



Regularities of Crystallization Heat Release During Solidification of Alloyed Cast Irons

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Abstract

The chemical composition of alloys plays an important role at their crystallization and influences the solid phase formation, and thus, microstructure and properties. The present paper studies the release of the heat of crystallization of alloyed wear-resistant cast irons in order to determine the quantitative patterns of the chemical composition influence to the kinetics of crystallization. The differential thermal analysis was applied to get the data of heat release, its rate at cast iron temperature decrease. The normalized dependence of the amount of crystallization heat over time was obtained. The main temperature parameters were analyzed and four stages at irons crystallization were established and characterized with their duration and released heat. The multiple correlation analysis allowed considering a numerous physical and chemical factors and distinguishing their role at crystallization of irons. As a result, the quantitative regularities are determined of influencing the content of alloying elements, impurities and carbides on a heat and time of crystallization at the different stages of solidification, which are of great importance in developing alloyed irons with required quality and properties.

Keywords: Regularities, Crystallization Heat, Solidification, Cast Iron, Alloying

1. Introduction

It is known that the influence of the chemical composition of metals and alloys on their crystallization is mainly associated with a change in the thermophysical properties of the melt and the conditions of the solid phase formation [1-3]. It was previously shown that the solid phase grows under concentration supercooling, determined by the content and diffusion of the dissolved elements, the energy of the boundary between liquid and solid phases of the melt, and the temperature field in front of the growing solid phase [4, 5]. A change in the temperature field can not only enhance or weaken the concentration supercooling, but also completely eliminate it at a negative temperature gradient in front of the moving crystallization front [5]. The temperature

distribution in the casting after melt pouring into the mold is determined by the conditions of heat removal and the release kinetics of heat of overheating and crystallization.

One of the effective methods to study the crystallization process of metals and alloys is the differential thermal analysis (DTA) [6-8]. It allowed particularly to investigate the graphitization ability of spheroidal graphite cast iron processed by Al, Zr, Ca-FeSi [9], solidification influence in the control of inoculation effects in ductile cast irons [10], solidification pattern of Si-alloyed, inoculated ductile cast irons [11], the influence of final inoculation on the metallurgical quality of nodular cast iron [12] and an increasing precision and yield at casting production by simulation of the solidification process based on realistic material data evaluated from thermal analysis [13].



The kinetics of heat of superheating release is studied and given in the numerous works [1-5, 14], while the regularities of the release of the heat of crystallization of multicomponent metal systems have not been studied enough.

The aim of the present work is to study the release of the heat of crystallization of alloyed wear-resistant cast irons in order to determine the quantitative patterns of the chemical composition influence to the kinetics of crystallization.

2. Methodology

The alloyed wear-resistant cast irons of different grades were used in the study (Table 1). The temperatures of liquidus (t_l) and solidus (t_s), heat (L) and time (τ) of crystallization of the irons at cooling in helium at a rate of 20 K/min, as well as regularities of change in the rate of crystallization heat release were determined by the method of differential thermal analysis (DTA) with thermoanalyzer GDTD-24AV (SETARAM, France) on the samples with a diameter of 3 mm and a length of 6 mm.

The surface of solidified samples was etched with 2-4 wt. % nitric acid solution to analyze microstructure. It was done by MIM-10 optical microscope, JEOL JSM-35CF electron microscope and INCA Energy 350 (Oxford Instruments) energy dispersion analyzer.

For a more accurate comparison of the crystallization heat release kinetics of the alloys with different chemical composition, analytical dependences were plotted in relative time coordinates (the ratio of the current time to the total solidification time) and crystallization heat (the ratio of the current value of the crystallization heat to the one released till complete solidification of the sample). The values were changed from 0 to 1, where 0 means the beginning of the process, whereas 1 means its end.

These regularities were determined by analyzing the polynomial in the form

$$Y = A_0 + A_1 \cdot x + A_2 \cdot x^2 + \dots + A_n \cdot x^n \quad (1)$$

were: Y - rate of crystallization heat release,
 A_0, A_1, \dots, A_n - polynomial coefficients,
 x - time.

This equation approximated the experimental data on the rate changes in crystallization heat release.

After determining the coefficients Equation 1 was integrated in the range from 0 to 1 and the normalized dependence of the amount of crystallization heat (L) over time (τ) was obtained as below:

$$L = A_0 \cdot x + \frac{A_1}{2} \cdot x^2 + \frac{A_2}{3} \cdot x^3 + \dots + \frac{A_n}{n+1} \cdot x^{n+1} \quad (2)$$

The coefficients (A_i) of the regression Equation 1, multiple correlation (R_i) and the relative approximation error (δ) were determined according to the method described in [15].

3. Results and discussion

The chemical composition, the temperatures of liquidus (t_l) and solidus (t_s), heat of crystallization (L) and solidification time (τ) of the studied cast irons are presented in Table 1 and the rates of crystallization heat release of alloyed cast irons are shown in Figure 1.

The Table 2 shows the parameters of Equation 1 and the regularities of crystallization heat release calculated by Equation 2 in relative and absolute values shown in Figure 2.

Correlation analysis showed that the polynomial of degree 16 of Equation 1 describes the data shown in Fig. 1 with a sufficient degree of reliability. The correlation coefficient (R) varies from 0.992 to 0.999, and the average approximation error (δ) - from 3.9 to 9.2%. When the number of variables is less than 16 the degree of reliability decreases and the approximation error increases. When the number of variables exceeds 16, Equation 1 becomes more complicated.

The data analysis of the Figures 1 and 2 shows that the crystallization process of the studied irons consists of the following stages:

1. The beginning of the austenite precipitation process with an increase in the rate of crystallization heat release to a local maximum,
2. Completion the process of austenite precipitation with a decrease in the rate of crystallization heat release to a local minimum,
3. The beginning of the eutectic precipitation process with an increase in the rate of crystallization heat release to a maximum,
4. Completion of the eutectic precipitation process with a decrease in the rate of crystallization heat release to zero at the moment of the end of solidification.

The results of determining the duration of the above stages and the amount of crystallization heat release in this case are shown in Table 3.

Analysis of the data in Figure 2 and Table 3 shows that, depending on the chemical composition of cast irons, the duration of the first stage of solidification is from 11 to 22% of the total solidification time, the second - 20 - 60%, the third - 17 - 35%, and the fourth - 12 - 27%. The amount of released crystallization heat at the first stage varies from 7 to 13% of the total heat of crystallization, at the second - from 14 to 46%, at the third - from 29 to 55% and at the fourth - from 17 to 29%.

Table 1.

The chemical composition, liquidus (t_l) and solidus (t_s) temperatures, heat of crystallization (L) and solidification time (τ) of cast irons

No.	Alloy Grade	Content of elements, wt. %							t_l , °C	t_s , °C	L, kJ/kg	τ , s
		C	Si	Mn	Cr	Mo	S	P				
1	240Kh16	2.37	0.83	0.78	17.12	-	0.028	0.054	1360	1234	221	356
2	260Kh28	2.55	0.57	0.93	28.84	-	0.031	0.049	1338	1275	238	261
3	300Kh22	3.18	0.46	2.08	23.44	-	0.030	0.051	1287	1224	276	231
4	300Kh12M	2.93	0.61	0.85	16.36	1.42	0.029	0.054	1295	1180	249	343
5	300Kh12G5	2.87	0.54	4.62	15.23	-	0.031	0.050	1288	1200	251	262
6	300Kh12G3M	3.07	0.68	3.44	14.95	0.63	0.027	0.048	1290	1225	212	270

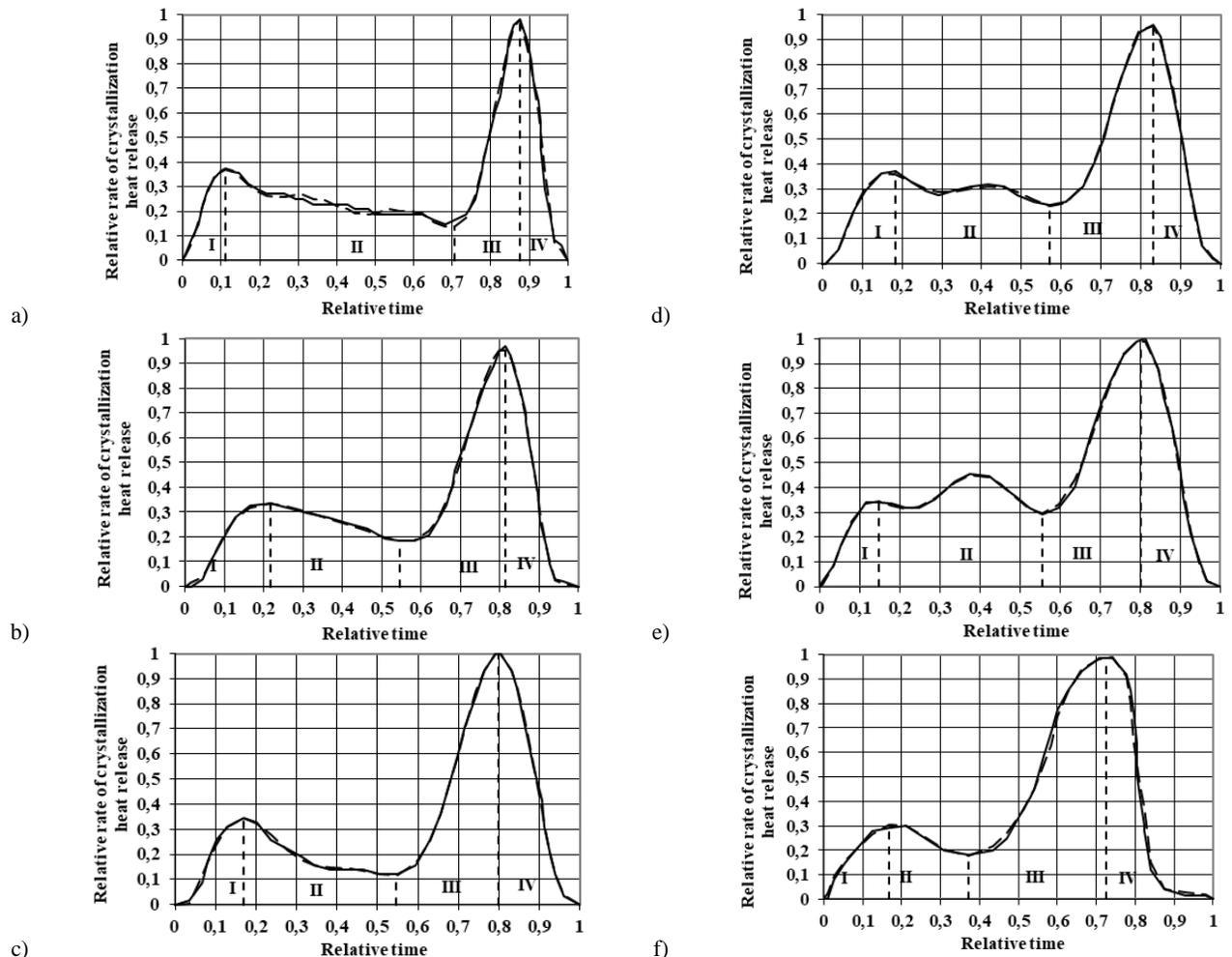


Fig. 1. Influence of the chemical composition on the rate of heat of crystallization release of alloyed cast irons. a) 240Kh16; b) 260Kh28; c) 300Kh12G3M; d) 300Kh12G5; e) 300Kh12M; f) 300Kh22; solid lines – experiment; dotted lines - calculation.

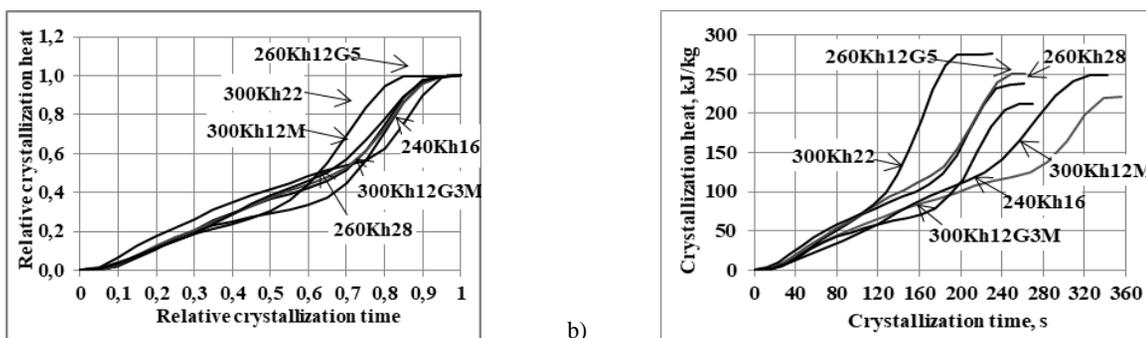


Fig. 2. Kinetics of the release of heat of crystallization of alloyed cast irons in relative (a) and absolute (b) values

Table 2.

Coefficients (A_i) of the regression Equation 1, multiple correlation (R_i) and relative approximation error (δ) for determining the rate of release of heat of crystallization of alloy cast irons

Parameter	Cast iron grade					
	240Kh16	260Kh28	300Kh22	300Kh12M	300Kh12G5	300Kh12G3M
A_0	$1.59 \cdot 10^{-2}$	$8.79 \cdot 10^{-3}$	$-2.70 \cdot 10^{-2}$	$1.03 \cdot 10^{-2}$	$7.06 \cdot 10^{-3}$	$2.53 \cdot 10^{-3}$
A_1	-2.00	-3.51	6.79	-1.00	-3.16	-3.18
A_2	241	146	-110	141	157	122
A_3	$-3.37 \cdot 10^3$	$-1.49 \cdot 10^3$	$1.21 \cdot 10^3$	$-1.66 \cdot 10^3$	$-1.50 \cdot 10^3$	-896
A_4	$20.9 \cdot 10^3$	$7.89 \cdot 10^3$	$-7.16 \cdot 10^3$	$8.26 \cdot 10^3$	$6.46 \cdot 10^3$	$2.48 \cdot 10^3$
A_5	$-69.4 \cdot 10^3$	$-25.2 \cdot 10^3$	$22.0 \cdot 10^3$	$-20.2 \cdot 10^3$	$-14.3 \cdot 10^3$	$-1.52 \cdot 10^3$
A_6	$124.3 \cdot 10^3$	$49.2 \cdot 10^3$	$-30.8 \cdot 10^3$	$21.8 \cdot 10^3$	$14.3 \cdot 10^3$	$-5.16 \cdot 10^3$
A_7	$-102.3 \cdot 10^3$	$-55.1 \cdot 10^3$	0	0	0	$8.44 \cdot 10^3$
A_8	0	$27.8 \cdot 10^3$	$51.5 \cdot 10^3$	$-16.1 \cdot 10^3$	$-10.2 \cdot 10^3$	0
A_9	$43.0 \cdot 10^3$	0	$-46.4 \cdot 10^3$	0	0	$-5.16 \cdot 10^3$
A_{10}	0	0	0	$12.1 \cdot 10^3$	$8.36 \cdot 10^3$	0
A_{12}	$-25.3 \cdot 10^3$	$-7.83 \cdot 10^3$	$15.6 \cdot 10^3$	0	0	$2.84 \cdot 10^3$
A_{13}	0	0	0	$-9.27 \cdot 10^3$	$-8.07 \cdot 10^3$	0
A_{14}	$15.3 \cdot 10^3$	$6.41 \cdot 10^3$	0	0	0	$-1.33 \cdot 10^3$
A_{15}	0	0	0	$8.93 \cdot 10^3$	$8.98 \cdot 10^3$	0
A_{16}	$-3.43 \cdot 10^3$	$-1.81 \cdot 10^3$	0	$-3.99 \cdot 10^3$	$-4.26 \cdot 10^3$	184
R	0.992	0.999	0.979	0.998	0.999	0.999
$\delta, \%$	7.5	4.8	9.2	5.2	3.9	5.8

Table 3.

The duration of the stage (τ_i) and the amount of released heat of crystallization (L_i) during the solidification of alloy cast irons*

Stage	Parameter	Units	Cast iron grade					
			240Kh16	260Kh28	300Kh22	300Kh12M	300Kh12G5	300Kh12G3M
I	τ	=	<u>0.111</u>	<u>0.216</u>	<u>0.168</u>	<u>0.148</u>	<u>0.184</u>	<u>0.169</u>
		s	39.5	56.4	38.8	50.8	48.2	45.6
I	L	=	<u>0.079</u>	<u>0.127</u>	<u>0.087</u>	<u>0.074</u>	<u>0.108</u>	<u>0.090</u>
		kJ/kg	17.5	30.1	24.1	18.2	27.2	17.2
II	τ	=	<u>0.595</u>	<u>0.329</u>	<u>0.204</u>	<u>0.409</u>	<u>0.387</u>	<u>0.378</u>
		s	211.8	85.9	47.1	140.3	101.4	102.1
II	L	=	<u>0.461</u>	<u>0.265</u>	<u>0.135</u>	<u>0.352</u>	<u>0.313</u>	<u>0.223</u>
		kJ/kg	101.9	62.0	37.3	87.7	78.5	42.8
III	τ	=	<u>0.170</u>	<u>0.268</u>	<u>0.354</u>	<u>0.245</u>	<u>0.259</u>	<u>0.251</u>
		s	60.5	69.9	81.8	84.0	67.9	67.8
III	L	=	<u>0.286</u>	<u>0.395</u>	<u>0.547</u>	<u>0.360</u>	<u>0.387</u>	<u>0.395</u>
		kJ/kg	63.3	94.1	151.0	89.7	97.1	75.9
IV	τ	=	<u>0.124</u>	<u>0.187</u>	<u>0.274</u>	<u>0.198</u>	<u>0.170</u>	<u>0.202</u>
		s	44.2	48.8	63.3	67.9	44.5	54.5
IV	L	=	<u>0.174</u>	<u>0.213</u>	<u>0.230</u>	<u>0.214</u>	<u>0.192</u>	<u>0.292</u>
		kJ/kg	38.3	50.8	63.6	53.4	48.2	56.1

* the relative and absolute values of the parameters are respectively given in the numerator and denominator.

It is known [4, 5] that the value of the crystallization heat of an alloy is directly proportional to the number of atoms passed from a liquid solution to a solid state. Consequently, the accumulation of the elements and mainly carbide phases at the interface between the liquid and solid phases during solidification should affect the crystallization heat of the alloys. From one hand solid carbides act like obstacles for atoms to pass from a liquid solution to a solid state and though decrease the crystallization heat. From another hand increase in solid carbides areas lead to crystallization heat increase.

The accumulation of the elements at the interface between the liquid and solid phases is possible both due to a change in solubility and the occurrence of adsorption and desorption processes. At the same time, at the initial moment of crystallization, the content of the element (i) in the liquid ahead of the flat crystallization front (C_{li}) due to the change in solubility is determined by the following dependence [4]:

$$C_{li} = C_i / K_0 \quad (3)$$

where K_0 - equilibrium distribution coefficient; C_i is the volumetric content of the i -th element in the melt, %.

The values of equilibrium distribution coefficients in austenite are given in Table 4.

Table 4.
Average values of the coefficients of equilibrium distribution of elements in $\gamma - 0$ [16-18].

Element	C	Si	Mn	Cr
$K_{0\gamma}$	0.340	0.543	0.77	0.865
Element	Mo	S	P	Ni
$K_{0\gamma}$	0.591	0.0263	0.085	0.87

The accumulation efficiency of elements at the interface between the liquid and solid phases as a result of adsorption processes (Γ_i) is determined by Gibbs equation:

$$\Gamma_i = -(C_i / R \cdot T) \cdot (\partial \sigma_i / \partial C_i) \quad (4)$$

where T is the temperature of the melt, K; R - universal gas constant ($R = 8.32 \text{ J/(K}\cdot\text{mol)}$); $\partial \sigma_i / \partial C_i$ - partial derivative of the energy of the boundary between liquid and solid phases with respect to the content of the i -th element in the melt, mN/%;

σ_i - the energy of the boundary between liquid and solid phases, which is determined by the equation given in [19]:

$$\sigma_i = 0.33 \cdot \sigma_{l-s} \quad (5)$$

where σ_{l-s} is the energy of the boundary between liquid and solid phases, N/m.

The quantitative regularity of the influence of the chemical composition on the energy of the boundary between liquid and solid phases of iron-carbon melts was determined according to the experimental data in [20-22].

The established regularity has the following form:

$$\begin{aligned} \sigma_i = & 132 - 13.9 \cdot C - 4.18 \cdot Si - 4.18 \cdot P + 0.418 \cdot Mn - 5.57 \cdot S - \\ & - 0.975 \cdot Ni - 0.696 \cdot Cr - 1.03 \cdot Cu - 3.48 \cdot Al + 146 \cdot Mo + 0.206 \cdot t \\ R_p = & 0.7; \delta = 4.8\%, \end{aligned} \quad (6)$$

where $C, Si, Mn, Cr, Ni, P, S, Mo$ are the content of these elements in the melt, respectively, %; t is the temperature of the melt, °C; R_p - correlation coefficient; δ - relative approximation error, %.

It was shown in [23-25] that at the ratio of the concentrations $Cr/C=3-10$, the crystallization of cast irons begins with the formation of austenite, and the eutectic is formed with the formation of austenite and carbides of $(Cr, Fe)_7C_3$ type, which contain from 50 to 70% chromium [23].

The regularity of the influence of elements on the amount of carbides (K) of $(Cr, Fe)_7C_3$ type in cast irons containing from 1.96 to 3.03% C; 0.3 to 0.75% Si; 0.64 to 4.6% Mn; 12.7 to 36% Cr; up to 11.4% Ni; up to 2.6% Mo, were determined from the experimental data given in [23].

The results of the mathematical analysis showed that the equation has the following form:

$$\begin{aligned} K = & 18.2 - 9.697 Si - 1.454 Mn + 0.6624 Ni + \\ & + 3.538 Mo + 0.2718 C \cdot Cr \\ R_p = & 0.999; \delta = 0.31\%. \end{aligned} \quad (7)$$

The results of calculating the total content of elements in a liquid at the interface between the liquid and solid phases at the initial moment of crystallization due to the different solubility of elements in the liquid and austenite (ΣC_{il-a}), as a result of adsorption at temperatures of liquidus ($\Sigma \Gamma_{il}$), solidus ($\Sigma \Gamma_{is}$) and in the middle of the solidification interval ($\Sigma \Gamma_{il-s}$), as well as the amount of carbides (K) are given in Table 5.

Table 5.
Results of calculating the values of $K, \Sigma C_{il-a}, \Sigma \Gamma_{il}, \Sigma \Gamma_{is}, \Sigma \Gamma_{il-s}$

No	Irons Grade	K, %	ΣC_{il-a} , %	$\Sigma \Gamma_{il}$	$\Sigma \Gamma_{is}$	$\Sigma \Gamma_{il-s}$
				mol/m ²		
1	240Kh16	20.05	12.00	$3.59 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.73 \cdot 10^{-6}$
2	260Kh28	31.31	18.34	$4.35 \cdot 10^{-6}$	$4.53 \cdot 10^{-6}$	$4.44 \cdot 10^{-6}$
3	300Kh22	30.98	16.49	$4.85 \cdot 10^{-6}$	$5.05 \cdot 10^{-6}$	$4.95 \cdot 10^{-6}$
4	300Kh12M	29.10	12.80	$4.23 \cdot 10^{-6}$	$4.56 \cdot 10^{-6}$	$4.39 \cdot 10^{-6}$
5	300Kh12G5	18.13	13.34	$4.10 \cdot 10^{-6}$	$4.34 \cdot 10^{-6}$	$4.22 \cdot 10^{-6}$
6	300Kh12G3M	21.31	13.16	$4.41 \cdot 10^{-6}$	$4.66 \cdot 10^{-6}$	$4.53 \cdot 10^{-6}$

Carbides amount (30.98%) calculated by Equation (7) in 300Kh22 cast iron, for which a significant increase in the heat of crystallization was observed, is compared to the experimental values (32.7%) (Fig. 3). Analysis showed that the difference is of 1.7% that is acceptable at modeling of the structure.

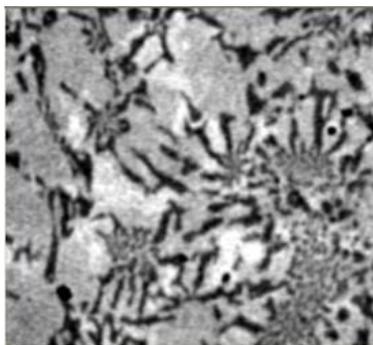


Fig. 3. Carbides in 300Kh22 iron. x 100

Analysis of elements content in carbides (Fig. 4 a), between carbides (Fig. 4 b) and in solid solution (Fig. 4 c) showed that chromium in carbides varies from 25.6 to 46.43 % wt. (average 37.9%), silicon from 0.12 to 0.54% (0.219%), manganese from 3.2 to 3.8% wt. (3.52%) (Table 6).

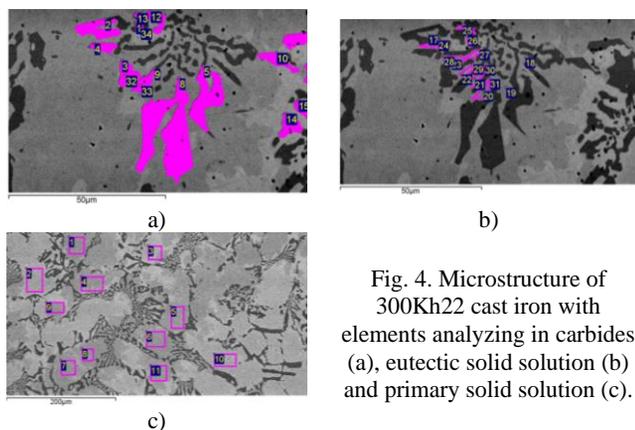


Fig. 4. Microstructure of 300Kh22 cast iron with elements analyzing in carbides (a), eutectic solid solution (b) and primary solid solution (c).

Table 6. Contents of C, Si, Cr and Mn (wt. %) in carbides, eutectic solid solution, primary solid solution of 300Kh22 iron as cast

Parameter	C	Si	Cr	Mn	Fe
Carbides (Fig. 4 a)					
Average	5.02	0.21	37.90	3.52	rest
Std. deviation	0.87	0.15	6.29	0.20	-
Max.	6.74	0.54	46.43	3.80	rest
Min.	3.44	0.12	25.60	3.02	rest
Eutectic solid solution (Fig. 4 b)					
Average	1.26	0.94	7.63	2.81	rest
Std. deviation	0.74	0.06	0.80	0.09	-
Max.	3.53	1.05	9.90	2.96	rest
Min.	0.49	0.83	6.56	2.70	rest
Cast primary solid solution (Fig. 4 c)					
Average	1.04	0.86	8.91	2.73	rest
Std. deviation	0.21	0.04	0.41	0.17	-
Max.	1.57	0.92	10.10	3.00	rest
Min.	0.85	0.80	8.64	2.46	rest

Average content of carbon in eutectic solid solution is of 1.26 %, silicon – 0.94 %, chromium – 7.63 %, manganese – 2.81 %. At

the same time cast primary solid solution contains lower elements C=1.04 %, Si=0.86 %, Mn=0.73 % and higher content of Cr=8.91 %.

An assessment of carbides influence on crystallization heat shows that their increase from 18 to 21% correlates with a decrease in the crystallization heat (correlation coefficient $r = 0.983$). Further carbides increase from 21 to 31% opposite trend is observed (correlation coefficient $r = 0.793$)

Taking as independent factors the amount of carbides (K) formed during the eutectic formation, the total content of elements in the liquid at the interface between the liquid and solid phases at the initial moment of crystallization due to the different solubility of elements in the liquid and austenite (ΣC_{il-a}) and as a result of adsorption at temperatures of liquidus ($\Sigma \Gamma_{il}$), solidus ($\Sigma \Gamma_{is}$) and in the middle of the solidification interval ($\Sigma \Gamma_{il-s}$), the effectiveness of their combined effect on the kinetics of heat of crystallization release of high-alloy cast irons at various stages of solidification was investigated.

Multiple correlation analysis with the 1st degree polynomial showed that the efficiency of accumulation of the elements on the surface of crystallization centers and growing austenite crystals as a result of adsorption at the liquidus temperature ($\Sigma \Gamma_{il}$) and in the middle of the solidification interval ($\Sigma \Gamma_{il-s}$) determines the duration of stages I and II of crystallization, respectively. In the transition to the eutectic crystallization, an additional significant factor is the release of carbides, the amount of which (K) simultaneously with the efficiency of accumulation of elements on the surface of growing crystals as a result of adsorption at a solidus temperature ($\Sigma \Gamma_{is}$) determines the duration of stages III and IV of crystallization.

At eutectic crystallization austenite and carbides serve as accumulators, since the solubility of elements in them is less than in the melt.

The coefficients ($A_i - A_{\Sigma \Gamma_{il}}, A_{\Sigma \Gamma_{icp}}, A_{\Sigma \Gamma_{ic}}, A_K$) of the 1st degree polynomial at $A_0=0$, multiple correlation (R_i) and the relative approximation error (δ) are shown in Table 7.

An analysis of the regularities representing by this table shows that the accumulation of elements and phases ahead of the crystallization front slows down its progress and leads to an increase in the crystallization time. Evaluation of the effectiveness of the influence of factors according to the Student's criterion (t_{st}) showed that the influence of elements adsorbed on the interface of the liquid and solid phases is 2.2–3.6 times higher than the influence of carbides.

Table 7.

The parameters of the 1st degree polynomial calculated at different stages of irons solidification

Stage	$\frac{A_{\Sigma \Gamma_{il}}}{t_{st}}$	$\frac{A_{\Sigma \Gamma_{icp}}}{t_{st}}$	$\frac{A_{\Sigma \Gamma_{ic}}}{t_{st}}$	$\frac{A_K}{t_{st}}$	R	$\delta, \%$
1	$\frac{108 \cdot 10^5}{14,3}$	0	0	0	0.988	5.5
2	0	$\frac{251 \cdot 10^5}{4,1}$	0	0	0.879	9.9
3	0	$\frac{129 \cdot 10^5}{3,8}$	0	$\frac{0.612}{1,1}$	0.998	5.2
4	0	0	$\frac{828 \cdot 10^4}{2,1}$	$\frac{0.661}{0,96}$	0.994	6.9

It is seen that at the beginning of the precipitation of austenite and eutectic (stages I and III), the amount of heat depends on the duration of the stages (τ_i). At the final stages of austenite and eutectic separation (stages II and IV), an additional influence is exerted by the accumulation of the elements in the liquid at the interface between the liquid and solid phases, which is formed as a result of different solubility of elements in the melt and austenite (ΣC_{il-a}).

The coefficients ($A_i - A_{\tau_i}$, $A_{\Sigma C_{il-a}}$) of the regression of the 1st degree polynomial at $A_0 = 0$, multiple correlation (R_i) and relative approximation error (δ) are shown in Table 8.

Table 8.

The parameters of the 1st degree polynomial calculated at different stages of solidification of the irons

Stage	A_{τ_i}	$A_{\Sigma C_{il-a}}$	R	$\delta, \%$
1	0.421	0	0.953	15.5
2	0.517	0.481	0.987	12.5
3	1.153	0	0.958	14.4
4	0.933	0.752	0.969	12.8

Analysis of the data given in Table 8 shows that the amount of heat of crystallization released at all stages depends on the duration of the process.

The experimental results and analysis show that the release of crystallization heat depends mainly, according with Student's criterion (t_{α}), on the efficiency of accumulation of alloying elements, impurities and carbides on the interfacial surface.

4. Conclusions

The study of the crystallization kinetics for different grades of alloyed wear-resistant cast irons revealed four stages at their solidification with subsequent austenite and eutectic precipitation, which are distinguished by the duration and released heat.

The chemical composition of irons influences to the crystallization kinetics and increase of heat release through the concentrations gradient of the elements at the solid-liquid interface and their accumulation on the surface of growing crystals. The impurities and precipitated carbides are found to play an important role in the intensification of crystallization heat release due to their barrier effect on the advancement of growing austenite crystals.

The quantitative regularities determined in this study could be useful at the development of alloyed cast irons of required quality and properties. Particularly, they can be used for modeling the process of alloyed cast irons solidification and predicting the development of casting defects in castings.

References

- [1] Girshovich, N.G. (1966). *Crystallization and properties of cast iron in castings*. M., L.: Mashinostroenie. (in Russian)
- [2] Khudokormov, D.P. (1968). *The role of impurities in the process of graphitization of cast irons*. Moscow: Science and technology.
- [3] Levi, L.I. & Nikitichin, A.M. (1973). On the influence of the hereditary properties of ferrosilicon on the structure and properties of cast iron in castings. *Foundry production*. 11, 23-25.
- [4] Chalmers, B. (1968). *Theory of solidification*. Trans. from English M.: Metallurgy.
- [5] Kan, R. (1968). *Physical metallurgy*. Vol. 3. Mir: Moscow.
- [6] Stefanescu, D.M. (2015). Thermal analysis—theory and applications in metalcasting. *International Journal of Metalcasting*. 9, 7-22. <https://doi.org/10.1007/BF03355598>.
- [7] Stefanescu, D.M., Suarez, R. & Kim, S.B. (2020). 90 years of thermal analysis as a control tool in the melting of cast iron. *China Foundry*. 17(2), 69-84. <https://doi.org/10.1007/s41230-020-0039-x>.
- [8] Ignaszak, Z., Popielarski, P. & Codina, E. (2015). Methodology of comparative validation of selected foundry simulation codes. *Archives of Foundry Engineering*. 15(4), 37-44. DOI: 10.1515/afe-2015-0076.
- [9] Bhat, M.N., Khan, D.M.A. & Singh, K.K. (2019). Thermal analysis and graphitization ability of spheroidal graphite cast iron preconditioned by Al,Zr,Ca-FeSi. *International Journal of metal casting*. 13(4), 928-936. DOI 10.1007/s40962-019-00311-6.
- [10] Cojocar, A.M., Riposan, I. & Stan, S. (2019). Solidification influence in the control of inoculation effects in ductile cast irons by thermal analysis. *Journal of thermal analysis and calorimetry*. 138(3), 2131-2143. <https://doi.org/10.1007/s10973-019-08808-2>.
- [11] Stan, I., Anca, D., Stan, S., Riposan, I. (2021). Solidification pattern of Si-alloyed, inoculated ductile cast irons, evaluated by thermal analysis. *Metals*. 11(5), 846, 1-16. <https://doi.org/10.3390/met11050846>.
- [12] Dwulat, R., Janerka, K. & Grzesiak, K. (2021). The influence of final inoculation on the metallurgical quality of nodular cast iron. *Archives of Foundry Engineering*. 21(4), 5-14. DOI: 10.24425/afe.2021.138673.
- [13] Persson, P.E., Ignaszak, Z. & Kump, A. (2019). Increasing precision and yield in casting production by simulation of the solidification process based on realistic material data evaluated from thermal analysis (using the ATAS MetStar system). *Archives of Foundry Engineering*. 19(1), 117-126. DOI: 10.24425/afe.2019.127104.
- [14] Gulyaev, B.B. (1960). *Foundry processes*. Moscow: Mashgiz.
- [15] Shvedkov, E.L. (1975). *Elementary mathematical statistics in experimental problems of materials science*. Kyiv: Naukova Dumka. (in Russian)
- [16] Ono, A. (1980). *Solidification of metals*. M.: Metallurgy.
- [17] Hein, K., Buriga, E. (1987). *Crystallization from melts. Handbook*. M.: Metallurgy.
- [18] Morita, Z. & Tanaka, T. (1988). Thermodynamics and coefficients of equilibrium distribution of dissolved elements between solid and liquid phases in iron alloys. *Tetsu to hagane. Transactions of the Iron and Steel Institute of Japan*. 74(7), 1210-1218.
- [19] Popel, S.I. (1971). *Theory of metallurgical processes*. M.: VINITI.
- [20] Arsentiev, P.P., Koledov, L.A. (1976). *Metal melts and their properties*. Moscow: Metallurgy.

- [21] Andronov, V.N., Chekin, B.V., Nesterenko, S.V. (1976). *Liquid metals and slags*. M.: Metallurgy.
- [22] Ershov, G.S., Bychkov, Yu.B. (1983). *Properties of metallurgical melts and their interaction in steelmaking processes*. M.: Metallurgy.
- [23] Garber, M.E. (1972). *Castings from white wear-resistant cast irons*. M.: Mashinostroenie.
- [24] Maratray, F. (1971). *Memoires scientifiques de la revue de metallurgie*. 68(2), 67-74
- [25] Tsypin, I.I. (1983). *White wear-resistant cast irons*. M.: Metallurgy.