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## Solidification Front of Oriented Ledeburite

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### Abstract

Directional solidification of the Fe - 4,3 wt % C alloy was performed with the pulling rate equal to  $v=83 \mu\text{m/s}$ . Sample was frozen during solidification to reveal the shape of the solid/liquid interface. Structures eutectic pyramid and spherulitic eutectic were observed. The solidification front of ledeburite eutectic was revealed. The leading phase was identified and defined.

**Keywords:** Ledeburite, Directional solidification, Eutectic, Solid/liquid interface, Leading phase

### 1. Introduction

Eutectic crystallisation is an important stage during the crystallisation of white iron. At this stage, the nucleation and growth of eutectic cells (consisting of carbide or cementite + austenite) occur. The carbide in eutectic cells is the main hard and brittle phase structure which has an important effect on the properties of white iron. If there the primary carbide in the structure, the effect of eutectic carbide is more prominent.

The eutectic solidification of a white iron is a crystallisation process in which cementite+austenite eutectic (eutectic cells) form the main structure. According to the principle of eutectic crystallisation, the formation of the second phase on the leading phase and their restricted cooperative growth is the key to eutectic cell formation [1].

Based on the morphology of cementite and austenite in eutectic, authors [2] divided the eutectic structure of normal white iron into two types: honeycomb ledeburite and plate cementite.

Directional solidification technique is applied to the research on the basic solidification theory [3,4]. V.L. Davies [5] was first to show the role of leading phases in eutectics. The theoretical

investigations of solid/liquid interface formation during oriented eutectic growth are revealed in [6-11].

### 2. Experimental procedure

The Fe - 4,3wt % C eutectic sample were prepared from Armco and pure graphite electrodes purity in a graphite crucible under the protection of argon gas in Balzers-type heater. After dross removal and homogenization, the molten alloy was poured into a permanent mold and cast into rod 12 mm in diameter. The samples were then machined to approximately 5 mm in diameter using a wire cutting process because of the high brittleness of the metals at this composition. After that, the samples were positioned in a alumina tube with an inner diameter of 6 mm at the center of the vacuum Bridgman-type furnace. Under an argon atmosphere, the samples were heated to a temperature of 1450°C. After stabilizing the thermal conditions, the samples were lowered at a given rate from the heating part to the cooling part of the furnace, with Ga-In-Sn liquid metal used as the coolant. The sample was grown by pulling it downwards at a constant pulling rate  $v=83 \mu\text{m/s}$  and at a constant temperature gradient  $G=33,5 \text{ K/mm}$  by means of

motor. Then the sample was frozen (immediately taken off the cooler). This is described in more detail in [12,13].

The research of directional solidification were performed in the Department of Casting at the AGH University of Science and Technology in Cracow.

### 3. Formation of ledeburite matrix

Ledeburite, which is the regular eutectic, nucleates in the form of a colony. The initial phase of eutectic solidification is cementite. In the middle of each ledeburite colony the base lamella of initial cementite is located (Fig. 1). The establishment of connection between the first crystals and eutectic colonies appears to be difficult if the last ones are of fine structure [14].

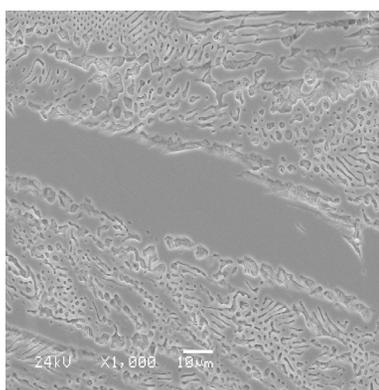


Fig. 1. The morphology of base lamella of initial cementite. Own research, SEM

The appearance of second eutectic phase nuclei on the initial - base crystal, as well as its dendritic development and growth in the branches of base phase does not create the matrix of colony yet, if the double-phase layer, which the regular eutectic structure is developed out of, is understood under this description [15].

The possibility of colony creation concerning the ledeburite formation according to Fe-Fe<sub>3</sub>C system, is based on the formation of second phase of the eutectic structure on the base continuous surface. All variants known from professional literature referring to the formation of this eutectic system determine the main idea of eutectic colony matrix formation on the base phase crystal as it happens in terms of all regular eutectics [14].

Observing the development of eutectic colony, their classification into honeycomb and skeleton eutectics. Among these types there is a difference in growth mechanism and structure. It consists in formation of matrix of honeycomb eutectic with no presence of initial crystals of base phase. This phenomenon is showed in the picture of set structures of both phases (Fig. 2). The middle set arises as a result of alternative creation of heteronymous plates and is a product of longitudinal growth [14].

The formation of honeycomb structure is described as perpendicular growth of a colony. It is determined that there are two types of cementite plates: longitudinally growing in middle set; and growing perpendicularly - in honeycomb eutectics. The middle set is a product of a separate solidification of phases:

firstly, the plates of one phase are growing out of the liquid, then in interspaces the second phase is crystallizing. Honeycomb structure represents normal eutectic system, namely with coupled growth of both phases [14].

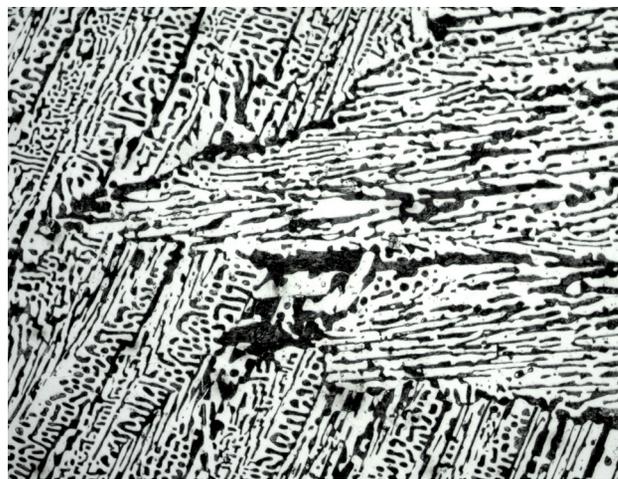


Fig. 2. Two types of cementite plates: longitudinally growing in middle set; and growing perpendicularly - in honeycomb eutectics. Own research, LM x 200

#### 3.1. Honeycomb ledeburite

In special conditions of solidification, especially with high rates of alloy cooling, the formation of discontinuous, dispersed structures is possible. In alloys applied in practice, the eutectic structure has got the construction of colony and consists of two crystals.

The most general model of binary eutectic is as follows: one of phases, the one with greater volume is a matrix of a colony, on the surface of which the dendrites of second phase are growing. Depending on the place of leading phase in this structure, the skeleton and honeycomb eutectic shall be defined. The skeleton structure is formed when the leading phase grows in the shape of branched skeleton and stands for the reinforcement of a colonies while the second phase fills the spaces between the branches and stands for the matrix of a structure.

Leading phase may create not only the skeleton, but also the matrix of a colony. In this case the structures called honeycomb are produced. This name is proper not only because formally it presents the morphological construction of a structure. To a certain extent, it presents the order of phase solidification - i.e. during the generation of honeycombs the wax matrix comes first, then the fills of the canals takes place [14].

The mechanism of honeycomb eutectic formation may be analysed on the basis of the Fe-Fe<sub>3</sub>C eutectic growth. The basic characteristics of this process is connected with layer growth of leading phase, being dependent on anisotropy of interatomic bonds strength. There is no clear image of leading, which characterizes the skeleton eutectics. The eutectic pyramid grows into the liquid with a surface of lower energy, the front of double-phase solidification seems to be plain (Fig.3). The microsection of eutectic pyramids has no extended branches of leading phases.

The detailed analysis of many examples of similar type enables, however, for presenting the fact of overtake and for determination of its distance [14].

Honeycomb ledeburite consist of eutectic cells in which many austenite rods, along [001], are embedded into cementite plates (or blocs) based on (001) plane. The eutectic cells show a lamellar or plate shape: their length and width are far greater than their thickness. Therefore, under microscope, only the transverse section of the austenite rods are observed, after etching, they show as dark round spots on a white substrate (cementite) [1].

The matrix of honeycomb eutectics is more hard and fragile leading phase than the characteristics of alloy may indicate. In honeycomb colony of such as ledeburite, there are fragments, namely the eutectic pyramids, having typical skeleton structure (Fig. 4). That is why as far as the evaluation of the influence of eutectic structure elements on the characteristics of alloys the orientation of colonies in stress field should be considered [14].

### 3.2. Sectoral structure of ledeburite colony

Eutectic structures may grow by many layers, depositing consecutively on nucleating base crystal. If it is a polyhedron, the formulation of a colonies arises by creation of chamfered double-phase pyramids. Appropriate edges of base crystal are the small bases of these pyramids, whereas extrapolated apices meet in geometric centre of crystal growth. The sides of the pyramids which are subsequently the borders between them, create ribs of base polyhedron by consecutive displacements, while the ribs of the pyramids are the traces of their apices' displacement. In the Figure 3 the model of eutectic pyramid shaping is presented. The protrusion of rib branches was slightly exaggerated, however in special case they can considerably preceded the large bases of eutectic pyramids coming out of liquid, which are the edges of eutectic rhombohedron [14].

If the anisotropy phase with complex crystal and chemical structure stands for the base phase, the sectoral structure of a colony becomes more complicated, and explanation of morphological details is possible only with help of extended stereometric analysis.

The analysis of ledeburite may be presented on the scheme, where eight most characteristic cross-sections of colony were showed (Fig. 5). The basic phase of Fe-Fe<sub>3</sub>C eutectic structure is iron carbide, that is why the morphological characteristics of a colony is strictly connected with features of structural construction and with growth of cementite. The colony has a form of parallelepiped. In its central part there is a surface of basic phase - carbide. On this surface there are six eutectic growth pyramids, being formed in pairs:  $\langle 100 \rangle$ ,  $\langle \bar{1}00 \rangle$ ,  $\langle 010 \rangle$ ,  $\langle 0\bar{1}0 \rangle$ ,  $\langle 001 \rangle$ ,  $\langle 00\bar{1} \rangle$ . Formation of a colony base begins with dendritic accumulation of second phase on the basic crystal. Both surfaces of carbide (001) are covered with austenite dendrites which are visible on cross-sections 1, 4 and 5 (Fig.5) as a thickened dotted lines [14].

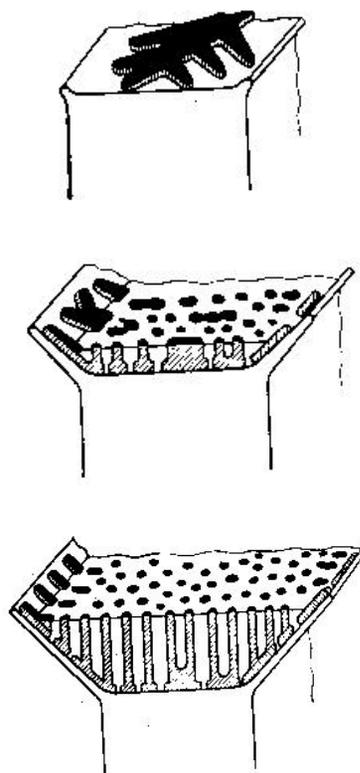


Fig. 3. The model forming of eutectic pyramid [14]

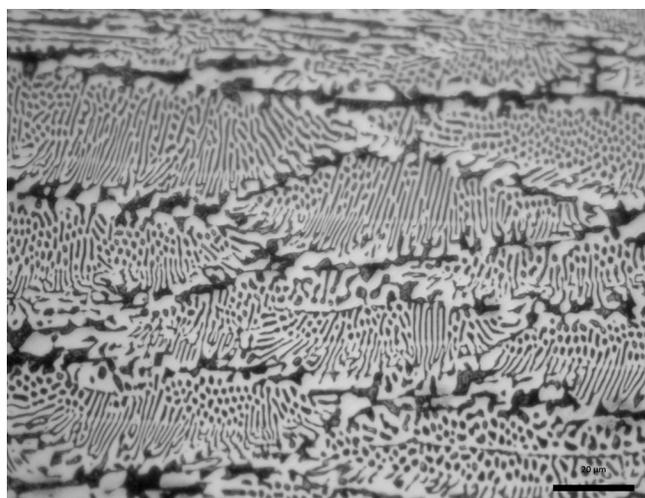


Fig. 4. Structure of eutectic pyramid in ledeburite, LM

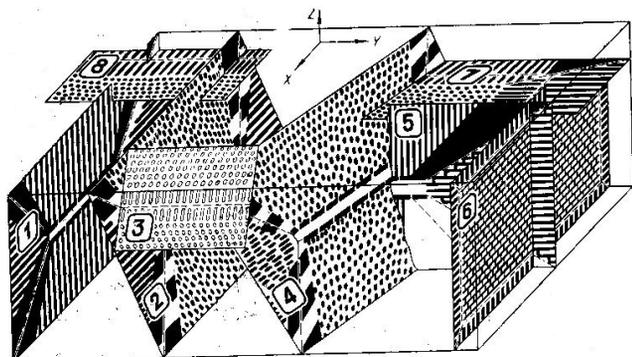


Fig. 5. The cross sections in scheme of construction sectoral structure of ledeburite [14]

Figure 6 and 7 show the sectoral construction observed in ledeburite structure of the sample.

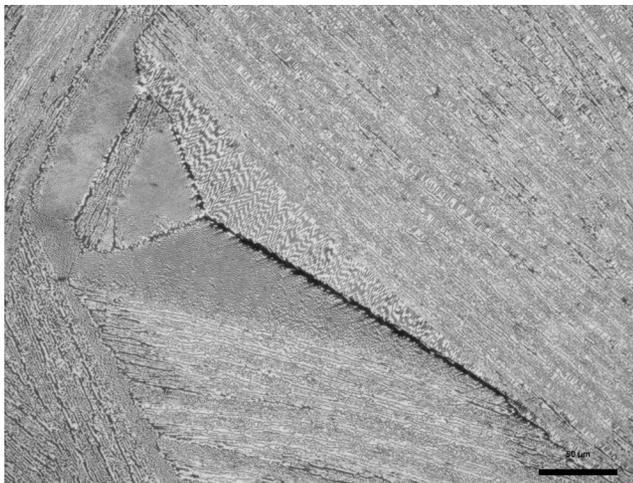


Fig. 6. Structure of eutectic pyramid of researched sample, light microscopy

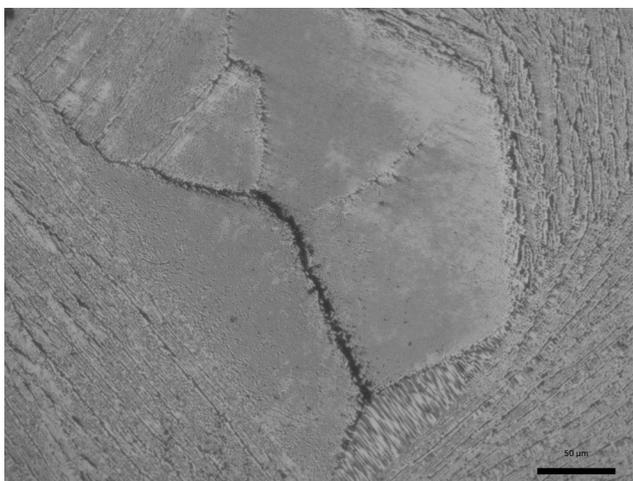


Fig. 7. Structure of eutectic pyramid of researched sample, light microscopy

### 3.3. Solidification of spherulitic eutectic

The formation of typical eutectic spherulites refers to these systems where the spherulitic colonies are created, so in the cases when both components of a structure are characterized by highly symmetric density compaction and metallic bonds. The significant thing is that in the indication of spherical eutectic formation the non-crystal furcation is the point - the branching of leading phase crystal. The process arises when the leading phase of eutectic holds visible anisotropy of a structure and properties [14].

If the anisotropy of leading phase is weakly expressed, the special conditions of cooling are required to spherulitic solidification uprising. Amongst well-known metal layouts the alloys Fe-C are the most efficient to be analysed. The tendency of iron carbide crystals to non-crystallographic branching during the growth is connected with the specific of its layer crystal structure. The conditions of reception and morphology of radial branch of carbon crystals. If eutectic solidification is done in large undercooled solution, the processing dispersion of flat carbon branches which leads the eutectic growth, and causes the transfer to plate colony to the spherulite.

The increase of the undercooling leads to double-sided, fan-shaped branching of flat phases forming the centre of ledeburite colony (Fig. 8). During the research of thin-walled castings of Fe-C alloys, there may be noticed the structures arising as a result of further development of fan-shaped dispersion of leading phase (Fig. 8). Such colony cannot be yet described as a typical spherulitic. However, here there is already the realization of a Lemán Schubnikov scheme in application of double-phase flat set: creation of double-leaf with radially-increasing branch of its fronts. The basic role of the colony volume is made of the flat structure, while in the free spaces between flat branches there are fragments of honeycomb structure [14].

With further increase of undercooling, the fan-shaped twist of branches and its thinning lead to the spherulitic formation. Spherulites are characterized by the sectoral, fan-shaped and arcuate structure. Each sector is a fan-shaped branch of plate ledeburite.

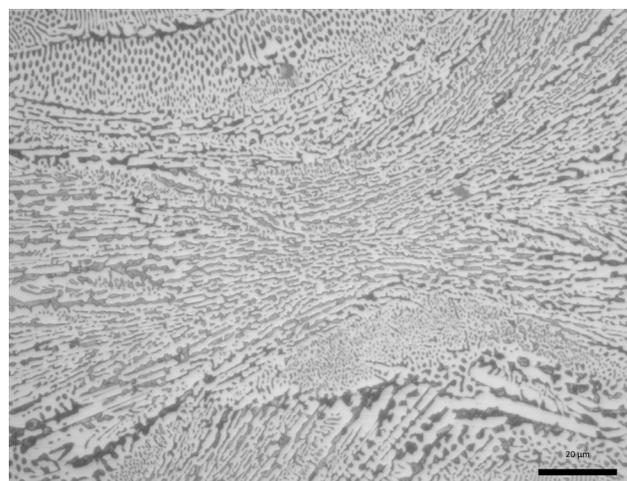


Fig. 8. Fan-shaped branching of lamellar phases forming the centre of ledeburite colony of researched sample, light microscopy

Influence of undercooling on the structure and shape of a ledeburite colony (with anisotropic leading phase) is presented on the scheme (Fig.9). With small undercooling the eutectics are growing in the form of a plate the matrix of which is a honeycomb structure (Fig. 9a). Together with undercooling increase the development of center takes place. Respectively, the part of a volume of colony characterized by cellular structure is decreasing. At the time of increase of these amendments the fan-shaped branching of flat set is initiated and the general plate form of a colony is deforming (Fig. 9b). In case of more increase of undercooling the dispersion of leading phase leads to formation of extensively branched colonies, the basic volume of which is a plate structure (Fig. 9b). In this process the sectoral division of a colony is noticed, which reaches its final development in spherulites (Fig. 9c), that are created in highly undercooled solutions. The spherulitic colony arises by strong branching of monocrystal eutectic phases. In spherulite the one of the phases - the leading one, being the continuous phase, is not a monocrystal in metallographic cognition, because the orientations of its parts differ in tens of degrees [14,16].

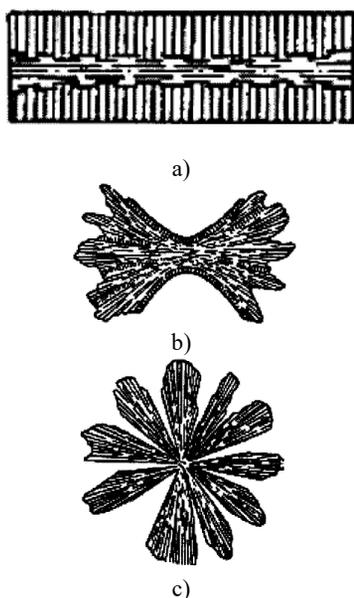


Fig. 9. The changes scheme during solidification of the eutectic with increasing undercooling [16]

#### 4. Leading phase of oriented solidification front

During the formation of regular eutectic, one of crystal phases plays the leading role (Fig.10). Generally, to determine this phase the distance of leading should be determined. However, the analysis of nucleation, growth and structure of eutectic colonies presents more general but more real criterion of leading phase identification as an eutectic associate, determining the basic rules of multi-phase crystallizations [5,14].

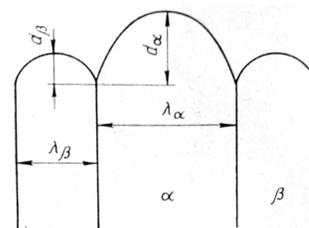


Fig. 10. The parameters of solidification front of regular eutectic:  $\alpha$  - leading phase,  $d = d_\alpha - d_\beta$  protrusion  $\alpha$  phase [5]

The leading phase of solidification eutectic is the base phase (nucleating), which gives the shape and sector structure to the eutectic colony that are the characteristics of monocrystals of this phase, being formed in the process of autonomic growth for similar conditions of alloy cooling.

The occurrence of the leading does not indicate for the different rates of eutectic phase growth. The analysis of the structure of hardened alloys revealed in the whole time of eutectic transformation that the distance of leading is constant from the matrix formation to the finalization of growth stadium, until the chemical contents of small amounts of liquid phase does not change. The acceleration of one phase support results in acceleration of growth of another phase branches. Otherwise, the character of multi-phase solidification is fractured. The more significant is the distance of leading, the more extended are the possibilities of free branched of leading phase which cause the decrease of structure regularity [5,14].

The morphological analysis of eutectic colonies having a shape of polydendrites (often expressed by sectoral structure), enables for consideration of leading phase notion. In Bochvar's monograph, the phase was determined as a phase governing the eutectic solidification and forming a skeleton of a colony due to higher line rate of crystallization and to leading transformation into liquid. The study of nucleation process of eutectic colonies and the uniqueness of their structure enabled for explanation and enlarge a notion of leading phase, considering all stages of colony formation. The research of initial stage showed that in any double system only one of phases, called the base phase stands for the matrix of the eutectic system - by nucleation process or implantation of eutectic second phase on the out-line. Next, the dominating role of one phase determines the coupled eutectic crystallization in the initial moment [5,14].

The fronts of austenite fibres, in high rates, are covered with cementite plate branches, indicating the localization of austenite solidification front (Fig. 11 - level L). The austenite branches surround the ledges of carbon phase, enabling to reveal their loading placement (level M).

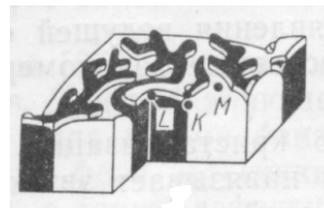


Fig. 11. The characteristic points of solid/liquid interface [14]

Figure 12 the scheme of leading phase in ledeburite and distance between levels L, M, K shows.

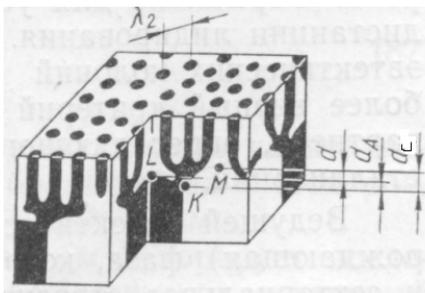


Fig. 12. The scheme of a leading phase in ledeburite [14]

The difference in levels L and M corresponds with the distance of leading which is associated with interphase recess (level K), it may be described as [14]:

$$d = d_{\text{cem}} - d_{\text{aust}} \quad (1)$$

$$d_{\text{aust}} = d_K - d_L \quad (2)$$

$$d_{\text{cem}} = d_K - d_M \quad (3)$$

$$d = d_K - d_M - (d_K - d_L) = d_L - d_M \quad (4)$$

During the research of solidification of ledeburite freezing of samples was made. The aim was to capture the leading phase in ledeburite.

The distance  $d$  between cementite and austenite phase is a leading distance in ledeburite eutectic. Figure 13 show the distance in researched sample of ledeburite eutectic. This is the distance between level L and level M. The distance  $d_K - d_L$  (2) corresponds to a dimension of perlite phase. The leading phase is cementite.

## 5. Concluding remarks

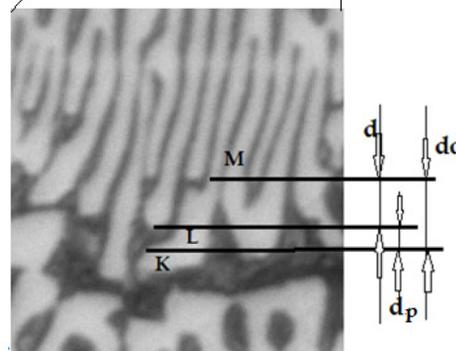
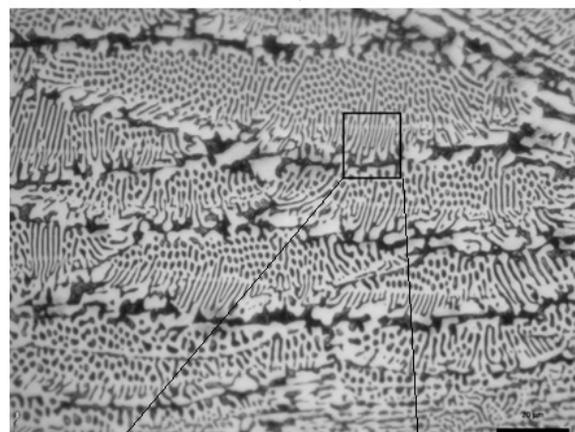
The solidification front in oriented ledeburite eutectic was observed. The presence of a leading phase – cementite was revealed (Fig.13).

The theoretical existence of leading distance in directional solidification eutectics has been demonstrated in work [11]. There were performed mass balance for solid/liquid interface and the couplet growth was defined.

This work experimentally confirmed the phenomenon, which has been theoretically anticipated by Wołczyński [11].

In obtained structure the eutectic pyramids were observed. These pyramids are typical for sectoral eutectic structure (Fig. 6 and Fig. 7). The fan-shaped branching of lamellar phases (Fig. 8) characteristic for spherulitic eutectic was shown.

a)



b)

Fig. 13. The distance in researched sample of ledeburite eutectic,  
 a) light microscope x500,  
 b) higher magnification of selected rectangle

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