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Evaluation of Precipitates Type in Brasses as a Function of Charge Material

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Abstract

Trial series of cast alloy MO59 obtained from qualified scrap was investigated. SEM and TEM of resulting precipitates were conducted. The SEM analysis demonstrated the dependence of silicon, phosphorus, iron, chromium and nickel in the composition of the so-called hard precipitates. TEM analysis showed the formation of phase AlFeSi and AlCr. Made studies have shown the important role of the composition of the batch melts brass CuZn39Pb2 type. The analysis of SEM and TEM resulting precipitates pointed to the formation of various forms of divisions, only one of which was described in the literature character of the so-called hard inclusions. The SEM studies demonstrated the dependence of the occurrence of inclusions rich in silicon, phosphorus, iron, chromium and nickel. In contrast, additional TEM analysis indicated the formation of AlFeSi phase type and AlCr. The results of the analyses referred to the structure of the batch. Due to the difficulty of obtaining recycled materials that do not contain these elements necessary to carry out further analyzes in the direction of defining the role of phosphorus in the formation of the so-called hard inclusions.

Keywords: Metallography, Leaded brass, Precipitates, Scraps

1. Introduction

The aim of the study is to analyze the structure of the charge and its influence on the structure obtained during the processing of metallurgical brass from recycled materials.

The previous studies [1-12] allow drawing the conclusion that there is a strong correlation between the nature of the ingots structure and formation of electron phases such as BCC β phase and HCP ε phase in the case of exceeding particular elements solubility limits [1-3]. It has been observed that formation of β and ε is complex due to mutual interactions between particular elements, which in turn make difficulties in its clear description and led to huge interpretation discrepancies presented in the literature [5-12].

Additionally, elements like oxygen, phosphorous, fluorine, chlorine and sulfur affect formation of β and ε electron phases, which make a phase analysis even more difficult.

Due to high production costs, foundry industry starts to produce alloys based on recycled materials like scraps, wastes etc. Hence, it is very important to characterize the effect of initial chemical composition of the charge on the structure of as cast materials.

2. Research programme

Research programme involves several types of recycled materials.

Table 1.
Description of the initial materials subjected to melting process

No.	Type of raw material	Trade name of the raw material	Description of the material	The type and amount of metallic impurities	The type and amount of contamination of non-metallic
1.	Scrap copper	Copper winding	Scrap in the form of: lacquered cooper wires with the dimension of ~ 1mm, cooper pipe	Scrap metal having impurities mainly: Fe, Sn, Pb, Al, Zn in a total amount up to 2%	The layers of lacquer, paint, plastics, sealants used in various types of installations. A total amount of impurities up to 5.0%
2.	Scrap brass	Leaded brass (MO59)	Lump scrap in the form of castings in various grades of brass	Scrap contaminated by Fe (screws, nuts, fittings, springs, etc.) Al (plates, fittings, pads), Sn, Pb (Sn-Pb solder).	Scale, paint, insulation, thermal plastic. The total amount of impurities up to 5.0%
3.	Scrap zinc	Zinc coated sheet	Scrap in the form of roof sheets and rain gutters	Scrap contaminated with Sn-Pb solder, fittings Fe, Pb in the form of collars window and roof trims	Scrap contaminated with dirt, moisture, tar paper in a total amount up to 6%
4.	Scrap lead	Scrap lead (fat)	Scrap in the form of protective cable coatings with power cables	Scrap free of metallic impurities	Scrap holding a thin layer of grease, soaked or dry paper, bituminous coatings (tape) and soaked jute twine. The total amount of pollution up to 8%

2.1. Melting brass

Melting was carried out in an induction furnace with a capacity of 50 kg. The collected samples were melted in a graphite crucible without using protective coverings. Chemical composition of melted samples is given in Table 2 (Tab. 2). In Table 1 (Tab. 1) is description of the initial materials subjected to melting process.

Table 2.
Result of chemical analysis performed for initial materials shown in Table 1 (selected components). Results are in weight %.

	Copper winding	Leaded brass (MO59)	Zinc coated sheet	Lead scrap (fat)
Al	0,14	0,18	0,058	0,001
Cu	98,64	58,1	0,103	0,027
Fe	0,45	0,19	0,003	0,006
Ni	0,07	0,07	0,003	0,001
P	0,04	0,01	-	0,0002
Pb	0,16	1,9	0,69	99,44
Sb	0,03	0,011	0,002	0,456
Sn	0,24	0,22	0,298	0,002
Zn	0,12	39,23	98,69	0,002
Mn	0,06	0,023	0,001	-
Ti	-	-	0,119	-
Cr	0,001	-	0,003	-
Si	0,02	0,04	-	-

Based on the chemical analysis results (Table 2) the following feedstocks were prepared to produce lead content brass alloys:
- Feed structure I: leaded brass (MO59) + correction composition (Pure Zn)
- Feed structure II: copper winding, zinc coated sheet, lead scrap.

Calculations based on assumption that cooper solution is solvent for the metallic zinc have been carried out. Based on calculated theoretical compositions of charge, some composition corrections were made due to material loses occurring during melting processes. In accordance with the decrease in the thermodynamic potential at 500K, the potential of copper oxides formation is approx. -120 KJ / mol, lead oxides -176 kJ / mol, and zinc oxides approx. -300 KJ / mol. Based on this data it has been decided to increase cooper amount of no more than 0.3% and lead amount by 0.5%. It has been expected that zinc losses will be the largest during melting process, thus in order to limits its loses, the amount of zinc has been reduced no more than 0.8% at the initial stage of melting and compensated at the final stage of melting process.

2.2. The results of structural analysis

Structural analysis was carried out by using Nikon EPIPHOT 200 light microscopy (LM), which enables microstructure studies at low magnifications and Hitachi SU-70 scanning electron microscopy (SEM), which allows microstructure imaging at higher magnifications and chemical analysis of structural components by using EDS. A typical microstructure of alloys obtained by the light microscopy. Alloys microstructure is characterized by two phases α and β commonly observed in brass alloys and large amount of fine particles almost uniform distributed in the matrix. Qualitative and quantitative analysis of visible particles was carried out based on the analysis of SEM and TEM EDS analysis.

SEM photos of the microstructures produced using SE detector (Secondary Electrons) and BSE (Back-Scattered Electrons), which exhibits high sensitivity to the atomic mass of the individual elements. In the case of alloy MO59, where the main components are: Cu (atomic mass 63), Zn (atomic mass 65), and Pb (atomic mass 207) may be expected high contrast originating from particles that are enriched in lead. This structure is shown in Figure 1 (Fig. 1).

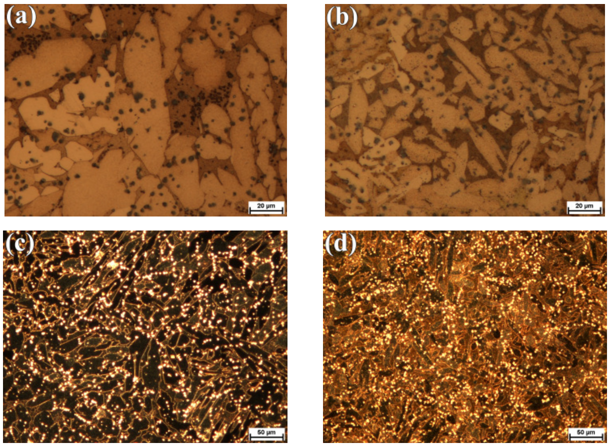

Fig. 1. The microstructure of MO59 alloy - the feed structure I (a, c) and the feed structure II (b, d) observed by means of light microscopy (LM); (a, b) bright field images, (c, d) dark field images

Typical SEM microstructures of tested alloys are shown in Figure 2. SEM imaging was performed by using SE (Secondary Electrons) and BSE (Back-Scatterd Electrons) detectors. The latter is particularly useful to detect contrast between areas with different chemical compositions. BSE images display atomic number (Z) contrast with brighter regions being generated from areas of higher average atomic number. In the case of MO59 alloy the basic components are: Cu (Z=29), Zn (Z=30), and Pb (Z=82), thus it is expected that the brighter BSE intensity might be originated from particles that are enriched in Pb.

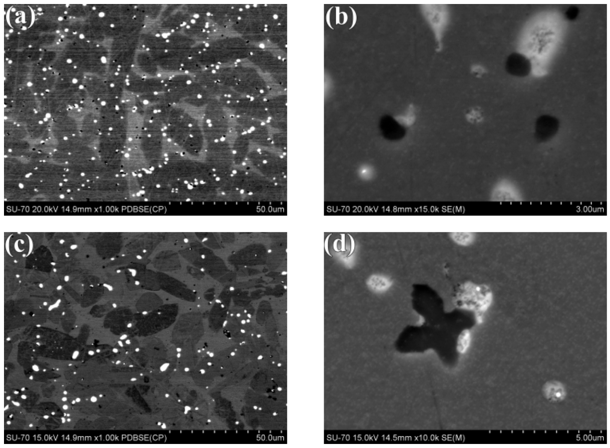

Fig. 2. The microstructure of MO59 alloy - the feed structure I (a, b) and the feed structure II (c, d) observed by means of scanning electron microscopy (SEM)

Figure 2 (a,b) presents typical microstructure of MO59 alloy – the feed structure I. Similar to light microscopy observations, alloy shows dual phase character with large volume fraction of white and dark particles. It is worth to note that dark particles usually occur around white particles, which suggests heterogeneous nucleation of such phases (Fig. 2b).

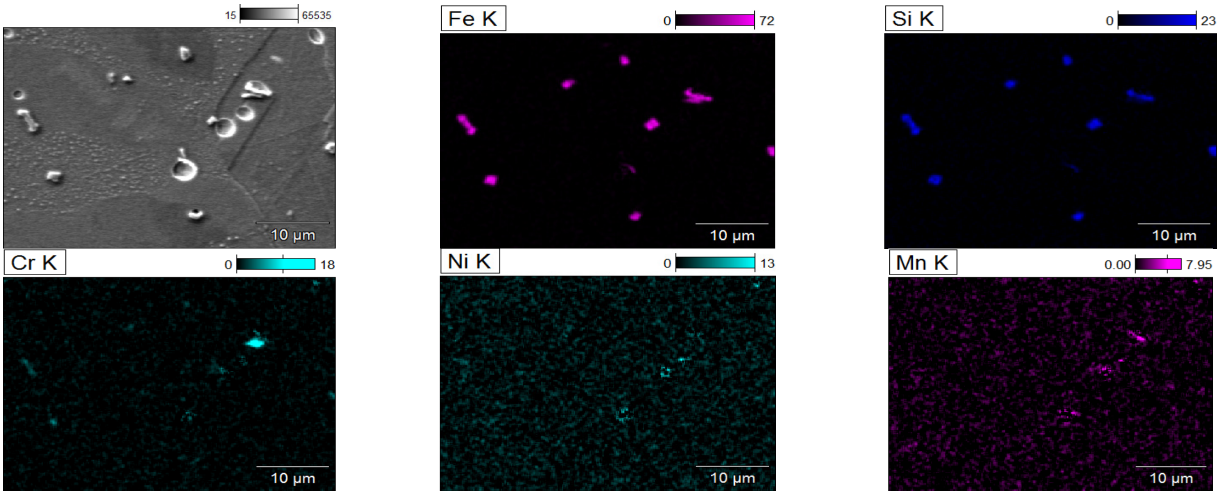

Fig. 3. Element map distribution of different elements received for MO59 alloy - the feed structure I (SEM mapping, atomic %)

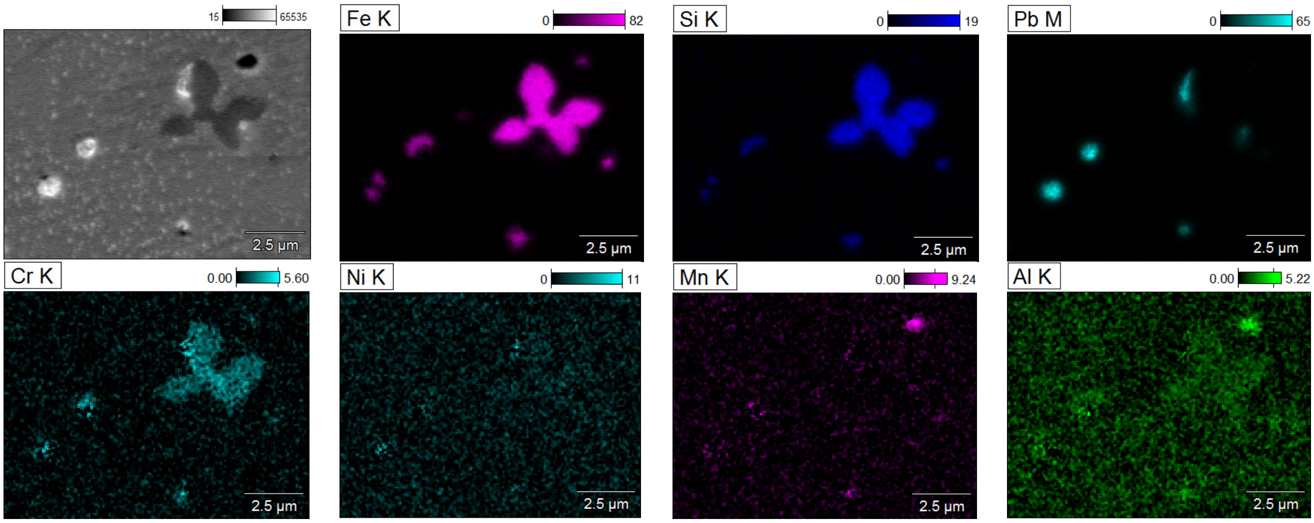

Fig 4. Element map distribution of different elements received for MO59 alloy - the feed structure II (SEM mapping). Results are in atomic %

Preliminary identification of particles composition in tested alloy is performed by means of SEM/EDS analysis. Element mapping results shown in Fig. 3 confirmed that the white phases observed in the microstructures are lead-rich particles. Additionally, the development of multi-component intermetallic phases of Fe-Si-Mn-Cr-Ni is observed (Fig.3). Some segregation of phosphorous (P) element around lead particles is also noticeable. The alloy matrix consists of cooper, zinc and small amounts of aluminum and tin as evidenced in Fig.3. Distribution of particular elements is supported by point analysis performed at different points further below. Received results are shown in Table 3.

The microstructure of the MO59 alloy – feed structure II is shown in Figure 2 (c, d). The alloy exhibits similar features as observed for MO59 alloy – feed structure I, i.e.: two phases α and β and two kinds of particles visible as white and black spots in the microstructure. One can observe that particles have different shape and morphology; bright particles are rather spherical while dark phases exhibit irregular shape. Bright phases are identified as Pb-rich particles and dark phases were found to be complex intermetallic phases that might consists of iron, chromium, silicon, phosphorus and traceable amounts of manganese and nickel (Fig. 4, Fig. 5b and Table 4).

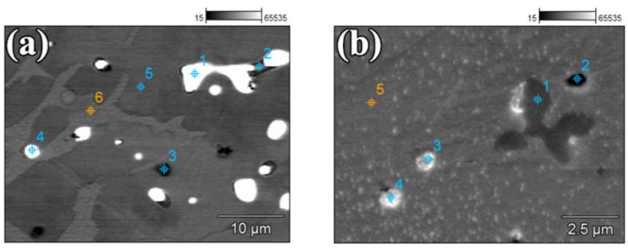

Fig 5. The microstructure of MO59 alloy - the feed structure I (a) and the feed structure II (b) observed by means of scanning electron microscopy (SEM). SEM/EDS analysis was performed at points number 1, 2, 3, 4, 5, and 6.

Summarized in Table 3 and Table 4 results of chemical analysis indicate large differences in the chemical composition of the different phases which occur in the tested samples.

Contaminants derived from scraps introduced in metallurgical process are the source of structure inhomogenity. The inhomogenity in sample labeled as feed Structure I is manifested in certain areas by the local presence of Fe precipitates, known as „hard particles" (see point 3, Figure 5). It is interesting to note the presence of phosphorous in the particles composition, which does not occur with any other phases.

Chemical analysis performed for charge feed Structure II also distinguishes two kinds of "hard precipitates" (Fig. 5b, Tab. 4). Similar to feed Structure II sample, phosphorus element is also detected as particles constituent.

More detailed chemical analysis was performed by using transmission electron microscopy.
Figure 6 shows TEM image and results of chemical analysis of particles visible in the structure. Alloy microstructure is characterized by α phase and dark lead-rich particles. Diffraction analysis, not discussed here, allows to identify grains of both α and β phases. Large phases, like quasi-spherical Pb particles, which are a few micrometers in size, can be analyzed using linear analysis (Fig. 6). It is more difficult to perform quantitative analysis of very fine, nanometers in size Fe-rich particles. During the analysis of such particles strong signal from alloy matrix is obtained.

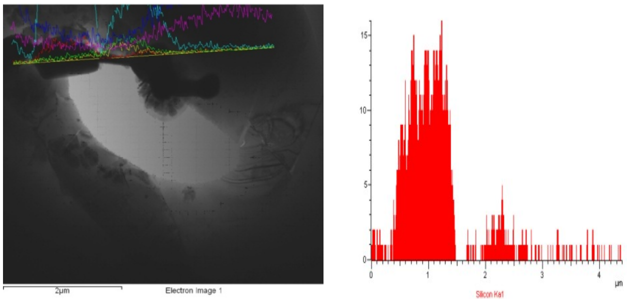

Fig.6. a) TEM image, b) Results of linear analysis. From left particles of: Al-Fe-Si, middle – Al-Cr and right - α CuZn phases

TEM analysis indicates the important role of iron, silicon and aluminum in the formation of precipitates in the Cu-Zn-Pb alloys. Similar conclusion can be drawn based on SEM observations and chemical analysis.

The interesting discovery is formation of particles enrich with phosphorous in both Feed structure I and Feed structure II samples. It is important to determine and understand role of phosphorous in the formation of precipitates in brasses. Details will be raveled in future by further SEM and TEM investigations.

Table 3.
Results of SEM/EDS analysis performed at 1, 2, 3, 4, 5, and 6 as marked in Figure 5a. Results are in weight %

	Al-K	Si-K	P-K	Cr-K	Mn-K	Fe-K	Cu-K	Zn-K	Sn-L	Pb-M
Point 1						0.01	5.69	3.71		90.59
Point 2		0.03			0.20	0.24	66.20	33.00		0.27
Point 3	0.19	7.95	3.06	3.95	0.56	49.09	23.70	11.31		0.19
Point 4	0.34	0.04				-	40.80	23.39		35.43
Point 5	0.39						66.01	33.60		
Point 6	0.58						58.42	39.54	1.46	

Table 4.
Results of SEM/EDS analysis performed at 1, 2, 3, 4, 5, and 6 as marked in Figure 5b. Results are in weight %

	Mg-K	Al-K	Si-K	P-K	Cr-K	Mn-K	Fe-K	Ni-K	Cu-K	Zn-K	Pb-M
Point 1		0.49	9.46	0.12	2.38		78.90	0.81	4.25	3.02	0.56
Point 2	4.20	0.27	1.09	0.37	1.23	1.89	21.97	0.55	41.25	21.88	5.29
Point 3		0.23					1.36		26.66	18.46	53.29
Point 4		0.27					0.40		29.11	20.39	49.83
Point 5		0.38							56.78	42.84	

In Table 3 (Tab. 3) and Table 4 (Tab. 4) are shown SEM/EDS analysis was performed at 1, 2, 3, 4, 5, and 6 and received results.

3. Summary and Conclusions

Recent studies have shown the important role of the composition of the batch melts of brass CuZn39Pb2 alloy type. Results of SEM and TEM analysis indicate on formation of different types of precipitates. Particles, known in the literature as “hard inclusions” have also been detected. The SEM studies have shown formation of these particles in areas enrich with silicon, phosphorous, iron, chromium and nickel. Complementary TEM analysis, have indicated on formation of Al-Fe-Si and Al-Cr phases. Due to the difficulty of obtaining contaminated-free scrap materials it is necessary to carry out further structural analysis in order to determine the role of phosphorous and other elements in the formation of “hard inclusions”.

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References

[1] Biernat, S. & Bydałek, A.W. (2014). Optimization of the brass melting. *Archives of Foundry Engineering.* 14(3), 5-10. ISSN (1897-3310).

[2] Bydałek, A.W. & Bydałek, A. (2014). The results of the brass refining process in the reducer conditions. *Archives of Foundry Engineering.* 14(1), 21-24. ISSN (1897-3310).

[3] Bydałek, A.W. & Biernat, S. (2012). The estimation of quality refining slag for the brass gas – slag refining.

Archives of Foundry Engineering. 12(2), 15-18. ISSN (1897-3310).

[4] Bydałek, A.W., Paul, H., Najman, K., Balcerek, D. & Janas, K. (2006). Intermatalic phasis in the brass in the continous casting. *Archives of Foundry*. 6(18), 251-256. ISSN 1642-5308. (in Polish).

[5] Romankiewicz, F. (1994). *Materials of the Conference of Dolnośląskiej,* Szklarska Poręba, 213.

[6] Wierzbicka, B. & Czyż, M. (1999). *Acta Metallurgica* Slovaca. 5(2), 443.

[7] Bydałek, A.W. (2001). *Conf. Proced. Technologia 2001*, Bratyslawa, 663.

[8] Ellner, M. & Predel, B. (1995). *Intermetallic Compounds*, Principles and Practice, J.H. Westbrook and R. Fleischer (eds.), John Wiley & Sons Ltd, 1 (91).

[9] Stolarz, S. (1974). *Compounds and high-melting phases*. Katowice: Publisher Śląsk.

[10] Biernat, S., Bydałek, A.W., Wołczyński, W. & Najman, K. Analysis of the possibility of calculating the mass on the example of brass. *Archives of Foundry Engineering.* (in print).

[11] Kondracki, M. & Szajnar, J. (2007). Possibilities for leaded brass replacement with multi-component brass. *Archives of Foundry Engineering.* 7(2), 57-64. ISSN 1897-3310.

[12] Kondracki, M., Gawroński, J. & Szajnar, J. (2006). TDA method application for structure evaluation of non-leaded fixture brasses. *Archives of Foundry.* 6(19), 149-156. ISSN1642-5308.