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Influence Cr on Crystallization and the Phase Transformations of the Bronze BA1044

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Abstract

The investigations were introduced in the paper, method of thermal and derivative analysis (TDA), the process of crystallization and phase transformation in the solid state of the aluminium bronze CuA110Fe4Ni4 (BA1044) and with the addition 0.3% Cr. Two intermetallic phase were identified in the microstructure of the bronze BA1044: κ_{Fe1} - rich in Fe and Cu and κ_{Fe2} - rich in Fe, and in the microstructure of the bronze BA1044+0.3 % Cr only one phase κ_{Fe1} - rich in Fe, Cu and Cr. The presence of chrome in the bronze BA1044 reduce size the primary crystals of the phase β, reduces the dynamics of the processes of thermal phase transformation in the solid state and lengthens the time their of duration.

Keywords: Innovative materials and casting technologies, Aluminium bronze, Cr, Crystallization, TDA method

1. Introduction

Near content 5% Ni and 5% Fe crystallize in the Cu-Al-Ni-Fe bronzes intermetallic phases on the base of phases Al_3Fe and Al_3Ni (or the complex phase of Al(Fe, Ni, Cu) - κ), and the eutectoid transformation of the phase β draws ahead in the range of the temperature about 580÷ 600°C [1]. The investigations of the influence of chrome were conducted for Cu-Al-Cr bronzes [2÷4], Cu-Al-Ni [5], Cu-Al-Fe, Cu-Al-Fe-Mn-Ni [6]. Affirm, that Cr influences microstructure, mechanical properties and corrosive resistance profitably, it shows border solubility in the phase α and the high-temperature phase β, as also size reduction of crystallites and the components of microstructure modify works on bronzes but was not examined, the method of thermal and derivative analysis (TDA), its influence in CuA110Fe4Ni4 bronze on the course of his crystallization and phase transformation in the solid state. In the aim of size reduction of microstructure, and in the consequence this obtainment of the essential improvement of the mechanical property of the bronzes of Cu-Al-Fe and Cu-Al-Fe-Mn complies the modifiers in which they are basic elements: B, Ti, Zr or Ca in quantity from 0.04 ÷ 0.06 % [7-12].

2. Methodic of research

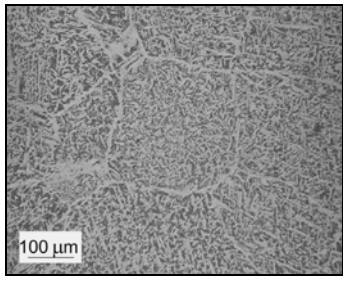
The CuA110Fe4Ni4 bronze (W1) about chemical composition: 10.60 % Al, 4.83 % Fe, 4.70 % Ni, 0.26 % Mn, 0.15 % Zn, 0.42 % Si and CuAl10Fe4Ni4Cr (W2) about chemical composition: 10.41 % Al, 4.78 % Fe, 4.67 % Ni, 0.25 % Mn, 0.15 % Zn, 0.40 % Si with the addition 0.31 % Cr was fused in the laboratory inductive furnace. Overheat charge about the mass 3.5 kg to the temperature 1250°C and it was kept under the layer of charcoal isothermal. Alloys were refined the Bronoxal. After 10 minutes, since the moment of the addition of refiner, the liquid alloy about the temperature 1200°C was cast to testing probe TDA-10. Microsections execute in the area of the center of the thermal cast from testing probe and digest the Mi17Cu reagent. Metallographic

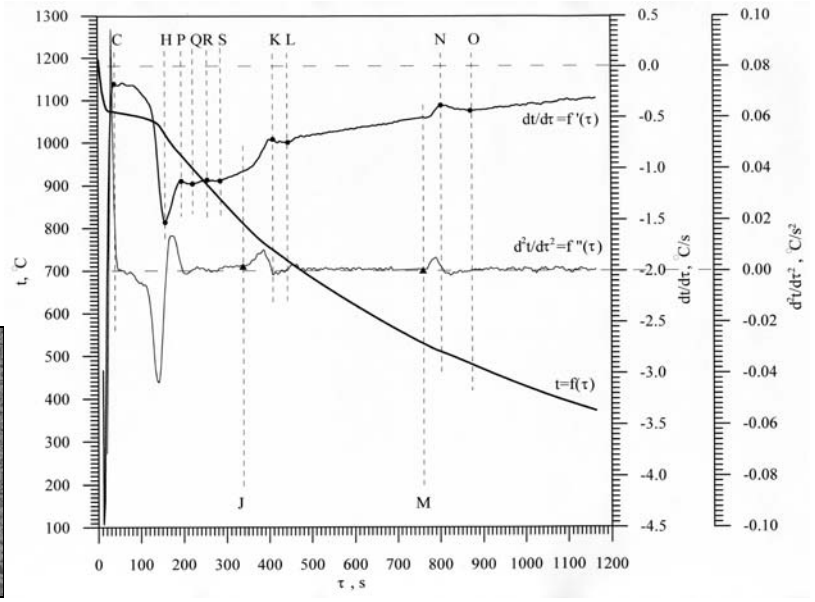
investigations were executed on the optical and electron scanning microscope of the firm Thermo Electro Corporation.
The punctual microanalysis of the concentration of elements was executed on the microanalyzer of the firm Thermo Electro Corporation. The process of crystallization and phase transformation in the solid state was studied the method of the thermal and derivative analysis (TDA). These processes were described following quantity: time τ, temperature t, the speed of cooling down $dt/d\tau$, the dynamics of thermal processes Z. The dynamics thermal processes Z it was described the unit about the of second derivative temperature after the time ($d^2t/d\tau^2$). There is equal the tangent angle of the inclination of straight line (contiguous to curve $dt/d\tau$) on characteristic sections, before and after the maximum of the effects of the thermal crystallizations of phase or the system of phases, described on curves TDA the points: C, P, R, K, N. Beginning and the end of the suitable stages of crystallization and phase transformation in the solid state describe (in pairs) points suitably : C, H; H, Q; Q, S; J, L; M, O.

3. The results of investigations

3.1. Thermal effects of the crystallization of phases

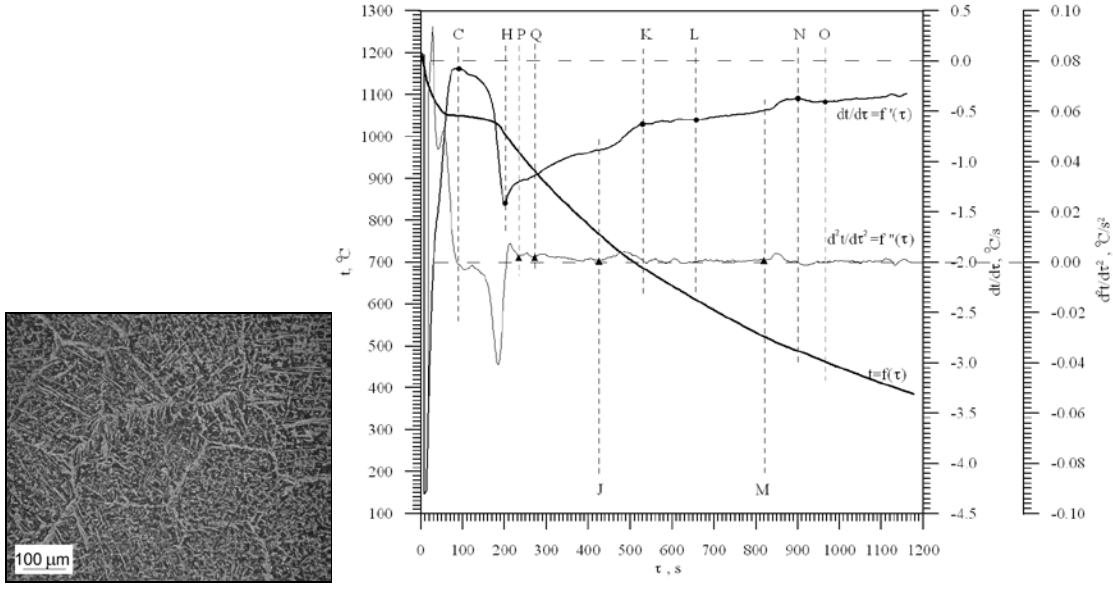
Representative microstructure and the TDA curves of the W1 bronze and with the addition 0.3 % Cr W2 was presented on figures 1 and 2 suitably.





Points	τ	t	dt/dτ	Z
	s	°C	°C/s	$*10^{-3}$, °C/s^2
C	30	1072	-0,172	-1,49
H	157	1020	-1,527	-63,78
P	195	971	-1,125	15,92
Q	221	941	-1,152	-
R	255	902	-1,115	1,70
S	285	869	-1,121	-
J	338	812	-1,031	-
K	409	749	-0,718	8,91
L	444	723	-0,749	-0,65
M	760	529	-0,504	-
N	802	509	-0,385	7,92
O	871	481	-0,439	-0,80

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



Points	τ	t	dt/dτ	Z
	s	°C	°C/s	$*10^{-3}$, °C/s^2
C	90	1050	-0,071	-1,71
H	201	1006	-1,412	-60,48
P	233	964	-1,279	8,67
Q	271	919	-1,142	-
J	425	767	-0,884	-
K	530	687	-0,626	3,48
L	657	610	-0,586	0,35
M	820	522	-0,490	-
N	900	489	-0,372	2,98
O	965	463	-0,405	-0,68

Fig. 2. Microstructure and the TDA curves of the BA1044+0,3%Cr (W2) bronze

The scanning photographs of microstructure of the studied bronze and the punctual microanalysis of the concentration of elements in rich phases in the iron were presented on figures 3 and 4, suitably for W1 (fig. 3) and W2 (fig. 4). However the results of the microanalysis of the concentration of elements in phase κ_{Fe1} and phase κ_{Fe2} of the bronze W1 were introduced in the table l, and in phase κ_{Fe1} of the bronze W2 in table 2.

The characteristic temperatures of phase transformations of studied bronzes (W1,W2) were presented on the figure 5 on the background of the system of Cu-Al [13] and Cu-Al-5% Ni-5% Fe [14], for „supplementary" the content of Al in studied bronzes - accept according to [5] the foundation, that 1% addition of Si are equivalent (for the alloys of Al) 1,6 % the Al.

The primary and secondary crystallization of the BA1044 (W1) bronze causes on derivative curve ($dt/d\tau$) creation of following thermal effects (fig. 1 and 5):

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

The crystallization of the (W1) bronze begins from nucleation and the growth of the primary phase β (β - the solid solution on base Cu_3Al_4) in the temperature tC=1072°C, primary crystallization ends in the temperature tH=1020°C. After finishing the crystallization of the bronze, its phase transformations begin in the solid state.

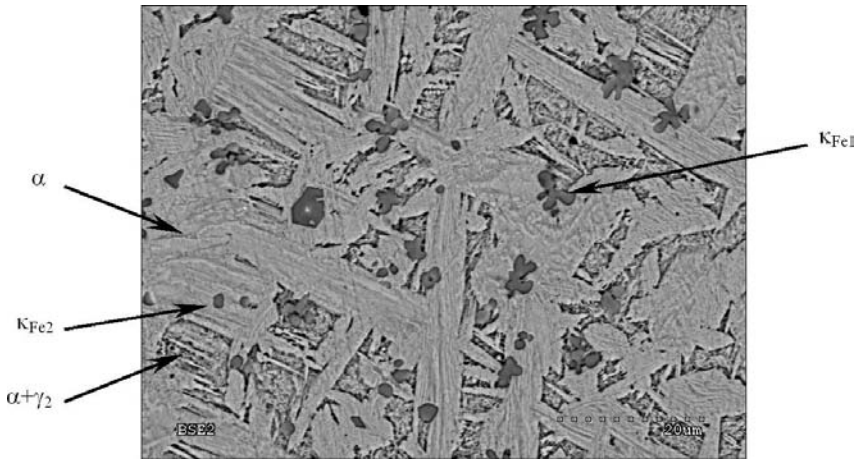
Intermetallic rich in the iron phases in temperature tP and tR crystallize (built on base intermetallic phase Al_3Fe). In the temperature tK=749°C, in the result of the fall of the solubility of Al in the solution β, draws ahead the partial transformation of the phase β→α, and in the temperature tN=509°C draws ahead

the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$ (γ_2 - the solid solution on base Cu_9Al_4).

It results that this bronze in the temperature of surroundings has the complex structure from the crystals of the primary phase α and eutectoid $\alpha + \gamma_2$ mainly from analysis of microstructure, alloy W1 (fig. 3). The crystals of the intermetallic phase κ_{Fe1} and comparatively small quantities of the crystals of the intermetallic phase κ_{Fe2} step out in microstructure.

Analysing the size of effects thermal P, R and characteristic for them temperature tP=971°C and tR=902°C you should accept that the phase κ_{Fe1} crystallizes in the temperature tP, then in the temperature tR the phase κ_{Fe2}. Because of the small quantity of the phase κ_{Fe2} in microstructure, it will come into being them the emission of the small quantity causes the heat crystallization - small effects thermal QRS on derivative curve (fig. 1).

The crystallization of the phase κ_{Fe1} causes on the derivative curve larger thermal effect HPQ, and see considerably larger quantity of the crystals of the phase κ_{Fe1} in microstructure than phase κ_{Fe2} (fig. 3).



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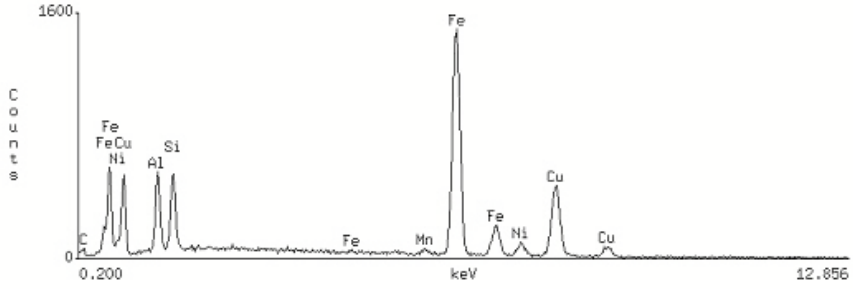
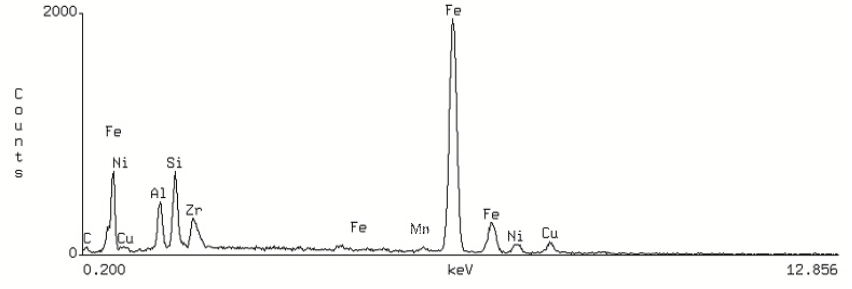
Live Time: 60 seconds Dead Time: 15.936



Phase κ_{Fe1}



Phase κ_{Fe2}

Fig. 3. The microstructure of the CuAl10Fe4Ni4 (W1) bronze and the punctual microanalysis of the concentration of elements in the phase κ_{Fe1} and κ_{Fe2}

Table 1.
The results of the microanalysis of the concentration of elements in the phase κ_{Fe1} and κ_{Fe2} of the BA1044 (W1) bronze

Phase κ_{Fe1}				
Element	k-ratio (calc.)	Concentration		Wt % Err (1-Sigma)
		Atom %	Wt %	
Si-K	0.0273	11.66	6.39	+/-0.16
Mn-K	0.0133	2.79	1.75	+/-0.24
Fe-K	0.4957	42.54	48.90	+/-0.55
Ni-K	0.0397	5.07	4.69	+/-0.23
Cu-K	0.2749	24.31	30.99	+/-0.76
Al-K	0.0240	13.63	7.28	+/-0.17
Total		100.00	100.00	
Phase κ_{Fe2}				
Element	k-ratio (calc.)	Concentration		Wt % Err (1-Sigma)
		Atom %	Wt %	
Si-K	0.0343	11.60	6.71	+/-0.17
Zr-L	0.0404	3.40	6.64	+/-0.32
Mn-K	0.0153	3.57	1.96	+/-0.08
Fe-K	0.6587	58.49	68.03	+/-0.63
Ni-K	0.0364	5.54	4.76	+/-0.43
Cu-K	0.0472	6.29	6.12	+/-0.51
Al-K	0.0198	11.11	5.78	+/-0.15
Total		100.00	100.00	

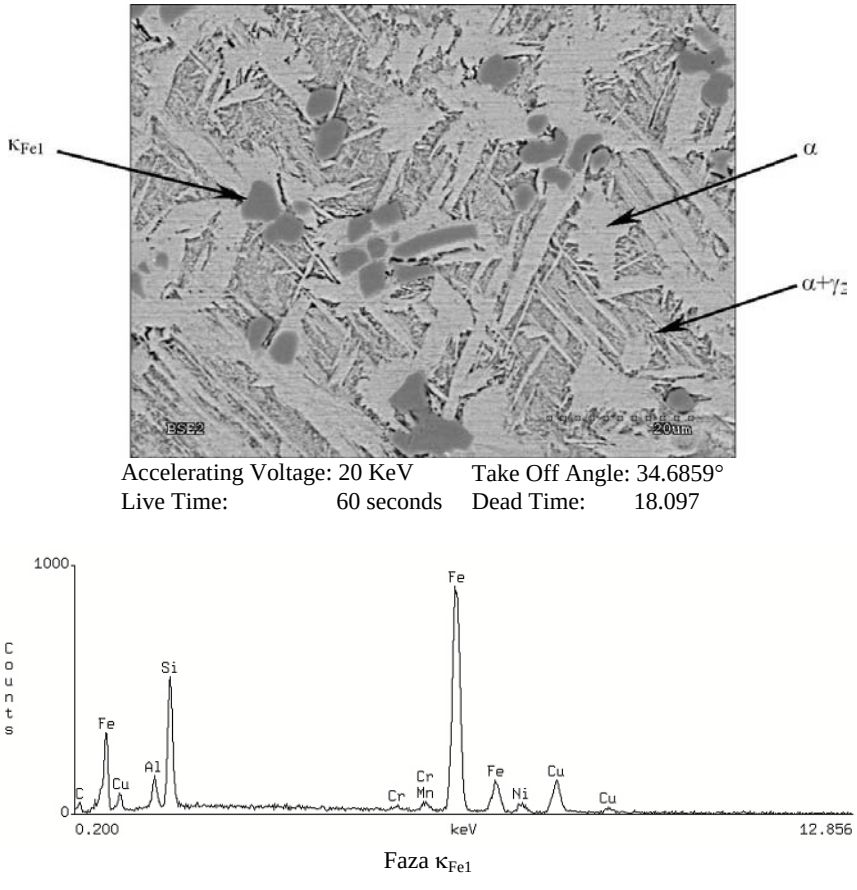


Fig. 4. The microstructure of the CuAl10Fe4Ni4+0.3%Cr (W2) bronze and the punctual microanalysis of the concentration of elements in the phase κ_{Fe1}

Table 2.
The results of the microanalysis of the concentration of elements in the phase κ_{Fe1} of the BA1044+0.3%Cr (W2) bronze

Phase κ_{Fe1}				
Element	k-ratio (calc.)	Concentration		Wt % Err (1-Sigma)
		Atom. %	Wt %	
Si-K	0.0343	11.16	6.71	+/-0.22
Cr-K	0.0055	3.74	1.48	+/-0.10
Mn-K	0.0220	5.07	3.30	+/-0.19
Fe-K	0.5702	53.75	64.26	+/-0.81
Ni-K	0.0328	5.89	4.64	+/-0.29
Cu-K	0.1300	12.94	15.92	+/-0.84
Al-K	0.0101	7.45	3.69	+/-0.11
Total		100.00	100.00	

Investigations the X-ray punctual microanalysis showed (table 1) that the concentrations of predominant elements in intermetallic phases κ_{Fel} and κ_{Fe2} were following:

- κ_{Fel}

  Fe(Cu,Al,Si,Ni,Mn) the concentration of Fe=49% and raised occur, in the comparison with the phase κ_{Fe2}, the concentration Cu=31%, and the concentrations of remaining elements change in borders 7÷ 2%,

- κ_{Fe2}

  Fe(Si,Al,Cu,Ni,Mn,Zr) mass concentrations occur Fe=68%, and the concentrations of remaining elements change in borders 7 ÷ 2% (Cu=6%).

The vestigial presence of Si was identified the punctual microanalysis of elements in the phase α, if also in eutectoid $\alpha + \gamma_2$. This comparatively high concentration of this element in phases κ_{Fel} and κ_{Fe2} explains.

It results that silicon is the element from this pushed aside before the front of the crystallization of phase β from all elements creators of solid solutions with the copper the most intensely, and created intermetallic phases rich in iron and silicon can have the structure of the complex silicides of the iron.
However the presence Zr in the studied bronze, you should chain the bronze CuCrZr (applied on electrodes to welding) with the small impurities of the metal charge on the stage of the production of the bronze CuA110Fe4Ni4 in the foundry. In the case of the phase κ_{Fe2} the dissolved particle including Zr ($ZrAl_3$, ZrC, ZrB_2 [10]) it made up the cluster of nucleation for this phase.

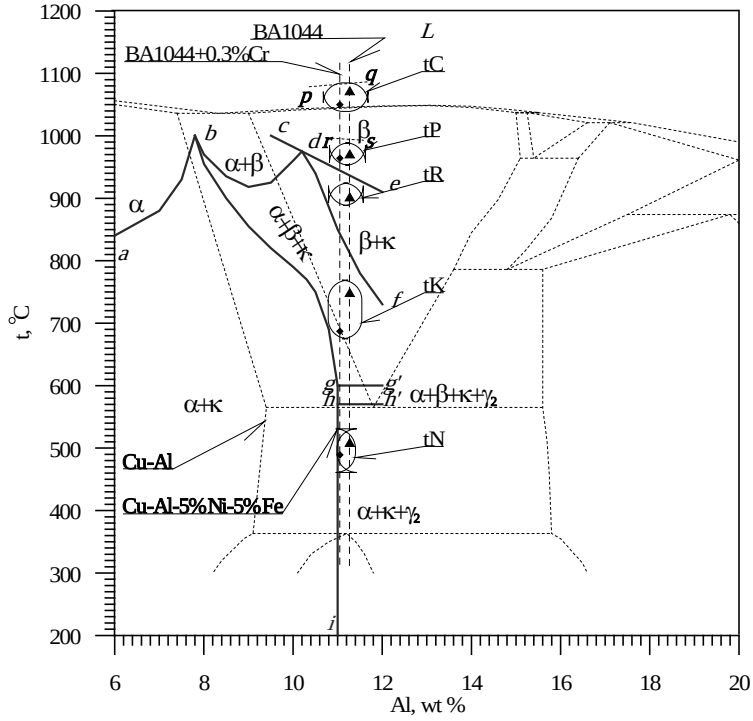


Fig. 5. The characteristic temperatures of phase transformations of studied bronzes on the background of diagrams Cu-Al [13] and Cu-Al-5%Ni-5%Fe [14]

The bronze W1, in the process of the production, not is modified in the foundry, and the presence (in insignificant quantities) of this element can act modify on it.
It was not identified in studied bronzes the X-ray microanalysis of the phase κ_{Ni}.

Primary and secondary crystallization of the BA1044 bronze with the addition 0.3 % Cr (W2) generates on derivative curve ($dt/d\tau$) creation of following thermal effects (fig. 2 and 5):

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

The crystallization of the bronze (W2) begins from nucleation and the growth of the primary phase β (β - the solid solution on base of Cu_3Al_4) in the temperature tC=1050°C, primary crystallization ends in the temperature tH=1006°C. After finishing the crystallization of the bronze, its phase transformations begin in the solid state.
In the temperature tP=967°C crystallizes the intermetallic rich phase in iron (built on the base of the intermetallic phase Al_3Fe). In the temperature tK=687°C, in the result of the fall of the dissolubility of Al in the solution β, draws ahead the partial transformation of the phase $\beta \rightarrow \alpha$, and in the temperature tN=489°C draws ahead the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$ (γ_2 – the solid solution on base of Cu_9Al_4).

In the temperature of surroundings occur in microstructure of W2 bronze (fig. 4), similarly how in the alloy without the addition Cr, the phase α and eutectoid $\alpha + \gamma_2$. The crystals of the intermetallic phase Fe(Si,Cu,Al,Ni,Mn,Cr) rich in the iron were identified in the microstructure of this bronze, comparatively large. Because of the content of Fe approx. 64% and Cu approx. 16% was accepted for its, similarly as in case of bronze without addition Cr, sign κ_{Fe1} (table 2). Added to the W1 bronze chrome accumulates first of all in the phase κ_{Fe1} - Cr approx. 1,5 %. However remaining elements have the concentration, similarly as in the bronze without the addition Cr, from 7% to 3%. The phase κ_{Fe2} was not identified in the field of the observation, and on derivative curve lack of thermal effect R (fig. 2).

Addition 0.3% Cr to the BA1044 bronze caused size reduction of primary phase β (fig. 1 and 2), crystallization of only one intermetallic phase κ_{Fe1}, rich in Fe, Cu and Cr, about the larger sizes of crystals in comparison with the crystals of intermetallic phases in bronze without the addition of chrome. It does not change the kinetics significantly ($dt/d\tau$) the thermal processes of crystallizations and phase transformation, however he influences on decrease of the dynamics (Z) beginning and the end of phase transformations in the solid state:

- the crystallization of the phase κ_{Fe1}:

	W1	W2	
ZP	15,92	8,67	$*10^{-3}$ °C/s^2,

- the partial transformation $\beta \rightarrow \alpha$:

	W1	W2	
ZK	8,91	3,48	$*10^{-3}$ °C/s^2,
ZL	-0,65	0,35	$*10^{-3}$ °C/s^2,

- the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$:

	W1	W2	
ZN	7,92	2,98	$*10^{-3}$ °C/s^2,
ZO	-0,80	-0,68	$*10^{-3}$ °C/s^2.

The decrease, under the influence of the addition of chrome, the dynamics of the thermal processes (Z) of phase transformation in the solid state, influences aspect ratio the time (τ) their of duration.

In the comparison with the equilibrium temperature both for the diagram of Cu-Al as and Cu-Al-5% Ni-5% Fe % (fig. 5) studied bronzes W1 and W2, in the result the presence in them different yet the elements (e.g.: Si, Mn, Cr), they are characterize the higher equilibrium temperature liquidus - the line *p-q*, how also additional temperature of the changing solubility of admixtures in the solution β (diminishing together with the fall of the temperature) - the line *r-s* - for intermetallic crystals type κ_{Fe1}. Taking into account the necessity of occurrence of the overcooling of the real temperature of crystallization in the relation to equilibrium the positions of these lines was added in the approximation.

4. Conclusions

From the presented investigations of the bronze CuA110Fe4Ni4 (W1) and CuA110Fe4Ni4 + 0.3 % Cr (W2), following conclusions result:

- the bronze W1 (BA1044) has compound microstructure from phases: α, γ_2, κ_{Fe1}, κ_{Fe2},
  - the intermetallic phase κ_{Fel} include first of all iron and copper,
  - the intermetallic phase κ_{Fe2} include first of all the iron,
- the bronze W2 (BA1044+0.3% Cr) he has compound microstructure from phases: α, γ_2, κ_{Fe1},
  - the intermetallic phase κ_{Fe1} include first of all iron, copper and chrome,
- intermetallic phases crystallize in the following order κ_{Fe1}, κ_{Fe2},
- addition 0.3% Cr to the bronze BA1044:
  - reduce size of the phase β,
  - it does not change the kinetics of the thermal processes of crystallization and phase transformation significantly,
  - it reduces the dynamics of the beginning of transformation and the end of phase transformation in the solid state and lengthens the time their of duration.

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