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Researching the Influence of Chemical Composition and Technological Parameters on the Quality of Copper Alloys

S. Rzadkosz [a,]*, J. Kozana, M. Kranc [b]

[a] Department of Moulding Materials, Mould Technology and Foundry of Non-Ferrous Metals,
The AGH Faculty of Foundry Engineering, Reymonta St.23, 30-059 Krakow, Poland
[b] Foundry Research Institute, Zakopiańska St.73, 30-418 Krakow, Poland
*Corresponding author. E-mail address: rzadkosz@agh.edu.pl

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Abstract

The work presents the results of process efficiency of refining liquid copper with special refining agents and the analysis results of the influence of alloying components on the structure and properties of the chosen alloys. The research undertaken aimed at evaluation of the influence of alloying additives, such as aluminium, silicon and also cobalt in the chosen Cu-Zn alloys. The microstructures were researched with the help of light and scanning microscopy together with X-ray microanalysis to determine significant changes of mechanical properties.

Keywords: Copper, Cu-Zn alloys, Microstructure, Mechanical properties, Alloying additives, Refining

1. Introduction:

The research focused on refining copper and copper matrix alloys. The main copper impurities are hydrogen and oxygen present in the solution, phases and also in the form of gas bubbles. The remaining impurities of copper matrix alloys are non-metallic precipitates belonging to oxides, nitrides, sulfides, carbides and complex precipitates. The presence of oxygen additives in copper causes, in the final stages of solidification, as the result of segregation phenomena, intensified reactions with other impurities. The final product and effect of these reactions may be gasses and other impurities causing an increase in porosity in the inner layers of casts.

To avoid these effects it is necessary, before casting into a mould, to apply deoxidation of the metal bath with active agents. Their choice is based on their sufficient affinity for oxygen. Besides, the deoxidation agent should be applied in a form easy to introduce into the metal bath.

The deoxidation products should be released as vapours or easily pass into the slag, and the excess of deoxidating substance should not have a negative influence on the properties of the deoxidised alloy. To deoxidise copper, some bronzes and brasses additions of such elements as phosphorus, magnesium, sometimes aluminium are used in casting practice, respectively in the amount of 0,1% and 0,05% mass of the metal stock. An excessive amount of deoxidising substance increases the gas level and the tendency to fracture. Also positive results come from using agents containing small amounts (up to 0,05%) of other elements, such as sodium, lithium, zirconium, boron and others belonging to micro-additives with modifying influence. They show high chemical activity, interact with impurities, oxide, nitrogen and others. In many cases complex refining agents cause not only a change in the original structure of the alloys, but also the phenomena of degassing and removing non-metallic precipitates from the metal bath or neutralising some impurities.

In the second part the effectiveness of synthesizing multicomponent special brasses is analysed. In foundry of non-ferrous alloys they are a very important group of materials. In many cases they show properties similar to bronzes and they are their cheaper but equivalent substitutes. The alloys of copper that were examined as cast, are characterised by soft and plastic matrix, built from solid solution crystallites α or β. At their interface there are hardening phase components in the peritectic form or free intermetallic phases. The microstructural composition has a decisive influence on the properties of the casting materials. By using chosen alloying additives in optimal amounts it is possible to obtain brasses with very high mechanical, technological and practical properties.

2. Methodology and conditions of research

The results presented in this article were obtained as part of the research conducted at the Laboratory of Non-Ferrous Metals Foundry, at the Faculty of Foundry Engineering of the AGH in Krakow.

The melts were obtained from an induction furnace.
As the stock the following materials were used:
-electrolytic cathodic copper in the form of plates, the minimum copper content of 99,99% according to PN-EN 1978,
-electrolytic zinc Z1 according to PN EN 1179,
-electrolytic aluminium AR1, according to PN EN 573-3
-cobalt and initial alloy of CuSi16.

The prepared alloys were cast into metal moulds taking care to preserve the conditions of melting and casting for the successive casts.

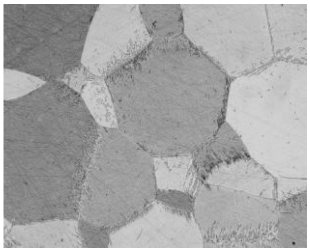
During melting the oxidised copper on the metal surface a protective and refining slag was applied. After melting the bath was overheated and next the deoxidation and modification were carried out, afterward the molten metal was cast into moulds.

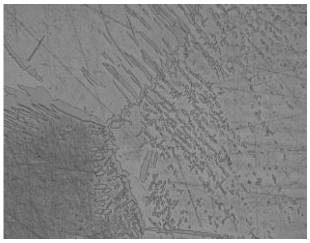
From the obtained experimental casts samples were prepared for the planned research.

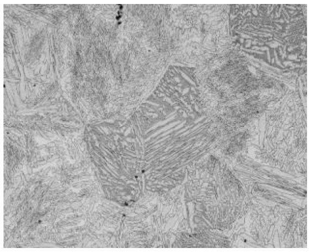
2.1. Researching cobalt influence on the microstructure and properties of CuZn alloys

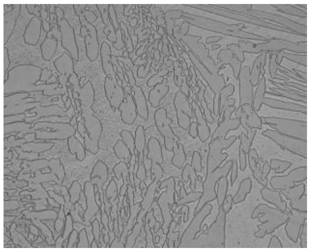
The research involved assessing cobalt influence on the microstructure and chosen properties of CuZn alloys, with changeable percentage of basic alloy components, namely from the interface areas of α/β' and β'/γ. Into the prepared CuZn44 and CuZn52 alloys changeable cobalt amounts were added, in the range from 0.5 to 2%.

Sample metallographic analyses are presented in pictures 1-10.

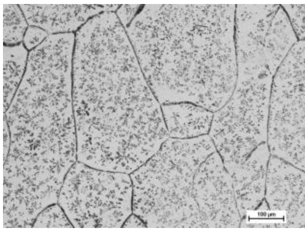

Picture 1: CuZn44Co0.5 alloy microstructure, magnification 100x.

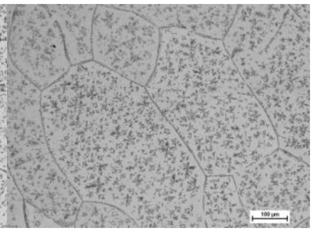

Picture 2: CuZn44Co0.5 alloy microstructure, magnification 500x.

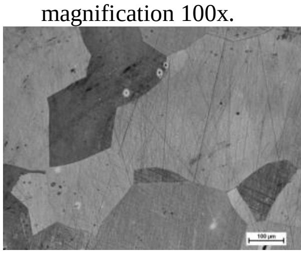

Picture 3: CuZn44Co2 alloy microstructure, magnification 100x.

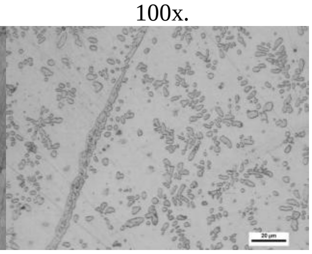

Picture 4: CuZn44Co2 alloy microstructure, magnification 500x.

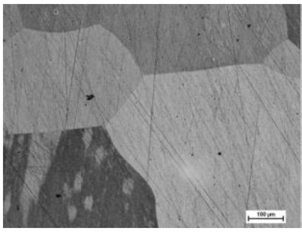
It can be concluded from the microstructure pictures above, that the cobalt introduced into brass with the β' phase structure with some precipitates of α phase causes size reduction of the grain and creates precipitates at the grain boundry; and with greater cobalt content (within 2%) it causes precipitation of the needle phases similar to phase α on the background of β'; the so called 'packet arrangement', so, in fact, it shifts the arrangement towards the $\alpha+\beta'$ structure.


Picture 5: CuZn52Co0.5 alloy microstructure, magnification 100x.

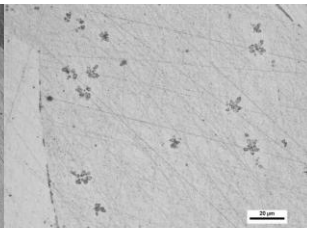

Picture 6: CuZn52Co1 alloy microstructure, magnification 100x.


Picture 7: CuZn52Co1.5 alloy microstructure, magnification 100x.


Picture 8: CuZn52Co0.5 alloy microstructure, magnification 500x.



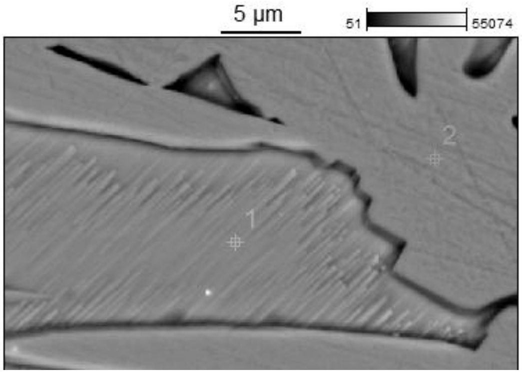
Picture 9: CuZn52Co2 alloy microstructure, magnification 100x.



Picture 10: CuZn52Co1.5 alloy microstructure, magnification 500x.

Analysing the metallographic test results a strong influence of cobalt can be seen in the alloys examined. Already at 1.5% addition of cobalt, phase γ disappeared almost completely.

In order to conduct a more detailed microstructure analysis scanning microscopy was used. The results of these analyses are presented in picture 11 and in table 1.

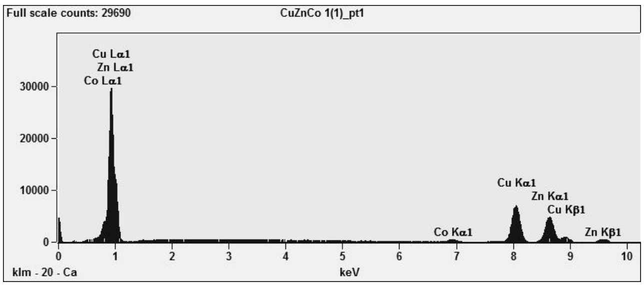


Picture 11: The surface of the CuZn44Co0.5 with the microanalysis points marked.

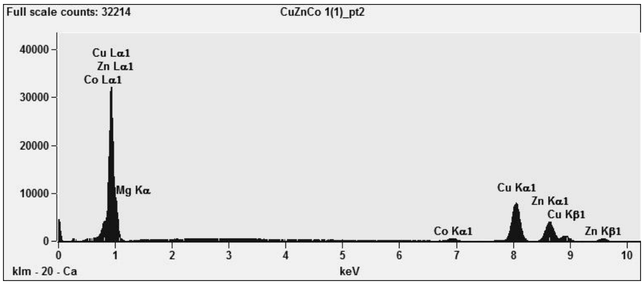
Table 1.
Microanalysis results for points from picture 11.

Analysis point	Co, mass %	Cu, mass %	Zn, mass %
C1x_pt1	1.428	53.504	45.068
C1x_pt2	1.646	61.562	36.784

In pictures 12-13 there are characteristic X-ray spectra, emitted from the micro-area analysed. There reflexes visible come from the elements present in the alloy examined.



Picture 12. X-Ray spectrum for picture 11, point 1.



Picture 13. X-Ray spectrum for picture 11, point 2.

The research of the influence of cobalt in CuZn52 brass showed, that cobalt has a great influence on the peritectic transformation, and as the result, the precipitation of the γ phase is stopped in the brasses examined. Cobalt additive (about 1.5%) will be enough to eliminate the γ phase from the microstructure of the tested CuZn52Co brass.

The mechanical tests showed, that the cobalt addition of above 1.5% improves the tensile strength R_m by 50%, reaching the value of 375 MPa, and also it increases elongationA_5 – almost threefold (picture 14).

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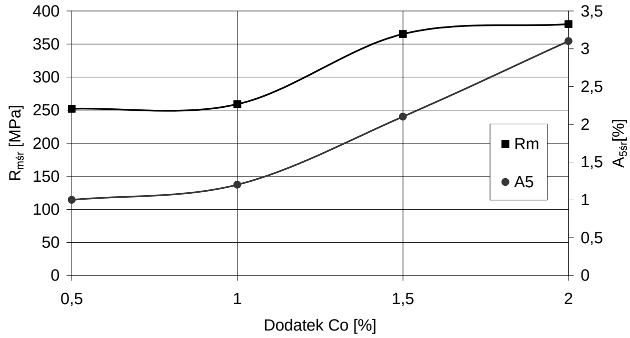


Picture 14. The influence of cobalt additive on R_m and A_5 of the CuZn52 brass.

At the same time it should be noted, that the hardenss of the alloys tested which contained cobalt decreased.

Because of the fact, that some results point to positive influence of cobalt additive on the improvement of properties of the brasses tested; and – above others – it clearly influences the γ phase blockage, so at the next stage of our work an attempt was made to optimise the content of the aluminium-silicon brasses with the addition of cobalt.

2.2. The research of aluminium-silicon-cobalt brasses

In order to specify the influence of the chosen alloying elements in multi-component brass a series of casts was made with their content specified. The contents of the planned and received alloying components are presented in tables 2 and 3.

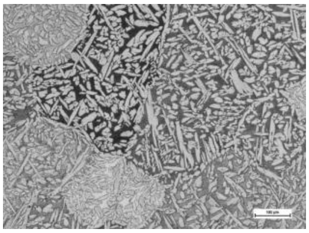
Table 2.
The planned content of the alloying elements

Matrix CuZn34AlSiCo				
	Al	Si	Co	cast number
1	1,8	1,2	2	C3x
2	1,2	1,2	2	C2x
3	1,2	0,8	2	C1x
4	1,8	0,8	2	C7x
5	1,8	1,2	3	C6x
6	1,2	1,2	3	C5x
7	1,2	0,8	3	C4x
8	1,8	0,8	3	C8x

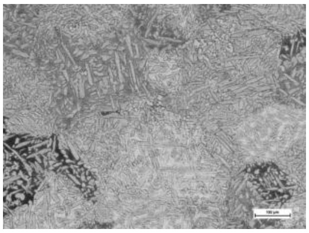
Table 3.
The received content of the alloying emenents

Matrix CuZn34AlSiCo				
	Al	Si	Co	cast number
1	1,82	1,24	2,14	C3x
2	1,24	1,23	2,07	C2x
3	1,21	0, 75	2,0	C1x
4	1,86	0,74	2,03	C7x
5	1,82	1,23	3,3	C6x
6	1,21	1,19	2,95	C5x
7	1,17	0,75	2,93	C4x
8	1,16	0,72	3,11	C8x

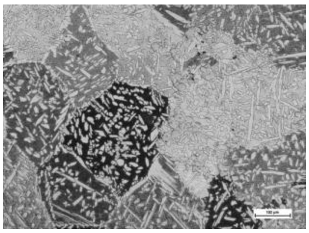
In further part of the article, in pictures 15–22, sample microstrucures of the examined alloys are presented.



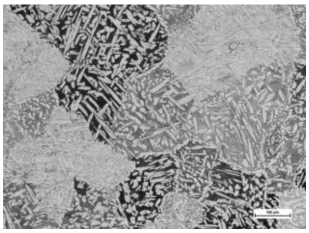
Picture 15.: Sample C1x microstructure, magnification 100x



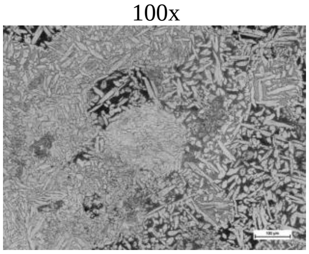
Picture 16.: Sample C2x microstructure, magnification 100x



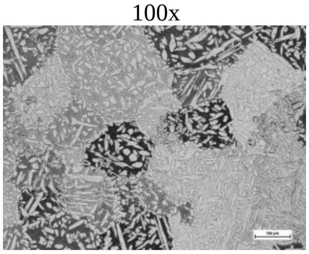
Picture 17.: Sample C3x microstructure, magnification 100x



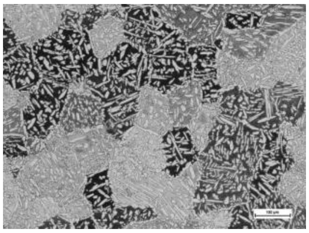
Picture 18.: Sample C4x microstructure, magnification 100x



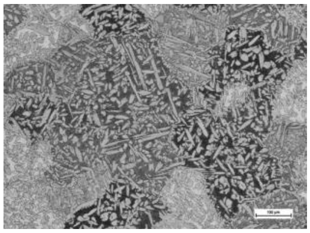
Picture 19.: Sample C5x microstructure, magnification 100x



Picture 20.: Sample C6x microstructure, magnification 100x



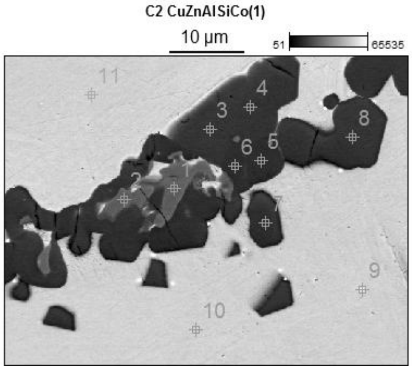
Picture 21.: Sample C7x microstructure, magnification 100x



Picture 22.: Sample C8x microstructure, magnification 100x

The analysis of the microstructures presented in pictures 15-22 indicates, that cobalt used as an alloying additive in the amount of 2 to 3 mass % causes in the CuZn34AlSiCo alloys grey precipitates, and also it influenced diminishing grain size of β' phase, which can be clearly seen in picture 21.

The precipitates visible underwent X-ray microanalysis in order to specify roughly the kind of the phase crystalised. The results of scanning tests are presented in picture 23 and in table 4. The clearly visible precipitates are placed in groups.



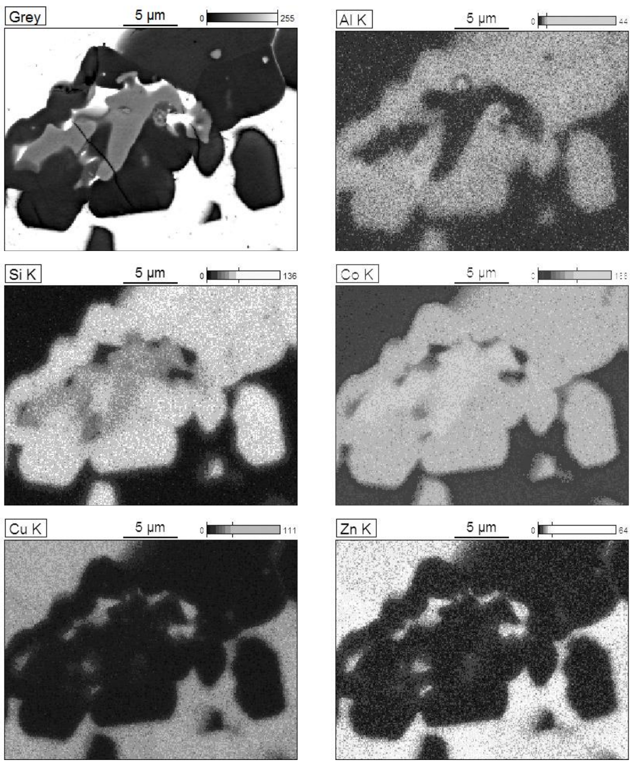
Picture 23. The surface of the C8x sample with the microanalysis points marked.

Table 4.
The microanalysis results for picture 25. The percent composition is by mass.

	Al	Si	Co	Cu	Zn	Pb
pt1	0.332	18.830	77.945	2.892		
pt2	0.591	18.437	76.395	3.319	1.25	
pt3	5.204	26.027	66.860	1.909		
pt4	5.055	26.007	64.822	2.351	1.76	
pt5	4.971	25.197	66.656	1.581	1.59	
pt6	5.238	24.926	66.766	1.549	1.52	
pt7	4.764	25.840	68.103	1.293		
pt8	4.914	26.246	67.606	1.234		
pt9	1.186	0.692	1.696	53.395	32.58	10.44
pt10	0.852	0.521	2.278	65.500	30.84	
pt11	0.790	0.448	0.947	66.994	30.82	

Analysing the picture of the sample surface with the help of reflected electrons (PDBSE) (picture 23) it can be concluded, that the alloying elements, as the result of phase transformations, lead to creating two kinds of intermetallic phases in the microstructure, seen as light grey and dark/black phase precipitates of cobalt-silicon compound, following the Co-Si equilibrium diagram. The differences in content and in morphology of these two phases result from the speed of solidification.

To conduct a more thorough analysis of both the matrix and precipitates in the alloys examined, apart from the point analysis also the test of elements distribution on the area tested was conducted. So the maps showing their distribution in the matrix and in the specific precipitates can be seen in picture 24.



Picture 24.:The elements distribution in the area analysed of the C8x sample.

Analysing the elements distribution in the area tested it can be seen that the precipitates visible are rich in aluminium, silicon and cobalt, and the matrix is mainly built of zinc and copper solution, with a small amount of aluminium.

2.2. Research of copper refinement processes

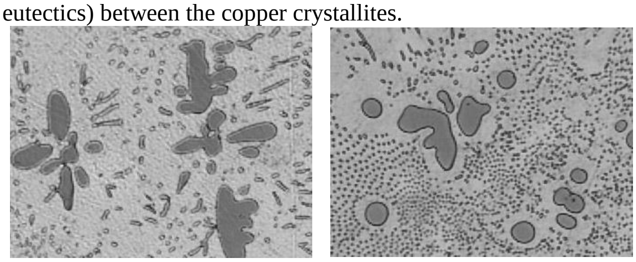
The research results concerning the intensity of copper deoxidation with the help of refining and modifying agents are shown in table 5.

Table 5.
The influence of deoxidation processes on the oxygen content in copper.

agent	agent content [%]	time after the treatment	oxygen content [ppm]	electric conductivity MS/m
-	-	-	5224	32
-	-	-	2129	33
CuP10	0,1	5 min	60	53
OMB2M	0,05	5 min	89	51
Kupmod 2B	0,03	5min	67	50
OBC2	0,05	5 min	26	57
OBZ4	0,05	5 min	33	55

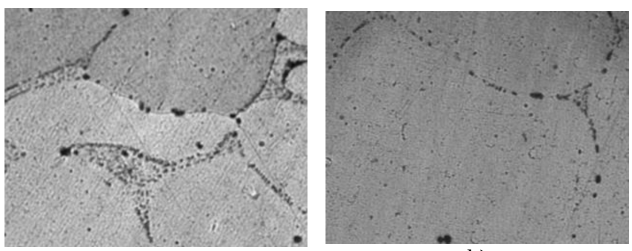
The analyses results of oxygen content in copper were compared with microstructure analyses. The sample results of this comparison are in pictures 25 – 27.

The comparison of microstructures of copper casts with different content of oxygen eutectic after the deoxidation treatment points to a comparatively strong deoxidation result obtained with the help of deoxidising and deoxidising-modifying agents. Before the process copper contains oxygen eutectic throughout the whole area visible as well as overeutectic precipitates of Cu_2O phase. After deoxidation copper phase grains dominate with very thin precipitates of oxygen phase (Cu-Cu_2O eutectics) between the copper crystallites.



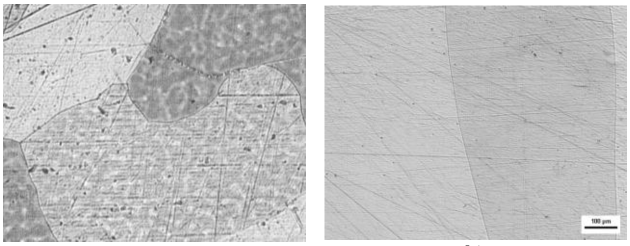
a) b)

Picture 25.: The microstructure of copper melted in the oxidising atmosphere and cast into a metal mould containing oxygen in the amount of a) 5224 [ppm], (b) 4450 [ppm]. Etched with Mi15Cu. Mag. 500x.



a) b)

Picture 26.: The microstructure of copper melted and cast into a metal mould after a deoxidising treatment with CuP10, 0.01 % of the amount, containing 1220 [ppm] of oxygen: (a) and after deoxidising with the OMB2M agent, 0.05% of the amount, containing 89 [ppm] of oxygen (b) Mag. 200x, etched with Mi15Cu.



a) b)

Picture 27.: The microstructure of copper melted and cast into a metal mould after a deoxidising treatment with (a) OBC2 agent, 0.05% of the amount, containing 26 [ppm] of oxygen, (b) with OBZ4 agent, 0.05% of the amount, containing 33 [ppm] of oxygen. Mag. 200x, etched with Mi15Cu.

3. Conclusions

From the comparative data obtained, concerning the influence of the refining agents of the oxidising and modifying kind it can be concluded that:

- in the microstructure of melted oxidised copper there appear primary precipitates of the Cu_2O phase against the background of oxygen eutectics of Cu- Cu_2O,
- the effect of deoxidising copper with the help of deoxidising or deoxidising-modifying agents is clear; the strongest influence however is exerted by the formulas containing microadditives of boron (agent OBM2M and OBC4).
- as the result of deoxidising of the eutectic mixture of Cu_2O the content of oxygen eutectics decreases significantly, and after the deoxidation very small amounts of of Cu_2O phase remain in the microstructure in the form of strands at the boundries of copper grains.

The influence of cobalt introduced into brass with β' phase structure with small α precipitates leads to reducing grain size and precipitates appear at the grain boundry. Greater cobalt content, up to 2%, causes precipitation of the needle phases similar to α phase against the β', so called 'packet arrangement', , so, in fact, it shifts the arrangement towards the α+β' structure. In the CuZn alloys with β' structure with γ phase precipitates the cobalt addition of 1.5% leads to complete disappearance of γ phase. From chemical analysis of the precipitates visible it can be concluded, that cobalt used as an additive to CuZn44 alloys solves both in the matrix, this means in β' phase, and in solid solution α.

The research on cobalt influence in CuZn52 brass showed, that cobalt has a very strong influence on peritectic transformation and as the result the precipitation of the γ phase is blocked in the brasses examined. Already 1.5% addition of cobalt almost completely eliminated gamma phase from the CuZn52Co brass. Mechanical tests showed that cobalt addition above 1.5% improved tensile strength as well as it increased elongation.

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