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Analysis of the Impact of Modifiers on the Formation of Non-metallic Inclusions During Continuous Casting of CuZn39Pb2 Brass

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Abstract

In this paper results of microstructural observations for series of CuZn39Pb2 alloys produced from qualified scraps are presented. The individual alloy melts were differentiated in terms of thermal parameters of continuous casting as well as refining methods and modifications. Structural observations performed by SEM and TEM revealed formation of different types of intermetallic phases including "hard particles". EDS results show that "hard particles" are enrich in silicon, phosphorus, iron, chromium and nickel elements. Additionally, formation of Al-Fe-Si and Al-Cr in alloy melts was observed as well. It was found that quantity and morphology of intermetallic phases strongly depends upon the chemical composition of raw materials, process parameters, modifiers and refining procedure applied during casting. It was observed that refining process results in very effective refinement of intermetallic phases, whereas modifiers, particularly carbon-based, results in formation of large particles in the microstructure.

Keywords: Continuous casting, Leaded brass, Precipitates, Metallography, Scraps

1. Introduction

The continuous casting method is commonly used in the manufacturing process of brass [1-4]. Determination of process parameters refers to the formation of a liquid and solid phase separation layer [5 - 7]. The use of waste materials results in distortion of this layer, which in turn does not allow for the adoption of already known models [8-12]. The problem is particularly exaggerated when raw materials are of quite different composition [13-15]. It is therefore necessary to focus on optimization of casting parameters in relation to the recyclable materials used in the process.

2. Experimental Research

The tested material was CuZn39Pb2 (according to European Standard CW612N) brass with the use of continuous casting and different parameters of the process. The influence of the amount of spent cooling liquid in primary circulation, times of granulation stops and casting quality feed were tested.

The material for testing was metal scrap. In order to approach the industrial conditions, the raw material was pre-selected using mobile spectrometers. The size of the raw material corresponded to 2Mg of the complete CuZn39Pb2 alloy.
The continuous casting process took place in a semi-industrial installation intended for testing such processes. the test stand consisted of a melting furnace. The alloy was refined using carbon, calcium carbide and complex R1 carbide with synthetic refiner RZ [16]. A graphite crystalliser with a nominal diameter of 300 mm was used. A cooling system was used with the possibility of adjusting water flow and temperature. Metal temperature - 1030 °C, water - 18 °C. Summary of casting conditions is presented in table 1. A series of 4 industrial casts was made.

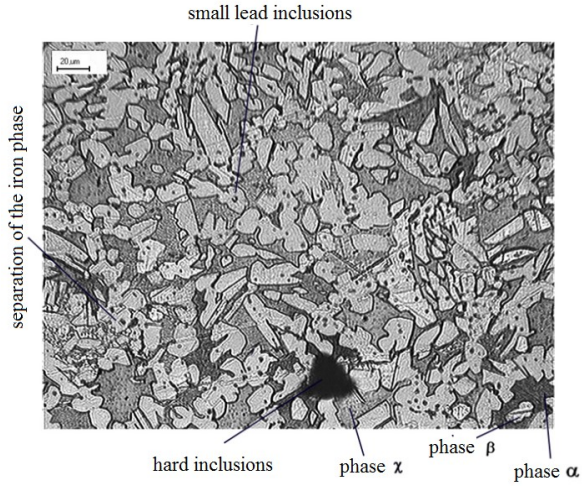


Fig. 1. Microstructure of CuZn39Pb2 alloy after wood-based refining upon casting conditions of 2mm/5s, 0.7l/min: a) without modification, b) after modification with titanium (0.05% by mass)

Figure 1 and 2 show typical microstructure of CuZn39Pb2 brass after wood-based or calcium carbide refining with and without titanium modification observed by means of light microscopy. Alloys microstructure is characterized by two phases α and β and large amount of fine lead-rich particles homogenously distributed in the cooper-zinc matrix.

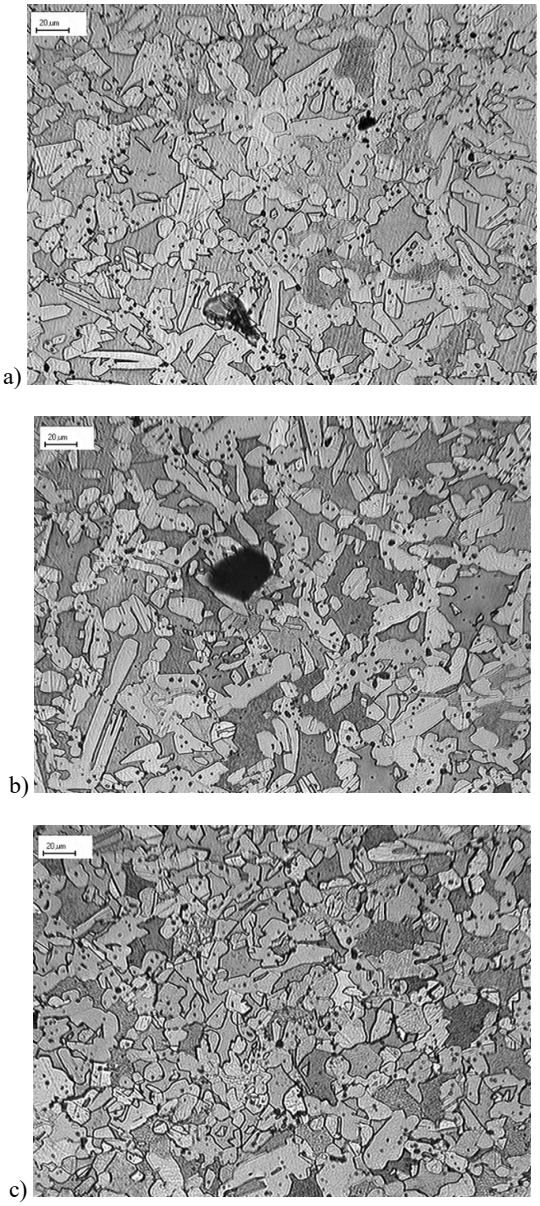


Fig. 2. Microstructure of CuZn39Pb2 alloy after calcium carbide refining upon casting conditions of 2mm/5s, 0.7l min: a) without modification, b) after modification with titanium (0.05% by mass), c) modification with titanium (0, 1% by mass)

Detailed analysis of the microstructural features of selected materials was performed by SEM and TEM techniques. Figure 3 shows the typical set of particles identified in the microstructure of Cu-Zn39-Pb2 alloy refined by calcium and cast according to conditions given for sample #7 (see Table 1). Chemical composition of micro-inclusions indicates that the white particles observed in the microstructure are enriched with lead (Pb). Additionally, complex phases imaged here as dark particles consist of zinc (Zn), sulfur (S) and trace amounts of manganese (Mn) and silicon (Si) can be identified as well (Table 2). It is worth to notice that around dark particles increased concentration of lead element can be observed

(Fig. 3). The alloy exhibits two-phase nature, alpha (α) and beta (β), as evidenced by distribution of copper and zinc in the matrix (Table 2). Figure 4 presents the microstructure of Cu-Zn39-Pb2 alloy received by casting conditions given for sample #1 (Table 1). Similar to previous observations, alloy exhibit two phase character with multi-component particles and intermetallic phases. White particles are recognized as lead-rich phases which in most cases coexists with phases enrich in silicon (Si), manganese (Mn) and iron (Fe) (Table 3). Additionally, single particles which consists of silicon (Si), phosphorus (P), chromium (Cr), manganese (Mn), iron (Fe) and traceable amounts of lead (Pb) are also identified (pt. 3) (Fig. 4, Table 3). Complex type of intermetallic phases has also been found for samples labeled as 13 and 14 shown in Figure 5. Analysis of the composition of intermetallic phases in samples 13 and 14 indicates the presence of hard particles: pt. 1 - sample 13, Figure 5a and pts. 1, 5 - sample 14, Figure 5b. They also show transition areas: pts. 2 and 3 – Fig. 5a and pts. 2 and 6 - Fig. 5b. Transition areas are characterized by a reduced or absence of: iron, chromium and manganese (pollution from the secondary circuit). The areas containing only iron were also identified (pt. 6). This analysis shows the diversity of the chemical composition of hard particles. After introducing the modifier in the form of zirconium, traces of this element were present - always in the system with silicon and iron (Figure 5c).

As a result of conducted chemical analyzes, it was found that the so-called hard precipitates in the brass are formed in the liquid phase during the synthesis of elements from secondary materials, creating large particles of 10-30 μm (randomly even reaching 50 μm). The slow crystallization caused by the slow displacement of ingots in the crystallizer promotes dissolution in the liquid phase and solid phase diffusion of these precipitates, which affects the formation of finer particles, 1-5 μm in size and smaller than 1 μm; the area 1 visible in Figure 4 is a depleted fragment after the original hard particle. TEM analysis also confirmed formation of intermetallic phases and agree well with SEM results and conclusions which arising from the experiment (Figure 6). Visible hard particles are the results of the crystallization process.

Table 1.
List of melting, casting and macroscopic parameters used in the experiment (* gray highlightes refer to structures in Figure 1-2)

#	refining	modification *	Casting parameters *		number of inclusions	
					minor below 1μm / from 1-5μm (counts on 0.001 mm^2)	large single separation 10 - 30μm (counts on 1cm^2)
1	refining using charcoal (wood-based)	---	2mm/5s	0.7 l/min	10/10	4
2		---	5mm/1s	6.6 l/min	5/5	8
3		---	5mm/5s	0.7 l/min	10/20	6
4		titanium (0.05% mas)	2mm/5s	0.7 l/min	85/2	1
5		titanium (0.05% mas)	5mm/1s	6.6 l/min	50/30	4
6		titanium (0.05% mas)	5mm/5s	0.7 l/min	30/15	2
7	calcium carbide refining	---	2mm/5s	0.7 l/min	30/10	6
8		titanium (0.05% mas)	2mm/5s	0.7 l/min	20/3	3
9		titanium (0.05% mas)	5mm/1s	6.6 l/min	40/20	2
10		titanium (0.05% mas)	5mm/5s	0.7 l/min	30/20	0
11		titanium (0.1% mas)	2mm/5s	0.7 l/min	30/10	0
12	refining carbide composite R1	---	2mm/5s	0.7l/min	10/20	7
13		zirconium (0.1%)	2mm/5s	0.7 l/min	15/10	3
14		zirconium (0.1%)	5mm/1s	6.6 l/min	30/30	4
15		zirconium (0.1%)	5mm/5s	0.7 l/min	20/15	2
16		titanium (0.05% mas) and zirconium (0.1%)	2mm/5s	0.7 l/min	40/20	0

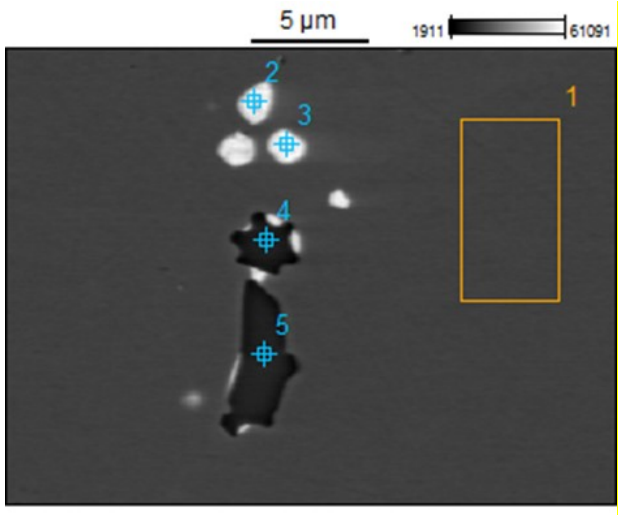


Fig. 3. SEM microstructure of Cu-Zn39-Pb2 alloy refined by calcium and casted according to conditions given in Table 1 for sample 7. SEM/EDS analysis was performed at points and areas marked in image (Table 2)

Table 2.
Results of chemical point analysis performed at points marked in Fig. 3. Results are given in mass %.

No	Analyzed elements					
	O	Si	Mn	Cu	Zn	Pb
1				65.54	34.46	
2	8.85	2.16		5.59	4.06	79.35
3	7.76	2.03		6.63	4.60	78.98
4			0.72		69.38	
5			0.55		68.58	

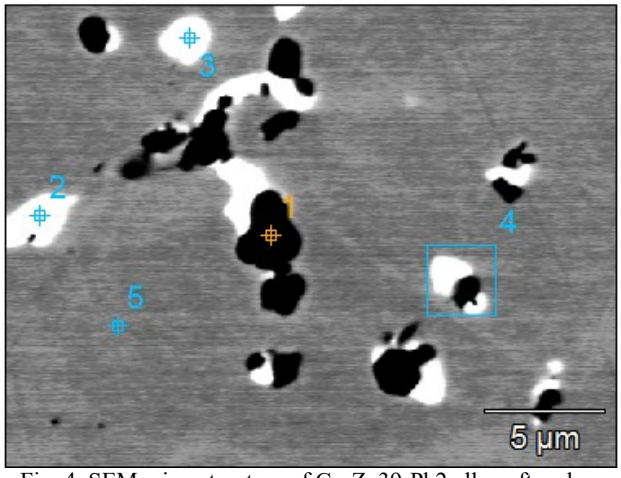
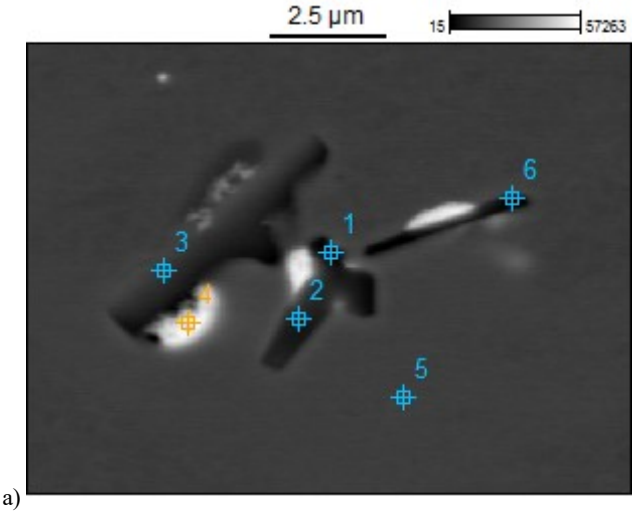


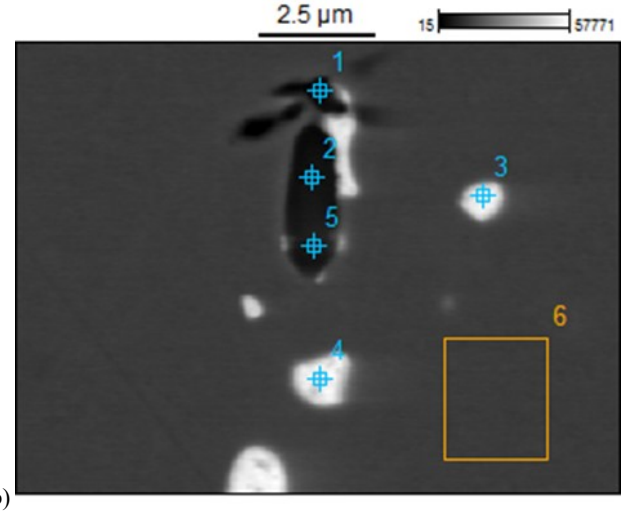
Fig. 4. SEM microstructure of Cu-Zn39-Pb2 alloy after slow crystallization conditions given for sample 1 in Table 1. SEM/EDS analysis was performed at points marked in image. Results of chemical analysis are shown in Table 3

Table. 3.
Results of chemical point analysis performed at points marked in Fig. 4. Results are given in mass %

No	Analyzed elements									
	Ca	Al	Si	P	Cr	M	Fe	Cu	Zn	Pb
1	74.8	0.9		0.6	4.9	0.4	11.6	6.9		
2		0.2					1.1	16.5	0.2	72.0
3		0.2					0.4	32.7	19.4	47.3
4	1.3	0.2	0.4	0.3	2.2		9.6	42.7	24.6	18.8
5		0.3	0.8				0.5	63.7	34.8	



a)



b)

Fig. 5. SEM microstructure of Cu-Zn39-Pb2 alloy for: (a) sample 13 and (b) sample 14 produced according to conditions given in Table 1. SEM/EDS analysis was performed at points marked in image. Results of chemical analysis - Table 4 and Table 5

Table 4.
Results of chemical point analysis performed at points marked in Fig. 5a. Results are given in mass %

No	Analyzed elements							
	Si	P	Cr	Mn	Fe	Cu	Zn	Pb
1	0.43	0.67	1.79	5.46			68.26	
2							71.22	
3						40.39	50.72	
4						8.92	8.99	82.09
5						54.61	45.39	
6		0.15			1.54	37.48	50.81	

Table 5.
Results of chemical point analysis performed at points marked in Fig. 5b. Results are given in mass %

No	Analyzed elements							
	Si	P	Cr	Mn	Fe	Cu	Zn	Pb
1		0.32	0.95	1.41			51.63	45.69
2	1.10			0.51			69.21	
3						12.39	6.60	81.01
4						8.09	4.85	87.06
5					0.63		69.06	
6					0.25	65.22	34.53	

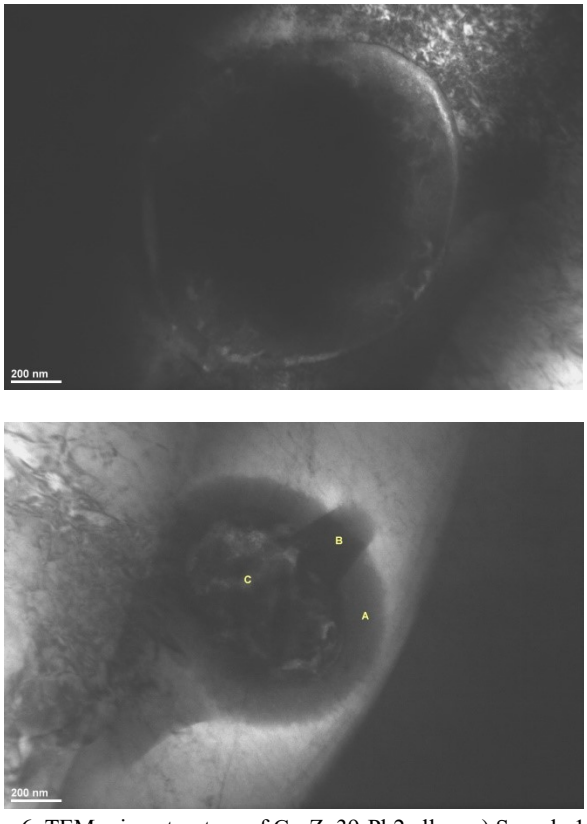


Fig. 6. TEM microstructure of Cu-Zn39-Pb2 alloy. a) Sample 1 and b) EDS analysis sample 1 produced according to conditions given in Table 1. (The chemical composition of the material at the point of EDS point analysis indicated in Fig. 6b on the Table 6.)

Table 6.
The chemical composition of the material at the point of EDS point analysis indicated in Fig. 6b. Processing option: All elements analysed (Normalised)

Spectrum TEM	O	Si	Mn	Fe	Cu	Zn	Pb
03A				0.36	64.03	34.29	1.32
03C	4.99				57.80	31.81	5.40
03B				0.38	63.42	34.40	1.81
04 incl.	15.10	0.46		0.58	47.64	27.71	8.50
05 incl.		0.37		0.43	57.91	33.58	7.71
05 incl.	9.90			0.53	51.38	30.13	8.06
05 incl.	4.98			0.46	54.17	31.63	8.75
06 incl.	10.98			0.60	51.44	29.24	7.75
07A	2.88	6.34		0.96	45.36	39.32	5.14
07B		9.30	0.28	1.37	42.07	46.10	0.89
07C base				0.40	62.00	36.76	0.85
07D bas				0.42	63.68	35.90	
08A				0.49	62.23	34.21	3.08
08B	5.86	0.40		0.33	53.21	31.47	8.74

All results in atomic %

3. Summary and Conclusions

The presented article shows the influence of titanium and zirconium on the number of inclusions and their composition. The impact of the modification procedure indicates that the quantity and quality of hard inclusions should depend on the type of modifier. The modification effect is visible in a reduced number of non-metallic inclusions - as indicated in the works [3, 13]. In addition, a reduction in the number of large particles was particularly noted. As a novelty, it was shown that after the introduction of the modifier in the form of zirconium traces of this element were present - always in the system with silicon and iron.
During the tests, the coefficient of cooling of ingots with the presence of hard inclusions was demonstrated. The slow crystallization caused by the slow movement of the ingots into the crystallizer promotes liquid phase dissolution and solid phase diffusion of these deposits, which affects the formation of finer particles with a size of 1-5 μm and less than 1 μm. This can be explained by similarly observed changes in the structure of brass ingots exposed to the magnetic field [3] or other impacts [2, 4, 5, 11, 12] affecting the formation of dendrites.
The analyzes also showed that the refining process reduces the number of non-metallic inclusions. At the same time, refining reduces the number of large deposits at the expense of growing small particles. Similar conclusions were presented in [1-3, 13-16].

Based on received results following conclusions can be drawn:

- so-called hard inclusions in brass are formed in the liquid phase; slow crystallization promotes the dissolution of precipitates in the liquid phase,

- refining treatment reduces the number of non-metallic inclusions, while affecting the reduction of the number of large precipitates at the expense of the amount of fine precipitates,
- the effect of the modification procedure on the quantity and quality of hard inclusions depends on the type of modifier - according to the analysis, it appears that the more carbide-forming adversely affect the final effect, increasing the number of large non-metallic inclusions.

Acknowledgements

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