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STRUCTURE ANALYSIS AND PROPERTIES OF UNLEADED BRASSES

ANALIZA STRUKTURY I WŁAŚCIWOŚCI MOSIĄDZÓW BEZOŁOWIOWYCH

The analysis of brasses regarding their microstructure, mechanical properties and ecological characteristics has been presented. The influence of characteristic alloying elements contained in the brasses and the possibilities of replacing them with other elements have been assessed. The paper contains the results of studies on the influence of chosen additional elements shaping the structure and properties of unleaded alloys based on Cu-Zn system as the matrix. The research aimed at determining the mechanism and the intensity of influence of such additives as tellurium and bismuth. The microstructures were investigated with the help of light microscopy and scanning electron microscopy with X-ray microanalysis (SEM-EDS) for determining significant changes of the properties.

Keywords: Environmental protection, unleaded brasses, alloying elements, mechanical properties, microstructure

Przedstawiono analizę mosiądzów w zakresie mikrostruktury, właściwości wytrzymałościowych oraz charakterystyki ekologicznej. Poddano ocenie wpływ charakterystycznych pierwiastków stopowych zawartych w mosiądzach i możliwości zastąpienia ich innymi. W pracy ujęto wyniki badań wpływu wybranych dodatkowych pierwiastków kształtujących strukturę i właściwości bezołowiowych stopów na osnowie układu Cu-Zn. Podjęte badania miały na celu określenie mechanizmu i intensywności oddziaływania dodatków takich jak: tellur i bizmut. Przeprowadzono badania mikrostruktur z wykorzystaniem mikroskopii świetlnej oraz mikroskopii skaningowej z mikroanalizą rentgenowską SEM-EDS, dla określenia istotnych zmian właściwości.

1. Introduction

The requirements of high quality regarding special brass casts impose the application of increasingly better, multicomponent alloys, containing different alloying elements which shape the special properties of the casts. At present, there are tendencies to limit some kinds of brasses and to introduce some others, which are more resistant to chemical and mechanical wear and more environmentally friendly. To these efforts also belongs researching the effects of introducing different alloying elements, which enhance ecological aspect of the materials, their resistance to dezincification, resistance to corrosion or improving the strength properties and technological parameters of the alloys, and sometimes even the improvement of surface and workability.

Constraints appear mainly with regard to lead as an alloying additive in brasses, because of its toxicity. The much-discussed [1-7] issue of replacing lead with bismuth has not been widely accepted yet in engineering, in spite of its good ecological characteristics and clearly similar influence on the structure and properties of the alloys. Also, rational criteria of using such elements as tellurium, arsenic and others are discussed [5]. Regarding the structure of the brasses, good strengthening possibilities are connected with the application of nickel and manganese as alloying elements, with some reservations concerning nickel as a harmful element. The alternative is using manganese or cobalt as a strengthening component of the alloy.

As part of the research, feasibility study was conducted on using the chosen elements in the Cu-Zn matrix alloys, and the practical benefits of their application were assessed. The assessment of limitations of structure shaping and special properties of the alloys aims at analysing the possibility of using lead-free brasses, the alloys containing bismuth and tellurium additions.

In Poland the most popular are common brasses, called 'leaded' – CuZn39Pb2 (MO59), CuZn38Pb2 (MO60), which according to the standards (PN-H-87026:1991; PN-EN 1982:2010) are used for production of fittings and fixtures. In the case of special fittings production technologies, there are also fitting brasses of the MOA and MOS types used [1-3, 8-10]. Most of these alloys used for production of fittings contain 1÷3% Pb.

The presence of lead in the alloys creates a hazard of contamination, which can happen during:

- melting, and especially during superheating and casting of fitting brasses, as a result of emission of lead vapours;
- in the process of casting of the fittings, through lead tran-

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sition to the core compounds and subsequent washing the lead out from the stored scrap material to the groundwater;
- during exploitation of the house fittings as the result of washing the lead particles by water stream from the outside surface of the elements.

Lead causes many toxic effects but, despite that, the attempts at replacing it with other elements in brasses used for fittings are not quite successful, because of:

- significant price differences between the elements such as bismuth and tellurium in comparison to lead (lead is the cheapest metal),
- a less effective influence on workability and chip character during machining,
- other influence mechanisms of different elements,
- other methods preventing solving of lead contained in the casts in the environments with low pH.

The results of comparative analysis of the influence of lead, tellurium and bismuth show: a different character of the phase arrangement in the microstructure, similar influence during the machining tests, different resistance to corrosion and different strengthening effects.

By using optimal alloying additives it is possible to obtain brasses with high mechanical, technological and utilitarian properties.

1.1. Washing out of lead from core compounds

The hazard of lead pollution resulting from lead particles transition form the alloy to core compounds and to the dusts coming from the cleaning and grinding shops was shown in the studies [3,9,11]. The level of washed-out lead and other heavy metals was assessed by testing the used core compounds coming from mould cores filled with leaded brass. The cores made in hot-box technology, were placed in a metal mould, heated to 185÷ 190°C, and next the mould was filled with molten MOS alloy containing 62,1% Cu, 0,9% Pb, 0,25% Al, 0,12% Sn, 0,001% Si, 0,0007% P, 0,001% Mn, 0,002% Ni and the rest of Zn.

The samples for assessing the erosion degree of lead and also of other heavy metals, such as zinc, cadmium and copper, were prepared according to a standard procedure, preserving the mass; liquid proportion of 1:10. The tests conducted using the stripping voltamperometric method showed the condensation of:

– Pb in the filtrate – 0,06 mg/dm^3,
– Cu in the filtrate – 0,06 mg/dm^3,
– Zn in the filtrate – 1,83 mg/dm^3,
– Cd in the filtrate – <0,003 mg/dm^3.

The core compound contamination with lead is comparatively low, but it can be significantly higher in case of a higher lead concentration in alloys and casts of higher mass, solidifying with lower speed [3,9,11].

1.2. Washing out of lead during the exploitation of fittings and fixtures

The ecological issues arising during the exploitation of the house fittings made from brasses containing lead, were discussed and analysed in several works [3,4,12].

The probability of lead being dissolved and washed out from fitting alloy is very low, even more so, because during the exploitation the surface in direct contact with running water is efficiently covered with a layer of mineral deposits. Lead is difficult to solve in alkaline environments, that is why there are formulas used that increase the pH of water (e.g. the addition of Ca^{2+} ions). In effect, very soon the direct transfer of brass lead into the water stream is inhibited [13].

A variety of corrosion in high-zinc brasses is the phenomenon of dezincification. One of the methods of increasing the resistivity to dezincification is applying small additions of arsenic into the brass [5]. In two-phases $\alpha + \beta$‘ casting brasses, containing a high proportion of the β‘ phase, the use of arsenic is not effective, and increasing the copper content too much clearly decreases the casting properties. Besides, arsenic creates toxic compounds and accumulates in the human body, which causes poisoning even with low dosage.

1.3. Other investigation methods concerning the chemical content choice in brasses

During the research, the influence of other elements replacing the lead addition, such as, e.g. bismuth, tellurium, indium, tin and antimony was analysed.

Comparative analyses were conducted based on the example of alloys with similar chemical composition to fitting alloys of MOA type, which are currently used in the production but not containing lead [4,5,8,10,14-16].

The exemplary research of the bismuth and tellurium influence on the strength properties and workability of brass Cu-Zn was conducted in many research studies [1,3,9,17-18]. As a brass workability criterium, the changes of chip shape coefficient were accepted and the changes of the chips apparent density indicator obtained from a machineability test. The increasing values of the indicators are the measure of increasing workability. According to the obtained results, the added elements significantly decrease the strength properties and they greatly improve workability. The chip shape indicator changes from about 0.5 for the initial alloy to about 0.9 for the alloys with bismuth additives. Similarly, after introducing the addition of bismuth, the value of apparent density increases, which can be a workability indicator. The influence of bismuth and tellurium on the Cu-Zn36-Al brass workability is comparable to the influence of lead. Other elements have less influence.

From an environmental protection point of view, the best equivalent of lead can be bismuth as an element of law toxicity for the human body and the environment.

Another direction of ecological research of new brasses is reflected in studying the silicon, manganese-silicon and low-zinc brasses. An example here can be the brasses of C87800 types – Cu-Zn14-Si3.8 or C87420M – Cu-Zn15-Si2.2-Sb0.3-Fe0.12 [8,10,14].

1.4. Vapour emissions during melting

The research of the concentration level of lead in the direct vicinity of the furnace during melting and overheating of brass for fittings containing 1.5% of Pb showed a very insignificant content of lead vapours, with a simultaneous relatively high concentration of zinc vapours. The contamination with lead of the laboratory area around the furnace was assessed as insignificant because of low lead concentration in the alloy, incomparable to the zinc content. Nevertheless, there was a trace contamination of the furnace area with lead and the presence of significant amounts of zinc vapours. Zinc vapours are dangerous for health. In industry, remelting of brasses and bronzes in induction and flame furnaces causes emissions of dusts containing heavy metals, including about 0,06% of lead [3,9,11].

2. Methodology and research conditions

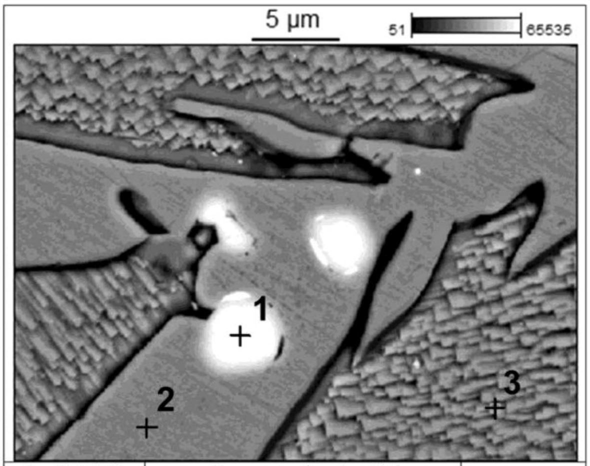
The alloys were melted in an induction thyristor furnace of medium frequency with chamotte- graphite crucible. As the charge, the following materials were used: electrolytic cathode copper in the form of sheets (min. 99.99% Cu, according to PN-EN 1978:2000), electrolytic zinc, bismuth, tellurium and lead, according to PN-EN 1179:2005. During the melting, protective refining slags were placed on the surface of charge. Next, the alloying additions were introduced, the bath was overheated and next the molten alloy was cast into the moulds. From the casts obtained in this way the samples for research were prepared.

The analysis included metallographic studies with the use of light microscopy, scanning microscopy with X-ray analysis SEM-EDS and the tests of basic strength properties.

3. The tellurium influence on the microstructure and properties of CuZn alloys

For research, the initial alloys with the phase structure of α/β (Cu-Zn44) and β'/γ (Cu-Zn52) were chosen, applying varied additions of tellurium and bismuth.

The microstructure tests showed that the addition of tellurium changes the conditions of peritectic transformation in the alloys analysed, and it limits the amount of γ phase at the grain boundaries and also inside the grain. In searching for the mechanism of these changes, X-ray analysis can be applied to determine the phases visible (Fig. 1).



Cu-Zn44-Te	Concentration [wt.%]			Phase
No	Cu	Zn	Te	
1	-	33.05	66.95	ZnTe
2	62.41	37.59	-	α
3	56.32	43.68	-	β'

Fig. 1. Microstructure of Cu-Zn52-Te sample, with chemical content analysis in microareas (SEM-EDS)

The conclusions made about the mechanism of γ phase disappearance based on metallographic tests are confirmed by the scanning research results. Fine, light precipitates on the background of β' and γ phases showed, that the chemical content of these precipitates is consistent with the Zn-Te equilibrium diagram. The microareas analysis points to the presence of intermetallic ZnTe phase. Combining some amount of zinc in the zinc-tellurium phase results in shifting the equilibrium diagram towards smaller zinc contents and thereby the limitation of precipitation of the hard and brittle γ phase.

The intermetallic phases created in the microstructure, with tellurium content of about 2%, cause a distinct increase in tensile strength and plasticity (Fig. 2).

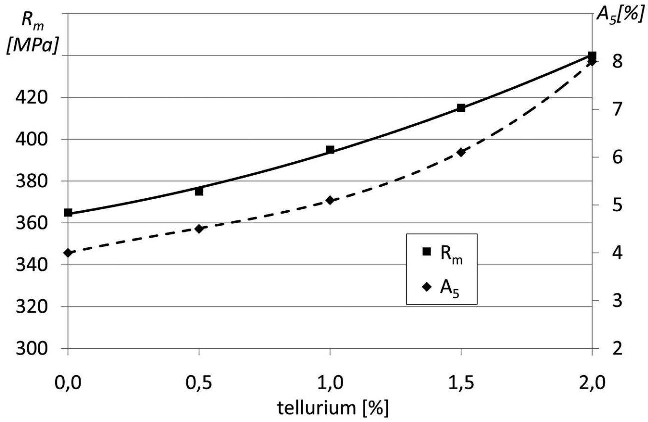


Fig. 2. Tellurium influence on the Cu-Zn52 alloy properties

In the case of the alloys with higher zinc content Cu-Zn52, tellurium additions (up to 2%) increased tensile strength R_m by 70 MPa, and the elongation A_5 from 4 to 8%. Its effect on hardness is slight and rather varied. With the tellurium addition of up to about 0.5% the hardness of the alloy under investigation increases, but beyond the addition of 1.5% the hardness of the alloy tested decreases.

The explanation for this diversification can result form the way the γ phase is affected by tellurium, which binds some of the zinc to create the intermetallic phase ZnTe. In step with increasing the tellurium addition, there appear intermetallic phase precipitates ZnTe and they cause hardening of the alloy, and with a higher dosage (2% of Te), tellurium stronger affects the disappearance of γ phase than it works by hardening the material through creating a phase with zinc.

Continuing the research with the aim of finding so called 'lead replacements' in order to improve the machineability of the tested Cu-Zn alloys, the machineability tests were conducted for Cu-Zn alloys with varied tellurium additions.

4. Influence of bismuth on the microstructure and properties of CuZn alloys

As part of the research, the influence of bismuth on the brass properties of the chosen Cu-Zn alloys was analysed. As an alternative for lead bismuth was used within the range of 0÷4%. Two alloys with characteristic microstructure, this is $\beta'+\gamma$ and $\alpha+\beta'$, were chosen for the tests.

Bismuth introduced into the brass analysed, precipitates as globular or elongated oval forms, which are uniformly spaced on the whole surface, with slight predominance at the grain boundaries. This kind of form and distribution of bismuth in brass is similar to lead precipitates in bathroom fittings and fixtures.

Increasing the bismuth addition to about 1%, in the microstructure there appear very fine, light precipitates within both brass phases (Fig. 3-5).

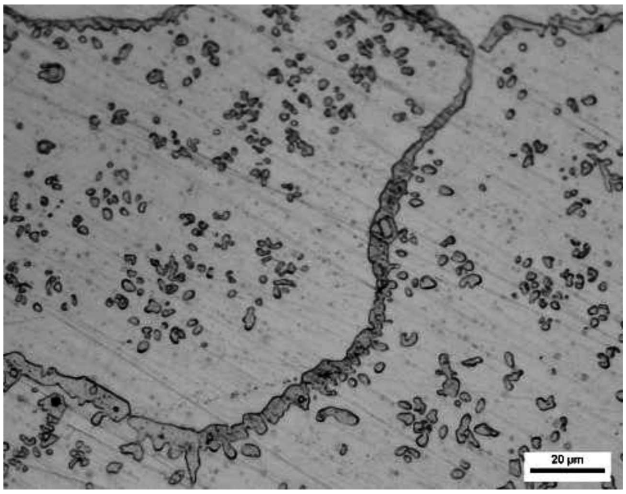
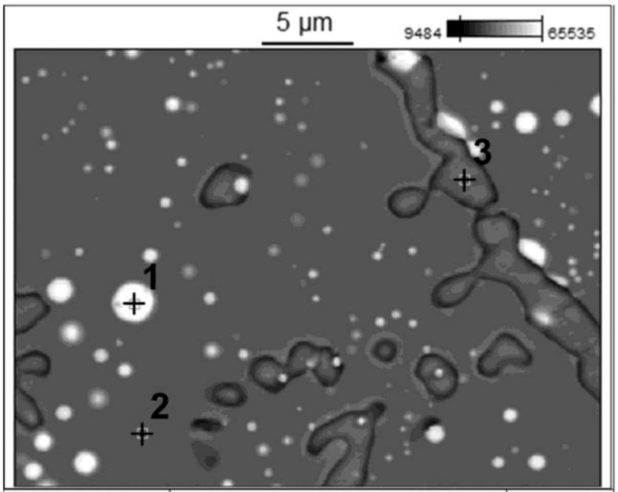


Fig. 3. β'+γ microstructure of Cu-Zn52-Bi4 alloy, 500x

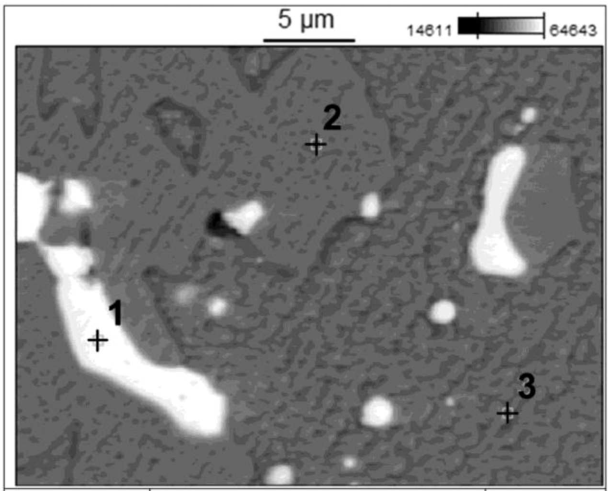
The X-ray microanalysis of the phases visible allows to conclude that the matrix of Cu-Zn52-Bi4 brass is made of β' phase with the precipitates of γ phase, and against the background of these, there are light, bismuth precipitates with slight participation of copper and zinc.



Cu-Zn52-Bi4	Concentration [wt.%]			Phase
No	Cu	Zn	Bi	
1	5.75	6.03	88.22	
2	51.69	48.31	-	β'
3	43.00	57.01	-	γ

Fig. 4. Microstructure of Cu-Zn52-Bi4 sample with chemical content analysis in microareas (SEM/EDS)

Analysing the test results concerning the influence of bismuth additions on microstructure and properties of brasses it can be ascertained that in the microstructure there are fine, globular bismuth precipitates (white) against the β' phase and the precipitates of γ phase. The picture of the sample surface (SE) points unequivocally to the uniform distribution of globular bismuth precipitates throughout the whole surface that was analysed. The hardness tests showed, that the addition of 2% of bismuth causes slight decrease in hardness of the alloys analysed.



Cu-Zn44-Bi	Concentration [wt.%]			Phase
No	Cu	Zn	Bi	
1	4.62	3.23	92.15	Bi
2	62.13	37.87	-	α
3	54.69	45.32	-	β'

Fig. 5. Microstructure of Cu-Zn44-Bi2 sample with chemical content analysis in microareas (SEM/EDS)

The research conducted, in line with the Keep-Bauer method that was adopted, allowed to show a positive effect of the bismuth and tellurium additions used in Cu-Zn alloys for the speed of hole drilling with constant advancing force [16-18]. From the obtained results the cutting speed was determined, which is shown in Table 1.

TABLE 1

Exemplary influence of variable additions of tellurium, bismuth and lead on machineability of the chosen Cu-Zn alloys

Addition share [%]	0	0.5	1	1.5	2	3
	Cutting speed [mm/s]					
Cu-Zn44-Te	0.35	0.40	0.58	0.70	0.85	–
Cu-Zn52-Te	0.80	0.90	0.96	1.00	1.28	–
Cu-Zn44-Bi	0.30	1.08	1.55	1.75	1.93	–
Cu-Zn52-Bi	0.81	1.05	1.24	1.38	1.23	–
Cu-Zn44-Pb	0.40	1.24	–	–	1.75	1.60

From the standpoint of mechanical working, the form and shape of chips resulting from machining process are important. The examples of chips resulting from conducting the machining tests by drilling with constant advancing force are presented in Figures 6-7.

The additions of bismuth used in the tests cause shortening of the length of helical chips. In the Cu-Zn alloys with 4% of bismuth addition, the resulting chips are light, with small dimensions.

Fig. 6. Form of Cu-Zn44 alloy chips

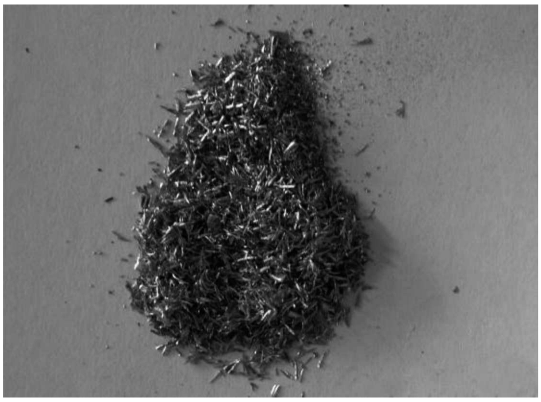


Fig. 7. Form of Cu-Zn44-Bi4 alloy chips

5. Summary of the research results and conclusions

Based on the research conducted and the industrial experiments, it can be concluded that:

- in the light of discussions on lead-related hazards, it is advisable to replace it with other elements, e.g. bismuth;
- many of the currently used fittings and fixture brasses do not meet technological or ecological criteria;
- bismuth introduced into Cu-Zn44 and Cu-Zn52 alloys appears in the microstructure in the form of globular or elongated precipitates throughout the whole surface of the intersection, which is advantageous for machining properties because the chips break; at the same time the uniform, dispersive bismuth precipitations do not lower the strength properties of the alloys analysed;
- tellurium additions change the structure of brasses, causing the γ phase to disappear through binding a part of zinc inside the ZnTe intermetallic phases. The precipitations of ZnTe phases show a more beneficial influence on the properties of the analysed brasses in comparison to the rich in γ phase low-copper brasses.

From the perspective of mechanical working, the form and shape of the chips resulting from machining process is important. The applied additions of bismuth and tellurium cause distinct shortening of the helical chips length and they improve workability. With regard to environmental issues, in line with the 2006/11 WE directive, eliminating harmful elements is recommended, among others tellurium and lead, from the water environment. In connection with the above-mentioned facts, a prospective alloying element is bismuth.

In spite of a significant volume of research on replacing lead in brasses, which suggests making casts from unleaded brasses, in reality the casting industry is unwilling to embrace the suggestions to change the content of these alloys.

The experience of producing brass points to the necessity to choose charge materials very carefully and thoroughly analyse various impurities present in brasses. It seems worthwhile to further research the issue of lead replacements and disseminating the research results.

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