

Research on Technology of Alloyed Copper Casting

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Abstract

The work presents experiment results from the area of copper casting technology and chosen examples of alloyed copper. At present, copper casting technology is applied in many branches of industrial manufacturing, especially in the sector of construction, communications, arms and power engineering. Alloyed copper, containing slight additions of different elements and having special physio-chemical properties, is used in a special range of applications. Copper technology and alloyed copper analyses have been presented, these materials being used for cast manufacturing for power engineering. The quality of casts has been assessed, based on their microstructure analysis, chemical content and the cast properties. During the research, special deoxidizing and modifying agents were applied for copper and chosen examples of alloyed copper; also exemplary samples were tested with the help of metallographic analysis, electrical conductivity and gaseous impurities research.

Keywords: Casting technology, Copper, Alloyed copper, Copper deoxidation, Heat treatment

1. Introduction

Modern industry, and especially the sector of power engineering and electronics, sets very high standards for the materials used there. They should be characterised by high physical and functional properties, such as high electrical and thermal conductivity, high strength, resistance to abrasion and corrosion [1-4]. The basic material used for casts manufactured for power engineering industry is copper. Its electrical conductivity is the highest of all technical metals used in casting (58MS). However, the mechanical properties of copper are relatively low, that is why, often small additions of other elements are introduced, which improve resistance to mechanical wear. One of the copper alloys meeting high strength and functionality requirements, and also characterised by good thermal and electrical conductivity is chromium copper. [5]

Producing chromium copper casts is connected with technological problems, especially during melting and liquid metal preparation process. This is caused by unfavourable properties of the material, among others significant differences in melting temperature and specific gravity of the alloyed elements, namely of Cu and Cr. But the greatest difficulties are caused by their different oxygen affinity. [5]

Copper, having low activity in comparison to oxygen, creates easily soluble oxides, while chromium creates Cr_2O_3 , which is insoluble and difficult to remove from the bath. It is the reason of many defects lowering the cast properties, mainly through creating discontinuities of structure, which has direct influence on strength parameters; thermal and electrical conductivity. High shrinkage and the proclivity to create slag which is difficult to remove, causes the appearance of shrinkage cavities and slag inclusions. A negative phenomenon resulting from high chromium affinity for oxygen is a significant melting loss,

causing changes of chemical composition and physio-chemical properties of the material melted. [7-8]

The difficult technology of melting and casting copper and alloyed copper poses a set of challenges. Conducting research and attempts of optimization of the melting technology and refining the metal bath of copper and alloyed copper is indispensable for achieving the highest levels of cast quality.

2. Researching copper casts

2.1. Researching copper melting and deoxidation technologies

Copper casts were analysed from the perspective of melting parameters and the efficiency of the influence of deoxidation technology on the structure and properties of copper and copper alloys. Also, the influence of modifying elements applied in the refining agents was tested in order to obtain the optimal cast properties, of among others, primary coils used in power engineering. Microstructure changes and cast properties were analysed. The most important copper properties are electrical and thermal conductivity as well as mechanical properties of casts. Next, the resistivity to corrosion was tested. The high values of the above-mentioned properties are obtained by the proper preparation of liquid metal, mainly by removing gaseous impurities. Oxygen and hydrogen are gasses, which are absorbed in copper. Their presence causes porosity (Fig. 1) and unfavourable eutectic microstructure in casts. [6-8]

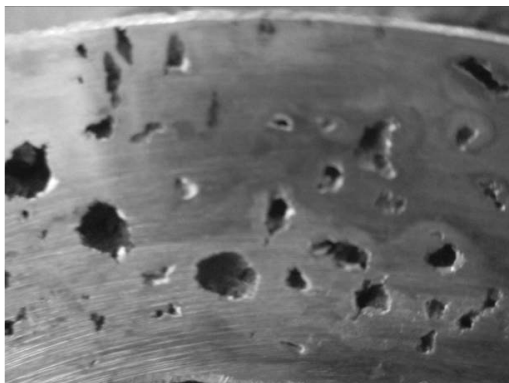


Fig. 1. Gaseous porosity in the copper cast section

Nowadays, to remove impurities a range of elements with high affinity for oxygen is used, the most important of them being phosphorus, lithium, magnesium, boron and beryllium. Electrical conductivity was analysed with the help of SIGMA TEST 2.067, a conductivity testing appliance, manufactured by Forster. Strength parameters were tested on the machined samples cast into ceramic moulds. The samples cut from the casts were machined with Metasinx metallographic grinder, and next the samples were polished using Montasupal machine. The polished sections were etched by a mixture of acids. The microstructures were observed with the help of metallographic microscope of

Nikon Eclipse LV150 type, with a magnification of 50x – 500x. The exemplary results for copper deoxidized with different agents are collated in Table 1.

Table 1. Deoxidizing influence on the oxygen content and electrical conductivity of copper

	Agent	Amount,%	Electrical conductivity MS	Oxygen content O ₂ [ppm]
1	-	-	24	2260
2	-	-	30	1290
4	Logas	0,15	54	73
5	CuP12	0,2	48	98
6	CuP12	0,3	55	34
8	Li	0,05	54	39
9	P3	0,5	55	93
10	ODM2	0,3	55	16
11	Kupmod 2B	0,2	53	24

The analysis of deoxidizing treatments shows varied influence of different agents. Phosphor introduced into the metal bath causes reduction of copper oxide (I) $5\text{Cu}_2\text{O} + 2\text{P} = \text{P}_2\text{O}_5 + 10\text{Cu}$ [1], and in the final stage it increases the flowing power of the liquid metal, which allows the slags, oxides and other impurities to float to the surface of copper bath. This treatment makes it possible to obtain a structure free from solid non-metallic inclusions, which in an obvious way influences technological properties of an alloy.

Introducing active lithium into the metal bath causes an intense reaction with oxygen in the deoxidizing process temperature, according to $2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O} + 136 \text{ kcal}$. Also, it reacts with hydrogen, according to $\text{Li} + \frac{1}{2}\text{H}_2 = \text{LiH} + 22 \text{ kcal}$. The created lithium oxide floats to the surface and passes into the slag, but the lithium hydride solves into the bath and lowers the metal properties [2]. Strong deoxidizing properties of boron are connected with active binding of oxygen into an oxide. B_2O_3 oxide reacts with oxidized copper, creating $2\text{Cu}_2\text{O} \cdot \text{B}_2\text{O}_3$ [6]. The addition of 0,02% of beryllium is introduced into copper in CuBe treatments. Copper deoxidized with beryllium does not show porosity or surface defects, also it has high thermal conductivity and increased strength. Microstructures characteristic for copper in the original state, and also after melting and deoxidizing process are presented in Figure 2.

Modern refining technologies for liquid metal that is designed for special casts are more and more efficient and they make it possible to obtain high purity material.

The effect observed in copper caused by different deoxidizing or deoxidizing and modifying agents is distinctly visible. Also, deoxidizing copper with the help of different complex formulas is interesting because they influence the microstructure and oxygen content to a significant degree.

Copper as matrix shows high values of electrical and thermal conductivity and it is rather resistant to atmospheric corrosion, however, pure copper has relatively low strength.

Well-deoxidized copper was used in further research for preparing melts of alloyed copper. Within the scope of our research, structure and properties of various kinds of alloyed

copper were investigated, including slight additions of, e.g., chromium, nickel, zirconium, silicon, beryllium, iron, titanium and other elements.

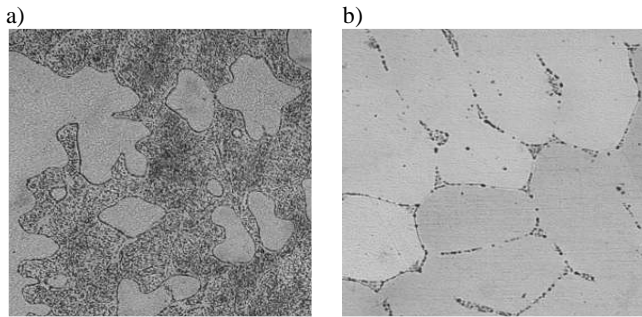


Fig. 2. Original copper microstructure. Oxygen content 2600 ppm. Dendritic crystallites of copper are visible (light) on the Cu-Cu₂O eutectic background (dark) (a). Copper microstructure after the deoxidizing CuP treatment. Oxygen content 230 ppm. Dendritic crystallites of copper are visible (light) and Cu-Cu₂O eutectic precipitates (dark) in the interdendritic regions (b). Magn. 200x.

Particular properties of some kinds of alloyed copper are connected not only with its chemical content but also with the alloy structure and the refining treatment applied. These alloys show relatively low technological properties as well as a tendency for many casting defects, which decrease their physio-chemical properties.

A difficult technology of the above-mentioned materials requires further research aimed at implementing new solutions that would result in their increased quality. [9-12]

A lot of attention is paid to the problems of shaping structures of the Cu-Cr, Cu-Cr-Zr, Cu-Ni-Si, Cu-Ni-Cr alloy types, among others. Within the research framework, macro- and microstructure of the alloys was analysed, as well as their intermetallic phases and properties of the chosen alloys. The influence of deoxidation processes, refining and modifications on the structure and properties of the alloys was investigated. Protective and refining slags were applied during melting, as well as characteristic micro-additives, deoxidizing and modifying the structure of the chosen alloys. Also, the properties were analysed in connection with the heat treatment parameters. During the stock melting process, to minimize the non-returnable losses, the argon protective atmosphere was used or protective coating in the form of charcoal, as well as protective-refining slags, with fluoride salts were applied. The effects were assessed from the point of view of changes in macro- and microstructure, changes of mechanical properties and electrical conductivity. High conductivity copper and electrolytic copper were used as metal stock.

2.2. Casting of chromium copper

Chromium copper is used for manufacturing welding electrodes, electrical cable connectors, switches, collectors, machine parts subject to intense abrasion under electric voltage and high temperatures, heat exchangers, parts of blast-furnace burners and blowpipes as well as parts of valves, nuclear reactors

and rocket engines. A characteristic feature of this material is its relatively high electrical conductivity in comparison with other copper alloys. A great advantage of chromium copper is its heat workability, resulting from changeable solubility of chromium in copper. The maximum solubility of chromium in copper in solid state is in the temperature of 1076.6°C and it equals 0.89%. It decreases in step with decreasing temperature, and, for example in 700°C – 0.07%, in 400°C it is 0.02% and it falls to 0.01% in room temperature [5].

Table 2.

The influence of chromium additions on copper properties

Cr addition, %	Rm, MPa	A5, %	MS	HV
0	150,20	48	57	50
0,4	192,50	36,1	45,2	105
0,8	255,30	30,8	35,4	162
1,3	271,00	22,2	27,4	191
1,6	282,70	20,8	23	210
2,1	270,50	15	19,5	208
2,4	248,10	11,4	16	214

The attempts at obtaining chromium copper with optimal functional properties are connected with examining the deoxidation process. The tests were carried out on samples obtained from alloys containing from 0.4 to 2.4 % of Cr (Table 2). The electrical conductivity tests show that this property decreases as the chromium content grows. During our investigations different formulas were used, but in this paper the exemplary results are shown for the formulas containing phosphorus and boron in Table 3 and in Figure 3-4.

Table 3.

The influence of deoxidation on electrical conductivity of chromium copper

No.	Alloy	Deoxidizer	Conductivity, MS	Oxygen, ppm
13	pure Cu	-	53	200
14	CuCr (1,4%Cr)	-	26	61
15	CuCr (1,4%Cr)	CuP (0,22%)	27	75
16	CuCr (1,8%Cr)	-	20	550
17	CuCr (1,8%Cr)	Desofin0,26 %	24	50
18	CuCr (1,8%Cr)	CuB ₂ 1,5%	23	65

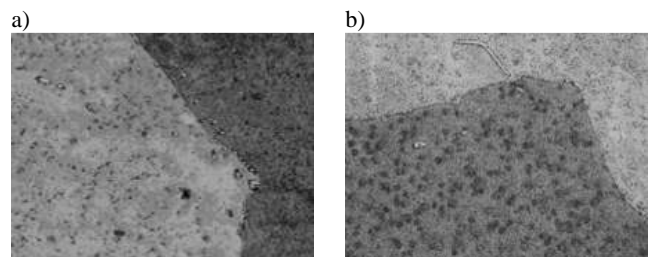


Fig. 3. The microstructure of chromium copper CuCr1.3, cast into a ceramic mould. Magnification 500x. Etched with Mi 17 (a). The microstructure of chromium copper CuCr1.3, deoxidized with 0.1% P, cast into a ceramic mould. Magnification 500x. Etched with Mi 17 (b)

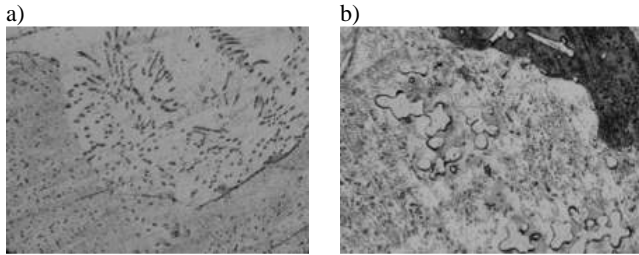


Fig. 4. The microstructure of chromium copper CuCr1.8, cast into a ceramic mould. Magnification 500x. Etched with Mi 17 (a). The microstructure of chromium copper CuCr1.8 with 1% CuB2 addition, cast into a ceramic mould. Magnification 500x. Etched with Mi 17 (b)

2.3. The influence of zirconium additions

Among many modifying agents, there were analysed additions of nucleation elements such as zirconium, boron, titanium, vanadium, tungsten, as well as salt formulas of the above-mentioned elements; used as modifying mixtures or complex, modifying and oxidizing slags (Table 4). After introducing zirconium additions its positive influence on the structure of chromium copper can be observed.

At the same time, zirconium additions lower electrical conductivity of chromium copper.

Table 4.
The conductivity of alloyed copper CuCr and CuCrZr

No.	Alloy	Conductivity, MS
1	pure Cu	50
2	CuCr (1,5%Cr)	24
3	CuCr (1,5%Cr)	22
4	CuCr (2,2%Cr)	22,5
5	CuCrZr (2,2%Cr, 0,2%Zr)	20,5
6	CuCrZr (2,2%Cr, 0,2%Zr)	20
7	CuCrZr (2,2%Cr, 0,2%Zr)	18,5
8	CuCrZr (2,16%Cr, 0,2%Zr)	18,5

2.4. Heat treatment

Heat treatment is an important element of technological process, and it is applied with the aim of obtaining casts with high functional properties. This process consists of two parts: solution heat treatment and ageing. During solution heat treatment the casts are first held at the temperature of 20-50°C above the solidus line, and next there is a quick cooling, most often in water, with the aim of arresting chromium in the matrix. Soaking time should be long enough to ensure that all of the chromium is solved within the whole volume of the cast [7-8]. Solution heat treatment causes lowering electrical conductivity to the value of 20–24 MS (Table 5).

The second stage of heat treatment is ageing. It consists of re-heating and air cooling. Ageing aims at precipitation of Cr from supersaturated solution in the form of precipitates, which significantly increase alloy strength. The process is conducted in the temperature of 450-510°C. The heating takes from 1,5 to 4 h.

After the heat treatment, in the microstructure, there are spherical chromium precipitates against the background of equiaxial, recrystallized grains of chromium in copper solution; the hardness increase after ageing results from dispersive chromium precipitates in the grains.

Table 5.
The influence of ageing on properties

Time, h	HB hardness				Conductivity, MS			
	Ageing temperature				Ageing temperature			
0	600	500	450	400	600	500	450	400
0,1	41	41	41	41	20	20	20	20
0,2	42	43	42	41	21	21	21	21
0,5	100	130	62	43	24	22	22	23
1,0	90	120	115	122	34	28	24	38
2,0	80	105	120	130	37	35	32	40
4,0	70	100	115	122	40	40	37	41
8,0	60	100	110	117	40	41	39	41

3. The influence of silicon additions on the CuNiSi alloy properties

A series of tests were conducted of the influence of nickel, chromium and silicon additions on the structure and properties of CuNi2SiCr copper. Next, the simultaneous influence of these elements was researched, with a changeable amount of silicon addition. The range of metals examined makes an interesting group of copper matrix materials, with good physio-chemical properties, and especially good mechanical features, accompanied by good thermal and electrical properties. The influence of varied chromium additions was analysed, within the range of up to 0.6%, as well as varied silicon additions of up to 2.2%. Microstructure changes were analysed, as well as changes in hardness and electrical conductivity. These characteristics are typical of the group of alloys researched, and are decisive about their application in engineering.

The research conducted showed, that the alloy hardness increases significantly after introducing 0.6% chromium addition. It is connected with the fact that in the microstructure there are chromium phases appearing, located inside the grains at their boundaries. Also, after introducing into deoxidized copper the additions of chromium (0.8%) and nickel (2.1%), and casting the initial samples, the varied additions of silicone were administered, in the amounts ranging from 0.4 to 2.2%. The tests results were compared with the test results for the initial sample (Table 6).

Table 6.
The influence of silicone additions on the CuNi2,1Cr0,6Si, cast into metal mould

No.	Addition Si, %	Rm, MPa	HB	A ₅ , %	Conductivity, MS
0	0	148,4	55	48,8	34
1	0,8	332,6	98	26,8	12,6
2	1,3	360,1	132	14,6	10,1
3	1,7	420,6	145	9,6	9
4	2,2	355,8	164	6	6,5

The microstructure was assessed on the basis of the chosen micro sections. A coarse-grained macro-structure of equiaxial grains was established, with clearly seen dendritic heterogeneity, without any gas or shrinkage porosity.

For further investigations the CuNi2Si0,8 alloy was chosen. The samples to be investigated were cast into metal and sand moulds. The chosen samples were heat-treated, in order to establish the possibility of dispersive strengthening of the cast structure. The exemplary research results of macro- and microstructures are collated in Figures 5 and 6.

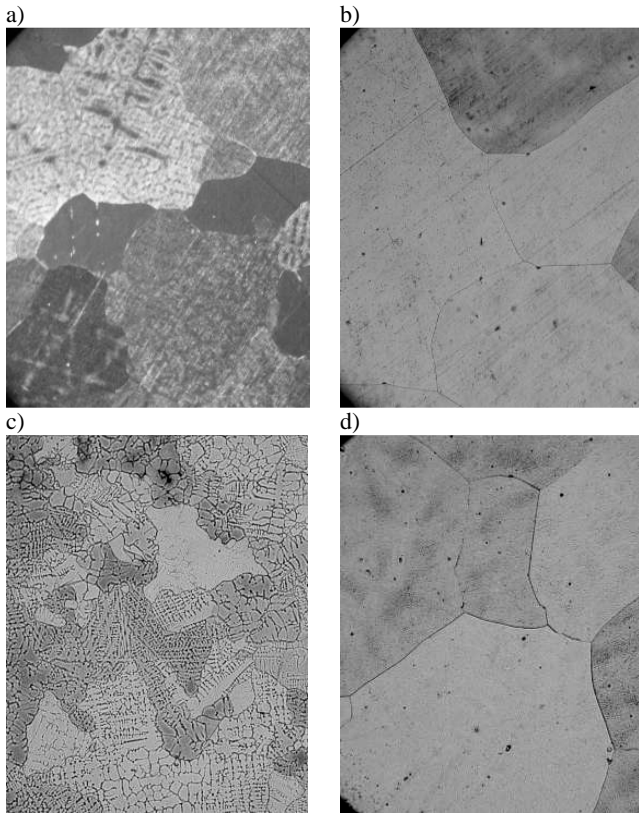


Fig. 5. The microstructure CuNi2Si0,8 sand moulds (a, b), metal moulds (c,d). Etched with Mi21, Magnification 50x (a,c), 500x (b,d)

The microstructure of the alloys researched has dendritic character with small precipitates of intermetallic phases in interdendritic regions. In the case of metal moulds a greater size reduction of primary structure is visible, and clearly compact structure of the solid state. In the sand moulds slow solidification is conducive to microporosity appearing at places.

After the heat treatment the heterogeneity disappears. There are only grain outlines of solid state visible in the microstructure, without the intermetallic phase precipitates from the interdendritic regions. The changes in microstructure cause changes in strength properties. The exemplary results of strength tests are collated in Table 7.

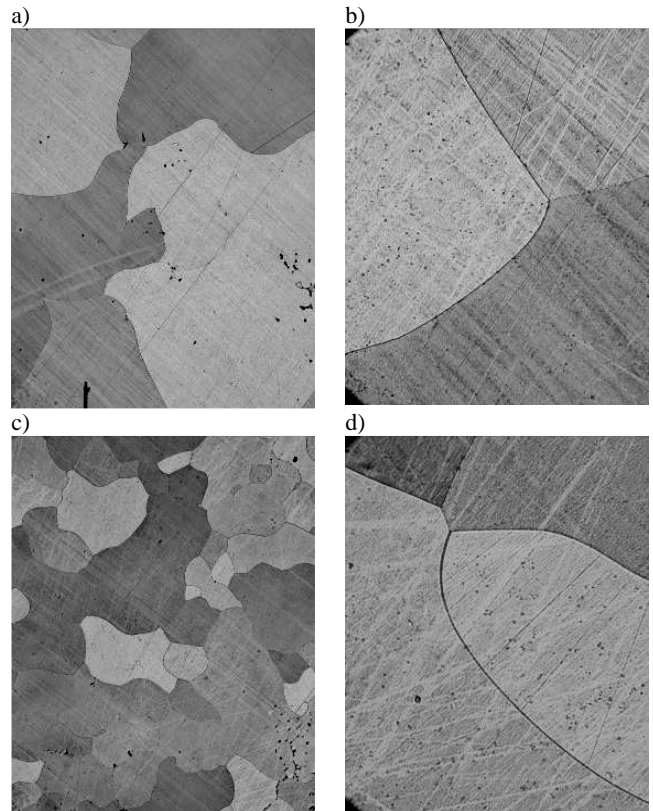


Fig. 6. The microstructure CuNi2Si0,8 after the heat treatment, sand moulds (a, b), metal moulds (c,d). Etched with Mi21, Magnification 50x (a,c), 500x (b,d)

Table 7.

Mechanical properties of the CuNi2Si0,8 alloy

No.	Alloy state	Conductivity, MS	R _m , MPa	A ₅ , %	HV
1	Lp	9,5	235	7,6	80
2	Lk	15	380	15,2	91
3	Lp-R6	16	320	3,2	118
4	Lk-R6	13	600	2,5	148

Based on the microscopic analysis it can be ascertained that increasing the chromium content above 0.8% brings about appearing the intermetallic phase precipitates, especially at the boundary of intercrystalline grains. According to the data, it is the original chromium phase. The addition of silicon and nickel causes the fact that in the microstructure there is a clear, dendritic, reduced in size structure of solid state, and in the interdendritic region there may appear Ni₂Si phases (Fig 5).

The results of a microstructure (Fig. 7), research conducted with the help of scanning microscope Hitachi S-4200 coupled with the system detecting and analysing EDS type of X-ray, registered at the 15kV accelerating voltage showed - Table 8.

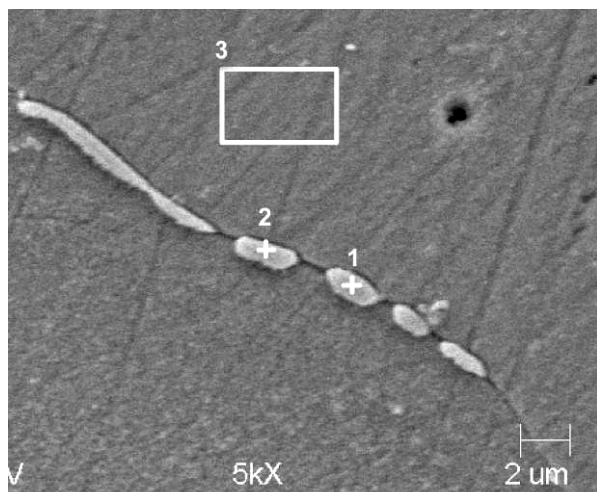


Fig. 7. The microstructure CuNi₂Si_{0.8}

Table 8.

The microanalysis of phases results for CuNi₂Si_{0.8} alloy (Fig.8)

Element	Int. c/s	Atomic, %	Conc, %	
Si	11.69	13.721	6.623	s1mar1
Mn	0.30	0.171	0.161	
Fe	0.98	0.552	0.530	
Ni	10.68	7.123	7.185	
Cu	62.52	78.211	85.409	
Si	26.95	27.673	15.041	s2mar2
Mn	0.49	0.275	0.293	
Fe	2.60	1.481	1.600	
Ni	38.85	35.818	40.685	
Cu	28.56	34.283	42.160	
Si	3.45	4.325	1.964	s2mar3
Mn	0.00	0.000	0.000	
Fe	0.62	0.289	0.261	
Ni	2.00	0.940	0.892	
Cu	73.24	94.200	96.78	

4. Conclusions

In the course of our research it was established that:

- the most important element in copper and alloyed copper casting is creating the optimal conditions of melting and efficient impurities extraction with the help of oxygen and hydrogen. During melting, the possibility of contact of the bath with any sources of impurities should be limited, through applying proper protective atmosphere and protective-refining slags.
- as stock materials pure kinds of copper should be used, electrolytic copper and CuCr12 master alloy. The furnaces used should enable fast melting of the metal stock, limiting the possibility of polluting the metal. One of the ways of checking the alloy quality is measuring electrical conductivity of copper. Lower conductivity may indicate

pollution of the bath. An important element of refining chromium copper is the deoxidation process conducted most easily with deoxidizing master alloys, such as CuP, CuB₂.

- applying modifying treatments causes slight improvement in the degree of grain size-reduction,
- there is a clear increase in strength parameters and electrical conductivity after the heat treatment of chromium copper,
- the research confirmed the engineering difficulties present during the melting process – during the melting and pouring the liquid metal into the moulds, the parameters must be strictly observed,
- silicon additions in multicomponent materials on copper matrix, also with chromium and nickel, clearly improve technological properties, and, at the same time, their strength properties.

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