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Possibilities for leaded brass replacement with multi-component brass

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Abstract

Leaded brasses are most commonly used Cu alloys, especially for home fixture. High toxicity of lead to human caused tendency to eliminate this additions from these alloys. In this work a discussion of solutions to this problem is shown and possibilities of leaded brasses replacement with multi – component non – leaded brasses. In this work general properties of multi – component brasses are investigated (mechanical, technological and operating properties) as well as its structure and their correlation with chemical composition. Some interactions of additions are shown with physical and mathematical model of its influence on properties. It was found that in a complex of additions (closed system) the interactions can be described by physical model and mathematical equations showing properties in function of chemical composition can be used to optimize chemical composition for engineering alloys with known properties. However, introducing new elements to the system (chemical composition) will disturb the created models (physical and mathematical). It must be said that for investigated alloys optimal properties can be ensured using presented models. Presented approach enables optimization of alloy properties for particular application. Properties can be introduced to the mathematical model which with use of optimization methods will return needed chemical composition. Alloys engineered with use of presented approach have properties close to leaded brass with low increase in total production costs.

Key words: materials, metallic alloys, Cu alloys, non – leaded brass, properties optimization

1. Introduction

Among cast Cu alloys the most important are brasses. About 20% of world Cu production is assigned for these alloys. Lead is a common addition to brasses (about 80% of Cu-Zn alloys is produced with lead addition – up to 3% mass), which ensures proper technological and operating properties like castability, corrosion resistance and most of all machinability. Leaded brasses are used in many fields, especially in fixture production. Typical structure of this alloy is shown in fig. 1.

High toxicity of lead caused a strong tendency to eliminate lead from all products being in contact with human. World Health Organization (WHO) worked out some recommendations for lead content in drinking water, to which lead penetrates from fixture elements made from leaded brasses. In many countries legal acts arose forcing fixture manufacturers to eliminate leaded brasses from fixture production [1 – 3].

First actions taken to prevent lead leakage form the brass fixture was to modified lead inclusions distribution and size [6, 12]. In non-modified alloy lead inclusions are rather big and concentrated near the center of the casting. Modification with use of elements, which create with lead stable phases caused refinement of lead inclusions and equalization of their distribution.

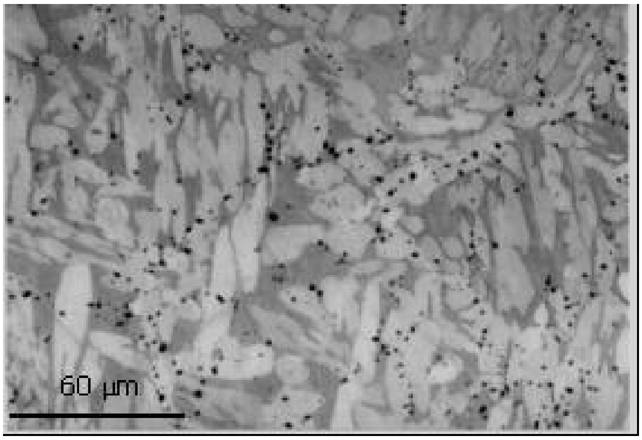

Fig. 1. Structure of leaded brass CuZn39Pb2, light α phase on dark β' background, small black Pb inclusions, $K_3Cr_2O_7$ etched [1]

Lead leakage from modified alloys was too high and efforts were put in another direction. Some works described the process of casting inner surface passivation to eliminate lead from this region [6, 13] but other works show, that only lead grinded during machining is washed out. Castings passivated are more susceptible to dezincification. Passivation increases also the costs and time of production [6, 13]. Other works were aimed on finding element influencing brass properties similar to lead an was not toxic to human. The biggest interest was directed bismuth [1, 2, 6, 13]. In many cases it acts similar to lead and by many is seen as non – harmful to human. It must be said, that bismuth is in Cu alloys the most detrimental impurity. It causes dramatic increase in brittleness. Because of great wettability and low melting point it creates a thin film distributed around the growing crystals [1, 6, 13]. Such distribution deteriorates the mechanical properties of alloy. However it also causes reduction in cutting forces during machining and appropriate chip shape and size fig. 2 and 3) [1, 2, 6, 13].

To improve bismuth distribution some additions are introduced: P, Sn, In or Sb. They change the wetting angle and cause the bismuth to occur as globular inclusions. The best results are observed with use of In. Bismuth can be also introduced to the alloy as a compound with other elements: S, Se or Te. Alloys with Bi and Se (compound Bi_2Se_3 with 64% Bi and 36% Se mass content) additions have very similar properties to leaded brasses. These alloys are more susceptible to corrosion than leaded brasses and much more expensive. Moreover many studies show that bismuth is only slightly less harmful to human than lead (selenium is more toxic than lead, fig. 4) [19] and with higher tendency to corrosivity their "ecological value" is very doubtful.

Few publications are dedicated to substitution of leaded CuZn alloys by multi – component brasses. The main reason is here the possibility of many phase transitions and synergic influence of alloy additions on structure and properties of the alloy.

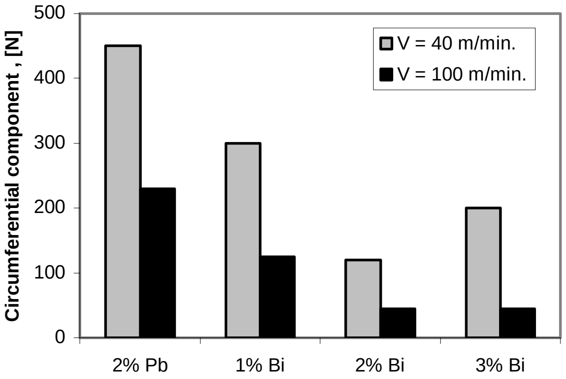

Fig. 2. Circumferential component of cutting force for various cutting speed and brasses with different additions [1]

Precise knowledge about this influence and elements interactions would enable alloy properties control. Mathematical model for these interactions would enable optimization of alloy chemical composition for particular application. Presented work show methodology and some results obtained in this field.

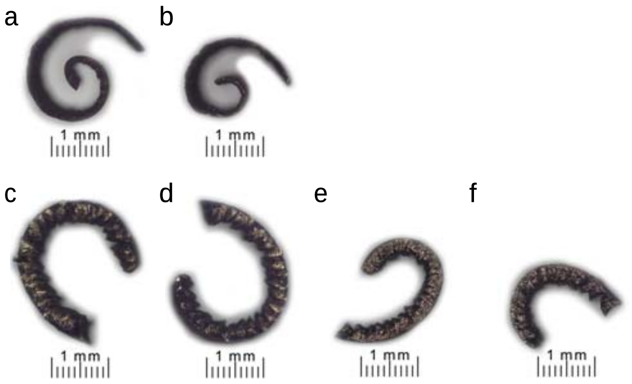

Fig. 3. Chip shape for CuZn alloys containing (in mass %): (a, b) 2% Pb, (c) 1% Bi, (d) 1,5% Bi, (e) 2% Bi, (f) 3% Bi [1]

2. Studies and results

In presented studies additions interactions and influence were investigated for multi – component brasses. Cu content was remained equal in all alloys (59% mass). To the alloy following addition were introduced: Al, Si, Ni, Fe, Sn and P. Alloy was prepared from pure elements (Cu99,99; Zn99,9; Sn99,9) or preliminary alloys (CuNi13, CuFe12, CuSi16, CuAl50, CuP10) in induction furnace according to brass technology. All casts were made up to the active experiment with changing chemical composition. During the studies different properties were observed to get the complete model of occurring interactions and their influence on alloy properties.

Chemical composition of investigated alloys was examined on rontgenographic spectrometer ALR type 8420+XRS. Precision of this apparatus was 0,15% mass for Cu content and 0,004% for other elements.

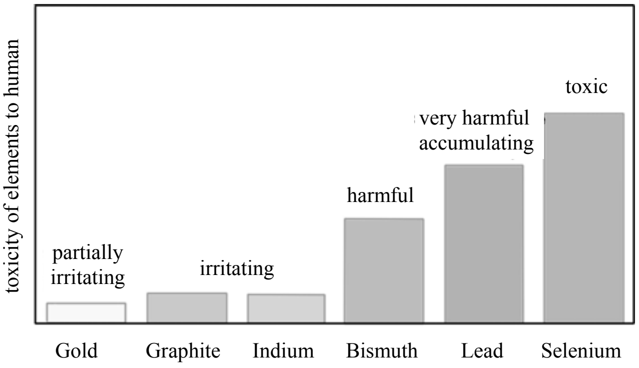

Fig. 4. Evaluation of toxicity to human for different elements, gold given for comparison [19]

2.1. Crystallization process

For each alloy thermal and derivative analysis has been conducted [1, 4, 5, 10, 14, 15, 17]. The scheme for this measurement is shown on fig. 5.

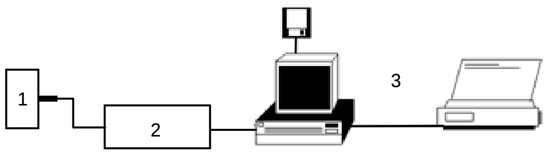

Fig. 5. Scheme for TDA apparatus: 1 – mould with NiCr – Ni thermocouple, 2 – A/C converter, 3 – computer system [5]

Data collected from TDA analysis can be used for observation of structure occurring in the alloy during solidification. Figures 5 and 6 show cooling and crystallization curves for fixture brass with two – phase structure (fig. 6 - α+β' brass) and one – phase structure (fig. 7 - β' brass). With use of information about structural components quantity a mathematical and phenomenological model can be proposed for quantitative structure observation during that stage of alloy manufacturing [5, 17]. Experimental verification showed that fraction of main structural components can be with high precision described with use of TDA curves characteristic points parameters [5, 17].

For occurring points on crystallization curve (first derivative of temperature after time) physical interpretation is following: points A, B and C are connected with heat effect related to solidification (L→β), points D, E and F are connected with heat effect related to α phase occurrence and are registered in solid state (β→α+β). By lower temperature also other heat effects can be observed; one connected with β→β' transition and in alloys containing lead heat effect related to lead solidification [5, 17].

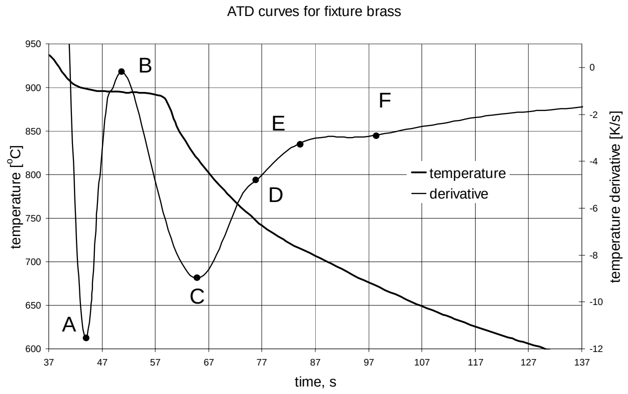

Fig. 6. Thermal and derivative analysis curves (cooling T(t) and crystallization dT/dt(t) curve) for two – phase brass (α+β'), letters indicate the characteristic points on crystallization curve

Data from thermal and derivative analysis was also used to create phenomenological and mathematical model of chemical composition influence on temperature registered in characteristic points. This model was also verified in experiment and showed good agreement of experimental data.

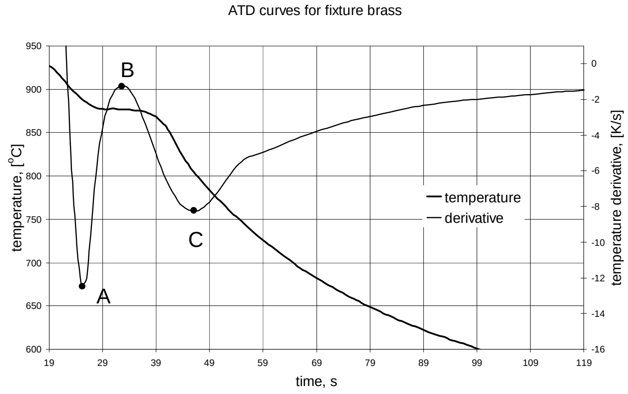

Fig. 7. Thermal and derivative analysis curves (cooling T(t) and crystallization dT/dt(t) curve) for one – phase brass (β'), letters indicate the characteristic points on crystallization curve

2.2. Structure

Structure of alloys was investigated using light microscopy, quantitative analysis with image analysis (Multiscan v13.01) and rontgenographic microanalysis on scanning microscope with EDAX attachment – used for structural components identification [4, 8]. These results have shown which elements have the strongest influence on intermetallic phases occurrence [8].

In studied alloys different types of structure were observed. Examples of obtained structure are shown on fig. 8 – 12. Typical two – phase structure is shown on fig. 8.

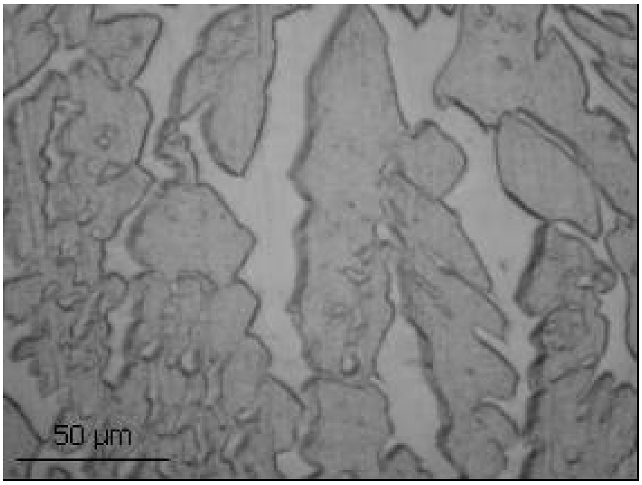

Fig. 8. Typical structure for two – phase brass, dark α phase on β' background, HNO_3 etched

With growing content of alloy additions more structural components occurred. Some additions caused occurrence of γ phase (fig. 9) and other phases out of Cu – Zn system (fig. 10, 11 and 12).

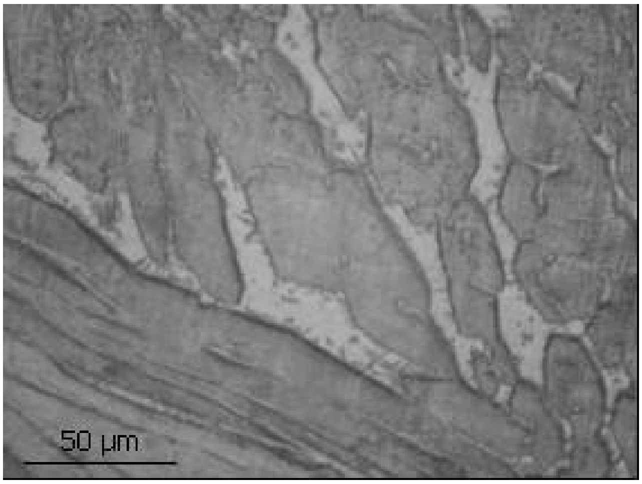

Fig. 9. Structure for three – phase brass, dark α phase on β' background, small γ phase particles on α/β' interface, HNO_3 etched

In some cases, especially by high aluminum and silicon content only β' phase in microstructure was observed (fig. 11). High content of phosphorus caused occurrence of numerous intermetallic phases (fig. 12).

To examine chemical composition of additional structural components rontgenographic microanalysis was conducted. It has revealed that by high iron and silicon content occurring phases are reach in these elements (fig. 13 and 14). Map of elements distribution confirmed these results (fig. 15).

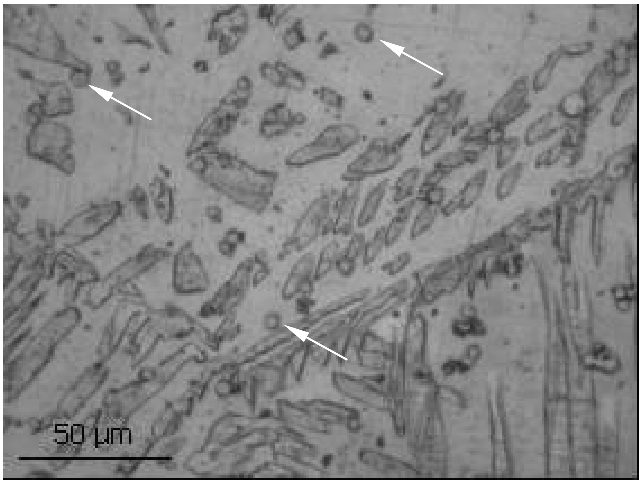

Fig. 10. Structure for three – phase brass, dark α phase on β' background, small intermetallic phases (arrows), HNO_3 etched

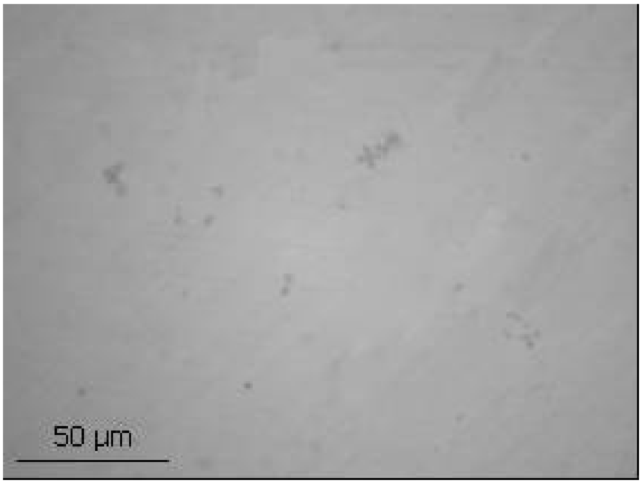

Fig. 11. Structure for two – phase brass, dark intermetallic phases on β' background, not etched

Introduction of phosphorus to the alloy caused occurrence of phases reach in that addition. These phases have strong influence on all properties of the alloy.

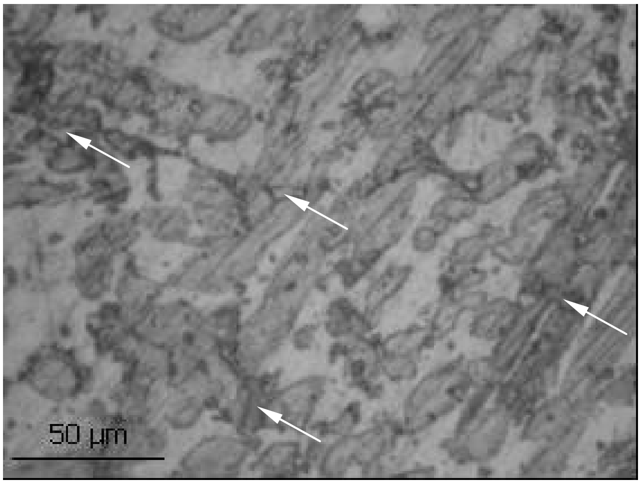

Fig. 12. Structure for multi – phase brass, dark α phase on β' background, small numerous intermetallic phases, HNO_3 etched

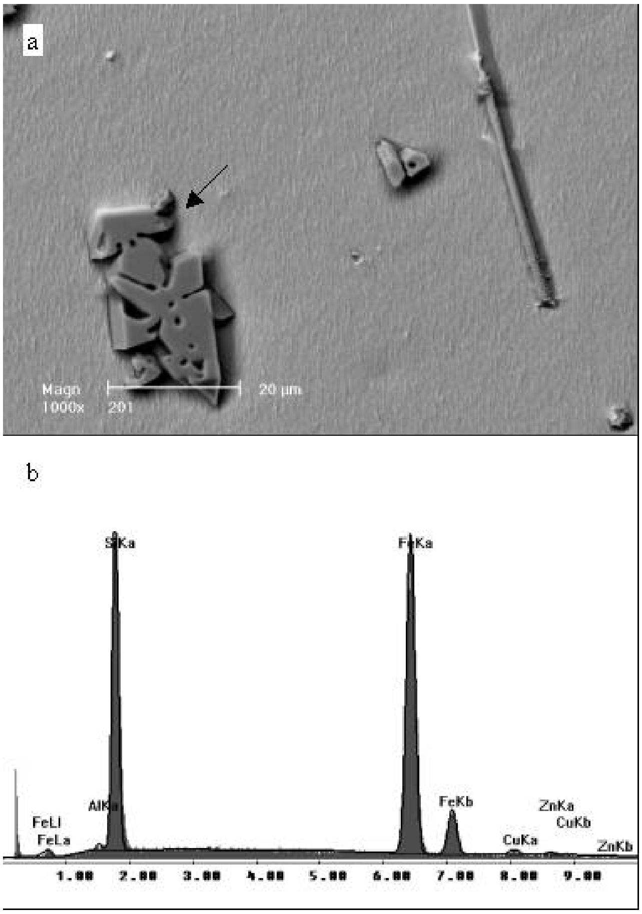

Figure 13. Rontgenographic microanalysis of hard inclusions; a) measuring field, b) point analysis of the inclusion pointed by arrow (% mas. content: 71.15 Fe, 25.35 Si, 1.72 Cu, 1.17 Zn, 0.60 Al)

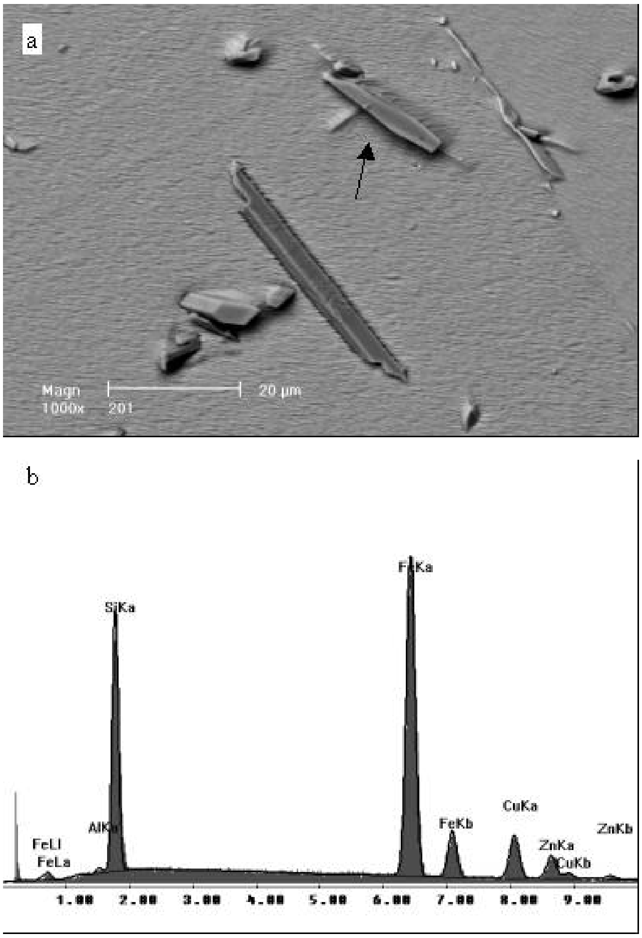

Figure 14. Roentgenographic analysis of hard inclusions; a) measuring field, b) point analysis of the inclusion pointed by arrow (%mas. content: 59.61 Fe, 18.22 Si, 11.54 Cu, 10.23 Zn, 0.40 Al)

2.3. Mechanical properties

Some standard mechanical tests were conducted showing influence of chemical composition and structural components influence on mechanical properties of multi – component brasses. These were tensile test, hardness and impact resistance.

Results obtained in mechanical testing were used for multi – component properties optimization. It must be said that multi – component alloys have much higher mechanical properties than typical leaded brasses. Moreover it is possible to obtain high strength simultaneously with high plastic properties. Such solutions have been achieved and experimentally verified.

2.4. Technological properties

In scope of technological and operating properties investigation three tests were conducted: castability with use of

Navarro – Alcacero technological test, machinability during drilling with constant force [18] and corosivity in solution creating conditions for dezincification.

Castability test revealed which additions have the strongest influence on this property, although as a technological test it has been imposed with some uncertainty, the direction of elements influence was determined. Studied multi – component alloys show castability in wide range, often higher than laded brasses.

Test used for machinability evaluation was based on Dagnell's method of drilling with constant force. This method was selected because it is very sensitive to every structure or chemical composition changes. Dagnell's test enables observation of several parameters connected with machinabilty: cutting resistance, influence of machined material on tool wear and chip shape.

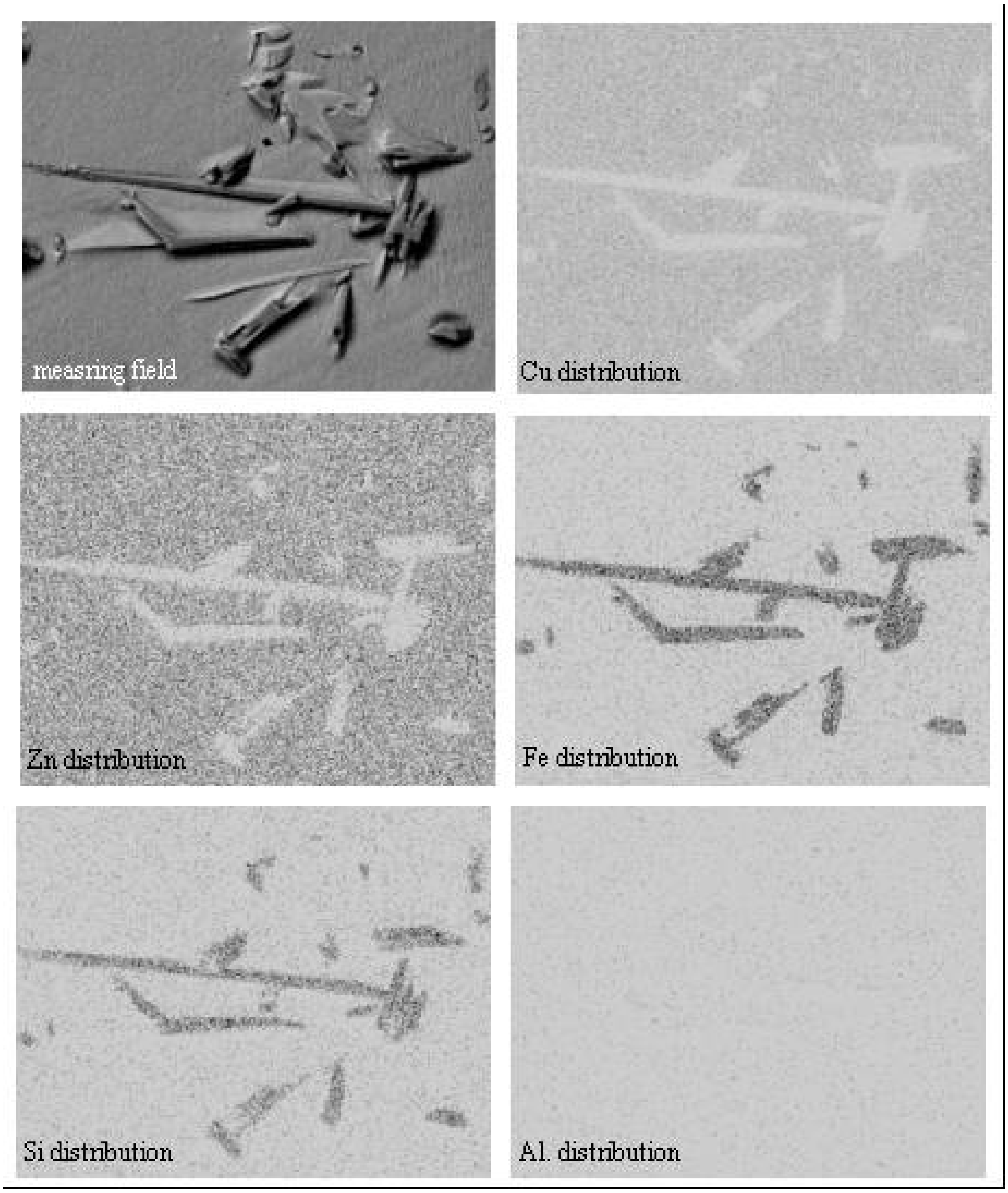

Fig. 15. Maps of elements distribution and measuring field, greater content of specific element is shown with more dots (darker field)

Parameters obtained during tests permit after some equation transformations [18] to represent the drilling time in function of hole depth. Difference in drilling time for investigated alloys is shown on fig. 16. As can be seen from this diagram multi – component brasses show different machinability. From results analysis it must be said, that machinability close to leaded brass can be achieved with maintenance of high other properties – it has been experimentally verified.

On fig. 17 and 18 a comparison of chip shape and size for leaded brass and studied multi – component brasses is illustrated. For many investigated alloys fine chips were obtained which do not effect machining process and were ease to remove from machine tool.

With use of statistical analysis some mathematical models describing machinability parameters in function of chemical composition were proposed. Their experimental validation confirmed possibility of alloy design with assumed properties.

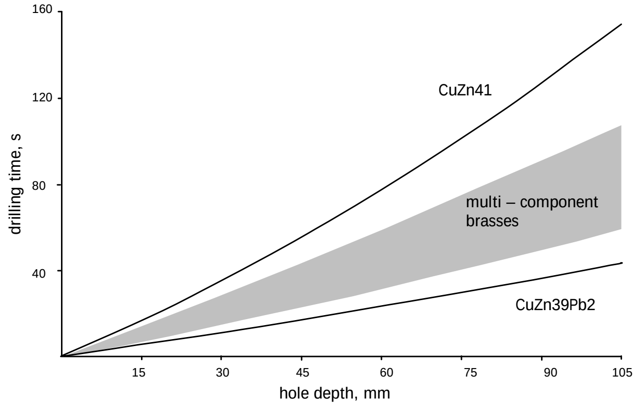

Fig. 16. Drilling time in function of hole depth for different CuZn alloys [16]

3. Conclusions

Conducted studies show that in closed system additions interactions can be described by phenomenological and mathematical model what can be used for optimization of alloy properties and their chemical composition engineering. Validation of created equations showed good agreement with experimental results.

In this studies phenomenological and mathematical model were also created for dependence of structural components quantity and chemical composition of multi – component brasses.

Observation of TDA curves during solidification enables structure forecasting. This part of studies was also verified experimentally and has shown good agreement.

It must be said that presented approach enables engineering of multi – component brasses with technological properties comparable to leaded brass with only slight increase of costs.

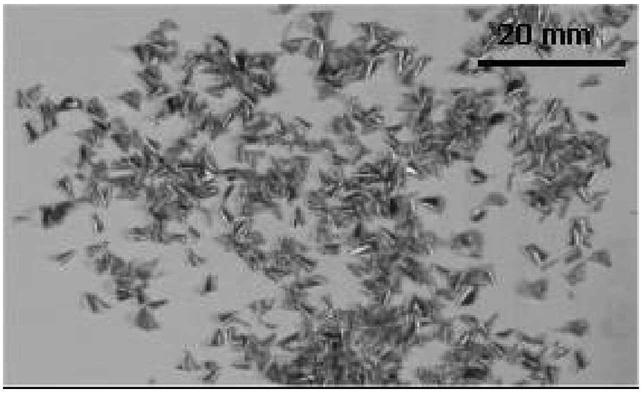

Fig. 17. Chip shape for classic leaded brass CuZn39Pb2 alloy

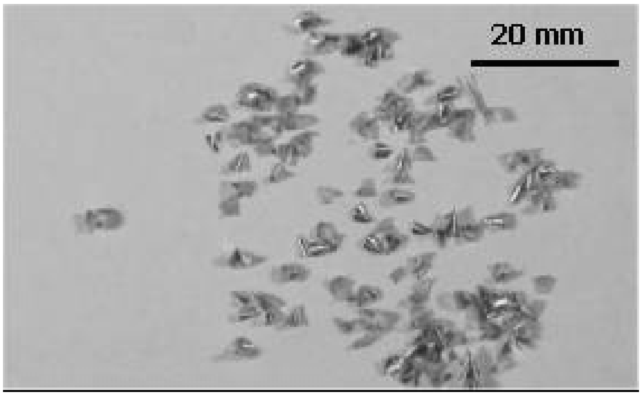

Fig. 18. Chip shape for multi – component alloys investigated

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