The role of interfacial energies in the crystallisation of graphite in cast iron

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SYNOPSIS

The mechanism of nodular crystallisation of graphite in the production of spheroidal cast iron is not fully understood. The work reported in this paper confirms that in cast iron melts having a high interfacial tension against the environmental atmosphere, the graphite tends to crystallise in nodules during solidification. The influence of interfacial tension between melt and solid graphite is similar.

SINOPSIS

Die kristallisasie meganisme van knolvormige grafiet gedurende die produksie van sferoidale gegote yster word nie tenvolle begryp nie. Die werk wat in hierdie skrif behandel word, bewys dat grafiet die neiging toon om uit te kristalliseer in knolle gedurende die stollings proses van gesmelte gegote yster wat 'n hoë interfase spanning toon in vergelyking met die omgewings atmosfeer. Die invloed van interfase spanning op solide grafiet in gesmelte metaal is soortgelyks.

INTRODUCTION

The mechanism of nodular crystallisation of graphite in the production of spheroidal graphite cast iron is still not completely understood. In several recent attempts to explain the development of graphite spherulites, the opinion has been expressed that high surface tension of the cast iron initiates the spheroidal graphite crystallisation. In the present paper an attempt is made to relate surface or interfacial tension of liquid cast iron samples with the shape of the graphite crystals obtained after solidification. A critical review of the theories of the nodular graphite crystallisation previously propounded is given, experimental techniques are described and the results of some research on the subject obtained in the Metal Mechanics Division of the CSIR's National Mechanical Engineering Research Institute, are compared with the findings of other research workers.

THEORIES OF NODULAR GRAPHITE CRYSTALLISATION

Gas pore theory

Some authors[1,2,3,4] favour the hypothesis that graphite spherulites develop at an interface between a gas pore and the surrounding melt. This hypothesis proposes that graphite in cast iron can crystallise only in the presence of gas-liquid or gas-solid interfaces. Thus graphite starts to solidify on the surface of gas bubbles, the bubble surfaces becoming partially or entirely covered with a thin film of graphite. When, for some reason, the gas pressure inside the bubbles decreases due, for example, to gas absorption, the bubbles collapse. The graphite covering the surfaces of the bubbles then remains in the cast iron in the form of lamellae. If, on the other hand, the pressure is maintained for a sufficient long interval during solidification and if the melt contains sufficient carbon, the graphite fills the entire bubble and forms a sphere. Carbon deficiency results in hollow spheres which have occasionally[4,5,6] been found in nodular cast iron.

It has been suggested that evaporating nodulising elements (e.g. Mg, Ce, Ca) provide the gas voids in which the graphite starts to grow as indicated in Fig. 1.

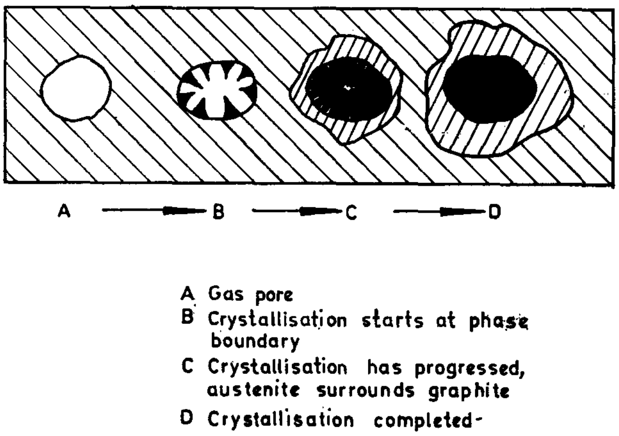

Fig. 1—Development of a graphite spheriod in a gas pore

Gas for formation of pores is present in large quantities in cast iron melts after the nodulising treatment. Most of the elements which modify the graphite to spherulitic shape have, in the range of the treatment temperatures, a vapour pressure exceeding atmospheric pressure, and therefore, under normal pressure conditions, are in their gas phase.

One of the shortcomings of the 'gas pore theory' is that it does not explain why only gases of specific (namely nodulising) elements cause the graphite to crystallise in the form of spheres. It is impossible to nodulise a melt just by passing any gas through it.

Another argument against this theory stems from the nodulising treatment of cast iron melts under high pressure. In this process a high environmental pressure suppresses the evaporation of nodulising elements in order to improve their recovery. The graphite obtained after this treatment is completely nodular in spite of the absence or at least reduction of gas voids

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*Mechanical Engineering Division Council for Scientific and Industrial Research in the melt as compared with melts treated under normal atmospheric pressure.

Nucleation theory

Foreign nuclei predetermine, according to De Sy and Colette[7,8], the shape of the graphite crystals in cast iron. Nuclei having a hexagonal lattice, for example SiO_2, SiC and FeS, cause the development of lamellar graphite and nuclei having a cubic lattice, for example MgO, MgS and Ce_2O_3, cause the development of nodular graphite. Lyubchenko[9] and Rosenstiel[10] have found a high concentration of the nodulising elements in the centre of graphite spherulites as shown in Fig. 2.

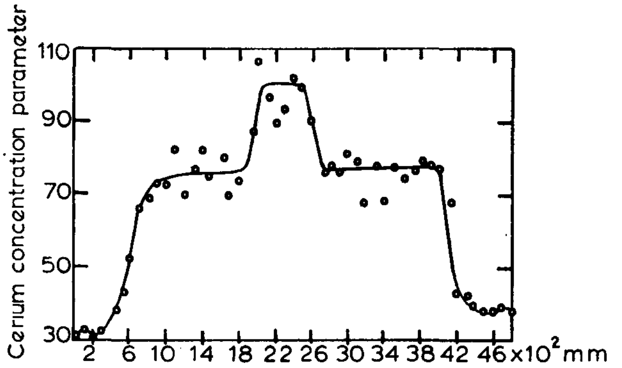

Fig. 2—Distribution of cerium across a graphite spheriod (According Lyubchenko)

Views on the distribution of nodulising elements in spherulites differ and are sometimes even in complete disagreement. Some authors[11,12] have found that nodulising elements are not found in high concentrations in graphite spherulites.

Fischer and Leis[13] obtained spherulitic graphite without the addition of nodulising agents by melting cast iron in crystallised lime crucibles. The presence of nodulising elements in the centres of spheroids was not checked in their investigations, but since no nodulisers were added to the melt, it is highly improbable that the spherulites contained nodulising nuclei.

Crystal Lattice growth theory

In normal grey cast iron the crystallisation of graphite progresses mainly by the growth of basal lattice planes. The crystallisation of nodular graphite can only progress by the development of new basal lattice planes. It has been suggested that spheroidising additions inhibit the growth of already present basal planes of the graphite crystal lattice and facilitate the development of new basal planes.

Because it is possible, however, to obtain graphite nodules without nodulising additions only by the application of certain melting or heat treatment procedures, the habitus change of graphite from lamellar to nodular is also not satisfactorily explained by this theory.

Surface tension theory

Frequently the modification of graphite habitus from lamellar to spherulitic is explained in terms of increase in surface tension of the cast iron melt. The surface tension theory has been favoured by several authors. Their publications are reviewed by Wastschenko and Sofroni[14].

The difficulty of the practical measurement of surface tension of cast iron melts causes quantitative differences in the results of the various authors, although qualitatively there is agreement. The surface tension theory in fact gives the best explanation of spherulitic graphite crystallisation and will therefore be discussed in more detail.

INFLUENCE OF SURFACE TENSION ON GRAPHITE CRYSTALLISATION

Basic considerations

The metal atoms on the surface of liquid cast iron have fewer neighbouring atoms as compared to atoms in the centre. This causes unbalanced attraction forces directed to the centre of the melt. The result is the surface tension. It forces the melt to assume the smallest possible outside surface. Gravitation, friction and other influencing factors act against the surface tension in its tendency to reduce the outside surface of liquid cast iron.

Additions of foreign elements usually decrease the surface tension of liquid cast iron. Additions of nodulising elements increase the surface tension of cast iron considerably. A possible explanation for this unusual reaction is that the nodulising elements bind other elements normally present in cast iron, e.g. sulphur or phosphorus both of which lower the surface tension of cast iron. The two elements mentioned are also known to inhibit the growth of nodular graphite and their absence in cast iron has been found to cause graphite to crystallise in the form of nodules without any nodulising additions[13].

An increase of surface tension of a cast iron melt could be considered as an indication for the absence or a reduced content of elements inhibiting the nodular crystallisation of nodular graphite.

Experiments

In order to determine the relationship between surface tension of cast iron melts and the form of graphite (whether flakes or nodules) in solidified cast iron, measurements of interfacial tensions and metallographic examinations of differently treated cast iron samples were carried out as described below.

The surface tension, i.e. interfacial tension between melt and environmental atmosphere, σ_{lg}, was determined by means of the so-called oscillating stream method[15]. In this method cast iron melt is forced through an elliptical nozzle. After leaving the nozzle, the surface tension of the liquid metal tends to reduce the surface area of the stream to a minimum and forces it to assume a circular cross-section. Inertia forces the liquid metal to assume an elliptical shape again. This cycle is repeated resulting in an oscillation in the metal stream. Viewed from the side, the edges of the metal stream have a wave form as shown in Fig. 3. The distance between adjacent peaks or valleys give the wave length λ of one complete oscillation.

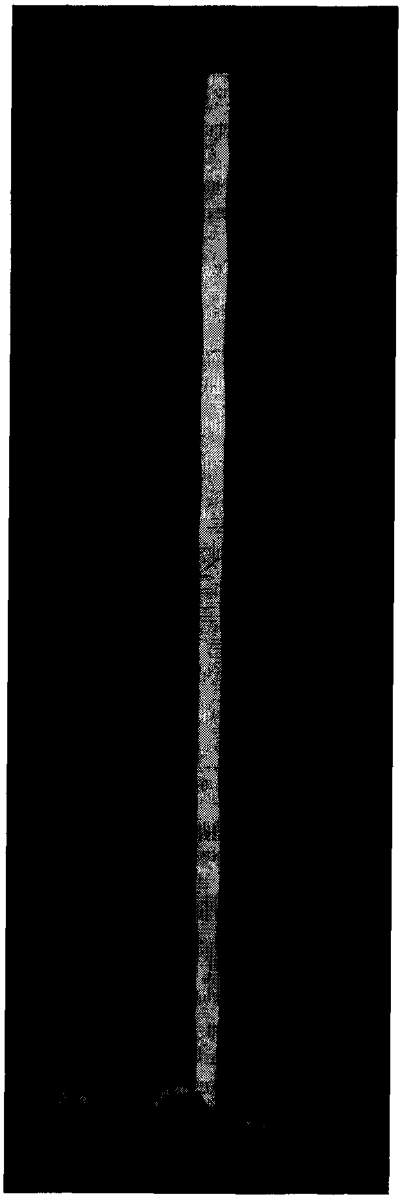

Fig. 3—Oscillating stream of liquid cast iron

The interfacial tension σ_{lg} can then be calculated using the equation:

$$\sigma_{lg} = \frac{2\pi^2 . a^3 . \rho}{3\tau^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 1$$

where

σ_{lg} = interfacial tension between the liquid iron and the atmosphere (N/m)

a = median radius of the nozzle forming the elliptic stream (m)

ρ = density of the liquid cast iron (kg/m³)

τ = period of oscillation (sec)

The period of oscillation τ can be determined from

$\tau = \lambda / c$

where

λ = wave length (m)

c = flow speed (m/s)

Cast iron melts produced from a pig iron having the composition given in Table I with Mg contents ranging from less than 0,002 to 0,06 per cent were investigated.

TABLE I

COMPOSITION OF PIG IRON USED IN THE INVESTIGATION

C	Si	Mn	P	S
4,03	1,69	0,35	0,028	0,014

After the surface tension measurement, the melts were cast into cylindrical specimens of different diameters ranging from 10 to 60 mm. The relation between number of nodules and lamellae in the cast specimen was determined. The interfacial tensions and the percentage of nodules versus the residual magnesium contents are plotted in the graph in Fig. 4 from which it can be seen that the maximum nodule count occurs at the maximum interfacial tension σ_{lg}. The maxima of nodule count and interfacial tension do not coincide with the maximum residual magnesium content.

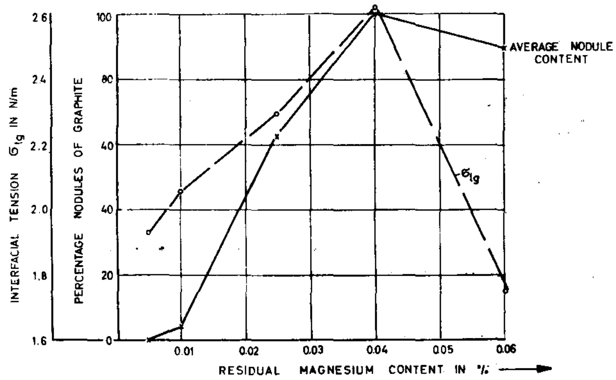

Fig. 4—Interfacial tension σ_{lg} of liquid cast iron and graphite shape versus residual magnesium content

The experimental results represented in Fig. 4 show clearly that a higher interfacial tension σ_{lg} between melt and environmental atmosphere is associated with nodular graphite in the solidified cast iron and lower interfacial tensions σ_{lg} result completely or partly in lamellar graphite crystallisation. But because graphite spherulites crystallise directly from the melt[16], it can be assumed that the interfacial tension σ_{sl} between liquid iron and solid graphite crystals has an even more significant influence on the development of nodules than the interfacial tension σ_{lg}, between melt and atmosphere.

INFLUENCE OF INTERFACIAL TENSION BETWEEN MELT AND GRAPHITE ON GRAPHITE CRYSTALLISATION

Basic considerations

During solidification of a graphite crystal from a cast iron melt, part of the latent energy of the melt is released as free energy H, of which—in turn—part is converted into new forms of latent energy, namely the interfacial energy $A.\sigma_{sl}$ to develop the interface between the solid graphite crystal and the surrounding melt, and if the graphite crystal consists of a number of crystallites, the interfacial energy $\Sigma a\sigma_{ss}$ to develop the interfaces between individual crystallites. The balance of the free energy is emitted from the system as kinetic energy (heat) E, thus

$$H = A.\sigma_{sl} + \Sigma a\sigma_{ss} + E \quad \ldots\ldots\ldots\ 2$$

where

H = free energy (J)
A = surface area of graphite crystal (m^2)
σ_{sl} = specific interfacial tension between graphite and melt (N/m)
Σa = surface area between individual crystallites inside the graphite crystal (m^2)
σ_{ss} = specific interfacial tension between individual crystallites (N/m)
E = energy emitted from the system (J)

Graphite in solidifying cast iron crystallises either in the form of flakes or in the form of nodules. Obviously, the amount of energy E released differs for both crystallisation processes and according to fundamental knowledge that form of crystallisation will develop in a given melt which releases the greater amount of energy E. This may be explained in more detail as follows:

Graphite flakes may be considered as single crystals (see Fig. 5a). The surface area Σa_F between individual crystallites in a graphite flake is therefore so small that the interfacial energy $\Sigma a_F.\sigma_{ss}$ may be neglected. Thus the energy released in flake forming, E_F, may be expressed as:

$$E_F = H - A_F \,.\, \sigma_{sl} \quad \ldots\ldots\ldots\ldots\ 3$$

A graphite nodule consists of a large number of crystallites in which the basal lattice planes are oriented normal to the radius of the nodule as depicted in Fig. 5b. Thus, the surface area Σa_N between individual crystallites may not be neglected as in the case of flakes. Thus,

$$E_N = H - A_N \,.\, \sigma_{sl} - \Sigma a_N \,.\, \sigma_{ss} \quad \ldots\ldots\ldots\ 4$$

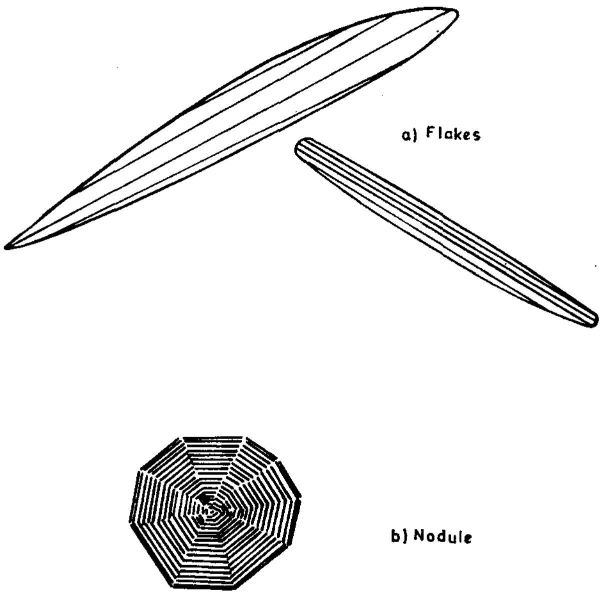

Fig. 5—Cross sections of graphite crystals (Schematic) the straight lines represent basal lattice planes

Fig. 6 shows the energies released in flake forming (E_F) as well as in nodule forming (E_N) versus the interfacial tension σ_{sl}. It will be noted from this figure that at low interfacial tension E_F is greater than E_N, thus flakes are formed. For greater values of interfacial tension E_N is greater than E_F and nodules are formed. As can be seen in Fig. 6, there exists a critical interfacial tension $\sigma_{sl_{crit}}$, which is a transition point at which flakes as well as nodules could develop, because at this point $E_F = E_N$.

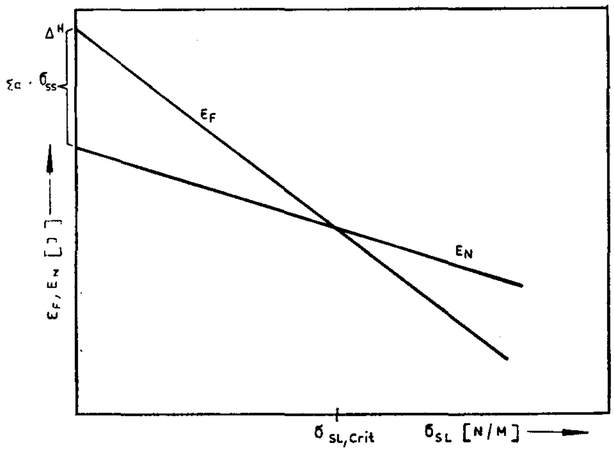

Fig. 6—Free energy of solidifying flake (*E*) and nodular graphite (*E*) versus interfacial tension (Schematic)

The reason for this behaviour is obvious from a comparison of equations 3 and 4 which shows that in the one case $\Sigma a\sigma_{ss}$ is neglected and in the other not. The E_N curve therefore crosses the ordinate of the graph in Fig. 6 ($\sigma_{sl}=0$) lower than the E_F curve.

The surface areas A_F and A_N determine the slopes of the curves obtained from equations 3 and 4. The surface area A_F of a flake is greater than that of a nodule A_N of equal volume and, accordingly, the slope of the E_F curve in Fig. 6 is steeper than that of the E_N curve.

Different values for the critical interfacial tension $\sigma_{sl_{crit}}$ were found by different authors. According to Marincek[17] values between 0,8 and 1,1 N/m are associated with lamellar graphite and values greater than 1,4 N/m with spheres, while Wassiljew and Barsilowitsch, according to Geilenberg[18], found a value of 0,9 N/m for the critical interfacial tension.

Experiments

In Fig. 6 a possible relationship between σ_{sl} and the resulting graphite shape has been shown. In order to prove the hypothesis represented by Fig. 6, the interfacial tensions between graphite and liquid samples of flake and nodular cast iron were measured. The oscillating metal stream method is unsuitable for the determination of the interfacial tension σ_{sl} between liquid melt and solid graphite. An alternative method the so-called sessile drop method, was used for subsequent measurements described below. In this method interfacial tensions are calculated from the shape of a drop of liquid iron resting on a substrate consisting of the material against which the interfacial tension is required as shown in Fig. 7.

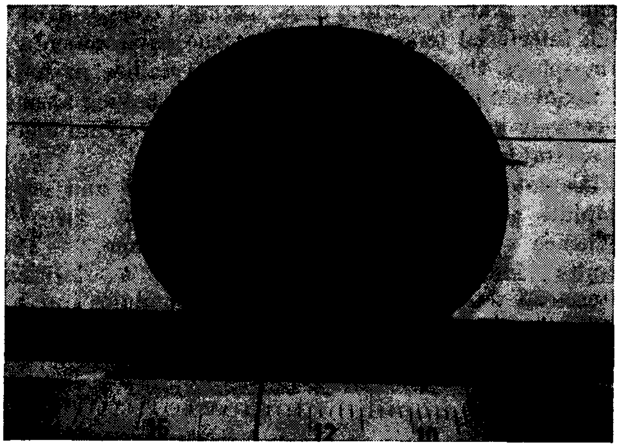

Fig. 7—Droplet of liquid cast iron on solid substrate

This method is based on the following considerations: For a drop of liquid resting on a solid plane (substrate) in a gas atmosphere the three interfacial energies between the three substances (liquid, solid and gas) as illustrated in Fig. 8, are related to each other by Youngs' equation. The three components of surface tension are in balance:

$$\sigma_{sg} - \sigma_{sl} = \sigma_{lg} \, . \cos\phi \qquad \ldots\ldots\ldots\ldots 5$$

where

σ_{sg} = interfacial tension between solid substrate and gas
σ_{sl} = interfacial tension between liquid and solid substrate
σ_{lg} = interfacial tension between liquid and gas
ϕ = angle of contact

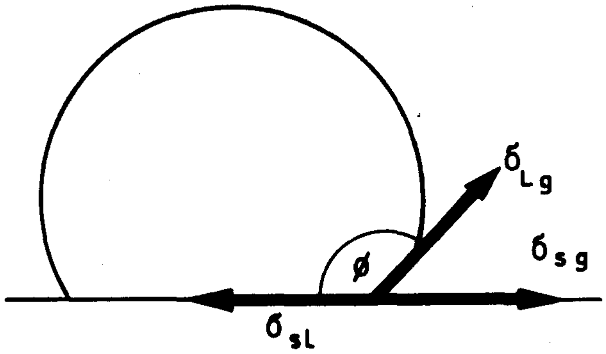

Fig. 8—Sectioned cast iron drop on solid substrate

The measurement of the interfacial energy between substrate and gas atmosphere, σ_{sg}, poses experimental difficulties. This parameter can, however, be considered to be constant for any solid material in contact with a specified gas atmosphere at a specified temperature, provided that there is no reaction between the two.

For the determination of the interfacial tension σ_{lg}, tables given by Bashforth and Adams[19] were used. For droplets having contact angles greater than 90° the following equation applies:

$$\sigma_{lg} = \frac{g \, . \, \rho \, . \, b^2}{\beta \, . \, 10^6} \qquad \ldots\ldots\ldots\ldots 6$$

where

σ_{lg} = interfacial tension between liquid and gas (N/m)
g = acceleration due to gravity (9,81 m/sec^2)
ρ = density of the iron (6,9 . 10^3 kg/m^3)[20]
b = intermediate value from Table I in reference 19 (m)
β = intermediate value from Table II in reference 19

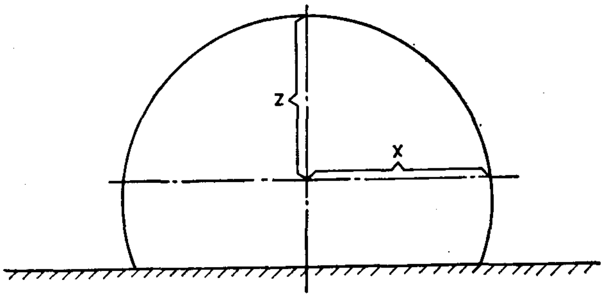

Fig. 9—Distances to be measured on drop for determination of surface tension and contact angle

The intermediate values β and b are determined in the following way: To obtain β the maximal horizontal radius x of the droplet is divided by the distance z between vertex and equator of the droplet (see Fig. 9). Table I in reference 19 gives values for b in relation to the x/z ratio. Table II in reference 19 gives numerical values for x/b and z/b in dependence of β and the contact angle ϕ . b can be eliminated from both x/b and z/b. For droplets having contact angles smaller than 90° a different method[21] of evaluation, but also based on Bashforth's and Adam's[19] tables, was used. The following function was applied for calculation of the surface tension:

$$\sigma_{lg} = a^2 \, . \, \rho \, . \, g \, . \, 10^{-6} \qquad \ldots\ldots\ldots\ldots 7$$

where

σ_{lg} = surface tension (N/m)
ρ = density of the iron (6,9 . 10^3 kg/m^3)[20]
g = acceleration due to gravity (9,81 m/sec^2)
a = intermediate value (m)

The intermediate value a was determined in the following manner:

For the distances x_1, x_2, z_1 and z_2 (see Fig. 10) the values h_1 and h_2 are calculated from
$h_i = x_i \, . \tan\phi - z_i$

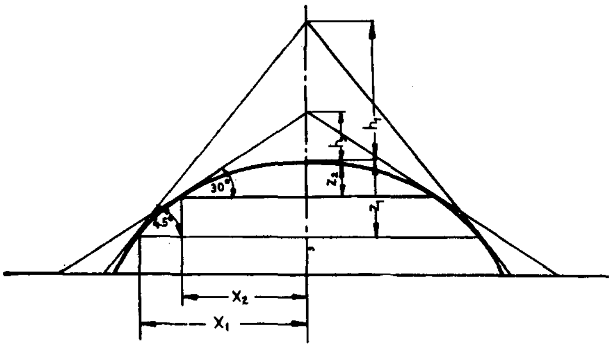

Fig. 10—Measurement on droplets having contact angle smaller than 90°

Ivashenko, Eremenko and Bogatyrenko[21] drew up a table of values of a^2/h^2_2 from Bashforth's and Adam's tables from which a^2 can be easily eliminated.

Measurements were carried out with ordinary cast iron having lamellar graphite and nodular cast iron. The chemical compositions of the two cast iron samples are given in Table II.

TABLE II

CHEMICAL COMPOSITION OF CAST IRON TESTED

	C%	Si%	Mn%	p%	S%	Mg%	0_2 ppm
Lamellar Graphite	3,88	1,58	1,22	0,028	0,015	0,002	49
Nodular Graphite	3,35	3,09	0,60	0,023	0,012	0,049	9

Pyrolytic graphite in which more than 99 per cent of all the graphite crystallites are oriented parallel to each other was used as the substrate in the investigation. The basal lattice surface of the pyrolytic graphite was the contact surface with the iron droplet. This simulated conditions prevailing in solidifying cast iron, where the contact (outer) surfaces of crystallising flakes or nodules with the still liquid melt consist mainly of basal lattice planes (see Fig. 3).

The interfacial tensions σ_{lg} were calculated using equations 6 or 7. Young's equation 5 was used to determine $\sigma_{lg}-\sigma_{sl}$.

As pointed out earlier, a direct measurement of the interfacial tension σ_{sg} between graphite and gas could not be carried out.

Patterson and Amman[22] have calculated the value $\sigma_s e=0,562$ N/m for the graphite base planes. This value was used to calculate the interfacial tension σ_{sl} given in Table III and in Fig. 11, from which it can be seen that the interfacial tension σ_{sl} between melt and basal lattice surface of pyrolytic graphite for nodular iron was, on the average, about 0,9 N/m higher than for the lamellar iron sample. Fig. 11 also indicates that the critical surface tension σ_{sl} crit for the two cast iron melts considered in this figure had a value between 0,8 and 1,0 N/m.

TABLE III

INTERFACIAL TENSION σ_{sl} BETWEEN BASAL LATTICE PLANES OF GRAPHITE AND LIQUID CAST IRON IN N/m

Time* (min)	1	2	3	4	5	Average
Alloy**						
1	0,746		0,550	0,550	0,520	0,574
2	2,285	1,387	1,073	1,207		1,488

*Time after sample attained measurement temperature (1 300 °C)

**Composition of the two alloys is given in Table II

SUMMARY

The results of tests described in the present paper confirmed that in cast iron melts having a comparatively high interfacial tention σ_{lg} against the environmental atmosphere the graphite tends to crystallise in form of nodules during solidification. In melts having a comparatively low interfacial tension σ_{lg} the graphite tends to crystallise in form of flakes.

The interfacial tension σ_{sl} between melt and solid graphite showed the same tendency in its influence on the graphite shape. The results indicate the existence of a critical interfacial tension $\sigma_{sl_{crit}}$ above which nodules and below which flakes are developing. The value of $\sigma_{sl_{crit}}$ was determined to be approximately 0,9 N/m.

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