MONITORING OF COPPER ALLOYS STRUCTURES DURING SOLIDIFICATION AND COOLING OF CASTINGS

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Abstract

In this year at our workplace (the Department of Engineering Technology - Technical University of Liberec) we were engaged in metallurgical research on copper and its alloys, especially crystallization. This research was never widely performed in the Czech Republic (even in times of Czechoslovakia) it was due to the demanding technologies of copper alloy castings and also because the melting of alloys must be provided with the necessary melting facilities. This paper contains a description of the crystallization of copper alloys and their equilibrium diagrams, experimental casting of selected copper alloys, melt metallurgical preparation and metallographic evaluation of the structure of castings.

Keywords: Copper alloys, brass, crystallization, solidification, structure

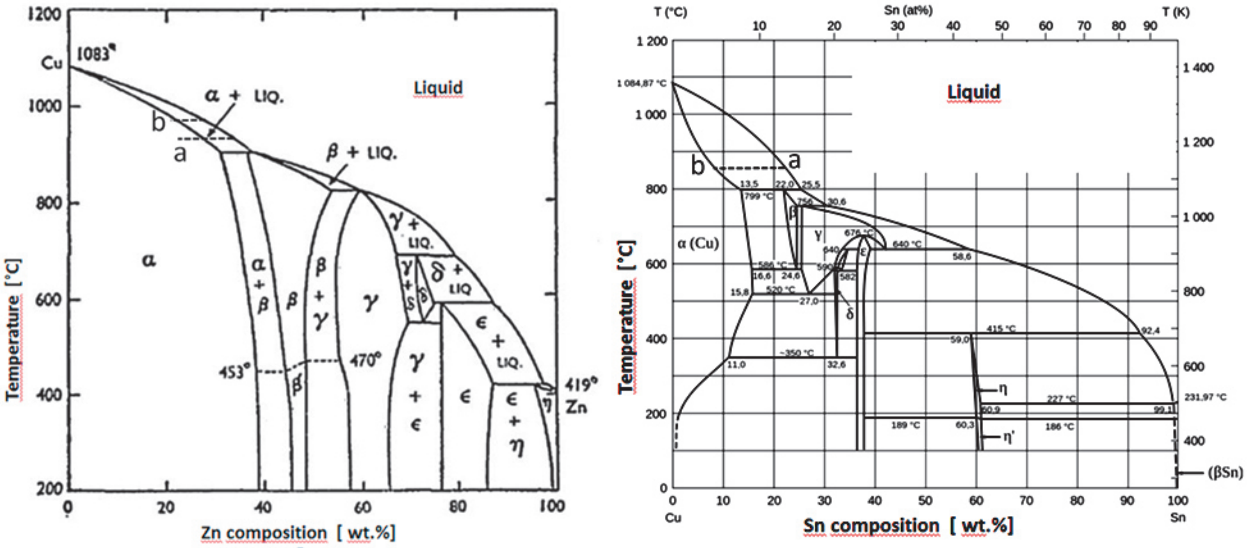
1. INTRODUCTION

Currently, copper alloy castings are increasingly applied in various industrial branches. Their production is relatively expensive and technically difficult. Their utilization is associated with high thermal conductivity and corrosion resistance. This issue has been addressed in publications [1-5]. For the foundry industry are used both known groups of copper alloys - bronzes and brasses. Bronzes are used for manufacturing of highly stressed components e.g. wreaths gears, worm gears, the housing, saddles of pumps, valves for high pressure. Brasses are used for the production of gear wheels, special nuts, bearing housings, parts of pumps, valves, and they have a good resistance to seawater. Currently electric conductive copper begins exceptionally be used for the manufacture of special, very small castings. Therefore, copper and its alloys retain long historic role since the time of Eneolith (about 7000 years BC) to the present.

2. CRYSTALLIZATION OF COPPER ALLOYS WITH EQUILIBRIUM DIAGRAMS

Crystallization of copper alloys depends on the thermodynamic conditions of phase transition. The copper alloys melt becomes the crystalline phase occur if the thermodynamic conditions, i.e. the Gibbs energy decreases. This assumes that the crystallization occurs at constant temperature and constant pressure. Another condition for crystal formation is hypothermia of the melt. This is going on at castings due to thermal accumulation ability of foundry mould. The crystallization process is also practically governed by method of heat removal from the melt. The crystallization nuclei are the driving force of crystallization. At non-homogenous melts form upon crystallization nuclei during heterogeneous nucleation. In practice occurs this type of nuclei formation. The melt always contains foreign particles, whether these residues of slag, fragments of furnace linings, oxides, silicates, but also sometimes intentionally added inoculants and modifiers. These particles facilitate to crystallization, because at heterogeneous nucleation is sufficient undercooling 0.02 T_{KR} [6, 7]. The basis for the crystallization of copper alloys or for brass is an equilibrium diagram Cu - Zn, see **Fig. 1a**, and for crystallization of tin bronzes diagram Cu - Sn, see **Fig. 1b**. Bronze structure Cu-12Sn after crystallization and cooling is conditioned by low value of the partition coefficient Sn in Cu, this leads to considerable tin microsegregation and in the structure at normal temperature occurs δ phase also in alloys with substantially lower tin content than corresponds to its maximum solubility (15.8 wt.% Sn), see **Fig. 1b**.

Crystallization of multicomponent copper alloys, e.g. brass Cu-31Zn-1Mn-1Al is very complicated. These systems are characterized by a series of intermediate phases and chemical compounds [6 to 13].



a) b)

Fig. 1 The equilibrium diagram a) Cu - Zn; b) Cu - Sn [13]

For brass alloys containing 30 wt. % of zinc proceeds crystallization according to the following scheme:

$$L_{(30\%Zn)} \xrightarrow{950\,till\,915^{\circ}C} \alpha_{(Cu)} \tag{1}$$

In the Cu-30Zn alloy is α phase rich on copper, which crystallized with the FCC lattice of dimensions $3.608\cdot10^{-10}$ m. It is a typical solid solution of substitution type where parts of the copper atoms are replaced by atoms of zinc.

Bronze with a tin content of 12 wt. % is located in the equilibrium diagram. Here are formed four temperature areas of transformation (1000 °C, 799 °C and 586 °C, 520 °C, 350 °C) and runs to form a biphasic structure. Crystallization of this bronze proceeds in two stages. The first stage takes place in temperature range 1000 to 799 °C:

$$L_{(12\%Sn)} \xrightarrow{1000-799^{\circ}C} \alpha_{(b-p)} + L_{(a-q)} \tag{2}$$

Note: a, b, d, p, q there are imaginary points corresponding to places in equilibrium diagram according to the specific crystallization.

The solid solution α is a substitution solid solution of tin in copper. It has a face-centered cubic lattice. The second stage takes place at temperature 799 ° C:

$$L_{(q)} + \alpha_{(p)} \xrightarrow{799^{\circ}C} \beta_{(k)} + \alpha_{(p)} residual \tag{3}$$

Note: This reaction proceeds in non-equilibrium conditions.

In further cooling down at temperature 586 °C is going on eutectoid disintegration of β phase:

$$\beta_{(d)} \xrightarrow{586^{\circ}C} \alpha + \gamma \tag{4}$$

Note: In brackets is α phase composition.

High temperature intermetallic phase β is an electron compound Cu_5Sn, which has a body centred cubic lattice and electron concentration of 3:2. Another high-temperature intermetallic phase γ is the electron compounds $Cu_{31}Sn_8$. $Cu_{31}Sn_8$ has a body centred cubic lattice and electron concentration 21:13. After the end of eutectoid disintegration consists the alloy structure of a solid solution α, the mixture of phases $(\alpha + \gamma)$.

3. EXPERIMENTAL CASTING OF SELECTED COPPER ALLOYS

The aim of this paper was to evaluate the crystalline structure of castings, cast into a metal and into a sand mould. At the same time it was worked with the assumption that the metal mould had a great heat accumulation ability causing smaller crystalline structure than castings cast into a sand mould. It was also monitored microstructure and hardness of the castings. Used alloys are listed in **Table 1**. Conductive copper was used from a purely experimental aspect for comparing the results of crystallization. **Table 1** shows the chemical composition of the materials, which was monitored at analyzer BRUKER Q4 TASMAN.

Table 1 Detected chemical composition of copper alloy cast plates

Alloy	Chemical composition (wt. %)								
	Zn	Sn	Al	Si	Mn	Ni	Pb	Cu	Others
Cu-30Zn	31.00	0.59	0.650	0.042	0.64	0.18	0.47	66.30	0.128
Conductive copper	0.006	0.29	0.005	0.180	0.002	0.06	0.01	99.35	0.095
Cu-12Sn	0.021	12.61	0.005	0.017	0.002	0.16	0.15	86.87	0.309
Cu-31Zn-1Mn-1Al	39.58	0.77	1.16	0.17	1.15	0.25	0.74	55.86	0.320

Copper smelting and smelting of the selected alloys (see **Table 1**) was carried out in an electric resistance melting furnace type 11016S from CLASIC company. The whole experimental material was melted in a graphite crucible by using a small amount of charcoal. For casting test was used a metal mould whose cavity is plate-shaped with dimensions 80 x 80 x 10 mm see **Fig. 2**.

Used alloys were after melting process metallurgic treated and gradually poured from a purely research purposes into the mould at 20 °C. The face of the mould was treated with paint DICOM 5 of the thickness of 0.2 mm. Used sand mould was prepared from bentonite mixture at our department. Casting temperature for all used alloys was 50 °C above the liquid temperature of the specific alloy. Filling time for all used moulds was 3 seconds. In this way were castings produced from all used copper alloys. By the experiments into the metal mould was cooling rate 40 °C/s. By the experiments into the sand mould was cooling rate 5 °C/s. Hardness measurement was conducted pursuant to Brinell according to standard ČSN EN ISO 6506-1. The hardness values of the copper alloy castings are listed in **Table 2**.

Table 2 The measured hardness values HBS (∅ 5mm; *F* = 2450 N)

Alkou	Measuring points							Sample average hardness HBS	The standard deviation of hardness HBS	Coefficient of variation [%]
	1	**2**	**3**	**4**	**5**	**6**	**7**			
Poured into the metal mould preheated to 200 ° C										
Cu-30Zn	51	52	54	53	52	54	52	52.6	1.05	1.99
Conductive Cu	46	48	49	47	48	48	47	47.6	0.90	1.89
Cu-12Sn	131	131	130	132	128	129	128	129.9	1.46	1.15
Cu-31Zn-1Mn-1Al	170	173	171	171	171	172	172	171.4	0.91	0.53
Poured into the sand mould										
Cu-12Sn	128	129	127	130	127	127	126	127.7	1.28	1.00
Cu-31Zn-1Mn-1Al	165	168	166	168	165	166	168	166.6	1.29	0.77

Fig. 2 The metal mould used for gravity die casting with Cu-30Zn alloy sample

4. METALLOGRAPHIC STRUCTURE EVALUATION OF THE CASTINGS

Metallographic evaluation of the copper structure was performed on the light microscope Neophot 21 (Carl Zeiss Jena). For metallographic observation were samples prepared by standard metallographic method (grinding, polishing and etching). To emphasize the microstructure were used in some cases two types of etchants. Samples were observed at various magnifications. During the metallographic evaluation of the copper alloys structures were applied knowledge of [8, 10-13]. Composition of the etchant: 2 g potassium dichromate, 8 ml sulfuric acid, 4 ml saturated NaCl solution and 100 ml distilled water. **Figs. 3 to 6** show the structures of copper alloys filled into the metal mould. Due to that for casting production were frequently used Cu-12Sn and Cu-31Zn-1Mn-1Al alloys, therefore was monitored their crystalline structure after casting into the sand moulds, see **Figs. 7, 8** and **Fig. 9**.

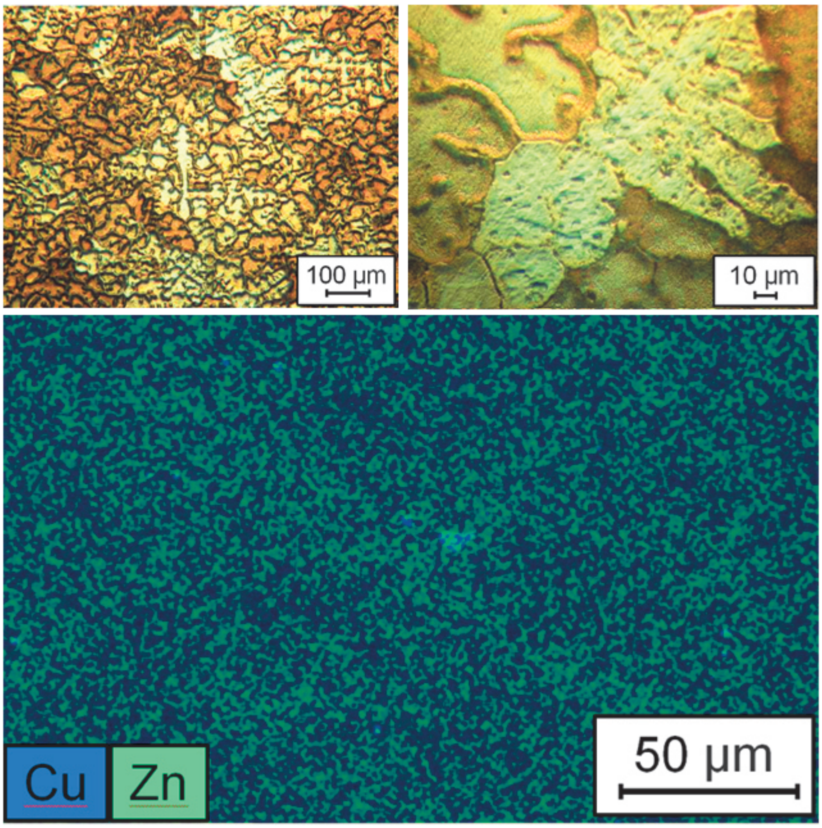


Fig. 3 Structure of Cu-30Zn alloy, poured into the metal mould, etched

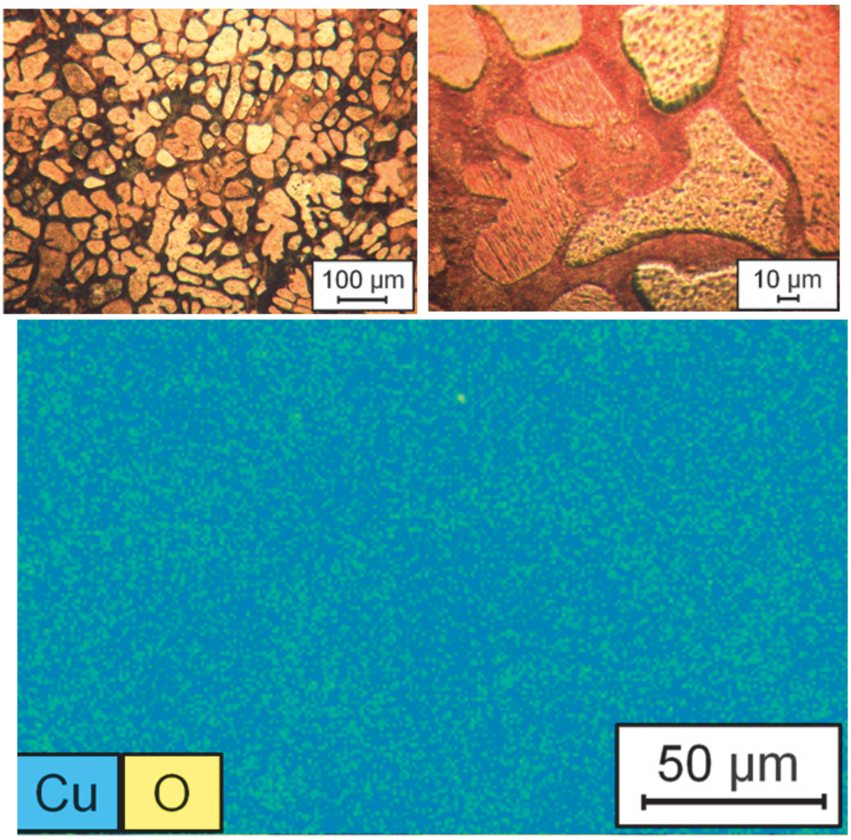


Fig. 4 Structure of the conductive copper, poured into the metal mould, etched

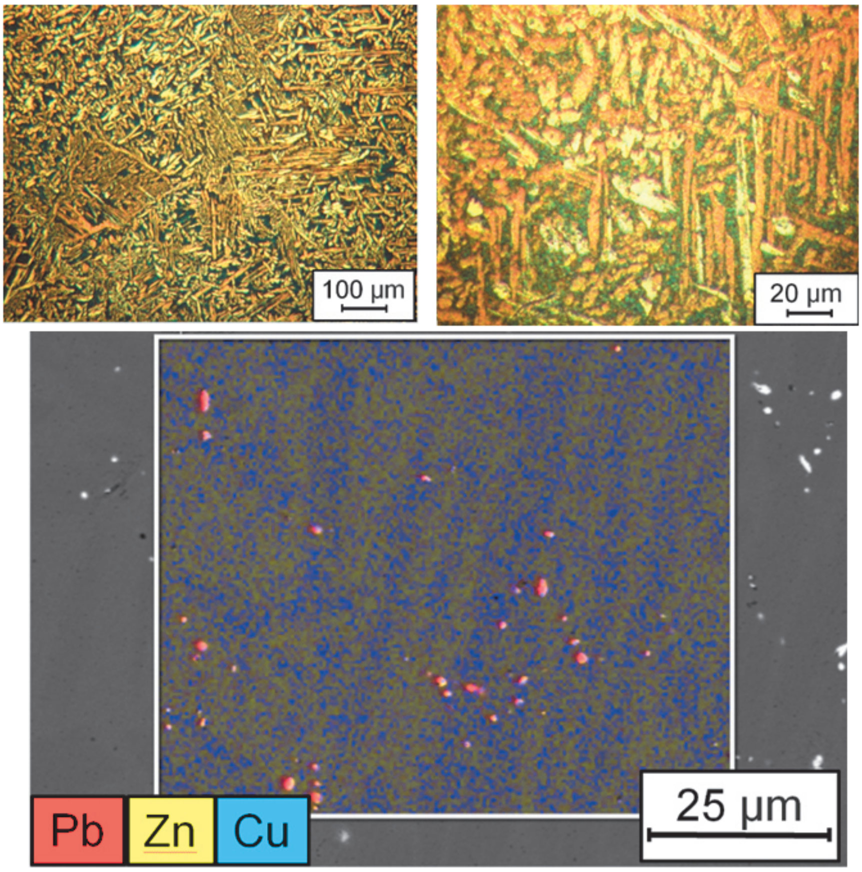


Fig. 5 Structure of Cu-31Zn-1Mn-1Al alloy poured into the metal mould, etched

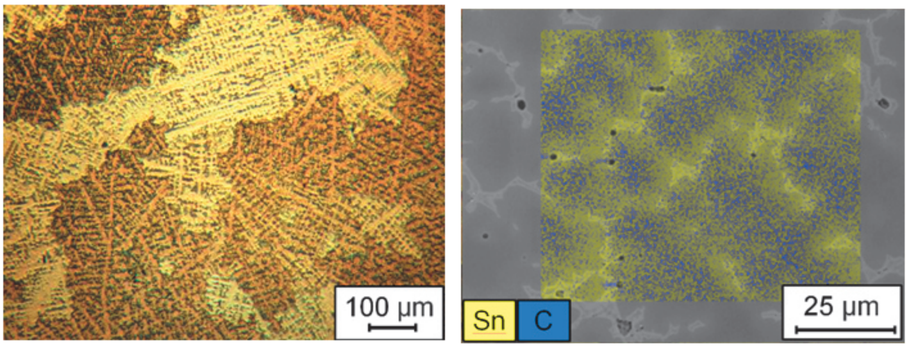


Fig. 6 Structure of Cu-12Sn copper alloys, poured into the metal mould, etched

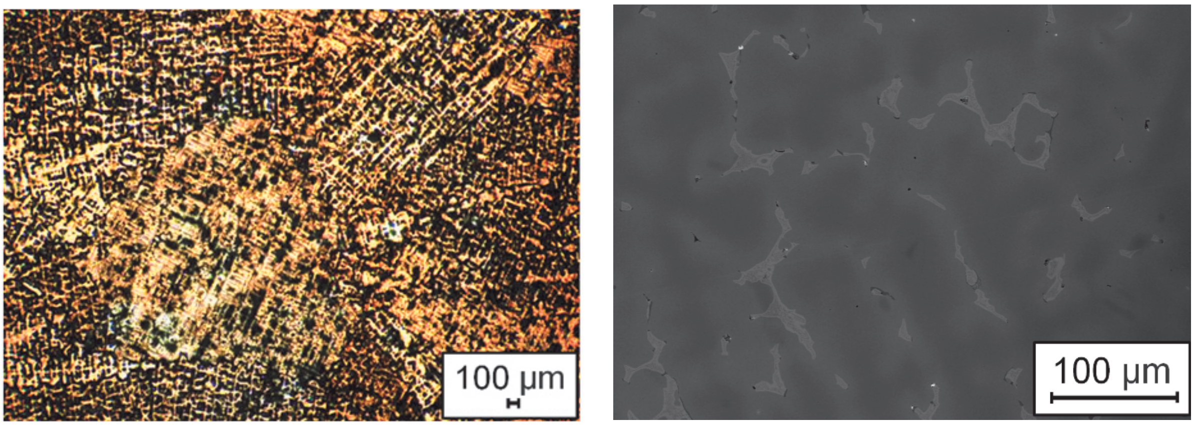


Fig. 7 Structure of Cu-12Sn copper alloys, poured into the sand mould, etched

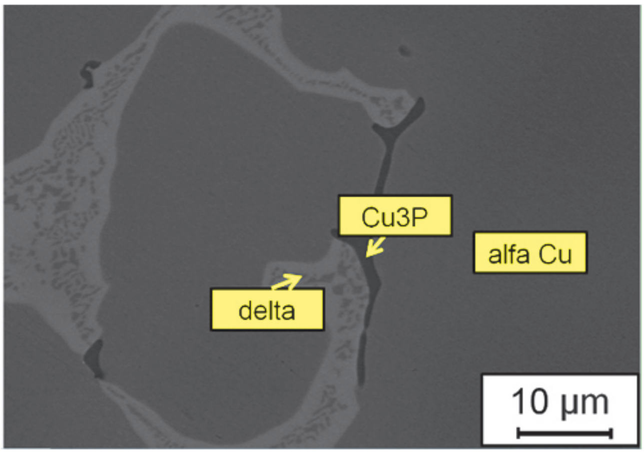


Fig. 8 Structure of the Cu-12Sn alloy, poured into the sand mould, etched

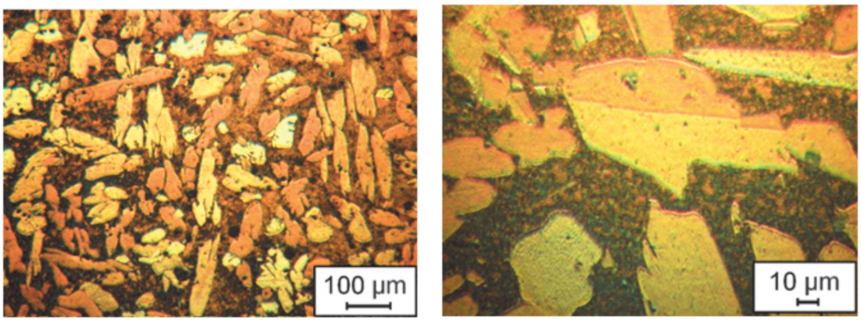


Fig. 9 Structure of the Cu-31Zn-1Mn-1Al alloy, poured into the sand mould, etched

Cu-30Zn - after casting into metal moulds (**Fig. 3**) had a brass structure formed by equiaxed dendrites. Equiaxed dendrites which crystallize in the final stage of crystallization were formed by a solid solution which was enriched with zinc (dark places) in the structure of the brass. The crystalline structure of the dendrites had a length from 45 to 230 µm.

Conductive copper - after casting into the metal moulds were in the structure areas with the contents of oxides. Copper crystals are shown in **Fig. 4**. The crystals had a typical dissected shape and reach a length from 20 to 120 µm. The width of the dendrites reached up to 30 µm. For a better view we would for further experiments have to electrolytically polished samples.

Cu-12Sn - after casting into the metal mould ran complicated crystallization even cooling of this bronze, according to the equilibrium diagram Cu - Sn. The resulting structure was composed of a α solid solution and of (α+δ). Phase (α+δ) is shown in **Fig. 5**.

Cu-12Sn - after casting into a sand mould ran complicated crystallization and by slow cooling of bronze arised a dendritic structure. Eutectoid ($\alpha + \delta$) was excluded between the grains of solid solution α (see **Figs. 7** and **8**). The basis of the eutectoid was the phase δ ($Cu_{41}Sn_{11}$). Structural components formed a solid solution α and eutectoid mixture $\alpha + \delta$. The dark areas in the structure in **Fig. 8** of bronze form the α phase. Bright areas form eutectoid see **Fig. 8**.

Cu-31Zn-1Mn-1Al - after casting into metal moulds crystallized brass in the shape of fine elongate grains (see **Fig. 6**) formed by a mixture of solid solution α rich in copper (light grains) and β solid solution rich on zinc (dark areas).

Cu-31Zn-1Mn-1l - after casting into a sand mould crystallized this multi-component brass in shaped coarse elongated grains (see **Fig. 9**), consisting of a mixture of solid solution α rich on copper (light grains) and further consisting in solid solution β rich on zinc (dark areas). When comparing the crystallization Cu-31Zn-1Mn-1Al in the sand and in the metal mould than crystal size when casting into a sand mould were elongated with a maximum length of 162 µm and width of 50 µm. The size of the crystals during die casting was finer and crystals reached a maximum length of 70 µm and maximum width of 12 µm.

5. CONCLUSION

Crystallization, solidification and cooling of copper alloys cast is related to the character of foundry moulds and the heat dissipation from the solidifying casting. Crystallization of the tin bronzes is influenced by the cooling rate. During solidification of bronzes arrive the crystallization in a narrow temperature range. In the process of cooling they exhibit substantial volumetric and also linear shrinkage. The crystalline structure of tin bronze was formed by solid solution α and by eutectoid which is a mixture $\alpha + \delta$ ($Cu_{41}Sn_{11}$). When we compare the crystallization of the corresponding alloy casted into a sand mould and into the metal mould it was obvious that the metal mould have a higher accumulative capability than sand mould. In the metal moulds were constituted a more favorable thermal ratio and then crystallization for the given alloy was more fine. When we compare the crystallization Cu-31Zn-1Mn-1Al in the sand and in the metal mould than crystal size when casting into a sand mould were elongated with a maximum length of 162 µm and width of 50 µm. The size of the crystals during die casting was finer and dendrites reached a maximum length of 70 µm and maximum width of 12 µm. The Cu-30Zn crystalline structure of the dendrites had a length from 45 to 230 µm (casted into metal mould). The crystals of conductive copper have had a typical dissected shape and reached a length from 20 to 120 µm (casted into metal mould). The width of this dendrites reached up to 30 µm (casted into metal mould).

ACKNOWLEDGEMENTS

This paper is published with the support of the project "Support of the creation of excellent research and development teams at the Technical University of Liberec" No. CZ.1.07/2.3.00/30.0065.

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