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INFLUENCE OF REFINING OPERATIONS ON A STRUCTURE AND PROPERTIES OF COPPER AND ITS SELECTED ALLOYS

WPŁYW ZABIEGÓW USZLACHETNIAJĄCYCH NA STRUKTURĘ I WŁAŚCIWOŚCI MIEDZI I WYBRANYCH STOPÓW MIEDZI

The analysis of the refining effwctiveness of the liquid copper and selected copper alloys by various micro additions and special refining substances – was performed. Examinations of an influence of purifying, modifying and deoxidation operations performed in a metal bath on the properties of ceratin selected alloys based on copper matrix – were made.

Refining substances, protecting-purifying slag, deoxidation and modifying substances containing micro additions of such elements as: zirconium, boron, phosphor, sodium, lithium, or their compounds introduced in orfder to change micro structures and properties of alloys, were applied in examinations. A special attention was directed to macro and micro structures of alloys, thier tensile and elongation strength and hot-cracks sensitivity. Refining effects were estimated by comparing the effectiveness of micro structure changes with property changes of copper and its selected alloys from the group of tin bronzes.

Keywords: copper alloys, tin bronzes, refining processes, structures and propereties of alloys

W ramach badań poddano ocenie analizę skutechności procesów uszlachetniania ciekłej mie4dzi i wybranych stopów miedzi różnymi mikrodatkami i specjalnymi preparatami uszlachetniającymi. Przeprowadzono badania wpływu zabiegów rafinujących, modyfikujących lub odtleniających dokonanych w kąpieli metalowej na właściwości wybranych tworzyw na osnowie miedzi.

Do badań zastosowano preparaty uszlachetniające tj. żużle ochronno-rafinujące, preparaty odtleniające i modyfikujące, zawierające różn e mikrododatki pierwiastków m.in. cyrkonu, boru, fosforu, sodu, litu, lub ich związki w postaci specjalnych preparatów wprowadzonych w celu zmiany mikrostruktury i właściwości stopów. Szczególną uwagę skierowano na makro i mikrostrukturę stopów, na zmainy wytrzymałości na rozciąganie i wydłużenie oraz na skłonność do pęknięć na gorąco. Efekty uszlachetniania oceniono – porównując efektywność zmian w mikrostrukturze i zmian właściwości miedzi i wybranych stopów miedzi z grupy brązów cynowych.

1. Introduction

Within investigations of refining processes of liquid copper and the selected copper alloys performed by various micro additions and special refining compounds the analysis of influence of deoxidising and modifying elements on microstructure and mechanical properties of alloys made on the basis of copper – was carried on. Protecting and purifying slag was applied in copper alloys since, regardless of the quality of charge materials and a participation of own wastes, a problem of increasing amounts of wastes and contaminations in a metal bath appears.

To assure a repeatability of the remelted metal charges quality the refining and coating slag containing, among others, borax, carbonates and activating additives were applied in examinations. The selected compositions of protecting and purifying slag – from the point of view of interfacial tension for metal-slag-oxide – were verified to find the influence of the composition on metallurgical yield and strength properties of alloys remelted in contact with those kinds of slag. The basic purpose of protecting and purifying slag – in the melting technology of non ferrous metal alloys – is the protection of liquid metals or alloys against a furnace atmosphere as well as physical and chemical influence assuring removal of non metallic contaminations from a metal bath. Main alloy contaminations constitute non-metallic inclusions such as oxides, nitrates, carbides and oxide-hydrogen complexes. Remaining contaminations of copper alloys are hydrogen and oxygen present in a solution in phases and in a free form as blowholes.

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Continuing examinations of a modification and dendritic segregation of casting alloys (on a copper matrix) an influence of alloy components and micro additions of deoxidising and modifying elements on the microstructure and on mechanical properties of such alloys was investigated. A presence of oxygen contaminations causes – in the final stage of a solidification process – an increased reactivity with other contaminations. Gases and other contaminations causing a porosity increase – since they entrapped in internal layers of castings – are the effect of those reactions. To avoid such situations it is necessary to apply deoxidising of a metal bath before pouring liquid metal into casting moulds. In order to remove oxygen strong deoxidising agents should be used. Their selection should be based on a relatively large affinity to oxygen. In addition, this deoxidising substance should be used in a form which is easy to be introduced into a metal bath, deoxidation products should either evolve as vapours or easily enter slag, and a substance excess should not influence negatively properties of the alloy. Addition of such elements as phosphor and magnesium, (sometimes aluminium) in amounts of 0.1% and 0.5% of a metal charge respectively, are used in foundry practice for deoxidation of copper, certain bronzes and brasses. An excess of deoxidising substance increases an amount of gases and inclination for cracking. Positive results are also obtained by using sodium and lithium, however, in very small amounts (up to 0.05%). Other elements counted also as micro additions of modifying influence, such as e.g. zirconium and boron, characterised by a high chemical activity, react with contaminations such as oxygen, nitrogen and others providing a deoxidation. In many cases complex refining compounds cause often not only a change of the primary alloy structure but also phenomena of alloy degassing, removal of non metallic inclusions or neutralisation of certain contaminations [1, 2, 3, 4, 5, 6].

2. Examination method

An analysis of an influence effectiveness of the selected deoxidising and modifying substances on the structure and properties of copper and its alloys, among others tin bronze – was performed. Examinations were carried on in the Non Ferrous Metals Casting Laboratory. The metal charge was melted in an induction furnace in chamotte-graphite crucible of a capacity of 10 kg. During melting of copper or CuSn7Ni alloy a protecting and purifying slag was placed on the metal surface. After melting the bath was overheated and then deoxidation and modification performed. At the end the liquid metal was poured into moulds.

3. Testing of deoxidation intensity of copper and its alloys

The results of the deoxidation intensity tests of copper performed by means of deoxidation and modifying substances are listed in Table 1.

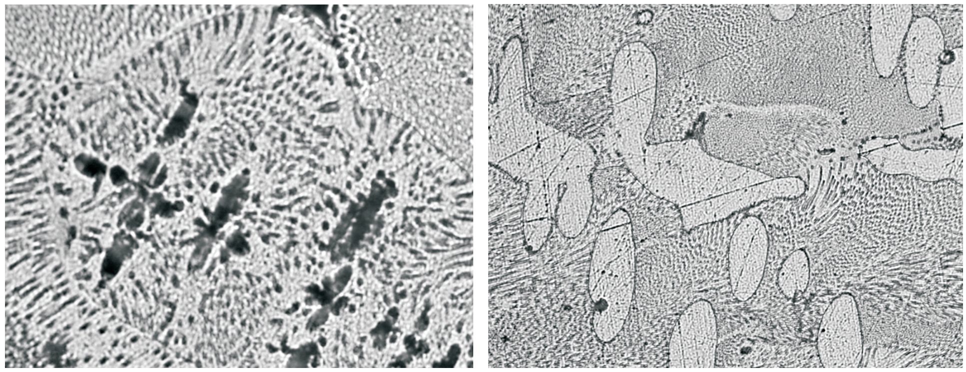
TABLE 1

Influence of deoxidation operations on oxygen content in copper

Substance	Amount of substance [%]	Time after operation	Oxygen content [ppm]	Remarks
–	–	–	5224	Oxidised charge
–	–	–	2129	melt., slag WB
CuP10	0.1	5 min	60	–
CuP10	0.2	5 min	31	
OMB2M	0.03	5 min	89	
OMB2M	0.1	15 min	22	
Kupmod 2B	0.03	5min	67	
OBC2	0.05	5 min	26	
OBZ4	0.05	5 min	33	

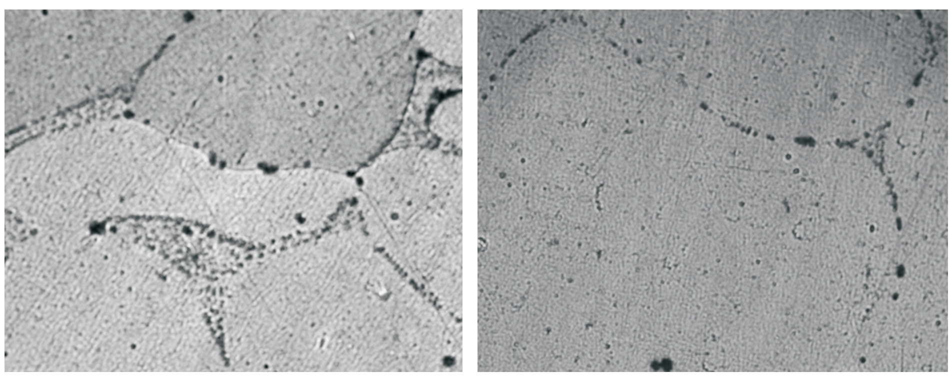
The results of oxygen content in copper were compared with the results of microstructure testing. Some examples are shown in Fig. 1-3.

Exhibited microstructures of copper castings – of a various content of oxygen eutectic – after deoxidising procedures indicate a relatively strong effect of deoxidising and modifying substances. Copper in its initial state contains oxygen eutectic in the whole field of view and hypereutectic precipitates of Cu_2O. After deoxidation the copper grains with very thin precipitates of Cu-Cu_2O eutectics in between copper crystallites – dominate in the structure.



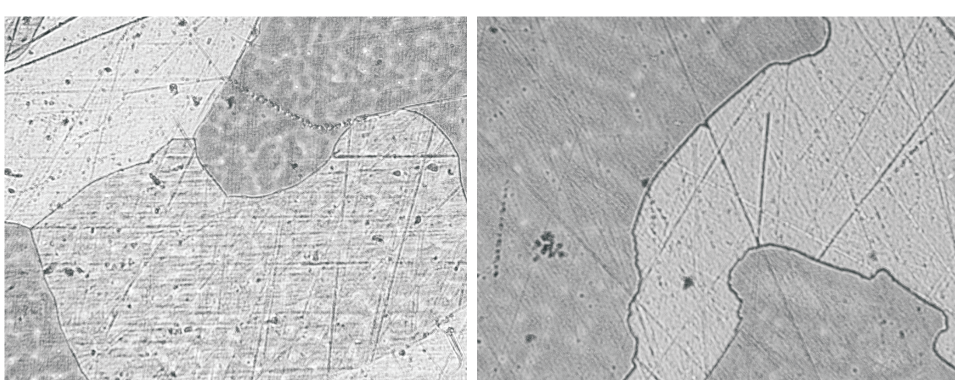
a) b)

Fig. 1. Microstructure of copper remelted under conditions of an oxidising atmosphere and cast into a metal mould. Oxygen content: (a) 5224 [ppm], (b) 4450 [ppm]. Etched by Mi15Cu reagent. Magnification 200x



a) b)

Fig. 2. Microstructure of copper remelted and cast into a metal mould after the deoxidising procedure performed by means of: (a) CuP10 substance (0.01‘%) – containing 1220 [ppm] of oxygen, (b) OMB2M substance (0.03%) – containing 89 ppm of oxygen (b). Magnification 200x. Etched by Mi15Cu reagent



a) b)

Fig. 3. Microstructure of copper remelted and cast into a metal mould after the deoxidising procedure performed by means of: (a) OBC2 substance (0.05%) – containing 26 [ppm] of oxygen, (b) OBZ4 substance (0.05%) – containing 33 [ppm] of oxygen. Magnification 200x. Etched by Mi15Cu reagent

4. Testing of CuSn7Ni bronze modification intensity

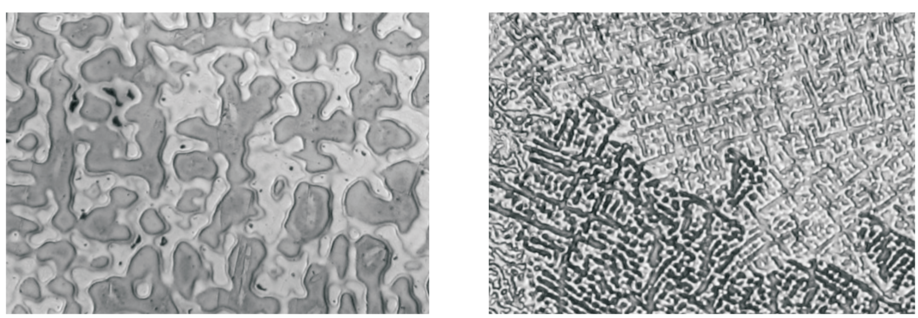
In subsequent castings the protecting and purifying slag was used for testing the structure and properties of CuSn7Ni bronze. Some examples of the results obtained for CuSn7Ni bronze are shown in Table 2.

TABLE 2

Influence of the refining performed by the selected substances on strength properties and a macrostructure of CuSn7Ni bronze

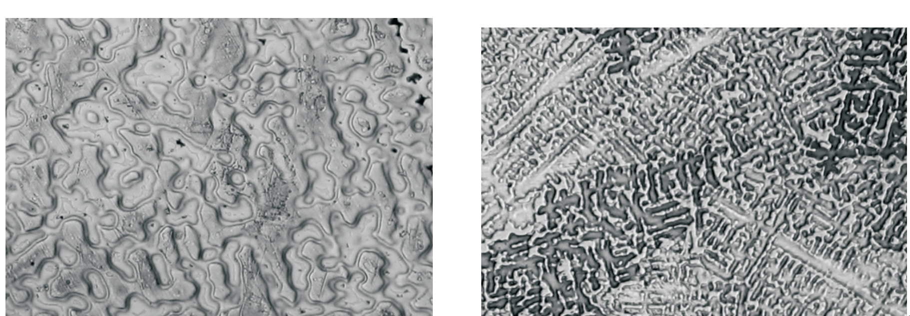
Modificator in [%] of a charge	R_m average [MPa]	A5 average [%]	Average number of grains in 1 [cm^2]
–	294	6.2	4
0.1% DSF	322	7.5	12
0.2% DSF	334	8.2	29
–	305	6.5	6
0.1% Kuprum 2	322	7.0	17
0.2% Kuprum 2	334	8.6	26
0.1% Kupmod 3	326	7.8	38
0.2% Kupmod 3	345	8.8	42
0.2% BZF4	319	9.0	43
0.3% BZF4	352	9.8	52

The results of metallographic examinations of CuSn7Ni bronze are presented in Figures 4 to 9.



a) b)

Fig. 4. Microstructure of CuSn7Ni bronze cast into a dried sand mould (a) and to a metal mould (b). Etched by Mi22Cu reagent. Magnification 100x



a) b)

Fig. 5. Microstructure of CuSn7Ni bronze after a modification by DSF substance (0.1 %) cast into a dried sand mould (a) and to a metal mould (b). Etched by Mi22Cu reagent. Magnification 100x

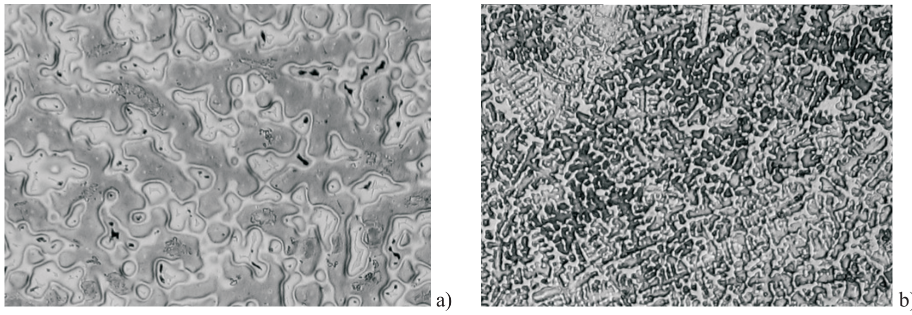


Fig. 6. Microstructure of CuSn7Ni bronze after a modification by DSF substance (0.2 %) cast into a dried sand mould (a) and to a metal mould (b). Etched by Mi22Cu reagent. Magnification 100x

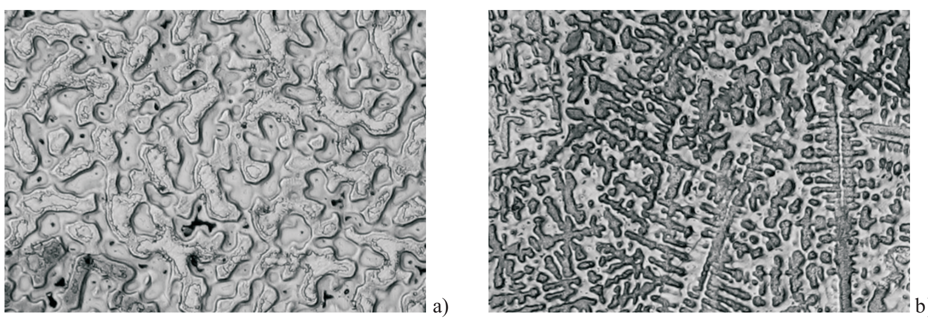


Fig. 7. Microstructure of CuSn7Ni bronze after a modification by Kuprum 2 substance (0.1 %) cast into a dried sand mould (a) and to a metal mould (c). Etched by Mi22Cu reagent. Magnification 100x

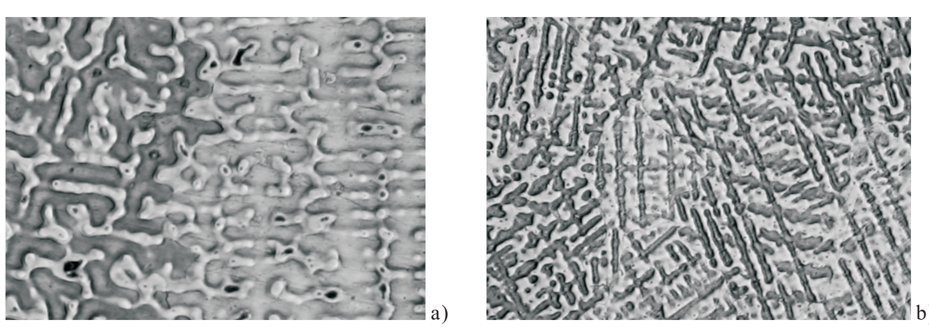
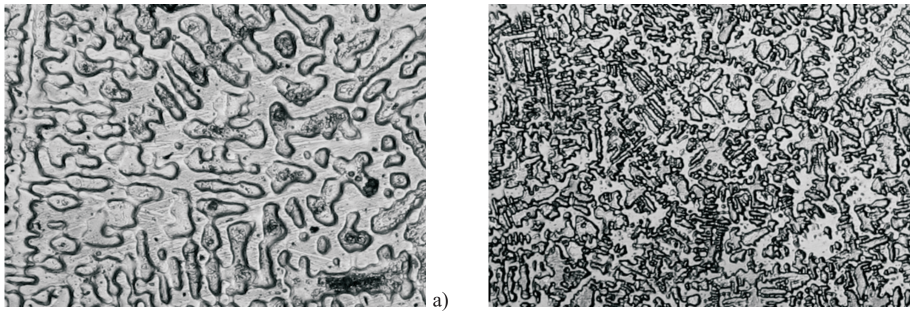


Fig. 8. Microstructure of CuSn7Ni bronze after a modification by Kuprum 2 substance (0.2 %) cast into a dried sand mould (a) and to a metal mould (c). Etched by Mi22Cu reagent. Magnification 100x



a) b)

Fig. 9. Microstructure of CuSn7Ni bronze after a modification by slag modifying substance BZF4 (0.3 %) cast into a dried sand mould (a) and to a metal mould (b). Etched by Mi22Cu reagent. Magnification 100x

5. Conclusions

The following conclusions can be suggested on the basis of examinations of the influence of refining substances of a deoxidising and modifying character:

- The effect of copper deoxidation performed by means of deoxidising or modifying substances is significant. Copper deoxidation by complex substances has quite intensive influence on a microstructure and oxygen content. In the microstructure of the remelted copper the primary precipitates of Cu_2O phase at the background of oxygen eutectic Cu-Cu_2O occur.
- Contents of an oxygen eutectic decreases significantly as the result of deoxidation of the eutectic mixture Cu_2O, and only small amounts of the Cu_2O phase in a form of very thin strips at the copper grains boundary remain.
- There is a relatively large intensity diversification when comparing influence of various modifying substances. However, it should be emphasised that BZF4 and Kupmod 3 substances have a strong modifying influence on the structure and strength properties of the tested bronze.
- Similarly a significant influence was observed in the case when the modifying substances of the DSF 2 type were used.
- It was also noted that the modifying substance of the BZF4 type containing nucleus formation elements exhibits some deoxidation properties and lowers a tendency for cracking in high temperatures. Also other modifying substances have a positive influence for hot-cracks.

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