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# Lead-Free Casting Brasses. Investigations of the Corrosion Resistance and Shaping of Microstructure and Properties

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## Abstract

The ecological factor is very important in shaping properties of alloys. It leads to a limitation or elimination, from the surroundings, of harmful elements from the heavy metals group. The so-called eco-brasses group comprises common lead-free brasses containing 10 to 40% of zinc and arsenic brasses of a high dezincification resistance. Among standardized alloys, CW511L alloy ( acc. to EN standard) or MS-60 alloy (acc. to DIN) can be mentioned. Investigations were performed on two different kinds of metal charges: ingots cast by gravity and the ones obtained in the semi-continuous casting technology with using crystallizers. The casting quality was analysed on the basis of the microstructure images and mechanical properties. The investigations also concerned increasing the corrosion resistance of lead-free alloys. This resistance was determined by the dezincification tendency of alloys after the introduction of alloying additions, i.e. aluminium, arsenic and tin. The investigations focused on the fact that not only alloying additions but also the production methods of charge materials are essential for the quality of produced castings. The introduced additions of aluminium and tin in amounts: 0÷1.2 wt% decreased the dezincification tendency, while arsenic, already in the amount of 0.033 wt%, significantly stopped corrosion, limiting the dezincification process of lead-free CuZn37 brass. At higher arsenic contents, corrosion occurs only within the thin surface layer of the casting (20 μ).

**Keywords**: Innovative foundry technologies and materials, Lead-free casting brasses, Mechanical properties, microstructure, Environmental protection

## 1. Introduction

Among casting alloys, widely described in the scientific domestic and foreign literature [1-4], casting bronzes and brasses constitute one of the most important groups, used for many years and still developed, since they create certain technological problems [5-6]. Various copper- and zinc-based alloys developed and assessed under laboratory [4-9] and industrial conditions [10-12] indicate several advantageous properties. They also indicate different, both mechanical and technological properties and corrosion/erosion [13] resistance.

However, currently more and more emphasis, in the context of forming alloys properties, is being attached to the ecological factor [14-17] and virtualization and process modeling [18-19]. Harmful elements from the group of heavy metals should be, in a maximal possible way, eliminated from alloys, i.e. from the

human environment. Ordinary casting lead-free brasses, containing 10 to 40% of zinc, as well as arsenic brasses of an increased resistance to dezincification are well suited for the so-called eco-brasses.
A wide group of Cu-Zn alloys, mainly low-zinc, is applied for producing semi-products and elements of machines and devices in the form of sections - extruded and drawn - of various dimensions and cross-sections [19]. Ordinary brasses are also casting brasses. Several brasses included in the ecological group occur in standards, e.g. acc. to DIN the alloy marked by MS-60, or acc. to EN12164 -CW511L.
Apart from copper, zinc and additions of tin, arsenic, and aluminium, these alloys contain also contaminations but within the standard limits. They are produced mostly in three forms: as extruded or drawn sections and as casting materials, the so-called pigs obtained by gravity casting and with applying the crystallizer and semi-continuous casting.
The form/quality of the charge material for melting, or more precisely the way of its production, is very important for the quality of produced castings. By analogy to the similar way of producing casting alloys from the group of AlSi alloys (pigs and ingots),slightly better properties could be expected in these alloys. This is related to the quality of precipitates occurring in the microstructure, which can essentially influence the final quality of castings.
The results of investigations indicating differences in properties of produced castings in dependence of the charge quality, mould technology and applications of alloying additions are presented in the this paper.

## 2. Investigation methodology

The performed investigations used the following research process:

- preparation of the induction melting furnace and melting the metal charge in a chamotte-graphite crucible,
- heating the metal bath up to a temperature of 1005°C, bath purification,
- the addition of alloying elements, i.e. Sn, Al, As,
- casting of alloys into permanent and sand moulds.

The samples for investigating the chemical composition as well as microstructure, using optical microscopy, were taken from the obtained castings. The specimens for assessing mechanical properties and resistance to dezincification were also prepared. The investigations were performed in the Laboratory of Non-ferrous Metals Casting at the Faculty of Foundry Engineering of the AGH University of Science and Technology in Krakow.

## 3. Results of own research

The investigations were performed for two kinds of metal charge. In the first case, the charge constituted pigs cast to the die (Fig. 1). The second charge was an ingot obtained in the semi-continuous casting technology with using a crystallizer (direct chill casting) (Fig. 2).

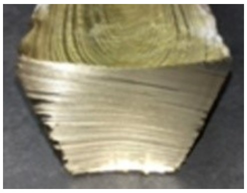
Fig. 1. Pig cast to the die

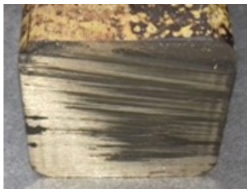
Fig. 2. Ingot from the crystallizer

The analysis of the chemical composition of the samples taken from the charge material is presented in Table 1. The metal charges subjected to investigations satisfied, in respect of their chemical composition, the criteria determined in the DIN 17660 standard. The obtained results do not exhibit essential differences.

Table 1.
The results of the chemical composition analysis of CuZn39 (MS-60, CW511L)

| **Charge form** | **Cu** (wt%) | **Pb** (wt%) | **metalliccontamin ations** (wt%) | **Zn** (wt%) |
|---|---|---|---|---|
| Pig cast to the die MS-60 | 60.81 | <0.3 | <0.5 | rest |
| Ingot from the crystallizer CW511L | 60.9 | <0.3 | <0.5 | rest |

In the further part of investigations, melting was performed and castings were made in three different moulds. These moulds are characterised by different conditions and different cooling rates. Test castings were made in: wet sand mould, sand mould with oil binder (OBB Sand) and metal mould. Photographs of equipment and moulds are presented in Figs 3-6.

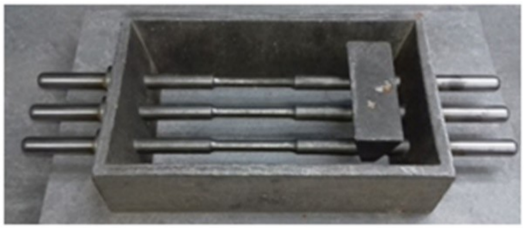
Fig. 3. The set-up for making sand moulds

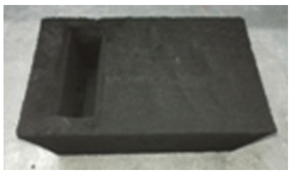
Fig. 4. A wet sand mould

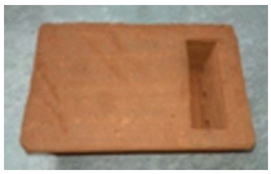
Fig. 5. A sand mould with an oil binder, OBB Sand


Fig. 6. A divided metal mould

The samples for metallographic, strength and corrosion resistance tests were prepared from the obtained castings.Examples of the obtained images of microstructures are shown in Figs7-12.

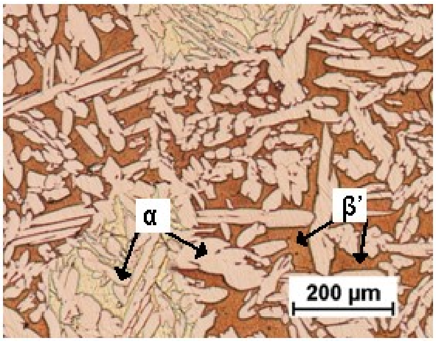

Fig. 7. The microstructure of MS-60 alloy, the casting from the wet sand mould obtained from the charge in the form of ingots

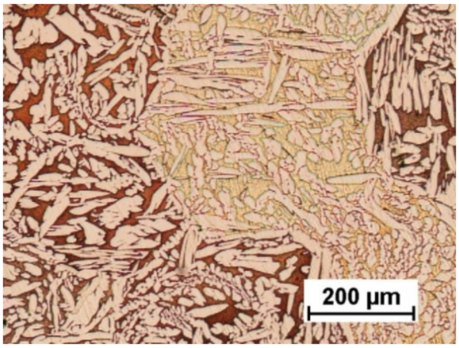

Fig. 8. The microstructure of MS-60 alloy, the casting from the OBB Sand mould obtained from the charge inthe form of ingots

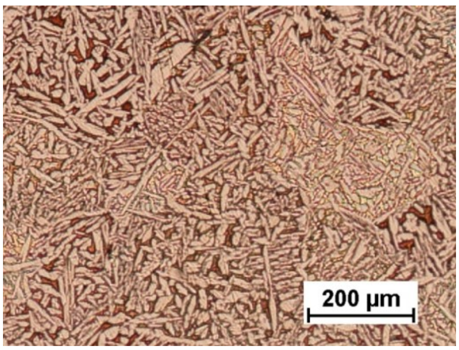

Fig. 9. The microstructure of MS-60 alloy, the casting from the metal mould obtained from the charge in the form of ingots

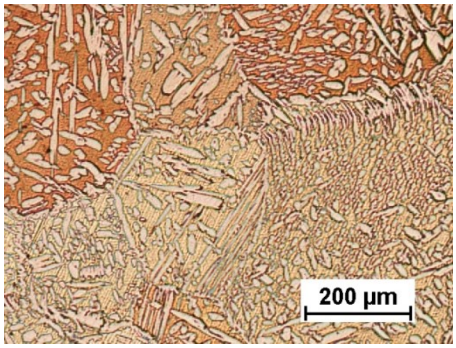

Fig. 10. The microstructure of MS-60 alloy, the casting from the wet sand mould obtained from the charge in the form of pigs

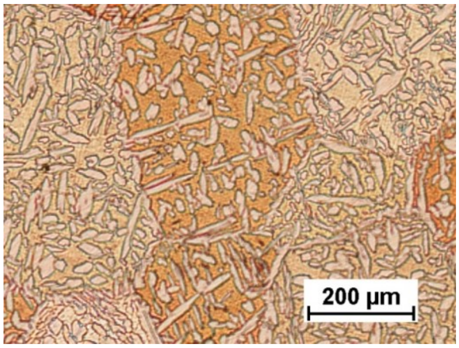

Fig. 11. The microstructure of MS-60 alloy, the casting from the OBB Sand mould obtained from the charge in the form of pigs

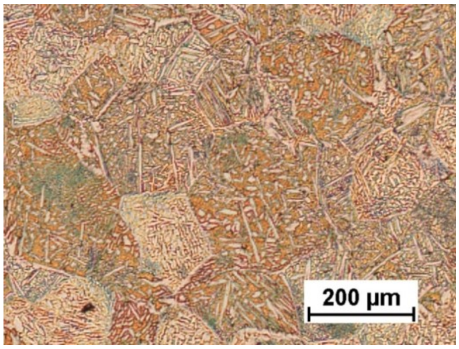

Fig. 12. The microstructure of MS-60 alloy, the casting from the metal mould, obtained from the charge in the form of ingots cast by gravity

The obtained images of microstructures shown in Figs 7-12 present the characteristic microstructure of this group of alloys. At the background of dark phaseβ', bright precipitates of phase α occur. Neither shapes nor sizes of solid solution α precipitates indicate essential differences in dependence of the applied kind of charge (pig, ingot). Of course, there are differences in the microstructure of CuZn39 alloy, solidifying under various conditions of heat dissipation (wet sand mould, OBB Sand mould, metal mould).The results of the mechanical properties investigations of CuZn39 alloy are presented in Fig. 13 and Fig. 14.The analysed castings were obtained from two kinds of charge materials: pigs and ingots. The alloy was cast into three various moulds

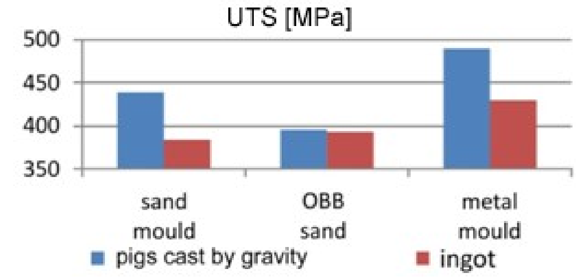


Fig. 13. The tensile strength results of the samples made of MS-60 alloy

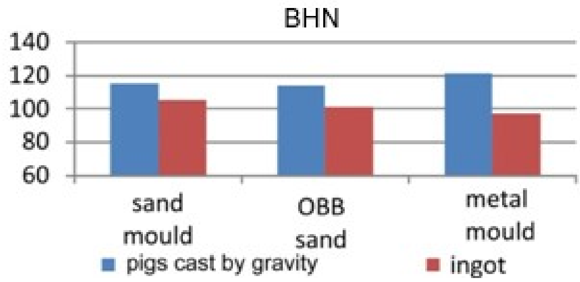


Fig. 14. The results of the hardness tests of the samples made of MS-60 alloy

The obtained results indicated higher UTS and BHN values of the samples obtained from the charge in the form of ingots cast by gravity. The highest values were obtained for the castings produced in the metal moulds.

The next stage of the investigations constituted the determination of the dezincification resistance of alloys from the lead-free brasses group. Lead-free CuZn37 brass was chosen as the material for analysis. Aluminium, arsenic and tin were introduced into the alloy in four doses. The samples after the mechanical working were chemically analysed with a spark spectrometer SPECTROMAXx. The obtained results are shown in Table 2.

Table 2.
The results of the chemical composition analysis

| | Contents of elements(wt%) | | | | | |
|---|---|---|---|---|---|---|
| | **Cu** | **Pb** | **Sn** | **Al** | **As** | **Zn** |
| **CuZnAl** | 65.76 | 0.002 | <0.001 | 0.001 | <0.001 | rest |
| | 65.41 | 0.001 | <0.001 | 0.480 | <0.001 | rest |
| | 65.18 | 0.002 | <0.001 | 0.750 | <0.001 | rest |
| | 64.92 | 0.001 | <0.001 | 0.990 | <0.001 | rest |
| | 65.01 | 0.005 | <0.001 | 1.210 | <0.001 | rest |
| **CuZnAs** | 65.41 | 0.003 | <0.001 | <0.001 | 0.001 | rest |
| | 65.56 | 0.003 | <0.001 | <0.001 | 0.033 | rest |
| | 65.83 | 0.002 | <0.001 | <0.001 | 0.055 | rest |
| | 66.01 | 0.003 | <0.001 | <0.001 | 0.170 | rest |
| | 66.26 | 0.003 | <0.001 | <0.001 | 0.370 | rest |
| **CuZnSn** | 65.66 | 0.002 | 0.011 | <0.001 | <0.001 | rest |
| | 65.47 | 0.010 | 0.290 | <0.001 | <0.001 | rest |
| | 65.03 | 0.015 | 0.710 | <0.001 | <0.001 | rest |
| | 65.00 | 0.010 | 0.950 | <0.001 | <0.001 | rest |
| | 64.90 | 0.008 | 1.240 | <0.001 | <0.001 | rest |

Then the samples were subjected to dezincification testing according to PN-EN ISO 6509 standard. To this aim, the prepared specimens of dimensions 10x10x10 [mm] were immersed in a solution causing corrosion by dezincification. After the determined time, the specimens were purified, cut and subjected to metallographic analysis using an optical microscope with a camera and software for image analysing. The obtained results are shown in Table 3.

Table3.
Results of dezincification measurements

| | **Alloy** | **Dezincificationlevel [µm]** |
|---|---|---|
| **CuZnAl** | CuZnAl0.001 | 450 |
| | CuZnAl0.480 | 440 |
| | CuZnAl0.750 | 400 |
| | CuZnAl0.990 | 320 |
| | CuZnAl1.210 | 290 |
| **CuZnAs** | CuZnAs0.001 | 245 |
| | CuZnAs0.033 | 85 |
| | CuZnAs0.055 | 65 |
| | CuZnAs0.170 | 40 |
| | CuZnAs 0.370 | 20 |
| **CuZnSn** | CuZnSn0.001 | 400 |
| | CuZnSn0.290 | 410 |
| | CuZnSn0.710 | 240 |
| | CuZnSn0.950 | 220 |
| | CuZnSn1.240 | 225 |

The obtained dezincification results constitutes the sample area which was dezincified, leaving a sponge structure of the solid solution α. The additions of aluminium, tin and, first of all, the additions of arsenic caused an increased corrosion resistance of CuZn37 alloy. At the additions of aluminium and tin, the dezincification level decreases approximately by half. In alloys with arsenic additions, already in the amount of 0.033 wt%, the corrosion resistance increases very intensively. When 0.4 wt% of arsenic is added only the sample surface layer (20 µm) is dezincified. Selected images of microstructures with a visible dezincified layer are presented in Figs. 15-22.

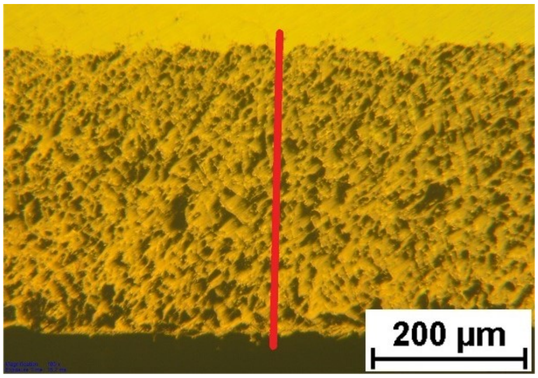


Fig. 15. The image of the surface layer of CuZn37Al0.001 alloy. Dezincification 450µm

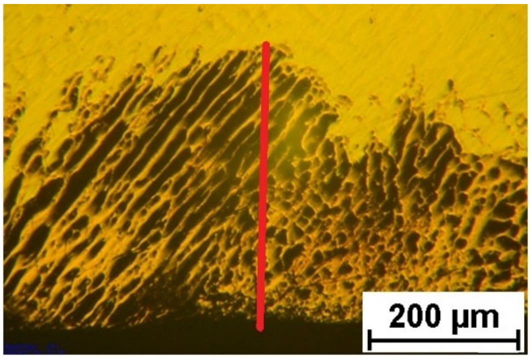

Fig. 16. The image of the surface layer of CuZn37Al0.75 alloy. Dezincification 400µm

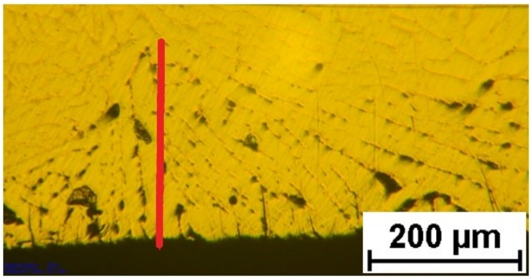

Fig. 17. The image of the surface layer of CuZn37Al1.21 alloy. Dezincification 290µm

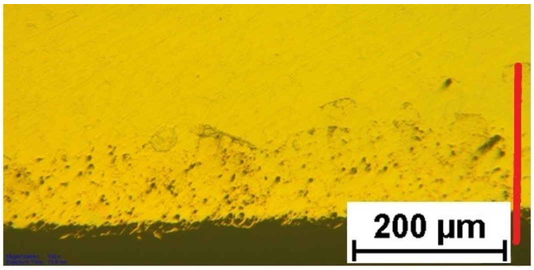

Fig. 18. The image of the surface layer of CuZn37Sn0.71 alloy. Dezincification 240µm

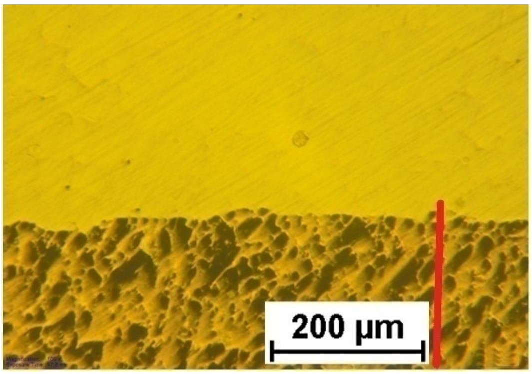

Fig. 19. The image of the surface layer of CuZn37Sn1.24 alloy. Dezincification225µm

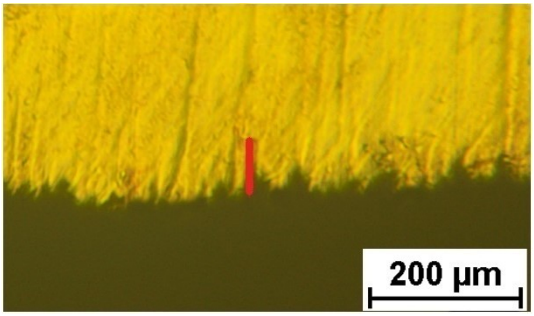

Fig. 20. The image of the surface layer of CuZn37As0.033 alloy. Dezincification85µm

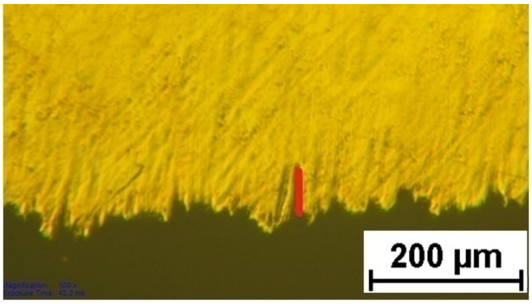

Fig. 21. The image of the surface layer of CuZn37As0.055 alloy. Dezincification 65µm

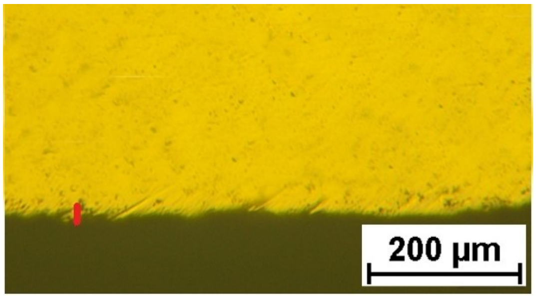

Fig. 22. The image of the surface layer of CuZn37As0.37 alloy. Dezincification 20µm

Thus, it can be stated that, along with increasing the aluminium content in CuZn37 alloy, the dezincification level insignificantly decreases and the pitting amounts in the material decrease. Even the smallest amount of arsenic (0.033 wt%) influences favourably the dezincification inhibition. At 0.37 wt% of As, the dezincification disappears nearly completely. The tin content, in a similar fashion as in the case of aluminium, does not have a significant influence on the decrease in dezincification. However, it can be noticed that the alloy dezincification slightly decreases when the Sn content increases. The dezincification changes have a linear character in the case of each of the applied alloying additions.

# 4. Conclusions

The obtained results concerning lead-free brasses indicate the possibility of obtaining various mechanical properties of the same alloy (CuZn39), but produced from different charges and by different metallurgical process. The discrepancies in the obtained strength and hardness values are mainly related to differences in microstructures. In the case of alloys with an established chemical composition, grain sizes and micro-contaminations decide on the achieved results. Regardless of the chemical composition, being in agreement with the standard and nearly identical for both kinds of charges, the average tensile strength and hardness results differ by approximately 20%. They are better when pigs cast by gravity are used as the charge. The analysed properties of the castings made of the charge produced by means of the semi-continuous casting technology are lower, regardless of the solidification conditions of experimental castings (wet sand mould, OBB Sand mould and metal mould).

The second stage of the investigations of lead-free brasses concerned increasing their corrosion resistance. Various additions of aluminium, arsenic and tin to CuZn37 alloy caused essential changes in the corrosion resistance determined by the dezincification tendency. Additions of aluminium and tin in the amount of 0÷1.2 wt% decreased the dezincification tendency, while arsenic, already 0.033 wt%, significantly hampered corrosion, limiting the dezincification process of lead-free CuZn37 alloy nearly to the surface layer of the casting.

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