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Structure and properties of new ecological copper alloys for fittings

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Abstract

The article presents the results of studies concerning the selection of the chemical composition of the new ecological copper alloys for fittings. It was analyzed, among other things, the impact of the content of bismuth, aluminum, iron and boron. Their solidification process was characterized on the grounds of thermal and derivative analysis (TDA). Also the microstructure and mechanical properties were analyzed. Casting properties were determined by the castability spiral test. It was found that zinc is an essential component of the tested group of alloys, determining the course of their crystallization, phase composition and microstructure. There was no significant effect from the other elements on the course of crystallization. The obtained results revealed that bismuth is the element of the strongest impact on the castability changes. The formulated alloys surpass the commonly used standardized alloy intended for components of fittings, namely MO59, in terms of casting and mechanical (hardness) properties.

Keywords: Innovative casting materials and technologies, Ecological brass, TDA, Castability, Microstructure

1. Introduction

The strong emphasis on ecological activities, observed in recent years, enforces the need to reduce or completely eliminate certain harmful substances, including lead, from the industrial practice. These activities were directly reflected in the legislation of legal acts regulating the allowable emission standards. One of the existing national documents of this type is the National Strategy for Reduction of Emissions of Heavy Metals, developed by the Ministry of Environment in 2002. This document includes the restriction of the use of harmful elements (lead, cadmium, mercury), among others in the metallurgy of nonferrous metals and processes used in non-ferrous metals industry [1].

The need to eliminate lead-containing copper alloys results from two main reasons related to this element emission to the environment. The first and most important results from the widespread use of these materials on the components of water systems, including those intended for drinking water transfer. The second is associated with a strong emission of lead vapors and dust during the process of melting and casting, as well as waste such as molding sand generated after the process [2].

Ever increasing limitations in the scope of drinking water purity resulted in the adoption of stringent quality requirements, and thus drew attention to the fittings made of copper alloys containing lead additive. In the result thereof the USA Congress has introduced the amendments to the Safe Drinking Water Act (SWDA) in force, which concerned the limitation of application of certain materials intended for water supply system fittings to lead-free materials. Also in Europe the restrictions on the allowable amount of lead in drinking water have been introduced. Currently, the European Union Directive 98/83/EC [2÷4] applies, which limits the allowable lead content in drinking water to 25 μg/l, from 1 January 2006. At the same time the allowable selenium content is 10 μg/l and the copper content is 2 mg/l. This directive provides for further limitations on lead content to 10 μg/l to be introduced from 2013. These provisions have been implemented into the scope of the Act on collective water supply and wastewater removal. Thus, our limitations in force are far less restrictive for a while.

Addressing the issue of drastic reduction of lead emissions into the environment, in relation to drinking water and atmosphere during production, can be achieved through various activities, namely:

- formulation of the copper alloys, in which the addition of lead would be replaced by another element,
- significant reduction of lead content in used copper alloys, while maintaining the required performance characteristics,
- introduction of other casting copper alloys to replace the currently used alloys containing lead,
- application of additional treatment technologies during melting the alloys, which would reduce lead emissions.

The literature analysis [2, 5÷6] shows that it is possible to replace lead by another ingredient that should meet the following criteria:

- posses sufficient solubility in copper in the liquid state,
- show low solubility in copper in the solid state,
- be characterized by the presence of low melting eutectic (mono-eutectic),
- should not form intermetallic phases with copper,
- should be characterized by availability and relatively low price.

Analysis of the possibility of using the elements other than Pb indicates [2, 6÷7] that these criteria are met by such components as: mercury, bismuth, and to a lesser extent, sulfur, selenium and tellurium. Due to the strong toxicity of mercury it can not be used for these purposes, while selenium, tellurium and sulfur are used as additives improving the machinability. Among these elements, the most advantageous seems to be bismuth, which is confirmed by the results of published studies [8÷9]. The test results of CuSn3Zn8 bronze with Bi and Pb additive contained in [7] indicate a strong similarity of both the microstructure and properties of these alloys, and thus the possibility of full replacement of lead additive with bismuth. The tests carried out for CuZn39Pb2 and CuZn39Bi2 [8] also confirmed the possibility of using Bi additive in place of lead, being found that it causes also the improvement of mechanical properties and machinability, and allows for more fine-grained microstructure.

Based on the analysis of literature and own experiences a group of copper alloys with low lead content and lead-free ones was formulated, by replacing it with the addition of bismuth.

2. Materials and methodology

The alloys from Cu-Zn-Bi system were selected to tests, which were the basic material for further composition modifications. As alloy additives the following elements were applied: Fe, Al, Sn, P, B, Ni and Pb. MO59 (CuZn39Pb2) brass was used as a comparative alloy. The assumed chemical composition is shown in Table 1.

Alloys were prepared by melting and casting in the induction crucible furnace with a capacity of 10 kg Cu. Batch materials were copper, zinc, tin, lead, bismuth of technical purity, and initial alloys in the grades: CuP14, 7; CuFe20; CuNi8; CuAl50, CuB2 obtained in the Casting Laboratory of the Institute of Non-Ferrous Metals.

Table 1.
Nominal chemical composition, % wt.

Alloy grade	Cu	Zn	Fe	Al	Sn	P	Bi	B	Ni	Pb
CuZnBi1,8	rest	36	0,3	0,6	0,2	0,1	1,8	-	0,3	-
CuZnBi2,2		36	0,3	0,6	0,2	0,1	2,2	-	0,3	-
CuZnBi1,8Pb		36	0,3	0,6	0,2	0,1	1,8	-	0,3	0,5
CuZnBi2,2Pb		36	0,3	0,6	0,2	0,1	2,2	-	0,3	0,5
CuZnBi1,8B		36	0,3	0,6	0,2	0,1	1,8	0,05	0,3	-
CuZnBi2,2B		36	0,3	0,6	0,2	0,1	2,2	0,05	0,3	-
CuZnBi1,8BPb		36	0,3	0,6	0,2	0,1	1,8	0,05	0,3	0,5
CuZnBi2,2BPb		36	0,3	0,6	0,2	0,1	2,2	0,05	0,3	0,5

Alloys overheated to a temperature from the range of 1040÷1080°C were poured into cast iron molds. The cast iron molds were pre-heated to a temperature of approximately 350°C. The ingots were obtained in the form of bars with a diameter of ø 12, 20 and 40 mm, h = 300 mm. The remaining material was cast in the form of blocks. A detailed chemical composition of the obtained alloys is given in Table 2. The analysis of results of these tests shows that the content of elements is consistent with the assumed composition, which proves the right choice of batch material recipes. At the stage of casting the alloys, also the castability tests were made by pouring into the spiral shaped shell molds.

Table 2.
Results of chemical composition analysis (% wt.) of obtained alloys

Alloy grade	Cu	Zn	Fe	Al	Sn	P	Bi	B	Ni	Pb
CuZnBi1,8	rest	34,6	0,27	0,57	0,21	0,06	1,84	-	0,29	-
CuZnBi2,2		34,4	0,28	0,57	0,19	0,06	2,36	-	0,29	-
CuZnBi1,8Pb		35,8	0,70	0,59	0,33	0,08	1,86	-	0,32	0,66
CuZnBi2,2Pb		35,9	0,41	0,57	<0,15	0,07	2,36	-	0,32	0,61
CuZnBi1,8B		34,6	0,10	0,64	0,22	0,06	1,88	0,02	0,29	-
CuZnBi2,2B		34,7	0,13	0,60	0,24	0,06	2,20	0,03	0,28	-
CuZnBi1,8BPb		36,1	0,36	0,58	0,33	0,08	1,89	0,019	0,31	0,72
CuZnBi2,2BPb		35,4	0,37	0,58	0,31	0,08	2,33	0,02	0,31	0,67

To assess the course of solidification of the newly formulated alloys the method of thermal and derivative analysis (TDA) [10÷12] was employed. To this end the control and measuring instrument "Crystaldigraf NT3-8K" was used. The thermal effects associated with the secretion of the crystallization heat during solidification of alloys were registered in the form of solidification diagrams showing the solidification temperature changes as a function of time T = f (t) and the rate of temperature changes T'= dT/dt.

The structure characteristic was made using the light microscope Olympus GX71F. Evaluation of mechanical properties was based on the Brinell hardness tests using a ball with a diameter of 2.5 mm and 612.9 N load.

3. Results and discussion

In order to determine the solidification parameters of the tested alloys the TDA analysis was performed. The liquid alloy was cast into a standard sampler, in which a thermocouple was mounted, connected to Crystaldigraf NT3-8K. The casting temperature of the tested alloys amounted to about 1050°C. The characteristic points determined on the differential curve of crystallization after their projection onto the solidification curve have determined the values of temperatures that characterize the successive stages of solidification of tested alloys, namely.:

- maximum temperature (point A),
- first crystals formation temperature T_{lik} (point B),
- crystallization completion temperature T_{sol} (point C).

Sample results of TDA analysis covering graph T = f (t) with first derivative dT / dt with plotted characteristic points are shown in Figures 1 and 2. In addition, Table 3 presents the results of the characteristic points of a selected group of alloys.

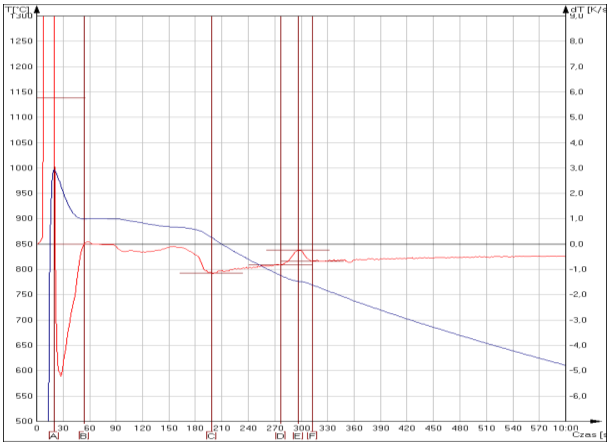

Fig. 1. TDA diagram of CuZnBi2,2 alloy

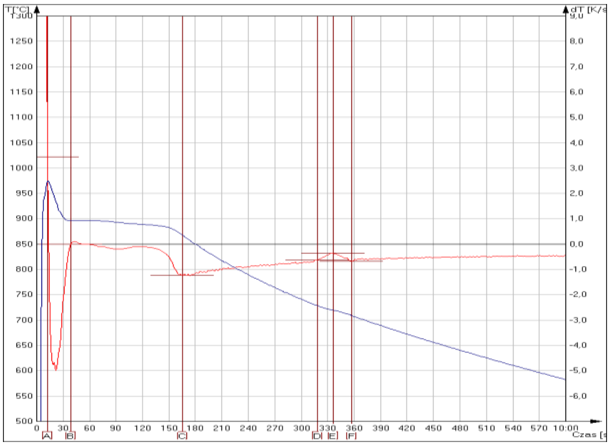

Fig. 2. TDA diagram of CuZnBi2,2Pb alloy

It was found that zinc is the most important component affecting the course of solidification, phase composition and microstructure. In the obtained alloys (Fig. 1, 2) the differences in the temperature of the first crystal formation are insignificant and amount to about 4°C. These differences are correlated with changes in zinc content.

A greater zinc content (35.9% wt.) affects T_{liq} temperature decrease. Similar differences were recorded for T_{sol} temperature. Other constituent components of alloys do not affect the solidification parameters.

In the course of derivatives (Fig. 1, 2) at the temperatures of 777°C and 720°C for CuZnBi2,2 (Fig. 1) and CuZnBi2,2Pb (Fig. 2) respectively, the thermal effects are observed in the solid state. Probably these effects are related to the secretion of β phase from supercooled solid solution α (zinc in copper). The confirmation of this fact can be the Cu-Zn [13] phase equilibrium system, where at the zinc content of > 35% wt., in the temperature range from 902 to 454°C, one can observe the occurrence of the two-phase area: α + β. Additionally, the increase in the range of occurrence of that area is influenced by the presence of aluminum [14].

Table 3.
Results of TDA analysis of tested alloys

Alloy	T_{max}, °C	T_{liq} °C	T_{sol} °C	T_{β} °C
CuZnBi2,2	997	900	863	777
CuZnBi2,2B	983	900	859	772
CuZnBi2,2Pb	975	896	868	720
CuZnBi2,2BPb	984	900	858	726

One of the most important technological parameters of the alloys intended for fittings is the ability to fill the mold determined in the castability test. The sample castability spirals and results of the tests are given in Figures 3 and 4. The castability of obtained alloys is in the range from 510 to 725 mm and dependents on the chemical composition. The highest castability on the level of 725 and 715 mm was obtained for CuZnBi2,2B and CuZnBi2,2Pb alloys, respectively. Slightly worse results were obtained for the CuZnBi,8Pb alloy, which exhibits castability at the level of 675 mm. The presence of bismuth content (~ 2.2% wt.) in alloy, at a simultaneous high aluminum content of 0.6% wt., results in good casting properties. A similar effect can be achieved applying additionally about 0.6 % wt. of lead. The obtained results indicate that bismuth is the component influencing the changes in castability to the greatest extent. The hardness measurements of tested alloys showed a beneficial effect of bismuth and iron. The greatest hardness of 113 HB was obtained for CuZnBi1,8Pb alloy, containing bismuth and lead, and the highest iron content at 0.7% wt. Also CuZnBi2,2Pb, CuZnBi1,8BPb, CuZnBi2,2BPb and CuZnBi2,2B alloys are characterized by a considerable hardness above 100 HB. It should be highlighted also that the newly developed alloys exceeds the casting and mechanical properties (hardness) of common, standardized MO59 alloy used for fittings (Fig. 4, 5).

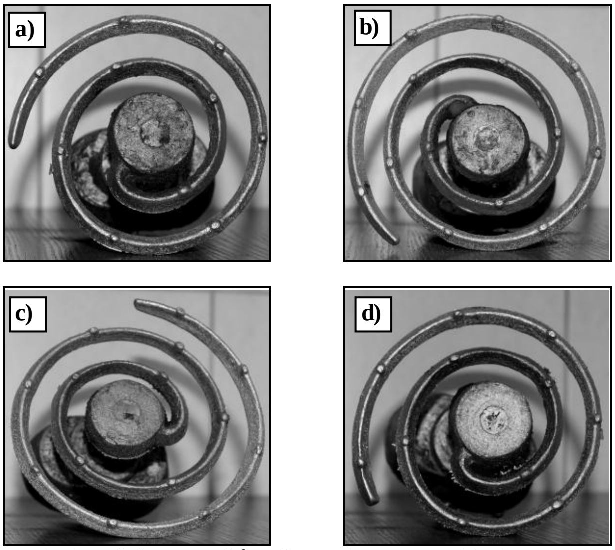

Fig. 3. Castability spiral for alloys: CuZnBi2,2 (a), CuZnBi2,2B (b), CuZnBi2,2Pb (c), CuZnBi1,8BPb (d)

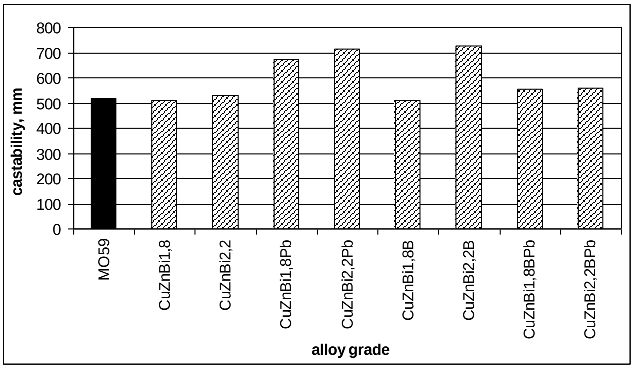

Fig. 4. Comparison of castability for the tested alloys

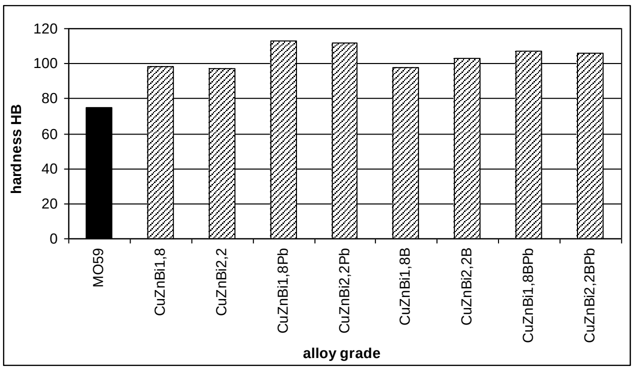

Fig. 5. Comparison of hardness for the tested alloys

The exemplary results of the observation of macro and microstructure of tested alloys are given in Figures 6÷8. Observations were carried out on transverse microsections. The structure of the alloys was revealed by etching in the reagent having the following chemical composition: 2 g of $K_2Cr_2O_7$, 100 cm^3 of H_2O, 4 cm^3 of NaCl, 8 cm^3 of H_2SO_4. As shown in Figure 6 the castings reveal on the cross section very fine-grained zone of equiaxial crystals with a great homogeneity. There were no casting defects observed.

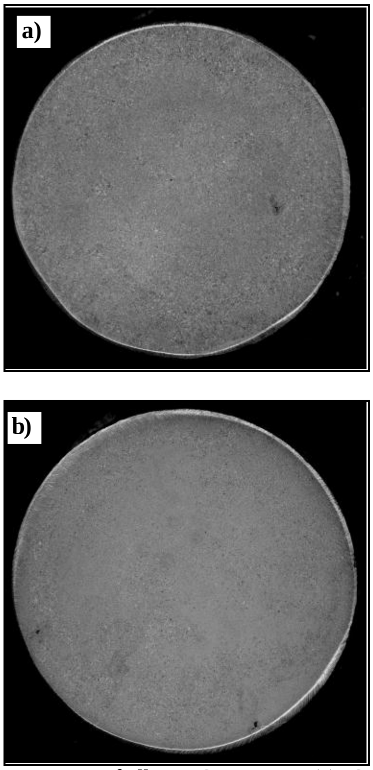

Fig. 6. Macrostructure of alloys: CuZnBi2,2 (a), CuZnBi2,2B (b)

Phase composition of these alloys is the mixture of α solid solution and β` phase (Fig. 7, 8). The CuZnBi2,2 alloy reveals the differentiated morphology of the grains of these phases from narrow and strongly elongated to equiaxial ones. The microstructure of CuZnBi2, 2BPb reveals the coagulation of grains of individual phases, probably due to the presence of a small amount of boron (0.02% wt.) in the alloy. Also the areas with a larger volume fraction of β`phase (Fig. 8) can be observed. No solubility of bismuth and lead in copper and low solidification temperature in comparison with copper causes that these constituent components evolve as the last one in pure form at grain boundaries and in spaces among the dendrite arms (Fig. 7 b, 8 b). To confirm this the preliminary results of X-ray phase analysis are shown in Figure 9.

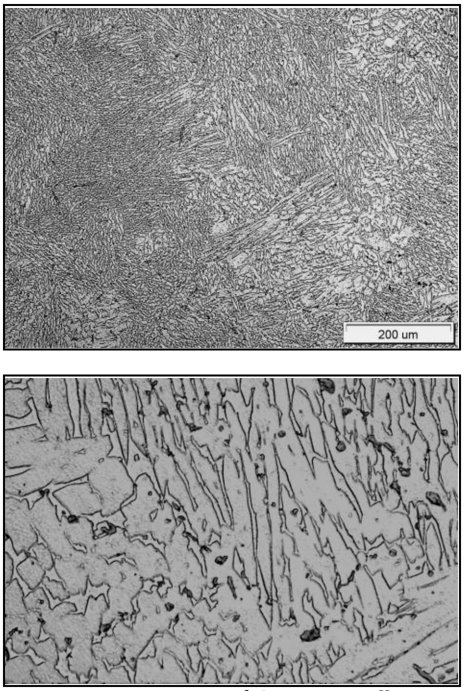

Fig. 7. Microstructure of CuZnBi2,2 alloy

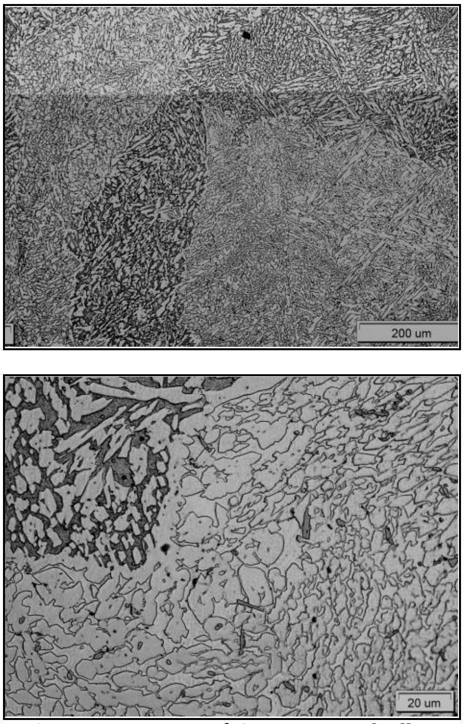

Fig. 8. Microstructure of CuZnBi2,2BPb alloy

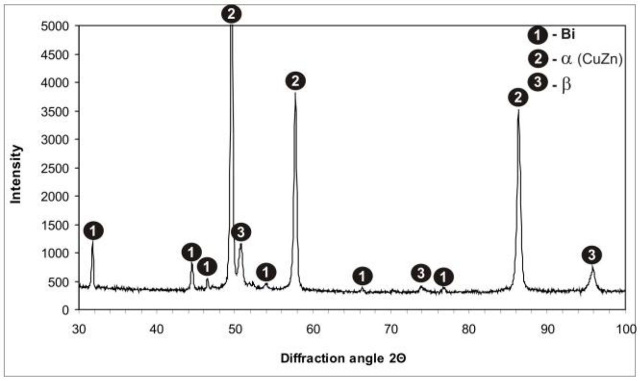

Fig. 9. X-ray diffraction of CuZnBi2,2 alloy

4. Conclusions

Effective control of the properties of final products is dependent on knowledge in the relationship between chemical composition, manufacturing process parameters and the course of the crystallization process, obtained phase composition and structure.

TDA analysis showed that zinc is a component of the strongest influence on the solidification process (T_{liq}, T_{sol}). Influence of other alloying elements on the process of crystallization is negligible. This means that small differences in the content of these ingredients does not cause a significant change in the process of melting and solidification. Zinc also determines the phase composition and microstructure. The phase composition of obtained alloys is constituted by the solid solution of zinc in copper (α) and β' phase. Due to the lack of solubility of bismuth and lead in copper, you can observe the spheroidal inclusions of these components in the microstructure on the grain boundaries of the mixture of α + β' phases.

The preliminary results presented in this paper have shown that there is a possibility to replace harmful lead with bismuth.

Changes in chemical composition in terms of quality and quantity of individual components such as bismuth, aluminum, iron, nickel and boron positively affected both the casting and mechanical properties of obtained alloys. Based on the performed tests it was found that the casting and mechanical properties of newly developed alloys are better than MO59 alloy commonly used in the fittings.

The component affecting the castability the most advantageously is bismuth, added in the amount of about 2% wt. Aluminum also positively affects the castability. The test results show that the greatest hardness is characteristic for alloys containing bismuth and lead and iron above 0.4% wt. This statement, however, requires extended strength investigations.

The gradual elimination of lead from the previously used casting copper alloys shall contribute to the reduction of existing post-production scrap in circulation, and thus reduce the emission to air of harmful lead vapors.

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