REFINING PROCESSES IN THE COPPER CASTING TECHNOLOGY

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The paper presents the analysis of technology of copper and alloyed copper destined for power engineering casts. The casts quality was assessed based on microstructure, chemical content analysis and strength properties tests. Characteristic deoxidising (Logas, Cup) and modifying (ODM2, Kupmod2) formulas were used for the copper where high electrical conductivity was required. Chosen examples of alloyed copper with varied Cr and Zr content were studied, and the optimal heat treatment parameters were tested for a chosen chromium copper content, based on the criterion of hardness and electrical conductivity tests. Searching for materials with high wear resistance, the influence of variable silicone content on the properties of CuNiSi alloy was researched.

Key words: copper, casting technology, refining alloy, microstructure, properties

INTRODUCTION

Modern industry stets very high standards for the materials applied. They should be resistant to mechanical and chemical wear. Many branches of industry demand materials with high physio-chemical and functional properties, such as high electrical and thermal conductivity, high strength, resistivity to abrasion and resistivity to corrosion. The material meeting these criteria is copper and its alloys. Copper as matrix material has high thermal and electrical conductivity, the highest of all materials used in casting of technical metals (58 MS). That is why it is the main material used in cast manufacturing for power engineering sector. But mechanical properties of copper are relatively low that is why often additions of other elements are introduced, to improve its resistivity to mechanical wear. Copper with these small additions constitutes the group of alloyed copper, showing high mechanical and functional properties, as well as good thermal and electrical conductivity. An example here is chromium copper, as well as other examples of alloyed copper, e.g beryllium (up to 2 %), nickel (up to 2,5 %), chromium (up to 1,2 %), manganese (up to 1,3 %) as well as cadmium and zirconium copper [1-4]. Bigger amounts of alloying additives create other groups of special bronzes, among which there are multicomponent bronzes resistant to wear, among others aluminium, nickel, manganese, aluminium-iron bronzes, as well as nickel-silicone CuAlFeNi and CuAlFeMn bronzes. In these bronzes a special role is played by manganese and nickel additions. An especially strengthening influence on the structure and properties of the aluminium bronzes is noticed in the case of interaction of manganese and

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silicone additions. They cause special physio-chemical and technological properties of the casts made from aluminium-silicone bronzes [5-7].

A heightened interest in special bronzes showing high resistance to mechanical and chemical wear creates favourable conditions for researching new materials, the influence of melting conditions and impurities and micro-additions on physio-chemical properties of the casts. A significant attention is paid to the issues of heat treatment and problems of special technologies of manufacturing casts from these alloys [1-5].

Manufacturing castings from chromium copper is connected with technological problems during melting and the process of preparing liquid metal, because, among other issues, there is a significant difference between the melting temperatures and specific gravities of the alloying elements (Cu and Cr). But the greatest difficulty is caused by their high affinity for oxygen [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. High shrinkage and the proclivity to create slag, which is difficult to remove, cause the appearance of shrinkage cavities and slag inclusions. The difficult technology of melting and casting copper and alloyed copper poses a set of challenges [1-5].

RESEARCHING COPPER CASTS

Copper castings 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 [1,3,6].

Nowadays, to remove impurities a range of elements with high affinity for oxygen is used, the most important of them being phosphorus, lithium, magnesium,

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boron and beryllium. Electrical conductivity was analysed with the help of SIGMA TEST 2.067. Strength parameters were tested on the machined samples cast into ceramic moulds. The microstructures were observed with the help of metallographic microscope of Nikon Eclipse LV150 type, with a magnification of 100 x - 500 x. The exemplary results for copper deoxidized with different agents are collated in Table 1.

No	Agent	Amount /%	Electrical con- ductivity / MS	Oxygen con- tent O ₂ / ppm
1	-	-	24	2260
2	Logas	0,15	54	73
3	CuP12	0,2	48	98
4	CuP12	0,3	55	34
5	Li	0,05	54	39
6	P3	0,5	55	93
7	ODM2	0,3	55	16
8	Kupmod 2B	0,2	53	24

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

The analysis of deoxidizing treatments shows varied influence of different agents, Phosphor introduced into the metal bath causes reduction of copper oxide(I) $5 \text{ Cu}_2\text{O} + 2 \text{ P} = \text{P}_2\text{O}_5 + 10 \text{ Cu}$ [3-5], and in the final stage it increases the fluidity of the liquid metal, which allows the slags, oxides and other impurities) to float to the surface of copper bath.

Introducing active lithium into the metal bath causes an intense reaction with oxygen in the deoxidizing process temperature, according to 2 Li + $\frac{1}{2}$ O₂ \rightarrow Li₂O; Li + $\frac{1}{2}$ H₂ \rightarrow LiH [4].

Strong deoxidizing properties of boron are connected with active binding of oxygen into an oxide, B_2O_3 oxide reacts with oxidized copper, creating $2Cu_2O \cdot B_2O_3$ [3-5].

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 Figure 1.

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.



Figure 1 Copper casting for power engineering

That is why various kinds of alloyed copper are used, including slight additions of, e,g, chromium, beryllium, iron, titanium and other elements. These alloys are characterised by relatively low technological properties and proclivity for casting defects, which lower their physiochemical properties.

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, 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 [7-14].

CASTING OF CHROMIUM COPPER

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.

copper							
Alloy	Deoxidation	/ MS	0 ₂ /ppm				
Cu	-	53	200				
CuCr 1,3	-	26	61				
CuCr 1,3	CuP	27	75				
CuCr1,5	-	24	-				
CuCr1,8	-	22	550				
CuCr1,8	Desof	24	50				
CuCr1,8	CuB ₂	23	65				
CuCr 2,16	-	22,5	-				
CuCr 2,16	Zr 0,2	20,5	-				
CuCr 216	Zr 0.2	20	-				

Table 2 The influence of zirconium, chromium anddeoxidation on electrical conductivity of chromium

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 [4-7]. Solution heat treatment causes lowering electrical conductivity to the value of 20 - 24 MS.

The second stage of heat treatment is ageing, Is 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 in 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 3).

Table 3 The influence of ageing on properties of chromium copper CuCr0,6

Time		Н	В		C	onduct	ivity / M	S
/ h	Ageing				Ageing			
	temperature / °C			temperature / °C				
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

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 silicon 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 4).

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 (Table 5).

Table 4 The influence of silicon additions on the CuNi2,1Cr0,6Si, cast into metal mould

No	Addition Si / %	<i>R</i> / MPa	HB	A ₅ /%	Conductivity / MS
0	0	148,4	55	48,8	34,0
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	9,0
4	2,2	355,8	164	6	6,5

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.

Table 5 Mechanical properties of the CuNi2Si0,8 alloy

Alloy state		/ MS	R _m / MPa	A ₅ /%	HV
CuNi2Si0,8	Lp	9,5	235	7,6	80
	Lk	15	380	15,2	91
	Lp-R6	16	320	3,2	118
	Lk-R6	13	600	2,5	148

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.

CONCLUSIONS

During the research it was established that:

- in copper and alloyed copper casting, the most important element is creating the optimal conditions of melting, together with limiting the contact with oxygen and hydrogen. During melting, the possibility of the bath coming in contact with impurities should be limited, through applying proper protective atmosphere and protective-refining slags,
- physio-chemical and functional properties of copper and alloyed copper casts depend on the efficiency of deoxidation treatments,
- additions of chromium and nickel lower the electrical conductivity of copper; the addition of silicon has a more adverse effect,
- silicon additions clearly improve technological properties of the materials researched, and, at the same time, their strength properties,
- applying modifying treatments causes slight improvement in the degree of grain size-reduction,
- there is a clear increase in strength parameters and electrical conductivity improvement after heat treatment of the alloys researched.

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