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Influence of the Rate of Cooling/Solidification on the Location of Characteristic Points on the AT and ADT Curves of Cast Iron

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Abstract

The paper presents the results of the analysis of cooling curves of cast iron with approximately eutectic composition rasterized at different rates of cooling and ingot crystallization. The test samples were in the form of rods with a diameter of 30,0.mm and a coagulation modulus M=0.75 cm. They were cast in a sand mould made of furan mass placed on a chill in the form of a cast-iron plate, with which one of the front surfaces of the rod casting was in contact. In this way, a differentiated cooling rate along the rod was achieved. At selected distances from the chiller (5, 15, 25, 25 and 45 mm) thermocouple moulds were placed in the cavity to record the cooling curves used in thermal (AT) and derivation (ATD) analysis. The solidification time of the ingot in the part farthest from the chiller was about 200s, which corresponds to the solidification time in the test cup AT. An analysis of the recorded cooling curves was performed in order to determine the values of characteristic points on the AT curve (Tsol. Tliq, Δ Trecal., τ clot, etc.). Relationships between cooling time and rate and characteristic points on AT and ATD curves were developed. For example, Tsol min changes in the range of 1115 - 1145 for the range of cast iron solidification times in the selected ingot zone from \sim 70 to \sim 200 s, which corresponds to the process speed from 0.0047 to 0.014 [1/s]. The work also includes an analysis of other characteristic points on the AT and ATD curves as functions of the solidification rate of cast iron of the same composition.

Keywords: thermal analysis, cast iron, cooling/solidification rate, cups AT

1. Introduction

The thermal analysis (AT) of alloys based on recording their cooling curves and interpreting the obtained results, is presently wider and wider applied in the foundry engineering, especially in iron casting. It is used in assessing the chemical composition or its

indicators (Sc, CE), mechanical properties, tendency for graphitic corrosion, etc. [1-3].

The AT is ranked the fast method of assessing the liquid metal quality, mainly cast iron. A wide application of the thermal (AT) and thermal-derivative (ATD) analyses, results from their reliability, simplicity, relatively low costs of the needed equipment and short test time (~3.0min). More and more often, in order to



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achieve the total assessment of the cast iron quality, in parallel to the AT analysis the investigations of the contents are performed by means of spectrometry. Forecasting for the nearest future expects further propagation of AT and ATD in practice, which is confirmed in numerous publications [1,4,5,6,7,9,10,14,15,16]. Several systems of a complex cast iron assessment, such as NOVOCAST and ATAS, were developed on the AT bases. The control of the physical-chemical state of metal, when it is still liquid, and the introduction of corrections of this state done on the basis of AT results, allows to avoid several defects in castings. This concerns mainly such defects as PN -85/H-83105: hard spots (W-411), greyness (W-412), incomplete fillings (W-102), dressings (W-206), shrinkage cavities (W-403) [14,15]. The control of a preparation process of a liquid metal as well as the efficiency of its secondary metallurgy (inoculation, spheroidization, vermicularization) performed by AT and ATD methods are the efficient ways of controlling the process and avoiding/limiting several casting defects. It is assumed in the measuring procedure and interpretation of AT and ATD results, that the pathways of curves only depend on the chemical composition of cast iron and its physical-chemical state. According to the author of the hereby paper too small attention is focused on the dependence of the curve pathway (Fig.1) on the cast iron cooling rate in the place of measuring and recording the temperature. Placements of such characteristic points on the cooling curve as: Tliq, Tsol, TEmin, TEmax determined under conditions which differ from the equilibrium solidification are changing their locations. The general tendency is as follows: the higher cooling and solidification rates the lower values of these characteristic temperatures. It is interesting how the cooling rate and its fluctuations influence values of characteristic points on the AT curve for ingots, made in AT samplers. This decides upon the accuracy of measurements performed by means of these methods and upon the credibility of the cast iron quality assessment. The construction of modern temperature sensors (thermocouples and their miniature covers) allows very precise temperature measurements and their digital recording. Thus, this means that also temperature fluctuations, caused by changes of cooling rates, will be also recorded. These issues will be addressed in the hereby

2. Own investigations

2.1. The aim and methodology of investigations

Two aims were realised in investigations:

- 1- The determination of the influence of cooling rate of cast iron (of a near eutectic composition) on the placement of characteristic points on the cooling curve (Fig. 1).
- 2- The determination how much shapes and dimensions of AT samplers as well as their filling ratio with liquid metal (cast iron) influence the pathway of the cooling curve.

The chemical composition of the cast iron applied in investigations is listed in Table 1.

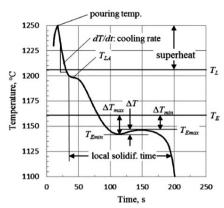


Fig. 1. The AT curve and its characteristic points utilised in the control of the casting process [8]

2.2. Influence of the cooling rate

In a majority of studies aimed at determining the influence of cooling and solidification rates of casting alloys on the structure and physical or mechanical properties the step-like sample is cast. The test casting is then shaped as the plate of a thickness - of individual segments - changing step by step. In this study, in continuation of the previous research of the author [9], different solutions are applied to achieve variable cooling rate in the test sample. The test sample of the shape of a rod is cast in sand mould, placed on a chill. The mould cavity reproducing the rod of a constant cross-section is opened on both sides. Its bottom surface is adhered to the chill, as shown in Fig. 2. The bottom/face surface of the metal poured into the mould is in a direct contact with a chill. At the selected distances from the face surface of the cooling test sample the thermocouples - with measuring points in the test sample axis - were placed. The test sample has a thickness of 30mm and a cross-section of a regular hexagon.





Fig. 2. Draft of the concept and the test sample cast on a chill: idea according to [9], b/cast iron sample

After pouring a mould the continued recording of the AT cooling curves starts. Pathways of temperature changes of cast iron (of a composition shown in Table 1) were recorded by means of the universal multichannel meter, Agilent type, Fig. 3.

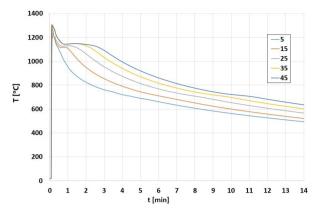


Fig. 3. Pathways of cooling (AT) of cast iron in the ingot placed on a chill at distances: 5; 15; 25; 35 and 45 mm

Table 1. Chemical composition of cast iron

С	Si	Mn	P	S	Cu	Cr	Sc
4,14	1,76	0,10	0,027	0,01	0,01	0,001	1,04

Results of the classic ATD analysis are presented in Fig. 4. As a distance from a chill increases the solidification time prolongs and values of a maximal under-cooling, at the final period of crystalizing, decrease.

The fuller picture of the kinetics of cooling and solidification processes can be obtained, when the temperature in the measuring point will be ascribed to the momentary cooling rate (ATD). Such dependence is shown in Fig. 5. It can be noticed, that an increase of cooling rates shifts characteristic points on the cooling curve (mainly $T_{\rm Emin}$, $T_{\rm Emax}$) to lower values. In addition, it narrows the temperature range of an eutectic transformation (Fig. 6).

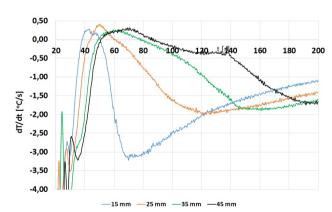


Fig. 4. Pathways of the cooling rates ATD of cast iron in the ingot on a chill

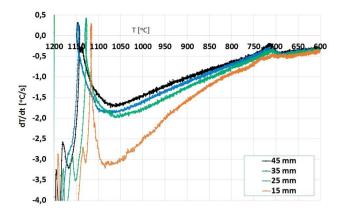


Fig. 5. Pathways of the cooling rates as a function of a momentary temperature of the ingot in the measuring point

This can be even more precisely analysed on the sector of the diagram from Fig 5, after narrowing axis x to the temperature range being near the eutectic transformation (Fig.6).

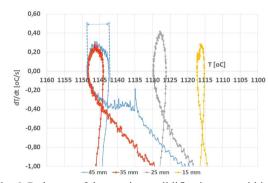


Fig. 6. Pathways of the cast iron solidification rate within the recalescence temperature range

It is difficult to define the velocity of the cast iron crystallization process, especially cast iron of a circum-eutectic composition, which is applied in the production of cast iron with a compact and nodular graphite. Since the range of changes between $T_{\rm liq}-T_{\rm sol}$ is small, the original crystallization does not decide on a rate understood as dT/dt. In addition, a solidification of the circum-eutectic cast iron has a volumetric character, which means that it is difficult to determine the moving rate of the crystallization front in the ingot. The growth rate of eutectic cells is the formal measure of the crystallization rate, but in the AT this indicator cannot be determined. As an apparent indicator of the crystallization rate the solidification time of the eutectic $(\tau_{\rm cut})$ in the selected place of the sample (casting) or the reversal of this time - $1/\tau_{\rm cut}$, can be used.

Solidification times of the eutectic in the performed tests were determined in accordance with figure 4. On the basis of the determined times and values of characteristic temperatures T_{Emin} and T_{Emax} the dependencies - presented in figures 7 and 8 - were

detected.

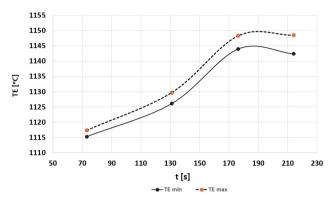


Fig. 7. Influence of the solidification time of circum-eutectic cast iron on values of characteristic temperatures TEmin and TEmax

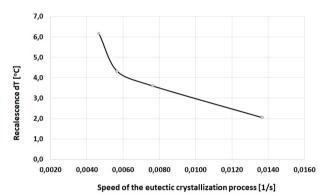


Fig. 8. Influence of the crystallization rate of circum-eutectic cast iron on the recalescence temperature range

Prolongation of the crystallization time from ~70 to 200s leads to increasing temperatures $T_{\rm Emin}$ from approximately 1115°C to ~ 1145, it means by 30°C. The value of the temperature $T_{\rm Emax}$ (Fig. 7) is the subject to a similar change. If it is assumed, that the described dependence, within the range of cooling/solidification times 70-180s, is of a linear character it can be stated that each 1 second change of cooling/solidification times causes the temperature $T_{\rm Emin}$ and $T_{\rm Emax}$ change by approximately $0.30^{\circ}C$. When the crystallization rate is characterised by the inverse of the time of transferring from a liquid to solid state $(1/\tau_{\rm cukt})$, the dependence presented in Fig. 8 will be obtained. The crystallization rate defined in such way influences the recalescence range of the eutectic transformation. Generally, the higher process rate the lower recalescence values.

2.3. Cast iron crystallization rate in AT samplers

Assessments of the cast iron quality by means of AT and ATD methods under industrial conditions, are usually performed using samplers produced by means of the hot-box technology. Measuring junction of the thermocouple is placed in a geometric centre of the sampler and this is the point, in which the temperature

is recorded. In a visual way, heat fluxes flowing from individual surfaces of a cooling sample are marked with arrows in Fig.9a. The largest flux is flowing from the upper uncovered surface, smaller fluxes from side walls, while the smallest one from the bottom of the sample. Thus, the heat centre of solidifying sample is admittedly in its geometric axis but below the half of the sampler cavity height. It means, that the heat centre of the cast iron sample and the point of temperature measuring are not situated in the same place.

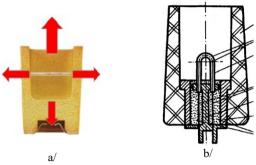


Fig. 9. Samplers for the thermal analysis (AT); a/ presently used [8], b/ previous version [11-13]

Such placement of the measuring point causes, that the test is sensitive to the sampler filling ratio with a liquid metal. When the sampler is not full, its upper, intensely cooling metal surface is approaching the measuring point AT, which causes changing of the crystallization rate in the measurement point. Previously [11-13] samplers shown in Fig. 9b, which had the measurement points situated significantly below the half of the sampler height, were popularly applied. Such samplers were less sensitive to the described effect of 'not total slash' of metal. In order to verify the thesis of an essential influence of the sampler filling ratio on pathways of AT curves and on T_{Emin}, T_{Emax}, values, several tests, in which the filling ratios with cast iron were intentionally changed, were performed.

The research set up of the AT, during tests with the controlled filling ratio of the sampler is presented in Fig. 10 Cuts made at the top of opposite walls in the sampler allowed to fill it with a liquid metal in: 70, 80 and 100 %. In samplers with cuts, the upper metal surface was moving closer to the measurement point and the geometric modulus of the ingot was changing within the range: M=0.52÷0.60cm. This test reproduced the situation, which would occur in practice when the AT sampler is not completely filled.





Fig. 10. a/ AT samplers filled to the height, h: 28.0, 34.0 and 40.0mm and with the geometric solidification modulus, M: 0.52, 0.56 and 0.60cm, b/ he stand of pouring AT samplers

Recorded pathways of AT curves are shown in Fig. 11. The solidification time recorded in subsequent samplers was changing, following the test sample modulus and stayed within the range of less than 200s.

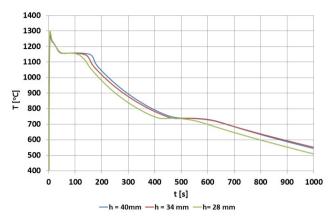


Fig. 11. Pathways of AT curves for test samplers of heights, h = 28; 34 and 40mm

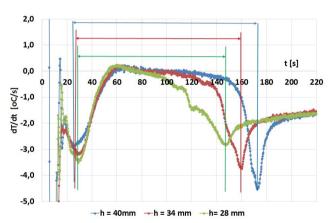


Fig. 12. Pathways of ATD curves obtained in samplers filled in various ratios, from 70 to 100%

Differences in pathways of cooling and solidification curves of cast iron are even more visible in classic ATD curves (Fig. 12). The new point of view of ATD curves, presented in figures 13 and 14, constitute the supplement of the previously shown AT and ATD curves. The analysis of these results (Fig. 13) confirms that the cast iron was cooled/solidified in subsequent samplers with different rates, which caused different cooling/solidification times. The ATD pathways presented as dT/dt = f(T) indicate that temperatures of individual points in the AT curve are also subjected to changes. The decrease of the solidification module (smaller filling of a sampler) causes an increase of the crystallization rate and shifting characteristic temperatures TEmin and TEmax in the direction of lower values. The temperature range of the eutectic solidification is also widening (Fig.14).

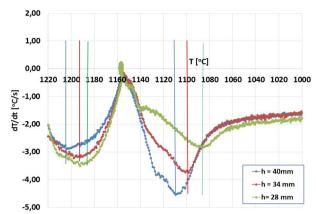


Fig. 13. Characteristic temperatures of the beginning and end of the graphite eutectic solidification in cubs filled in 70 - 100%

Characteristic temperatures from the recalescence range, $T_{E(min)}$ and $T_{E(max)}$, are also changing (Fig. 16). In a similar way as in the analysis of the whole range of the eutectic solidification, in the recalescence range a certain rule can be noticed: when the cooling rate is increasing (decreasing of the modulus) the temperature range of recalescence is widening. Differences are visible even when changes of the modulus are quite small, (M=0.60÷0.52cm). For M=0.60 the recalescence temperatures range ΔT_{recal} = 1156.1 ÷1158.2°C, while for M=0.52cm, ΔT_{recal} = 1155.5 ÷1158.2°C.

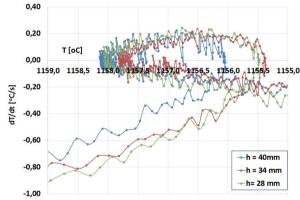


Fig. 14. Pathways of the recalescence temperature of cast iron in AT cups filled in different ratios: 70 - 100%

Shapes of AT samplers and their cavities are influenced by continues changes. Samplers, presently available in the market, are shown in Fig. 15. One of the samplers has a cavity of a square cross-section, while another one - of a circular cross-section. Temperature sensors (thermocouples) in both samplers are localised in the geometric axis at the half of the cavity height. Test samples obtained from the samplers have different solidification modulus, respectively: $M_{square} = 0.64 \text{cm}$, $M_{circle} = 0.60 \text{cm}$. They also differ in volume: $V_{square} = 56 \text{cm}^3$, $V_{circle} = 38.5 \text{cm}^3$.



Fig. 15. Presently used AT samplers for cast iron [6,7]

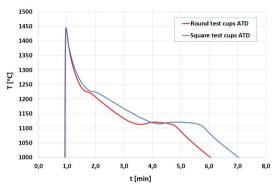


Fig. 16. AT curves recorded in samplers of a square and circular cross-sections

Pathways of cooling hypoeutectic cast iron in both samplers poured at the same temperature, were recorded. Pathways of the AT curves in a classic perspective: T = f(t) are shown in Fig.16, while pathways of the ADT curves in a new perspective: dT/dt = f(T) in Fig. 17.

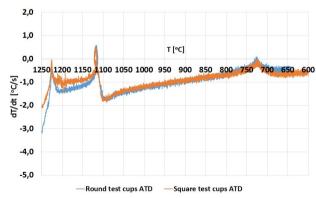


Fig. 17. Pathways of ATD curves of hypocutectic cast iron in samplers of square and circular cross-sections

It can be noticed in the analysis of AT and ATD curves recorded in samplers of square and circular cross-section, that the characteristic temperature values T_{Emin} and T_{Emax} differ by a few degrees. Ranges of the recalescence temperatures are also different (Fig. 18). In the circular sampler (smaller solidification modulus) the recalescence temperature range is wider. The recalescence range is used in assessments of the cast iron quality, more precisely: its ability of graphitization. The smaller this range -- the

higher ability of graphitization. Thus, by changing samplers a different quality assessment can be obtained.

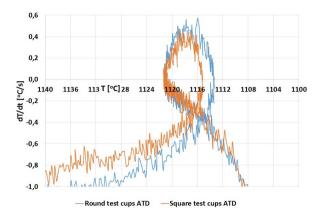


Fig. 18. Range of the recalescence temperatures of cast iron solidifying in cups of square and circular cross-sections

3. Discussions concerning investigation results

Analysis of investigation results of the crystallization process of the ingot placed on the chiller indicate, that shortening of its solidification process from approximately 200s to 70s causes (in accordance with Fig. 7) decreasing of values of characteristic temperatures of the eutectic transformation (T_{Emin},) by approximately 30°C from T_{Emin} = 1145°C to 1115°C. In a similar way values of T_{Emax} will change. Further prolongations of the solidification time is not causing essential changes of T_{Emin} and T_{Emax} (Fig.7). Within solidification times shortening/prolongation by 10s changes the analysed temperature by approximately 3°C. Within the range 70 – 180s of solidification times the recalescence range, in the 'point' of temperature measuring, changes ΔT_E from ~ 2.0 at the solidification time of 200s to over 4.0°C – at 70s (Fig. 8). In effect the change of T_{Emin}, and T_{Emax} by a couple of degrees occurs. This can be a reason of the erroneous assessment of the cast iron quality by the ITACA or ATAS systems. Every time the source of changes of characteristic temperatures on the AT curve constitutes the change of the cooling/solidifying rate.

4. Conclusions

Written below conclusions were drawn on the basis of analyses of the achieved results.

- The solidification time in the measuring point (τ_{cryst}) or its inverse 1/(τ_{cryst}) can be a good indicator of the cooling/solidification rate of cast iron in the thermal AT analysis.
- In standard AT samplers used for cast iron this time is wit hin: 180 – 200s, while the rate: 0.0055 – 0.0050 1/s.

- Decreasing of the solidification time (increased process speed) leads to a decrease of values of the characteristic AT points, including T_{Emin} and T_{Emax} - on the average - by 0.30°C for each second of the time shortening.
- A source of potential errors in industrial AT can constitute not complete filling of AT samplers or changes of their size or shape. Such changes lead to increase/decrease of the modulus of ingot solidification in a sampler and shortening/elongation of the solidification time. It can lead to obtaining erroneous pathways of AT and ATD curves and erroneous cast iron assessments.

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