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Influence of the Superheating Temperature of Metal Melts on their Supercooling before Crystallization

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This work is devoted to the study of the effect of overheating of metal melts on their supercooling before crystallization. Melting and crystallization are important technological processes for producing high-quality castings. The direct study of the processes involved in casting metals and their alloys is extremely difficult because they are opaque, take place at very high temperatures and sometimes occur in aggressive environments. In this regard, we have applied the physical modelling method to conduct these studies, using the low-temperature metal alloys Wood and Rose and the organic media diphenylamine and camphene as objects of study. To conduct the research, a special experimental setup was created and a physical modelling technique is developed. In the experiments, three prototypes of equal weight were prepared from each model alloy on an electronic balance with a weighing accuracy of 0.01 g. To ensure the absolute identity of the melting and crystallization conditions of the model alloys, all three test samples were simultaneously placed in a thermostatically controlled chamber. The samples are gradually heated to melt and superheat to a certain level. After the melt is held in the superheated state, it is cooled to the temperature of nucleation, which is recorded using thermocouples. The signal from the thermocouples is observed on the screen of the potentiometer in the form of absolute digital temperature values, and on the laptop screen in the form of temperature curves of cooling

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of the melts of the test media. The magnitude of melt supercooling, at which crystals nucleate, is determined by characteristic features on the cooling temperature curve of the model medium, *i.e.*, the appearance of boards on them due to the release of crystallization heat. In experiments on transparent organic media (camphene and diphenylamine), the accuracy of fixing the amount of supercooling in their melts using thermocouples is also controlled visually by observing the moment of crystal nucleation in them. As a result of the research, it is found that the effect of overheating on supercooling of the studied alloys is most likely due to a change in the concentration of limitedly soluble impurities. This assumption is based on the fact that the dissolution of impurities in the melt of any metal occurs as a result of diffusion, which is a relatively time-consuming process, and to obtain greater homogeneity of the metal melt, it is necessary either to increase the temperature of its overheating or to ensure its longer holding in the overheated state. The results of our research confirmed these assumptions. With an increase in the degree of dissolution of impurities, the supercooling of model melts changes, which is due to a change in the physical and chemical properties during the nucleation of crystals.

Key words: model alloys, metal melt, overheating temperature, supercooling, limited soluble impurities, crystal nucleation.

Робота присвячена вивченню впливу перегріву розтопів металів на їх переохолодження перед кристалізацією. Топлення та кристалізація — це важливі технологічні процеси для одержання якісних литих заготовок. Безпосереднє вивчення процесів, пов'язаних з розливкою металів та їх стопів надзвичайно ускладнене тим, що вони є непрозорими, протікають за дуже високих температур та іноді проходять в агресивному середовищі. У зв'язку з цим для проведення даних досліджень нами застосований метод фізичного моделювання, в яких як об'єкти вивчення, використані низькотемпературні металеві стопи Вуда та Розе та органічні середовища дифеніламін та камфен. Для проведення досліджень було створено спеціяльну експериментальну установку та розроблено методику фізичного моделювання. В експериментах з кожного модельного стопу на електронних вагах з точністю зважування 0,01 г готували по три дослідних зразка однакової маси. Для забезпечення абсолютної ідентичності умов топлення та кристалізації модельних стопів усі три дослідні зразки одночасно поміщали у камеру, що термостатується. Зразки поступово нагрівалися до розтоплення та перегріву до певного рівня. Після витримки розтопу в перегрітому стані його охолоджували до температури утворення зародків, яку фіксували за допомогою термопар. Сигнал від термопар спостерігали на екрані потенціометра у вигляді абсолютних цифрових значень температур, а на екрані ноутбука — у вигляді температурних кривих охолодження розтопів дослідних середовищ. Величину переохолодження розтопу, при якому у них відбувається зародження кристалів, визначали за характерними ознаками на температурній кривій охолодження модельного середовища — появі плат на них через виділення тепла кристалізації. В експериментах на прозорих органічних середовищах (камфен та дифеніламін) точність фіксації величини переохолодження в їх розтопах за допомогою термопар контролювали ще й візуально, спостерігаючи за моментом зародження кристалів у них. В результаті проведених досліджень встановлено, що вплив перегріву на переохолодження досліджених стопів, найімовірніше, обумовлений зміною концентрації обмежено розчинних домішок. Таке припущення ґрунтується на тому, що розчинення домішок у розтопі будь-якого металу відбувається внаслідок дифузії, що є відносно тривалим у часі процесом і для отримання більшої однорідності розтопу металу необхідно або підвищити температуру його перегріву, або забезпечити тривалішу його витримку в перегрітому стані. Результати проведених досліджень підтвердили ці припущення. Із підвищенням ступеня розчинення домішок змінюється переохолодження модельних розтопів, що обумовлено зміною фізико-хемічних властивостей при зародженні кристалів.

Ключові слова: модельні стопи, розтоп металу, температура перегріву, переохолодження, обмежено розчинні домішки, зародження кристалів.

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1. INTRODUCTION

The properties of the final metal product are mainly determined by the characteristics of the primary crystal structure of the billets at the stage of casting. And the structure and properties of cast metal are primarily determined by the conditions of the crystallization process, *i.e.* the rate of nucleation and growth of crystallization centres. Accordingly, in order to control the structure formation process of cast billets, it is necessary to be able to influence the nucleation and growth of crystals in solidifying metal melts. An important parameter that significantly affects the nucleation and growth of crystals and, accordingly, the structure of cast billets is the supercooling (Δt^{-}) of the metal melt before crystallization. Therefore, many studies have been devoted to the problem of crystal nucleation and growth, which confirm the importance of supercooling in crystallization processes and the general pattern of its gradual increase with increasing degree (temperature) of overheating (Δt^{+}) of the melt with gradual reaching a plateau (saturation) [1–6].

Despite a large number of researches on this problem, there are various theories explaining the dependence of melt supercooling on overheating, which can be divided into surface and bulk crystallization theories. In the first case, it is believed that crystallization begins on the surface between the melt and the crucible (or oxide film) and that overheating affects the state of this surface (it is assumed that the solid metal remains in the pores of the crucible or in the pores of the oxide film when overheated to a certain critical temperature) [7–9]. The theory of bulk crystallization assumes the existence of microgroups of atoms (clusters) in the melt, which are preserved at a slight overheating of the melt above the liquidus and serve as nuclei during crystalliza-

TABLE 1. Properties of modelling environments.

Properties \ Environment	Wood alloy	Rose alloy	Camphene	Diphenylamine
Density, kg/m^3	9720	7600	845	1200
Liquidus temperature, °C	68	94	45	53
Solidus temperature, °C	68	94	42	53
Crystallization interval, °C	0	0	3	0

tion, but are destroyed at higher overheats [2, 10, 11]. However, both theories have been only partially confirmed experimentally in experiments with pure metals.

In our opinion, the contradictory nature of the known results is due to the different content of soluble impurities in the studied metals, changes in their concentration during melting, and, accordingly, the instability of the microscopic state of melts in the superheated state. In addition, this is due to the lack of reliable methods for determining the moment of crystal nucleation in metal melts, especially in metals with a low impurity content, in which crystal nucleation occurs at high supersaturations (supercoolings). Therefore, this work was aimed at, first, developing a reliable methodology for fixing the moment of crystal nucleation in metal melts and, second, studying the dependence of supercooling of the experimental alloys on their melting (*i.e.*, superheating temperature and holding time in the superheated state) and solidification modes.

2. MATERIALS AND METHODOLOGY

To create new and improve existing metallurgical technologies related to the casting of metals and their alloys, it is necessary to study processes that operate at very high temperatures, are opaque and sometimes take place in aggressive environments. Direct study of such processes is extremely difficult. To solve this problem, indirect methods of study in the laboratory are widely used, in particular, the method of physical modelling of natural objects on low-temperature alloys [12–14]. In conducting these studies, the method of physical modelling was also applied, and low-temperature metal alloys and organic media were used as objects for study. These materials were chosen based on the following considerations: the nature of crystallization is similar to metals and alloys with a high melting point; transparency (for organic media) provides visualization of the processes under study; melting point not exceeding 100°C provides convenience of experiments, *etc.* Taking into account the above requirements, the following materials were used as objects for study: low-temperature metal alloys Wood (12.5% tin, 25% lead, 50% bismuth, 12.5% cadmium) and Rose (25% tin, 25% lead, 50% cadmium) and transparent organic substances diphenylamine ($C_{12}H_{11}N$) and camphene ($C_{10}H_{16}$) (Table 1).

In this work, we investigated the effect of the melt superheat temperature of the experimental alloys on its supercooling, at which crystal nucleation occurs. To conduct the research, a physical modelling technique was developed and a special experimental setup was created (Fig. 1).

The research was carried out according to the following procedure. At the beginning of the experiments, three test samples of the same mass were prepared from each model alloy on an electronic balance (with a weighing accuracy of 0.01 g.) in quartz tubes with a diameter of 5 mm. To ensure the absolute identity of the melting and crystallization conditions of the model alloys, all three test tubes with the test samples *1* were simultaneously placed in a chamber *3* using a special mount (cassette) *2*, into which a transparent coolant (water) was supplied from a thermostat *4* by a circulating pump. The temperature in the chamber was gradually increased at a given rate to a certain level in order to melt and superheat the model alloy. After appropriate exposure of the melt in the superheated state, it was cooled at a certain rate by cooling the coolant in the thermostat *3*. To record the temperature of nucleation, thermocouples 5 were lowered into test tubes *1* with test samples, the signal from which, in the form of absolute temperature values in digits, was observed on the screen of a digital potentiometer *6*

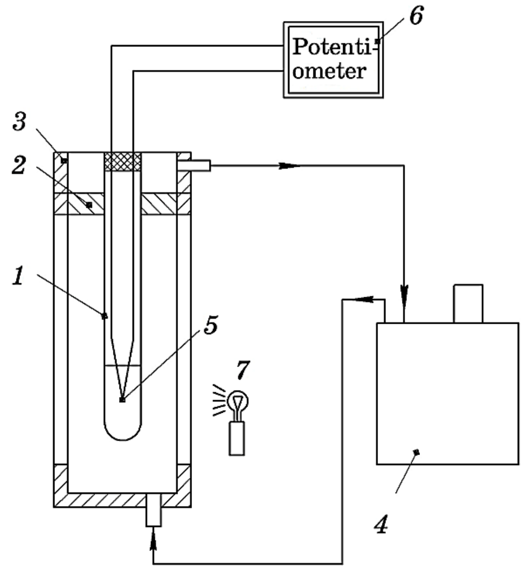

Fig. 1. General scheme of the experimental setup.

and stored on a memory card. From the memory card, these digital temperature values were converted into temperature curves for cooling the melts of the test media using a laptop in a special program. Characteristic features on the cooling temperature curve of the model medium (*i.e.*, when boards appear on it due to the release of crystallization heat) determined the amount of melt supercooling at which crystals are formed. In the experiments with a transparent model medium (diphenylamine, camphene), the nucleation of crystals was also observed visually through the transparent faces of the chamber. To improve the observation of the crystallization processes through the transparent faces of the chamber *3*, the chamber was illuminated with a lamp *7*.

3. RESULTS AND DISCUSSION

Initially, when developing the methodology, it was found that the range of supercooling (Δt^{-}) for the experimental metal alloys (Wood, Rose), ceteris paribus, was equal to ± 1°C. The range of supercooling (Δt^{-}) for organic media (diphenylamine, camphene) depended on their moisture saturation (they are hygroscopic substances) and, depending on the degree of their saturation, could differ from each other up to 5 times (Fig. 2, curves *1*, *3*). Therefore, the experimental samples from organic media were subjected to preliminary heat treatment at a temperature of 95°C for 60 minutes, after which they were tightly closed with a cork to prevent contact with the atmosphere. After the heat treatment, the scatter of supercooling (Δt^{-}) of the test samples from these media did not exceed ± 3°C (Fig. 2, curves *2*, *4*).

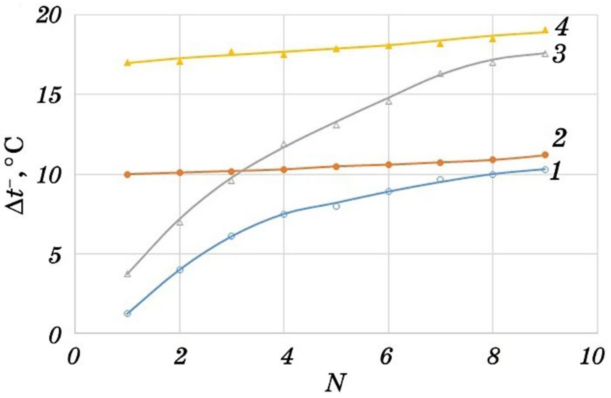

Fig. 2. Dependence of supercooling of camphene (*1*, *2*) and diphenylamine (*3*, *4*) alloys on the number of repeated tests of samples with a volume of $12\cdot10^{-6}$ m^3 at overheating $\Delta t^{+} = 10$°C: *1*, *3* without heat treatment; *2*, *4*—with heat treatment at 95°C for 60 min.

In the course of further studies, classical curves were obtained for all model media, confirming the dependence of supercooling before crystallization (Δt^{-}) on the magnitude of overheating of their melts (Δt^{+}) (Fig. 3). This pattern is explained in the literature by the deactivation of solid substrates and the melting of the crystalline phase in micropores on their surfaces [1]. However, we have previously obtained results in other experimental environments that show that the effect of melt overheating on its supercooling can be caused by a change in the concentration of limitedly soluble impurities [15]. In work [15], we saturated the salol melt with water vapor, as a result of which, during the first crystallization, its supercooling, ceteris paribus, was 6–7 times less than for an unsaturated melt. With an increase in the superheating temperature of the moisture-saturated melt of lard, its supercooling increased. Such an effect of the superheating temperature on the supercooling of the saturated with water vapor melt of the lard is most logically explained by a change in the concentration of a soluble impurity (water) in it. It is obvious that the solubility of water in the lard melt increases with increasing temperature, which results in changes in its physicochemical properties [15].

These researches on other model alloys (camphene, diphenylamine, Wood and Rose alloys) confirmed the results of our previous researches on salol and gallium. In addition, new data were obtained for all of the experimental alloys, confirming our hypothesis about the crucial role of limitedly soluble impurities in the dependence of the supercooling of metals before crystallization on the superheat temperature of their melts.

Let us consider the results obtained for the example of Wood and camphene alloys. Thus, Figure 4 shows the dependence of supercooling

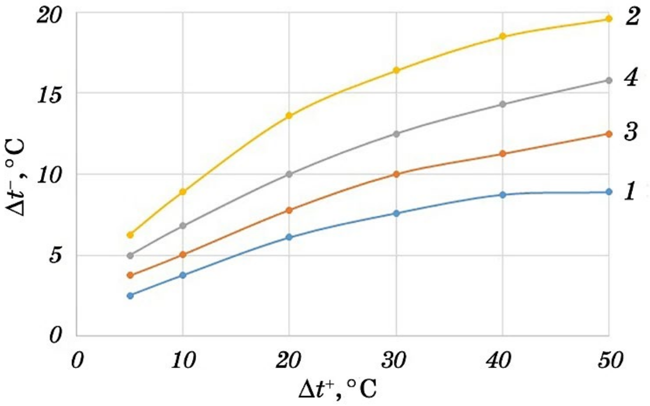

Fig. 3. Dependence of supercooling of samples from the studied model alloys with a volume of $12\cdot10^{-6}$ m^3 on the overheating temperature for 2 min: Rose alloy (*1*); Wood alloy (*2*); camphene (*3*); diphenylamine (*4*).

(Δt^-) of Wood alloy on the volume of test samples for two superheat temperatures $\Delta t^+ = 10$°C (curve *1*) and $\Delta t^+ = 25$°C (curve *3*) with holding in the superheated state for 2 minutes under other identical experimental conditions. Curve *2* in Fig. 4 is based on the test data of samples obtained by combining two identical alloy samples that were overheated by 10°C and 25°C, respectively. Before combining, the temperature of the 25°C sample was slowly lowered to the overheating temperature of the other sample (*i.e.*, $\Delta t^+ = 10$°C). Then the samples were combined into one tube (shown by arrows in Fig. 4) and the amount of supercooling (t^-) of the new sample obtained by mixing them was determined. As a result of the research, it was recorded that the supercooling for the new sample (Fig. 4, curve *2*) was higher than the supercooling of sample 1 (Fig. 4, curve *1*), which was overheated by $\Delta t^+ = 10$°C.

In our opinion, the experiments with the combination of two identical samples superheated to different temperatures convincingly demonstrate that the change in their supercooling is not due to the deactivation of mechanical impurities. It would seem that no matter how much volume was added to the sample that produced a lower supercooling, the activity of the mechanical impurities or the crystals remaining in the pores on them should not have changed. However, more supercooling was required for the crystallization of all new samples (combined). This indicates that overheating changes the amount of supercooling of Wood alloy precisely due to changes in the concentration of limitedly soluble impurities.

In this case, the amount of supercooling should depend on the heating rate of the test sample, since it takes time for the concentration of soluble impurities to equalize throughout its volume by diffusion. The

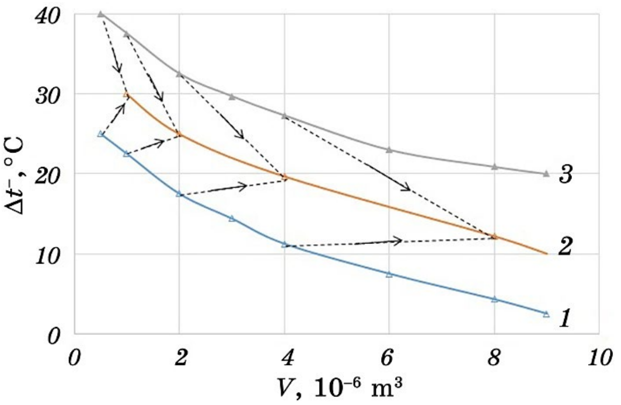

Fig. 4. Dependence of Wood alloy supercooling on the volume of the test sample: with overheating $\Delta t^+ = 10$°C (*1*); $\Delta t^+ = 25$°C (*3*); samples obtained by combining the corresponding samples of curves *1* and *2* (*2*).

corresponding experiment for all the test alloys confirmed that their supercooling significantly depends on the heating rate, ceteris paribus. Figure 5 shows the curves of dependence of Wood alloy supercooling on its heating rate and holding time in the superheated state. We can see that with an increase in the heating rate of Wood alloy from 2°C/min to 44°C/min with a short holding time in the overheated state ($\tau \leq 1$ min.), its supercooling decreases by more than 3 times. This result, in our opinion, is explained by the different degree of dissolution of the same impurities in the melt of this alloy. The dissolution of impurities in the melt of any metal occurs as a result of diffusion, which is a relatively long process in time. To ensure the homogeneity of the metal melt, it is necessary to ensure that it is held in an overheated state for a longer period of time. Indeed, a significant increase in the holding time of the Wood alloy melt in an overheated state ($\tau \geq 50$ min) has levelled this dependence.

In the next experiment, quartz powder (particle diameter 0.2 mm) was added to the camphene melt with a volume of $2\cdot10^{-6}$ m^3 in a 1:1 ratio. The purpose of this study was, firstly, to determine their effect on the diffusion of soluble impurities, and, secondly, to introduce additional crystallization centres (each powder particle should theoretically be a potential nucleus in the melt). To activate the quartz powder particles, several recrystallizations of the prototypes were performed. It was assumed that the effect of overheating on the melt supercooling was due to the influence of mechanical impurities, and that after activation of the quartz particles that had been in the solidified camphene, the supercooling should have decreased. But this did not happen in any of the repeated experiments.

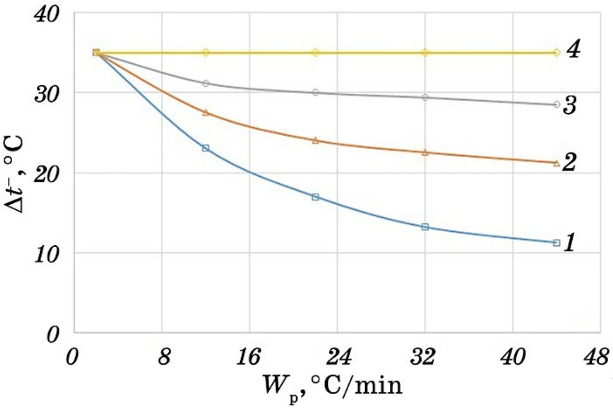

Fig. 5. Influence of the heating rate of a prototype sample of Wood alloy with a volume of $2\cdot10^{-6}$ m^3 on its supercooling: $\tau = 1$ min (*1*); $\tau = 20$ min (*2*); $\tau = 40$ min (*3*); $\tau = 50$ min (*4*).

The presence of quartz particles in the test sample of camphene led to an increase in the dependence of its supercooling on the holding time in the superheated state, in contrast to the control samples (Fig. 6). We can see that at low values of the holding time of the camphene melt in the superheated state ($\tau \leq 3$ min), its supercooling is less than for the control sample. At higher values of the holding time ($\tau \geq 3$ min), on the contrary, the supercooling of the powdered camphene is greater than for the control sample.

The obtained character of the supercooling curves in this figure, in our opinion, is due to the fact that in samples of camphene with quartz powder, the diffusion of soluble impurities is hampered both during heating and when the temperature decreases. That is, at low values of the holding time of camphene with powder in an overheated state ($\tau \leq 3$ min), impurities do not have time to completely dissolve (diffuse) in its melt and, accordingly, it crystallizes at a lower supercooling than the control sample. At high values of the holding time of camphene with powder ($\tau \geq 3$ min), impurities are completely dissolved in the melt, so their 'reverse diffusion' requires more time, during which its supercooling increases.

These results convincingly prove the decisive influence of soluble impurities on the dependence of supercooling of the studied model alloys on the superheat temperature of their melts. In general, the interest in this problem is due to the fact that the degree of supercooling of the metal melt (Δt^-) before crystallization affects the crystallization rate and the dispersion of the crystal structure of the cast metal [16]. The crystallization of metals is known to occur by the mechanism of normal crystal growth, in which the rate of crystal growth (R) is directly proportional to the supercooling of the melt (Δt^-) at the interface [16]:

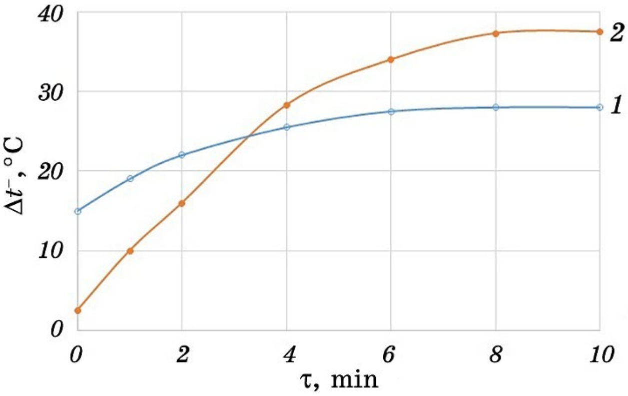

Fig. 6. Dependence of supercooling of a $2 \cdot 10^{-6}$ m^3 camphene sample on the time of holding its melt in an overheated state: control sample (*1*); sample with quartz powder (*2*).

Fig. 7. The macrostructure of camphene depending on the supercooling at which it crystallizes: $\Delta t^- = 2°C$ (*a*); $\Delta t^- = 12°C$ (*b*); $\Delta t^- = 36°C$ (*c*).

$$R = k \cdot \Delta t^-, \tag{1}$$

where k is the kinetic coefficient, which for metals has a value in the range of (1–40) m/s°C.

The effect of supercooling on the dispersion of the cast structure can be clearly seen on the example of crystallization of the model medium of camphene (Fig. 7), for which the size of the macro-grain of the ingot decreases significantly with increasing supercooling.

4. CONCLUSION

An original method of physical modelling was developed to study the effect of overheating of experimental alloy melts on their supercooling before crystallization, which allowed us to reliably record the moments of crystal nucleation in them. Using metal alloys (Wood and Rose) and organic media (diphenylamine and camphene), it was found that the effect of the melting superheat temperature on the degree of their supercooling before crystallization is due to the temperature dependence of the concentration of limitedly soluble impurities present in them.

It has been shown that by changing such parameters of melting and casting of metal alloys as superheat temperature, holding time in the superheated state, heating and cooling rates, *etc.*, it is possible to control the degree of supercooling of metal melts before their crystallization, and, accordingly, to influence the dispersion of the structures of cast billets (*i.e.*, the physical and mechanical properties of the cast metal).

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