SECON D PHASE MORPHOLOGY IN THE Zn-Ti0.1-Cu0.1 SINGLE CRYSTALS OBTAINED AT DIFFERENT GROWTH RATES

MORFOLOGIA DRUGIEJ FAZY W MONOKRYSZTAŁACH Zn-Ti0.1-Cu0.1 OTRZYMYWANYCH PRZY RÓŻNYCH SZYBKOŚCIACH WZROSTU

The influence of growth rate on a morphology, distribution and crystallographic relationship of the intermetallic phase Zn$\text{\textsubscript{16}}$Ti in Zn-Ti0.1-Cu0.1 single crystals were investigated. The crystals obtained at rates in range of from 1.8mm/h to 16mm/h were tested. In all cases a strong elongation of the Zn$\text{\textsubscript{16}}$Ti particles along the [11-20] direction is observed. Moreover, it is found that a lamellar phase existing in the crystals develop in range of the growth rate from 6 to 10 mm/h and grows in the {10-11} planes. In the case of the growth rate of 16mm/h oval-shaped areas of $\alpha$ phase (solid solution of zinc and 0.1wt.% of copper with trace content of titanium) elongated along [10-10] direction and surrounded by needle shaped precipitations are formed in the structure.

Keywords: Crystal structure, Crystal morphology, Single crystal growth, Zinc compounds

1. Introduction

The zinc alloys with additions of titanium and copper are known to be hardened even by small contents of alloying components [1-4]. Single crystals which include about 0.1wt.% of Ti (0.14at.%) represent quite complicated structure of the precipitates (Fig. 1) [3-7]. It is induced by very low solubility of titanium in zinc at the room temperature (below 0.0005wt.%) and strong anisotropy of diffusion coefficients of the alloying components in hexagonal lattice and elastic constants in the zinc single crystals [8-10].

In all investigated structures, only one type of the precipitates was observed, namely Zn$\text{\textsubscript{16}}$Ti intermetallic phase [11]. To confirm the phase careful analysis by EB-SD method and evaluation of chemical composition were conducted. The Zn$\text{\textsubscript{16}}$Ti intermetallic phase (containing 6.3 at.% of Ti) contains only one atom of the titanium per 16 zinc atoms, what possibly generates above 2% of the phase in the single crystal volume at the content of only 0.14 at.% of Ti in the alloy [4,5].
The preferable growth direction of the Zn$_{16}$Ti phase is [11-20], which is the close packed direction in hexagonal structure of the zinc. Direct consequence is a growth anisotropy of the second phase particles. The titanium content in the investigated alloy Zn-Ti0.1-Cu0.1 is located in hypereutectic range of the Zn-Ti phase diagram. The whole copper addition is solved in zinc as the alpha phase. Microanalysis of the chemical composition of the matrix showed additionally a small 0.022 wt.% titanium content [4,5].

The work concentrates on investigations of the growth rate of the Zn-Ti0.1-Cu0.1 single crystals on the morphology and distribution of the intermetallic phase Zn$_{16}$Ti. Previous researches showed that an increase of movement rate of the crystallization front induced a structural transformations in these crystals according to scheme (Fig. 2):
oscillatory structure [5,6,12] $\rightarrow$ continuous structure $\rightarrow$ cellular/tube structure.

Together with foregoing transformations, shapes of the precipitates of the Zn$_{16}$Ti phase evolve too. For small growth rates (1.8mm/h) an irregular rods with low degree of order were observed. On contrary, at 6mm/h the lamellar phase with the high degree of order arose (Fig. 3). The further increase of the growth rate up to 10mm/h activates a lamellar-to-needle transformation (Fig. 5 and 6). This is also the critical growth rate where, at the same time, in the core of the single crystal the cellular structure with needle-shape precipitates is being formed. With the growth rate of 16mm/h a whole volume of the single crystal is transformed and an arrangement of the long needles as on a Figures 2 and 4 is observed [3,5-7].
2. Methods

The Zn-Ti0.1-Cu0.1 single crystals were produced by modified Bridgmann method in the argon atmosphere [13]. Growth processes was carried out in spectral-pure graphite crucible. The final crystals had the dimensions of 7x7x150 mm. Four different growth rates of the single crystals were applied: 1.8mm/h, 6mm/h, 10mm/h and 16mm/h. The choice of the rates was dictated by observations of the structural changes. The single crystals were oriented on X-ray diffractometer Bruker D8 Advance, and afterwards cut on samples either with (0001) or (11-20) plane as the observation surface. The observed surfaces were polished on sand papers, then etched by a chromium reagent [14]. Deep etching was applied in order to reveal the real 3-D shapes of the precipitates and to investigate crystallographic relationships of the particles with the matrix. Structural observations were carried out at scanning electron microscopes Hitachi 3300 AN with EDS and EBSD and Tesla-302.
3. Results and discussion

Figure 3 and Figures 5-8 presents a structure of the Zn-Ti0.1-Cu0.1 single crystals obtained with the growth rate in range from 6 to 10mm/h. The characteristic feature is highly ordered structure of the precipitates in the crystal structure strongly connected with crystallography of the matrix. The Zn$_{16}$Ti intermetallic phase characterized by the tetragonal structure exists in the material in a form of lamellae. The growth direction of the lamellae corresponds to the [11-20] direction in the matrix. The [11-20] direction is at the same time the growth direction of the whole single crystal. Previous EBSD results have showed that between the orientations of matrix and the Zn$_{16}$Ti phase strong connection exist, i.e. [11-20] direction in the matrix is parallel to the [100] direction of the intermetallic phase. These dependencies together with the proper growth rate (6...10mm/h for Zn-Ti0.1-Cu0.1 single crystals) exact the lamellar shape of the precipitates while keeping a high symmetry of the creating structure (Fig. 3, 7 and 8). The side surfaces of the lamellae coincide with {10-11}planes of the matrix. Due to the fact, that for every <11-20> direction two equally important {10-11} planes are present, thus the lamellae are located in those two planes in the structure. Measurement of an angle between the lamellae growing on the different planes is equal to $49^\circ \pm 3^\circ$, what is in a good correspondence with the angle between two {10-11} planes in zinc structure with respect of a $c/a$ ratio equal to 1.85 [8,15,16].

Fig. 7. The lamellar structure observed on the (11-20) plane of the Zn-Ti0.1-Cu0.1 single crystals obtained at 6mm/h growth rate

Fig. 8. The Zn$_{16}$Ti lamellar phase crystallographic configuration. The $50^\circ \pm 0.5$ angle respect $c/a$ coefficient for pure zinc (1.85) and lattice expansion by copper addition.
The lower growth rate (1.8mm/h) generates the precipitates elongated along [11-20] direction in the matrix. They are not regular lamella but have highly developed cross-sections with many side branches (Fig. 9). It is a consequence of strong anisotropy of the diffusion coefficient and elastic constants in hexagonal metals depending on the crystallographic orientation.

At the temperature of 293K, the auto-diffusion coefficient in zinc in the <11-20> direction is $0.58 \times 10^{-4} \text{m}^2\text{s}^{-1}$, and for the [0001] direction is $0.13 \times 10^{-4} \text{m}^2\text{s}^{-1}$ only [8]. Similar situation follows in case of the elastic constants: $K_{||}[0001]=13.1$ and $K[0001]=1.93 \text{cm}^2\text{dyne}^{-1} \times 10^{-13}$ (Bridgmann) [10]. The results of other authors suggest that elasticity of zinc is very sensitive to small variations in amount and kinds of impurities [9,10]. Considering the inhomogeneous distribution of the alloying elements in the matrix of the Zn-Ti0.1-Cu0.1 single crystals, the local growth rate of the Zn$_{16}$Ti phase particles could change. Moreover, the low growth rate of the single crystals allows for expansion of the Zn$_{16}$Ti phase precipitates along the low-diffusion-coefficient directions, different from the direction of the matrix growth [11-20]. The intensity of the side expansion is negligible at high growth rates in the range of 10...16mm/h. The high growth rate of the Zn-Ti0.1-Cu0.1 single crystals (>10mm/h) favors the growth of the needle-shaped particles (Fig. 3). It is caused by the reduction of the diffusion to the one direction [11-20] only, when the diffusion goes fastest.

Another consequence of the high growth rate are local thermal fluctuations on the surface of the crystallization front. The direct effect is cellular/tube structure with oval regions of the $\alpha$ phase without any precipitates, as shown in Figs 5 and 6a. These areas are characterized by elongation along the [10-10] direction, correlated with the anisotropy of the growth direction of the Zn$_{16}$Ti phase on <10-11> directions. Although individual “cells” seem to be separate, the matrix preserve crystallographic homogeneity in the whole volume of the single crystal. It is proved by EBSD measurements [5]. Exclusively above the growth rate of 16mm/h crystallographic continuum of the $\alpha$ phase is lost and elongated multicrystal structure forms.

4. Summary

Strong crystallographic dependencies between the $\alpha$ phase of the matrix and intermetallic phase Zn$_{16}$Ti as well as knowledge about the influence of the growth rate on diffusion processes in the hexagonal single crystals Zn-Ti0.1-Cu0.1 allows for a structure control. These results together with investigations of chemical composition on the stability and shape of the surface of the crystallization front allow to create the mathematical model of developing structure for the hexagonal-based crystals.

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