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Primary Crystallization of High Chromium Cast Steel in Metastable Conditions

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Abstract

The analysis of the primary crystallization of wear corrosive-erosive high chromium cast steel was introduced in the article on the basis of investigations the widened method of the differential thermal analysis with testers DTA-C and DTA-Is. The use of these testers enabled the analysis of crystallization for the various rates of cooling.

Keywords: Chromium cast steel, Primary crystallization, DTA method

1. Introduction

Chromium is one of the most often applied elements in the ferroalloys. Its content carries out from approx. 0,5 to even above 30 %. Such large extension causes the differentiation of structure, from here we ferroalloys with chromium are classified in relation to the structure on:

1. martensitic, in which the total transformation of ferrite into austenite proceeds,
2. half ferritic, in which only part of the ferrite changes into austenite,
3. ferritic in which ferrite phase is stable and phase transformations do not set.

In all three groups in equilibrium state the matrix carbides can occur. Following carbides step out in the practical ranges of the chemical composition: $(Fe, Cr)_3 C$, $(Cr, Fe)_7 C_3$, $(Cr, Fe)_{23} C_6$ in dependence to the content of carbon and chromium.

Chromium creating carbides increases the resistance to abrasive wear and when introduced in large quantities also the resistance to corrosion and heat-resistance. Chromium is introduced in constructional, abrasive wear, tool, heat-proof, stainless steels, cast steel etc. [1-3]. Though it belongs to ferrite forming elements in the presence of carbon it stabilizes the austenite. Chromium dissolved in austenite increases hardenability, increases the temperature of eutectoid and eutectic transformation, and also the eutectoid and moves the eutectic point to the lower contents of carbon.

One distinguishes hypoeutectoid, hypereutectoid and ledeburite alloys, among the steels and cast steels in which the transformation of the ferrite proceeds in the austenite, e.g. steel X210 Cr12 (NC11) [1, 4]. Such alloys should be classified as cast irons due to the occurrence of the eutectic, however from the attention to the fact, that they are malleable they were classified to the group of steel. They are comprise in this group of alloys both constructional, tool, abrasive wear and corrosion resistant cast steels. The L35H17N2 cast steel taking out from X20CrNi172 (H17N2) steel for toughening with high resistance to sea water is one of the alloys fulfilling described criteria. Specified alloy belongs to tool cast steel group, for which standards do not require specified mechanical proprieties. One can only suppose, that in the relationship with the use (e.g. defiberizer in the paper industry), mechanical proprieties should be satisfactory. Due to high content of chromium this cast steel is resistant to corrosion

and hardened in the air it possesses high hardness what acts it on low the abrasive wear.

Presented in the article investigations relate to the analyses of the primary crystallization of high chromium cast steel. The analysis was conducted on the base of the graphs of the cooling and crystallization, and structural investigations which were performed in Department of Foundry of Silesian University of Technology. Using the Crystaldigraph-PC apparatus with the standard tester DTA-C and isolated tester DTA-Is the registration of the cooling curves for sample castings were conducted in metastable conditions [8, 9, 11].

2. Experiment - material and research methods

The analysis of the primary crystallization of high chromium cast steel was conducted on the base of six melts, which were conducted in the laboratory conditions in Department of Foundry. Melts were performed according to the method of recasting in the inductive crucible furnace with neutral lining and capacity of 20 kg.

The foundry mixtures of added materials were composed from generally accessible materials eg. steel scrap-iron, ferroalloys. Molten cast steel was deoxidized with use of ferrosilicon and aluminium, and subjected to modification with ferrovanadium and ferrotitanium. Cast steel appointed as T6 was subjected to argon refining before tapping. The chemical composition for studied cast steels is shown in table 1.

The Crystaldigraph-PC apparatus was applied to cooling curve registrations of sample castings with set of two measuring testers with diverse thermal parameters of used sandmix, giving in return the different cooling rates. The conditions of cooling for sample castings on the applied stand resulted in metastable crystallization of the alloys. The pattern of the investigative stand and the photograph of the set of measuring testers were shown in Fig. 1. Sample castings, in shape of cylinders cooled down in testers DTA-C and DTA-Is. In the tester DTA-Is the isolating aluminosilicate material was applied, elongating almost twice the time of primary crystallization of studied alloys. The average cooling rate in the range of primary crystallization in applied testers was:

DTA-C 100 K/min.; DTA-Is 50 K/min.

Table 1.
Chemical composition of research cast steels in % weight

no	mark	C	Mn	Si	P	S	Cr	Ni	Mo	V	Cu	Al	Ti
1	T1	0,51	0,50	0,63	0,014	0,013	16,27	0,55	1,28	0	0,19	0,012	0
2	T2	0,48	0,45	0,77	0,014	0,013	16,80	0,56	1,23	0,22	0,18	0,016	0,22
3	T3	0,51	0,45	0,78	0,016	0,013	16,42	0,54	2,87	0,28	0,19	0,011	0,28
4	T4	0,49	0,43	0,79	0,007	0,014	16,47	2,43	1,22	0,26	0,19	0,011	0,26
5	T5	0,57	0,55	0,49	0,015	0,009	18,50	1,70	0,80	0,04	0,18	0,004	0
6	T6	0,56	0,51	0,58	0,015	0,011	18,30	1,69	0,80	0,32	0,18	0,006	0,12

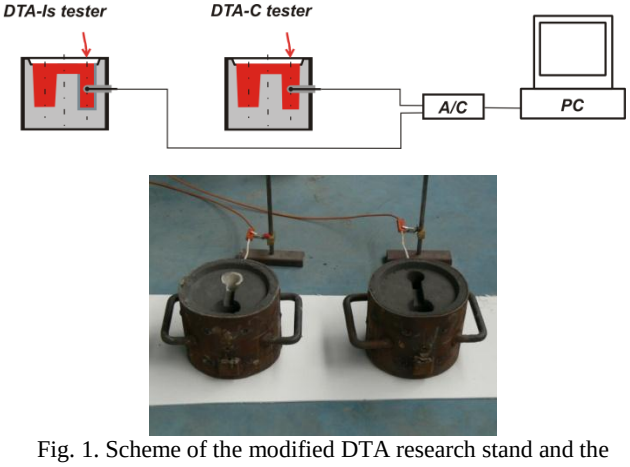


Fig. 1. Scheme of the modified DTA research stand and the photograph of the set of measuring testers

The method of X-ray diffraction was used for identification of phases. The studies of X-ray diffraction were conducted on diffractometer Panalytical X-ray X´Pert with utilization of the bar the code crystal set in range of angles 2Θ 30º -130º (λ_{What}=1,78901, step 0,05, the time counts impulses 10 seconds).

During studies the software X'Pert Date Collector and X'Pert Date Viewer were used.

The qualitative investigations of structures were conducted on the Nikon optical microscope for all studied cast steels. Specimens for metallographic investigations were cut out from sample castings DTA-C and DTA-Is, then prepared for etching with use of the Struers grinding-polishing machine. Etching was conducted using the Mi19Fe reagent to reveal matrix and carbides. Observations were performed using various magnifications.

3. Crystallization of chromium cast steel in stable conditions

The system phase equilibrium, which are the basis for crystallization analysis of alloys, are prepared using experimental results of alloys crystallization in stable conditions, i.e. by very low cooling rates [6]. Multi-thermal cross-section fragment of Fe-C-Cr system 17%wt. chromium was shown in Fig. 2. Four melts were marked on the graph (I, II, III and IV) at corresponding carbon content, for which the path of primary (Kp) and secondary (Kw) crystallization proceed differently. The analysis of alloys stable crystallization was the basis for experimental studies on

alloys crystallization within the realized work. Alloys I, II, III and IV have the following course of crystallization in the stable system:

Alloy I

Kp **L → L+α → L+α+γ → L+γ → γ**

Kw **γ → γ+K₁ → α+γ+K₁ → α+K₁**

Alloy II

Kp **L → L+α → L+α+γ → L+γ → γ**

Kw **γ → γ+K₂ → γ+K₂+K₁ → γ+K₁ → α+γ+K₁ → α+K₁**

Alloy III

Kp **L → L+α → L+α+γ → L+γ → L+γ+K₂ → γ+K₂**

Kw **γ+K₂ → γ+K₂+K₁ → γ+K₁ → α+γ+K₁ → α+K₁**

Alloy IV

Kp **L → L+γ → L+γ+K₂→ γ+K₂**

Kw **γ+K₂ → γ+ K₂+K₁ → γ+K₁ → α+γ+K₁ → α+K₁**

Analysing the paths of the crystallization of alloys I and II, can be seen that carbides distribute only in the range of secondary crystallization, that is already in the solid state. Precipitation of chromium carbides already happens during primary crystallization in case of alloys III and IV. These carbides crystallize in eutectic as the carbides K_2 type. Carbides of type K_1 always distribute from the solid phase. The structure of all analysed alloys crystallizing in the stable system after finishing primary and secondary crystallization consists of ferrite and chromium carbides of type K_1.

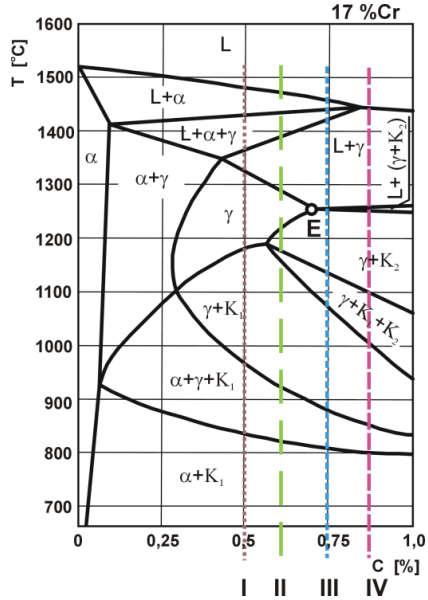
Additional alloy components introduced to the alloy Fe-C-Cr cause displacement of the characteristic points of equilibrium system. The majority of elements shifts the points towards the smaller content of carbon, e.g. Fig. 2, point E. This is connected with the change of dissolubility of carbon in austenite.

The content of the carbon in the point E regarding of alloy additions can be calculated using the formula [7]:

$$C_E=2{,}08+\sum m_X\cdot\%X \qquad (1)$$

where: m_X - experimental coefficient describing influence of given element X on dissolubility of carbon in austenite,
%X - content of element X in alloy [% weights.]

Introduced during experimental studies elements to chromium cast steel move the point E to the left side and therefore the course of crystallization of these cast steels should be based on stable crystallization analysis of alloys III and IV.



K_1 – $(Fe,Cr)_{23}C_6$ K_2 – $(Fe,Cr)_7C_3$

Fig. 2. Multi-thermal cross-section of Fe-C-Cr phase equilibrium system for 17% wt. of Cr [5]

4. Studies results and analysis

The description of DTA graphs (cooling and crystallization curves) was conducted according to principles applied in the standard DTA method. In Fig. 3 the analysed curves were described with characteristic points and the values of the chosen parameters of primary crystallization collted in table 2 for studied chromium cast steel. The denotation of points on crystallization curve colligates with the course of crystallization and were described according to standard applied in the DTA method. Point A describes maximum thermal effect of crystallization of primary phase (α or γ) and temperature in this point is recognised for the liquidus temperature of the analysed alloy. Point H describes the end of primary crystallization.

The course of crystallization curves for studied cast steels shows that the processes of primary crystallization confrms chromium cast steel with chemical composition assuring crystallization above the point E (according to equilibrium system, Fig. 2). Such course of crystallization, in spite of low content of carbon in studied cast steel is assured by elements such as: silicon, molybdenum, phosphorus, sulphur, titanium, which strongly move the position of the point E in direction of lower content of carbon (eq. 1). Difference in description of crystallization of chromium cast steel in equilibrium (stable system) and unequilibrium (metastable system) conditions consists in absence of total austenite- ferrite transformation during secondary crystallization in the metastable system. Qualitative metallographic investigations and X-ray diffraction results also confirm such course of primary and secondary crystallization. The examples of obtained structures for chromium cast steels were demonstrated in Fig. 4. Zones of eutectic carbides can be visible and were identified as typical carbides $(Fe, Cr)_7C_3$.

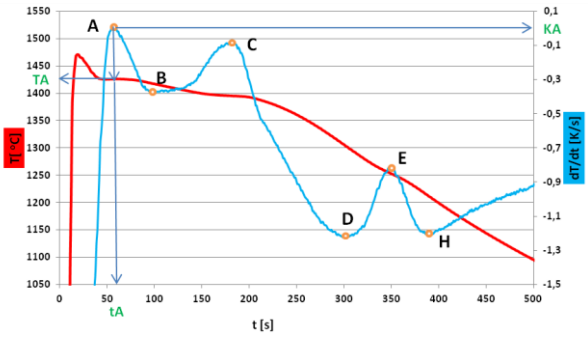


Fig. 3. DTA graph with marked points on crystallization curve and reading procedure of crystallization parameters (TA – temperature, KA – cooling rate, tA – time)

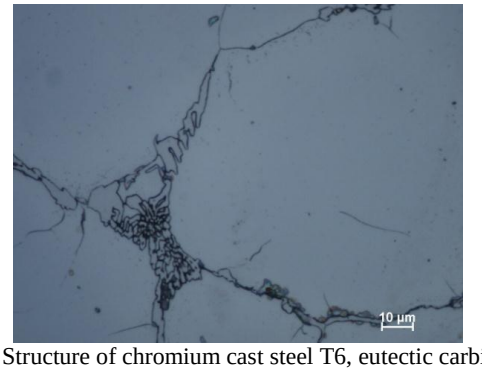


Fig. 4. Structure of chromium cast steel T6, eutectic carbides at grain boundaries of austenite, Mi19Fe etched

X-ray investigations show, that the matrix of studied cast steel consists of austenite mainly, small quantities of ferrite and carbides of type $(Fe, Cr)_{23}C_6$ and $(Fe, Cr)_7C_3$ (Fig. 5). Austenite of studied cast steel in raw state is very unstable and it undergoes the transformation quickly after repeated heating.

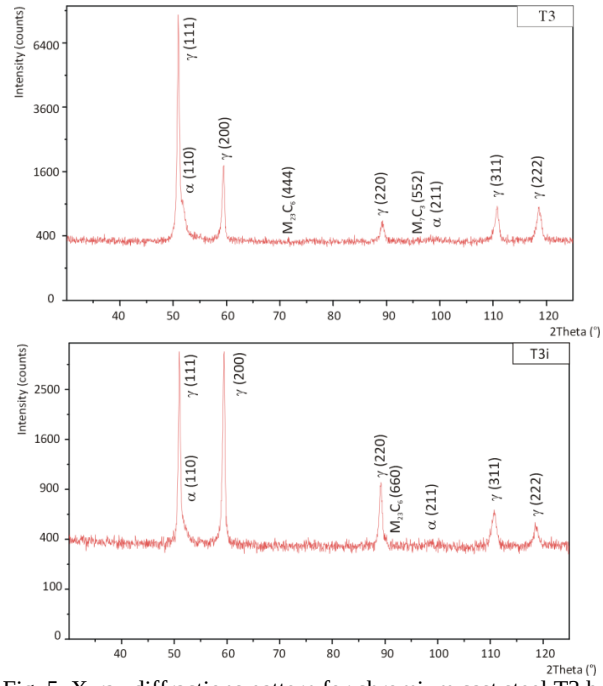


Fig. 5. X-ray diffractions pattern for chromium cast steel T3 by low and high cooling rates

In Figures 6 – 11 the set of cooling and primary crystallization graphs (DTA curves) of studied high chromium cast steels was presented. DTA curves were shown on one graph for sample castings at different cooling rates (DTA-C high cooling rate, DTA-Is low cooling rate). Metallographic structures obtained during the studies were shown in Figures 7 and 11. Difference of primary grain size can be seen.

Table 2.
Chosen DTA parameters of primary crystallization of studied high chromium cast steels

Melt	Tester	Temperature in °C					Time in sec.	
		TL=TA	TD	TE	TH	TL-TH	tD-tA	tH-tA
T1	*DTA-C*	1458	1307	1243	1206	252	113	162
	DTA-Is	**1458**	**1326**	**1253**	**1206**	**252**	**233**	**313**
T2	*DTA-C*	1453	1324	1233	1197	256	95	152
	DTA-Is	**1463**	**1336**	**1257**	**1214**	**249**	**228**	**305**
T3	*DTA-C*	1449	1316	1255	1222	227	110	159
	DTA-Is	**1448**	**1323**	**1269**	**1256**	**192**	**251**	**310**
T4	*DTA-C*	1441	1298	1216	1188	253	93	151
	DTA-Is	**1456**	**1311**	**1228**	**1197**	**259**	**253**	**354**
T5	*DTA-C*	1436	1317	1263	1231	205	84	130
	DTA-Is	**1426**	**1299**	**1255**	**1224**	**202**	**248**	**326**
T6	*DTA-C*	1431	1313	1260	1220	211	89	139
	DTA-Is	**1436**	**1319**	**1272**	**1238**	**198**	**244**	**324**

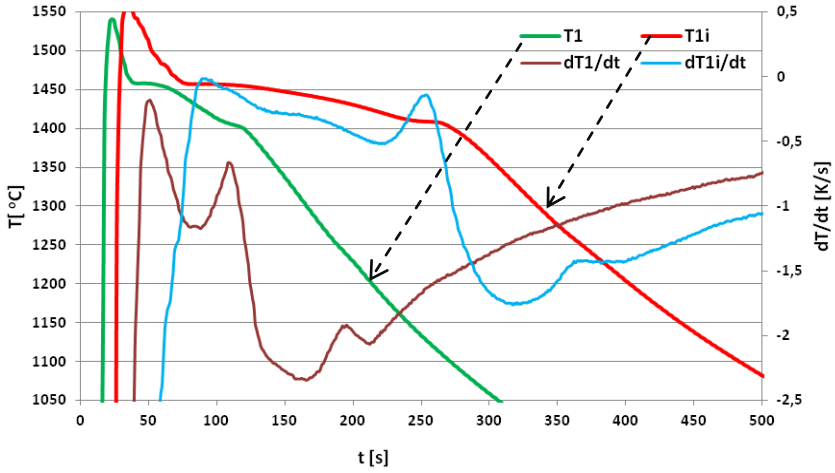
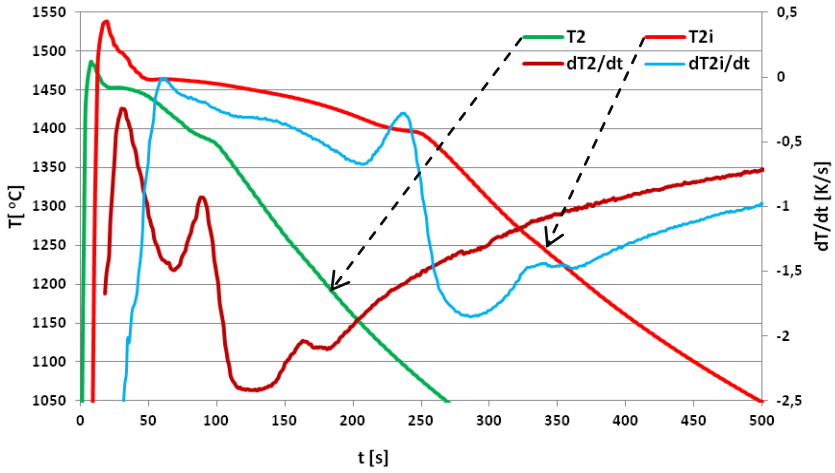
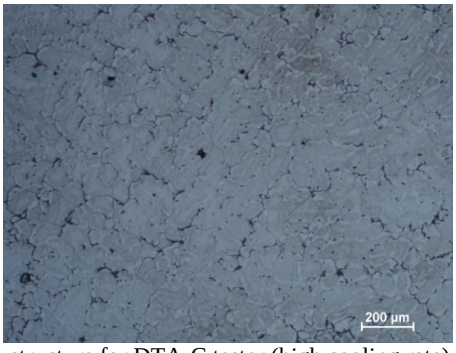
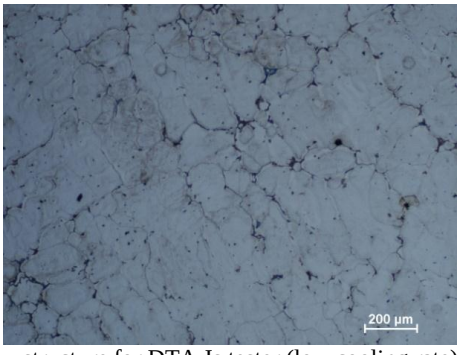


Fig. 6. Cooling and crystallization curves of high chromium cast steel T1





structure for DTA-C tester (high cooling rate)



structure for DTA-Is tester (low cooling rate)

Fig. 7. Cooling and crystallization curves of high chromium cast steel T2 and photographs of structure

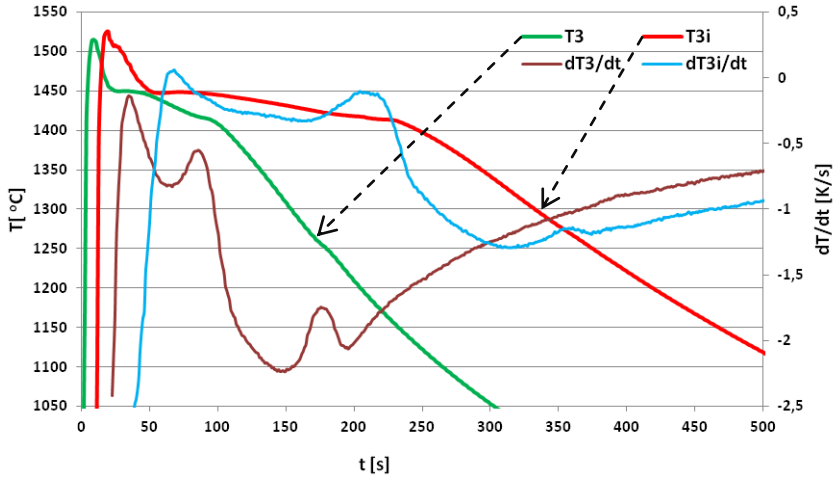


Fig. 8. Cooling and crystallization curves of high chromium cast steel T3

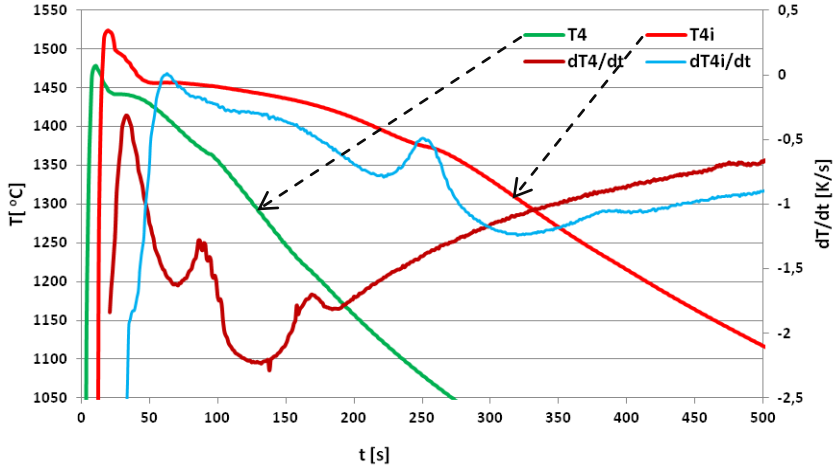


Fig. 9. Cooling and crystallization curves of high chromium cast steel T4

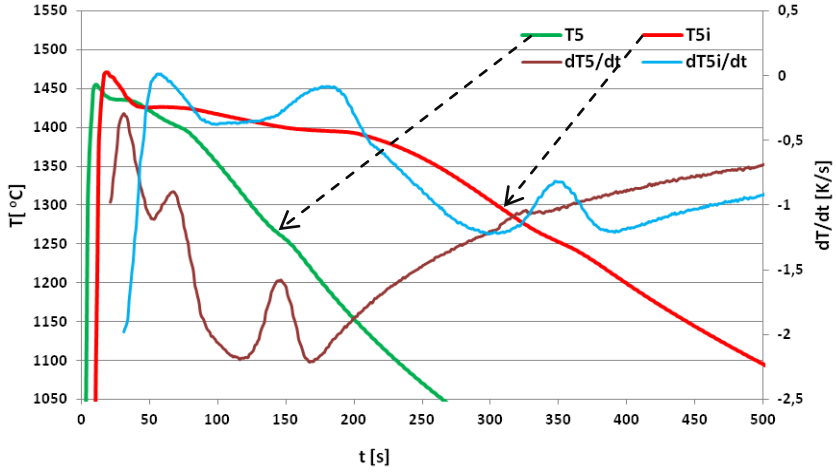
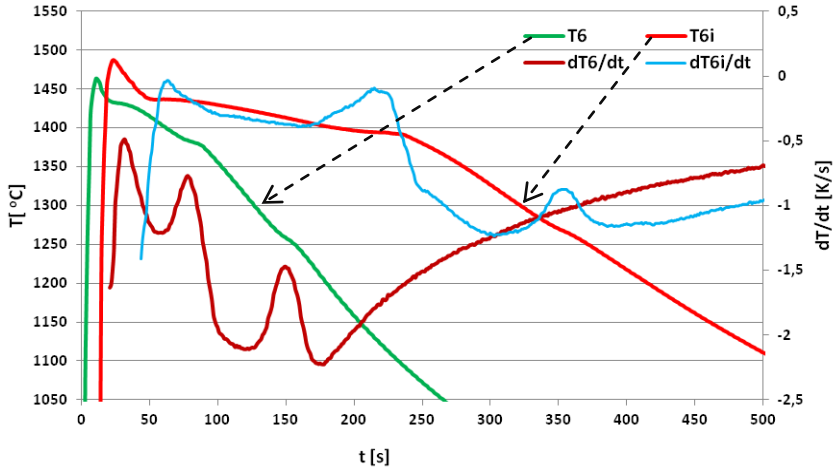
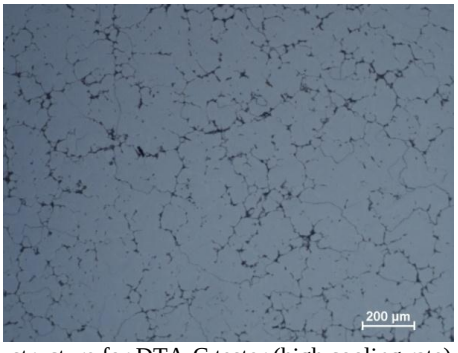
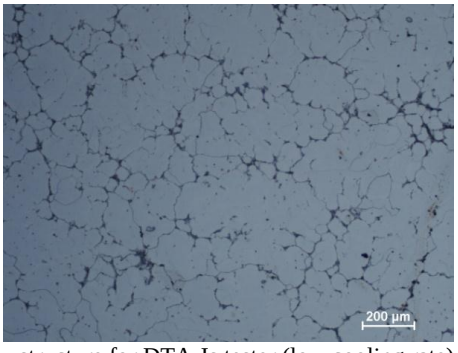


Fig. 10. Cooling and crystallization curves of high chromium cast steel T5





structure for DTA-C tester (high cooling rate)



structure for DTA-Is tester (low cooling rate)

Fig. 11. Cooling and crystallization curves of high chromium cast steel T6 and photographs of structure

5. Summary

The conducted studies of primary crystallization of high chromium cast steel with use of modified DTA method allowed complementation of crystallization process description in unequilibrium conditions, which occur during solidification of real castings. In Fig. 12 an attempt of primary crystallization description for high chromium cast steel T5 was presented (DTA-Is tester). The path of primary crystallization for studied high chromium cast steel can be described as follows:

$$\mathbf{L \rightarrow L+\alpha \rightarrow L+\alpha+\gamma \rightarrow L+\gamma \rightarrow L+\gamma+K_2 \rightarrow \gamma+K_2}$$

Individual pikes on curve crystallization characterize the component processes of primary crystallization of studied cast steel and according to equilibrium system (fig.2 – alloy III). Taking under consideration the additional elements in analysed cast steel T5, the position of point E moves towards the smaller carbon content (approx. 0,3% C counted according to equation 1). Peak size on curve crystallization provides information about force of given crystallization process and quantity of new forming phase. The curve crystallization is however a sum of whole transformation process from the liquid into the solid state and that is why it is hard to estimate quantity of separate phases. Additional quantitative investigations on image analyser can help in these estimations. The results of structural investigations demonstrate that carbide K_1 ($(Fe, Cr)_{23} C_6$) is also present in studied cast steel, which does not form from the liquid state directly and its precipitation proceeds in the solid state [10, 11]. Analysing the secondary crystallization curves the process was not observed The thermal effect of this process probably is too small due to the quantity of a new phase to became clearly registered.

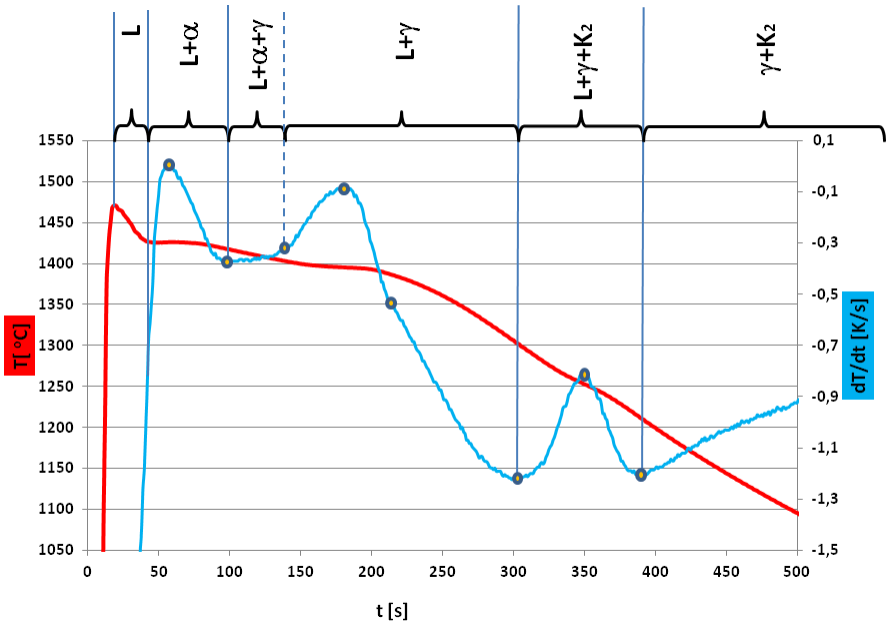


Fig. 12. Primary crystallization of high chromium cast steel T5 registered for DTA-Is tester

Acknowledgements

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References

[1] Sakwa W., Jura S., Sakwa J. (1980): Wear resistance iron alloys. Part II Cast steel. Publisher ZG STOP, Kraków (in Polish).

[2] Kniaginin G. (1972): Cast steel. Metallurgy and Founding. Publisher Śląsk, Katowice (in Polish).

[3] Kilarski J., Studnicki A., Suchoń J. (2011): The study of chromium cast steel on the liners of mining combines, Archives of Foundry Engineering, Publisher PAN Katowice, vol. 10, Special Issue 4, s. 31-36 (in Polish).

[4] Dobrzański L.A. (2004): Metal engineering materials. Publisher WNT Warszawa (in Polish).

[5] Malkiewicz T. (1971): Ferroalloys metal science. vol. II, Publisher PWN, Warszawa-Kraków (in Polish).

[6] Fraś E (2003): Metals crystallization. WNT, Warszawa (in Polish).

[7] Podrzucki Cz. (1991); Cast iron vol. I, Publisher ZG STOP, Kraków (in Polish).

[8] Gawroński J. (2004): Professor Stanisław Jura the creator of theory and the industrial uses of diagnostics and the wear of metals and alloys. Archive of Founding, special issue, vol.4, nr 16, Publisher PAN Katowice (in Polish).

[9] Cholewa M., Jura Z., Studnicki A. (2009): The development of thermal analysis and derivative method in Department of Foundry Silesian University of Technology, Progresses Theory and The Casting practice, Publisher PAN Katowice, rozdz. 4, 2009, s. 49-70 (in Polish).

[10] Przybył M., Studnicki A., Bartocha D. (2005): The decomposition of the austenite cooled alloys Fe-C-Cr about changing concentration of chromium, Procedings of the Third Scientific Conference Materiale Mechanical and Manufacturing Engineering M^3E, 2005, s. 549-553 (in Polish).

[11] Own studies, Department of Foundry, Faculty of Mechanical Engineering, Silesian University of Technology in Gliwice.