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Influence of Modification in Centrifugal Casting on Microstructure and Mechanical Properties of Silicon Bronzes

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Abstract

Silicon bronzes are characterised by good mechanical properties and by high corrosion and mechanical wear resistance. The process of sleeve casting by means of the centrifugal casting with the horizontal axis of the mould rotation was analysed. The assessment of the influence of modification and centrifugal casting parameters on the microstructure and mechanical properties of alloys was carried out in the hereby work. Zirconium was applied as a modifier. Speed of rotation of the mould was the variable parameter of the centrifugal casting. The investigation results were summarised on the basis of the microstructure analysis and mechanical properties determination: UTS, proof stress, A₁₀ and BHN. The experiment aimed at finding the information in which way the modification together with changing the pouring parameters influence the mechanical properties of the CuSi3Zn3FeMn alloy.

Keywords: Innovative Foundry Technologies and Materials, Cu-Si Alloys, Centrifugal Casting, Microstructure, Mechanical Properties

1. Introduction

Among several non-ferrous alloys used for building machines and devices, the copper alloys, described widely in references, constitute the important group [1-4].

The industry and research institutions are still interested in the oldest group of copper - tin alloys. Performed investigations contain analysis of the chemical composition influence as well as modification processes of copper [5] and copper alloys [6,7,8,9]. Due to economic reasons and also due to a possibility of obtaining different properties, investigations of brass and silicon bronzes are carried out [1].

Copper alloys with silicon and other elements are used in a form of products after casting and solidifying in a crystallizer and then

plastically shaped (extrusion, drawing, rolling etc.). They are also used as cast products, including the process performed by the centrifugal casting [10,11] with using the software for the process simulation [12].

Products made by means of plastic working are the most often produced from two-component alloys CuSi3 strengthened by alloying additions, e.g. tungsten [13]. The main strengthening process of this group of alloys is done by plastic working, which causes, among others, grain refinement [14]. Changes of the precipitated phases are also possible and in consequence improvement of selected properties by means of the heat treatment and fast cooling is noted [15]. Thermodynamic conditions during the crystallisation process are very important not only in shaping the microstructure and properties, but also because of the inverse

segregation [16] they can lead to creation of defects in castings of silicon bronzes.

Casting bronzes CuSi3Zn3FeMn exhibit good plastic properties and a very high corrosion resistance [1]. The zinc addition causes that these bronzes are characterised by a good fluidity, while the iron and manganese additions significantly improve their mechanical properties. Due to that, these bronzes have high mechanical properties both at a room temperature and at temperatures increased to 300°C. They are of a high wear resistance as well as of variable loads and abrasion resistance. Bronzes CuSi3Zn3FeMn are applied in production of machine parts and accessories (bearings, drive elements, pumps), which are exposed to corrosion and variable loads. Sleeves, rods, flat bars and shaped elements (rotors, bearings, pump housings) are cast from silicon bronzes, also for the aircraft industry, which requires excellent properties and reliability [17].

An important aspect in obtaining cast products of a high quality constitutes the metal bath quality in respect of contaminations and melting conditions [18,19].

After the proper preparation of the metal bath the refining process, such as grain refinement and the structure modification as well as the casting technology in respect of solidifying and cooling of the casting, is essential for obtaining the expected properties of castings.

Modification has advantageous influence on the structure formed in the primary crystallisation process. It is especially important in shaped elements, since their mechanical properties cannot be improved by means of plastic deformation processes and recrystallization. It is equally important for the majority of copper alloys, which contrary to ferrous alloys, do not have phase transformations (especially eutectoid transformations) allowing to improve mechanical properties by means of a heat treatment. Refinement of copper alloys structure advantageously influences strength as well as - in a certain range - plasticity expressed by elongation or reduction of area. The most generally it can be stated that, the modification process in Cu alloys can occur due to facilitating the nucleation process of the crystalline phase by heterogenic nucleation particles called 'crystallizers' or due to the inhibition of growing spontaneous (homogeneous) nucleation or crystals. The modification by inhibition of the crystals growth is called the surface active modification. This is the result of an increased concentration of the modifying element in the vicinity of growing crystals. Due to that, the diffusion of atoms of the given metal or alloy components to the surface of phase separation is rendered difficult. On the other side, by decreasing the surface tension it creates more favourable conditions for the spontaneous nucleation than for the growth of existing nuclei or crystals. In relation to a widely understood group of copper alloys one of the most active modifiers is zirconium. The addition of zirconium causes - in silicon bronzes - the formation of fine-grained, equiaxial structure, at decay of developed dendrites. In the case of several grades of bronzes, the modification effect is improved by a previous or simultaneous addition of phosphorus, which not only acts deoxidating but also protects the modifier (zirconium) against melting loss, thus improving its efficiency [20].

2. Methodology and conditions of research

The experiment of the sleeve casting of dimensions: 100x140x200 mm, weight ~12.5 kg (Fig. 1) was performed by the centrifugal casting method at variable rotation speeds. Tests were performed for the silicon bronze CuSi3Zn3FeMn approximate to CB245E (EN 1982:2017). The rotation speed was selected from the diagram in Fig. 2 [10], which takes into account the optimal number of rotations in dependence on the casting diameter. Each of the six stages of the experiment is characterised in Table 1. Pouring parameters were as follows: pouring time 3s, pouring temperature 1087-1099°C, mould temperature 247-268°C.

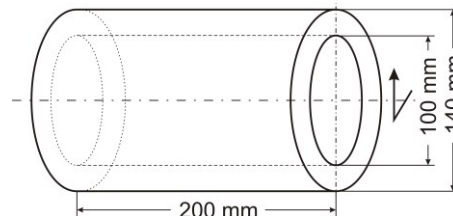


Fig. 1. Sleeve dimensions: 100x140x200 mm, ~12.5 kg

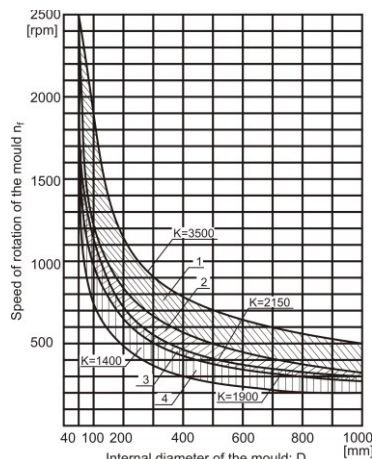








Fig. 2. Diagram of selecting the mould rotation speed, based on the Cammen's equation: 1- aluminium and aluminium alloys, 2- grey cast iron and bronzes, 3- cast steel, 4- lead and tin bronzes [10]

Table 1. Parameters of the sleeve casting in successive stages of the experiment

The mould rotation speed	Stages of the sleeve casting		
	0% Zr	0.2% Zr	0.2% Zr
990 rpm	0 min	7 min	30 min
	1. 	3. 	5. 
1500 rpm	0 min	10 min	37 min
	2. 	4. 	6. 

In the initial stage the sleeve was cast according to the standard parameters, applied usually in the centrifugal casting of silicon bronzes (990 rpm). In the second stage the sleeve casting was made

with applying the maximal rotations obtainable in the centrifugal machine (1500 rpm). In the third stage the initial speed was applied (990 rpm), and the modifying addition in a form of inoculant CuZr10 was used (0.2% Zr in relation to a metal charge). The fourth stage was performed with applying the maximal rotation speed (1500 rpm) and the CuZr10 inoculant. In the fifth and sixth stage the parameters were selected in a similar fashion as in the third and fourth stage, it means the time the alloy was held in the furnace - after addition of the CuZr10 inoculant - was prolonged from 7 to 37 minutes.

The results of the centrifugally cast samples were compared with the gravity casting material in molding sand (Stage 01-02).

The chemical composition of samples was tested by means of the emission spectroscopy Spectro Oxford PMI-Master 200. Macro- and microstructures were investigated by the NIKON SMZ 745Z and Eclipse LV 150 microscopes (OM). The further observations were performed at a scanning electron microscope (SEM) Hitachi S-3400N with Energy-Dispersive X-ray Spectrometer (EDS) by Thermo Noran. Samples were tested for mechanical properties at the INSTRON device, model 1115.

3. Results of chemical tests and their analysis

3.1. Influence of the mould rotation speed and modification on the microstructure

The chemical composition was verified on the basis of spectroscopic investigations (Table 2). The chemical composition of the sleeve, in each of the stages of the experiment was in agreement with the composition of the normalised alloy, containing: minimum 90% Cu, 3-5% Si, 3-5% Zn, 0.2% Pb, 0.2% Fe, 0.25% Mn.

Table 2.

Chemical composition of samples of the experiment

Stage	Concentration (wt.%)								
	Cu	Zn	Pb	Sn	Mn	Fe	Ni	Si	Zr
01	90,3	4.39	0,126	0.210	0.720	0.715	0.038	3.46	0
02	89.8	4.38	0.371	0.24	0.697	0.939	0.045	3.35	0.131
1	89.9	4.46	0.352	0.212	0.690	0.869	0.039	3.39	0
2	89.9	4.46	0.352	0.212	0.690	0.869	0.039	3.39	0
3	89.8	4.38	0.371	0.24	0.697	0.939	0.045	3.35	0.131
4	89.9	4.39	0.341	0.213	0.684	0.922	0.044	3.27	0.184
5	89.8	4.38	0.371	0.24	0.697	0.939	0.045	3.35	0.172
6	89.9	4.36	0.362	0.194	0.689	0.928	0.044	3.33	0.184

Samples for tests were cut crosswise the sleeve, observations were performed on the sleeve cross-section (B) as well as on the external (A) and internal (C) surface of the sleeve (Fig. 3). The images

pictures of the samples macro- and microstructure from selected stages in magnifications of 6.7x and 100x are presented below.

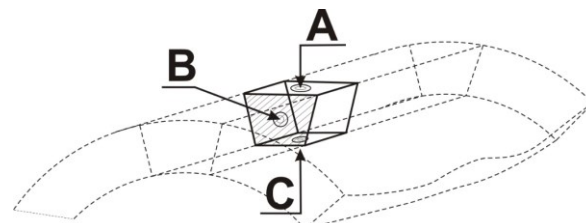


Fig. 3. Schematic presentation of samples cut from the sleeve for microstructure observations

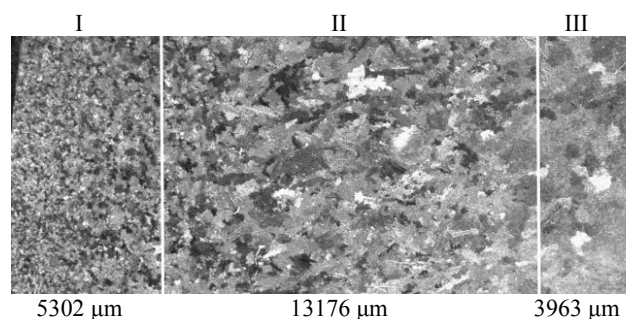


Fig. 4. Image of the macrostructure of the cut fragment of the sleeve with marked areas. Stage 2: CuSi3Zn3FeMn, 1500 rpm

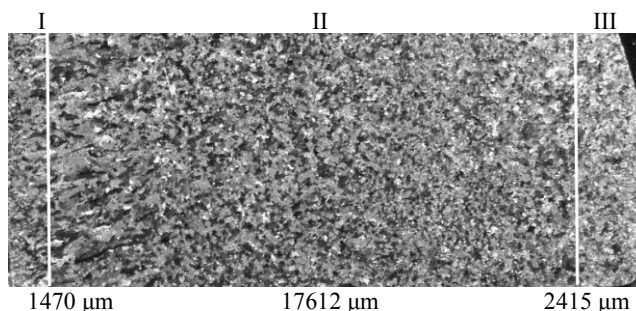


Fig. 5. Image of the macrostructure of the cut fragment of the sleeve with marked areas. Stage 3: CuSi3Zn3FeMn+Zr, 7 min, 990 rpm

Representative samples are presented in Figures 4 and 5. Three areas (I, II, III) - differing in grain sizes - can be singled out on the sleeve cross-section. These areas are the effect of variable rates of heat transfer, rotational speeds and zirconium influence, leading - in consequence - to changes in the crystallisation process.

The macrostructure presented in Figure 4 reveals two clearly visible edge areas with equiaxial crystals, the first one from the side of the metal mould (area I) and the second from the internal side of the sleeve casting (area III). The middle area (II) is characterised by the uniform grain refinement and constitutes the zone deciding on properties of the final casting, since the cast sleeves are subjected to machining, the so-called 'peeling'.

When analysing the cut fragment of the sleeve of bronze CuSi3Zn3FeMn with the addition of zirconium (Fig. 5), it is possible to notice two effects on the polished section: the middle area (II) is widening, while edge areas (I and III) are narrowing and

the grain sizes are diminishing, especially in the middle area (under the zirconium influence). Images of microstructures of analysed alloys are shown in Figures 6-11.

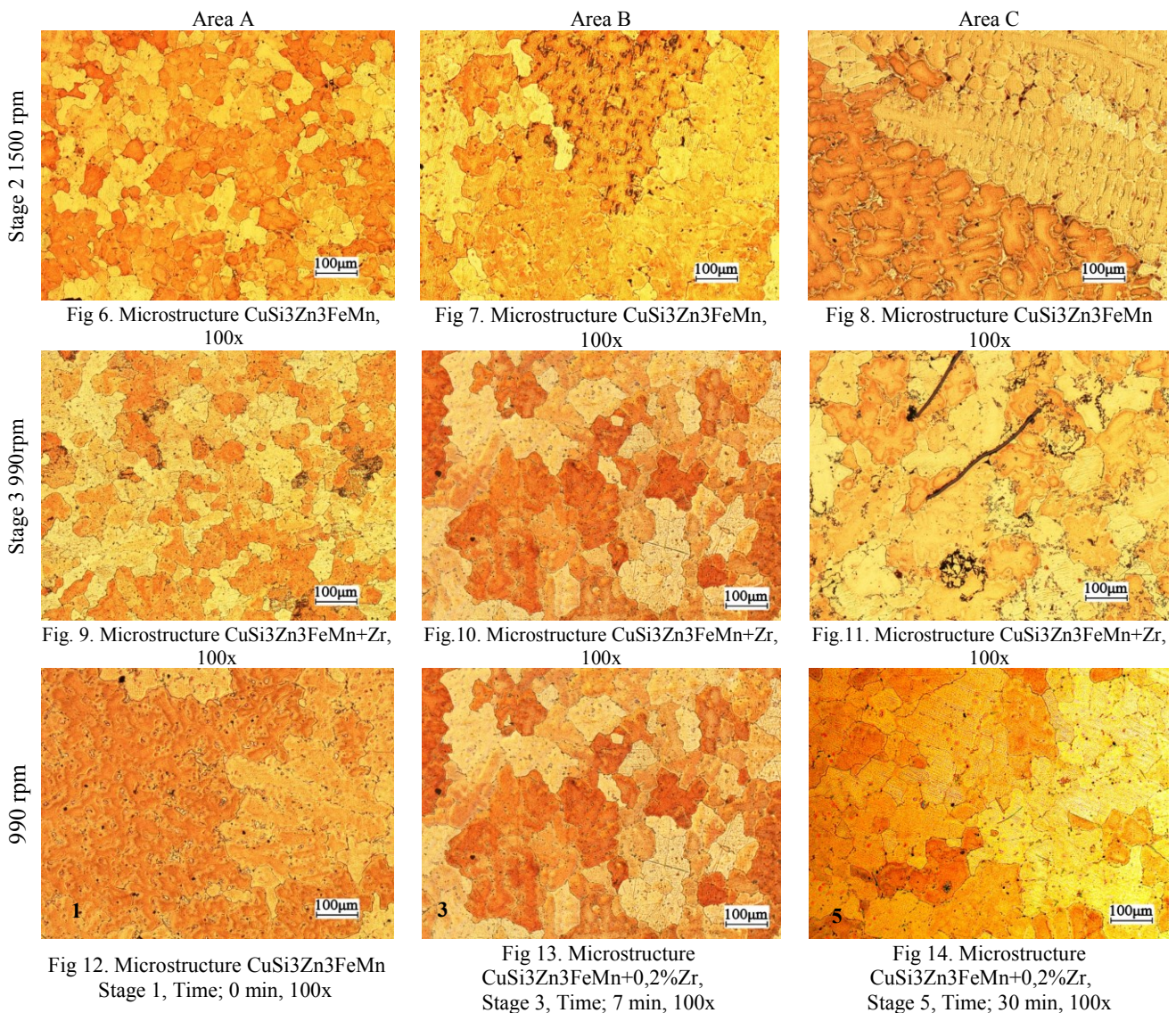
Fine equiaxial crystals formed due to an intensive cooling of the casting which external sleeve areas are in contact with the metal mould, can be observed in the sample cross-section (Fig. 6). Also larger crystals with developed dendrites of solid solution (Fig. 8) being the result of the increased temperature gradient and free cooling of casting in the open mould from the internal sleeve side (area III), can be seen. After introducing in the CuSi3Zn3FeMn bronze a modifier (Zr) in a form of CuZr10, the microstructure in areas II and III is changing (grains are diminishing). Not numerous, longitudinal dark precipitates, probably of partially undissolved zirconium being the effect of solidifying and shifting of the

solidification front in the direction of the axis of the mould rotation, were also observed.

Especially essential, from the point of view of functional properties, is the middle area of the casting (area II). Therefore, this area was subjected to the detailed metallographic analysis with using the optical and scanning microscopy with microanalysis SEM+EDS. The obtained results are shown in Figures 12-22 and Tables 4-6.

Grains of solid solution α and small precipitates on grain boundaries were observed in the microstructure of samples.

Grain sizes of samples were significantly different. The inoculant introduction and increasing of the rotation speed caused decreasing of grain sizes.



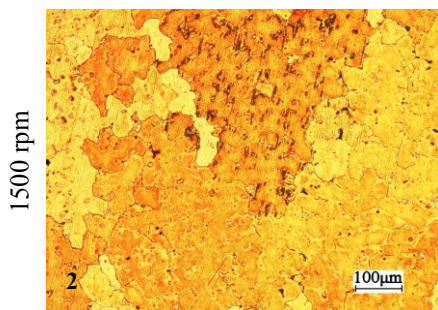


Fig 15. Microstructure CuSi₃Zn₃FeMn
Stage 2, Time; 0 min, 100x

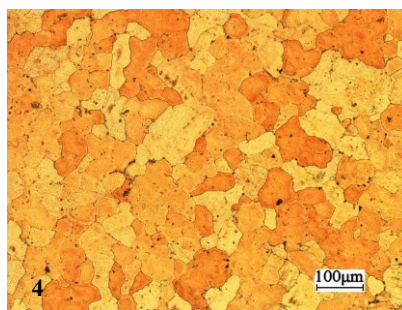


Fig 16. Microstructure
CuSi₃Zn₃FeMn+0,2%Zr
Stage 4, Time; 10 min, 100x

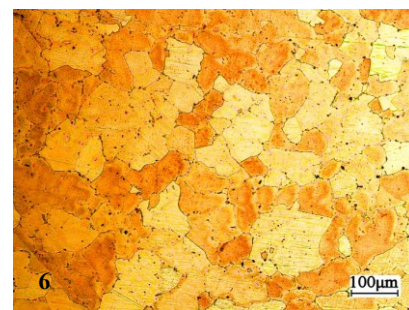


Fig 17. Microstructure
CuSi₃Zn₃FeMn+0,2%Zr,
Stage 6, Time; 37 min, 100x

Samples of the middle section before and after adding the inoculant were subjected to the microstructure analysis, using SEM+EDS. The obtained results are presented in Figures 18-21 and Tables 3-6.

The obtained investigation results of the CuSi₃Zn₃FeMn alloy indicate the microstructure consisted of the solid solution α of a composition similar to the composition of the analysed alloy with precipitates of fine silicon-iron and silicon-manganese phases on boundaries and inside grains. In bronzes of this group the solid solution α constitutes the soft matrix, while precipitates of intermetallic phases improve strength properties, especially increasing the abrasion resistance.

The investigation results of the CuSi₃Zn₃FeMn alloy with zirconium addition, begun with an unfortunate experiment where zirconium did not dissolve completely forming large needles (Fig. 18, Table 3). In Figure 19 and Table 4 are presented results of microanalysis indicating the grains—having the composition in accordance with the alloy composition and precipitates of complex phases containing silicon with iron and manganese (some with a significant fraction of zirconium). The morphology of precipitates takes also forms of ragged clusters (Fig. 20, Table 5) with the major fraction of zirconium with copper, iron and silicon.

The obtained distribution maps of elements occurring in the alloy presented on the microstructure background (Fig. 21) indicate that zirconium occurs in grains of the solid solution α , in dark precipitates of phases rich in Fe, Si, Mn and also in fair precipitates rich in zirconium.

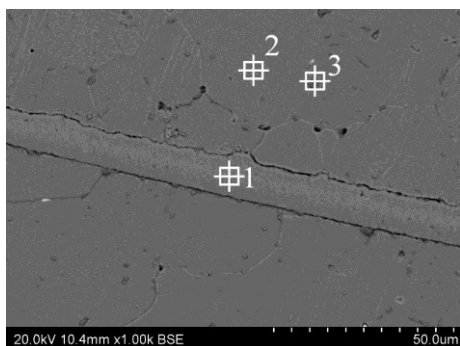


Fig. 18. The SEM-EDS. Stage 3 - CuSi₃Zn₃FeMn +0.2%Zr,
990 rpm (time 7 min) with indicated microanalysis points
(Table 4)

Table 3.

The results of microanalysis in microareas of Fig. 18

pt	Concentration (wt.%)							
	Al	Si	Mn	Fe	Ni	Cu	Zn	Zr
pt 1	-	-	-	-	-	2.97	-	97.03
pt 2	0.21	3.30	0.54	0.58	-	90.89	4.47	-
pt 3	-	17.35	3.41	27.09	0.41	49.50	2.24	-

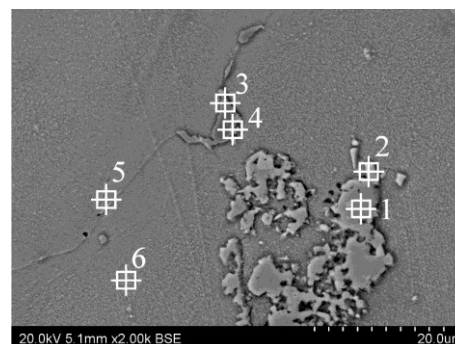


Fig. 19. The SEM-EDS. Stage 5 - CuSi₃Zn₃FeMn +0.2%Zr,
990 rpm (time 30 min) with indicated microanalysis points
(Table 5)

Table 4.

The results of microanalysis in microareas of Fig. 19

pt	Concentration (wt.%)						
	Si	Cr	Mn	Fe	Cu	Zn	Zr
pt 1	-	-	-	-	5.60	-	94.40
pt 2	3.37	-	-	24.34	7.20	-	65.09
pt 3	17.27	-	1.86	76.95	3.91	-	-
pt 4	7.25	0.98	2.84	40.28	15.95	-	32.69
pt 5	3.18	-	1.60	-	90.86	4.36	-
pt 6	3.23	-	-	0.80	91.75	4.23	-

Zirconium introduced into an alloy requires certain conditions to dissolve causing grain-refinement and formation of fine precipitates. Investigations of samples with zirconium additions indicated also the occurrence of longitudinal, acicular precipitates. The analysis performed in this microarea indicates that this is undissolved zirconium on the background of solid solution grains.

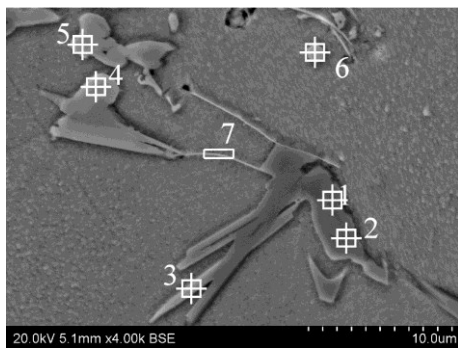


Fig. 20. The SEM-EDS. Stage 5 - CuSi₃Zn₃FeMn +0.2%Zr, 990 rpm (time 30 min) with indicated microanalysis points (Table 6)

Table 5.

The results of microanalysis in microareas of Fig. 20

pt	Concentration (wt.%)						
	Si	Mn	Fe	Ni	Cu	Zn	Zr
pt 1	16.19	2.28	77.05	-	4.48	-	-
pt 2	21.78	4.87	54.30	-	19.04	-	-
pt 3	13.10	4.20	16.00	-	64.04	2.67	-
pt 4	3.58	-	25.31	-	8.35	-	62.76
pt 5	6.99	3.04	42.98	1.10	14.57	-	31.33
pt 6	4.81	1.76	32.11	-	8.84	-	52.47
pt 7	3.97	0.89	0.98	-	85.02	4.05	5.07

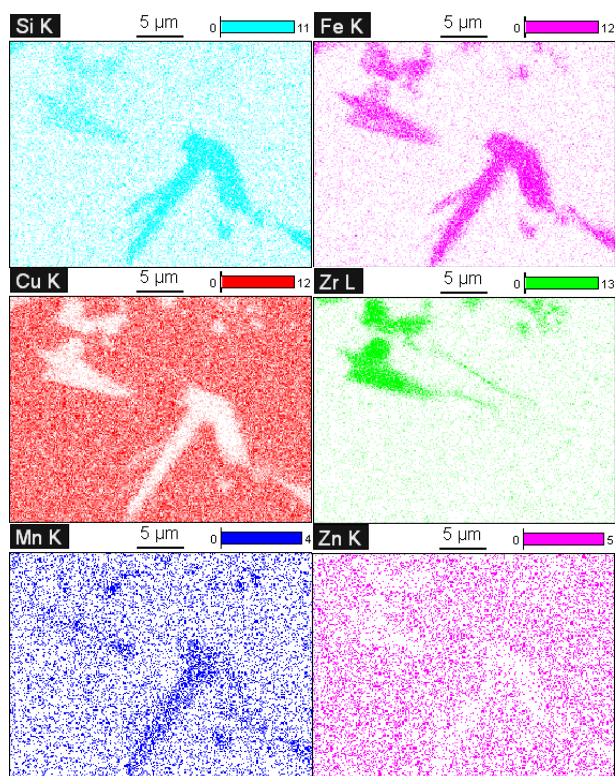


Fig. 21. The SEM-EDS. Stage 5 - CuSi₃Zn₃FeMn +0.2%Zr, 990 rpm (time 30 min).

Maps of main constituents: Cu, Mn, Fe, Si, Zr, Zn

Due to a high melting temperature of zirconium (1855°C) and small amounts of the applied modifying additions (0.02 - 0.04 wt.% Zr) it is essential to apply the modifier in a form of the master alloy CuZr10 or CuZr30. The lowest melting temperature indicates, according to the equilibrium system, the master alloy CuZr11.5 wt.%. The form of the master alloy is essential in the modification process (ingot, wire), homogeneity and micro structural build of the master alloy with the special attention to morphology and sizes of intermetallic precipitates e.g. Cu₉Zr₂, Cu₅₁Zr₁₄, Cu₈Zr₃. Undissolved, developed and high-melting intermetallic phases - introduced in the master alloy - not only will make the microstructure change impossible but remaining in this undissolved state they can lead to decreasing the properties of modified alloys.

3.2. Influence of the mould rotation speed and modification on mechanical properties

Tests of mechanical properties were performed on samples cut according from sleeve. An important aspect of the sleeve casting quality is the structure density with regard to porosity and inclusions. The analysis of castings, produced by means of centrifugal casting, indicates that especially the middle areas of castings are non-cohesive and contain significant amounts of oxide inclusions. This is related to a rotational motion of the liquid and crystallising alloy and to a fact that - in some ways - this area acts as a feeder during the solidification time. Because of these effects the structure in this area is heterogeneous and due to that a significant part of sleeve castings, cast by means of the centrifugal casting, is removed by machining.

On the bases of analyses of the casting process carried out under industrial conditions in the majority of cases even 1/3 of the casting is removed from the inner side of the sleeve. Therefore in order to determine mechanical properties of the casting the samples, for the UTS, proof stress, A₁₀ and BHN tests, were taken from the middle part of the sleeve cross-section subjected previously to machining to the state of the ready casting. The results of mechanical investigations are listed below (Table 6, Fig. 22). Comparison of experimental results of mechanical tests showed significant hardening effect by zirconium addition especially in samples cast into sand moulds; a considerable increase in tensile strength by over 50%, proof stress by about 70% at small decrease of plasticity expressed by A₁₀ parameter. Strong hardening of the analyzed alloys modified by zirconium addition is a result of a change in crystallization conditions, long solidification time, characteristic for the casts solidifying in sand moulds, and the same, at occurring full crystallization process of all microstructure components.

Comparing the results of mechanical tests of the samples cast into sand moulds and rotating metallic mould, it can be observed that UTS, proof stress and BHN significantly increase while A₁₀ elongation slightly decrease; this consists an obvious fact observed in a number of alloys connected with the heat transfer conditions. The results of mechanical test of the casts solidifying in a rotating metallic mould at various parameters of alloy preparation and pouring, achieve higher values in comparison to the original alloy solidifying in a sand mould. However, faster solidification process in a rotating mould blocks the crystallization process what results in slightly less effective hardening of the analyzed silicon bronzes.

Undoubtedly, the process of centrifugal casting of the analyzed bronzes with zirconium addition shows a positive effect on

densification of cast microstructure, especially in the part of the cast that carries loads during exploitation.

Table 6.

Results of testing mechanical properties of samples from individual experiments

Experiment	UTS [MPa]	Proof stres [MPa]	A ₁₀ [%]	BHN
Stage 01 Sand CuSi3Zn3FeMn	290.53	118.66	27	78
Stage 02 Sand CuSi3Zn3FeMn+0,2%Zr	441.67	203.24	23	112
Stage 1 990 rpm CuSi3Zn3FeMn	406.45	155.21	21.08	99
Stage 2 1500 rpm CuSi3Zn3FeMn	414.93	156.32	22.72	108
Stage 3 990 rpm CuSi3Zn3FeMn+0,2%Zr 7 min	386.97	149.05	15.67	107
Stage 4 1500 rpm CuSi3Zn3FeMn+0,2%Zr 10 min	375.57	155.37	14.03	109
Stage 5 990 rpm CuSi3Zn3FeMn+0,2%Zr 30 min	426.00	159.80	19.25	104
Stage 6 1500 rpm CuSi3Zn3FeMn+0,2%Zr 37 min	423.00	158.25	19.50	104

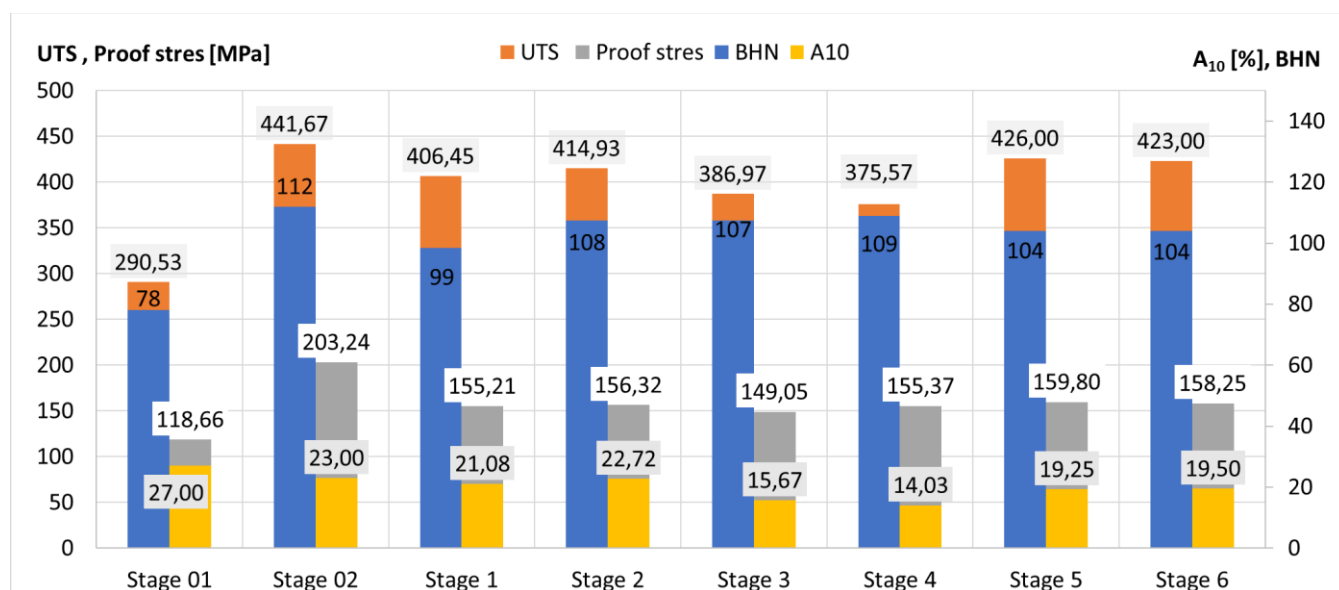


Fig. 22. Graphical listing of the mechanical properties results of samples from individual experiments

8. Conclusions

The aim of the experiment was finding the information in which way the modification effect together with changes of the pouring parameters influence the mechanical properties of the CuSi3Zn3FeMn alloy. Based on the research conducted and the industrial experiments, it can be concluded that:

- in the microstructure of silicon bronzes CuSi3Zn3FeMn was observed solid solution α and small precipitates of intermetallic phases (mainly at grain boundaries). Long needles of pure zirconium were seen in samples from stage 3 as a result of undissolved zirconium from Cu-10% Zr alloy,

- the microstructure of samples from stage 4 (increased rotational speed of the metal mould and the zirconium addition) is much more fine-grained than of samples 2 and 3. However, it is not reflected in the improvement of the mechanical properties, probably due to occurrence of long precipitates of undissolved zirconium, which decrease the tensile strength and plasticity,
- the influence of increased rotational speed (in stage 2) and addition of zirconium (in stage 3) on the alloy microstructure was distinctly noticeable in relation to the stage 1; the zirconium addition caused homogenizing of the microstructure together with minimization of the mould-edge

- effect. This in turn will guarantee a considerable decrease of machining,
- the obtained results showed that the mould rotational speeds within the range 990-1500 rpm do not have a decisive meaning in improving strength properties of the analysed silicon bronze,
 - increasing the rotational speed leads to densification of the structure and improve the efficiency casting of the sleeve without oxide inclusions.

The modification effect is observed mainly in the casts prepared in sand moulds. During centrifugal casting, the effect is almost unnoticed what is reflected in the strength parameters. The significant effect on these parameters has solubilizing time of Zr. Application of zirconium modification at optimal parameters of the alloy preparation and centrifugal velocity of a mould, allows to obtain casts with well-defined shape and decrease of machining allowance. Such castings also exhibit high densification, equiaxial and fine grains achieving high strength properties. Regardless very good properties, the silicon bronzes still represent a small part in the total production of the cast copper alloys. Improvement of the properties of the alloys may increase a range of their applications.

Acknowledgements

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