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STRUCTURE AND PROPERTIES RESEARCH OF CASTS MADE WITH COPPER ALLOYS MATRIX

BADANIA STRUKTURY I WŁAŚCIWOŚCI ODLEWÓW ZE STOPÓW NA OSNOWIE MIEDZI

The article presents the research results obtained at the Department of Foundry of Non-Ferrous Metals at the Foundry Faculty of AGH, the University of Science and Technology, in Krakow. The research comprises the processes connected with the technology of melting, refining and making casts based on copper matrix, both contemporary and historical, especially bronzes containing tin, zinc and lead. These issues are well-known but they still pose problems for contemporary foundries. The article presents the results of modifying formulas on the improvement of mechanical properties and limiting casting defects.
Keywords: copper, bronze, refining, modification

W artykule przedstawiono wyniki badań realizowanych w Pracowni Odlewnictwa Metali Nieżelaznych na Wydziale Odlewnictwa AGH w Krakowie. Badania obejmują procesy związane z technologią topienia, uszlachetniania oraz odlewania stopów na osnowie miedzi, zarówno współczesnych jak i historycznych, głównie brązów zawierających cynę, cynk i ołów. Poruszone zostały zagadnienia związane z procesem topienia oraz kształtowania struktury odlewów z miedzi. Problemy te znane są już od dawna, ale nadal stanowią aktualny problem współczesnych odlewni. Przedstawione zostały wyniki badań wpływu preparatów o charakterze modyfikującym na poprawę właściwości mechanicznych i ograniczenie wad odlewniczych.

1. Introduction

Copper alloys consist a group of materials used from the earliest stages of human civilisation, indispensable both in the technology development and artistic casting. Copper resulting from the old metallurgical processes, contained admixtures of other metals; still other additions were included purposefully to improve the alloy properties and broaden its range of applications [1-3].

Nowadays, copper alloys for industrial applications must be characterised by high mechanical properties, high strength sustained also in increased temperatures, resistivity to abrasion and corrosive agents; also high thermal and electrical conductivity. These properties result from a proper alloy composition as well as from a range of refining steps, such as de-oxidation, modification and others [4-8].

Researching the old metallurgical and copper foundry technologies on the bases of archival sources and historical works needs to be complemented with historical material analyses [3-6]. Archeological material was analysed quantitatively and qualitatively. For example, metallographic analyses were made using macro and microscopic observations, as well as with the help of scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS). Also, metallographic and strength tests were conducted, according to the EN-ISO 6892-1:2009 standard.

Exemplary test results of the chemical composition of the historical copper alloy casts, collated with contemporary copper casts, are presented in Table 1.

The results presented in the table prove a greatly varied content of impurities in individual copper samples. Contemporary copper products of highest quality contain minimal amount of impurities, whereas in non-alloyed copper finds there are significant amounts of lead, arsenic, antimony, sulphur, tin, zinc – up to 1%. Historical bronzes contain much bigger amounts of tin, lead, zinc and others. Exemplary micro-structures of the copper samples collated in Figure 1, show clearly the placement character of the admixtures. In the samples (Fig. 1a) they are visible as relatively big, coagulated intermetallic precipitates, whereas in the microstructures of contemporary copper of higher purity there are trace impurities of oxygen eutectics at the grain boundaries of pure copper (Fig. 1b). Such properties of copper microstructure result from a proper melting technology. A proper preparation of the melted metal guarantees good quality, also in the case of its alloys, that is bronzes and brasses.

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TABLE 1
Chemical analysis results of copper samples (wt%). K0, Ml, M7, P6, P7 (contemporary copper cast), G2-G3 (archeological samples), Bs, Ms1, Ms2 (historical casts)

Element	content(*wt%*)									
	KO	MI	M7	P6	P7	G2	G3	Bs	Ms1	Ms2
Cu	**99.97**	**99.93**	**99.94**	**99.87**	**99.88**	**98.96**	**99.00**	**83.41**	**79.98**	**88.47**
Zn	0.039	0.024	0.062	–	–	< 0.002	< 0.002	5.65	18.17	6.99
Pb	0.024	< 0.0039	< 0.004	0.009	0.004	0.837	0.809	2.41	1.26	1.24
Sn	0.026	0.012	0.014	–	–	0.108	0.068	5.06	0.59	0.28
P	< 0.0005	< 0.0001	< 0.0001	0.014	0.005	0.001	0.0005	–	–	–
Fe	0.025	0.0172	0.0229	0.002	–	0.004	0.014	1.12	–	0.19
Ni	0.004	< 0.0035	< 0.004	–	–	0.033	0.038	0.06	–	0.21
Mn	0.004	< 0.0005	< 0.0005	–	–	< 0.001	< 0.001	0.02	–	–
As	0.011	0.0038	0.0034	0.001	–	< 0.001	< 0.0017	0.2Sb	–	0.28Sb

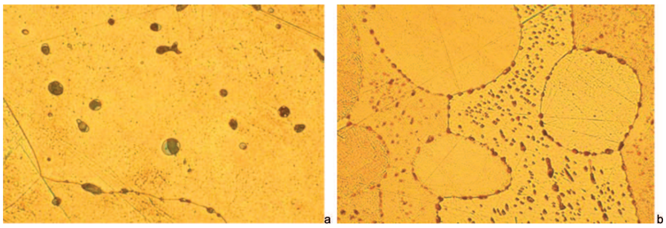

Fig. 1. Microstructure of historical copper cast (a) collated with contemporary copper (b). Magnification 1000x, etched

2. The influence of refining processes on the bronzes quality

At the next stage of research, the influence of refining molten metal bath on the structure of tin bronzes was analysed; the influence of chosen micro-additions of modifying and de-oxidising elements on the microstructure formation and the properties of copper matrix alloys was analysed.

At the final stages of solidification process, the presence of oxygen impurities causes intensified reactions with other impurities as a result of segregation phenomena. The final consequence of these reactions and the created gasses is an increase in porosity, because these gasses are arrested inside the casts. To avoid the consequences of this reaction it is necessary to de-oxidise the molten metal bath, before casting it into the mould. To this effect, with chosen tin bronzes, there were additions of such elements as phosphorus and magnesium used, in the amount of 0.02-0.1%, and sodium, calcium and lithium in the amount of 0.01-0.05% of the metal stock. Individual micro-additives were introduced as ready formulas in salt mixtures. During the analysis of the influence of some micro-additives, such as zirconium and boron, on the alloy structure, the effect of structure granularity was observed in the bronzes examined. The elements showing high chemical activity react with the impurities resulting in de-oxidation, or reacting with the alloy components they can become active nuclei causing changes in the primary structure of the alloys.

This paper presents exemplary results of the influence of the de-oxidising and modifying formulas on the structure and strength properties of the chosen tin bronzes (CuSn10P, CuSn10Zn and CuSn8Ni).

The metal stocks prepared during the laboratory research were refined after being melt, and then the samples were cast. Then, the chemical content of the alloy was analysed, as was its oxygen content, its structure and strength parameters.

The chosen results of this research is shown in Table 2.

TABLE 2
The influence of de-oxidising with various formulas on the strength parameters R_m (Mpa), A_5 (%) and oxygen content (ppm) in the CuSn8Ni microstructure

agent	agent content (%)	R_m (MPa)	A_5 (%)	O_2 (ppm)
–	–	281.2	9.5	110
–	–	262.6	10.6	54
CuPIO	0.05	318.0	12.8	34
Prep.-Li	0.03	309.8	18.4	21
Prep.OD-M2	0.03	322.5	16.8	24
Prep.ODM-B2	0.03	316.4	12.8	31
ODMB2	0.2	327.3	16.4	22
ODMBZ|	0.2	340.4	18.8	18

The influence of changeable additives of Kupmod B modifier on shaping the macrostructure of CuSn10Zn2 bronze is shown in Figure 2.

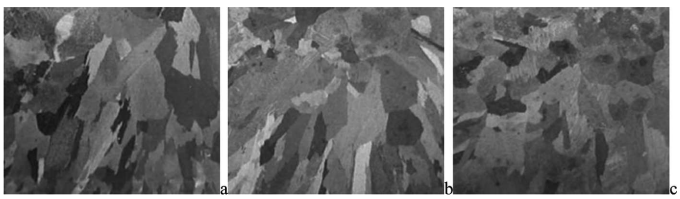

Fig. 2. CuSn10Zn2 bronze macrostructure. The initial alloy (a), after being modified by Kupmod B in the amount of 0.1% (b) and 0.2% of the metal stock mass (c)

The results of researching the influence of Kupmod modifier on the tensile strength R_m and elongation A_5 is presented in Tables 3 and 4 as well as graphically on the charts (Figure 3).

TABLE 3

Collation of results for the samples cast into a metal mould: the modifier addition (%), tensile strength R_m(MPa) and elongation A_5 (%)

bronze symbol	modifier	modifier addition (wt.%)	R_m (MPa)	A_5 (%)
CuSn10P	Kupmod B	–	343.6	8.6
		0.1	338.8	10.2
		0.2	342	11.4
		0.3	327.4	16
CuSn10Zn2	Kupmod B	-	265.3	10.2
		0.1	288.8	11.4
		0.2	302.4	16
		0.3	291.2	35
CuSn8Ni	Kupmod Z	-	258.8	18.2
		0.1	316.3	27.4
		0.2	364.2	32.0
		0.32	347.4	30.0

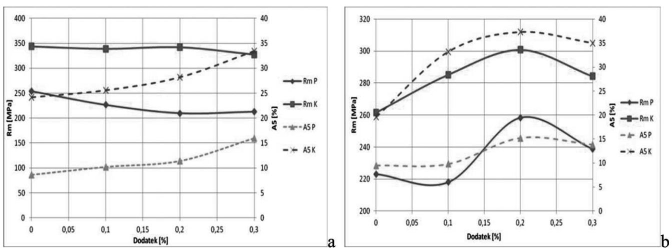

Fig. 3. Graphic representation of the CuSn10P(a) bronze and CuZn10Zn2(b) bronze; the samples cast into sand and metal moulds. Kupmod B modifier

TABLE 4

CuSn10P and CuSn10Zn2 alloys hardness, depending on the modifier

bronze symbol	modifier	modifier addition (wt.%)	HB
CuSn10P	Microsal	–	118.5
		0.1	126
		0.2	120.5
		0.4	115.7
CuSn10Zn2	Desofine	–	117
		0.05	112.5
		0.1	116.8
		0.2	117.4

The influence of different amounts of the modifier on the microstructure of the CuSn10Zn2 bronze alloy is shown in Figures 4 and 5.

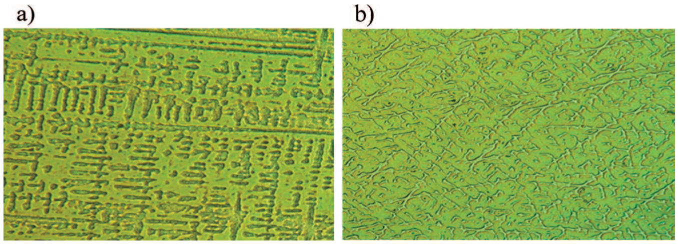

Fig. 4. CuSn10Zn2 bronze microstructure: initial alloy (a), after modification (b); Kupmod B modifier 0.2 % wt. magnification 200x

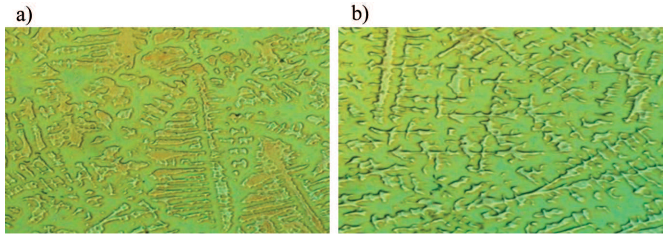

Fig. 5. CuSn10P bronze microstructure: initial alloy (a), after modification (b); Kupmod B modifier 0.2% wt. magnification 200x

The influence of modification on the CuSn8Ni macrostructure is presented in Figure 6.

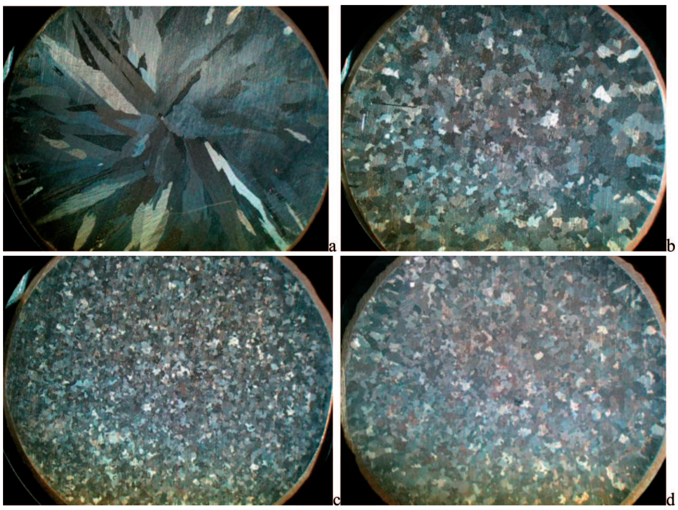

Fig. 6. CuSn8Ni ingot macro-structure cast into a metal mould without modification (a), after modification in the temperature of 1150°C with zirconium formula Kupmod Z, in the amount of 0.1% (b), 0.2% (c) and 0.3% (d) of the metal stock mass. Etched with a mixture of acids

Figure 7 shows changes in the micro-structure after the modification with the Kupmod Z formula.

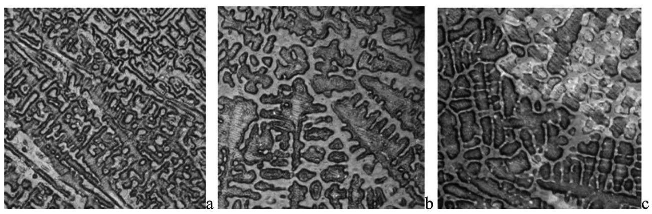

Fig. 7. CuSn8Ni bronze ingot micro-structure, cast into a metal mould before modification (a), after modification with Kupmod Z formula in the amount of 0.2% (b) and 0.3% of the metal stock weight (c). Magnification 300x, etched with a mixture of acids

3. Conclusions

Conducting metal relic research in a complex way – from historical, technological, metal science and corrosion angles – helps to increase our knowledge of foundry technology. From the comparison of chemical content of archeological and contemporary copper samples it can be concluded that the difference in copper contamination levels comes up to 1%. This testifies to a high level of knowledge and technology in the old copper smelters, and, at the same time, it shows how difficult it is to keep up the high level of copper purity. The modification process of bronzes with Kupmod type formulas causes changes in both macro- and microstructure; it changes solidification process from directional into volume-oriented one, which results in an increased tensile strength and plasticity. As a consequence, with more homogeneous microstructure, it improves the resistance to inter-crystalline fracturing.

In many cases, complex modifying formulas cause complex effects; often not only changing the initial structure of the alloys, but also the phenomena of alloy degassing, removing non-metallic inclusions and also neutralising some other impurities. In effect, applying modification formulas to copper alloys makes it possible to use bronzes for making complex shape casts effectively and efficiently.

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