



The crystallisation of the aluminium bronze with additions of Si, Cr, Mo and/or W

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ABSTRACT

Purpose: The aim of this paper is description of the process of the crystallization of new aluminium bronzes with the complex silicides of the iron.

Design/methodology/approach: Additions Cr, W, Mo and Si were introduced to create in the microstructure of the aluminium bronze of the complex silicides of the iron about high mechanical and physical proprieties to the bronze BA1044. The process of formation the microstructure of the bronze with use of the method of the thermal and derivative analysis (TDA) was analysed. The examinations under the microscope and X-ray microanalysis of the surface distribution of elements were conducted.

Findings: From carried research results, that in the aluminium bronze BA1044 after addition Si, Cr, Mo and/or W the phase κ_{Fe} , κ_{Ni} crystallize as the complex silicides of the iron. Elements such as: Fe and Si dissolve first of all in silicides in the smaller stage in the matrix of the bronze, Mn and Ni they dissolve in matrix and silicides, Cr dissolves in the larger stage in silicides than in the matrix, W and Mo dissolve in silicides however they crystallize as nanocrystals in the metal matrix and create with her composite.

Research limitations/implications: Results of investigations of aluminium bronze BA1044 and alloys after adding to him about 1% Si were introduced in the article and suitably: 1.22 % Cr; 0.82 % Mo; 0.020 % W; 0.60 % Cr, 0.17 % Mo and 0.017 % W.

Originality/value: The original results of the investigations of the crystallization of the new bronzes (innovative materials and casting technologies) for which the process of arising microstructure the method TDA was not analysed so far were introduced in the article. The article possesses cognitive values not only essential for researcher but and practician-melters.

Keywords: Metallic alloys; Aluminium bronze; Complex silicides of the iron; TDA method

MATERIALS

1. Introduction

The influence Al, Fe and Ni on microstructure and the proprieties of multiple aluminium bronzes it was introduced in works [1,2]. Microstructure of bronze about content about 10% Al, 4% Ni and 4% Fe are compound from the phase $\alpha + (\gamma_2$ near the higher concentration of Al in the melt) and occurrence of rich phases in nickel and iron, such possible is as $FeAl_3$, $NiAl_3$, $FeNiAl$, [1], if also compound nickielic phases κ_{Ni} $Ni(Fe,Al,Cu)$

and ferric κ_{Fe} $Fe(Al,Ni,Cu)$ [2]. Chrome in aluminium bronze as it is applicable so far more rarely, although it advantageous influence is written down on their microstructure and specificity ($CuAl_{11}NiCrFe$) [3].

In the literature the lack of exhausting information about the influence Cr, W, Mo and Si on the crystallization of bronzes from the group Cu-Al-Fe-Ni.

Well-known it is, that Si with elements, such as: Cu, Ni, Fe, Mn, Cr, Mo and W the number of silicides creates about the various configurations of the type Me_nSi_b [4]. From the point of

view of high mechanical specificity and physical they find as modern design materials more widest employment [5÷7].

Therefore, the investigations of the process of the crystallization of the aluminium bronze BA1044 with additions Cr, W, Mo and Si were conducted the method of thermal and derivative analysis in the aim of the identification of thermal effects of crystallizing phases. The examinations under the microscope and X-ray microanalysis of the surface distribution of elements were also conducted.

2. Methodic of research

The chemical composition of the studied bronze was introduced in table 1. Smelt multiple aluminium bronzes from pig sows BA1044 in the laboratory inductive stove in the graphite crucible, the surface of the liquid metal was isolated from the atmosphere of surroundings the layer DESULCO (99,9% C).

After overheating alloy for temperature 1200°C and it introduce removal slag, depending on kind of bronze, required amount of alloy addition: chrome technically clean (98,5% Cr), ferromolybdenum FeMo60, tungsten (99,9% W), metallic silicon (99% Si). The alloy was cast, after isothermal unbearable and removal of the slag, to testing set TDA then. The investigations of the process of crystallization were conducted the method of the thermal and derivative analysis (TDA) with utilization of the Crystaldigraph of the firm Z-Tech.

Investigations on the metallographic and electron microscope were conducted on samples low-cut from testing set TDA. Microsection on the sample from testing set TDA it was made on the height of the weld of thermocouple. Microsections was digested the reagent Mi17Cu.

The X-ray microanalysis of the surface distribution of elements were conducted on the microanalyzer of the firm Thermo Electro Corporation.

3. The results of investigations

3.1. The thermal effects of the crystallization of phases

Microstructure and characteristics TDA of alloys W1÷W5 (Tab. 1) were showed on Figures 1÷5.

The process of creating microstructure in analyzed alloys draws ahead in several stages, cause creation of the thermal effect in the form peaks on derivative characteristic $dt/d\tau$. The crystallization of the bronze W1 (BA1044) runs in following stages (Fig. 1):

- C-H → the primary crystallization of the phase β (the crystallization of the phase directly from the liquid),
- H-P-Q → crystallization of phase κ_{Fe} (first phase transformation in the solid state),
- Q-R-S → crystallization of phase κ_{Ni} ,
- J-K-L → the partial transformation $\beta \rightarrow \alpha$,
- M-NO → the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$.

In the result of the process of crystallization, in the temperature of surroundings, the bronze BA1044 has complex microstructure from phases $\alpha + \gamma_2 + \kappa_{Fe} + \kappa_{Ni}$.

Make additions to the studied bronze 1,22 % Cr and 1,03 % Si called out the considerable influence on the course of the process of the crystallization of the alloy (Fig. 2). From the analysis of the diagram of phase equilibrium Cu-Cr it results, that near the concentration 0,73 % Cr in the alloy with the copper crystallizes eutectic in the temperature 1077 °C (eutectic point 1,28 % Cr) [8]. In the multiple alloy of the copper, such what the bronze is studied (BA1044+1,03% Si+1,22% Cr, W1 Tab. 1), possible there is the shift of the eutectic point in the direction of the lower content of chrome in the relation to the diagram Cu-Cr, and in the diagram of Cu-Al the aspect ratio the eutectic transformation in the direction to the line higher concentrations of Al in the bronze.

The crystallization of the bronze W2 (BA1044+1,03% Si+1,22% Cr) it runs in following stages (Fig. 2):

- A-E → crystallization hypereutectic of the primary phase, probably complex the silicide of the iron κ_{FeCrSi} , rich phase in chrome (the crystallization directly from the liquid),
- B-H → crystallization of eutectic $\kappa_{FeCrSi} + \beta$,
- M-NO → the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$,
- X-Y-Z → the peritectoid transformation $\alpha + \gamma \rightarrow \nu$.

In the result of the process of crystallization, in the temperature of surroundings, the bronze has complex microstructure from phases $\nu + \kappa_{FeCrSi}$.

The copper with molybdenum does not create solid solutions [8]. The influence of molybdenum on the characteristic temperatures of the primary crystallization of the aluminium bronze similar is to the influence of chrome.

The crystallization of the bronze W3 (BA1044+1,00%Si+0,82%Mo) runs in following stages (Fig. 3):

- A-E → crystallization hypereutectic of the primary phase, probably complex the silicide of the iron κ_{FeMoSi} , rich phase in molybdenum,
- B-H → crystallization of eutectic $\kappa_{FeMoSi} + \beta$,
- J-K-L → the partial transformation $\beta \rightarrow \alpha$,
- M-NO → the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$.

In the result of the process of crystallization, in the temperature of surroundings, the bronze has complex microstructure from phases $\alpha + \gamma_2 + \kappa_{FeMoSi} + \text{nanocrystals Mo}$. The separate thermal effect of their crystallization was not registered because of the small quantity nanocrystals Mo.

Similarly as molybdenum, tungsten does not also create solid solutions with the copper [8]. Because of the high temperature of melting the tungsten (3422 °C) 0,020% W were successful to dissolve in the bronze BA1044 through diffusion.

The crystallization of the bronze W3 (BA1044+1,13%Si+0,020%W) runs in following stages (Fig. 4):

- C-H → the primary crystallization of the phase β ,
- P → crystallization of phase κ_{FeWSi} ,
- R → crystallization of phase κ_{NiWSi} ,
- J-K-L → the partial transformation $\beta \rightarrow \alpha$,
- M-N-O → the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$.

In the result of the process of crystallization, in the temperature of surroundings, the bronze has complex microstructure from phases $\alpha + \gamma_2 + \kappa_{FeWSi} + \text{nanocrystals W}$. The separate thermal effect of their crystallization was not registered because of the small quantity nanocrystals W. Simultaneous addition 1,30% Si, 0,60% Cr, 0,17% Mo and 0,017% W to the bronze BA1044 it caused that the crystallization of the bronze W5 ran in following stages (Fig. 5):

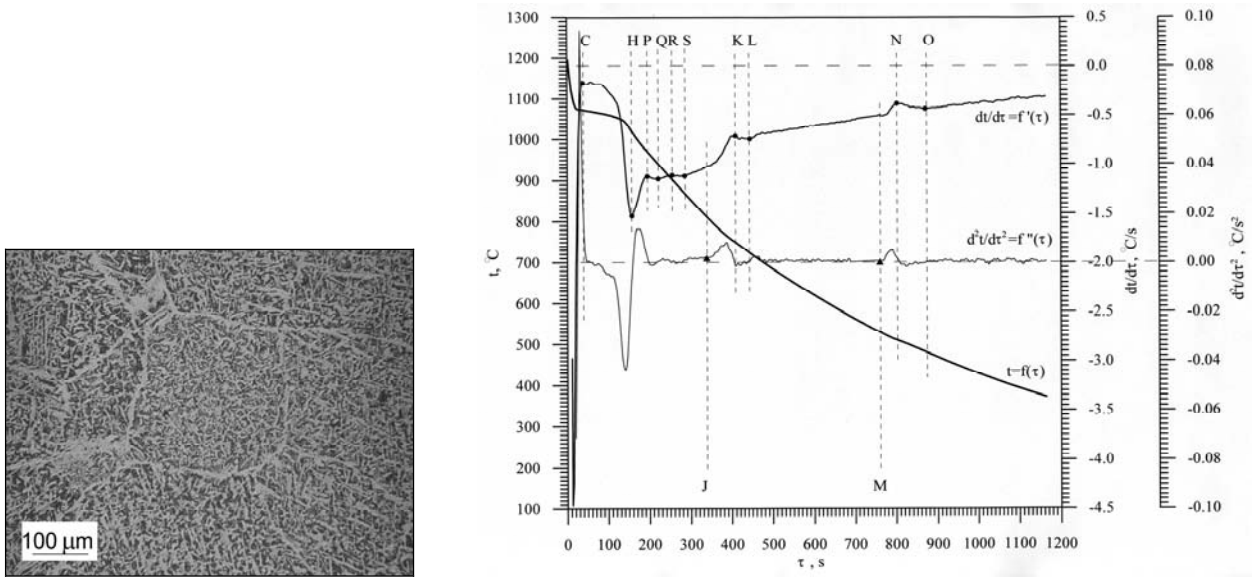


Fig. 1. Microstructure and characteristics TDA of the bronze W1 (BA1044)

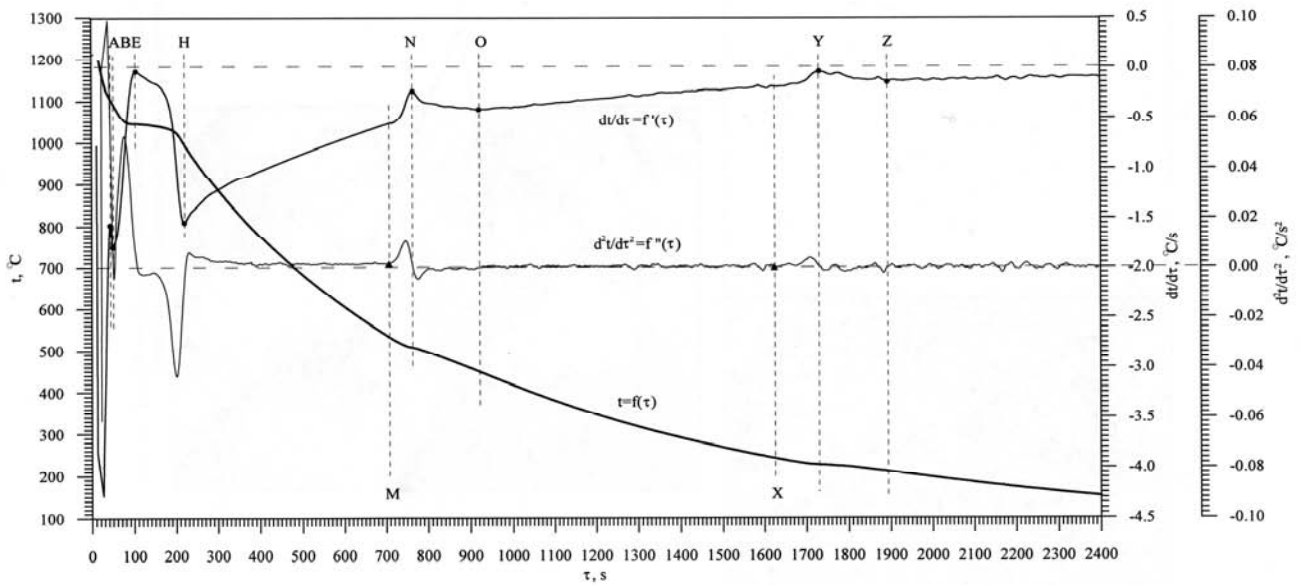
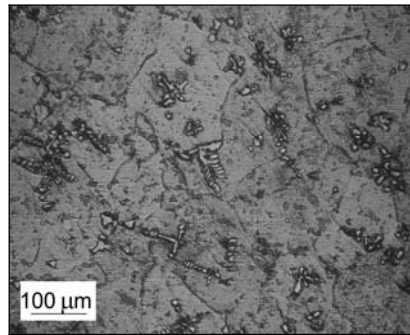


Fig. 2. Microstructure and characteristics TDA of the bronze W2 (BA1044+1,03%Si+1,22%Cr)

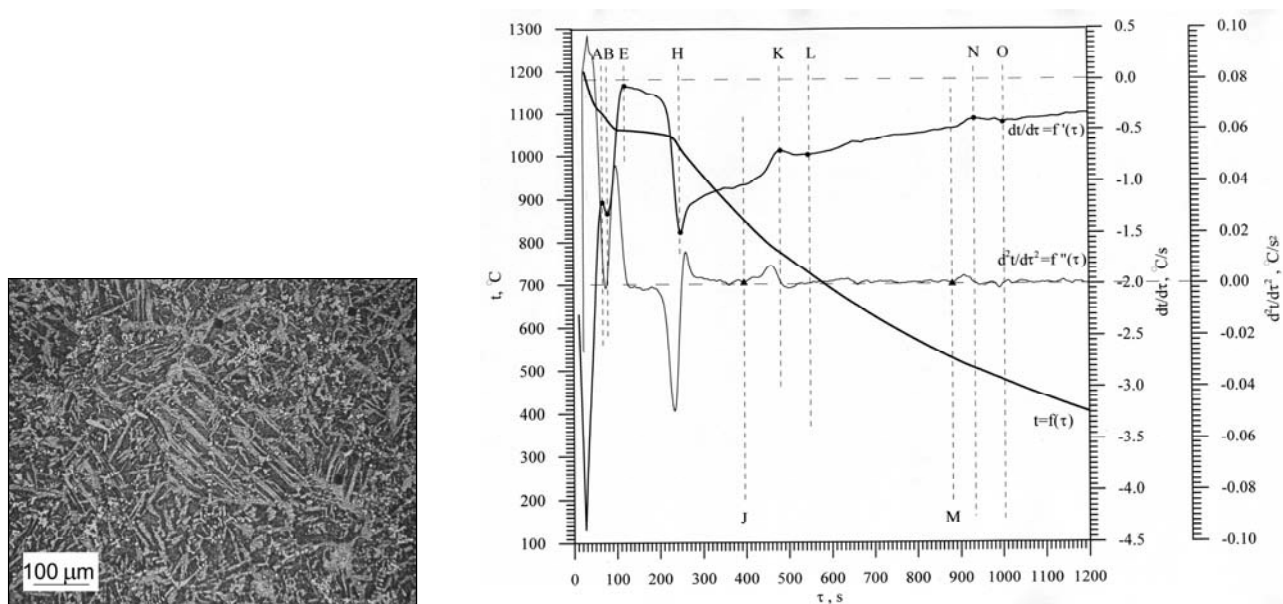


Fig. 3. Microstructure and characteristics TDA of the bronze W3 (BA1044+1,00%Si+0,82%Mo)

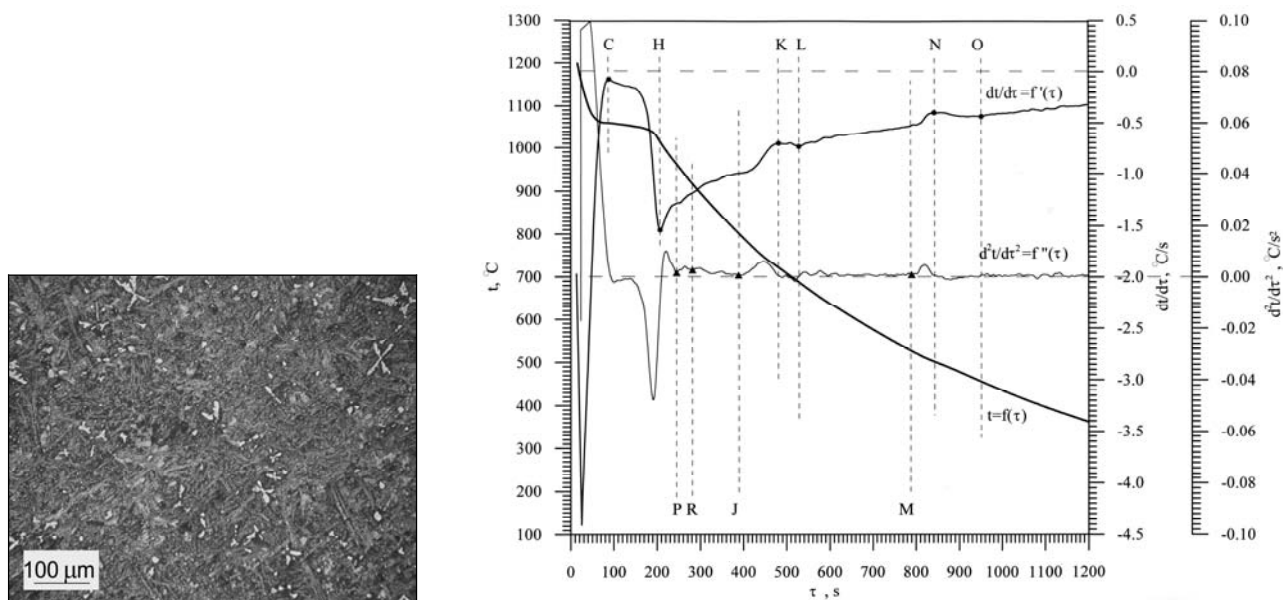


Fig. 4. Microstructure and characteristics TDA of the bronze W4 (BA1044+1,13%Si+0,020%W)

Table 1.
The chemical composition of the studied bronze

No. alloy	Chemical composition, %									
	Cu	Al	Fe	Ni	Si	Mn	Cr	Mo	W	Zn,Pb,Sn,P
W1	79,13	10,60	4,83	4,70	0,42	0,26	-	-	-	balance
W2	75,37	12,26	4,40	4,29	1,45	0,29	1,22	-	-	balance
W3	76,05	9,66	6,77	4,43	1,42	0,27	-	0,82	-	balance
W4	78,87	9,49	5,18	4,41	1,55	0,30	-	-	0,020	balance
W5	77,58	9,68	5,54	4,32	1,72	0,32	0,60	0,17	0,017	balance

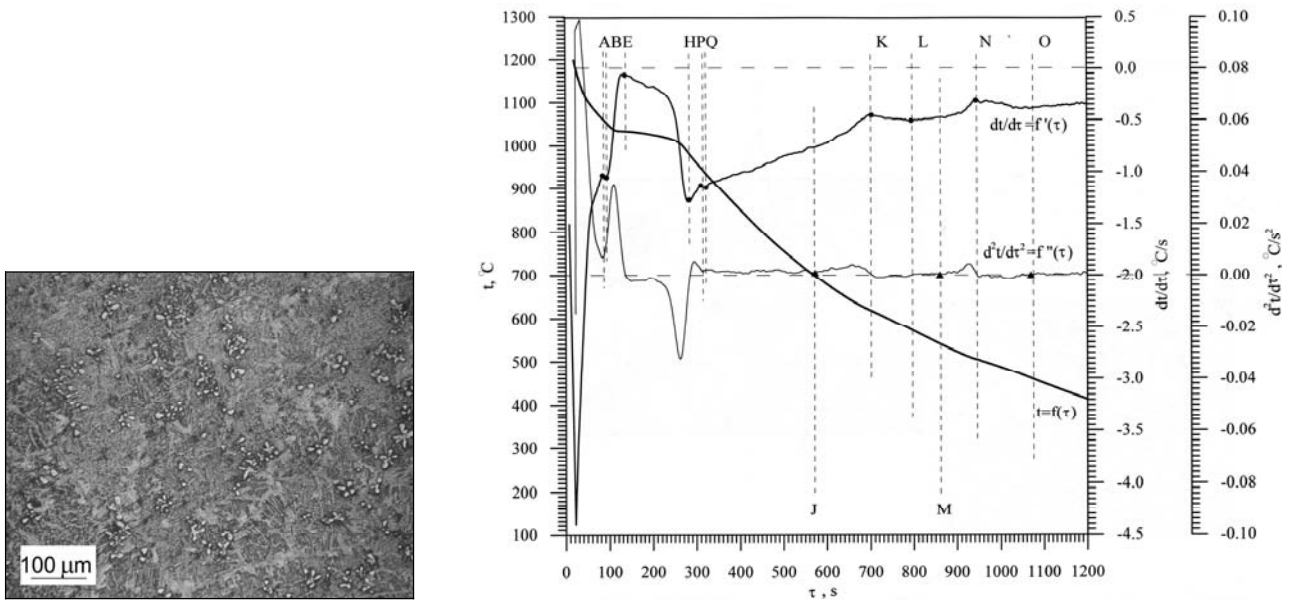


Fig. 5. Microstructure and characteristics TDA of the bronze W5 (BA1044+1,30%Si+0,60%Cr+0,17%Mo+0,017%W)

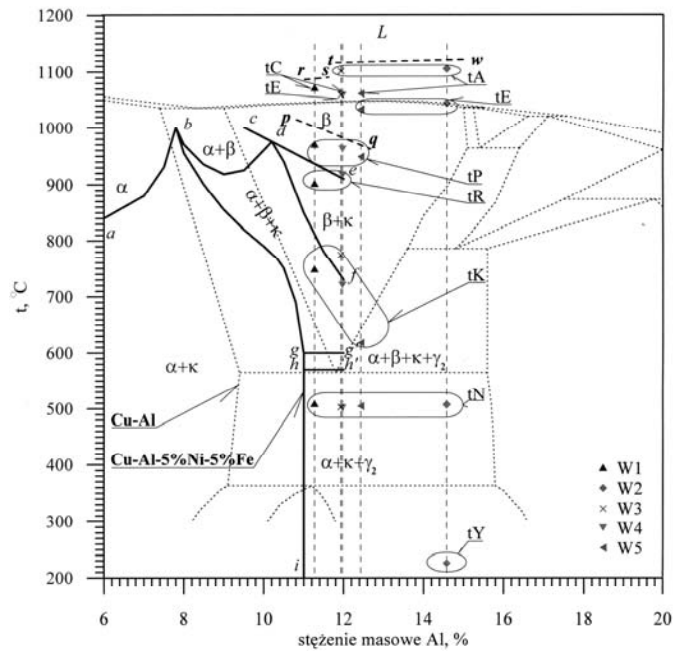


Fig. 6. The characteristic temperatures of phase transformations of studied bronzes on the background of the diagrams of Cu-Al [8] and Cu-Al-5%Ni-5%Fe [9]

- A-E → crystallization hypereutectic of the primary phase, probably complex the silicide of the iron $\kappa_{FeCrMoWSi}$,
- B-H → crystallization of eutectic $\kappa_{FeCrMoWSi} + \beta$,
- P → crystallization of phase $\kappa_{FeCrMoWSi}$,
- J-K-L → the partial transformation $\beta \rightarrow \alpha$,
- M-N-O → the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$.

In the result of the process of crystallization, in the temperature of surroundings, the bronze has complex microstructure from phases $\alpha + \gamma_2 + \kappa_{FeCrMoWSi} + \text{nanocrystals Mo} + \text{nanocrystals W}$. Because of the small quantity nanocrystals Mo as and W the separate thermal effect of their crystallization was not registered.

The characteristic temperatures of phase transformations of studied bronzes (W1÷W5 Tab.1) were introduced on the Figure 6 on the background of the diagram of Cu-Al [8] and Cu-Al-5% Ni-5% Fe [9], for „supplementary” the content of Al in studied bronzes - accept according to [10] the assumption, that 1% addition of Si (for the alloys of Cu-Al) is equivalent 1,6 % Al.

It was estimated on the basis of conducted investigations, in the relation to the diagram Cu-Al-5%Ni-5%Fe, the locations of the temperature of the crystallization of phases $\kappa_{Fe(CrMoW)Si}$ the line p-q and the temperature liquidus the line r-s and for alloys crystallizing hypereutectic the temperature liquidus the line t-w. Picture of microstructure was shown on Figures 7 and 8 properly and results of investigations of X-ray microanalysis of the surface distribution of elements in the microstructure of the bronze W5 (BA1044+1,30% Si, 0,60% Cr, 0,17% Mo and 0,017% W).

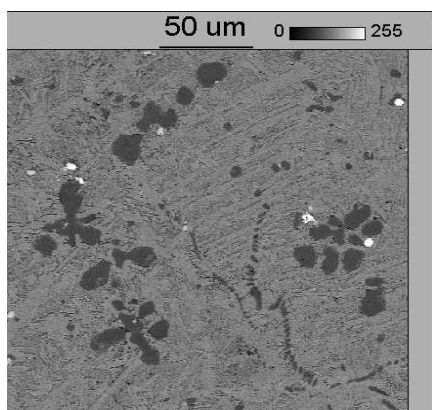


Fig. 7. The microstructure of the bronze W5 (the electron microscope - BSE)

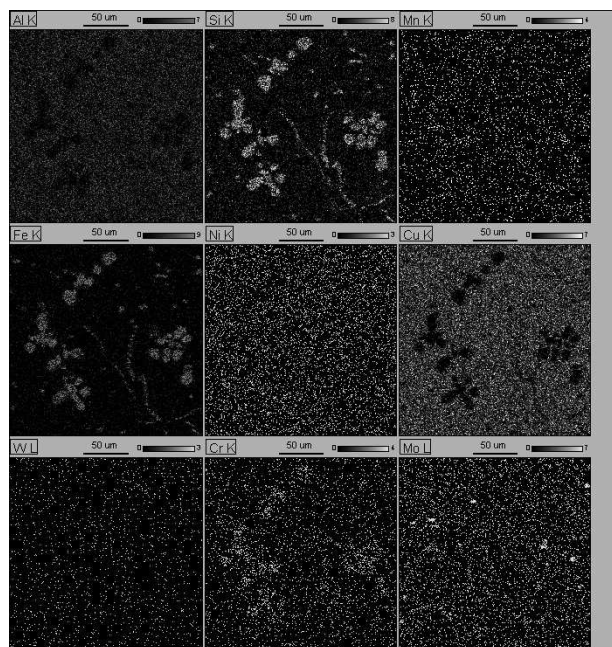


Fig. 8. The map of the surface distribution of elements in the microstructure of the bronze W5

From the carried analysis result, that Mn and Ni, how also Mo and W it is characterizes the comparatively even distribution in all phases of microstructure, Al and Cu first of all, it is located in the metal matrix of the bronze (β , γ_2), there is the basic components of the phases of type κ Fe and Si.

4. Conclusions

From the data disclosed in this study the following conclusions follow:

- in the aluminium bronze BA1044 after make additions Si, Cr, Mo and/or W the phases of the type κ_{Fe} , κ_{Ni} crystallize as the complex silicides of the iron,
- it dissolves Fe and Si first of all in silicides in the smaller measure in the metal matrix of the bronze,
- it dissolves Mn and Ni in the metal matrix and silicides,
- Cr dissolves in the larger stage in silicides than in the metal matrix,
- it dissolves W and Mo in silicides, however in the metal matrix crystallizes as nanocrystals creating with matrix composite.

References

- [1] Z. Górný, Casting aluminium bronzes, Part I and II, Institute of Casting, 2006 (in Polish).
- [2] T. Grzegorzewicz, Nickelless aluminium bronzes with increased durability and resistance on corrosion, University of technology Wrocław, 2005 (in Polish).
- [3] M. Wysięcki, The influence of chemical composition and structural building on the usable proprieties of multiple aluminium bronzes, Scientific Works of Institute of Machine Buildings, Szczecin University of Technology 57, 1976 (in Polish).
- [4] B. Aronsson, T. Lundström, S. Rundqvist, Borides, silicides and phosphides – a critical review of their preparation, Properties and Crystal Chemistry, John Wiley & sons INC, New York, 1965.
- [5] R.D Weir, Thermophysics of advanced engineering materials, Pure Applied Chemistry 71 (1999) 1215-1226.
- [6] S.V Raj, A preliminary assessment of the properties of a chromium silicide alloy for aerospace application, Materials Science and Engineering A 192/193 (1995) 583-589.
- [7] E. Ström, J. Zhang, S. Eriksson, C. Li, D. Feng, The influence of alloying elements on phase constitution and microstructure of $Mo_3M_2Si_3$ (M=Cr,Ti,Nb,Ni, or Co), Materials Science and Engineering A 329-331 (2002) 289-294.
- [8] M. Hansen, K. Anderko, Constitution of Binary Alloys, Mc Graw-Hill Book Comp., New York, 1958.
- [9] M. Cook, W.P. Fentiman, E. Davis, Observations on the structure and properties of wrought cooper-aluminium-nickel-iron alloys, Journal of the Institute of Metals 80 (1951/1952) 419-429.
- [10] K.P. Lebedev, L.S. Ranes, G.F. Šcemetev, A.D Gorjačev, Casting bronzes, Leningrad, 1973 (in Russian).