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New Ecological Cast Bronzes for Fittings Manufactured from Recycled Waste

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Abstract

The article presents tests on a new lead-free bronze CuSn4Zn2PS, intended for fittings for contact with drinking water, in which the addition of lead was replaced with sulphur. The subject of the experimental work was the production of semi-finished products from this alloy based on the charge coming entirely from waste generated after machining. A specialized pilot line was used for the tests, and after cleaning, the waste was melted and then were continuously cast in the form of rods and hollow rods. The cleaning efficiency was assessed, and the manufactured semi-finished products were subjected to tests, including the assessment of the chemical and mechanical homogeneity and the structure of the test batch of the semi-finished casting products in terms of the possibility of manufacturing products meeting the requirements of technical specifications. The obtained results, both in terms of a stable chemical composition, homogeneous and reproducible mechanical properties, fully compliant with the specifications for fittings bronzes (CC499K), as well as the lack of faults of the obtained semi-finished products, despite a very large share of waste material, indicate the possibility of using the tested recycling method for the production of semi-products of sulphur bronze, which is an alloy that is relatively difficult to manufacture.

Keywords: Wastes, Recycling, Continuous casting, Free machining bronze, Lead free copper alloy

1. Introduction

Removing lead which is a harmful element from all products manufactured globally has been ongoing for many years. This also applies to fittings, usually made of materials with very good machinability, and which are in contact with drinking water. At present, after the introduction of the new Directive 2020/2184 on the quality of water intended for human consumption [1], the limit content of lead in water is 5 μg/l, (this value shall be met, at the latest, by 12 January 2036, until that date shall be 10 μg/l). In addition, for the consistent implementation of these restrictions, the EU is to have a unified approach to the approval of materials for use in elements that come into contact with drinking water in supply systems and determination of permissible levels of, among others, lead content in materials used in drinking water supply systems (similar like in e.g. in USA). The existing so-called positive lists (materials approved for contact with water) are to be replaced by one, developed by the European Chemical Agency (ECHA). It should be accepted by the EC and subject to periodic reviews and, according to ECHA's announcement, should be approved by June 12, 2025. Thus, at present the legal status is still being shaped by local initiatives, the most important of which is the so-called 4Member State Common Approach, the result of which is the development and updating of a list of materials approved for contact with drinking water [2].

According to this list, in the area of casting bronzes for fittings, bronzes with a limited lead content should be distinguished (e.g., CC499K alloy introduced instead of CC491K), i.e., rather traditional materials, as well as new lead-free alloys (Ecocast, Rg +). In the case of the Ecocast alloy, which is a silicon brass CuZn21Si3P (CC768S), the obtained properties are significantly different from the replaced CuSnZnPb bronzes, in particular CC491K (Table 1). A much more interesting material introduced to the industry is a new alloy, which is bronze with an addition of sulphur CuSn4Zn2PS, with characteristics similar to CC491K, but without the addition of Pb [3]. This alloy is protected by a patent [4]. It should be noted that at the moment this alloy is not standardised [5] but has already been included in the 4MS CCL list [2]. There are many reasons to carefully analyse the possibility of its production due to the significant probability of wide use of this bronze in the field of fittings materials.

The research presented in this paper was undertaken based on the following premises:

- this alloy may, in the near future, become one of the main materials used for fittings (and not only) with a relatively large production volume,
- alloy production based on pure components is a challenge to master, but as in all cases, the more widespread the use of fittings products means large amounts of waste generated after machining and the need to manage it,
- the transition to the manufacturing of products based on large amounts of waste has a completely different specificity and requires gaining appropriate experience and conducting extended research.

These premises were the basis for the attempts to use a charge consisting of 100% waste, covering the entire process from subjecting it to cleaning, manufacturing of products, and determining the impact of the waste charge on the quality of the products obtained. The scope of the research covered the basic parameters of production indicators and the required properties of cast rods and hollow rods.

Table 1.
Comparison of properties of continuously cast products of selected fittings bronzes [6]

Material designation (EN 1982:2017)		R_m, MPa	$R_{p0,2}$, MPa	A, %	HBW	Machinability
		min	min	min	min	(CuZn39Pb3 = 100%)
CC491K	CuSn5Zn5Pb5	250	110	13	65	85 %
CC499K	CuSn5Zn5Pb2	250	110	13	65	70 %
–	CuSn4Zn2PS	250	110	13	65	70 %
CC768S	CuZn21Si3P	420	140	20	80	80 %

2. Research Methodology

The charge was waste in the form of fine chips after machining of fittings made of CuSn4Zn2PS bronze semi-finished products. The experimental part and research covered the manufacturing process with the use of the developed prototype pilot line, including waste cleaning operations, subsequent melting, and casting of semi-finished products together with finishing operations. The applied process is the subject of a patent application [7]. The schematic diagram of the pilot line is shown in Fig. 1, and its description is included in work [8]. A summary of the parameters used in the production of rods is given in Table 2. The tests included the assessment of the cleanliness of the charge before and after cleaning, analysis of the chemical composition of the cast material as a function of the process duration, macro- and microstructure tests of the cast products to determine their correctness, stability and lack of faults, control measurement of mechanical properties of semi-finished products, assessment of surface quality and dimensional stability.

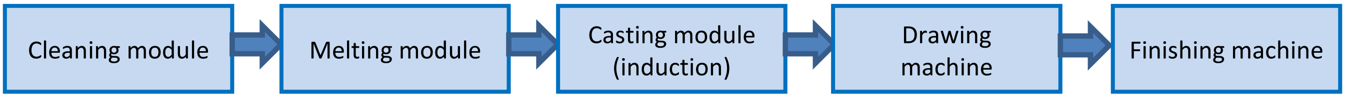


Fig. 1. General scheme of the pilot line

The degree of cleaning was assessed in accordance with the indications of PN-EN 12861 standard [9]. Chemical composition analyses were performed using a spectrometer (Thermo Scientific ARL 3460 OES). The tests of mechanical properties were carried out with the use of a testing machine (Instron 4505 / 5500K) according to PN-EN ISO 6892-1 standard, HBW hardness was measured using a hardness tester (Wolpert 2Rc) according to PN-EN ISO 6506 standard. The microscopic examinations were performed using the Olympus GX71 and SEM Zeiss EVO MA10 microscopes, and for the identification of the chemical composition in the micro-areas, the energy dispersion analysis (EDS) was performed using the Bruker XFlash® 5010 EDS spectrometer.

For the cleaning of waste, parameters analogous to those used with good effect for CC499K bronze waste were adopted, using the previously adopted assumption that the total moisture content of the melting charge may not exceed 1% (determined in accordance with the methodology specified in [9]).

Table 2.
Basic parameters of the conducted experimental casting

Parameter	**Description**
Charge	post-production waste from the production of installation fittings
Share of waste in the charge	100 %
Waste mass	about 13.4 Mg
Cleaning medium	Cystertol water solution (alkaline degreasing and washing preparation based on new generation, complex surfactants)
Screw conveyor speed	25 Hz

Air blower speed	60 Hz
Feed screw speed	25 Hz
Stirrer speed	50 Hz
Protective coating	Boron oxide flux
Semi-finished cast products	• rods ø 23 mm – 4 strand casting • rods ø 30 mm – double strand casting • hollow rods ø 45 × 10.5 mm – double strand casting • casting
Casting temperature	1180 ÷ 1200°C
Mass of cast rods	10.5 Mg

3. Results of examinations and discussion

The results of the evaluation of waste treatment efficiency are presented in the diagram in Fig. 2. The waste treatment process ensured that the charge was obtained with a total moisture content of less than 1%. The average value of chip moisture after cleaning the waste was 0.75%.

The test batches of rods and hollow rods produced were subjected to extensive testing. The average chemical composition of the cast material is shown in Table 3. This composition complied fully with the assumptions and met the requirements of the specification [3], with low amount of Pb (less than 0.1 %), and Ni, Fe impurities (much below 0.3 %). The second important parameter is the chemical homogeneity of the cast rods and hollow rods. The change in the content of alloying elements depending on the duration of the casting campaign is shown in Fig. 3. Very small variation in the content of alloying elements, especially sulphur (0.39 - 0.42 % S with permissible fluctuations in its content from 0.2 to 0.6 %), were obtained with appropriate adjustments of additives, and mainly by a stable charge obtained from waste.

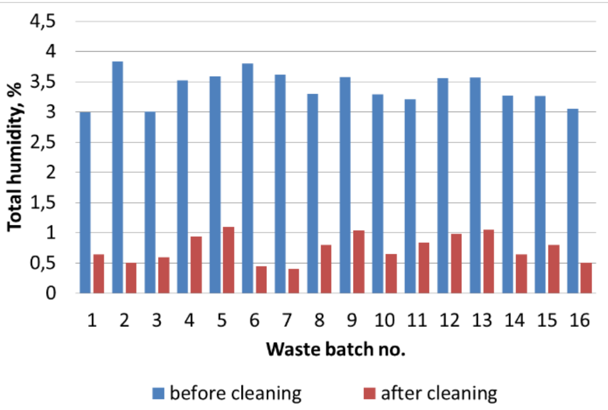


Fig. 2. Summary of test results for total moisture in chips before and after cleaning

The stability of the chemical composition of rods and hollow rods is beneficial for the casting process and for obtaining repeatable properties of the semi-finished casting products. Fig. 4 shows the cross-sectional and longitudinal macrostructure of ø 23 mm rods for samples taken at various stages of the casting process. The macrostructure is typical for this material and the method of casting, and its stability and the absence of casting defects are noteworthy. Similar casting effects were observed in the case of ø 30 mm rods and hollow rods (Fig. 5).

Table 3.
Average bronze material composition with impurities

Value	Sn	Pb	Zn	Fe	P	Ni	S	Cu
mean	4.15	0.069	1.60	0.088	0.033	0.060	0.405	93.578
std. dev.	0.048	0.010	0.150	0.014	0.013	0.015	0.010	0.187
max	4.26	0.089	1.79	0.11	0.06	0.09	0.42	94.12
min	4.07	0.05	1.19	0.07	0.018	0.04	0.39	93.3
DIN SPEC min	3.0	–	1.0	–	0.01	–	0.20	90.0
DIN SPEC max	5.0	0.10	3.0	0.3	0.10	0.3	0.6	96.0

Content of Mn, Al, Si, Sb, As, Bi - trace (0.001 ÷ 0.004 %)

The microscopic examination of the microstructure confirmed the good metallurgical quality and the absence of internal defects in the material. Tests carried out for the samples taken from rods after different casting times showed its very good stability. It was a typical dendritic casting structure, very homogeneous, with no visible casting and material internal defects, with a good and homogeneous sulphide particle distribution. An example of a typical microstructure is shown in Fig. 6 for a ø 23 mm rod.

In terms of the phase structure, a matrix in the form of a solid solution on a copper matrix with Sn and Zn additions should be distinguished, with the occurring effects of strong dendritic microsegregation, leading to the sporadic occurrence of eutectoid regions - α (Cu) + δ ($Cu_{41}Sn_{11}$) phases. In the near-surface zones of the rods and hollow rods, the eutectoid regions of the α + δ phases resulting from inverse segregation can be observed more often, as well as the typical tin sweating visible on the outer surface of the semi-products. Thus, the bronze CuSn4Zn2PS matrix after casting is similar to that of CC499K, with no significant changes. Throughout the volume of the matrix, fine spheroidal sulphide particles are visible, the distribution of which is relatively uniform throughout the cross-section. The sulphides present in bronze are predominantly Cu_2S, but in some places their mixed character of Cu_2S/ZnS can be observed. Their spheroidal shape is typical, which is favorable from the point of view of the properties of the products. Typical images of the phases occurring in the semi-finished casting products in the examined bronze are shown in Fig. 7.

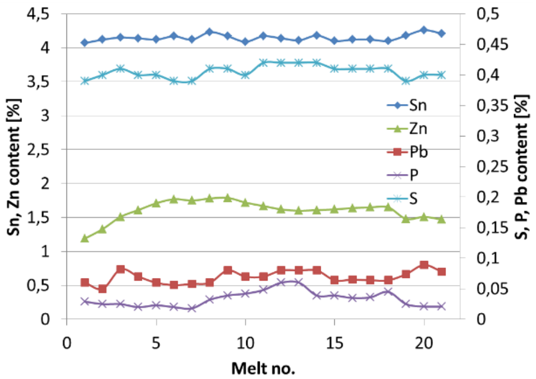


Fig. 3. Change in the content of alloying elements as a function of casting time

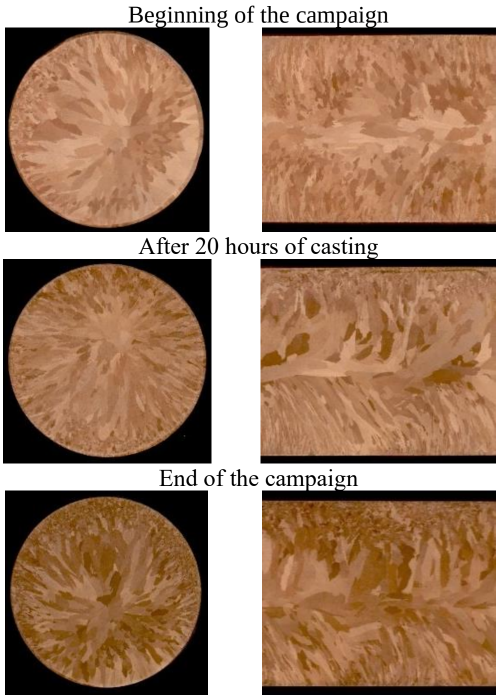


Fig. 4. Macrostructure of ø23 mm cast rods at various stages of the casting campaign

Fig. 5. Typical macrostructure of cast hollow rods ø 45 x 10.5 mm

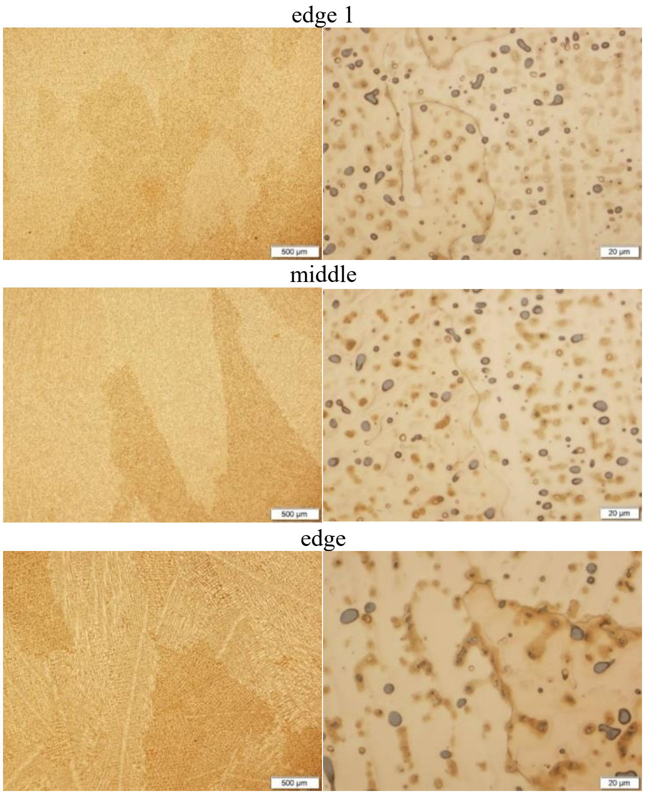
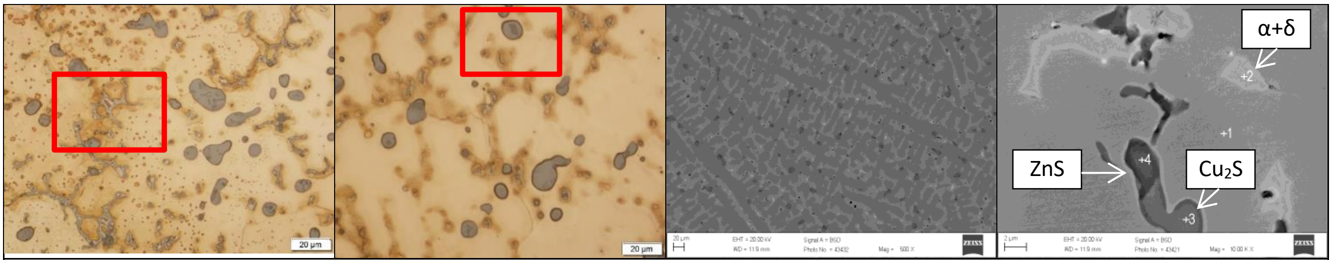


Fig. 6. Typical microstructure observed in different areas on the cross section of ø 23 mm cast rod



Element	Spot 1		Spot 2		Spot 3		Spot 4	
	Mass [%]	Atom [%]	Mass [%]	Atom [%]	Mass [%]	Atom [%]	Mass [%]	Atom [%]
Copper	94.84	96.16	74.83	84.74	79.54	66.23	10.13	7.86
Tin	2.83	1.54	25.17	15.26				
Zinc	2.34	2.30					58.75	44.30
Sulphur					20.46	33.77	31.12	47.85

Fig. 7. Microstructure of cast rods made of CuSn4Zn2PS alloy with examples of phases. The elements constituting the contamination of the sample surface: carbon and oxygen are omitted in the table of compositions

The very stable microstructure of the material is accompanied by the stability of the mechanical properties (Table 4), fully compliant with the requirements of the specification. The observed variation of properties for the samples taken during the entire casting campaign was small (low values of the standard deviation), which is also visible in the courses shown in Fig. 8 for the ø 23 mm rod. The mechanical properties are fully comparable to those of bronze CC499K, which is currently a kind of reference material used in the production of fittings. Very good plastic properties, significantly higher than those required by the specifications, should be emphasized. Also, the ductile nature of the fracture of the sample for the tensile strength tests (Fig. 9) is typical for a fully plastic material with a large plasticity margin.

Table 4.
Mechanical properties of CuSn4Zn2PS bronze semi-finished products continuously cast from treated waste and typical properties of CC499K and for comparison typical properties of CC499K bronze

Product	Value	R_m MPa	$R_{p0,2}$ MPa	A %	HBW
CuSn4Zn2PS ø 30 mm rods	mean	290	131	35.4	70.2
	std. dev.	2.12	1.51	3.25	1.65
CuSn4Zn2PS ø 23 mm rods	mean	298	130	33.2	72.8
	std. dev.	3.07	2.87	2.25	3.79
CuSn4Zn2PS ø 45 × 10.5 mm hollow rod	mean	281	131	27.9	73.0
	std.dev.	1.73	1.15	2.04	1.56
DIN SPEC 2701	min	250	110	13	65
PN-EN 1982 CC499K	min	250	110	13	65
CC499K ø 22 mm cont. cast rods	mean	310	141	36.5	69.4
	std. dev.	7.30	3.27	3.69	1.01

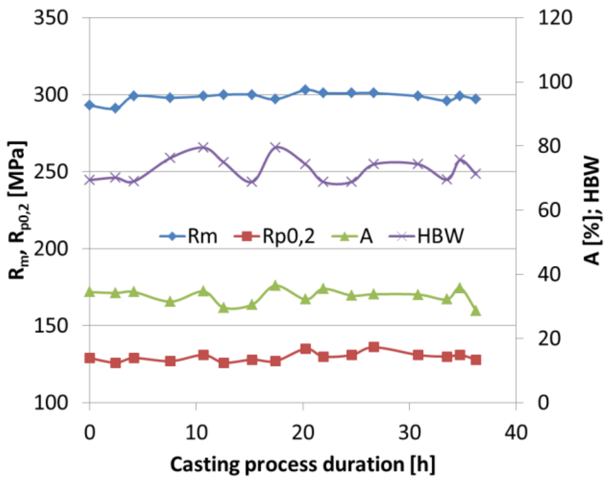
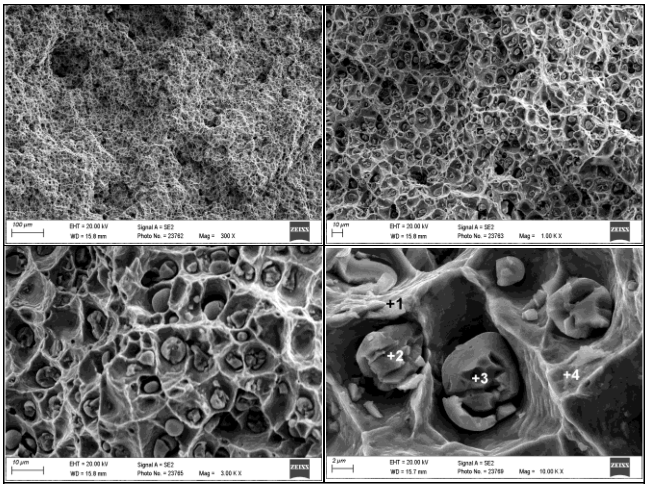


Fig. 8. Stability of mechanical properties of ø 23 mm cast rods as a function of the duration of the casting campaign

The use of large amounts of post-production waste as the input material is a necessity due to maintaining proper economy of the process and is a common practice. As a rule, however, a significant increase in the share of this component in the charge structure causes a significant deterioration in the quality of products, mainly due to the introduced impurities, and therefore their share is usually limited in industrial practice. The results of the tests and studies carried out show that the application of an additional purification process in accordance with the scheme presented in Fig. 1, together with a rigorous approach to the collection and storage of waste, allows for obtaining products practically not different in quality from those obtained with the use of the primary charge.



Element	Spot 1		Spot 2		Spot 3		Spot 4	
	Mass [%]	Atom [%]	Mass [%]	Atom [%]	Mass [%]	Atom [%]	Mass [%]	Atom [%]
Copper	65.26	30.33	71.66	44.01	78.21	54.11	82.96	53.46
Tin	2.11	0.53	0.26	0.09	0.37	0.14	1.73	0.60
Zinc	2.17	0.98					1.93	1.21
Sulphur	3.15	2.90	17.38	21.16	14.26	19.55	0.24	0.30

Fig. 9. The nature of the fracture of the ø 23 mm rod after the tensile test with visible numerous particles of sulphides, mainly Cu_2S. The elements constituting the contamination of the sample surface, carbon and oxygen, are omitted in the table of compositions

Table 5.
Technical and economic characteristics of the production of the new alloy from waste

Parameter	Value
Cast semi-finished products	10415 kg
Technological waste	1835 kg
Yield	96.1%
Melting loss	1.82%
Energy consumption	1060.5 kWh/Mg

4. Conclusions

All the experimental work and research can be summarised by the test evaluation parameters for the manufacturing of CuSn4Zn2PS sulphur bronze semi-finished products, given in Table 5. It should be emphasised that according to [10], sulphur bronze is in many respects similar to CC499K bronze, especially when it comes to corrosion resistance and, consequently, it may fully substitute material for lead-based free-cutting bronze in drinking water fittings.

The new alloy introduced into the field of fittings application has a great potential for dissemination, especially in the case of further significant reduction of the allowable Pb content in materials intended for contact with drinking water.

The conducted experimental work and research have shown that the contaminated post-production waste used as a charge, after its purification with the application of the pilot line used is a fully useful charge material. The obtained results both in terms of a stable chemical composition, homogeneous and reproducible mechanical properties, fully compliant with the specification for fitting bronzes (CC499K), as well as the lack of defects of the obtained semi-products, despite a very large share of waste material, indicate the possibility of using the tested recycling method for the production of semi-finished products made of sulphur bronze, which is an alloy that is relatively difficult to manufacture.

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