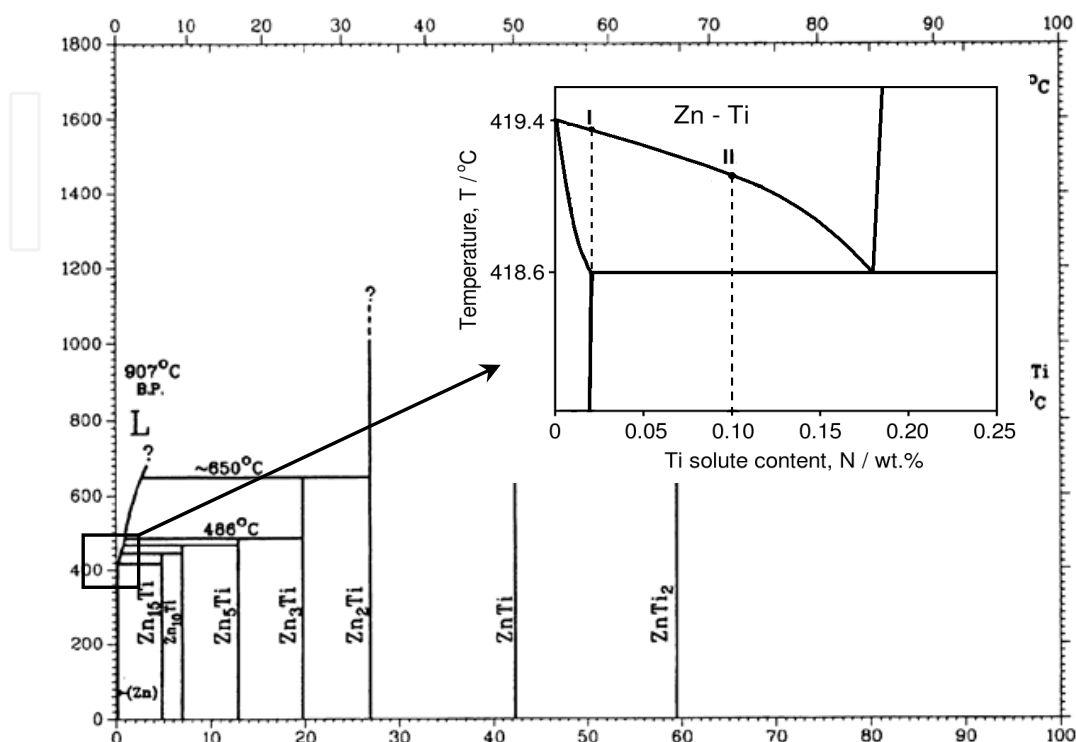


Fig. 1. The Zn-Ti phase diagram [5,6,7].

The specific crystallography of metals with a hexagonal structure, combined with the strong anisotropy of diffusion coefficients and elasticity constants has a strong influence on morphology of the obtained structures.

For example the elastic constants c of the pure zinc are property [16,17]:

- $c_{||}[0001] = 13.1 \text{ cm}^2 \text{ dyne}^{-1} \times 10^{-13}$
- $c_{\perp}[0001] = 1.93 \text{ cm}^2 \text{ dyne}^{-1} \times 10^{-13}$

The results of other authors suggest moreover, that elasticity of zinc is very sensitive to small variations in amount and kinds of impurities [15,17].

The additional special feature is also a strong influence of even small amounts of the alloying elements on the surface tension of molten zinc, which is a critical parameter for the process of monocrystallization [16,23,24,26].

Another important factor is the existence of a limited number of directions characterised by a high coefficient of diffusion and self-diffusion. At a temperature of 293K, the zinc coefficients of self-diffusion D_0 are, respectively [9]:

- $D_{0[0001]} = 0.13 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$
- $D_{0\langle 11-20 \rangle} = 0.58 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$

In hexagonal metals there are three directions preferred by the diffusion; these are the directions of the most dense packing $\langle 11-20 \rangle$ located in a hexagonal column on the plane (0001). These are also the privileged directions for the growth of a single crystal structure. This tendency is the stronger, the higher is the imposed from the outside speed of

crystallisation and the higher is the content of alloying elements. In the case of single crystals grown without a nucleus, this means a constant axial orientation consistent with the direction [11-20]. This effect is so strong that all attempts at obtaining an orientation different than the one preferred by the growth mechanism require, beside the presence of a nucleus of the desired orientation, also the crucible of special design [18].

Alloys based on hexagonal metals offer low solubility to other metals in the solid state and a tendency to create numerous intermetallic phases [5,6,19-22].

The structural anisotropy strongly influences the mode of nucleation and growth of the secondary phases in single crystals with a hexagonal structure. The large difference in elastic constants at different crystallographic directions of the hcp lattice [16,17] enforces some permanent relationships between the crystal lattice of the newly emerging intermetallic phases and matrix.

2. Methodology

Single crystals of Zn-Ti and Zn-Cu-Ti used in this study were grown by Bridgman method with sliding temperature gradient.

Bridgman’s original method [23], which consists in lowering a crucible with the charge inside through the zone of strong temperature gradient, was modified by application of the sliding motion of the furnace, while the nucleus and the charge were left immobile. The growth process was carried out in crucibles made of spectrally pure graphite. To prevent oxidation and also a reaction between the charge and the crucible material, an argon protective atmosphere was used. Permanent purging of the furnace chamber allowed the removal of oxygen and unwanted gaseous products formed during melting of charge. Compositions of the investigated single crystals and crystallisation speeds are summarised in Table 2. The resulting single crystals were oriented with a Bruker D8 Advance X-ray diffractometer, and were cut next into specimens with orientation of the observation planes (0001) and (11-20), respectively. The surfaces of the specimens were pre-polished with abrasive papers and diamond paste, first, and etched next with a chromium reagent. To reveal the shape of precipitates and determine the crystallographic relationship with the matrix, deep selective etching was used. Structural examinations were performed under Hitachi 3300 scanning microscopes with an EDS and EBSD attachments, and under the TESLA-302 microscope.

Single crystal chemical composition	Growth rate [mm/h]
Zn-Ti0.02 wt. %	3
Zn-Ti0.10 wt. %	3
Zn-Ti0.10 wt. % - Cu0.1 wt. %	1.8
	6
	10
	16
Zn-Ti0.2 wt. % - Cu0.15 wt. %	1.8

Table 2. The investigated single crystals and growth rates.

3. Characteristics of phases present in the examined Zn-Ti and Zn-Ti-Cu single crystals

3.1 Types of phase lattice

In the case of Zn-Ti and Zn-Ti-Cu single crystals analysed in this study, the only stable intermetallic phase observed in an around-eutectic range (titanium content in zinc of about 0.2 wt.%) is the $Zn_{16}Ti$ phase [10-14,25]. It is a tetragonal phase of Cmc_m structure containing 6.33 at.% of titanium. A single cell of this phase is built of 51 atoms. Each Ti atom is surrounded by 15 Zn atoms, with the additional 16th atom located in a space between the "chain" elements. The $Zn_{16}Ti$ phase has the following lattice parameters [25]:

- a. 772.0 pm
- b. 1144.9 pm
- c. 1177.5 pm

For pure zinc elemental cell has a dimensions [2,3]:

- a. 266.49 pm
- b. 266.49 pm
- c. 494.68 pm

Interplanar distances for the planes (0001) normal to the 'c' Zn direction are $d_{(0001)} = \frac{1}{2}c = 247.34$ pm. On the other hand, the 'a' parameter of the $Zn_{16}Ti$ phase is 772 pm which is the value roughly three times higher (3×247.34 pm = 742.02 pm). Hence, the edge length ratio $a_{Ti}/\frac{1}{2}c_{Zn}$ is $772\text{pm}/247.34\text{pm} = 3.12$.

Other combinations of ratios between the lattice constants of the $Zn_{16}Ti$ phase and the 'a' constant of a unit cell of zinc are:

- a. $Zn_{16}Ti / a_{Zn} \sim 2.9$
- b. $Zn_{16}Ti / a_{Zn} \sim 4.3$
- c. $Zn_{16}Ti / a_{Zn} \sim 4.42$

The edge ratio of $a_{Zn_{16}Ti}/a_{Zn} \sim 2.9$ is also close to an ideal multiple, but creating an interface of this configuration is energetically less favourable, as it does not affect the planes with the highest packed coefficient.

In this situation, one should expect a strong tendency to the formation of a crystallographic configuration, in which $a_{Zn_{16}Ti}$ edges of the phase cells and $c_{\alpha-Zn}$ edges of the matrix will be mutually parallel to each other.

3.2 Chemical composition and hardness of phases

Hardness of the $Zn_{16}Ti$ phase and of the α -Zn matrix was measured on the (0001) plane of a Zn-Ti0.2-Cu0.15 single crystal.

The α -Zn matrix of these single crystals contains 0.15 wt.% Cu and ~ 0.02 wt.% Ti. The measurements were taken using STRUERS microhardness tester, applying a load of 0.1 kg. To eliminate the error due to possible inhomogeneity of properties and small dimensions of the measured object, mapping was performed on the surface of 1.6×1.8 mm in the region containing a single exposed particle of $Zn_{16}Ti$ phase and pure matrix. Altogether, 80 measurements were taken. The results are shown in Figure 2 in the form of a 3D chart.

The obtained results showed that an average hardness of the $Zn_{16}Ti$ phase reaches 296 μHV as compared to 58 μHV of the matrix, with standard deviation not exceeding 8%. Previous studies performed on Zn-Ti and Zn-Ti-Cu alloys have proved that the $Zn_{16}Ti$ phase has little influence on hardening at the initial stage of deformation [11]. What predominates at that

stage is the effect of precipitation hardening derived from copper, which all enters into the solution, and from small amounts of titanium (at the level of hundredths of a weight percent). Its main role in the hardening effect, the $Zn_{16}Ti$ phase starts playing at higher deformations when, owing to their shape and dimensions, the needle-like particles of this phase are acting in a way analogous to fibres in composite materials. Partially coherent combination of the $Zn_{16}Ti$ phase with matrix confirmed by the results of EBSD [10,11,12] suggests good transfer of stresses from the matrix, while high hardness of this phase will increase the properties of the material taken as a whole.

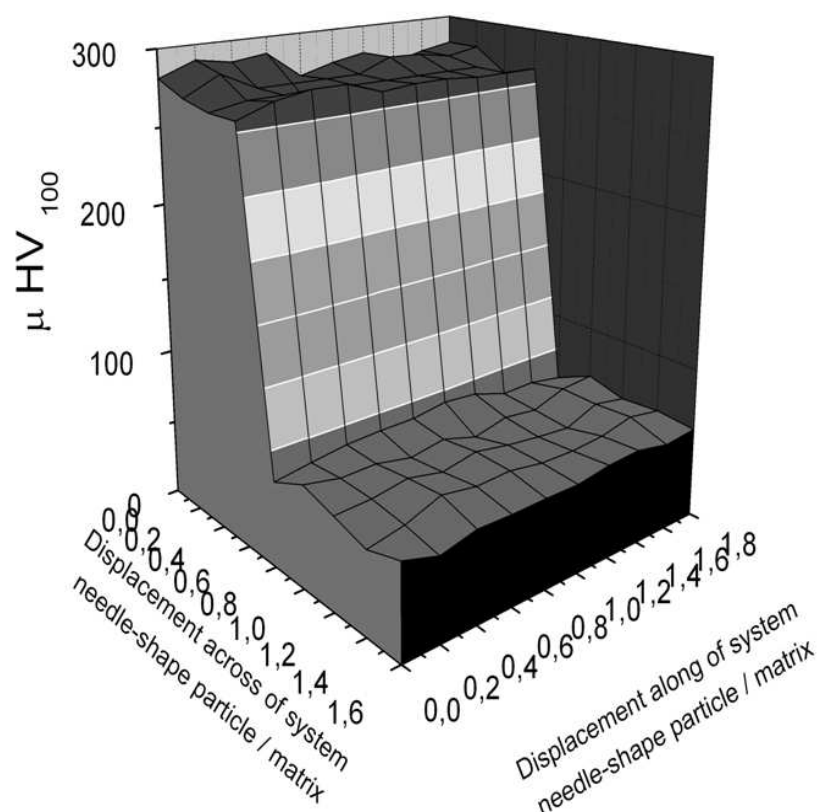


Fig. 2. Microhardness results for system $Zn_{16}Ti / \alpha_{Zn}$. Displacement in [mm].

4. Crystallographic relations in a matrix/precipitate system

The results of tests performed on Zn-Ti and Zn-Ti-Cu single crystals by TEM and EBSD techniques confirmed the existence of a close crystallographic relationship between the hexagonal crystal lattice of the matrix and the lattice of an intermetallic $Zn_{16}Ti$ phase. The $a_{Zn_{16}Ti}$ edges of the cells of the $Zn_{16}Ti$ phase and the $c_{\alpha-Zn}$ edges of the matrix are parallel to each other. At the same time, it has been observed that the direction of the $b_{Zn_{16}Ti}$ edges of the crystal cells in the $Zn_{16}Ti$ phase is in the majority of cases parallel to the $a_{\alpha-Zn}$ $\langle 11-20 \rangle$ direction of the hexagonal lattice of the matrix. This type of relationship proves an interrelation that exists between the phase lattice and the matrix lattice and, consequently, a partial coherence between the precipitates and the matrix.

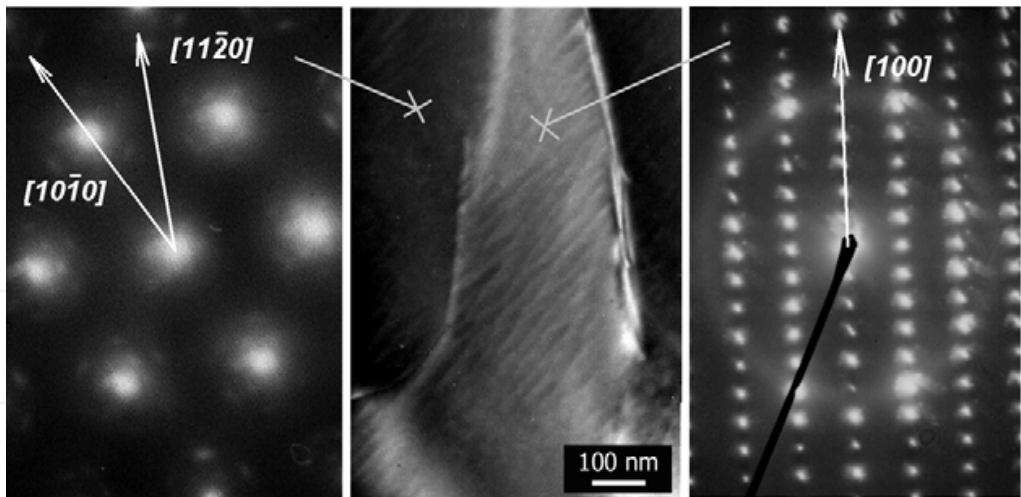


Fig. 3. TEM diffraction results from matrix and the $Zn_{16}Ti$ particle. Plane (0001) of the Zn-Ti0.1wt.% single crystal [11].

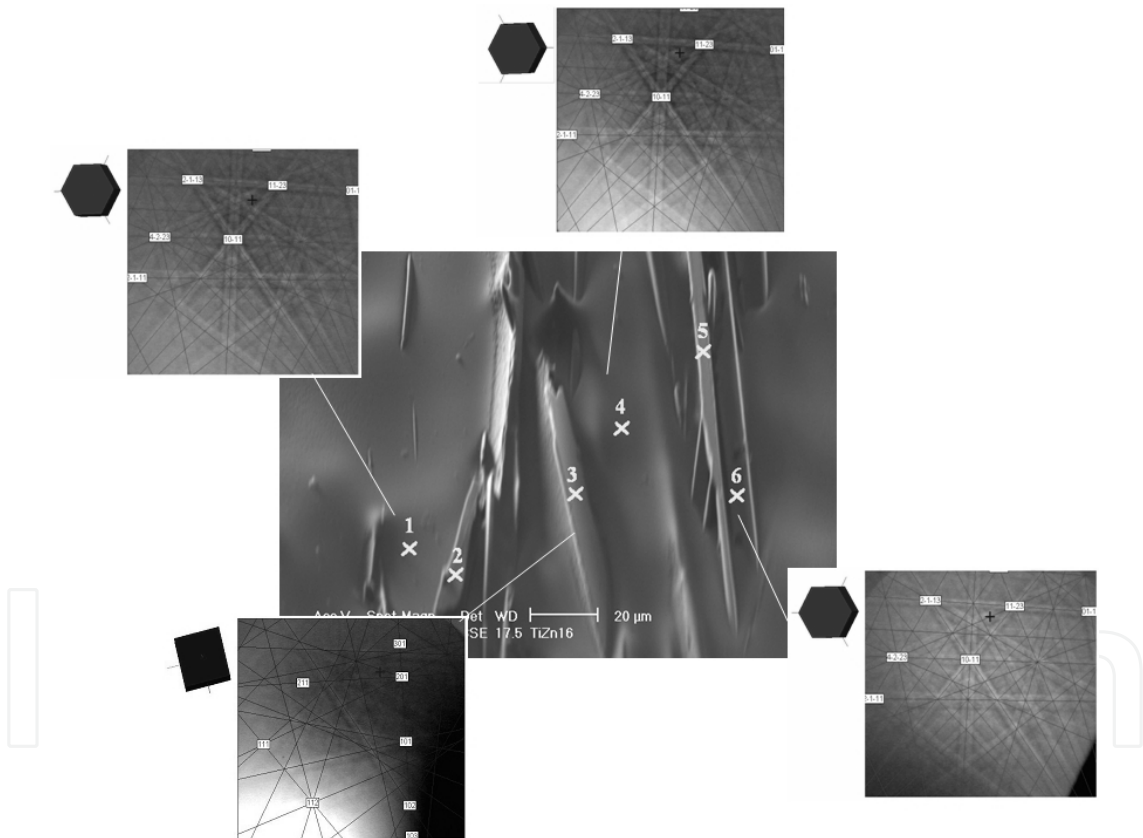


Fig. 4. EBSD results. Plane (0001) of the Zn-Ti0.1wt.% single crystal [26].

5. Control of the $Zn_{16}Ti$ phase morphology

The intermetallic $Zn_{16}Ti$ phase commonly occurs also in industrial zinc alloys. Due to its chemical composition, even alloys with a low content of titanium contain a large volume amount of this phase. This applies, first of all, to the hypoeutectic alloys with titanium content below 0.1 wt.%, which are used as a covering sheet metal in building constructions [26].

Previous studies have shown considerable potential for controlling the Zn_{16}Ti phase morphology through the choice of alloy composition and crystallisation speed. In the case of hypoeutectic binary Zn-Ti alloys, the capabilities of forming different structures are limited by the low stability of the crystallisation front which, in turn, translates into intensive nucleation and growth of intermetallic phases in the form of rods of complex cross-sections. This applies to single crystals obtained by Bridgman method, where the limit growth rate for Zn-Ti0.02wt.% alloys and Zn-Ti0.1 wt% alloys with single crystal matrix does not exceed 3 mm/h [26]. With the rate so low, the factor deciding about the morphology of the Zn_{16}Ti phase in a single crystal is the chemical composition. In the case of Zn-Ti0.02wt.% single crystals, the formation of needle-like crystallites is observed. The reason for this is a relatively low concentration of titanium, which forces predominant growth in the directions defined by diffusion and elastic constants of the crystal matrix. The result is an acicular form of precipitates of the Zn_{16}Ti phase.

Much higher content of titanium in Zn-Ti0.1wt.% single crystals enables the growth of crystallites of an intermetallic phase with larger and more complex cross-sections than in the previous case. The low growth rate combined with a high concentration of titanium allows for efficient growth, also on less preferred planes. The result is the presence of the intermetallic phase particles in the form of rods of irregular cross-sections (Figure 5).

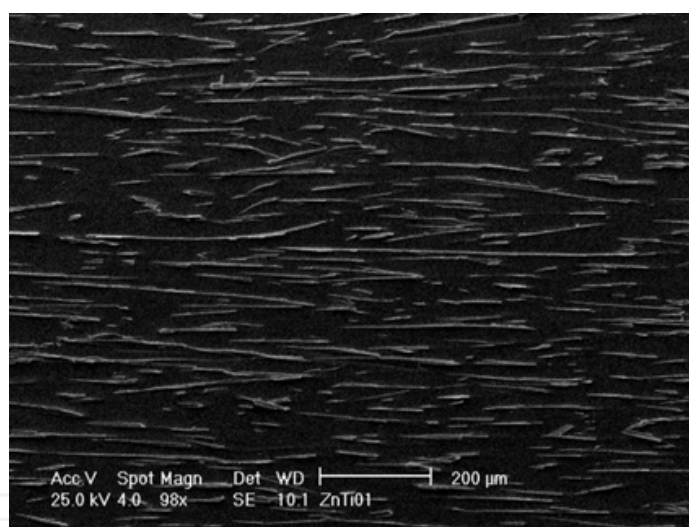


Fig. 5. The needle-shape form of the intermetallic phase Zn_{16}Ti observed on (0001) plane in Zn-Ti0.1wt.% single crystals obtained at growth rate of 3 mm/h.

Enhancing the capability of generating the particles with different morphologies is possible through stabilisation of the crystallisation front with an alloying addition increasing the surface tension of the front and thereby significantly limiting the amplitude of thermal fluctuations on its surface (Figure 6). In zinc alloys, very effective has proved to be copper, used in an amount of 0.075wt.% ... 0.15wt.% as a component of industrial Zn-Ti-Cu alloys. Copper addition to Zn-Ti0.1wt.%-Cu0.1wt.% single crystals allows increasing the crystallisation rate up to 16mm/h, which brings a wide range of changes to the morphology of particles produced in an intermetallic phase precipitating at the crystallisation front (morphology changing from columnar through lamellar to acicular) [18].

For a low rate of single crystal growth in the Zn-Ti0.1wt.%-Cu0.1wt.% alloy, i.e. 1.8mm/h, the intermetallic phase occurs in the form of rods of irregular cross-sections (Figure 7). This situation is analogous to the previously discussed single crystals of binary Zn-Ti alloys. The morphology of this phase is shown in Figure 5. Increasing the growth rate of single crystals in Zn-Ti0.1wt.%-Cu0.1wt.% alloy up to 6mm/h changes the $Zn_{16}Ti$ phase morphology from columnar to lamellar (Figure 8).

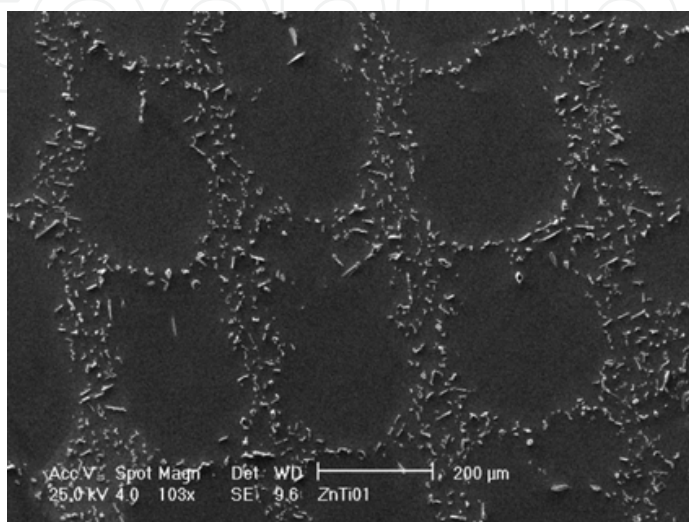


Fig. 6. Structure observed on (11-20) plane in Zn-Ti0.1wt.% single crystals obtained at growth rate of 3 mm/h.

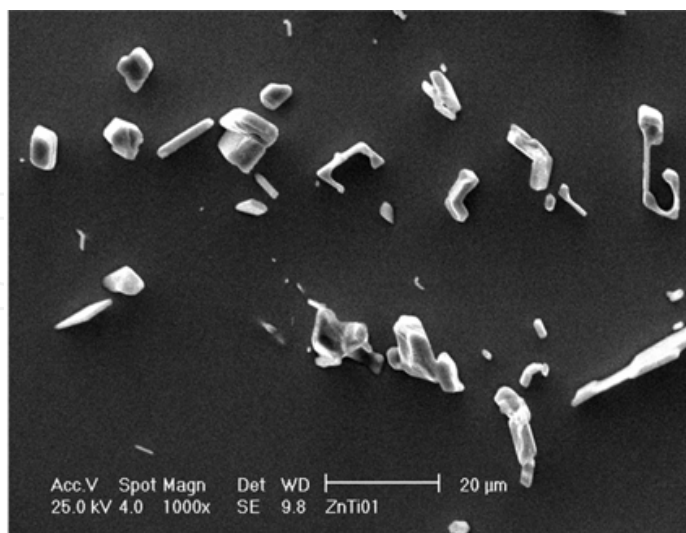


Fig. 7. The $Zn_{16}Ti$ intermetallic phase in a form of rods with irregular cross-sections, elongated on the [11-20] direction, observed in Zn-Ti0.1wt.%-Cu0.1wt.% single crystals obtained at growth rate of 1.8 mm/h.

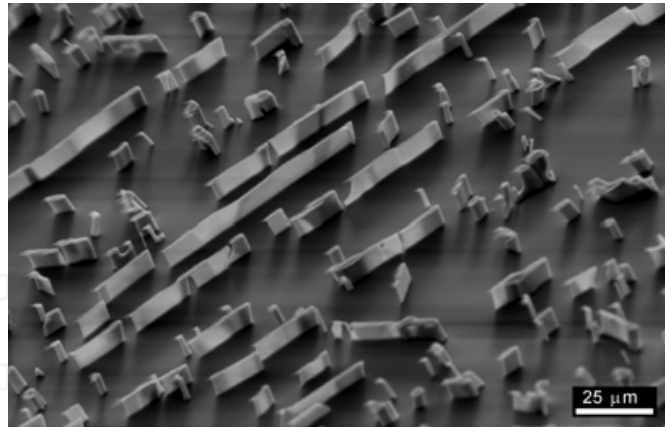


Fig. 8. The lamellar form of the $Zn_{16}Ti$ intermetallic phase observed in Zn-Ti0.1wt. %-Cu0.1wt. % single crystals obtained at growth rate of 6 mm/h. The (11-20) plane [18].

The resulting structure is characterised by a high degree of ordering. Constant crystallographic relationships have been observed between the arrangement of the $Zn_{16}Ti$ phase lamellae and matrix orientation. The precipitates of the $Zn_{16}Ti$ phase in the form of lamellae prefer for growth the pairs of planes from the family $\{10\bar{1}1\}$ which, in the case of zinc crystal lattice with the ratio of $c/a = 1.856$, are oriented at angles of 51° (Figure 9). The choice of a specific pair of planes is determined by the direction of growth of a single crystal belonging to the $\langle 11\bar{2}0 \rangle$ family, which also forms an axis for the band of the selected pair of planes (Figure 10).

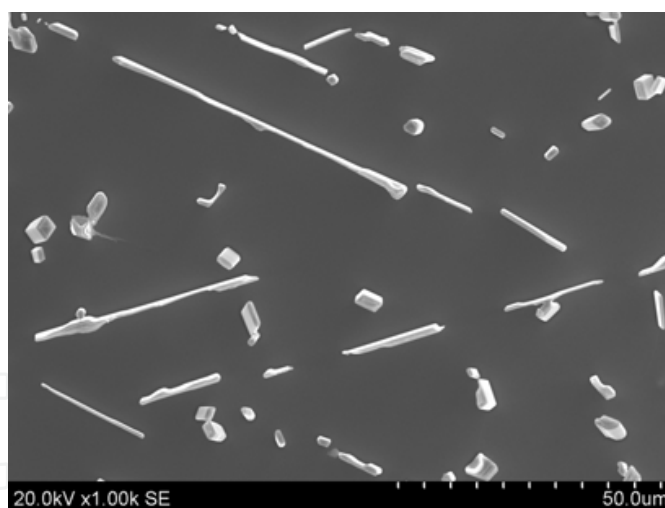


Fig. 9. The lamellar form of the $Zn_{16}Ti$ intermetallic phase observed in Zn-Ti0.1wt. %-Cu0.1wt. % single crystals obtained at growth rate of 6 mm/h. The (11-20) plane [14].

Another change in the morphology of the $Zn_{16}Ti$ intermetallic phase precipitates in single crystals of the Zn-Ti0.1wt. %-Cu0.1wt. % alloy is observed at the growth rate of 10mm/h. In the case of the examined alloy, this is the speed limit at which the crystallisation front is no longer a smooth surface because of the appearance of thermal fluctuations near the axis of growth. A consequence of this phenomenon is the locally varied growth rate of the single crystal matrix structure, changing the kinetics of growth of the intermetallic $Zn_{16}Ti$ phase precipitates at the crystallisation front. This situation is illustrated in Figure 11. The

structure visualised here was observed on the plane (11-20) perpendicular to the axis of growth. A clear difference is observed between the morphology of precipitates in the central part of the single crystal cross-section and outer zone close to the crystal faces. The $Zn_{16}Ti$ phase in the outer zone has a lamellar morphology, qualitatively identical with that occurring in single crystals at a growth speed of 6mm/h, while central zone is characterised by a morphology close to the acicular one. The reason accounting for this phenomenon is the structure growth velocity locally increased due to thermal fluctuations in the 'empty' oval areas free from the precipitates, and a small radius of the front curvature in these areas. Under such conditions, the nucleation and growth of an intermetallic phase takes place at the inflection points, which best serve this purpose because of the energy expenditure needed to create a nucleus. This situation is shown in Figure 12.

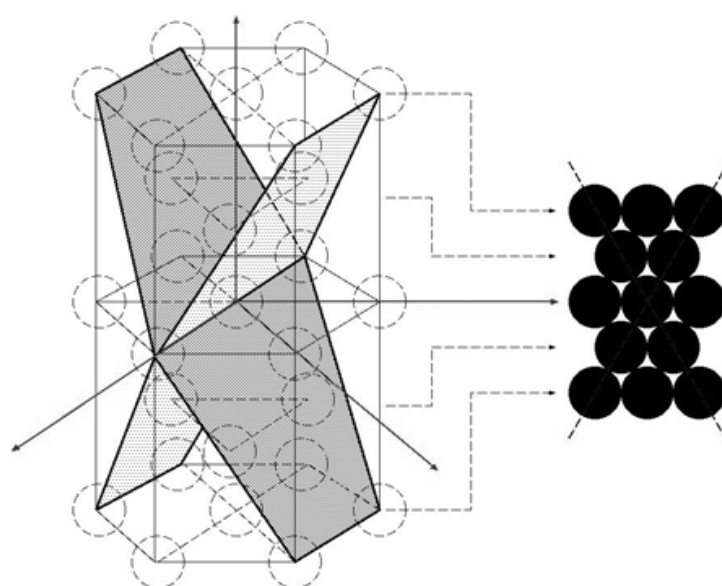


Fig. 10. The planes of preferred growth from {10-11} family, characteristic for lamellar shape of the $Zn_{16}Ti$ intermetallic phase.

With the speed of single crystals growth in the Zn-Ti0.1wt.-%-Cu0.1wt.-% alloy equal to 16 mm/h, the thermal fluctuations now cover the entire surface of the crystallisation front. This is shown in Figure 13. Within the whole examined area, the precipitates of purely acicular morphology arise. Compared to the previously discussed variant of a lower growth rate, the needles of the $Zn_{16}Ti$ phase now have round cross-sections, devoid of branches. It has also been observed that the oval areas devoid of precipitates show some degree of elongation on direction which is a trace of the plane (0001), characterised by the closest packing in a hexagonal structure (Figure 11, 12).

In the case of the Zn-Ti0.1wt.-%-Cu0.1wt.-% alloy, the speed of 16mm/h was the highest one for which a single crystal structure could be obtained (Figure 13,14). Therefore the next change to the morphology of precipitates was initiated by modification of the chemical composition. Considering the amount of the $Zn_{16}Ti$ phase formed in alloys with 0.1wt.-% of titanium, single crystals of the Zn-Ti0.2wt.-%-Cu0.15wt.-% alloy were obtained. It is a composition similar to the eutectic point which, on account of the Zn-Ti alloys belonging to the group of "off-eutectic" alloys, has not been at this rate accurately determined.

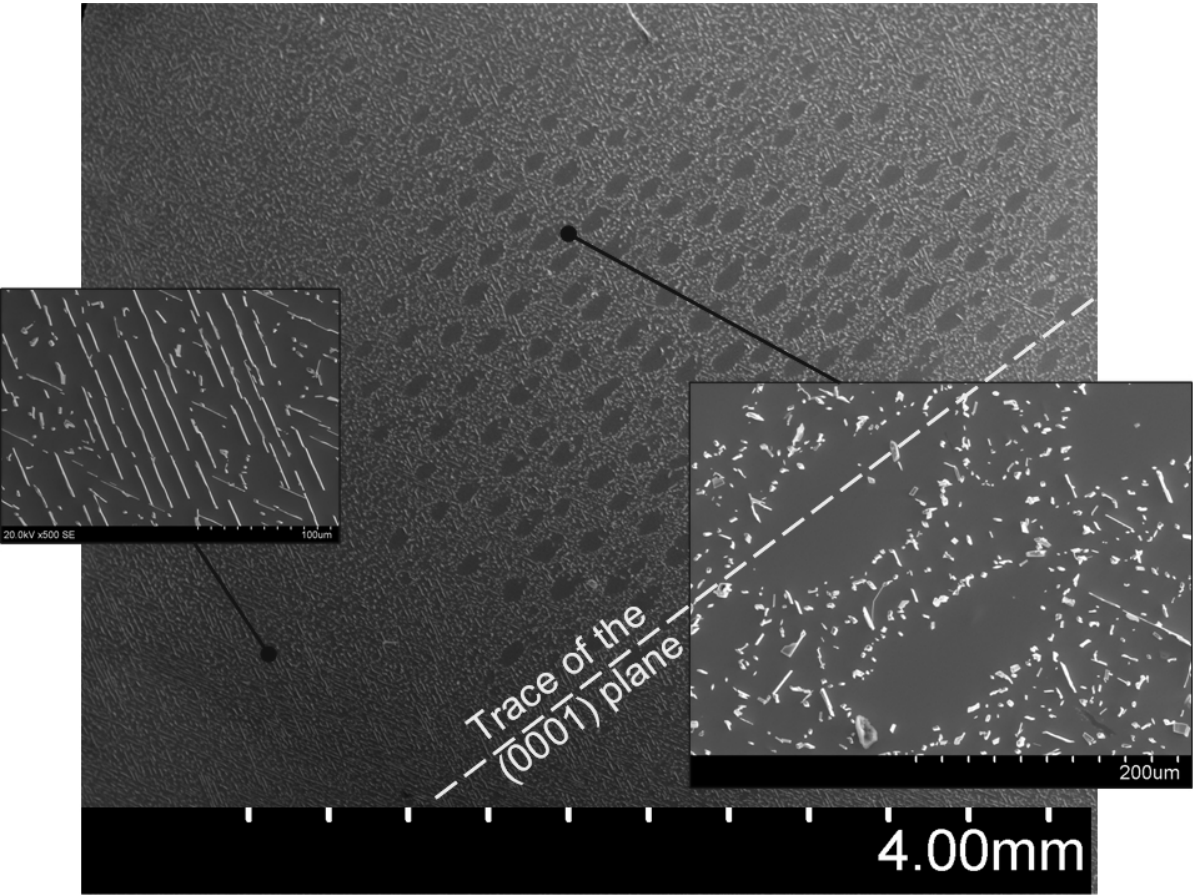


Fig. 11. Structure observed on (11-20) plane in Zn-Ti0.1wt.-%-Cu0.1wt.-% single crystals obtained at growth rate of 10 mm/h. Morphology of the precipitates in a core of crystals is different from morphology observed near outside walls of the crystal.

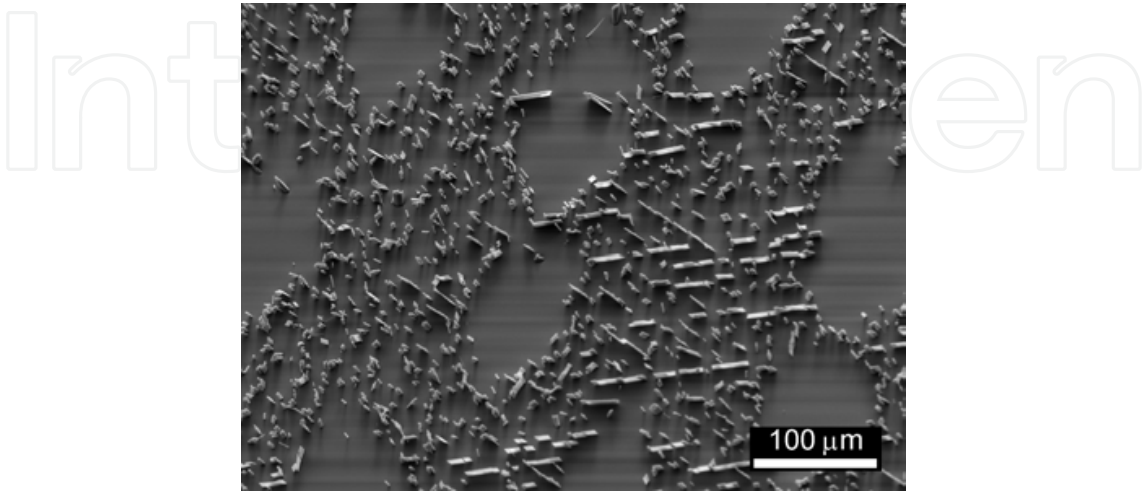


Fig. 12. The beginning of lamellar → fibre transformation observed in a core of the crystal.

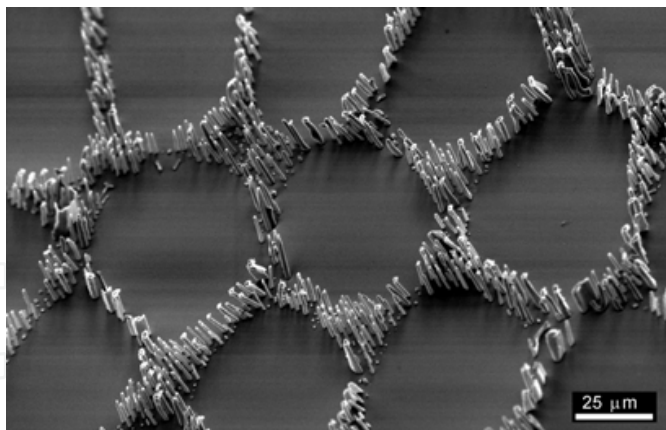


Fig. 13. Structure observed on (11-20) plane in Zn-Ti0.1wt.-%-Cu0.1wt.-% single crystals obtained at growth rate of 16 mm/h [18].

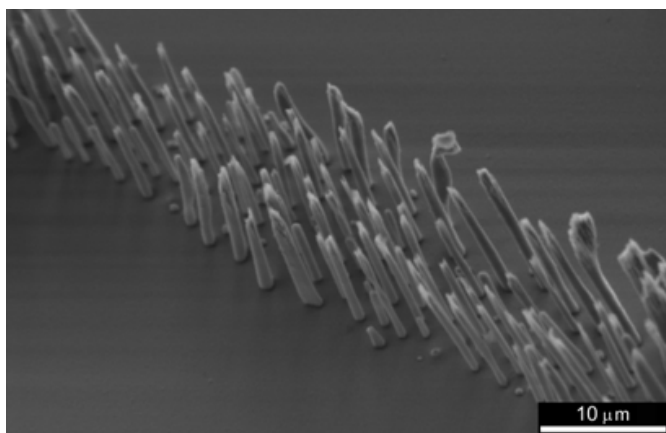


Fig. 14. Structure observed on (11-20) plane in Zn-Ti0.1wt.-%-Cu0.1wt.-% single crystals obtained at growth rate of 16 mm/h.

Single crystals in the Zn-Ti0.2wt.-%-Cu0.15wt.-% alloy were obtained at a speed of 1.8mm/h. Structural analysis revealed in the structure the presence of particles of very complex morphology (Figure 15). Observations revealed the existence of precipitates of an acicular morphology and macroparticles shaped like discs and polygons. The performed chemical analysis has shown that all the observed types of precipitates are composed of one intermetallic phase only, i.e. $Zn_{16}Ti$ [21]. Until now it has not been possible to identify clearly the reasons which have made one phase assume so many different types of morphologies. One of the reasons can be different mechanism of nucleation of the individual types of particles. The constitution of Zn-Ti0.2wt.-%-Cu0.15wt.-% macroparticles observed in the structure of Zn single crystals significantly deviates from previous observations of the $Zn_{16}Ti$ phase. In the case of macroparticles (Figure 16), the precipitates take the form of a eutectic system, in which there are alternately arranged lamellae of $Zn_{16}Ti$ / α / $Zn_{16}Ti$ / α / ... / α /. The nucleation of such a system is energetically privileged, compared to the process by which isolated particles of one phase only are expected to precipitate from the solution. This follows from the mechanism of the coupled growth of eutectic phases [27].

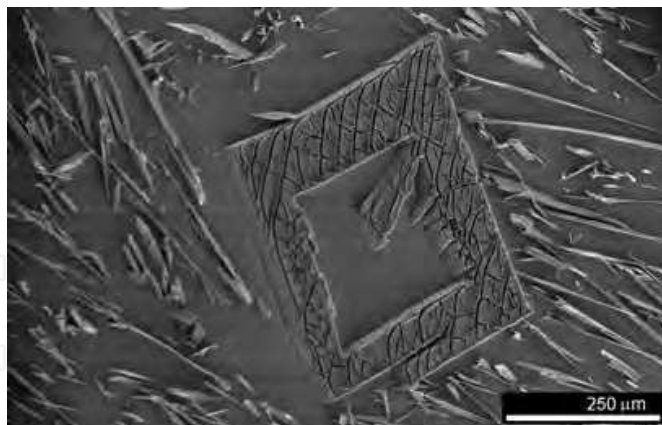


Fig. 15. Multishape morphology of the $Zn_{16}Ti$ intermetallic phase observed on (0001) plane in Zn-Ti0.2wt.-%-Cu0.15wt.-% single crystals obtained at growth rate of 1.8 mm/h.

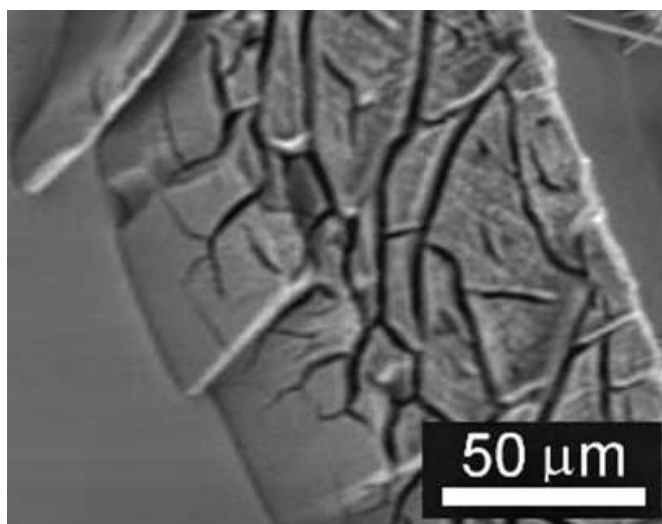


Fig. 16. The macroparticle as a eutectic form $Zn_{16}Ti/\alpha/ Zn_{16}Ti/\alpha/...$ observed on (0001) plane in Zn-Ti0.2wt.-%-Cu0.15wt.-% single crystals obtained at growth rate of 1.8 mm/h.

6. The distribution of $Zn_{16}Ti$ phase in function of growth conditions

6.1 Oscillatory structures

The conditions of growth and chemical composition affect not only the morphology of the $Zn_{16}Ti$ phase precipitates, but also distribution of this phase. A special case of the structure formed at low growth rates of the Zn-Ti and Zn-Ti-Cu single crystals is oscillatory structure [18,26,28]. It is characterised by the cyclic occurrence of typical elements, such as areas rich in precipitates interwoven with areas of pure matrix totally devoid of precipitates.

Oscillatory structures were observed for the first time in the peritectic Sn-Cd alloys [28]. They are formed as a result of changes in the concentration of an alloying constituent ahead of the moving crystallisation front, which affects the conditions necessary for nucleation of individual phases. With proper velocity of the crystallisation front movement, the preferred growth is alternately exhibited by phases a and b (Figure 17).

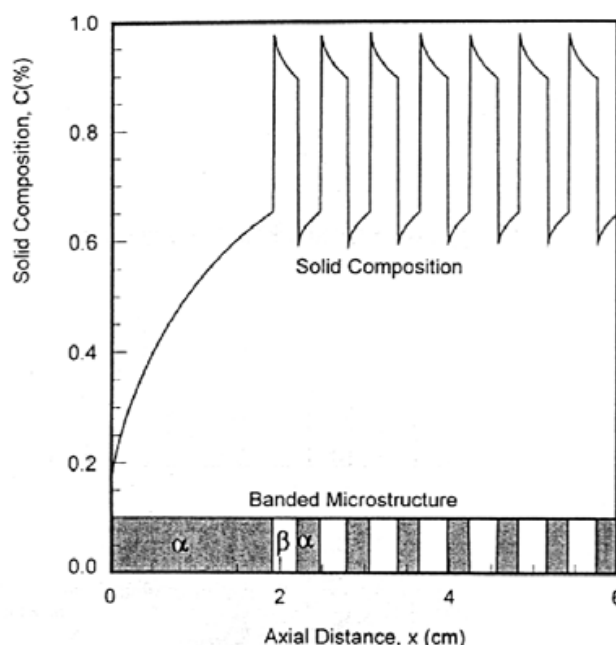


Fig. 17. Growth mechanism of the oscillatory structure in peritectic [28].

Massive macroparticles use in building of their structure a significant amount of titanium, thus reducing the concentration of this element in solution. Then, from the rest of the titanium-depleted solution, the precipitation of fine-grained phases occurs; on account of the low concentration of titanium, these phases do not form a eutectic system in the solution.

A similar phenomenon as described previously for the peritectic Sn-Cd alloys was also obtained in the eutectic Zn-Ti and Zn-Ti-Cu alloys. Studies showed that the condition necessary for the formation of such structures in single crystals based on zinc is low travel speed of the cooling zone, and hence low rate of the crystal growth. In cases under discussion, it did not exceed 6 mm/h. Additional important factors are the chemical composition of the alloy and differences in temperature between the melting point of pure metal (in this case zinc) and the eutectic point. The lower is the difference in temperatures, the stronger tendency the alloy shows to the formation of an oscillatory structure. Depending on the degree to which these conditions are satisfied, the following types of oscillatory structures can be obtained:

- a. purely oscillatory, i.e. a sequence of alternately occurring regions rich in inclusions of the second phase and layers of pure matrix (alpha phase) free from the precipitates [18],

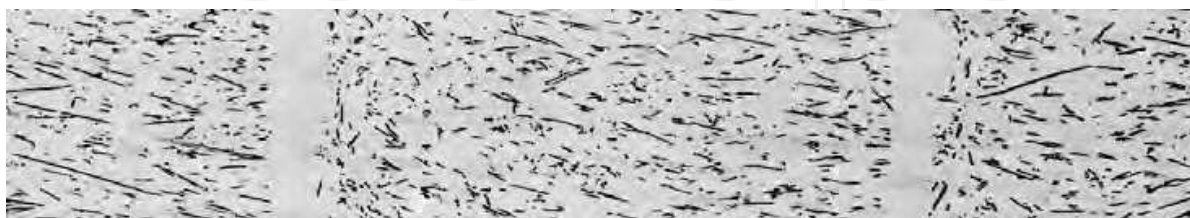


Fig. 18. Oscillatory structure of "a-type" observed in Zn-Ti-Cu single crystals.

- b. oscillatory, in the case of which areas totally free from the precipitates are not observed any longer, while the degree of filling the alternately occurring layers with inclusions of the intermetallic phases is periodically changing.

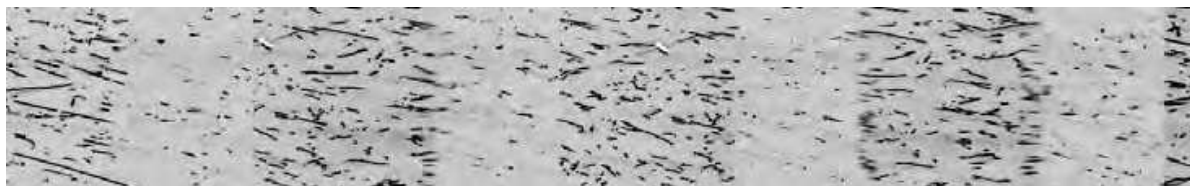


Fig. 19. Model of oscillatory structure of “b-type” observed in eutectic Zn-Ti-Cu single crystals.

Case (a) occurs in titanium alloys with 0.1 wt.% Ti and less. In alloys with the titanium content so low, the zonal segregation occurring during single crystal growth by Bridgman method is sufficiently strong to form areas with the concentration of alloying elements so low that the process of the second phase precipitation is inhibited.

Another phenomenon observed in the case of the oscillatory structures of type (a) is the, linearly changing along the growth direction, density of the inclusions of the second phase in areas rich in precipitates. This phenomenon is particularly evident in single crystals growing at the lowest rates (1.8mm/h). This is presented in Figure 20a. Increasing the growth rate to 6 mm/h makes the structure preserve its oscillatory character but with a uniform distribution of precipitates within the layer (Figure 20b). The reason for this is lower concentration of titanium ahead of the crystallisation front caused by a higher rate of the cooling zone transfer, which weakens the effect of zonal segregations, and consequently changes the conditions for nucleation of an intermetallic phase.

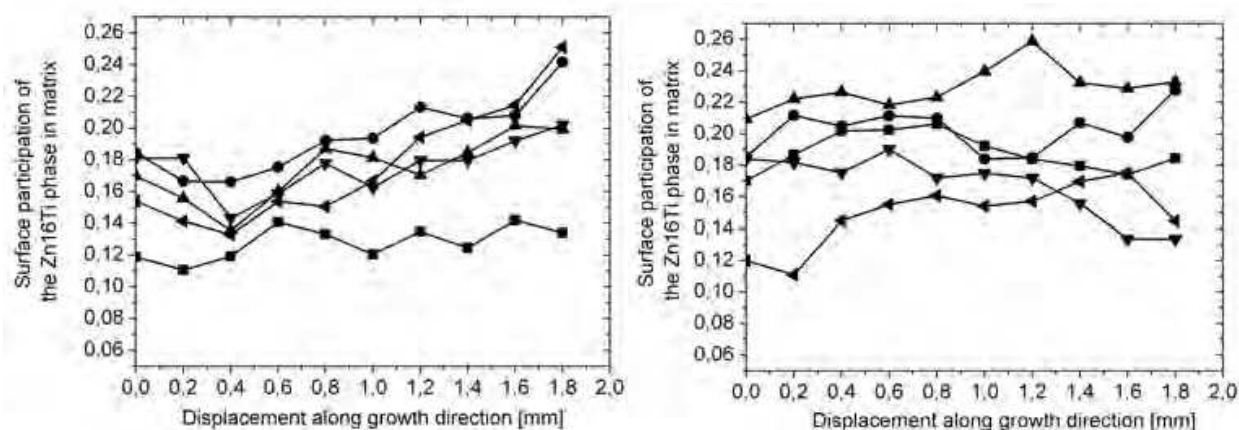


Fig. 20. The $Zn_{16}Ti$ phase distribution along of a precipitation-rich layer: a) oscillatory structure obtained at 1.8 mm/h growth rate; b) oscillatory structure obtained at 6 mm/h growth rate.

On the other hand, structures of type (b) have been observed in Zn-Ti-Cu alloys with around-eutectic titanium content. In this case, the concentration of titanium in the entire volume of the solution is so high that, regardless of the speed of crystal growth, there are conditions for the nucleation and growth of the $Zn_{16}Ti$ phase. What changes is only the intensity of this phenomenon, which manifests itself in an alternate occurrence in the structure of the layers of higher and lower concentration of the precipitates.

6.2 Model analysis of oscillatory structure

To better understand the growth mechanism of oscillatory structures, a mathematical model developed by Wolczynski has been used [29]. It allows us to estimate the impact of growth

conditions and chemical composition on the forming sequence of layers rich in an intermetallic phase and free from the precipitates [11,18,26,29,30]. This model has been developed for binary alloys and is based on the diffusion-related changes in alloying constituent concentration. It includes the three major processes occurring during alloy crystallisation:

1. changes in the concentration of alloying element depleting the liquid phase with progressing crystallisation along the liquidus line,

$$N^L(x; \alpha) = N_0 (1 + \alpha k x - x)^{(k-1)/(1-\alpha k)}$$

2. microsegregations at the crystallisation front, resulting from the constituent segregation,

$$N^S(x; \alpha) = k N_0 (1 + \alpha k x - x)^{(k-1)/(1-\alpha k)}$$

3. redistribution of alloying constituents in grains after the occurrence of reverse diffusion.

$$N^B(x; X^0, \alpha) = \left[k + \beta^{ex}(x; X^0) \beta^{in}(X^0, \alpha) \right] N^L(x; \alpha)$$

where:

- k - partition ratio, x - amount of growing crystal,
- N_0 - nominal concentration of the alloy, α - back-diffusion parameter,
- β^{ex} ; β^{in} - coefficients of the redistribution extension and intensity.

$$i_E(N_0) = i_K(1, N_0)$$

$$i_D(\alpha, N_0) = i_K(\alpha, N_0) - i_E(N_0)$$

$$i_K(\alpha, N_0) = 1 - x_K(\alpha, N_0)$$

$$x_K(\alpha, N_0) = \frac{1}{1 - \alpha k} \left[1 - \left(\frac{N_E}{N_0} \right)^p \right]$$

This method allows precise determination of the amount of precipitates of both equilibrium i_E and non-equilibrium i_D character, where x_K is the amount of pure single crystals between the fringes.

$$p = \frac{1 - \alpha k}{k - 1}$$

If α is equal to zero, then the model is diffusionless. Such simplification makes the model unrealistic, although it may serve as a benchmark or reference.

Two binary alloys, i.e. Zn-Ti0.02wt.% and Zn-Ti0.1wt.%, were selected for tests. The structures of single crystals of these alloys are of an oscillatory character, but differ considerably in respect of volume fraction of the Zn₁₆Ti phase and its distribution. Layers rich in precipitates observed in the Zn-Ti0.02wt.% alloy are much smaller in thickness than the layers without precipitates.

Single crystal	Titanium contents [wt.%]	Thickness of precipitation-rich layer [μm]	Thickness of precipitation-free layer [μm]
Zn-Ti0.02wt. %	0.023	10	120.4
Zn-Ti0.1wt. %	0.10	56.6	127.3

Table 3. Structural parameters of the Zn-Ti0.02wt.% and Zn-Ti0.1wt.% single crystals.

For single crystals of Zn-Ti.01wt.% alloy, the layers rich in precipitates are much thicker, while spacing between them is similar to that observed in single crystals of lower titanium content.

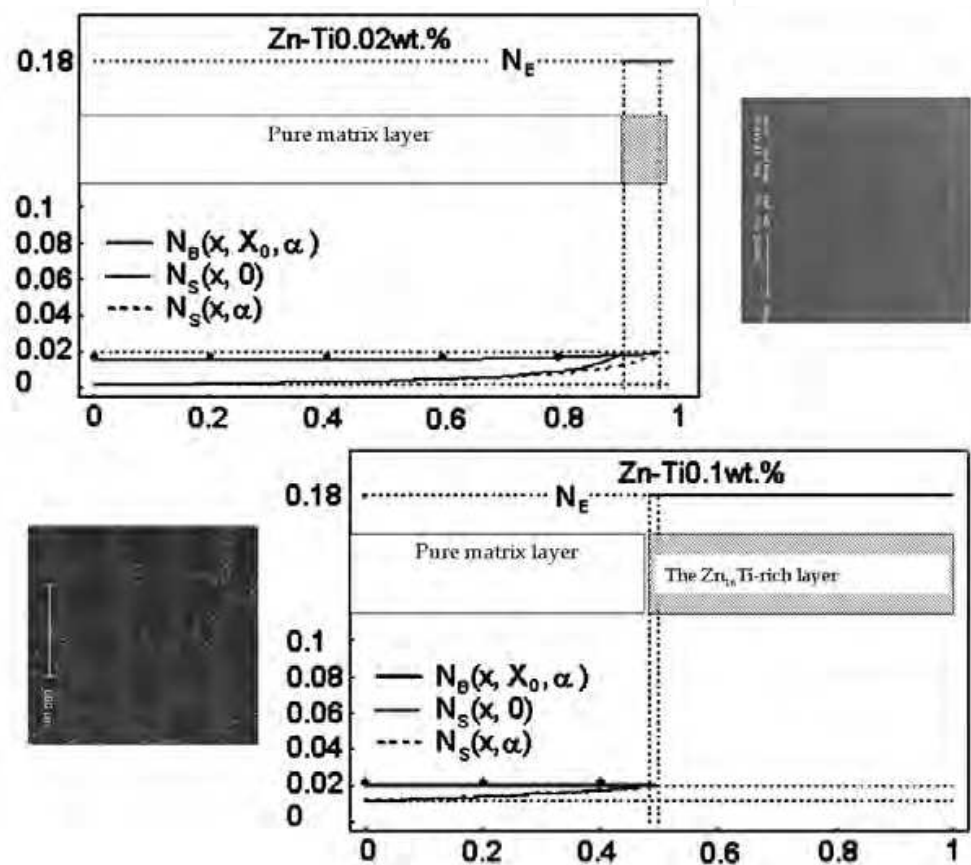


Fig. 21. Calculatin results obtained for the model.

Designations used in Figure 21:

- N_E - eutectic concentration of the Ti-solute [wt.%]
- N_B - solute redistribution after back-diffusion [wt.%]
- N_S - "historical" solute concentration on the solid/liquid interface
- α - back-diffusion parameter [wt.%]

The proposed model based on calculations of the diffusion of the alloying elements fairly well reflects the growth of an oscillatory structure in the binary Zn-Ti alloys. The compliance is particularly strong for the structure of single crystals of Zn-Ti0.02wt.%, where there is clear division between individual elements of the structure. In the case of single crystals of Zn-Ti0.1wt.%, a large amount of the alloying constituent disturbs the arrangement of layers because of "bridges" that are formed in between them. However, in the case of a model based

solely on theoretical data, the results obtained can be considered correct. Additionally, Figure 22 presents a hypothetical path of crystallisation for the Zn-Ti0.1wt.% alloy [30].

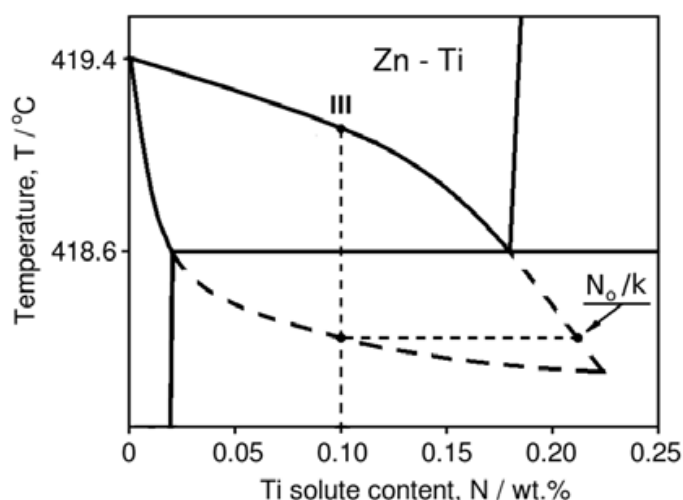


Fig. 22. Solidification $III \rightarrow N_0/k$ for an equilibrium solidification of the single crystal with $N_0 = III = 0.1$ [wt.%Ti] [30].

6.3 Continuous and cellular structure in single crystals of Zn-Ti0.1-Cu0.1

Increasing the growth rate of Zn-Ti-Cu single crystals leads to disappearance of oscillatory structure and formation of structures with a uniform distribution of inclusions of the second phase, accompanied by simultaneous change in the morphology of an intermetallic phase. In the case of an oscillatory structure, the observed phase has the form of rods with heterogeneous cross-sections, while with the crystallisation rates of 6.10 mm/h a lamellar phase appears [18].

The morphological transformation at 10mm/h is a consequence of the crystallisation front changing from flat to cellular. The changing character of the crystallisation front can affect the morphological transformation of the second phase. The phase transformation from lamellar to acicular takes place due to the change of nucleation conditions. According to the thermodynamic rules, the lamellae/rods transformation takes place if and when the minimum free energy for lamellae ΔG_L is equal to the minimum free energy for rods ΔG_R [24,29].

Further increase in the front travel rate brings next change to the distribution and morphology of an intermetallic phase. The distribution of precipitates starts changing from continuous to cellular. This transformation is also accompanied by the appearance of the $Zn_{16}Ti$ phase in the form of needles. The beginning of this transformation can be observed in the core of a single crystal, while near the outer walls, the continuous structure with lamellar morphology of the precipitates still prevails. This situation occurs at the rate of growth equal to 10 mm/h.

Thermal fluctuations at the crystallisation front are responsible for different growth rates in microregions, causing the appearance of pseudo-cellular structure. It has the appearance of a lattice with regularly spaced meshes free from the precipitates and surrounded by an acicular phase. The lattice meshes seen on the plane (11-20) are of an oval shape, elongated in the direction indicated by traces of the plane (0001). Observed on the plane (0001), this structure gives a picture of axial sections of the strongly elongated "rods" of pure matrix, enclosed from the outside by acicular precipitates.

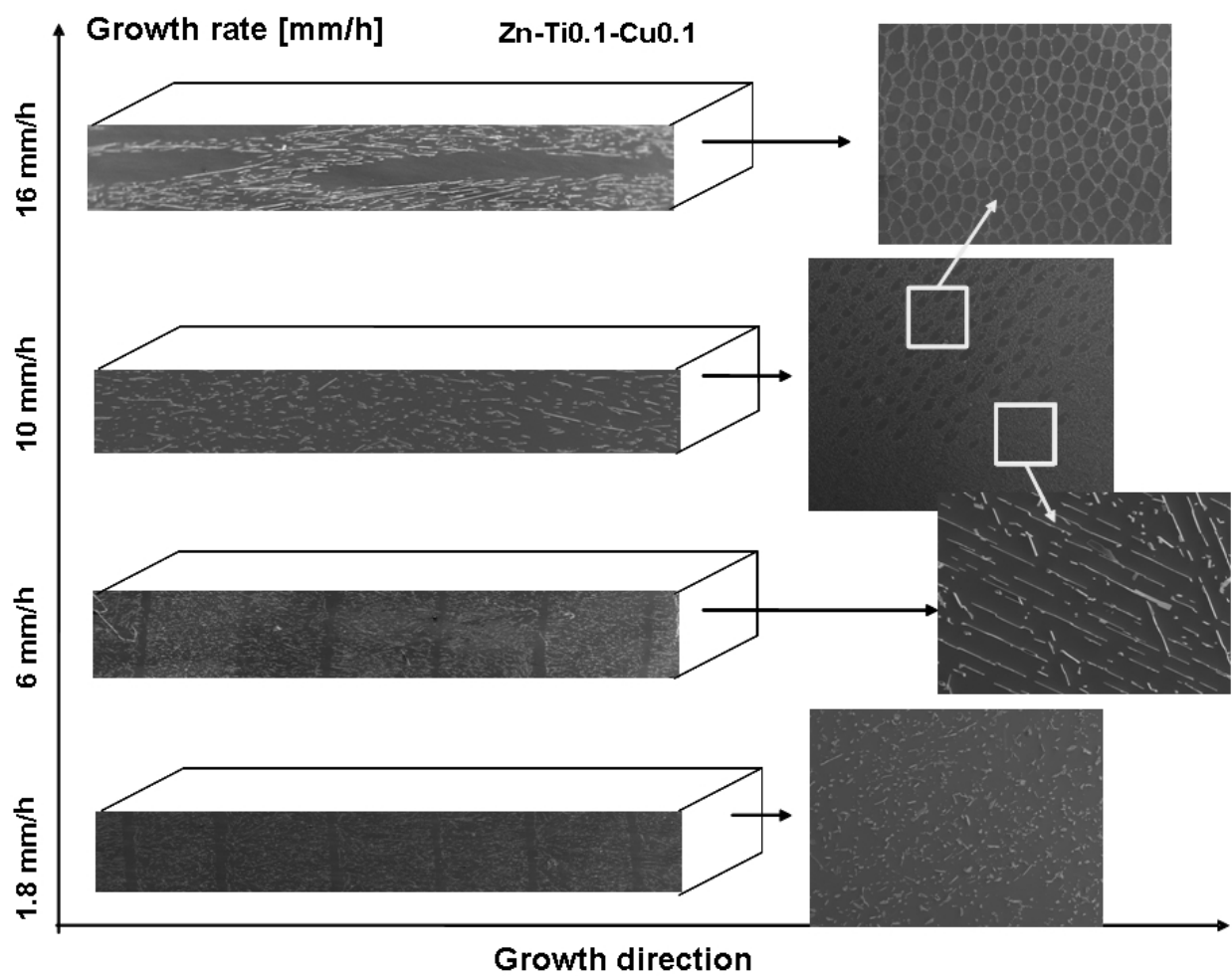


Fig. 23. Comparison of morphology and distribution of the $Zn_{16}Ti$ intermetallic phase in relationship to growth rate of the Zn-Ti0.1wt.-%-Cu0.1wt.-% single crystals.

An increase in the travel speed of the cooling zone to 16mm/h makes the whole crystal volume assume the form of a pseudo-cellular structure. The observed precipitates assume the form of strongly elongated needles with circular cross-sections, while areas surrounded by them are free from the precipitates and assume an equiaxial shape. Further increase in the crystallisation rate makes the matrix lose its crystallographic continuity and starts the formation of a structure with strongly elongated grains [17].

7. Summary

Regardless of the applied variant of the Zn-Cu-Ti Ti single crystals growth containing up to 0.2wt.% Ti, only one type of the intermetallic $Zn_{16}Ti$ phase was observed to occur. Changing the growth conditions and the chemical composition strongly affected the morphology and distribution of the precipitates of this phase in a single crystal matrix. It was found that low growth rates of zinc-based single crystals led to the formation of an oscillatory structure. At the same time, in the case of binary Zn-Ti alloys, it was the only available type of structure. Generating other types of structure required higher rates of the single crystals growth. On the other hand, the acceleration of the growth process required stabilised surface of the crystallisation front obtained by reduced thermal fluctuations. This

was achieved by adding copper to the Zn-Ti alloy, which resulted in increased surface tension at the crystallisation front and enabled generation of structures characterised by a single crystal matrix at rates in the range of 1.8 - 16 mm/h.

	Shape of the solid/liquid interface	Type of the structure	The intermetallic compound morphology
1.8 mm/h	almost plane	oscillatory	irregular bands
6 mm/h	concave, without instabilities	oscillatory	regular bands
10 mm/h	instabilities appear in the core	continous	bands/needles (fibres)
16 mm/h	instabilities on a whole surface	cellular/pipe	rod-like needles (fibres)

Table 4. Structure types and the intermetallic phase morphology obtained at different growth rates.

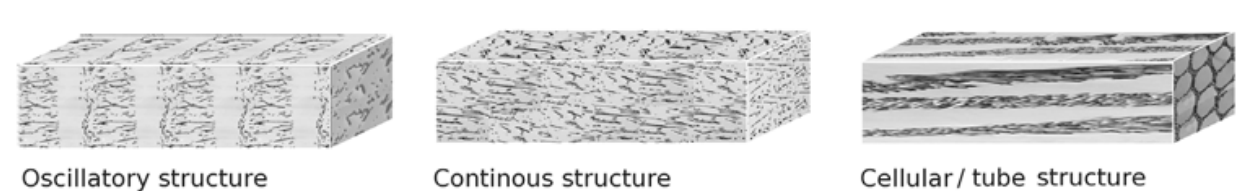
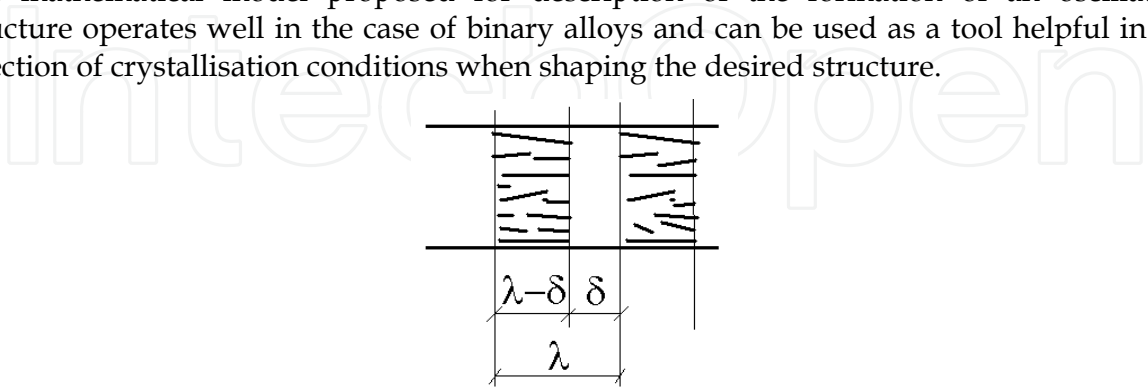


Fig. 24. Change of the intermetallic phase distribution in relationship to growth rate observed in the Zn-Ti0.1wt. %-Cu0.1wt. % single crystals.

Changing the speed of Zn-Ti0.1-Cu0.1 single crystals growth strongly influences the distribution of the Zn₁₆Ti phase in a single crystal matrix, as shown in Figures 23 and 24. In the case of oscillatory structures, the following relationships were observed:

- a. precipitates-free layers are located at the same distance, λ , for the growth rates 1.8 mm/h and 6 mm/h
- b. thickness of these layers, δ , decreases with the growth rate
- c. precipitates-rich layer thickness, $\lambda - \delta$, increases with the growth rate
- d. oscillatory structure vanishes, cells structure appears in the core of the single crystal, above the growth rate 10 mm/h.

The mathematical model proposed for description of the formation of an oscillatory structure operates well in the case of binary alloys and can be used as a tool helpful in the selection of crystallisation conditions when shaping the desired structure.

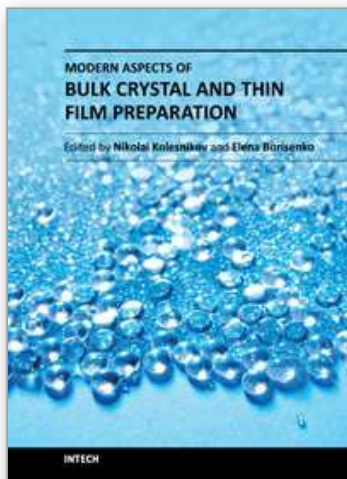


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