

## Influence of the Specific Heat Capacity, Thermal Conductivity Coefficient, Density and Cooling Rate on Formation of Crystallization Centers in Metallic Melts

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The influence of physical parameters (specific heat capacity, thermal conductivity coefficient, density, specific heat of crystallization) and their interactions on the formation of crystallization centers during homogeneous crystallization of metals at different cooling rates has been studied. Modeling and calculations were carried out for pure metals: Ag, Al, Au, Bi, Cu, Ni, Pb, Sn, and Zn. The indicators were obtained for each metal separately under ten different cooling rate conditions. The degree of influence of each physical parameter and their joint impact on the number of formed metal crystallization centers was determined by calculating the pair correlation coefficient. A simulation model for theoretically calculating the number of formed crystallization centers using a computer experiment made it possible to establish a functional relationship between the cooling rate and the number of formed crystallization centers. The determining influence of the specific heat capacity and density of metals on the number of crystallization centers has been established. In turn, there is a slight influence of the thermal conductivity index on the number of crystallization centers. However, this correlation has a variable value at low cooling rates. The effect of the heat of crystallization on the formation of crystallization centers is insignificant. The obtained values were analyzed for each metal separately, and, in addition, a comparative assessment of the same indicators characteristic of different metals under study was carried out among themselves.

**Keywords:** Crystallization centers, Simulation model, Correlation coefficient.

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### 1. INTRODUCTION

Crystallization underlies many technological processes for the production of metal products. Therefore, it is still the object of study. To date, a significant amount of experimental data has been accumulated in this direction and various theories have been developed both for bulk and film materials [1-5].

However, the available theories are often unable to adequately describe both the crystallization mechanism itself and its kinetics for real (nonequilibrium) conditions. It happens because to do so, it is necessary to solve a set of problems for each of the time points: calculation of the temperature field of the casting, thermodynamic assessment of the degree of phase stability at a given point in the system, assessment of the critical size of the solid phase nucleus, and, accordingly, the probability of formation of crystallization centers in local microvolumes of the melt, etc.

One of the promising directions of theoretical studies of metal crystallization is the description of the formation of solid structures using the methodology of synergetics. Synergetic methods allow a qualitatively new approach to solving the problem. Thus, for example, in [6-10], by using the method of analogies between the displacement of the liquid-solid interface and the propagation of a switching wave in a bistable trigger-type cellular automaton, a formula was proposed for determining the critical radius of the nucleus during crystallization:

$$r^* = K_f \frac{\lambda}{c\rho V_{cul}}, \quad (1)$$

where  $r^*$  – critical radius of the nucleus of the solid phase [m];  $\lambda$  – coefficient of thermal conductivity [W/(m K)];  $c$  – specific heat capacity [J/(kg K)];  $\rho$  – density [kg/m<sup>3</sup>];  $V_{cul}$  – cooling rate in the system under study [K/s];  $K_f$  is a coefficient having the dimension of the temperature gradient [K/m].

It should be emphasized that formula (1) takes into account the cooling rate of the metal during crystallization. This significantly distinguishes it from the classical formula:

$$r^* = 2 \frac{\gamma_{S-L}}{L} \cdot \frac{T_k}{\Delta T}, \quad (2)$$

where  $L$  is the latent specific heat of crystallization;  $T_k$  is the crystallization temperature;  $\Delta T = T_k - T$  is undercooling;  $\gamma_{S-L}$  is the free energy of the "liquid-solid" interface.

There is no cooling rate in expression (2), but cooling rate significantly affects the crystallization processes and the formation of the metal structure.

The characteristics of metals included in (1) are quite simply determined experimentally. A change in their values can affect the critical radius of the nucleus during homogeneous crystallization and, consequently, on the number of formed centers, which is reflected in the structure of the crystallized metal. An analysis of the influence of these physical parameters on the

formation of centers of the crystallization will simplify both the search for new methods for controlling the structure of metals and the creation of promising casting technologies.

The aim of the work is to study the influence of the physical characteristics of metals (specific heat capacity, thermal conductivity coefficient and density) on the formation of centers during homogeneous crystallization of metals.

## 2. MATERIALS AND METHODS

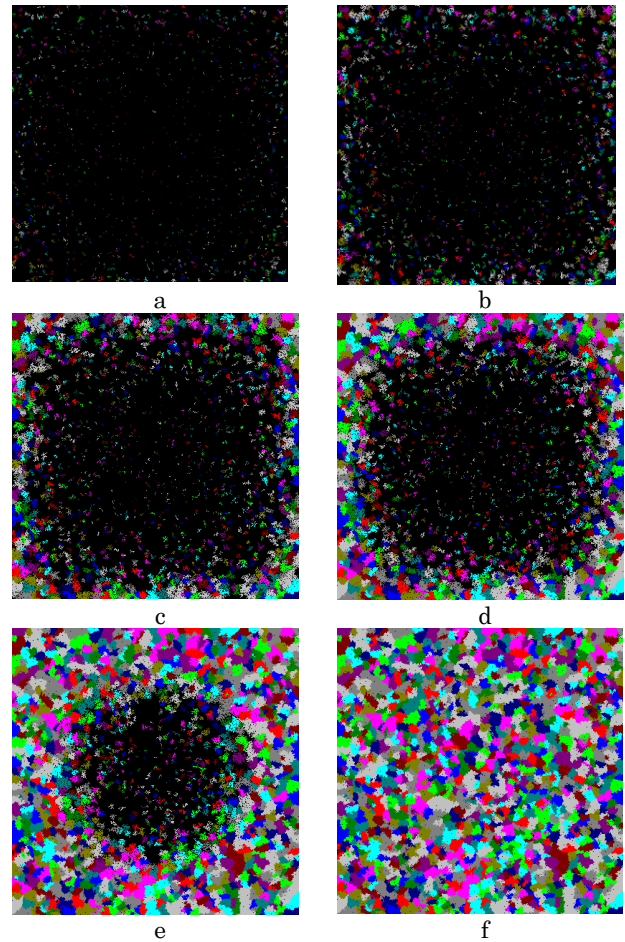
In this work, a simulation model of metal crystallization was used [11, 12]. With its help, computer experiments were carried out, simulating homogeneous crystallization, in which the number of emerging centers was determined. This model is based on a bistable probabilistic cellular automaton of a trigger type, whose operation algorithm is determined by the magnitude of undercooling. The value of undercooling in each of the local microvolumes of liquid metal is determined as the difference between the temperatures of its crystallization (which is the reference value) and the current temperature in the given microvolume of the system. The temperature field of the system is calculated by numerically solving the two-dimensional heat equation, taking into account the release of crystallization heat. This model makes it possible to reproduce and study the formation of the metal structure during crystallization under various cooling conditions, both for homogeneous and heterogeneous formation of crystallization centers.

It should be noted that the simulation model which was used does not allow to determine the critical size of the solid phase nucleus directly. This is due to the fact that the minimum size of the solid phase particle, which appeared as a result of the simulation, is equal to the size of the element (cell) of the cellular automaton. At the same time, the cell size is determined by the geometric dimensions of the system and the dimensions of the arrays specified when programming the algorithm of the model. The geometrical dimensions of the system are set during calibration of the model, while the dimensions of the arrays are determined by the characteristics of the monitor and the computational capabilities of the computer (memory size, speed, etc.). At that, it is important to mention that when calibrating the model for conducting a computer experiment, its parameters were chosen so that the cell size of the cellular automaton corresponded to the level of the critical size of the nucleus in the melt near the temperature of crystallization ( $10^{-6}$ - $10^{-5}$  m).

The technique for conducting computer experiments consisted in determining the number of homogeneously formed centers of crystallization at different cooling rates for various metals. The level of interrelation between the obtained values of the number of crystallization centers that formed and the physical characteristics of metals was determined by the method of correlation analysis.

Modeling and calculations were carried out for 9 metals: Ag, Al, Au, Bi, Cu, Ni, Pb, Sn, Zn at constant cooling rates (Fig. 1). In this model, a cooling curve is

calculated, according to which a different cooling rate was set by an appropriate choice of heat transfer coefficients from different sides of the system.



**Fig. 1** – Modeling of the crystallization process of aluminum structures in different periods of crystallization time: the beginning of crystallization (a), intermediate stages of crystallization (b-e), complete crystallization (f)

In a series of experiments for each of the metals, the cooling rate ( $V_{cool}$ ) was set according to the initial section of the cooling curve at levels: 0.17; 0.33; 0.67; 1.00; 1.67; 2.00; 3.50; 5.00; 6.00; 6.67 K/s. Crystallization was modeled for a two-dimensional sample with dimensions of  $0.02 \times 0.02$  m. Thus, the level of the linear size of a cellular automaton cell was  $10^{-5}$ . The dimension of the numerical arrays used in the computer model was  $400 \times 400$ . Average values of the corresponding quantities for metals in liquid and solid states were used as thermophysical parameters in the calculations. The heat released during crystallization was also taken into account (Table 1).

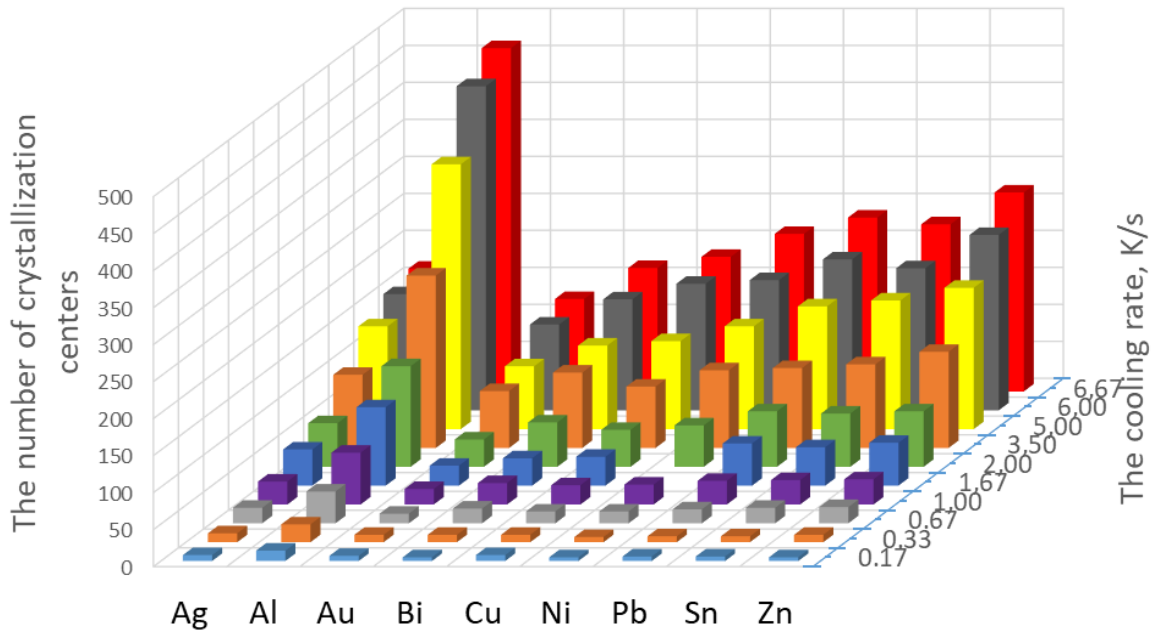
Using of a random number generator is the peculiarity of the simulation model used. As a result, each specific simulation result has a probabilistic character. Therefore, for each of the given values of the cooling rate and the thermal conductivity, the calculations were repeated 11 times and then the arithmetic mean values of the number of crystallization centers formed were determined  $\bar{N}$  (Table 2, Fig 2).

**Table 1** – Values of the physical characteristics of metals used in the simulation

Metal	$\rho$ , kg/m <sup>3</sup>	$c$ , J/(kg·K)	$\lambda$ , W/(m·K)	$L$ , kJ/kg	Molar mass, $\times 10^3$ kg/mol	Average molar heat capacity, J/(mol·K)
Ag	9600	305	260	105	107.87	32.9
Al	2700	1290	210	357	26.98	38.67
Au	17720	169	255	66	196.97	33.29
Bi	9900	145	10	54.07	208.98	30.3
Cu	8180	520	250	205	63.55	33.04
Ni	7850	680	74	297,6	58.71	39.92
Pb	10900	144	24	23,17	207.2	29.83
Sn	7080	255	45	60,2	118.7	30.27
Zn	6920	470	80	112	65.4	30.72

**Table 2** – Dependence of the number of crystallization centers during homogeneous crystallization on the cooling rate

Metal	$\bar{N}$ , thing (at $V_{cul}$ , K/s)									
	0.17	0.33	0.67	1.00	1.67	2.00	3.50	5.00	6.00	6.67
Ag	8	12	21	31	49	59	99	139	157	166
Al	14	24	43	70	106	136	233	358	438	464
Au	7	10	13	21	27	37	77	85	116	125
Bi	5	10	20	29	37	60	102	113	150	167
Cu	8	10	16	26	39	50	83	119	171	182
Ni	5	7	16	27	50	56	105	139	176	213
Pb	6	8	19	32	57	75	108	166	204	235
Sn	6	8	21	33	52	72	113	174	192	226
Zn	5	10	22	34	58	75	130	191	237	269



**Fig. 2** – Dependence of the number of formed crystallization centers on the cooling rate of metal melts

**Table 3** – Values of the pair correlation coefficients between the cooling rate and the number of crystallization centers

Metal	Ag	Al	Au	Bi	Cu	Ni	Pb	Sn	Zn
$R_{x,y}$	0.998	0.999	0.988	0.992	0.994	0.997	0.998	0.998	0.999

**Table 4** – Pair correlation coefficients between the number of crystallization centers, physical parameters of metals and their interactions at different cooling rates

Parameter	Correlation coefficients at $V$ , K/s									
	6.67	6.00	5.00	3.50	2.00	1.67	1.00	0.67	0.33	0.17
$\rho$	-0.84	-0.84	-0.82	-0.86	-0.85	-0.85	-0.84	-0.79	-0.65	-0.53
$c$	0.83	0.83	0.81	0.80	0.73	0.80	0.80	0.78	0.81	0.79
$\lambda$	-0.14	-0.09	-0.08	-0.11	-0.19	-0.13	-0.03	0.03	0.35	0.51
$L$	0.50	0.48	0.47	0.46	0.34	0.44	0.45	0.43	0.57	0.64
$\rho c$	0.12	0.12	0.06	0.06	-0.05	0.09	0.02	-0.32	0.09	0.17
$\rho \lambda$	-0.62	-0.59	-0.56	-0.61	-0.67	-0.63	-0.56	-0.48	-0.20	-0.03
$\rho L$	-0.40	-0.42	-0.42	-0.46	-0.57	-0.48	-0.47	-0.45	-0.23	-0.06
$c \lambda$	0.71	0.73	0.73	0.71	0.65	0.69	0.75	0.76	0.90	0.95
$c L$	0.82	0.80	0.80	0.80	0.73	0.78	0.80	0.79	0.84	0.83
$\lambda L$	0.39	0.40	0.40	0.36	0.27	0.33	0.41	0.43	0.68	0.81

The degree of influence of each of the physical parameters (as well as of their combinations) on the number of crystallization centers formed was determined by calculating the pair correlation coefficient.

### 3. RESULTS AND DISCUSSION

According to the calculation results for nine different metals, it was found that the values of the pair correlation coefficients ( $R_{N,V}$ ) between the number of crystallization centers formed and the cooling rate are positive and exceed 0.99 (Table 3). This is in good agreement with the well-known fact that with an increase of the cooling rate, number of crystallization centers also increases, which, in turn, contributes to the refinement of the structure of the solidified metal.

In addition, very large values of the correlation coefficients indicate that for all nine metals (i.e., regardless of the values of such physical characteristics as density, specific heat, thermal conductivity and specific heat of crystallization), the relationship between the cooling rate and the number of crystallization centers formed is actually functional. This fact can serve as an additional confirmation of the correctness of expression (1).

Based on the results of the analysis of the relationship between the physical characteristics of metals and the number of crystallization centers formed at different cooling rates (Table 4), it was found that at fixed initial cooling rates, the number of crystallization centers formed most strongly correlates with the density and specific heat of metals (Table 4, line 1 and 2). The average values of the correlation coefficient  $R_{x,y}$  are -0.79 and 0.80, respectively (estimated as a high degree of correlation [13]. The influence of thermal conductivity ( $\lambda$ ) is insignificant, and the influence of the heat of crystallization  $L$  on the formation of crystallization centers (line 4) is not decisive (0.48 – is weak correlation) (Table 4).

Special attention should be paid to the correlation between the density and the number of crystallization centers formed. The value of the density of a substance, among other things, depends on its atomic (molar) mass. As a rule, an increase in atomic mass is accompanied by an increase in density (Table 1). At least for the nine metals under consideration, the correlation coefficient between molar mass and density, as calculations show, is positive and amounts to 0.76. Therefore, the negative values of the correlation coefficient between the density ( $\rho$ ) and the number of crystallization

centers are quite understandable. This is because more massive atoms (atoms of substances with a higher density) with the same average value of kinetic energy (at the same temperature) have a lower speed.

That is, in melts of metals with a higher density, there is a lower diffusion rate, and, consequently, a lower probability of the formation of crystallization centers.

Attention should be paid to changes in the degree of connection between some physical parameters of metals and the number of crystallization centers that have appeared at low cooling rates (0.17 and 0.33 k/s). An increase of the correlation coefficient is especially noticeable for thermal conductivity  $\lambda$  (Table 4).

When analyzing the degree of influence of specific (per unit mass) heat capacity on the number of crystallization centers, it should be taken into account that, in the ideal case, the molar heat capacities of metals in the solid state are equal and remain constant over a wide temperature range (Dulong and Petit law). Even calculated from the average values of the specific heat for the solid and liquid states, the values of the molar heat capacities of metals can be considered equal with a sufficient degree of accuracy (Table 1). If we assume the values of the molar heat capacity for all metals to be the same, then higher values of the specific (per unit mass) heat capacity correspond to lower values of the molar mass (Table 1), and, consequently, lower values of density.

### 4. CONCLUSIONS

Taking into account the previously described influence of the metal density on the number of crystallization centers formed, and despite the large values of the correlation coefficient, there are absolutely no grounds to assert a direct causal relationship between the number of crystallization centers formed and the value of the specific heat capacity. All the apparent influence of specific heat is reduced to the fact that its large values correspond to lower values of density. Under conditions of constancy of the cooling rate, and assuming the molar heat capacities of various metals to be equal, it can be concluded that the density has a determining influence on the number of crystallization centers formed, and the value of the specific heat is mainly determined by the value of density. This is also evidenced by the almost equal in absolute value, but opposite in sign, correlation coefficients for density and specific heat, as well as the insignificance of their joint influence for all values of the cooling rate.

## REFERENCES

1. X. Liu, H. Li, M. Zhan, *Manufacturing Rev.* **5** No 10, 1 (2018).
2. A. Zyska, Z. Konopka, M. Łagiewka, M. Nadolski, *Archives of Foundry Eng.* **6** No 1, 99 (2016).
3. K.V. Tyshchenko, L.V. Odnodvoretz, I.Yu. Protsenko, *Metallofiz. Noveishie Tekhnol.* **33** No 10, 1351 (2011).
4. Yu. Berezhnyak, L. Odnodvoretz, D. Poduremne, I. Protsenko, Yu. Shabelnyk, *Springer Proceedings in Physics*, **210**, 17 (2018).
5. O. Lasyuchenko, L. Odnodvoretz, I. Protsenko, *Crystal Res. Technol.* **35** No 3, 329 (2000).
6. S.C. Michelic, J.M. Thuswaldner, Ch. Bernhard, *Acta Materialia* **58** No 7, 2738 (2010).
7. S.M. Elahi, R. Tavakoli, I. Romero, D. Tourret, *Comput. Mater. Sci.* **216**, 111882 (2023).
8. F.L. Mota, J. Pereda, K. Ji, Y. Song, R. Trivedi, A. Karma, N. Bergeon, *Acta Materialia* **204** No 1, 116500 (2021).
9. A. Zyska, *Materials* **14** No 12, 3393 (2021).
10. Jing Jing Wei, Xu Dong Wang, Lai Qiang Cai, Man Yao, *Journal: Steel Research International* **93** No 7, 2100793 (2022).
11. O. Donii, A. Kulinich, V. Khristenko, *International Scientific Journal. Mathematical Modeling* **1** No 4, 180 (2017).
12. T. Wang, Y. Cheng, L. Yong, N. Qu, Z. Lai, X. Zhang, J. Zhu, *J. Non-Crystal. Solid.* **600**, 121991 (2023).
13. J. Ofungwu, *Statistical Applications for Environmental Analysis and Risk Assessment (Statistics in Practice)* (Hackettstown: John Wiley & Sons, Inc.: 2014).

### Вплив питомої теплоємності, коефіцієнта теплопровідності, густини та швидкості охолодження на формування центрів кристалізації в металевих розплавах

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Досліджено вплив фізичних параметрів (питомої теплоємності, коефіцієнта теплопровідності, щільності, питомої теплоти кристалізації) та їх взаємодії на утворення центрів кристалізації при гомогенній кристалізації металів за різних швидкостей охолодження. Моделювання та розрахунки здійснювали для чистих металів: Ag, Al, Au, Bi, Cu, Ni, Pb, Sn, Zn. Зазначені показники отримували для кожного металу окремо за умов десяти різних швидкостей охолодження. Ступінь впливу кожного з фізичних параметрів та їх спільний вплив на кількість центрів кристалізації металів визначали, розраховуючи парний коефіцієнт кореляції. Імітаційна модель теоретичного розрахунку кількості центрів кристалізації за допомогою комп'ютерного експерименту дозволила встановити функціональну залежність між швидкістю охолодження і кількістю цих самих центрів кристалізації, що утворилися. Встановлено визначальний вплив питомої теплоємності та щільності металів на число центрів кристалізації. У свою чергу, відзначається незначний вплив показника теплопровідності на число центрів кристалізації. Однак це кореляція при невисоких швидкостях охолодження має змінне значення. Вплив теплоти кристалізації на формування центрів кристалізації не є значущим. Отримані значення проаналізовані для кожного металу окремо і крім того, проведена порівняльна оцінка одних і тих самих показників, характерних для різних досліджуваних металів, між собою.

**Ключові слова:** Центри кристалізації, Імітаційна модель, Коефіцієнт кореляції.