3,455,164

3,463,005

7/1969

8/1969

[45] June 20, 1972

[54] RAPID THERMAL ANALYSIS METHOD FOR PREDICTING NODULAR IRON PROPERTIES

[72]	Inventors:	Edward F. Ryntz, Jr., Warren; John F. Janowak, Saginaw; John F. Watton, Roseville, all of Mich.
[73]	Assignee:	General Motors Corporation, Detroit, Mich.
[22]	Filed:	May 28, 1971
[21]	Appl. No.:	147,836
[52]	U.S. Cl	73/17 R
[51]	Int. Cl	G01n 25/02
[58]	Field of Sea	rch73/15, 17, 354, 359
[56]		References Cited
	U	NITED STATES PATENTS

Boyle.....73/359

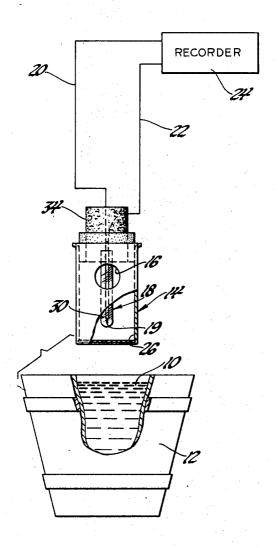
Hance.....73/354

Primary Examiner—Richard C. Queisser
Assistant Examiner—Herbert Goldstein
Attorney—Sidney Carter and Peter P. Kozak

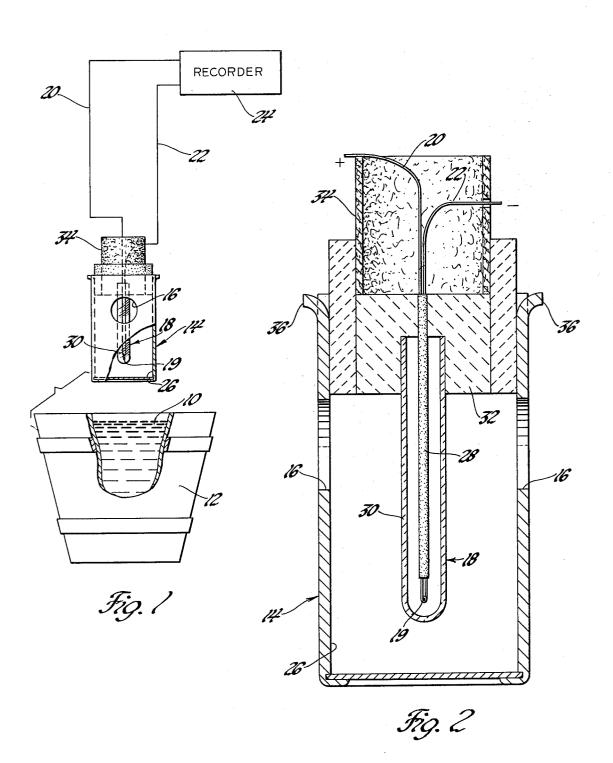
[57] ABSTRACT

A method of rapidly and accurately predicting the cast properties of nodular iron in foundry control operation is disclosed. A sample of nodular iron having a thermal mass such as to cool from 2,300° to 1,850° F in less than 4 minutes is extracted from a heat of molten cast iron immediately before the casting thereof. A cooling curve is generated and divided into characteristic curve segments indicative of the nucleation and growth reactions occurring on solidification. A comparison of the characteristic curve segments with respective families of like curve segments obtained from samples of known metallurgical properties yields one like curve segment from each family most like each characteristic curve segment. Correlation of most like curve segments with a known relationship between said families and nodular iron metallurgical properties yields the largest range of properties possible for the unknown sample on solidification.

4 Claims, 6 Drawing Figures

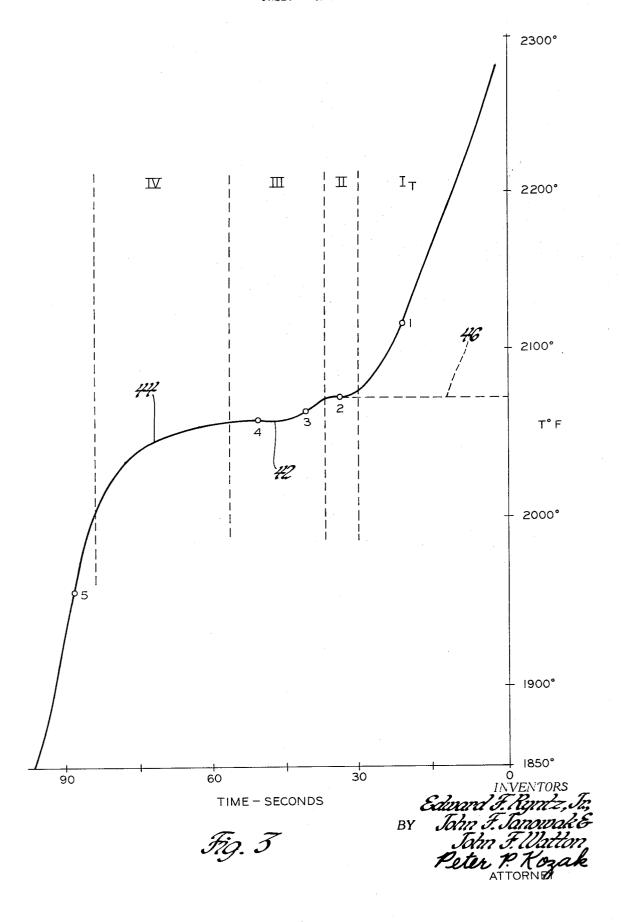


SHEET 1 OF 5

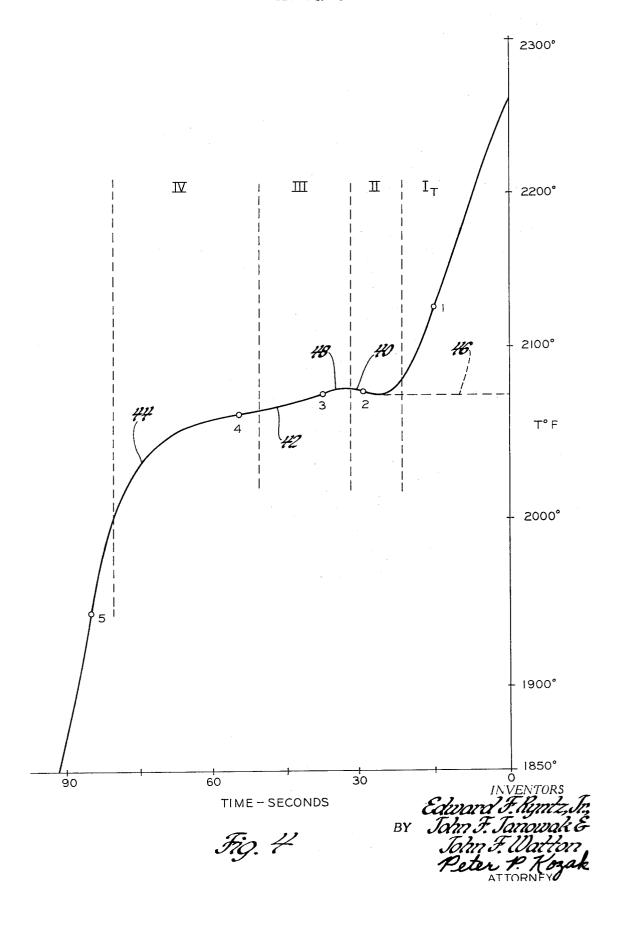


INVENTORS
Eclavard F. Kyrdz Jr.,
BY John F. Janowak &
John F. Waldon
Peter P. Kozak

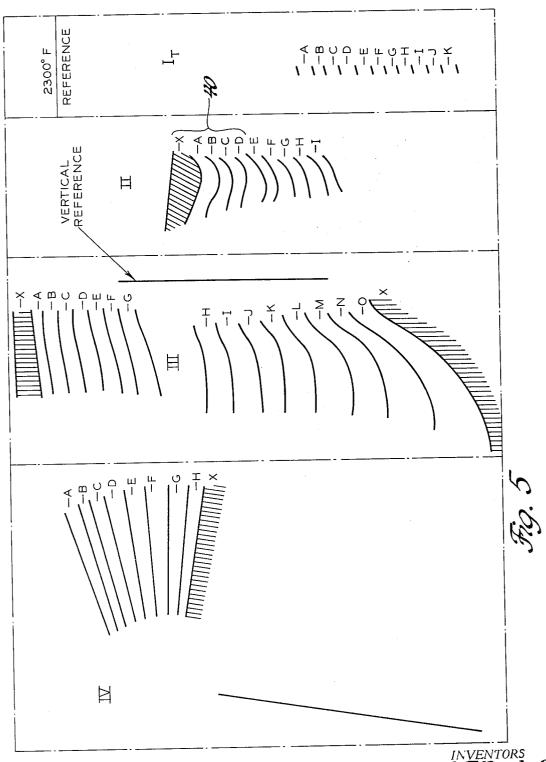
SHEET 2 OF 5



SHEET 3 OF 5



SHEET 4 OF 5



INVENTORS
Edward F. Rymz, I.,
BY John F. Janowak &
John F. Watton
Peter P. Kozak

ATTORNEY

SHEET S OF 5

_												T	1				
% NODULARITY ;	≤40	ABCD	EFG	F G H I	0 Ζ× Σ	т С		4.81 4.85	ტ	ВСР	FGH	C D E			Fig. 6		
	50	CDEF	СНГЭ	E S E E	ر × ا	O E F		4.76 4.80	I υ	A B C D E F	DEFG	ABCD					
	09	DEFG	НIЛ	я Х Х	×	D E F		4.71 4.75	T	C D E F G	A B C E F C	D E F	\ \ \ \		FGHIB	0 Z	F D
	70	DEFG	O I H	DE	L M	D F F	VALENT	4,66 4,70	GHIJ	ABCD EFX	A A C E E	CDEF	(20	G H	N N N	F G H
	80	ш	つ II I	D E F G H I	HI U K L M N	DEF	CARBON EQUIVALENT 4.56 4.60 4.61 4.65 4.66 4.7	H S	B C D E F G H	ABCD EFGH IJK	CDEFG	CARBIDES	2	E F G H I	z S	π Q	
	85	ட	つ I I	ABC D EFG	DEFGH IJKL	A B C D E F			E II	DEFG HIX	HIJKL MNX	DEFGH	% CAR	2	π Ω	ر 7× ⊼	E D H
	06	U	ы У	ABCD	ABCD	A B B C F F		4.51 4.55	E F G	C H I	Z Z J	ᄔ		ი	О П П К	ABCDE FGHIJ KLMX	CDEF
	92	Н		ø ∢	A B C	ABCD	-	4.46 4.50	ABCDE	II I	0	F G H		0	ABCDE	ABCD EFG	ABCD
			H H	Ħ	目	M	,		L H	H	Ħ	M			Ħ	Ħ	

INVENTORS
Edward F. Ryntz, Ir.,
BY John F. Janowak &
John F. Watton
Peter P. Kozak

RAPID THERMAL ANALYSIS METHOD FOR PREDICTING NODULAR IRON PROPERTIES

This invention relates to the production of nodular cast iron, and specifically, to a method of reliably predicting the cast structure of nodular iron from cooling curves in a foundry control operation. More specifically, this invention relates to a method of predicting, before the casting thereof, the microstructural and compositional properties of cast nodular iron.

In current production practice relatively soft based gray iron is rendered nodular by the small addition of magnesium which changes the shape of the flake graphite to a nodular or spheroidal form. After the magnesium inoculation a post-inoculation treatment of ferrosilicon is made to eliminate the carbide-forming tendency of the magnesium treated iron. It is known that successful processing of nodular iron is dependent on such process variables as the composition of the base gray iron, the adequacy and effectiveness of the inoculation and post-inoculation treatments, and the temperature of the molten cast iron and the holding time between the inoculation treatments and the casting of the iron. This latter effect, which is known as inoculation fade, results from the gradual loss of magnesium and consequently inoculation effectiveness as the molten cast iron is held before pouring. Residual magnesium levels in the normal range of 0.03-0.06 percent will result in acceptable nodular iron structures for a suitable gray iron composition. However, as the residual magnesium decreases below 0.03 percent, the spheroidal shape of the graphite rapidly deteriorates to a vermicular and finally to a flake form which is an unacceptable structure. The control of these process variables is important to the production of acceptable nodular iron castings due to their effect on the microstructural and compositional properties of the resulting castings, e.g., percent nodularity, percent carbides, percent ferrite and pearlite, and the percent carbon, silicon and magnesium which are related to the physical properties of the castings, e.g., tensile strength and ductility.

Because of the effect of the aforementioned variables, in production processes the base gray iron is treated in batches with test samples poured from each bath, cooled, and the 40microstructure examined metallographically to determine whether the treatments have been successful. Ideally, once a successful treatment schedule has been established in the foundry, its use should result in reproducible casting quality. However, the sensitivity of nodular iron production to these 45 variables and the processing difficulties inherent in a production operation preclude such a practice. Consequently, to insure high quality castings, commercial castings are also poured with a test sample portion which is cut from the casting and examined metallographically to determine the micros- 50 tructure of the casting. Failure to achieve an acceptable spheroidal graphitic structure in the sample means that the castings are unacceptable and must be scrapped. The difficulty in control of the composition and process treatments and the need for extensive quality control procedures thus has a significant 55 may be determined in less than 4 minutes thereby minimizing impact on the economics of the foundry operation not only in the possibility of a high rate of scrap castings but also in the time and facilities required to maintain quality control. It may be seen then that a reliable method for directly predicting the properties of the nodular iron castings before casting of the 60 molten iron is highly desirable.

Prior use of thermal analysis techniques has involved the determination of some constituents in molten hypoeutectic cast iron by a determination of its carbon equivalent, which may be defined as the total percent of carbon plus one-third of 65 the total percent of the silicon plus one-third of the total percent of the phosphorus contained in the iron sample based upon the total weight of the sample. These methods have, however, concentrated solely on the absolute temperature and the time at which the liquidus thermal arrest occurs. The 70 liquidus thermal arrest is determined by generating a cooling curve for a sample of molten cast iron. As the molten metal solidifies with either a single phase or multiphase microstructure, the heat of formation of new phases or of a change of

change in temperature with time of the solidifying sample, the temperature at which the heat liberated when the austenite starts to precipitate producing an isothermal arrest in the cooling curve may be determined. This temperature is the liquidus thermal arrest temperature. When accurately detected, the measurement of the liquidus thermal arrest is a reliable method of chemical analysis. However, absolute values of temperature and time are dependent on many influencing factors which cause the curve to shift to different temperatures and times. These factors include small changes in chemical composition, the heat transfer characteristics and mass of the solidifying sample, and the accuracy of positioning a thermocouple and determining temperatures. For example, small changes in chemical composition of nodular iron samples shift the temperatures at which solidification reactions occur due to the sloping regions of the ternary iron-carbon-silicon phase diagram. Further complications arise from the possible occurrence of either stable graphite or metastable carbide. This dif-20 ficulty in determining absolute temperatures and in defining absolute temperatures on the ternary iron-carbon-silicon phase diagram makes it difficult to associate specific reaction products, such as austenite, graphite, and carbide with an exact temperature on a nodular iron cooling curve.

Although absolute values of temperature and time are dependent on the aforementioned factors, these factors have been found not to cause a change in the general shape of the cooling curve. That is, we have found the existence of a relationship between the shape of the nodular iron cooling curve 30 and metallurgical structure whereby the shape of the nodular iron cooling curve can be correlated with a corresponding microstructure thus avoiding the many difficulties and inaccuracies inherent in the use of absolute temperatures and times.

The present invention thus provides a method of thermal 35 analysis which relies primarily on the shape of the entire nodular iron cooling curve rather than solely on the absolute temperature at which the liquidus thermal arrest occurs. Furthermore, by analysis of the subtle changes in shape of the cooling curve, as hereinafter fully explained, specific microstructural and compositional properties of the nodular iron on solidification may be predicted accurately and reliably before the casting thereof.

Accordingly, it is the principal object of this invention to provide a thermal analysis method for reliably and accurately predicting the microstructural and compositional properties of molten cast iron before the casting thereof.

It is another object of this invention to provide a thermal analysis method based on the shape of the entire nodular iron cooling curve, from the molten state to the solid state, for predicting the microstructural and compositional properties of both hypoeutectic and hypereutectic nodular cast irons.

It is a further object of this invention to provide a rapid thermal analysis method wherein the properties of the cast iron variations due to inoculation fade during the analysis period.

It is a still further object of this invention to provide a sampling device which will allow for the generation of a desired cooling curve from about 2,300° F to 1,850° F in about 0.5 to 4 minutes without masking the thermal effects of reactions which occur at different time intervals and without creating anomalous reactions.

These and other objects are accomplished in the preferred embodiment of the invention by first extracting a sample of molten cast iron from the holding furnace or ladle after the molten cast iron has been suitably inoculated with magnesium and ferrosilicon. The sample is of such a size and thermal mass as to allow for cooling from the molten region at about 2,300° F into the solid region at about 1,850° F in less than 4 minutes thereby providing a rapid analysis technique. The sample, after extraction, is allowed to cool and a thermocouple which extends to the center of the sample continuously measures the change in temperature of the sample with time whereby a cooling curve for the sample is generated. This cooling curve state alters the rate of temperature decrease. By plotting the 75 is then divided into characteristic curve segments indicative of

the nucleation and growth reactions occurring during solidification of the sample. For each of the characteristic curve segments a family of like curve segments obtained in like manner from nodular iron samples of known composition and microstructure are provided. By comparing the characteristic curve segments with their respective families a series of curve segments representing that member of each family most like each unknown curve segment is determined. This determination and further comparison with a known relationship between the families of curve segments and nodular iron metallurgical properties yields the largest range of microstructural and compositional properties possible for the sample of nodular iron based upon the total number of known curve segments. It will be seen that the present invention offers a rapid thermal analysis method which predicts many of the important microstructural and compositional properties of the cast iron and provides a reliable basis on which to accept or reject the heat of

Other objects and advantages of this invention will become more apparent from the following detailed description of the invention reference being had to the accompanying drawings of which:

FIG. 1 is a schematic illustration of the sampling technique the millivolt data from a thermocouple immersed in the sample being fed to a recorder;

FIG. 2 is a cross-sectional view of the sampling device employed in this invention:

FIG. 3 is a reproduction of an actual cooling curve for a 30 hypoeutectic cast iron generated in accordance with this invention:

FIG. 4 is a reproduction of an actual cooling curve for a hypereutectic cast iron generated in accordance with this in-

FIG. 5 is an illustration of families of known curve segments; and

FIG. 6 is a table used for correlating the unknown curve segments with the families of known curve segments shown in

Referring now to the drawings and particularly to FIG. 1, a heat of molten cast iron 10 suitably treated with magnesium and ferrosilicon is contained in a suitable holding vessel 12 at a temperature of about 2,600° F immediately prior to the pouring operation. A sampling device 14, shown in detail in 45 FIG. 2, is immersed in the holding vessel 12 allowing the molten cast iron 10 to flow through side holes 16 into the sampling device 14 activating a thermocouple 18 whose sensing junction 19 is located at the thermal center of the sample. After soaking for a few seconds to obtain thermal equilibrium, the sample is removed and air cooled through the eutectic temperature. The thermocouple leads 20, 22 are connected to a standard strip chart recorder 24 which continuously plots the change in temperature of the cast iron sample as sensed by the thermocouple 18 with time while the sample cools from its molten state to solid state to produce a cooling curve of the cast iron sample extending from about 2,300° F to 1,850° F.

The size and design of the sampling device 14 is critical to generating a cooling curve which will not mask the nucleation 60 and growth reactions occurring in the solidifying cast iron sample but which will provide sensitivity to inflections and arrests in the cooling curve resulting from the reactions occurring on solidification and which will cool sufficiently fast to provide the required temperature data, preferably in less than 65 four minutes. In general, the critical features of the cast iron sample and the sampling device are: sample means and soundness, sample surface area-to-volume ratio which determines the cooling rate, the wall thickness and material of the sampling device, and the position of the thermocouple in the sam- 70 pling device. These features are important in obtaining cooling curves which are responsive to changes in nodular iron processing which in turn affect the resulting microstructure. That is, if the sample is inordinately small resulting in a fast cooling rate, the microstructure of the sample will not be in- 75

dicative of the microstructure encountered in typical castings. For example, possible carbide formation and high graphite nodule counts will result from significantly smaller samples. If the sample is inordinately large resulting in a slow cooling rate, sensitivity to small inflections in the cooling curve representing variations in the microstructure will be lowered or masked. In addition, a slower cooling rate extends the time required in obtaining and analyzing the cooling curve which could result in low pouring temperatures and unacceptable castings.

The preferred form of the sampling device, as shown in detail in FIG. 2, is 1 inch in inside diameter, 11/2 inch in outside diameter, and is 3 inches in height. The device is made from a low carbon-low sulphur steel and provides a receiving basin 26 1 inch in diameter by 1% inch high. The two side holes 16 limit the height of the molten metal sample in the receiving basin 26. The thermocouple assembly 18 is formed of 24 gauge Chromel-Alumel thermocouple wires 20,22 insulated with a suitable ceramic 28 and sheathed in 3mm diameter Vycor tube 30. The thermocouple wires 20, 22 terminate in a sensing junction 19 which is located at the thermal center of the molten metal sample in the receiving basic 26. The thermocouple assembly is cemented in a ceramic sleeve 32 and the therfor extracting a sample from a heat of molten cast iron with 25 mocouple wires 20, 22 extend to a cardboard tube 34 which supports the thermocouple wires 20, 22 and allows for a quick connect and disconnect of the respective wires 20, 22 with the recorder 24. Metal clipping portions 36 serve to position and hold the thermocouple assembly in the receiving basin 26.

Referring now to FIGS. 3 and 4, there is reproduced actual cooling curves of a sample of a hypoeutectic casting iron and a hypereutectic cast iron, respectively, obtained in accordance with the present invention. That is, the sampling device 14 shown in FIG. 2 was immersed in a heat of molten cast iron 35 held at a temperature of about 2,600° F. Upon immersion, the molten cast iron flowed through the side holes 16 filling the receiving basin 26. The sampling device was held in the molten cast iron for a few seconds until a thermal equilibrium was established as indicated by the thermocouple 18 surrounded 40 by molten metal recording an equilibrium temperature. The sampling device 14 was then removed from the heat with the metal above the bottom of side holes 16 flowing out thereby establishing a constant volume sample in the basin 26 extending to the bottom of side holes 16. Extensive experimental investigations into the construction and assembly of the sampling device 14 had established that the thermocouple sensing junction 19, when constructed in accordance with the foregoing description, would be located at the approximate thermal center of the sample. The sample was then air cooled from the holding temperature of 2,600° F. A cooling curve was generated for the sample from a temperature of about 2,300° F to a temperature of about 1,850° F at which temperature the sample was completely solidified. As shown in FIGS. 3 and 4, the cooling time was about 90 seconds. During cooling the thermocouple sensing junction 19 continuously sensed the temperature change of the sample registering the thermal arrest and other thermal effects indicative of the various reactions taking place in the sample as the sample solidified. This temperature response data was plotted on a standard strip chart recorder 24 as a function of time to provide a cooling curve for the cast iron sample. As further shown in FIGS. 3 and 4, the cooling curves were then divided into characteristic curve segments indicated by numerals II, III and IV. Reference points have been placed on the curves at curve inflection points for purposes of the following description. As hereinafter more fully explained, these curve segments are indicative of the primary nucleation and growth reactions occurring on solidification of the sample.

The mechanisms of nodular iron solidification as indicated by the cooling curves shown in FIGS. 3 and 4 can be summarized as follows. As the molten metal sample cools, graphite nuclei, which formed at an elevated temperature after the magnesium treatment and silicon inoculation start to grow appreciably at a temperature between points 1 and 2. The

austenite shell, which surrounds the graphite nucleus also begins growing at this time. In hypoeutectic iron austenite dendrite growth is also initiated at this point. The section of the cooling curve corresponding to region II in FIGS. 3 and 4 marks the point of significant graphite nodule and austenite shell growth in nodular terms and also primary austenite dendrite growth in hypoeutectic irons. In addition, this section of the cooling curve has exhibited a high correlation with graphite nodularity in eutectic/hypereutectic irons. If the magnesium and silicon treatments are effective, resulting in wellformed graphite spheroids, recalescense occurs on this part of the curve for hypereutectic irons. Recalescense is indicated in region II of FIG. 4 by a temperature increase 40 caused by the rapid liberation of the latent heat of transformation. If for some reason the treatments were not effective, this section of the curve is displaced downwardly. This suppression of the curve has been related to increasing quantities of vermicular and flake graphite and carbides. A reversion of the graphite spheroids to essentially flake morphology also produces a recalescense in this section of the cooling curve. However, the curve segment becomes extended under these conditions. This deteriorated structure also produces characteristic changes in regions III and IV as discussed below.

The bulk eutectic arrest 42 during which the major portion 25 of growth occurs is represented by region III. For a eutectic/hypereutectic iron this section of the cooling curve has been related to the presence of carbides which form when the eutectic arrest temperature falls below the metastable eutectic temperature. The tendency to carbide formation results from 30 insufficient post-inoculation or face of the post-inoculation effect. An undercooling or rapid decrease in temperature in this curve section indicates that metastable iron carbide solidification has occurred. If the post-inoculation is sufficient to maintain solidification in the iron-graphite system, the temperature 35 decrease in this area is represented by a gradual slope in the curve. For properly inoculated iron with vermicular or flake graphite the curve segment in region III approaches the horizontal. The general shape of the cooling curve indicating carbides in eutectic/hypereutectic irons is also representative of acceptable hypoeutectic solidification.

The final stages of eutectic solidification occur in region IV of the cooling curve. This "knee" 44 of the curve exhibits a large angle between the curve sections for well-formed graphite spheroids in both hypoeutectic and eutectic/hypereutectic irons. The large angle between the bulk eutectic arrest 42 and the slope of the curve at point 5 is believed to result from decreased growth rates caused by the time dependent diffusion of carbon through the increasing austenite shell to the graphite nodule. Small angles between the line segments indicate carbide formation and/or a low percent nodularity. When region III exhibits large undercooling, sharp angles occur in region IV indicating that the last stages of growth occurred rapidly by massive carbide reaction rather than by a diffusion reaction required for complete graphitization. The formation of flake graphite produces a recalescense in region IV indicated by small angles which results from graphite growing in direct contact with the melt. As with carbide formation, perature to occur.

Because of the similarity of the hypereutectic iron cooling curves to the hypoeutectic curves, the two have been considered together in the foregoing discussion of solidification reactions. However, by recording the minimum temperature 46 just prior to inflection point 2, the difference between hypoeutectic and hypereutectic solidification may be determined. Hypereutectic nodular iron cooling curves also have an initial arrest 48 above the bulk eutectic arrest occurring in region III, as shown in FIG. 4 between points 2 and 3. The similarity between a hypoeutectic cooling curve of high nodularity and a eutectic/hypereutectic cooling curve of very high carbide content, however, requires a method of differentiation. The temperature at which the initial arrest occurs has

solidification modes, i.e., as the iron composition becomes increasingly hypoeutectic, the initial arrest occurs at higher temperatures. In addition, high carbide contents as indicated by region III of the curve also tends to lower the initial arrest temperature.

Although each of these characteristic cooling curve regions is representative of either graphite or matrix structures, the interrelationship of these regions must be considered in evaluating the curve to predict microstructure. Accordingly, as shown in FIG. 5, a family of curve segments II, III, and IV is provided for each of the characteristic curve segments II, III and IV shown in FIGS. 3 and 4. The curve segments shown in region I_T of FIG. 5 are not used for comparison with the curve segments I_T in FIGS. 3 and 4 in the same manner as those of families II, III and IV of FIG. 5. Rather they are used to determine the minimum temperature 46 just prior to inflection point 2 to differential hypoeutectic solidification from hypereutectic solidification. Accordingly, region I_{τ} has not been designated as a "characteristic curve segment," as used herein, and has been labeled with a subscript "T" to indicate temperature dependence. Although not required for prediction, it is possible, however, to differentiate the solidification modes by an analysis of curve shapes occurring in region I_T in the same manner as regions II, III, and IV. It will be noted that it is not critical to the practice of this invention that the cooling curves be divided into these regions only. Rather the curve can be divided into more regions determined by the maxima, minima and inflection points occurring in the curve depending on the accuracy of prediction required. However, there must be a family of curve segments corresponding to each characteristic curve segment of the cooling curve for prediction of the microstructural and compositional properties of the cast iron. We have found that the divisions shown in FIGS, 3, 4 and 5 and previously described identify the primary nucleation and growth reactions occurring on solidification and provides good predictability.

The families of curve segments shown in FIG. 5 were obtained in like manner as those of FIGS. 3 and 4. That is, a large number of nodular irons representing a wide range of chemistries and possible microstructures were provided and for each a cooling curve was generated by the method described above using the sampling device shown in FIG. 2. After generating a cooling curve, each solidified sample was sectioned and metallographic examination of the samples was performed. The composition and microstructural properties were then related to the shape of the cooling curves to provide a spectrum of curve shapes observed in regions I_T , II, III, and IV. FIG. 5 represents a compilation and analysis of over 100 cooling curves obtained from nodular irons representing a wide range of chemistries and microstructures. It will be recognized that, as in many methods based on correlating an unknown with a group of known samples, the accuracy of the method will depend on the total number of known samples available for correlation. We have found, however, that the use of the families of curve segments shown in FIG. 5 which were derived from over 100 cooling curves provides good predictability.

Briefly, some of the characteristics of the families of curve this reaction does not require a continuing decreasing tem- 60 segments shown in FIG. 5 may be described in relation to the previous discussion of the possible solidification reactions of cast iron. The area between each curve segment in the spectrum of curve shapes in each of the families I7, II, III, and IV has been identified with a letter designation for purposes of the discussion and for correlation of the curve segments as hereinafter described. As previously described, the section of the cooling curve corresponding to region II of FIGS. 3 and 4 and also region II of FIG. 5 marks the period of significant graphite nodule and austenite shell growth in nodular iron and also primary austenite dendrite growth in hypoeutectic irons. The recalescense 40 accompanying effective magnesium and silicon treatments is represented by the curve segments located toward the top of region II of FIG. 5 while curve suppression accompanying ineffective treatments is indicated by proven to be an adequate criterion for separating the two 75 the curve segments located toward the bottom. Extension of

the curve segment coupled with a recalescense in region II indicating a reversion of the graphite spheroids to a flake morphology is indicated by the shaded area X at the top of region II of FIG. 5. Referring briefly now to region III of FIG. 5, insufficient post-inoculation or post-inoculation fade resulting in a tendency to carbide formation is indicated by the curve segments located toward the bottom of that region. In region IV of FIG. 5, the possible angles occurring in the "knee" 44 of the curves shown in FIGS. 3 and 4 are indicated.

Accordingly, for each of the characteristic curve segments in FIGS. 3 and 4 there is provided a family of like curve segments obtained from samples of known composition and microstructure with each like curve segment in each of the families being related to a known range of microstructural and compositional properties. However, in evaluating the cooling curve of an unknown sample of cast iron to predict properties, these regions must be correlated to predict the largest possible range of properties mutually related to each serial combination of like curve segments of the respective families.

FIG. 6 is a tabular correlation which provides such an interrelationship of curve families for three properties of primary importance in nodular iron production-percent nodularity, carbon equivalent, and percent carbides. For each property a range is shown on the horizontal across the top of the table 25 and the designation of curve families I_T , II, III and IV of FIG. 5 is shown on the vertical at the left of the table. The table is compiled by determining from the known samples the range of properties possible for the shape of each curve segment in each family. For example, curve HI, (curve segment H in re- 3) gion I_T of FIG. 5) is known to indicate a nodularity of 50-95 percent; curve segment A_{II} is known to indicate a nodularity of 85-95 percent; curve segment A_{III} is known to indicate a nodularity of 90-95 percent; and curve segment A_{II} is known to indicate a nodularity of 85-95 percent. Serial correlation of 3. these curves segments, i.e., combining curve segment A from each family, H_{IT} , A_{II} , A_{III} , and A_{IV} , in that order and only in that order, produces a composite curve which is known to be representative of a nodular iron having a largest possible range of nodularities of 90-95 percent. This process can be repeated 40 for each possible serial combination of curve segments of each family for each property under consideration to produce a composite curve for each serial correlation of a curve segment chosen from each family. With this large number of composite cooling curves the cooling curve of an unknown sample can be 45 compared to find the one most like it in shape for each property whereby the properties of the unknown sample may be predicted. However, this process is inordinately time-consuming and, therefore, the serial correlations of curve families has been broken down into tabular form in FIG. 6.

Referring again to FIG. 3 for purposes of an example, it may be seen that the curve of the actual hypoeutectic iron sample was divided into regions characteristic of the primary nucleation and growth reactions occurring on solidification. The characteristic curve segments in regions II, III, and IV were compared with the spectrum of curves in the corresponding families of FIG. 5 to determine the member most like the respective segments. The curve segments in region I_T of FIG. 5 were used only to determine the minimum temperature 46 just 60prior to the second inflection point in order to differentiate hypoeutectic and hypereutectic solidification as previously described. Starting from a reference point of 2,300° F, it may be seen that this minimum temperature occurred at about 2,070° F which corresponds to area H of FIG. 5. Comparing 65 regions II, III, and IV of FIG. 3 with their respective families in FIG. 5, it may be seen that member F of region II, member K of region III, and member F of region IV are most like the respective characteristic curve segments of FIG. 3. Accordingly, a composite curve of known curve segments most 70 closely resembling the unknown hypoeutectic curve of FIG. 3 is formed by serially combining the like curve segments: $\mathbf{H}_{1\mathbf{r}}, \mathbf{F}_{II}, \mathbf{K}_{III}, \mathbf{F}_{IV}$

Referring now to FIG. 6, this correlated serial combination is known to indicate 80-85 percent nodularity. That is, H_{1_T} in-75

dicates a nodularity of 50-95 percent, F_{II} indicates a nodularity of 40-60 percent and 80-90 percent, K_{III} indicates a nodularity of 80-85 percent, and $F_{II'}$ indicates a nodularity of 40-90 percent. However, the four in serial combination indicate that 80-85 percent is the largest range of nodularities common to all four. A like analysis may be made for carbon equivalent (CE) and percent carbides, however, for percent carbides only regions II, III, and IV need be considered. Repeating the process for the serial combination $H_{IT'}$, $F_{II'}$, $K_{III'}$, $F_{II'}$ carbon equivalent (CE) in the range of 4.56-4.60 and percent carbides in the range of 5-10 percent is predicted. Actual metallographic analysis showed the cast iron sample to be of 90 percent nodularity and 8 percent carbides and to have a CE = 4.44.

Repeating the process for the hypereutectic iron cooling curve shown in FIG. 4, a composite curve H_{1T}, B_{II}, G_{III}, C_{II} most closely resembling the unknown curve was formed. Referring again to FIG. 6, this correlated serial combination is 20 known to indicate 85 percent nodularity, 0-5 percent carbides, and a carbon equivalent in the range of 4.76-4.80. Actual metallographic examination showed the cast iron sample to be of 90 percent nodularity and 3 percent carbides with a CE=4.62.

The results of the above described examples are summarized in tabular form below:

% NODULARITY

0				
	Sample Hypoeutectic Iron Hypereutectic Iron	Predicted 80–85 85	Actual 90 90	% Error 11% max 6%
5		% CARBIDES		
	Sample Hypoeutectic Iron Hypereutectic Iron	Predicted 5-10 0-5	Actual 8 3	% Error 0 0
0	CA	RBON EQUIVA	LENT	
	Sample Hypoeutectic Iron Hypereutectic Iron	Predicted 4.56–4.60 4.76–4.80	Actual 4.44 4.62	% Error 5% max 4% max

Both cooling curves were obtained in about 90 seconds and the predictions of the properties of primary importance were made in less than a total time, including sampling, of 2½ minutes. The predictions were made with excellent accuracy and both heats proved to be of acceptable quality.

Although our invention has been described in terms of specific examples, it is to be understood that other forms of the invention may be readily adapted with the skill of the art. For example, those skilled in the art will recognize that suitable families of curves can be generated and correlated to predict microstructural and compositional properties other than those described above which may be further related to predict physical properties of the cast iron.

We claim:

1. A method of predicting metallurgical properties of a molten cast iron treated to form nodular cast iron on solidification, comprising the steps of:

providing a heat of said molten cast iron,

extracting from said heat a sample of said molten cast iron, allowing said sample to cool from its molten state to a solid state.

generating a cooling curve of said molten cast iron sample, said curve being obtained by continuously measuring and plotting the change in temperature with time of said sample of said iron while said sample of said iron is cooling from the molten to the solid state,

dividing said cooling curve into characteristic curve segments indicative of the nucleation and growth reactions occurring during solidification of said sample of said iron,

10

25

generating for each of said characteristic curve segments a respective family of like curve segments obtained in like manner from like cast iron samples of known composition and microstructure wherein each curve segment in each of said respective families is related to a known range of metallurgical properties,

correlating said respective families of like curve segments to determine the largest range of metallurgical properties mutually related to each serial combination of said like curve segments of said respective families,

comparing the shape of each characteristic curve segment with its respective family of like curve segments to determine the curve segment in each of said respective families most like each characteristic curve segment,

serially combining said curve segments most like said 15 characteristic curve segments, and

determining from the serial correlation of the families of like curve segments the largest range of metallurgical properties possible for the serial combination of most like curve segments, said range indicating the metallurgical properties of said cast iron on solidification.

2. A method of predicting microstructural and compositional properties of a molten cast iron treated to form nodular cast iron on solidification, comprising the steps of:

providing a heat of said molten cast iron,

extracting from said heat a sample of said molten cast iron, said sample having a thermal mass such as to cool from about 2,300° F to 1,850° F in about 0.5 to 4 minutes,

allowing said sample to cool from its molten state to a solid state,

generating a cooling curve of said molten cast iron sample, said curve being obtained by continuously measuring and plotting the change in temperature with time of said sample of said iron while said sample of said iron is cooling from the molten to the solid state,

dividing said cooling curve into characteristic curve segments indicative of the nucleation and growth reactions occurring during solidification of said sample of said iron,

generating for each of said characteristic curve segments a respective family of like curve segments obtained in like manner from like cast iron samples of known composition and microstructure wherein each curve segment in each of said respective families is related to a known range of microstructural and compositional properties.

correlating said respective families of like curve segments to determine the largest range of microstructural and compositional properties mutually related to each serial combination of said like curve segments of said respective families,

comparing the shape of each characteristic curve segment with its respective family of like curve segments to determine the curve segment in each of said respective families most like each characteristic curve segment,

serially combining said curve segments most like said 55 characteristic curve segments, and

determining from the serial correlation of the families of like curve segments the largest range of microstructural and compositional properties possible for the serial combination of most like curve segments, said range indicating the microstructural and compositional properties of said cast iron on solidification.

3. A method of predicting the nodularity, carbon equivalent, and percent carbides of a molten cast iron treated to form nodular cast iron on solidification, comprising the 65 steps of:

providing a heat of said molten cast iron,

extracting from said heat a sample of said molten cast iron, said sample having a thermal mass such as to cool from about 2,300° F to 1,850° F in about 0.5 to 4 minutes, 70 allowing said sample to cool from its molten state to a solid

state,

generating a cooling curve of said molten cast iron sample, said curve being obtained by continuously measuring and plotting the change in temperature with time of said sample of said iron while said sample of said iron is cooling from the molten to the solid state,

dividing said cooling curve into characteristic curve segments indicative of the nucleation and growth reactions occurring during solidification of said sample of said iron.

generating for each of said characteristic curve segments a respective family of like curve segments obtained in like manner from like cast iron samples of known nodularity, carbon equivalent, and percent carbides, wherein each curve segment in each of said respective families is related to a known range of nodularities, carbon equivalents, and percent carbides,

correlating said respective families of like curve segments to determine the largest range of nodularities, carbon equivalents, and percent carbides mutually related to each serial combination of said like curve segments of said respective families.

comparing the shape of each characteristic curve segment with its respective family of like curve segments to determine the curve segment in each of said respective families most like each characteristic curve segment,

serially combining said curve segments most like said characteristic curve segments, and

determining from the serial correlation of the families of like curve segments the largest range of nodularities, carbon equivalents, and percent carbides possible for the serial combination of most like curve segments, said range indicating the nodularity, carbon equivalent, and percent carbides of said cast iron on solidification.

plotting the change in temperature with time of said sample of said iron is cooling 35 iron treated to form nodular cast iron on solidification, comfrom the molten to the solid state,

4. A method of predicting the nodularity of a molten cast iron treated to form nodular cast iron on solidification, comprising the steps of:

providing a heat of said molten cast iron,

extracting from said heat a sample of said molten cast iron, said sample having a thermal mass such as to cool from about 2,300° F to 1,850° F in about 0.5 to 4 minutes,

allowing said sample to cool from its molten state to a solid state,

generating a cooling curve of said molten cast iron sample, said curve being obtained by continuously measuring and plotting the change in temperature with time of said sample of said iron while said sample of said iron is cooling from the molten to the solid state,

dividing said cooling curve into characteristic curve segments indicative of the nucleation and growth reactions occurring during solidification of said sample of said iron,

generating for each of said characteristic curve segments a respective family of like curve segments obtained in like manner from like cast iron samples of known nodularity wherein each curve segment in each of said respective families is related to a known range of nodularties,

correlating said respective families of like curve segments to determine the largest range of nodularities mutually related to each serial combination of said like curve segments of said respective families,

comparing the shape of each characteristic curve segment with its respective family of like curve segments to determine the curve segment in each of said respective families most like each characteristic curve segment,

serially combining said curve segments most like said characteristic curve segments, and

determining from the serial correlation of the families of like curve segments the largest range of nodularities possible for the serial combination of most like curve segments, said range indicating the nodularity of said cast iron on solidification.

* * * * :