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Influence of selected modifiers on crystallization curve of chromium cast iron

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Abstract

In article was introduced the results of investigations of modified chromium cast iron crystallization process. It the cast iron about composition of basic elements C = 2,8 % and Cr = 18% was modified with five substances (boron carbide, ferrosilicon, ferrocalciumsilicon, ferroniobium and ferroniobium with ferrovanadium). Influence on course of primary and secondary crystallization process was observed. The investigations of crystallization was conducted DTA method in tester DTA - C.

Keywords: Chromium cast iron, Crystallization, Modification, DTA method

1. Introduction

Chromium cast iron, particularly with larger content of chrome is applied on casting, which works in conditions of abrasive wear. This material wide uses mining and processing industry. Chromium cast irons possess goods resistance on corrosive environments as well as resistance on serial strokes. In relation to work in large and changing loads conditions, the users of castings have the considerable doubts and fear which are not groundless.

The suitably high content of chrome and carbon assures formation in structure of chromic cast iron of hard carbides of type M_7C_3 (where M it represents mainly Cr or Fe) in matrix of austenite or products of its transformation. This two-phase structure guarantees high abrasive wear resistance, which is enlarged by heat treatment of castings. The improvement of resistance on works in percussive conditions across interventions of heat treatment does not let the waited results. The key to solution of this problem should was look for in suitable controling process of crystallization, particularly primary crystallization. During primary crystallization carbides M_7C_3 grow as rods and bars about longitudinal parallel axis to direction of warmth flow to casting form. In castings, these carbides are often large about superiority one dimension (length). Great size of carbides and unfavourable coefficient of their shape as well as creating of continuous mesh of carbides results in large brittleness of chromium cast iron. The cracks be initiated on carbides easily and further spread along mesh of carbides.

The modification treatments in cast process lead to sensible controling of crystallization process, which result in improvement of structure. In case of chromium cast iron the desirable effect concerns in ductile matrixwhich do not create the continuous mesh.

The authors of research works with range of modification of chromium cast iron obtain interesting results by introducing the different alloy additions, however is lack a good industrial solutions. The researchrs introduced to chromium cast iron among other things: the niobium[1-3], the cerium [4], the vanadium [5,6], the boron [7], the silicon [8,9], the titanium [10-13], the rare-earth elements [10,11], the nitrogen [14].

The author of present article realizes the systematic investigations [15-18] of the process of crystallization of wear resistance chromium cast iron which put to the test different interventions of modification (the different modifiers and technique of modification). In presented article were introduced the results of investigations of crystallization hypoeutectic chromium cast iron without and with modyfication.

2. Course of experiment

The investigations concern chromium cast iron named initial cast iron, which was melted in industrial arc electric furnace from standard charge materials applied to industrial melting of wear resistant chromium cast iron. The chemical composition of initial cast iron is presented in table 1.

Table 1.
The chemical composition of initial cast iron

Mark	Content of element in % weight					
	C	Cr	Si	Mn	S	P
K0	2,82	18,20	0,56	0,64	0,030	0,050

Melting experimental were conducted in crucible inductive furnace about indifferent lining and capacity 20 kg. All melting were executed according to the same procedure, applying the process of melting of initial cast iron K0. Before tapping temperature of metal bath was measured, which was 1480 ^{o}C. After obtaining of proper temperature, liquid metal was poured to warm ladle. Melt 1 (U1) only concerns melting at initial cast iron. Following melts (U2-U6) were conducted with modification of cast iron in moment of tapping. The put quantity of crumbled proper quantity of modifier was introduced on stream of liquid metal. In table 2 is presented plan of experimental melts.

After end of heat melt and waiting about 10 seconds was poured the tester DTA - C and next the mould (the metal mould as well as isolating mould –Sibral 300) of samples. The castings in shape of cylinder were used in more far metallographic investigations and investigations of fractures.

Principle investigations of process of crystallization chromium cast iron were conducted recording of curves of cooling in tester DTA - C with application of Crystaldigraph PC apparatus. The registration of temperature was finished when casting reached temperature below 500 ^{o}C. Such registration made possible the analysis of primary and secondary crystallization studied chromium cast iron. The time of registration carried out over 2000 seconds. The construction of DTA - C tester is presented on figure 1. The tester was made from classic moulding sand and was dried in ventricular dryer. The complete test stand was showed on figure 2.

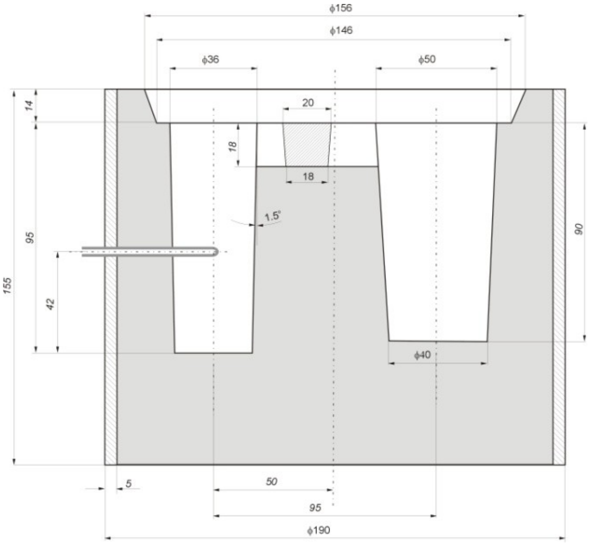

Fig. 1. Tester DTA-C

Table 2.
Plan of experimental melts of chromium cast iron

Mark of melt	Modifier	Quantity (% weight)
U1	absence	-
U2	boron carbide (B_4C) + borax	0,2% + 0,3%
U3	ferrosilicon (FeSi75) + borax	0,2% + 0,3%
U4	ferronobium (FeNb60) + borax	0,2% + 0,3%
U5	ferrocalciumsilicon (FeCaSi) + borax	0,2% + 0,3%
U6	ferronobium (FeNb60) + ferrovanadium (FeV70) + borax	0,1% + 0,1% + 0,2%

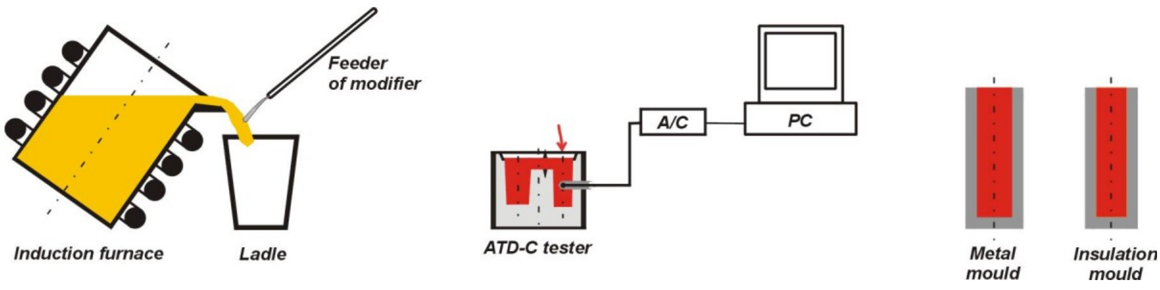

Fig. 2. Test stand

3. Curves of cooling and crystallization

On figures 3 - 8 are presented the curves of cooling and crystallization which were registered in whole range of studies (in range of primary and secondary crystallization). The changes were observed on curve of crystallization, in different degree for applied modifiers. In range of primary crystallization was been possible to notice the influence of boron carbide and ferrocalciumsilicon on course of curve dT/dt, particularly near at hand before end of crystallization process (the point H). Possible, that is a proof on creating of new phase.

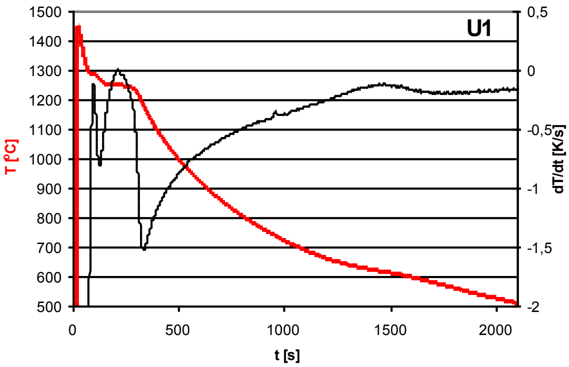

Fig. 3. Curves DTA of unmodified chromium cast iron

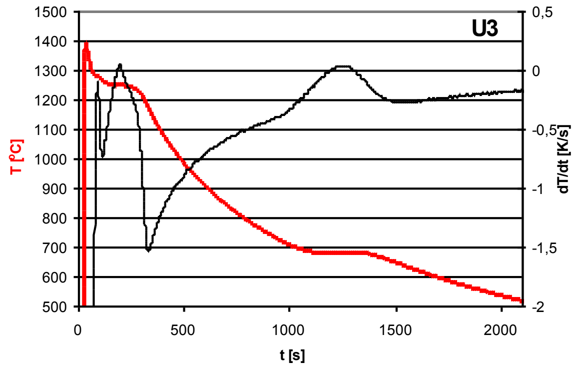

Fig. 5. Curves DTA of chromium cast iron modified ferrosilicon

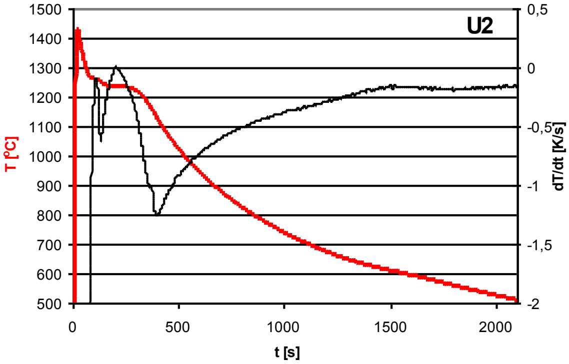

Fig. 4. Curves DTA of chromium cast iron modified B_4C

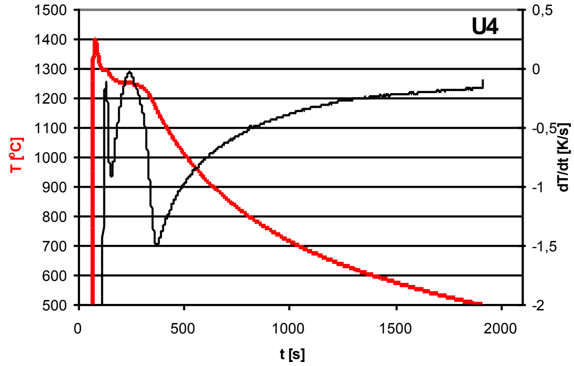

Fig. 6. Curves DTA of chromium cast iron modified ferronobium

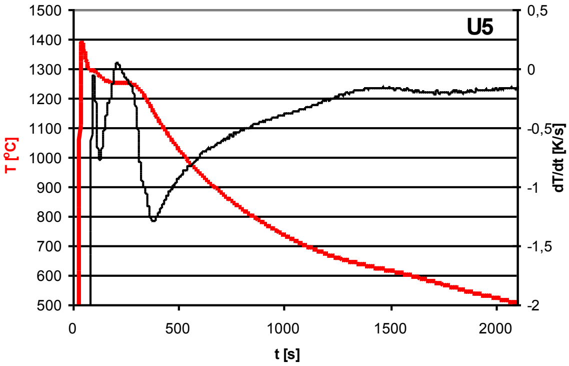

Fig. 7. Curves DTA of chromium cast iron modified ferrocalciumsilicon

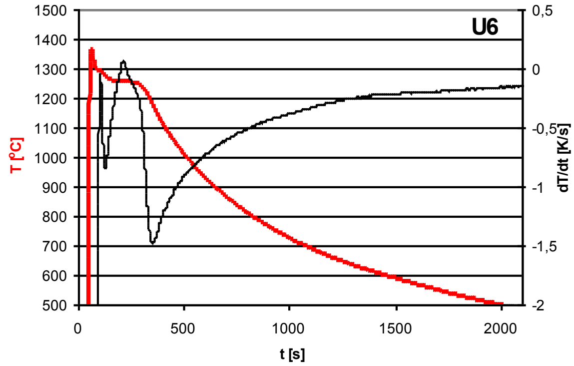

Fig. 8. Curves DTA of chromium cast iron modified ferronobium with ferrovanadium

Curves dT/dt in range of secondary crystallization change noticeable also. Modifiers consisting from carbides element (niobium, vanadium) minimalize eutectoid transformation clearly, thermal effect disappears almost entirely. The qualitative opinion of curves of crystallization does not let however the possibility of observation the change of individual parameters of curves DTA. The quantitative changes of parameters of crystallization were estimated really after accomplishment of description of characteristic points of dT/dt curves. The characteristic points were showed on crystallization curve in range of primary and secondary crystallization (fig. 9). The choice of points was executed from methodology applied by prof. Jura [19].

The additional point Pk was received according from hands prof. Pietrowski [20], which interprets as beginning the process of primary crystallization. In tables 3 - 5 are presented all parameters of crystallization from registered curves DTA.

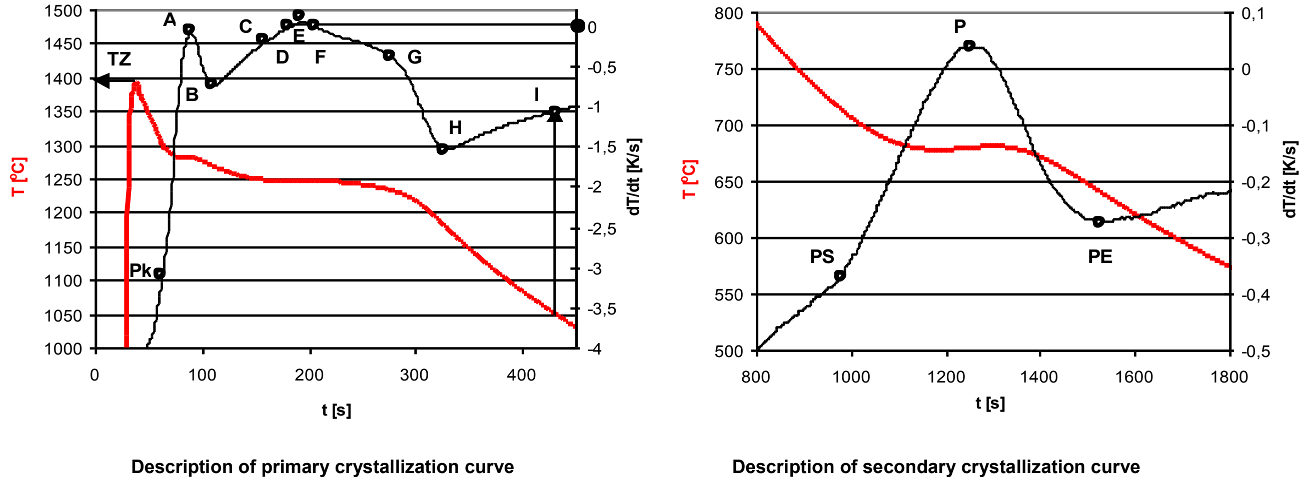

Fig. 9. Mark of characteristic points on curve of crystallization (curve dT/dt) – melt U3

Table 3.
Crystallization parameters – time in s

point \ melt	U1	U2	U3	U4	U5	U6
Z	27	22	39	80	47	64
Pk	**62**	**68**	**60**	**100**	**60**	**79**
A	**90**	**102**	**85**	**123**	**91**	**97**
B	**118**	**124**	**105**	**149**	**119**	**120**
C	**155**	**156**	**153**	**194**	**173**	**165**
D	**199**	**190**	**178**	**235**	**191**	**194**
E	**205**	**194**	**190**	**235**	**204**	**207**
F	**211**	**203**	**201**	**235**	**218**	**220**
G	**295**	**304**	**269**	**308**	**284**	**296**
H	**330**	**388**	**321**	**362**	**367**	**343**
I	442	471	430	461	474	459
PS	***979***	***1149***	***965***	***1128***	***1055***	***1229***
P	***1462***	***1514***	***1243***	***1319***	***1455***	***1427***
PE	***1772***	***1789***	***1497***	***1556***	***1733***	***1622***

Table 4.
Crystallization parameters – temperature in ^oC

point \ melt	U1	U2	U3	U4	U5	U6
Z	1447	1431	1393	1397	1386	1365
Pk	**1320**	**1289**	**1312**	**1326**	**1340**	**1313**
A	**1288**	**1261**	**1281**	**1293**	**1292**	**1294**
B	**1274**	**1254**	**1273**	**1280**	**1279**	**1283**
C	**1253**	**1241**	**1249**	**1252**	**1254**	**1258**
D	**1247**	**1237**	**1246**	**1247**	**1252**	**1255**
E	**1247**	**1237**	**1247**	**1247**	**1252**	**1255**
F	**1247**	**1237**	**1247**	**1247**	**1253**	**1256**
G	**1232**	**1218**	**1236**	**1233**	**1246**	**1243**
H	**1187**	**1142**	**1190**	**1178**	**1173**	**1192**
I	1050	1050	1050	1050	1050	1050
PS	***729***	***688***	***719***	***669***	***715***	***652***
P	***616***	***608***	***679***	***615***	***621***	***605***
PE	***566***	***562***	***648***	***561***	***571***	***565***

Table 5.
Crystallization parametres – derivative dT/dt in K/s

point \ melt	U1	U2	U3	U4	U5	U6
Z	-	-	-	-	-	-
Pk	**-2,75**	**-2,25**	**-3,08**	**-3,65**	**-3,71**	**-2,79**
A	**-0,08**	**-0,07**	**-0,03**	**-0,04**	**-0,04**	**0,06**
B	**-0,82**	**-0,67**	**-0,76**	**-0,93**	**-0,77**	**-0,86**
C	**-0,28**	**-0,23**	**-0,21**	**-0,29**	**-0,25**	**-0,26**
D	**0**	**0**	**0**	**-0,01**	**0**	**0**
E	**0,01**	**0,02**	**0,06**	**-0,01**	**0,06**	**0,07**
F	**0**	**0**	**0**	**-0,01**	**0**	**0**
G	**-0,66**	**-0,48**	**-0,33**	**-0,47**	**-0,25**	**-0,46**
H	**-1,53**	**-1,25**	**-1,55**	**-1,5**	**-1,29**	**-1,48**
I	-1	-0,97	-1,04	-1,06	-0,97	-0,99
PS	***-0,37***	***-0,3***	***-0,37***	***-0,32***	***-0,35***	***-0,27***
P	***-0,11***	***-0,15***	***0,04***	***-0,25***	***-0,17***	***-0,22***
PE	***-0,19***	***-0,18***	***-0,27***	***-0,21***	***-0,2***	***-0,2***

The method of introducing of crumbled modifier on stream of liquid cast iron during heat melt clearly reduces temperature TZ (Table 4), which determines the initial field of temperatures in casting and in connection with this influences on crystallization process.

The deeper analysis was subjected in chosen of crystallization parameters in points of DTA curve. On graphs (figs. 10-15) the changes of temperatures (figs. 10 and 13), derivative (figs. 11 and 14) and times (figs. 12 and 15) in range of primary and secondary crystallization, were showed.

The influence of modifiers without boron carbide on temperature TA (interpreted often as likwidus temperature) is minimum, however on temperature TPk is significant. The similar arrangement was observed in case of temperatures TE and TH. Temperature TE as solidus temperature changes slightly for all modifiers without B_4C. The change of TH (the end of primary crystallization) are clear. The lowest value was for boron carbide.

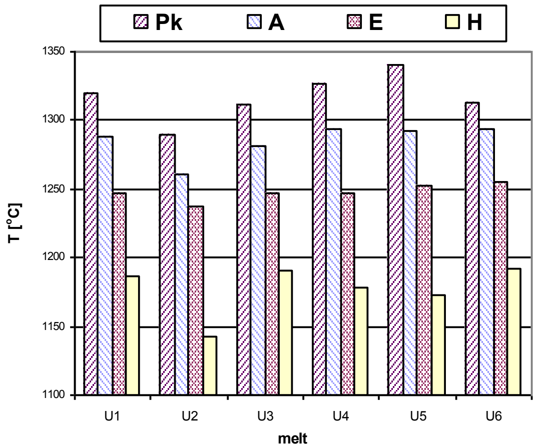

Fig. 10. Influence of studied modifiers on chosen characteristic temperatures of primary crystallization

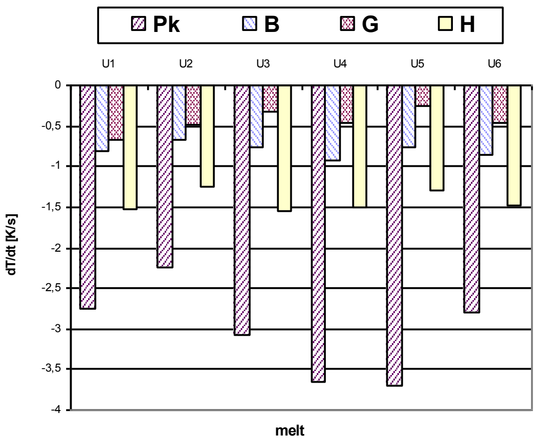

Fig. 11. The influence of studied modifiers on value of derivative in characteristic points of primary crystallization

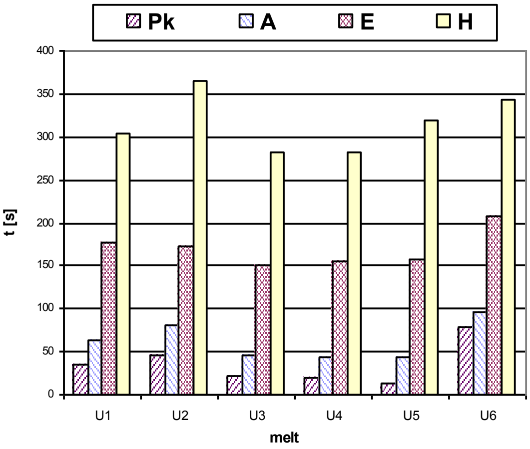

Fig. 12. Influence of studied modifiers on time of appearing of characteristic points of primary crystallization

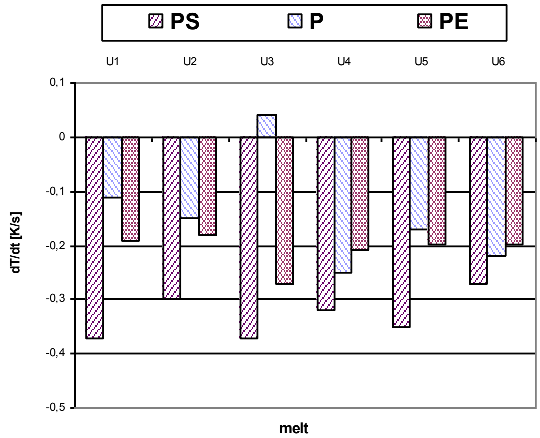

Fig. 14. The influence of studied modifiers on value of derivative in characteristic points of secondary crystallization

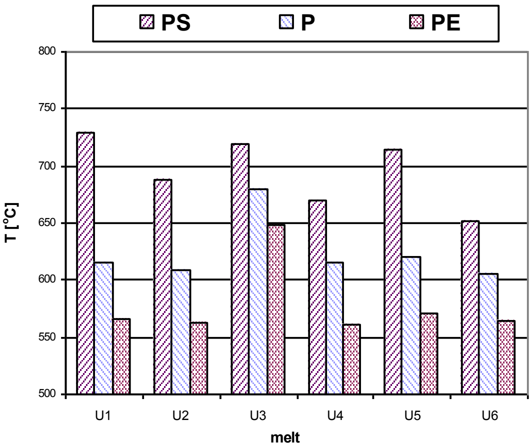

Fig. 13. Influence of studied modifiers on characteristic temperatures of secondary crystallization

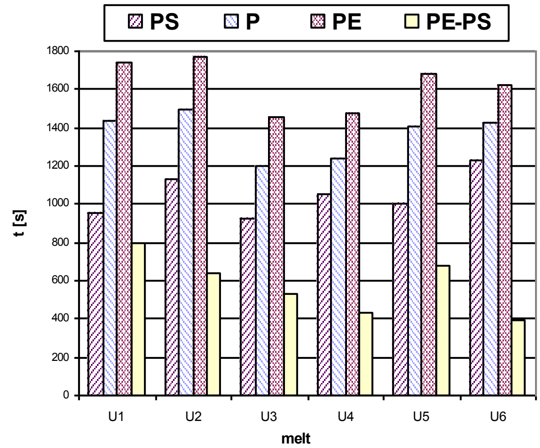

Fig. 15. Influence of studied modifiers on time of appearing of characteristic points of secondary crystallization

The changes of derivative dT/dt result from kinetics of crystallization process. Clear differentiation was observed for points Pk, B, G, H (fig. 11). The largest influence was observed for boron carbide. B_4C also influences strongly on time parameters of primary crystallization. The total time of primary crystallization (tH) has the largest value (fig. 12).

The analysis of chosen parameters of secondary crystallization are presented on figures 13-15. The largest thermal effect was observed in case of modification with ferrosilicon. The positive value of derivative dT/dt was registered in point P (fig. 14). Also the observations of curve crystallization in range of secondary crystallization were confirmed by qualitative investigations of metallographic structure. The pictures of structures are presented on figure 16 (etching Nital). The image of matrix of studied chromium cast iron is closely-coupled with secondary crystallization curve. There where was the eutectoid transformation that matrix etched clearly (fig. 16 U3). In case of melt U4 and U6 is predominant bright (unetched) matrix (fig. 16 U4 and U6), which testifies about lack of austenite transformation. On curves dT/dt in these cases was noticed minimum changes (fig. 6 and 8).

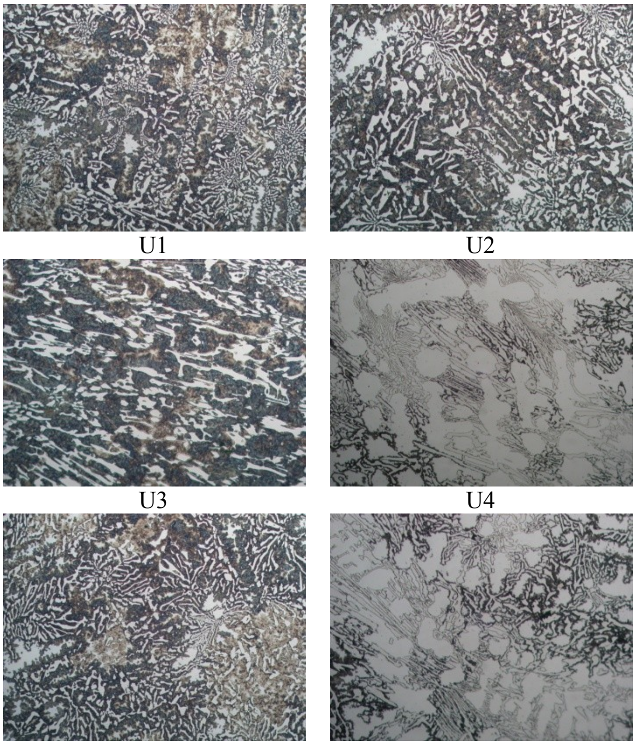

Fig. 16. The metallographic structures of studied chromium cast iron, etched Nital, magnification 200x

4. Summary

The introduced results of investigations show that method DTA makes possible the quantitative opinion of crystallization parameters of modified chromium cast iron. The small quantity of modifier and method of its applications during cast change noticeable the parameters of primary and secondary crystallization. The indication, which parameter of crystallization of chromium cast iron answers for formation of the profitable structure requires the executions of more far investigations, particularly the analysis of quantitative structure and identification phases as well as mechanical property.
On basis of conducted investigations was been possible to affirm that modification with boron carbide the most strongly influences on primary crystallization of studied chromium cast iron, however on secondary crystallization strongly influences ferroniobium and ferrovanadium as well as ferrosilicon.

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