Oct. 25, 1949. K. D. MILLIS ET AL 2,485,760

CAST FERROUS ALLOY

Filed Nov. 21, 1947 4 Sheets-Sheet 1

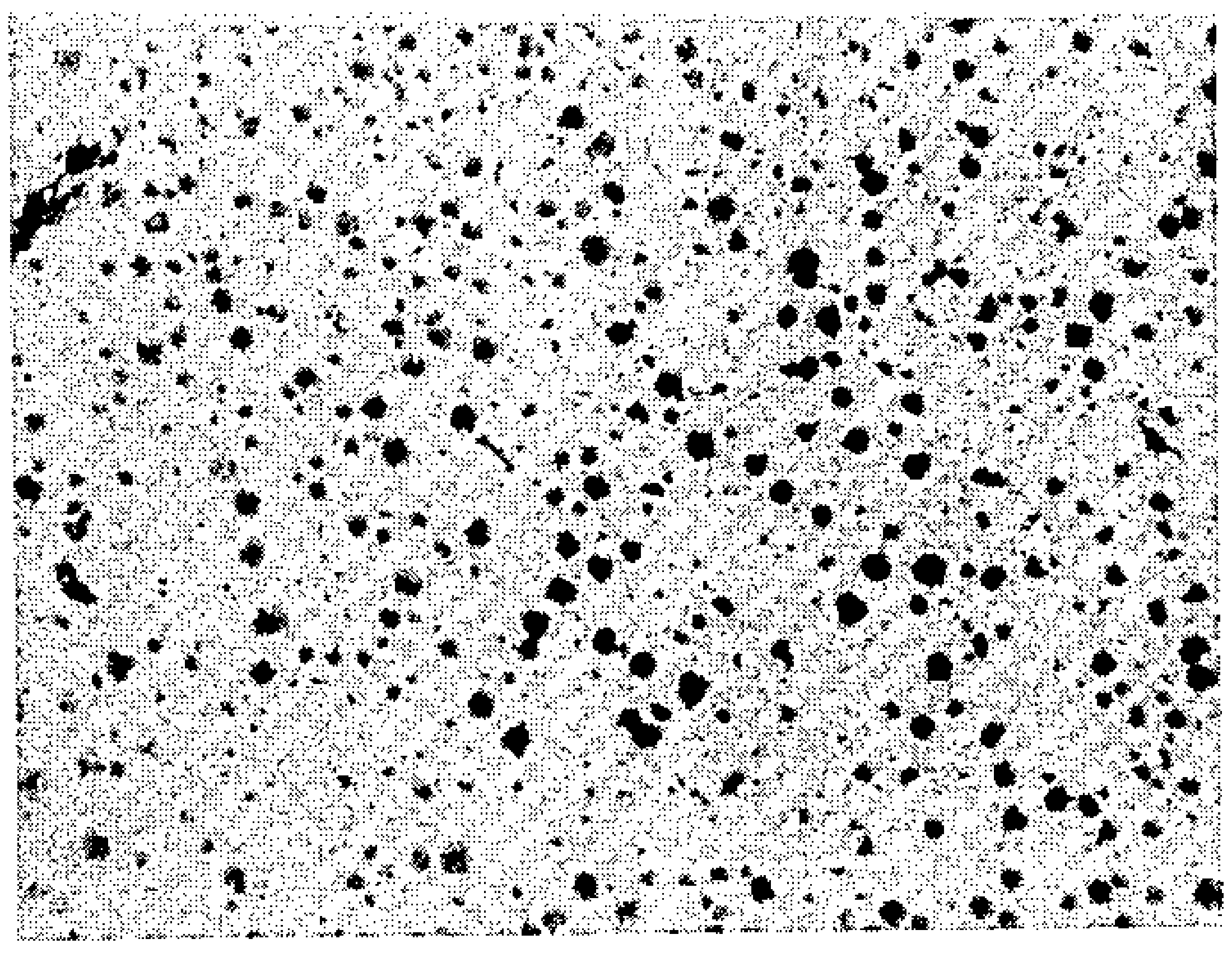

Fig. 1.

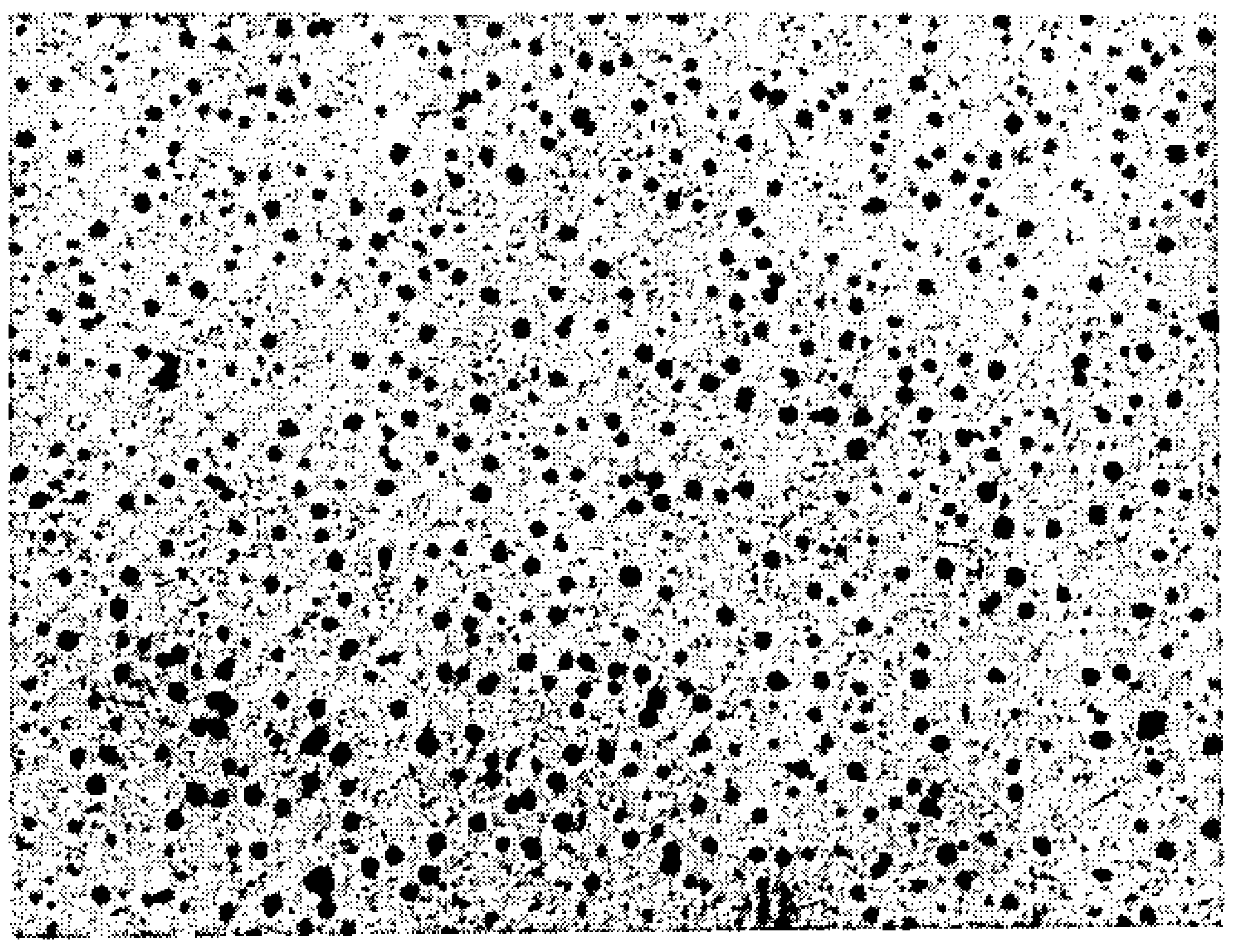

Fig. 2.

Fig. 3.

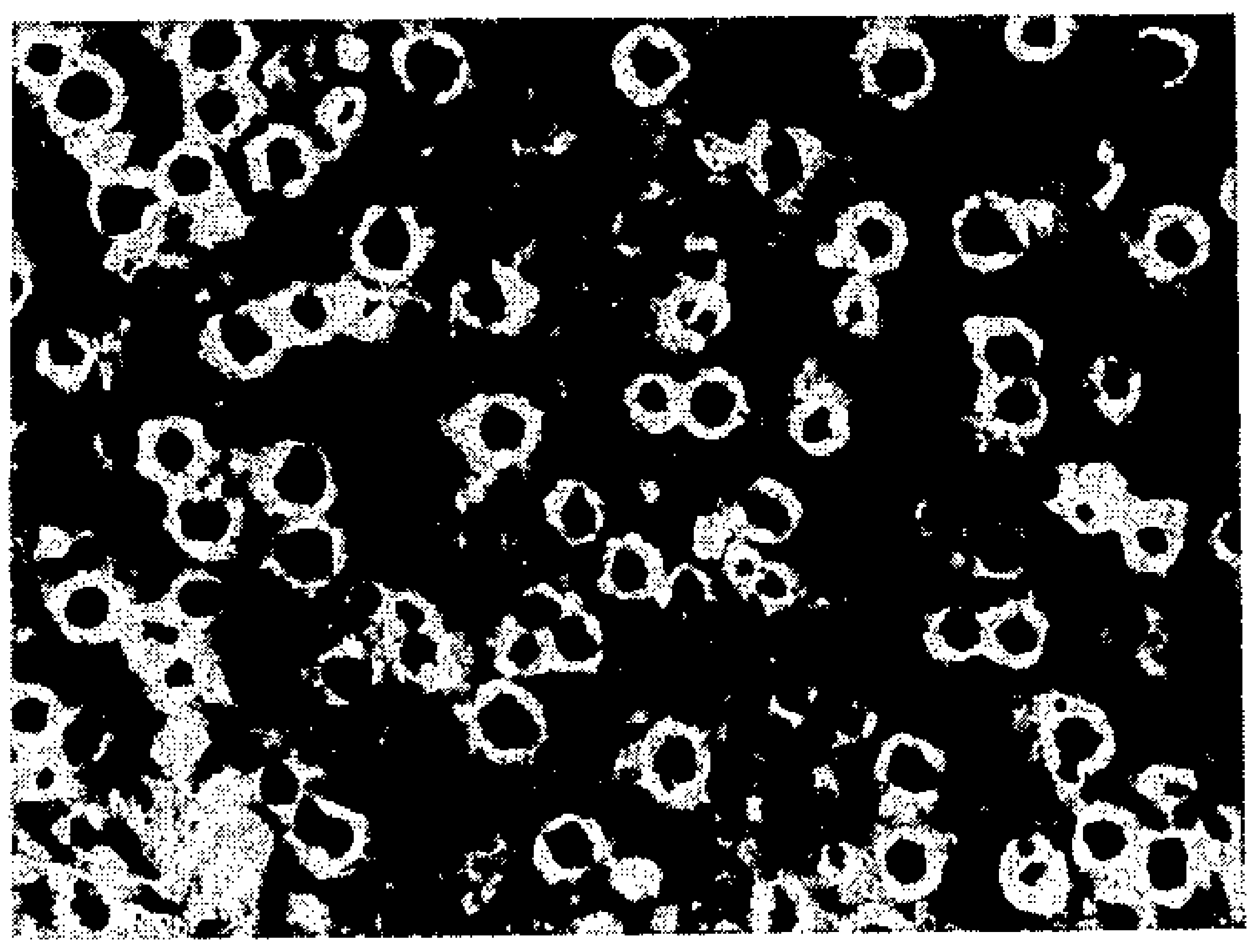

Fig. 4.

Fig. 5.

INVENTORS
KEITH DWIGHT MILLIS
ALBERT PAUL GAGNEBIN
NORMAN BODEN PILLING
BY
A. J. Weller
ATTORNEY

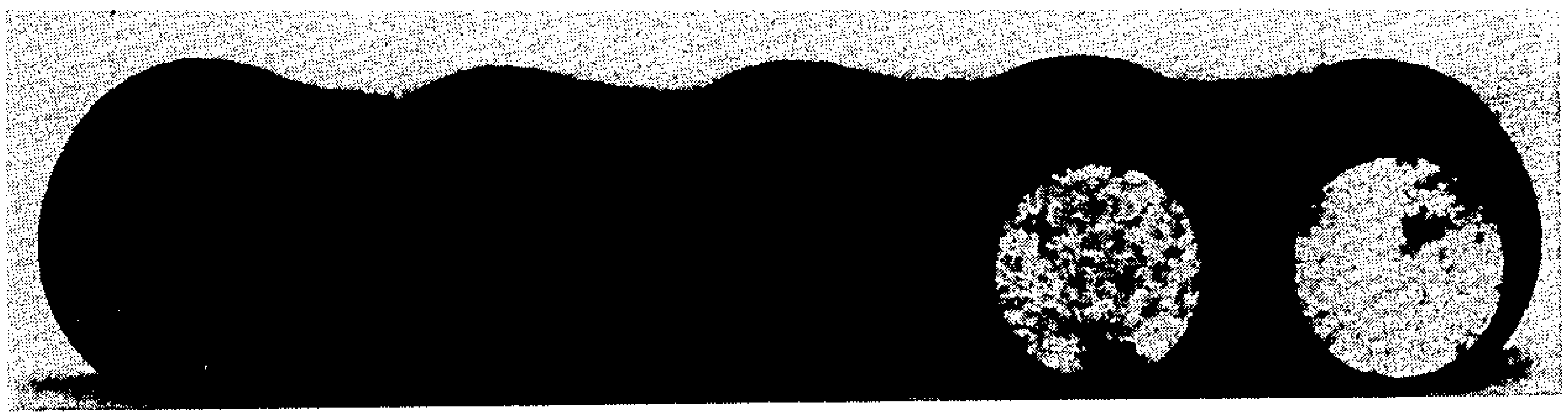

Fig. 6.

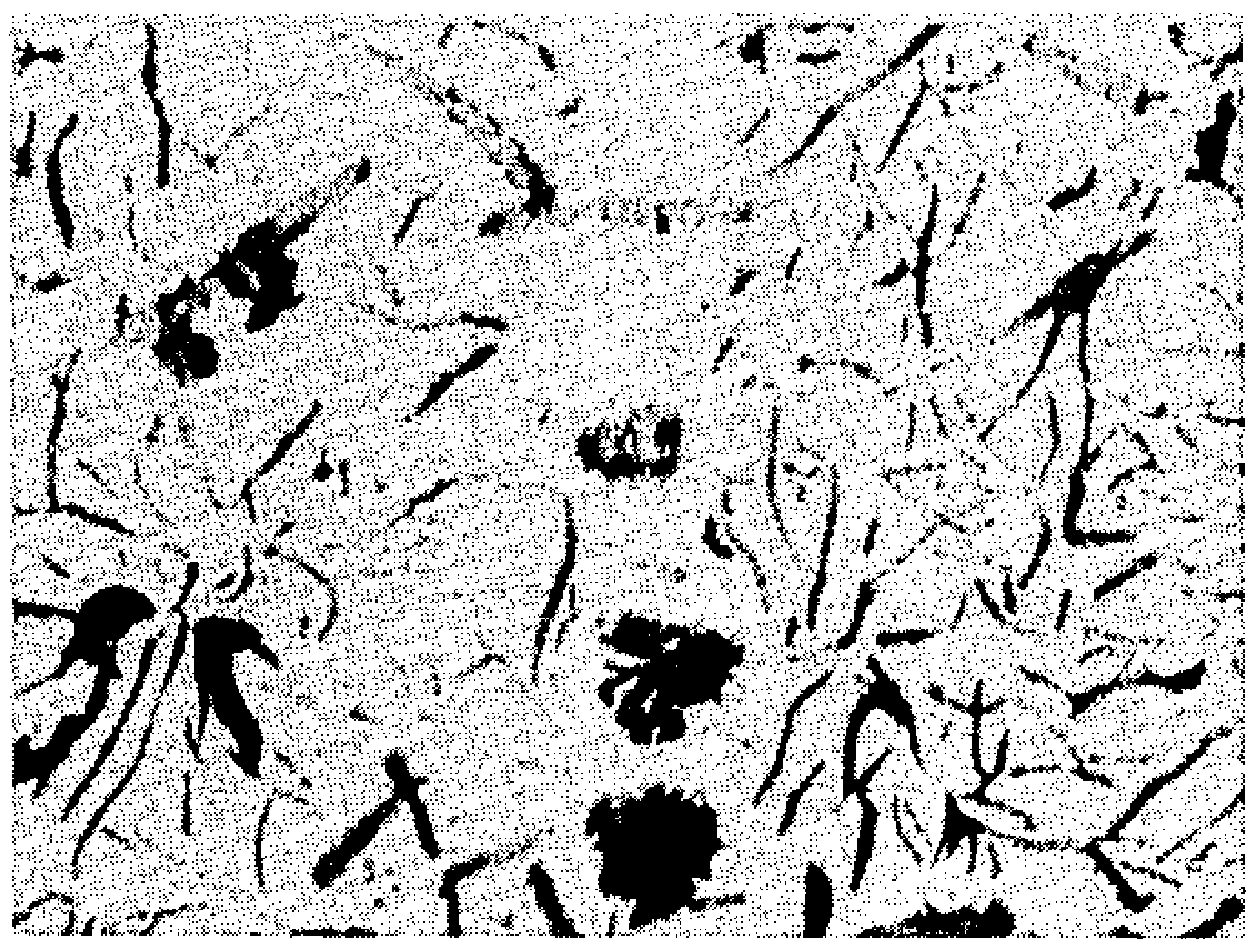

Fig. 7.

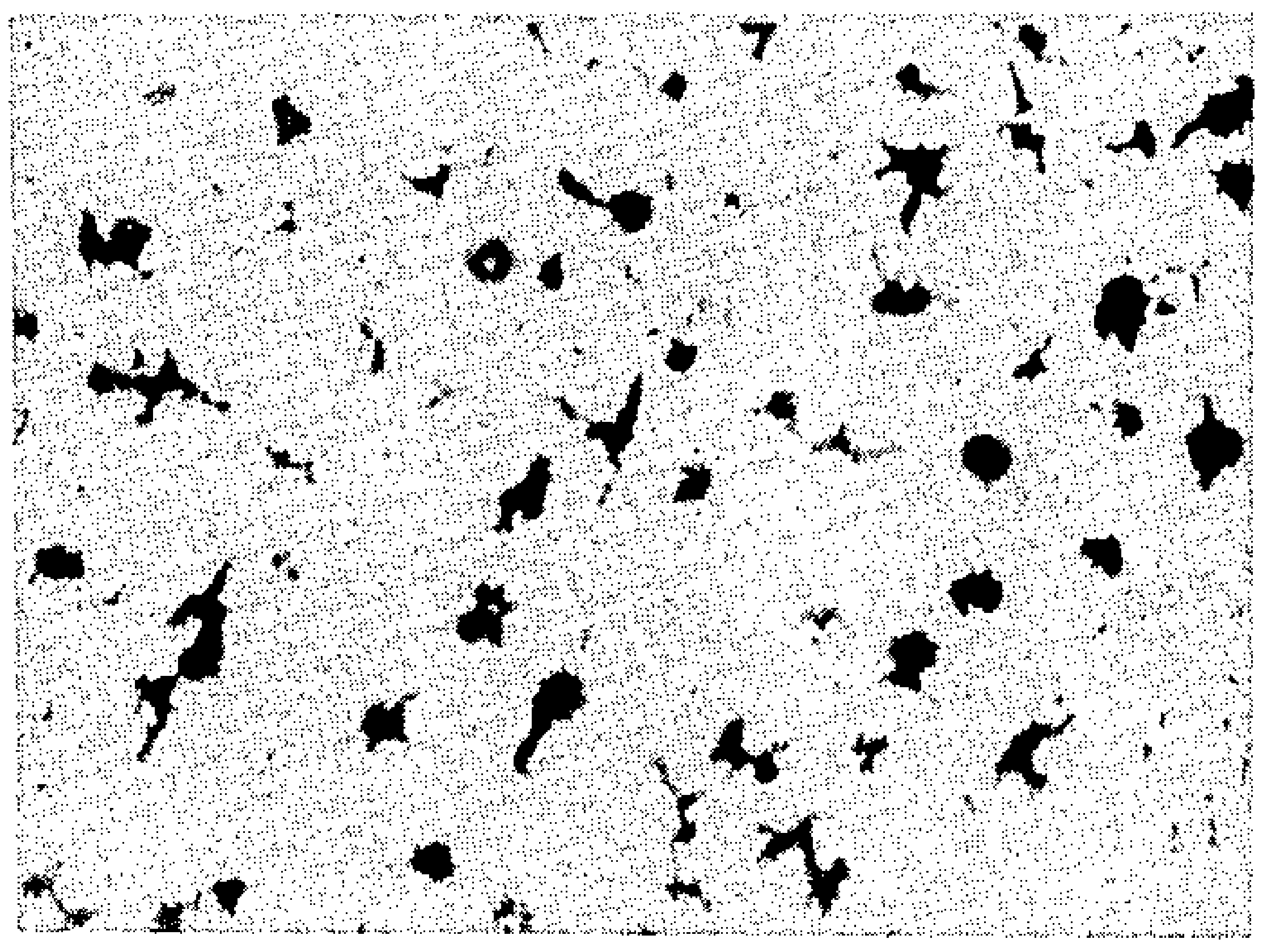

Fig. 8.

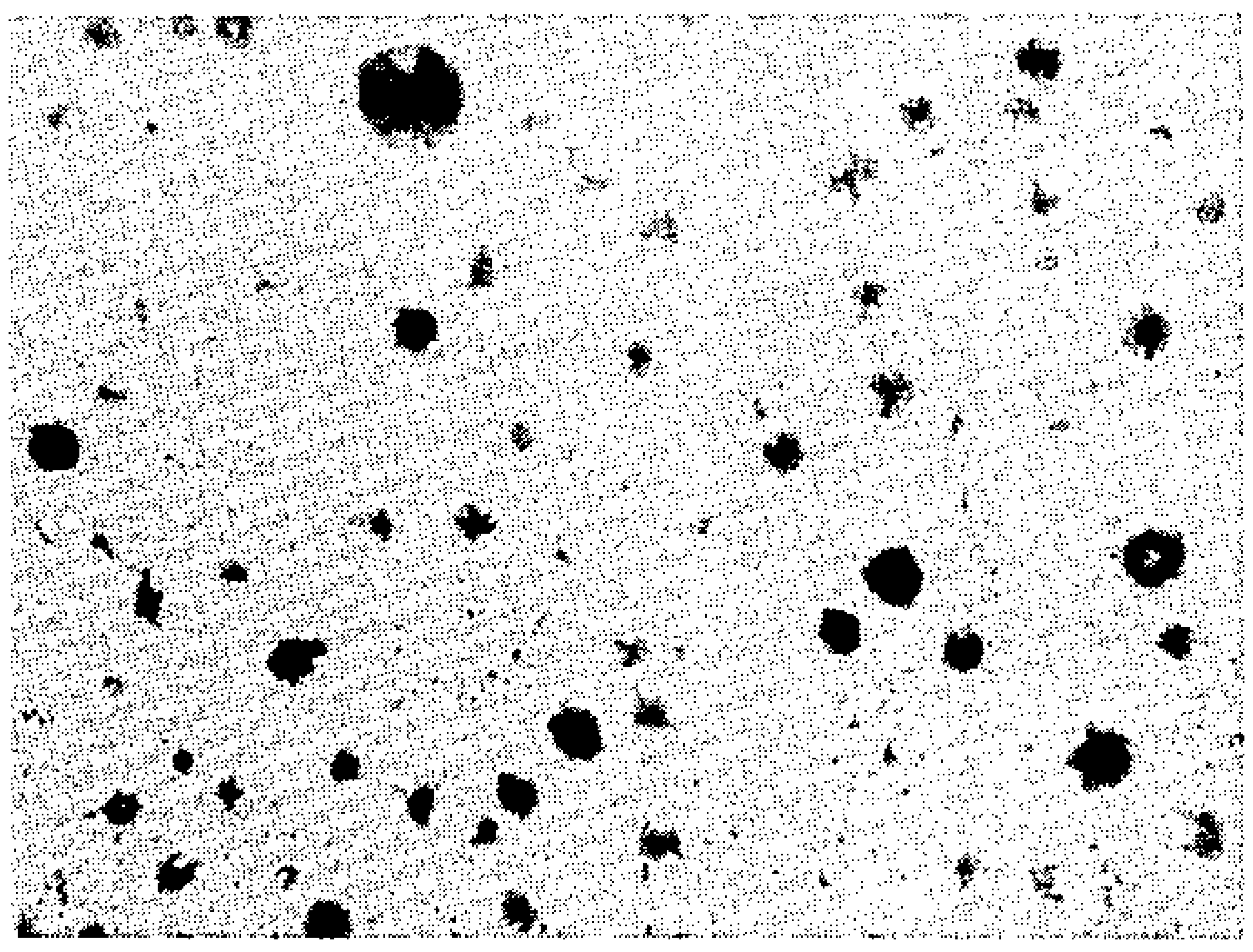

Fig. 9.

INVENTORS
KEITH DWIGHT MILLIS
ALBERT PAUL GAGNEBIN
NORMAN BODEN PILLING

BY

ATTORNEY

Oct. 25, 1949. K. D. MILLIS ET AL 2,485,760

CAST FERROUS ALLOY

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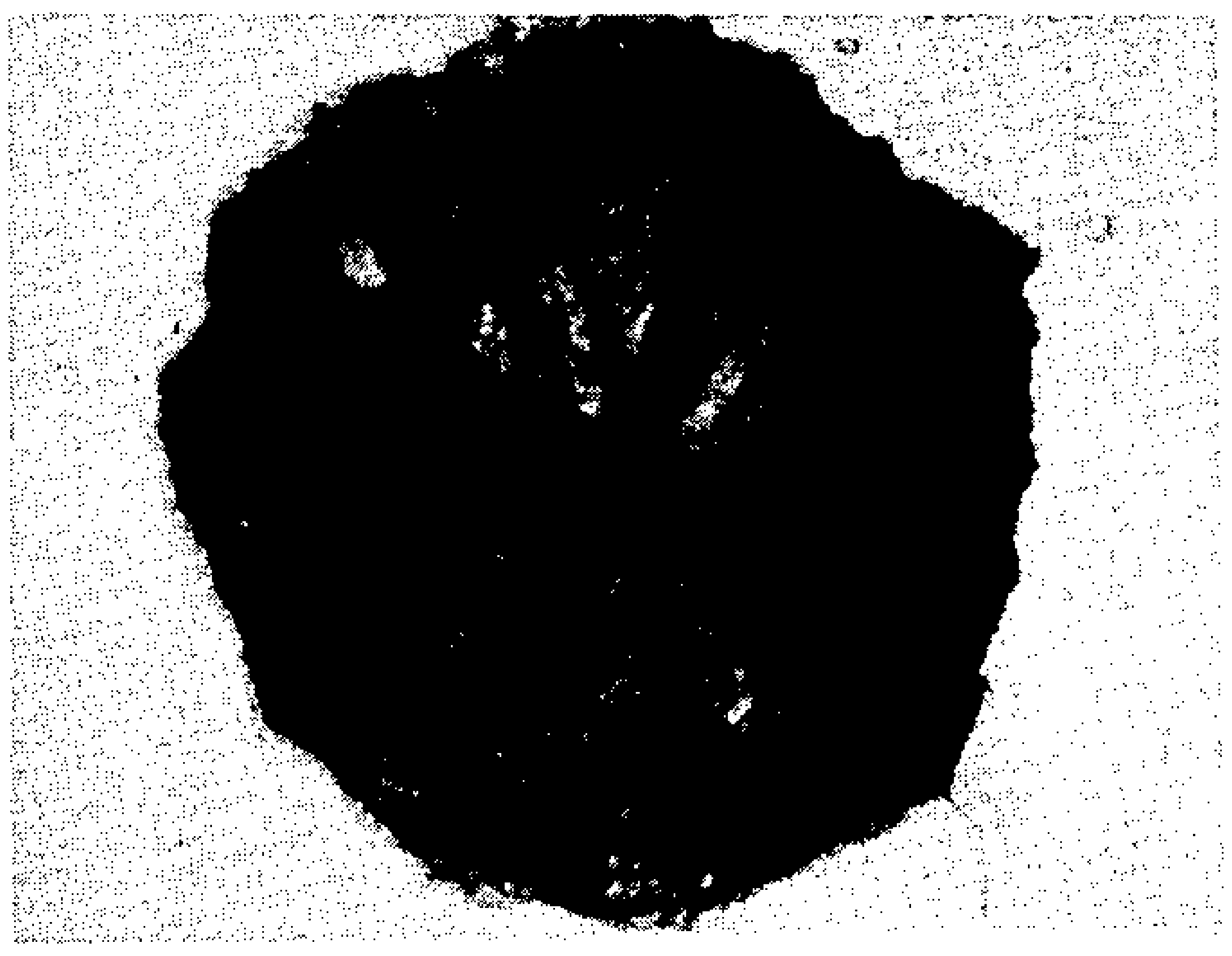

Fig. 10.

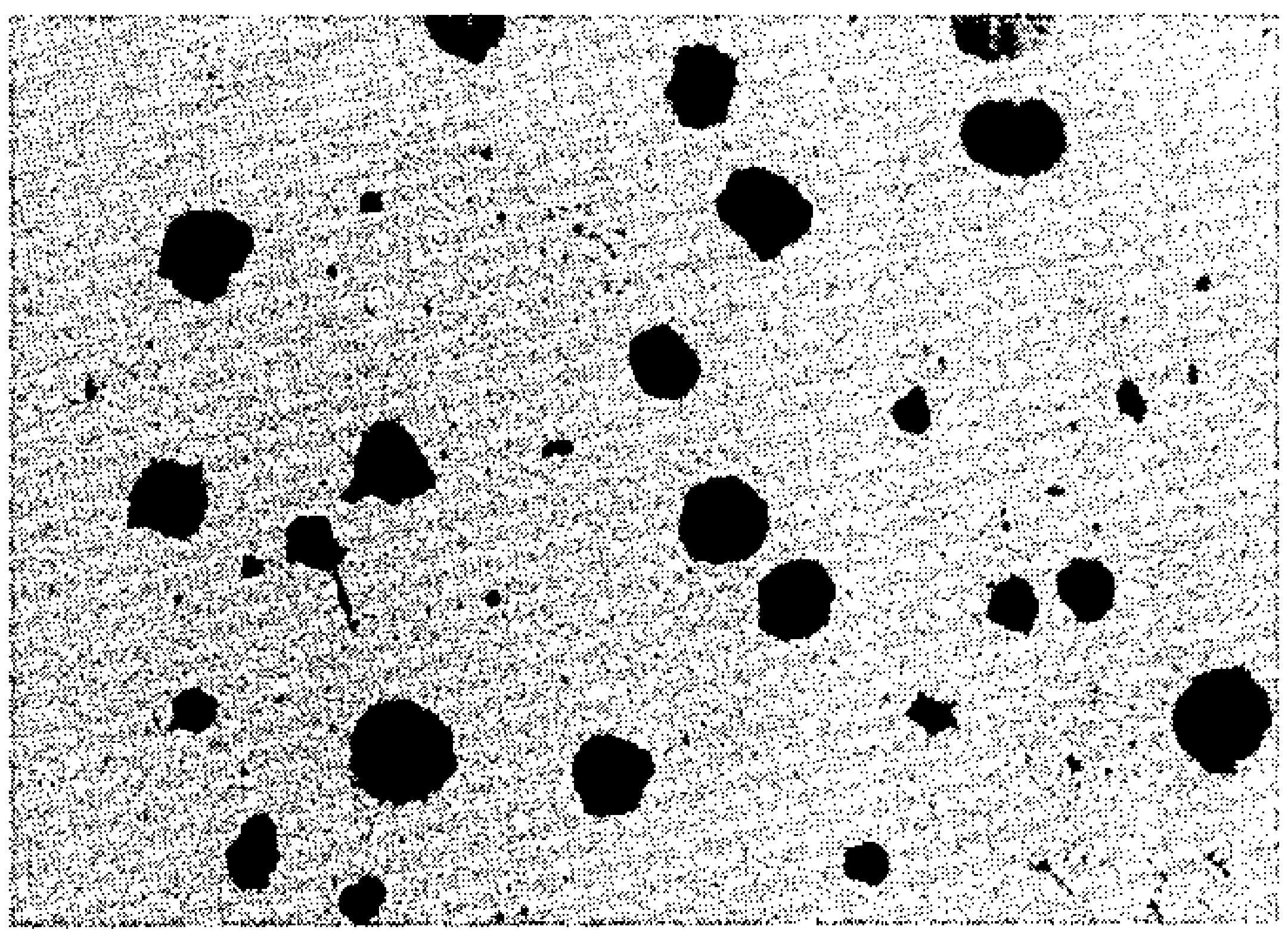

Fig. 11.

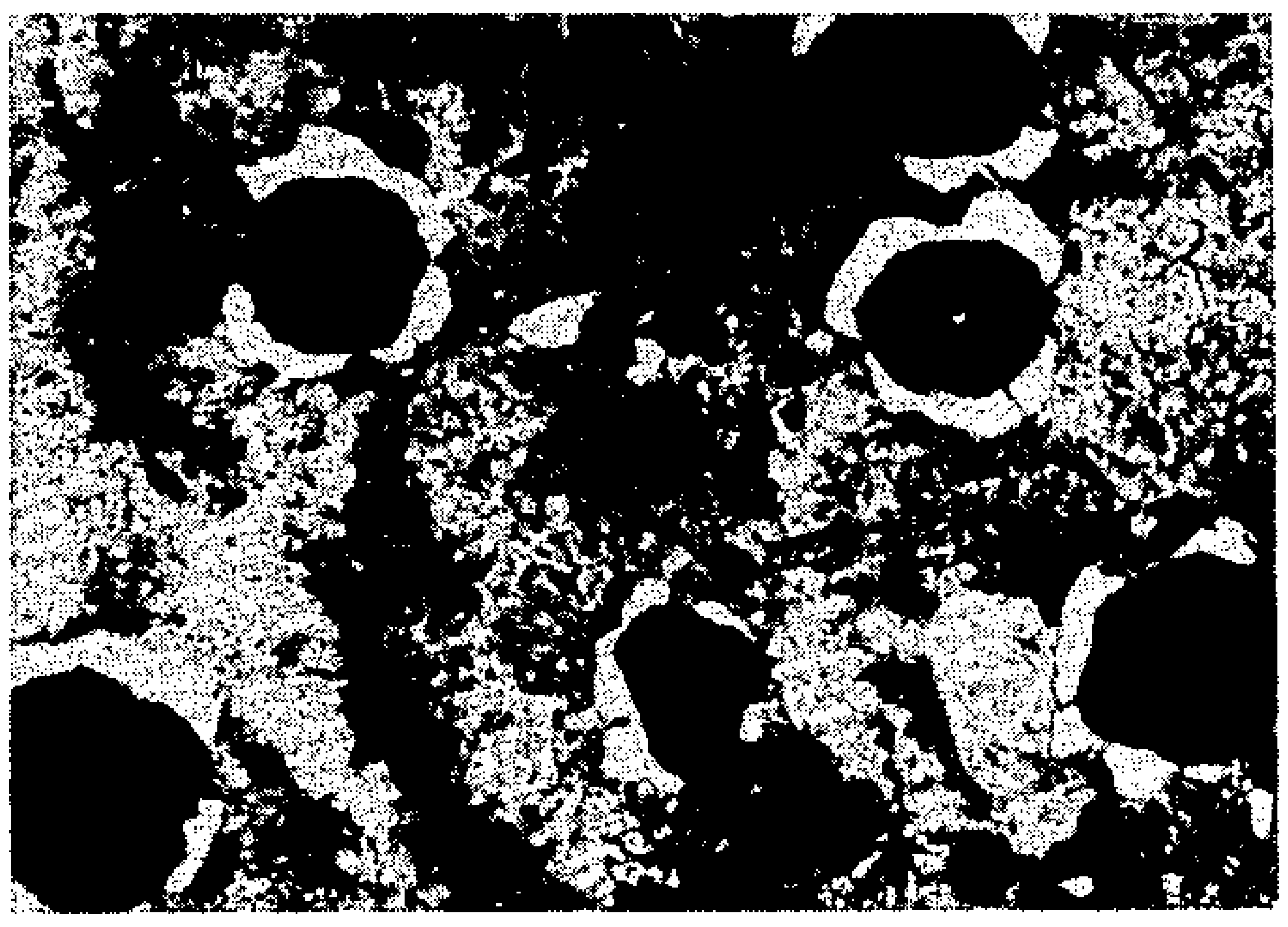

Fig. 12.

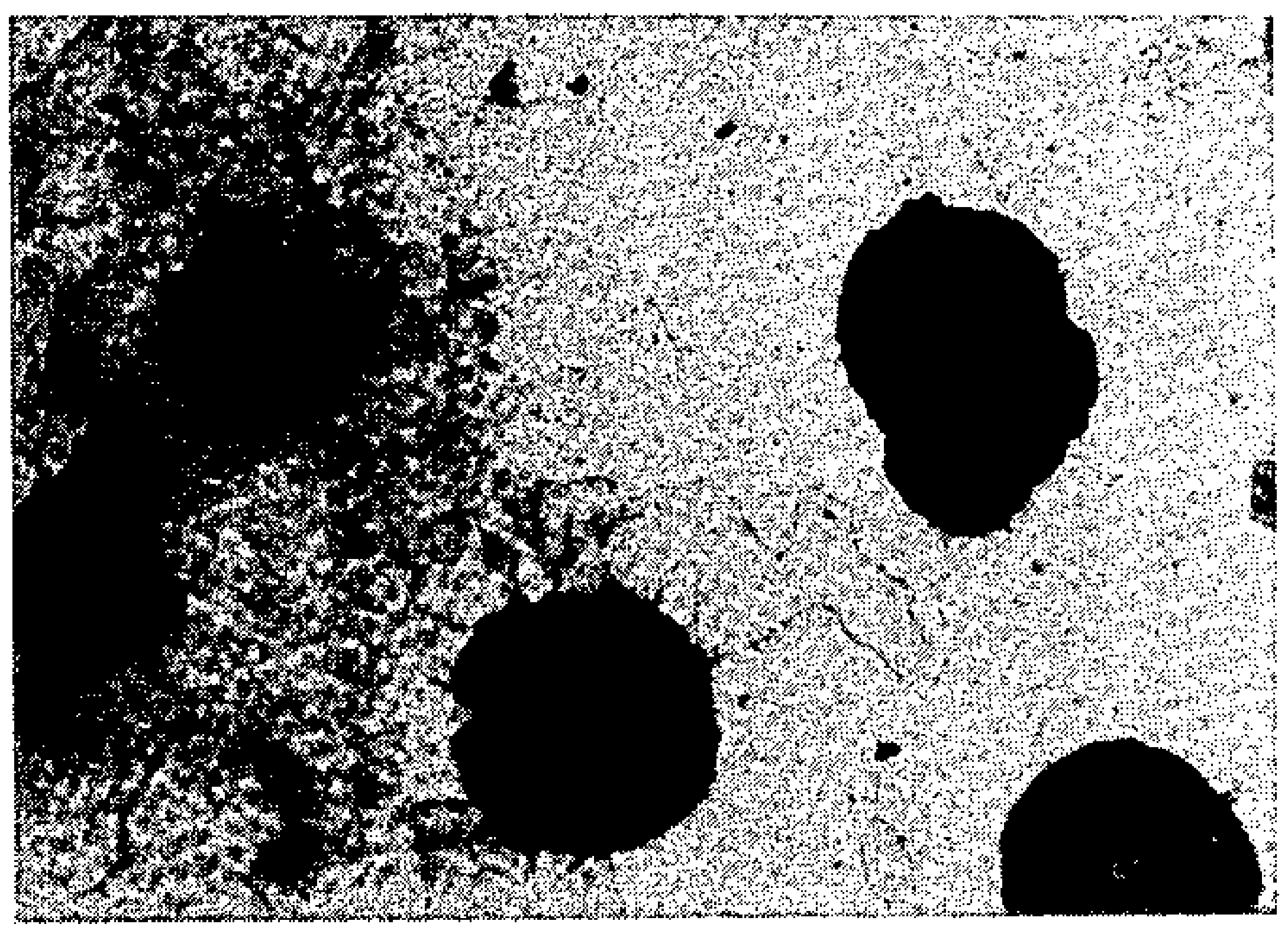

Fig. 13.

INVENTORS
KEITH DWIGHT MILLIS
ALBERT PAUL GAGNEBIN
NORMAN BODEN PILLING
BY

ATTORNEY

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CAST FERROUS ALLOY

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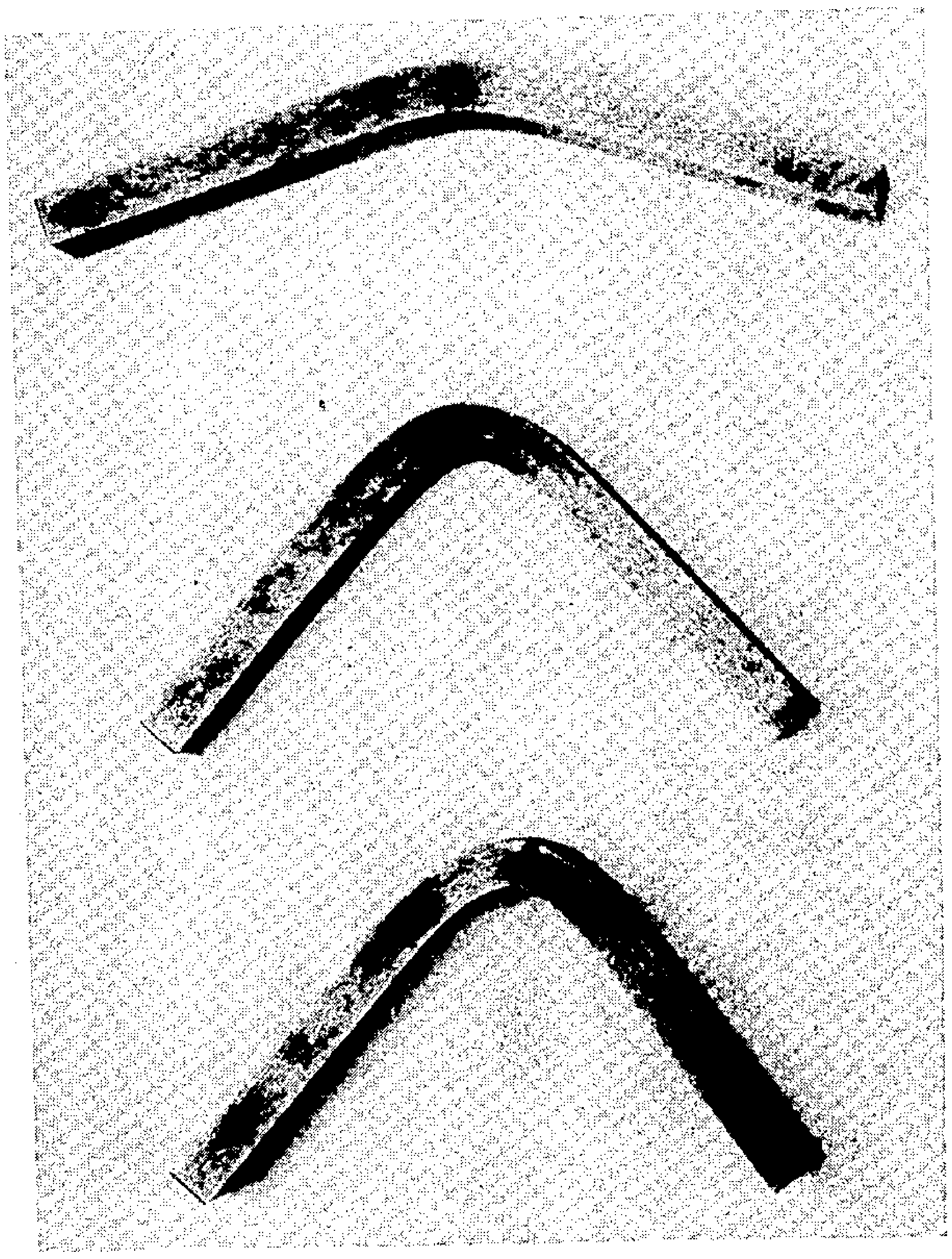

Fig. 14.

INVENTORS
KEITH DWIGHT MILLIS
ALBERT PAUL GAGNEBIN
NORMAN BODEN PILLING
BY
A. W. Deller
ATTORNEY

UNITED STATES PATENT OFFICE

2,485,760

CAST FERROUS ALLOY

Keith Dwight Millis, Rahway, Albert Paul Gagnebin, Red Bank, and Norman Boden Pilling, Westfield, N. J., assignors to The International Nickel Company, Inc., New York, N. Y., a corporation of Delaware

Application November 21, 1947, Serial No. 787,420
In Great Britain March 22, 1947

17 Claims. (Cl. 75—123)

The present invention relates to a unique ferrous alloy possessing advantageous features of gray cast iron and malleable iron, but devoid of defects and shortcomings thereof, and, more particularly, to a new ferrous product having improved and unusual combinations of properties, especially an improved and unusual combination of founding properties and mechanical and physical properties.

Cast iron is a eutectiferous alloy comprised mainly of iron, i. e., 50% or more of iron, and containing carbon, and usually a substantial amount of silicon, the carbon being present in excess of the amount which can go into solid solution in austenite at the eutectic temperature of the alloy, whereas steel is an alloy which contains less than this amount of carbon and which does not exhibit a eutectic of iron and carbon. Cast irons are usually considered as being either white cast iron or gray cast iron. Sometimes a cast iron which possesses some of the characteristics or structural features of a white cast iron and some of the characteristics or structural features of a gray cast iron is termed a "mottled cast iron," but for general purposes and for purposes of the present description, such a product is classified as either a white cast iron or a gray cast iron, depending upon which characteristics or structural features predominate. The kind of cast iron which has generally been most commonly used for centuries is gray cast iron, i. e., the soft and machinable kind in which the major part of the carbon not required to form the matrix structure is present as graphite in the "as-cast" condition. It has been recognized that the graphitic carbon occurs as elongated particles, commonly called "flake graphite," disseminated throughout the matrix. In polished gray cast iron sections, the flake graphite appears under the microscope as a grayish, soft constituent. The weakening discontinuities produced by flake graphite are reflected in the greatly reduced tensile strength, fatigue resistance, toughness and ductility of gray cast iron compared to a product made up entirely of the matrix component, e. g., a comparable steel. White cast iron is a harder, less ductile cast iron in which the major part of the excess carbon not required to form the matrix is present as combined carbon, i. e., as carbide, in the "as-cast" condition. While some advances, considered notable at the time, have been made in gray cast iron, no one has proposed a satisfactory, generally applicable method for eliminating from gray cast iron the detrimental effect of graphite due to its flake form in the "as-cast" condition. As a result, it has been necessary to resort to the use of ferritic or pearlitic malleable iron or even cast steel when higher properties or combinations of properties were required, although these engineering materials are considerably more expensive than gray cast iron and possess other disadvantages.

The present invention is based on the discovery that carbon in a high-carbon "as-cast" ferrous alloy, i. e., in an "as-cast" ferrous alloy containing carbon within the cast iron range, can be made to appear consistently and reproducibly in the form of dispersed gray-colored, soft particles substantially spheroidal or spherical in shape and having a radial structure, thereby eliminating the deleterious effects of flake graphite. In the ferrous alloy of the invention, this form of carbon can be obtained in the "as-cast" condition, i. e., without heat treatment, together with a combination of properties of an order entirely different from and higher than that obtained in gray cast iron.

It is among the objects of the present invention to provide a gray cast iron alloy or the like having an improved combination of properties.

Other objects and advantages of the present invention will be apparent to those skilled in the art from the following description taken in conjunction with the drawings in which:

Figs. 1 and 2 are reproductions of photomicrographs taken at a magnification of 25 diameters and showing, in polished sections of representative alloys, the spheroidal form of carbon obtained in the as-cast condition by the presence of a special element contemplated by the present invention;

Fig. 3 is a reproduction of a photomicrograph taken at a magnification of 250 diameters and showing the etched structure in the as-cast condition of an alloy produced in accordance with the present invention and containing the spheroidal form of carbon in a pearlitic matrix;

Fig. 4 is a reproduction of a photomicrograph taken at 50 diameters showing the occurrence of the spheroidal form of carbon in the etched structure of an alloy in the as-cast condition and produced in accordance with the invention;

Fig. 5 is a reproduction of a photomicrograph taken at a magnification of 1000 diameters of an etched specimen and showing in more detail the structure of the spheroidal form of carbon obtained in the alloys contemplated by the present invention in the as-cast condition;

Fig. 6 is a reproduction of a photograph at about natural size showing, from left to right, the fracture of a test specimen made from an as-cast ferrous base composition devoid of a special element contemplated by the invention and the fractures of test specimens made from a series of as-cast ferrous alloys containing increasing amounts of a special element contemplated by the present invention;

Figs. 7 to 9, inclusive, are reproductions of photomicrographs taken at a magnification of 100 diameters on polished sections and illustrating the as-cast structure of the alloys in the three right-hand test specimens shown in Fig. 6 and show the effect of progressively increasing the retained amount of a special element contemplated by the invention;

Fig. 10 is a reproduction of a photomicrograph taken at a magnification of 1000 diameters on an etched specimen and showing in detail the structure of the spheroidal form of carbon obtained in the alloys contemplated by the present invention after having been given a treatment to "ferritize" the matrix;

Figs. 11 and 12 are reproductions of photomicrographs taken at magnifications of 100 diameters and 250 diameters, respectively, and showing the polished and etched structures, respectively, of a composition in the as-cast condition after the introduction of a required retained amount of a special element contemplated by the present invention;

Fig. 13 is a reproduction of a photomicrograph taken at a magnification of 250 diameters and showing the etched structure of the alloy of Fig. 12 containing a special element contemplated by the invention after a treatment to ferritize the matrix; and

Fig. 14 is a reproduction of a photograph of three bend-test specimens made of the alloy contemplated by the present invention, one specimen having been tested in the as-cast condition and the other two specimens having been tested after different "ferritizing" treatments.

The present invention provides a novel ferrous product containing at least about 50% iron, carbon and silicon within the cast iron range, the carbon in excess of that required to form the matrix being predominantly in the uncombined form, and containing a controlled amount at least equal to a critical minimum of about 0.04% retained magnesium, preferably at least 0.05% retained magnesium. The product of the invention is characterized by a microstructure containing carbon in the form of randomly dispersed, soft, gray-colored, substantially spheroidal or spherical particles or agglomerates of such particles. In accordance with the present invention, the aforementioned microstructure of the product is obtained in the as-cast condition to provide a novel product characterized by an improved combination of properties and by a structure not reproducibly obtained prior to the present invention in cast irons in the as-cast condition. The product of the invention is preferably substantially devoid of flake graphite. Another distinguishing feature of the microstructure is that usually no sulfied particles are seen embedded in the matrix, whereas ordinary cast iron usually contains many easily recognized sulfide inclusions embedded in the matrix. The spheroidal form of carbon can be obtained in any matrix obtainable in known ferrous alloys which, as cast, contain flake graphite, such as gray cast irons. The ferrous matrix may be pearlite, ferrite, martensite, austenite, an acicular constituent (for example, bainite or other transformation products of austenite explained by the S-curve), tempered martensite or sorbite, etc., or the known combinations thereof. The matrix constituents, structure and properties can be controlled in well known manners by control of the composition without or with well known heat treatments. In ferrous-base compositions containing uncombined carbon embedded in ferrous matrices of the aforementioned kind, the presence of retained magnesium in accordance with the invention causes uncombined carbon to occur in the spheroidal form. The essential features of the novel magnesium-containing product of the invention are the presence of carbon in amounts within the cast iron range, the presence of a substantial amount of the carbon in the uncombined form, and the presence of about 0.04% or more retained magnesium with the remainder essentially iron to provide an as-cast ferrous matrix in which the soft, gray-colored spheroids of uncombined carbon are dispersed. Usually, silicon is also present in the novel product of the invention. In essence, the aforementioned novel ferrous alloy of the invention contains about 0.04% or more retained magnesium, the balance of the alloy being a gray cast iron composition, i. e., the balance being a composition which without magnesium would have the constitution of a gray cast iron normally having the uncombined carbon in the form of flakes.

Under the microscope, the difference between the as-cast product of the invention and gray cast iron is readily apparent. In polished sections of the as-cast novel product provided by the present invention, some or practically all of the spheroidal form of uncombined carbon appears as compact, soft, gray-colored, rounded particles, usually nearly circular, or as agglomerates or groups of such particles. The occurrence of the spheroidal form of carbon in polished (unetched) specimens of the magnesium-containing ferrous alloy in the as-cast condition is illustrated in Figs. 1 and 2. The appearance of the spheroidal form of carbon in etched sections of the alloy in the as-cast condition is illustrated in Fig. 3 wherein the spheroidal carbon occurs in a matrix of pearlite. When the composition is such that the matrix contains ferrite as well as pearlite in the as-cast condition, the ferrite often tends to occur around the spheroidal carbon particles, as illustrated in Fig. 4. In the as-polished condition and particularly in the etched condition, the rounded particles of carbon seen in properly polished sections have a well-defined radiating structure. Fig. 5 shows the representive radiating or radial structure of the spheroidal or rounded particles which at a magnification of 1000 diameters usually are about 1 to 2½ inches in average diameter. In polished sections of gray cast irons, the uncombined carbon has appeared entirely or almost entirely as elongated particles or flakes which are very long in comparison to their width. The spheroidal or rounded particle seen under the microscope in polished sections of the magnesium-containing alloy generally has the appearance of a plurality of crystals radiating from approximately the center, i. e., a radiating and polycrystalline appearance. When viewed under reflected polarized light through a microscope, radiating portions or sectors of the rounded particle (which apparently produce the radiating or radial structure of the particle) extinguish at different intervals as the stage of the microscope is revolved. In gray cast irons containing flake graphite, the entire flake, which has been recognized to be a single crystal, usually extinguishes at one time during the stage rotation.

RETENTION OF MAGNESIUM

A feature of the present invention in obtaining the aforementioned product having a microstructure containing the spheroidal form of carbon is the introduction of magnesium into the molten bath and the retention of at least a critical minimum amount of magnesium in the final product. It is not sufficient merely to add magnesium to the molten bath. The presence of retained magnesium in the aforementioned product is essential in order to obtain the aforementioned structure therein. While the theory of the magnesium effect on the form of carbon and on the properties of the new alloy is not fully apparent, it has been found that the presence of retained magnesium is required in order to obtain the compacted spheroidal or spherical, soft, gray-colored form of carbon and to obtain the high combination of properties in the ac-cast ferrous alloy of the present invention. If the final product contains no retained magnesium or too small an amount of retained magnesium, the results of the present invention as indicated by either the properties or the carbon form are not obtained.

PREFERRED COMPOSITIONS

The magnesium-containing preferred ferrous alloy having the higher order of properties and the spheroidal form of carbon in the as-cast condition will generally contain over 1.7% but less than 5% carbon. More preferably, the carbon content will fall within the range of about 2.0% to 4.5% or even within the range of about 2.5% to 4%. The carbon content of said alloy can vary considerably without adversely affecting the properties and, in this respect, differs from "high strength" gray cast irons which have been restricted to the lower carbon contents of the cast iron range, usually below 3% carbon, in order to obtain optimum strength properties. In fact, it has been found that the aforementioned alloy of the invention has high tensile strength when the carbon content is increased to between 3% and 4%. All the carbon need not be present in the form of soft, gray-colored spheroids. For example micro-constituents of the ferrous matrix usually contain combined carbon. In general, less than half of the carbon present in excess of that required to produce the matrix structure will be combined carbon in the aforementioned as-cast ferrous alloy of the invention. In most cases, alloys produced in accordance with the invention will have a combined carbon content not more than half of the total carbon content. The uncombined carbon will be present as compacted particles, at least some of these particles and more preferably most or even all of the particles occurring in a substantially spheroidal or spherical, soft, gray-colored form. The occurrence of some of the carbon in the very compact substantially spheroidal or spherical form in the as-cast condition is accompanied by a compacting of the remaining uncombined carbon, but this compacting may be to a leser extent. This compacting, including the presence of about 25% or more of the uncombined carbon as spheroids or spheres (in the presence of about 0.04% or more retained magnesium), indicates that a notably improved combination of properties will be obtained of an order different from and higher than that obtained when no magnesium or smaller amounts of magnesium are present. In its preferred embodiment, the as-cast product contains about 0.05% or more retained magnesium, e. g., about 0.05% to 0.2%, and contains uncombined carbon which occurs predominantly, and often occurs practically entirely, as substantially spheroidal compact particles of about the same size as, but different in shape and structure from, the irregular and fluffy-appearing patches or aggregates of temper carbon obtained in American malleable iron. Retained magnesium contents within the preferred range of 0.055% or 0.060% to 0.15% have given highly satisfactory results and, in general, have assured high properties as well as the presence of the uncombined carbon predominantly or practically entirely in the spheroidal or spherical form. A striking characteristic which is exhibited by the product, particularly in its preferred embodiment, is the steely appearance of its fracture as compared to the gray fracture of gray cast iron. The as-cast alloy also has the unexpected characteristic that when struck with or against a hard object, e. g., dropped upon a concrete floor, it emits a definite steel-like ring rather than the duller sound emitted by gray cast iron. The minimum retained magnesium content, at which the spheroidal form of uncombined carbon is induced, generally increases slightly with the carbon content and/or silicon content of the alloy and with the section size of the casting to be produced. It has been found that when some of the carbon is in the aforementioned spheroidal of spherical form, the use of a slightly higher amount of retained magnesium, for example, about 0.01% to 0.02% additional retained magnesium to bring the magnesium content above the preferred minimum of 0.05% to 0.06%, is sufficient in most cases to cause the uncombined carbon to appear predominantly in a substantially spheroidal or spherical form and to impart the markedly higher order of properties provided by the preferred alloy of the invention in the as-cast condition. A peculiar effect that has been observed in some compositions containing borderline amounts of retained magnesium, e. g., 0.035% to 0.043%, just sufficient to initiate the occurrence of the aforementioned spheroidal or spherical form of carbon, is that such occurrence is first noted in a zone near the surface of the casting. In a fractured standard 1.2-inch diameter arbitration bar, this effect near the surface is indicated by the presence of an outer rim having a steely appearance and containing the spheroidal or spherical form of carbon in the as-cast condition. The presence of this rim imparts a notable improvement in properties to the product but one which is not as high as when the product contains the spheroidal or spherical form of carbon throughout the cross section. The combined carbon in many alloys producible in accordance with the present invention will not exceed approximately 1.2%, e. g., will fall within the range of about 0.3% to 1.2%, in the as-cast condition. The foregoing range is illustrative of the amounts of combined carbon, but, as those skilled in the art will appreciate, the combined carbon may be outside this range. For example, in a composition having high graphitizing power and containing large amounts of silicon, the matrix may be practically all ferrite in which case the combined carbon will be very low. Usually, the preferred as-cast alloy of the invention will contain at least 1.3% or 1.5% uncombined carbon, and more usually over 2% uncombined carbon, in the as-cast condition. The silicon content of the preferred as-cast alloy having the spheroidal or spherical form of carbon will be at least 1% of the alloy and will usually fall within the range of 1.3% to 5% or 5.5% or even 6%, preferably within the range of 1.5% to 4.5%. It has been found desirable to maintain the silicon below about 3.5% or 3% or even 2.5% because increasing the silicon content over these amounts apparently lowers the mechanical properties, especially toughness, tensile strength and/or ductility, although the properties are at a very high level as compared to those of gray cast irons having similar high silicon contents. For some applications, it may be desirable to produce a product having a hard chilled surface portion or outer layer in which the carbon is in the combined form to provide wear resistance or the like while also obtaining in the product a core or body portion having substantial amounts of uncombined carbon in the spheroidal form and having the improved properties provided by the invention. Such products may be made by controlling the known factors which affect the amount of graphitization that will take place in the various portions of the product. A particularly responsive range of compositions having sufficient graphitizing power to avoid, under most practical foundry conditions, the occurrence of massive carbides or incidental chills in sections of 3/8" in thickness or greater, is defined by the carbon limits 2.5% to 4.5%, the silicon limits 1.0% to 4.0%, and the silicon content being so related to the carbon content that the sum of

$$\frac{\%\,\mathrm{Si}}{3.1}+\frac{\%\,\mathrm{C}}{4.5}$$

is greater than 1.00. It is desirable that within this range and especially toward the lower limits of carbon and silicon, the alloy product be substantially free from tellurium and bismuth in order to avoid vagaries in graphitizing power and irregular tendencies toward chilling.

The retained magnesium content of the as-cast alloy will be less than about 0.4% or 0.5% and will generally fall within the range of at least about 0.04% up to 0.25% or 0.3%. It is recognized that magnesium determinations of the order involved herein are difficult to make, and the values given herein are based upon analyses by a chemical wet method and are reproducible within about 0.005%. As the skilled analytical chemist will understand, the wet method for obtaining the correct values of retained magnesium in an iron-base composition must take into account the elements associated with magnesium in the product, for example, iron, phosphorus and other elements which may affect the values obtained for magnesium.

The as-cast alloy may be free from alloying elements or may contain substantial amounts of alloying elements. No common alloying elements in the usual amounts employed heretofore in gray cast iron, with the possible exception of large amounts of copper, have been found to have a marked detrimental effect in interfering with the desired function of magnesium or to prevent the results of the invention from being obtained in the as-cast condition. The alloying elements may be present to affect the matrix constituents, microstructure and/or properties in the manner well known to those skilled in the art. Examples of such alloying elements are nickel, molybdenum, chromium, manganese, silicon, etc. Thus, the invention includes cast iron compositions having a pearlitic matric (i. e., pearlitic cast iron compositions) and containing

2% nickel, martensitic cast iron compositions containing 4.5% or 5% nickel, austenitic cast iron compositions containing over 20% nickel (e. g., 21% or 36%), acicular cast iron compositions (such as disclosed by Reese et al. in U. S. Patent No. 2,324,322) containing 2% nickel and 0.6% molybdenum with or without up to 0.5% chromium and cast iron compositions containing large amounts of silicon (e. g., 4% or more) and having a predominantly ferritic matrix as cast. As will be apparent to those skilled in the art, the whitening or carbide-stabilizing properties of some alloying elements must be borne in mind in view of the requirement that the product contain a substantial amount of uncombined carbon. For this reason, it is preferred that the chromium content normally not exceed about 1%, more preferably not over about 0.5% or 0.6%. However, the amount of chromium that can be tolerated depends upon the composition of the product as a whole. Thus, satisfactory results were obtained in an as-cast austenitic ferrous product which contained about 2% chromium in addition to about 20% nickel, 1.2% manganese, 2.2% silicon, 2.6% carbon and 0.075% magnesium. Manganese, a milder whitener or carbide-stabilizer, can be tolerated in larger amounts, and the results of the invention have been obtained with as-cast compositions containing up to about 2.5% manganese. Larger amounts of manganese can be present when the alloy has an austenitic composition or matrix. In general, manganese tends to lower certain mechanical properties, especially in those as-cast alloys in which the iron is in the alpha form, and it is preferred that the manganese content not exceed 0.8% or 1%. Higher ductility and toughness are particularly notable in such alloys when the manganese content does not exceed about 0.3%. Aluminum decreases carbide stability and acts as a graphitizer but is not favored because of its adverse influence on casting properties. The term "alloying elements" includes residual amounts of those elements added as treating agents, degasifiers, etc., and those elements introduced along with the magnesium as carrier elements for magnesium or introduced by master alloys containing magnesium. When copper is present in large amounts, it interferes with the formation, in the as-cast condition, of the spheroidal or spherical form of carbon required by the present invention. For this reason, it is preferred that copper not be employed in amounts exceeding 3%, and more preferably not exceeding 2%, without first determining the effect of copper upon the carbon formation in the particular composition. Certain alloying elements such as nickel may in conjunction with copper increase the tolerance for the copper. It has been found that certain other elements comparatively rare in and not usually found in cast iron should be avoided or should be present only in traces or very small amounts because they interfere with the formation of the spheroidal form of carbon and/or the attainment of the high properties provided by the invention. These subversive elements include tin, lead, antimony, bismuth, arsenic, selenium, tellurium, etc. It may be possible to compensate for the presence of a small amount of these subversive elements, preferably less than about 0.1%, by increasing the amount of magnesium introduced into the bath and/or by the introduction of specific elements to form compounds of high stability with the subversive element. The addition of tin has been found to be particularly detrimental, and the tin content should be kept below 0.1%, preferably below 0.05%. It is more preferred that the alloy be devoid of tin. Phosphorus (which does not interfere with the formation of spheroidal carbon) is usually considered an impurity but may be added sometimes to obtain specific effects. The phosphorus content may be as high as 0.5% or more, but preferably should not exceed approximately 0.25% and more preferably should not be more than about 0.15%. Where high properties, especially impact properties and/or ductility, are desired in the as-cast ferrous alloy, it is recommended that the phosphorus content not exceed 0.06%, e. g., 0.02% to 0.06%. In the product of the present invention, the sulfur content is low, usually not exceeding about 0.02%, and is commonly between about 0.007% or 0.010% and 0.015% unless the raw materials and/or the process employed in producing the product introduce less sulfur. The balance of the composition of the magnesium-containing product is iron (including small amounts of impurities, preferably less than a total of about 0.5%). The iron content, in general, is at least 50% or 55% by weight of the alloy and in the case of unalloyed or low-alloyed magnesium-containing products will be at least about 90% or 87% of the total composition. In the case of the more highly alloyed compositions, usually having an austenitic matrix, the iron content may be considerably lower than 87%.

PRODUCTION OF CASTINGS

The product of the invention having high properties in the as-cast condition can be produced by a method which comprises establishing a molten ferrous alloy bath of such composition that if cast after inoculation it would be a gray cast iron, e. g., if cast in a sand mold or in the particular kind of mold to be employed (if it is a different mold) shortly after a late inoculating addition such as conventionally employed in treating cast iron, incorporating magnesium into said bath to provide the required retained magnesium content and inoculating the bath at least once (preferably with a late addition of at least 0.2%, or more preferably at least 0.3%, e. g., 0.3% to 2.5% or 3%, more preferably 0.4% to 1.2%, of silicon as a silicon-containing metallic agent such as ferro-silicon), and casting the inoculated bath. The treated inoculated metal can be cast in accordance with accepted foundry technique, bearing in mind that the shrinkage characteristics of the alloy are such that castings made from the alloy should be gated and risered more in conformity with the practice employed for steel than that employed for unalloyed or low-alloyed gray cast iron. In view of the fact that usually about 0.03% to 0.06% magnesium is lost, possibly by oxidation, in about ten minutes in hand ladles such as employed in a foundry and the effect of the inoculation is lost if the treated bath is held for too long a period, the magnesium treatment and the inoculation in actual practice should be carried out in such equipment that the magnesium-containing, inoculated metal can be cast shortly thereafter. The aforesaid bath to be treated with magnesium will have a rather high graphitizing power or potential. The graphitizing power or potential of the bath is the summation of a number of possible variable factors and conditions known by those skilled in the art to influence graphitization. In inoculating the magesium-containing bath, it is preferred that the graphitizing inoculant be separately introduced into the bath after the magnesium introduction. While inoculation with ferro-silicon, e. g., an iron alloy containing about 50% to 95% silicon, gives satisfactory results, inoculation with other metallic silicon-containing agents or alloys such as nickel-silicon alloys or nickel silicide, calcium-silicon alloys or calcium silicide, silicon metal, and various proprietary inoculating alloys commonly used for reducing dendriticism and reducing chill in foundry gray cast irons may be employed. Metallic aluminum-containing agents have a tendency to produce viscous slags difficult to separate from the metal. As magnesium has been found to have by itself a very strong whitening effect, very few molten baths employed in actual practice can be treated with magnesium in accordance with the invention and cast without inoculation to produce the novel product of the invention or to obtain the novel combination of properties provided by the invention. In some cases, where the graphitizing power of the magnesium-containing bath is very high, e. g., when the carbon plus one-third the silicon is approximately 5% or more at the time of the magnesium introduction, inoculation may not be necessary to insure that a sufficient amount of the total carbon will be in the uncombined form in the solidified casting, although it has been found that inoculation is always beneficial. If the inoculation precedes the introduction of the magnesium, it may not produce the desired results in the as-cast product. However, certain baths having high graphitizing power apparently can be inoculated prior to the magnesium introduction, for example, an inoculated bath containing 4% carbon and 2% silicon (including 0.75% silicon introduced for inoculation just prior to the magnesium introduction). By employing an agent containing both magnesium and the inoculating element, for example, a nickel-magnesium-silicon alloy containing about 30% or 50% or more silicon, it is possible to introduce the magnesium and the inoculant by means of a single addition agent. If the inoculating addition is ineffective or the effect of inoculation has been lost, this can be remedied by one or more re-inoculating additions (along with or after the magnesium introduction) which may each incorporate a smaller amount of the inoculant, e. g., as little as about 0.1% or 0.15% of silicon. The magnesium-treated reinoculated bath should be cast shortly after the last inoculation. By periodically inoculating the bath having the required retained magnesium content, it is possible to cast a large treated bath over a considerable period of time.

If any undesirable elements which tend to combine with and/or counteract the effect of magnesium, for example, sulfur, etc. (including oxygen, if any be present in the molten cast iron bath as is believed possible by some metallurgists), are present in the bath or are subsequently added, the amount of magnesium introduced should be increased by the amount required to counteract the effect of the presence of these elements or impurities by removing the elements or by otherwise overcoming their effects. Sulfur is the magnesium-counteracting element which is most likely to be present. It has been found that all the magnesium-containing agents which produced the spheroidal form of uncombined carbon obtained by the invention also introduced the magnesium in a form which combined with sulfur present in the bath with the result that the sulfur content was reduced to about 0.010% to 0.015%, e. g., 0.012%. The results also have clearly indicated that only the unconsumed excess of magnesium is then available to perform its function of controlling the form of the uncombined carbon and providing the required retained magnesium content. Since many baths that can be treated in accordance with the invention will usually contain sulfur in various amounts as high as even 0.3% or more, it is therefore necessary to add an amount of magnesium which is sufficient to introduce magnesium to combine with the sulfur and to provide an excess sufficient to give the retained magnesium content required by the invention. The introduction of about three parts by weight of magnesium is required to react with about four parts by weight of sulfur. In actual practice, it is preferred to introduce one part by weight of magnesium for each part by weight of sulfur to be removed. Thus, if the bath contains 0.155% sulfur and it is desired to obtain a retained magnesium content of 0.06%, then, since the sulfur content must first be reduced from 0.155% to about 0.015%, about 0.14% magnesium is introduced for this purpose and an additional 0.06% magnesium must be introduced to provide the desired retained magnesium content. A total of about 0.20% magnesium would therefore have to be introduced into the molten bath. The amount actually added to the bath would be even greater because in practically all cases, except when the more preferred magnesium addition agents described hereinafter are employed, it is possible to obtain an introduction of only a small amount of the magnesium added to the bath. This is apparently due mainly to its high volatility at the temperatures involved and also due to its low solubility in iron. The magnesium treatment very effectively removes sulfur from the molten ferrous bath even when it is under the influence of acidic conditions such as created by furnace linings, ladle linings, slags, etc., of a siliceous nature or other acidic nature as well as under neutral or basic conditions created by the furnace lining, the ladle lining, the slag, etc. Another unusual feature of the invention is that the removal of sulfur by the magnesium treatment does not require the presence of any slag and takes place regardless of whether a slag is or is not present.

The introduction of the essential amounts of magnesium required by the present invention can be accomplished in a number of ways. However, the amount of magnesium to be added to the bath will depend upon the retained magnesium desired, the additional amount of magnesium required to overcome the presence of interfering elements such as sulfur, etc., the amount of magnesium lost by delaying the casting of the bath after the introduction of the magnesium and the proportion of magnesium recovered in the bath from the magnesium addition agent. The last factor involves the losses of magnesium incurred in attempting to introduce the magnesium into the molten bath. This last factor presents considerable difficulties, as it has been found that in many cases no magnesium can be recovered from the addition agent employed or only a small amount recovered, e. g., 3% of the amount added. It is known that the temperatures of molten iron baths usually exceed the boiling temperature of magnesium. The fact that the introduction of solid elemental magnesium into molten iron baths produces a reaction of explosive violence has been well recognized in the art heretofore, and the introduction of magnesium into molten iron has been generally regarded as being impossible on a practical scale. Proposals have been made by the prior art to solve an analogous problem encountered in the introduction of various highly volatilizable elements into molten baths, for example, U. S. Patent No. 1,931,144 relating to the introduction of sodium as sodium vapors into a molten bath to purify the bath. It has been found that magnesium in the form of a solid magnesium-containing agent can be added in a number of ways to introduce into the molten bath magnesium in a form capable of acting as if it were introduced in elemental form, for example, in a form available to react with the sulfur which is usually present in the molten carbon-containing ferrous bath being treated. Metallic magnesium can be added with due caution in solid elemental form directly to the molten ferrous bath when the bath is "cold." Magnesium may also be aded in the form of briquettes with binders and the like to decrease the burning of the magnesium and to allow the magnesium to become incorporated more quietly and with greater recovery of the magnesium in the bath. Of course, briquettes may also be employed to introduce the magnesium in the other forms described herein, e. g., as magnesium-containing alloys.

It is preferred to add the magnesium as a metallic agent, such as an alloy, containing about 2% to about 40% magesium. Suitable alloys include those alloys which are sometimes referred to as intermetallic compounds, e. g., $MgNi_2$, or mixtures of an intermetallic compound with a metal or with another intermetallic compound, e. g., $MgNi_2+Ni$ or $MgNi_2+Mg_2Ni$. It has been found desirable to introduce the magnesium as an alloy with one or more metals in which the magnesium is soluble in the molten condition, these metals in turn being soluble in iron in the molten condition. In carrying the invention into practice, nickel, copper and/or silicon are the preferred metals with which the magnesium is alloyed to form the addition agent. The usefulness of copper is somewhat limited due to the desirability of not introducing excessive copper in the final product. In practice, very satisfactory results have been obtained with binary and more complex alloys of nickel and magnesium. A series of alloys which have given satisfactory results are the nickel-magnesium alloys containing from about 4% to about 20% magnesium. It has been found that when the nickel-magnesium alloys also contain carbon, for example, up to the maximum amount that the alloys will take up, the addition characteristics of the alloys, especially those containing about 10% to 15% magnesium, are improved. Furthermore, by first producing a molten nickel-carbon alloy and then introducing magnesium therein, the manufacture of a nickel-magnesium addition alloy is facilitated. Nickel-magnesium-carbon alloys containing 10% to 15% magnesium and containing carbon within the range of about 1% to 4%, preferably about 2% to 4%, have given good results when used as addition agents.

Various means may be employed to increase the proportion of magnesium introduced into the bath for any given composition, but the high reactivity of magnesium should always be borne in mind. The lower the temperature of the molten bath at the time of the magnesium introduction, whether as an alloy or in another form, the higher will be the proportion of magnesium introduced from a given agent. Likewise, the proportion of magnesium introduced can be increased by blowing a pulverulent or powdered magnesium-containing alloy through a tube or the like into the molten bath below the surface thereof by means of a gas which is inert or nonoxidizing with respect to magnesium. The proportion of magnesium introduced into the molten bath from a given magnesium-containing alloy of lower density than the molten bath being treated can be increased by submerging the addition alloy below the surface of the bath, e. g., by an inverted cup attached to a rod or handle or by adding the crushed addition alloy to a molten stream of the metal bath as the bath is being poured into a ladle. From the standpoint of ease of introduction of magnesium, the 96% nickel-4% magnesium alloy is very satisfactory because this alloy has about the same density as the molten bath and tends to sink therein so that substantially no burning of magnesium occurs. Because of the high nickel concentration of this addition alloy, substantial amounts of nickel are also introduced in the molten bath and carried over into the final product. As the magnesium concentration in the nickel-magnesium alloys is increased, the burning and loss of the magnesium is increased since the alloys become progressively less dense and are less immersed in the molten bath. The nickel-magnesium alloys may also contain other elements such as silicon, manganese, copper, iron, etc., but it has been found that, in general, the proportion of magnesium introduced into the molten bath from the addition alloy increases as the nickel content of the addition alloy increases. For example, replacing part of the nickel by iron usually decreases the proportion of magnesium introduced from the addition alloy. The following Table I sets forth the approximate composition of some magnesium-containing alloys which can be employed as addition agents for the purpose of introducing magnesium into the molten bath in the amounts required by the invention.

Table I

Alloy	Per Cent Mg	Per Cent Ni	Per Cent Si	Per Cent Cu	Per Cent C	Per Cent Mn	Per Cent Fe	Per Cent Others
A	2	98						
B	4	96						
C	5	95						
D	7	93						
E	10	90						
F	13	87						
G	19	81						
H	20	80						
I	14	Bal.			2-2.5			
J	12	Bal.			2.8			
K	14	Bal.			3.7			
L	5	75	20					
M	5	65	30					
N	5	64	30					1 Ca
O	5	45	50					
P	10	50	40					
Q	4	30			2.4		Bal.	
R	4	50			2.6		Bal.	
S	8	50			2.5		Bal.	
T	5-10	30	20				Bal.	
U	11	28	18				Bal.	
V	10		50				Bal.	
W	15		40			45		
X	20		40			40		
Y	5			52		43		
Z	14			58		Bal.		
AA	5			95				
BB	20			80				

PROPERTIES AND CHARACTERISTICS

The product provided by the present invention containing the spheroidal form of carbon in the as-cast condition provides the art with a new metallic engineering material. The as-cast alloy has excellent founding properties, e. g., it can be readily cast into molds of intricate design, the molds being made of the usual materials employed in molds for casting cast iron. The molten alloy has better castability than steel and has a castability comparable to, or even better than, many grades of cast iron, especially the higher quality gray cast irons which, in order to develop high mechanical properties, are limited to the lower carbon and silicon contents of the cast iron range. In addition, the aforementioned as-cast alloy of the invention has the desirable property of being strongly self-feeding in the mold, thus providing an automatic check on the quality of the castings made of the new alloy because improperly fed castings often will be misshapen and will exhibit depressed or shunken regions on the surface. It has been found that the magnesium-containing molten composition has a somewhat greater chilling propensity than has a similar magnesium-free gray cast iron composition but the chilling propensity is affected to a lesser extent by changes in the carbon content than is that of conventional gray cast iron. The as-cast product of the invention has an exceptionally high combination of strength and ductility in the as-cast condition and in this respect is far superior to any cast iron of comparable composition available heretofore. For comparable matrices, the improved mechanical or physical properties possessed by the as-cast product of the present invention include ductility values generally greatly superior to those possessed by prior art cast irons, yield strengths and tensile strengths higher than those possessed by ordinary gray cast iron and higher than many common grades of heat treated carbon steel castings (for example, the various Grade A and Grade B castings covered by the A. S. T. M. specification for carbon-steel casting A 27–44), unique elastic properties not possessed by gray cast iron (for example, a straight-line proportionality of stress to strain over a wide range of stresses, a high proportional limit and a consistently high tensile modulus of elasticity of about 25,000,000 pounds per square inch or greater), resistance to the combined effects of oxidation and heat (e. g., growth resistance) superior to that of gray cast iron, and other improved or high properties. In comparison to pearlitic malleable iron, the aforementioned as-cast product of the present invention (when it has a pearlitic matrix) often possesses in the as-cast condition higher tensile strength at an equivalent ductility level and higher ductility at an equivalent tensile strength level. In addition, it can be cast in larger section sizes than can be employed in the production of malleable iron and can contain larger amounts of carbon, silicon and other graphitizing elements. The alloy possesses the further advantage over high-grade malleable iron that it can be made from ferrous raw materials having better melting properties and can be produced from metal melted in the cupola furnace alone, whereas specifications for high-grade malleable iron generally require that it be processed in the less economical air furnace, electric furnace, open hearth furnace or by duplex operations in such a furnace following cupola melting. Of course, the alloy of the present invention may also be produced in an air furnace or other reverberatory furnace, an electric furnace, etc.

The product of the invention is preferably characterized by a microstructure in the as-cast condition in which the gray-colored carbon is present predominantly or substantially all in the form of fairly large, well-distributed, essentially equiaxed particles resembling spheroids or spheres. The magnesium-containing as-cast product having this structure possesses mechanical and/or physical properties, such as strength and ductility, greatly exceeding those which would have been obtained in the same base composition not treated with magnesium. In general, the tensile strength of the as-cast product will be more than 50% greater than would be obtained in the same composition not containing magnesium, and usually the improvement in tensile strength will be 100% or much more, as illustrated by data set forth herein. The amount of improvement depends upon the base composition and is greater in those base compositions which initially have the poorer tensile properties. Usually, the present invention improves the tensile strength of the base composition by at least about 40,000 pounds per square inch in as-cast, 1.2-inch diameter, standard arbitration bars when the magnesium content is 0.05% or more.

The high mechanical properties possessed by the as-cast product having the spheroidal form of carbon include high tensile strengths which in the pearlitic (i. e., generally preferred) compositions are usually of the order of 85,000 pounds to 120,000 pounds per square inch or even more. In those base compositions which produce a pearlitic or pearlitic-ferritic matrix, the improved ductility obtained by the invention is evidenced by elongations as high as 5%, or even more, but usually between about 2% and 4%, whereas prior art gray cast irons with similar matrices generally have low elongations usually below 1%.

ILLUSTRATIVE EXAMPLES AND DATA

For general use, a pearlitic matrix, e. g., a matrix comprised substantially all of pearlite or partly of pearlite as in a pearlite-ferrite matrix, is usually desired; and for this purpose, it is preferred, in carrying out the present invention to obtain an as-cast product containing the spheroidal form of carbon, to employ a composition containing the indicated amounts of the elements set forth in Table II.

Table II

Element	Range
	Per Cent
Carbon	2.8 to 3.8
Silicon	1.5 to 2.7
Magnesium	0.06 to 0.15
Nickel	0.5 to 3
Manganese	0.1 to 1

The composition may also contain chromium, e. g., up to 0.5%. The balance of the composition will be almost all iron except for incidental small amounts of impurities, etc. It is more preferred that the manganese content not exceed about 0.3%, particularly when good ductility and/or high impact properties are desired. Likewise, it is more preferred that phosphorus, if present at all, not exceed about 0.06%, as indicated hereinbefore. Of course, the final composition should preferably be correlated to the average section size of the final product to be produced. In general, the larger the average section size the higher should be the magnesium content and the lower should be the carbon content.

The necessity for having the required retained magnesium content in the as-cast product made in accordance with the present invention is illustrated by the data in Table IV setting forth the mechanical properties of similar iron-base compositions devoid of magnesium and containing various amounts of magnesium. The properties set forth in Table IV are the properties of the product in the as-cast condition determined from standard unmachined arbitration bars having a diameter of 1.2 inches, except for the tensile strength which was determined from a tensile specimen machined out of the arbitration bar. All the alloys referred to in Table IV were inoculated with a ladle addition of 0.5% silicon as ferro-silicon. The magnesium-containing alloys were inoculated shortly after the magnesium addition.

Table IV

[Composition: 3.6% C; 2.3% Si; 2% Ni; 0.7% Mn; 0.03% P]

Alloy No.	Per Cent Mg	Transverse		T. S.	BHN	Impact
		Defl.	Load			
1	None	0.170	2,180	18,440	158	19.5
2	0.02	0.169	2,600	22,260	165	21.0
3	0.039	0.180	4,530	41,800	228	38.0
4	0.067	0.240	8,980	112,000	290	84.0
5	0.096	0.248	9,040	102,020	302	54.0

Defl.= Deflection in inches in transverse test determined on arbitration bar over 12-inch span.
Load= Pounds required to fracture arbitration bar transversely over 12-inch span.
T. S.= Tensile strength in pounds per square inch.
BHN= Brinell hardness number.
Impact= Foot pounds required to break full-sized unnotched standard arbitration bar in Izod (120 ft.-lb.) impact testing machine.

The transverse breaking strength in pounds per square inch, sometimes referred to as the modulus of rupture, can be determined for each alloy in Table IV, or for any other alloy described herein, by multiplying the transverse load (determined on a 1.2-inch diameter bar tested over a 12-inch span) by the factor of 17.69. For the same bar tested over an 18-inch span, the factor would be 26.53. It will be observed from the foregoing that a notable improvement in properties takes place when the magnesium content is 0.039%. The improvement in properties becomes remarkably high when the magnesium content exceeds about 0.05%, e. g., 0.067% or 0.096%, as compared to the same composition devoid of magnesium or containing too little magnesium, e. g., only 0.02%. The importance of an inoculation after the introduction of the required amount of retained magnesium to obtain the high improvement in properties and the spheroidal form of carbon in the as-cast condition was illustrated by omitting the inoculation treatment from a portion of the molten magnesium-containing bath employed to produce alloy 4. Whereas inoculated alloy 4 had the typical steely fracture and contained the spheroidal form of carbon characteristic of the invention, the uninoculated magnesium-containing similar alloy (No. 4*a*) was hard, had a definite white fracture such as exhibited by white cast iron, and contained substantially all the excess carbon not required to form the matrix structure in the form of combined carbon.

In order that those skilled in the art have a better understanding of the properties which can be obtained by the present invention, the compositions of some as-cast ferrous-base alloys made in accordance with the invention and containing the spheroidal form of carbon are set forth in Table V and their properties are set forth in Table VI. The balance of the composition of the alloys set forth in Table V was iron except for small amounts of impurities. All the properties were determined on the alloys in the as-cast condition. The transverse properties and impact properties were determined from unmachined standard arbitration bars having a diameter of 1.2 inches. The yield strength, tensile strength and elongation were determined on a tensile specimen machined down to a diameter of 0.357 inch.

Table V

Alloy No.	Per Cent C	Per Cent Si	Per Cent Ni	Per Cent Mg	Per Cent Nn	Per Cent Others
6	3.5	2.3	0.6	0.050	0.1–0.2	
7	3.4	2.3	0.7	0.060	0.1–0.2	
8	3.7	2.1	0.7	0.053	0.1–0.2	
9	3.7	2.1	0.8	0.060	0.1–0.2	
10	3.4	2.7	0.9	0.056	0.8	
11	3.7	2.1	0.9	0.055	0.1–0.2	
12	3.7	2.1	1.0	0.065	0.1–0.2	
13	3.7	2.1	1.1	0.080	0.1–0.2	
14	3.4	2.2	1.2	0.068	0.7	
15	2.4	2.1	1.3	0.067	0.07	
16	3.4	2.3	1.4	0.071	0.1–0.2	
17	2.1	1.9	1.9	0.078	0.8	
18	2.6	2.3	1.9	0.072	0.9	
19	2.8	3.1	1.7	0.069	0.8	
20	3.1	1.8	2.0	0.062	0.66	
21	3.1	2.1	1.9	0.081	0.8	
22	3.2	2.0	1.9	0.073	0.8	
23	3.2	4.5	1.9	0.063	0.8	
24	3.3	2.7	1.8	0.058	0.8	
25	3.3	3.8	1.9	0.074	0.8	
26	3.4	2.0	1.9	0.058	0.8	
27	3.4	2.1	1.9	0.079	0.13	
28	3.4	2.3	1.9	0.066	0.8	
29	3.5	2.3	2.0	0.074	0.1–0.2	
30	3.5	2.4	1.9	0.066	0.8	
31	3.6	1.6	1.9	0.061	0.8	
32	3.6	2.1	1.9	0.075	0.09	
33	3.7	1.1	1.9	0.049	0.8	
34	3.7	1.9	1.9	0.075	0.8	
35	3.7	2.1	1.9	0.076	0.61	
36	3.7	2.2	1.9	0.067	0.1	
37	3.7	2.3	1.9	0.075	0.39	
38	3.8	1.3	1.9	0.055	0.8	
39	3.8	2.3	1.9	0.052	n. d.	
40	3.5	2	2.6	0.11	0.16	
41	3.4	2.4	2.8	0.049	0.18	
42	3.4	2.1	3.1	0.055	0.8	
43	3.6	2.3	3.6	0.084	0.73	
44	3.6	2.3	3.6	0.10	0.17	
45	3.6	2.1	3.7	0.079	0.8	
46	3.5	2	3.8	0.14	0.16	
47	3.6	2.1	4.7	0.053	0.8	
48	3.5	2	4.7	0.15	0.16	
49	3.6	2.1	7	0.05	0.8	
50	3.6	2.1	10	0.05	0.8	
51	3.6	2.1	15	0.05	0.8	
52	2.8	1.6	20.2	0.169	0.8	
53	2.9	2.0	21.1	0.12	0.15	
54	3.2	2.2	(*)	0.069	1.41	0.96 Cu
55	3.3	2.3	(*)	0.074	2.1	1.88 Cu
56	3.5	2.1	1.5	0.054	0.1	0.66 Mo
57	3.6	1.9	1.5	0.059	0.1	0.36 Cr
58	3.6	1.9	2.3	0.090	0.1	0.36 Cr
59	3.2	3.7	(*)	0.085	2.2	

*=No nickel added.
n. d.=Not determined.

Table VI

No.	Y. S.	T. S.	El.	Impact*	Transverse		HN
					Defl.*	Load*	
6		97,020			0.687	9,160	237
7		79,740		3 blows	0.675	8,760	223
8		83,300			0.377	7,400	215
9		81,260			0.498	7,950	215
10		90,100		34	0.187	8,880	293
11		91,760			0.404	7,950	228
12		102,860			0.505	7,730	229
13		88,940			0.662	9,390	236
14		97,460		2 blows	0.315	8,950	265
15	83,500	96,800	1.5				336
16		86,920		2 blows	0.485	9,160	252
17	84,500	110,300	1				347
18	78,000	89,200	0.8				296
19		97,580		65	0.156	7,820	275
20		91,960		104	0.343	10,170	302
21	71,000	100,300	1.8		0.270	9,990	298
22		96,000		65	0.224	9,510	300
23	70,100	76,100	0.5	19	0.127	5,940	283
24		96,840		3 blows	0.256	8,950	263
25	71,600	82,000	1	31	0.140	6,940	267
26	62,500	100,000	5	105	0.335	9,550	238
27	59,000	93,600	4				
28	65,000	84,700	2	55	0.230	8,870	247
29	60,100	96,300	7				238
30	67,000	100,000	5				258
31	66,000	110,000	3				280
32	60,000	98,000	5				234
33	64,500	83,200	1				303
34		120,400		1 blow	0.324	9,450	273
35		109,600		57	0.292	9,270	277
36		99,800		3 blows	0.755	9,630	237
37		108,760		2 blows	0.508	10,340	277
38	57,500	104,800	4.5				252
39		98,800		83	0.287	8,790	265
40		99,040		1 blow	0.359	10,130	284
41		101,900		2 blows	0.559	9,530	265
42		105,700		90	0.211	10,320	319
43	106,000	128,100	1.5	24	0.161	9,130	340
44	91,000	121,500	3	97	0.235	10,450	308
45	86,500	101,500	1	99	0.295	10,520	308
46		104,500		73	0.195	9,020	306
47	80,000	113,000		65	0.167	6,930	477
48		118,180			0.248	10,760	340
49				53	0.166	6,840	512
50				77	0.152	5,610	423
51				90	0.178	5,950	337
52		65,000		10 blows†	2,150	7,000	155
53	23,500	63,100	11.5				148
54		95,800		109	0.206	8,880	298
55		92,000		34	0.178	9,030	317
56		119,360		1 blow	0.314	10,320	298
57		116,860		82	0.345	9,360	282
58		102,100		2 blows	0.234	9,630	302
59		72,800		40	0.113	5,810	321

*=See footnotes of Table IV for key to terms or abbreviation.
†=Still unbroken after 10 blows.
Y. S.=Yield strength (0.2% offset) in pounds per square inch.
El.=Per cent elongation in 2 inches.
Impact=In foot pounds except where number of blows is specified; latter indicates number of full swings of Izod hammer withstood by specimen before fracturing.
HN=Hardness determined as Brinell or Vickers hardness numbers which are approximately equivalent.

Tables V and VI illustrate the application of the invention to as-cast ferrous alloys having a variety of matrix structures. Thus, alloy 26 illustrates the properties of an as-cast ferrous alloy made in accordance with the present invention and having a pearlitic matrix. Alloy 47 illustrates the properties obtained with a martensitic matrix, and alloy 56 illustrates the properties obtained with an as-cast acicular matrix. Alloys 52 and 53 indicate the properties obtained when the matrix is austenitic. In order that the improvement obtained by the invention in compositions having austenitic matrices be more fully appreciated, the properties of alloy 52 are compared in the following Table VII with the properties of a magnesium-free similar alloy (No. 52*a*) containing, in addition to iron, about 2.9% carbon, 1.7% silicon, 0.8% manganese and 20% nickel:

Table VII

Alloy No.	T. S.	Transverse		Impact	BHN
		Defl.	Load		
52a	15,800	1.250	2,470	2 blows	95
52	65,000	2.150	7,000	10 blows*	155

*=Still unbroken after 10 blows.

The product of the present invention possess unique elastic properties, including a straight-line proportional relationship between stress and strain over a wide range and a high proportional limit, whereas gray cast iron containing flake graphite does not have such properties. The unique elastic properties have been confirmed by plotting corresponding values of stress and strain over a wide range of stresses. The upper limit of the straight-line plot thus obtained determines the proportional limit, which for the product of the present invention is at a high stress level (e. g., about 30,000 to 55,000 pounds per square inch), and the slope of this straight-line plot determines the tensile modulus of elasticity, which for the product of the invention is of the high order of about 25,000,000 pounds per square inch or greater and is an indication of the high stiffness possessed by the product.

As indicated hereinbefore, the magnesium-containing alloy of the present invention is characterized by markedly improved resistance to the combined deleterious effects of heat and oxidation, e. g., growth resistance. The improved resistance to heat and oxidation is illustrated by tests conducted on four as-cast products similar in base composition to alloy 30 and containing about 3.5% carbon, about 2.4% to 2.6% silicon, 1.3% to 1.8% nickel and about 0.8% manganese. Two of the products (alloys 30*a* and 30*b*) were devoid of magnesium while the other two products (alloys 30A and 30B) contained 0.063% retained magnesium. In preparing these four products, all were inoculated shortly before casting. Pieces from each of the four products were subjected to a 100-cycle oxidation test, each cycle of which consisted in heating the piece in air to 1600° F. in about one-half hour, holding the piece for about one hour at 1600° F. in air and then air-cooling the piece for about one hour. The data obtained from these tests are given in the following Table VIII:

Table VIII

Alloy No.	Percent Mg	Length		Growth Percent Increase in Length
		Original	Final	
30A	0.063	3.122	3.185	2.01
30B	0.063	3.134	3.198	2.04
30*a*	none	3.130	3.483	11.30
30*b*	none	3.140	3.551	13.05

In Table VIII, the growth resistance is indicated by the per cent increase in length after the cyclic oxidation test and is markedly lower in the product provided by the invention than in a similar magnesium-free gray cast iron composition containing flake graphite. These tests also confirmed by the amount of oxidation that the product of the invention has resistance to oxidation at elevated temperatures superior to that of a similar magnesium-free gray cast iron composition containing flake graphite.

In producing the high quality gray cast irons of the prior art, the metallic raw materials of the charge could not be entirely pig iron but had to include at least a substantial amount of steel scrap. The exceptionally high combination of properties provided by the invention can be obtained from a charge in which the metallic raw materials contain a larger proportion of pig iron. To illustrate this, the following data are given:

A charge in which the metallic raw materials were entirely pig iron was melted in the usual manner to establish a bath having a proper temperature for casting. The charge was designed to produce a bath containing about 4.1% carbon, 1.25% silicon, 0.5% manganese and 0.03% phosphorus, the balance being essentially iron. Portions of the bath were separately transferred to a ladle and each portion treated in a different manner. One portion was not treated with magnesium but was inoculated with about 0.75% silicon as ferro-silicon containing about 85% silicon and then quickly cast into 1.2-inch diameter standard arbitration bars (alloy 60). Five other portions of the bath were treated in the ladle with various amounts of a nickel-magnesium alloy containing about 95% nickel and 5% magnesium to produce retained magnesium contents of 0.03%, 0.04%, 0.04%, 0.05% and 0.09% and cast into similar bars (alloys 61 to 65 respectively. All but one (alloy 62) of the magnesium-treated portions were inoculated (in the same manner as the portion not treated with magnesium) after the magnesium addition and shortly before casting. The fractures of machined tensile specimens made of the foregoing inoculated alloys (alloys 60, 61 and 63 to 65) are shown in Fig. 6. The form of uncombined carbon occurring in polished and unetched sections of alloys 63, 64 and 65, in the as-cast condition, are shown in Figs. 7 to 9. The occurrence of some carbon spheroids in the presence of short thick particles when the retained magnesium reaches about 0.04% is shown in Fig. 7 which depicts the structure of alloy 63 about half-way between the center and surface of the bar. Nearer the surface of the bar, a larger proportion of the uncombined carbon was in the spheroidal form. Figs. 8 and 9 illustrate the spheroidal form of uncombined carbon occurring in alloys 64 and 65. A very pronounced effect is obtained when the product has a retained magnesium content of about 0.04% and the magnesium addition is followed by an inoculation. The importance of sufficient graphitizing power, such as contributed by inoculation, is illustrated by the fact that alloy 62 had a white fracture and had a high hardness of 412 Brinell. The markedly improved results which begin to be evident with a retained magnesium content of about 0.04%, and which are very evident with a retained magnesium content of about 0.05%, are illustrated by comparing the tensile strength of alloy 60 with the tensile strength of alloys 63, 64 and 65. Alloy 60, made from a charge in which the metallic raw materials were all pig iron, had a tensile strength of only about 17,000 pounds per square inch. By introducing sufficient magnesium to produce a retained magnesium content of 0.04% (alloy 65), the tensile strength was raised well over 100%, i. e., to 44,000 pounds per square inch. With retained magnesium contents of 0.05% and 0.09% (alloys 64 and 65, respectively), the tensile strength was raised from about 17,000 pounds per square inch to 101,000 and 108,400 pounds per square inch, respectively, which represent increases in tensile strength of about 85,000 to 90,000 pounds per square inch.

It has been indicated hereinbefore that phosphorus should be maintained as low as practicable. The effect of phosphorus in the product of the present invention is very similar to its effect in gray cast iron, and while the present invention improves the properties of relatively high phosphorus compositions as well as the properties of low phosphorus compositions, the level of certain properties, e. g., ductility, toughness and tensile strength, is lowered by phosphorus in a manner analogous to its effect in gray cast iron. The effect of phosphorus on the tensile properties and hardness of the as-cast ferrous-base product of the invention is illustrated in Table XI.

Table XI

[Composition: 3.5% C; 2.4% Si; 0.05–0.08% Mg; 0.8% Mn; 1.9% Ni]

Alloy No.	Per cent P	Y. S.	T. S.	El.	VHN
30	0.015	67,000	100,000	5.0	258
30C	0.052	82,000	98,500	1.5	278
30D	0.089	75,000	90,100	1.5	264
30E	0.20	n. r.	83,500	------	307
30F	0.43	n. r.	68,800	------	269
30G	0.67	n. r.	67,600	0	312

VHN=Vickers hardness number.
n. r.=Not reached; specimen broke before 0.2% offset was attained

Where ductility and toughness, reflected by deflection under transverse loading (and by elongation or reduction of area under tensile loading) and impact respectively, are of prime consideration, it is usually preferred to maintain the manganese content of the as-cast product of the invention below 0.8% or 1%, and more preferably not over 0.3% or 0.4%. It has been found that as the manganese content decreases, the deflection and impact properties increase while the tensile strength and hardness decrease slightly. The trend of the manganese effect on the as-cast properties of the ferrous-base alloy of the invention in 1.2-inch diameter arbitration bars is indicated by the data in Table VII.

Table XII

[Composition: 3.7% C; 2.1–2.2% Si; 0.067–0.076% Mg; 1.9% Ni; 0.02% P]

Alloy No.	Per cent Mn	T. S.	Impact	Transverse		BHN
				Defl.	Load	
36	0.10	99,800	3 blows	0.755	9,630	237
36A	0.21	101,200	5 blows	0.491	9,200	255
35	0.61	109,600	57.0	0.292	9,270	277

HEAT TREATMENT

When it is desired to enhance certain particular properties or to modify the combination of properties, the alloy of the invention may be subjected to known heat treatments, including induction hardening, flame hardening and similar surface treatments, to affect particular properties or combinations of properties of ferrous alloys. Thus, the alloy of the invention can be subjected to heat treatments for stress relief, strengthening, hardening, toughening, etc. These heat treatments include so-called "isothermal" treatments or "austempering" treatments of ferrous alloys to transform austenite, including any retained austenite, to an acicular constituent at or near the temperatures corresponding to the nose of the S-curve or below said nose but above the martensite transformation temperature. Other illustrative heat treatments which may be employed to modify somewhat the properties of the as-cast alloy of the invention include quenching and drawing, normalizing and drawing, etc. For example, the product can be reheated above the critical transformation temperature, then cooled in air or quenched in oil or water, and then drawn at about 400° F. to about 1250° F. To illustrate some permissible heat treatments for modifying the properties, Tables VIII and XIV set forth three heat treatments and their influence upon the indicated properties of two as-cast alloys produced in accordance with the invention and containing the spheroidal form of carbon.

Table XIII

Treatment No.	Treatment
0	As cast.
1	Austempered by quenching from 1550° F. into salt bath at 800° F. and holding at 800° F. for five hours.
2	Quenched in oil from 1550° F. and drawn at 1100° F. for five hours.
3	Normalized from 1550° F. and drawn at 1100° F. for five hours.

Table XIV

Treatment No.	Alloy No.	Y. S.	T. S.	El.	VHN
0	18	78,000	89,200	0.8	296
0	21	71,000	100,300	1.8	298
1	18	103,000	118,600	0.5	344
1	21	109,000	127,200	1.5	328
2	18	96,000	101,200	2.0	280
2	21	92,000	97,500	2.5	264
3	18	74,000	111,400	2.5	299
3	21	78,500	113,300	3.8	285

A special heat treatment has been found which produced markedly improved ductility in combination with high tensile strength in those as-cast alloys described hereinbefore having a pearlitic matrix. This heat treatment involves treating such a pearlitic cast alloy within a range of temperatures slightly below the lower critical temperature, generally for at least about one hour. In practice, it is preferred to employ temperatures not more than 75° F. below the critical transformation temperature of the composition being treated and more preferably not more than 50° F. below said critical temperature (often also referred to as the critical point or the "A_1" point, i. e., the lowest temperature where the alpha-gamma transformation takes place in the particular composition involved). The critical temperature is influenced by many factors, including the composition, and these factors must be taken into consideration as is well known to those skilled in the art. In general, a temperature range of about 1270° F. to 1310° F. has given satisfactory results. It is also preferred that the heat treatment at an elevated temperature slightly below the critical temperature be conducted for at least about two hours. An advantage of this treatment at relatively low temperatures is that it can be carried out in comparatively short periods of time but there are no particular limitations on the maximum time of treatment. Treating times up to fifteen or twenty hours have given satisfactory results, e. g., five hours or ten hours.

It has been found that the aforementioned special heat treatment of the magnesium-containing, as-cast ferrous alloy having a pearlitic matrix at atmospheric temperatures and containing the spheroidal form of carbon produces an improved combination of properties, especially an improved combination of ductility and tensile properties, as compared to the properties of malleable iron, e. g., standard or ferritic malleable iron. Because the aforementioned special heat treatment has a ferritizing effect on the matrix, this heat treatment has been referred to as a "ferritizing" treatment and the product as a "ferritized" product. After the ferritizing heat treatment, the magnesium-containing product has a microstructure comprised predominantly or even substantially entirely of a ferrite matrix containing compacted and dense, randomly dispersed, substantially equiaxed particles of uncombined carbon, preferably spherulitoid, spheroidal or spherical in shape, of about the same size as the patches of temper carbon found in malleable iron. The spherulitoid or spheroidal particles in the ferritized product of the invention are similar in appearance and size to the particles in the as-cast product but are comprised of a large spheroidal or spherical body with a very thin irregular fringe, shell, edging or rim as shown in Fig. 10. The fringe or edging, which is very thin, has a rougher and pebbly appearance. This edging or fringe does not necessarily appear around the entire circumference of the body portion of the carbon particle.

A feature of the ferritized product is that it can have a high graphitizing power, such that the carbon content plus one-third the silicon content is over 3.5% or 3.7% or 4.2% or more, which cannot be present in compositions employed to produce malleable iron. In some instances, for example, when the heat treatment has not been conducted for a sufficiently long time and/or when the composition contains a substantial amount of carbide stabilizers such as chromium, manganese, etc., a minor proportion of combined carbon or carbides may be present in the final ferritized product. Retained magnesium in the amounts contemplated by the invention has been found to have a very strong whitening effect and to have a tendency to refine pearlite slightly. Although magnesium has a whitening effect, the ductile magnesium-containing ferritized product of the present invention can be obtained from the as-cast product of the invention with a considerably shorter heat treatment than is required to obtain ferritic malleable iron. Another feature of the ferritized alloy is that it can be produced in large section sizes, e. g., up to 4 or 5 inches or even more, without unduly sacrificing properties or appreciably increasing the heat treating time required and is not limited to the small section sizes, e. g., up to 1 inch and on occasion up to about 2 inches, which restrict the production of malleable iron products.

Ferritized products having compositions within the most preferred range of compositions, given in Table II, will generally have the following average properties:

Yield strength---45,000–55,000 p. s. i. (0.2% offset)
Tensile strength-63,000–75,000 p. s. i.
Elongation------12 to 18%
Hardness-------150 to 190 Vickers number

Table XV sets forth data showing the new combination of properties that were obtained in alloy 29 after a ferritizing treatment (No. 4) for five hours at 1300° F. as compared to the properties possessed by the pearlitic product in the as-cast condition.

Table XV

Property	As-cast	Ferritized
Per cent Elongation (2 in.)	7	20.6
Per cent Reduction of area	6.4	17.5
Yield strength (0.2%), p. s. i	60,100	48,500
Tensile strength, p. s. i	96,300	66,100
Vickers Hardness	238	181

In carrying the ferritizing heat treatment into practice, it is preferred to subject the casting having a pearlitic composition to temperatures above the critical temperature before subjecting it to temperatures just below the critical temperature in the manner described hereinbefore. The aforementioned higher temperature treatment assures that excessive amounts of free massive carbides will not exist in the final heat treated product and compensates for possible variables of production in the initial casting. The higher temperature treatment is satisfactorily accomplished by subjecting the castings to one or more temperatures between about 1800° F. and the critical temperature, preferably for at least about one hour and more preferably for at least two hours. There is no particular limitation upon the maximum time at temperature in this treatment, but generally satisfactory results are obtained in less than about 15 hours, e. g., in about 3 to 5 hours. A suitable treatment comprises subjecting the casting to temperatures between about 1750° F. and 1500° F.

The influence of magnesium on the structure in the as-cast condition and the influence of the ferritizing treatment on the matrix of the magnesium-containing as-cast alloy are illustrated in Figs. 11 to 13. Figs. 11 and 12 show the polished and etched as-cast structures at a magnification of 100 diameters and 250 diameters, respectively, of an inoculated gray cast iron composition containing about 3.6% carbon, 2.3% silicon and the required amount of retained magnesium to provide the spheroidal form of carbon in the as-cast condition. Fig. 13 shows the effect on the matrix structure shown in Fig. 12 of a ferritizing heat treatment, i. e., cooling slowly in a furnace from 1700° F. to 1280° F. and holding at 1280° F. for five hours. As illustrated by the etched structure in Fig. 13 (taken at a magnification of 250 diameters), the pearlite in the matrix has been converted by the heat treatment to ferrite.

In order that those skilled in the art may have a better understanding of some of the preferred embodiments of the ferritizing heat treatment and of the properties that can be obtained in the ferritized product, data have been set forth in Tables XVI, XVII and XVIII giving the composition (the balance being iron except for small amounts of impurities), the ferritizing heat treatment and the properties of ferritized products made in accordance with the invention from magnesium-containing ferrous alloy castings containing the spheroidal form of carbon in the as-cast condition.

Table XVI

Alloy No.	Per cent C	Per cent Si	Per cent Mg	Per cent Mn	Per cent P	Per cent Ni
15	2.4	2.1	0.067	0.07	0.02	1.3
66	3.3	2.7	0.058	0.8	0.02	1.6
17	2.1	1.9	0.078	0.8	0.01	1.9
67	2.4	1.9	0.060	0.07	0.02	1.9
18	2.6	2.3	0.072	0.9	0.07	1.9
21	3.1	2.1	0.081	0.8	0.06	1.9
26	3.4	2.0	0.058	0.8	0.02	1.9
27	3.4	2.1	0.079	0.13	0.02	1.9
29	3.5	2.3	0.074	0.1–0.2	*n. d.	2.0
30	3.5	2.4	0.066	0.8	0.02	1.9
31	3.6	1.6	0.061	0.8	0.02	1.9
32	3.6	2.1	0.075	0.09	0.02	1.9
33	3.7	1.1	0.049	0.8	0.02	1.9
68	3.8	1.4	0.050	0.8	0.08	1.9
69	3.8	1.9	0.083	0.8	0.02	1.9
64	4.2	2.3	0.054	0.5	0.03	2.3
41	3.4	2.4	0.049	0.18	0.04	2.8
65	4.2	2.3	0.092	0.5	0.03	3.0
42	3.4	2.1	0.055	0.8	0.02	3.1
44	3.6	2.3	0.10	0.17	0.04	3.6
43	3.6	2.3	0.084	0.73	0.04	3.6

*n. d.=Not determined, low.

Table XVII

No.	Heat Treatment
0	As cast (no heat treatment).
5	Cold castings heated to about 1750° F., held 5 hrs., furnace cooled to room temperature, reheated to about 1300° F., held 5 hrs.
6	Cold castings heated to about 1700° F., held 15 min., furnace or pit cooled to about 1280° F., held 5 hrs.
7	Red hot castings (stripped from mold) furnace or pit cooled from about 1700° F. to about 1275° F., held 2 hrs.
8	Red hot castings (stripped from mold) furnace or pit cooled from about 1700° F. to about 1275° F., held 5 hrs.
9	Cold castings normalized by holding for 1 hr. at about 1550° F. and air cooling to room temperature, reheated to about 1300° F., held for 5 hrs.
10	Cold castings heated to about 1550° F. and held for 1 hr., quenched in oil, reheated to about 1300° F., held for 5 hrs.

Table XVIII

Alloy No.	Treatment No.	El.	R. A.	VHN	Y. S.	T. S.
15	0	1.5	--------	336	83,500	96,800
15	5	14.0	14.0	190	52,500	80,200
15	6	12.0	11.4	187	54,500	73,100
66	5	19.0	19.6	195	54,400	73,300
17	0	1.0	1.1	347	84,500	109,500
17	5	16.0	13.0	223	55,500	92,600
67	0	0.5	--------	321	76,000	94,500
67	5	8.0	9.3	218	57,000	93,400
67	6	8.5	9.3	189	52,000	72,400
18	0	0.8	--------	296	78,000	89,200
18	5	8.5	7.1	201	47,500	73,100
18	6	8.5	8.2	210	57,000	75,300
18	9	7.5	6.7	222	63,000	80,900
18	10	6.5	6.0	222	63,500	83,200
21	0	1.8	2.3	298	71,000	100,300
21	6	7.0	8.8	186	54,000	67,300
21	9	13.0	10.9	197	58,500	75,000
26	0	5.0	4.9	238	62,500	100,000
26	5	15.0	14.6	187	48,000	70,000
26	6	13.5	13.0	192	49,000	72,400
27	0	4.0	4.4	--------	59,000	93,600
27	5	17.0	19.6	155	45,000	63,800
29	0	7.0	6.4	238	60,100	96,300
29	5	22.5	21.3	167	47,400	64,600
29	6	21.5	21.5	168	46,300	64,000
30	0	5.0	3.9	258	67,000	100,000
30	5	17.5	15.6	179	52,000	72,000
30	6	16.0	17.1	192	56,000	74,700
31	0	3.0	2.8	280	66,000	110,000
31	5	13.0	14.5	175	43,500	71,600
32	0	5.0	4.4	234	60,000	98,000
32	6	18.5	15.6	150	46,500	63,900
32	7	13.0	9.8	178	49,500	68,500
33	0	1.0	1.1	303	64,500	83,200
33	5	11.0	10.2	180	41,000	72,900
68	0	2.5	2.2	272	63,500	95,300
68	5	11.0	11.3	161	43,000	64,800
69	0	2.5	2.7	288	78,000	108,200
69	5	12.5	13.0	187	49,500	72,300
64	5	10.5	12.5	--------	51,000	67,400
41	0	2.5	--------	222	63,000	79,150
41	5	6.0	--------	176	49,500	60,000
65	5	6.0	8.8	--------	59,200	72,000
42	0	--------	--------	313	--------	--------
42	5	5.5	6.1	203	52,000	71,600
44	0	3.0	3.3	308	91,000	121,500
44	5	11.0	10.3	211	66,500	85,500
44	6	13.5	14.1	202	67,000	78,600
44	8	13.0	15.6	197	58,500	76,400
43	0	1.5	1.7	340	106,000	128,100
43	5	9.0	8.7	244	76,500	94,700

R. A.= Per cent reduction of area. See footnotes of other tables for key to terms, etc.

The improvement in ductility obtained by the ferritizing heat treatment is illustrated in Fig. 14 which depicts photographs of originally straight bend-test specimens, about 6 inches long, after said specimens had been subjected to a bend test to determine their ductility to the point of fracture. All three specimens were made of alloy 29. The top specimen shows the high ductility of the as-cast alloy. The middle specimen shows the ductility of the alloy after having been given heat treatment 6. The marked improvement in ductility over the as-cast ductility is shown by the greater amount of bend withstood by the specimen before cracking. The bottom specimen shows the ductility of the alloy after having been subjected to heat treatment 5,

By varying the ferritizing treatment, e. g., the temperatures, the time of treatment, etc., it is possible to obtain various different combinations of ductility and strength. In general, as the ductility is increased, the strength properties of the heat treated casting are decreased and vice versa. Thus, the ductility will usually be higher the longer the treating time just below the critical temperature of the composition. This effect of varying the treating time is illustrated in Table XIX which shows the effect on the properties of alloy 32 of a heat treatment comprising heating cold castings made of said alloy to about 1700° F., furnace cooling (e. g., cooling at an average rate of about 80° F. to 100° F. per hour) to about 1275° F., and holding at the latter temperature for the various periods of time indicated in Table XIX.

Table XIX

Holding Time	El.	R. A.	VHN	Y. S.	T. S.
30 min	8.0	8.8	190	50,500	78,200
1 hour	9.0	9.8	177	49,500	73,900
2 hours	15.0	12.5	179	48,500	69,700
5 hours	18.5	15.6	150	46,500	63,900

The phosphorus content of the ferritized casting is preferably maintained low, e. g., not more than about 0.06%. Increasing amounts of phosphorus have been found to lower the properties of the ferritized casting, particularly the tensile strength and the ductility (which is indicated by elongation and/or reduction of area). The effect of phosphorus is indicated in Table XX which gives the properties of alloy 30 containing 0.015% phosphorus and alloys 30C and 30E to 30G, which are similar alloys containing increasing amounts of phosphorus in the order given and in the amounts indicated in Table XX, after having been given ferritizing heat treatment 5 or 6 described hereinbefore.

Table XX

Alloy No.	30	30C	30E	30F	30G
Percent Phosphorus	0.015	0.052	0.20	0.43	0.67
Treatment No. 5:					
El	17.5	14.5	7.0	1.0	0
R. A	15.6	14.1	8.2	1.2	0
VHN	179	193	198	205	189
Y. S	52,000	60,000	61,500	69,000	* 53,000
T. S	72,000	77,900	75,300	73,100	53,900
Treatment No. 6:					
El	16.0	11.5	11.5	5.5	0
R. A	17.1	13.0	10.8	6.1	0
VHN	192	205	203	224	208
Y. S	56,000	62,000	60,500	70,500	67,000
T. S	74,700	82,000	80,300	77,000	67,000

* 0.1% offset; specimen fractured before 0.2% offset was reached.

It is also preferred that the manganese content of the ferritized product be low, e. g., not more than 0.3% or 0.4%. Manganese apparently stabilizes carbon in the form of carbides, for example, in the pearlite of the matrix, because as the manganese content increases, longer treating times below the critical temperature are required to obtain similar structures. Likewise, it is preferred that the silicon content of the ferritized product not be too high. It has been found that high silicon contents detrimentally affect the properties, particularly the ductility. Silicon in amounts from about 1% to about 3% does not appear to have any detrimental effect on the properties and, in fact, improves the properties as the silicon is increased above 1.5% within this range. A detrimental effect becomes evident at about 3% silicon and becomes quite pronounced when the silicon content exceeds about 3.5%.

Magnesium-containing alloys which as a result of production variables are carbidic as cast, such as magnesium-containing alloys which have not been very effectively inoculated, e. g., been held too long in the ladle after inoculation, can be heat treated to decompose the free carbides by means of the high temperature treatment above the critical temperature, whereby the amount of uncombined carbon in the form of spheroidal bodies increases without the development of graphite in flake form. When the magnesium-containing ferritic product is desired, this treatment is followed by treatment just below the critical temperature.

The ferritizing heat treatment has been found to produce particularly satisfactory results when applied to the treatment of magnesium-containing castings having a matrix comprised of pearlite in the as-cast condition. The ferritizing heat treatment can also be applied to other matrices containing combined carbon and having the iron in the alpha form at atmospheric temperatures, for example, matrices containing martensite, bainite, etc. However, these non-pearlitic matrices are more difficult to treat and in general require longer treating times to ferritize the matrix, e. g., at least about 3 or 4 hours. Castings having such a non-pearlitic matrix will usually contain larger amounts of alloying elements than will be present in a pearlitic casting of an analogous composition. Thus, the presence of about 4% or more of nickel, e. g., 4.7% nickel, will usually result in a casting having a martensitic matrix and having a lower critical temperature than if made of a similar pearlitic composition containing less nickel.

STATE OF CARBON

The exact nature of the soft, gray-colored spheroidal form of carbon having the radiating structure with a polycrystalline appearance has not been conclusively established, but in all tests conducted thereon, the spheroidal form of carbon has exhibited the same behavior, color and individual properties as graphite. Thus, the spheroidal form of carbon has a gray color the same as or very closely similar to that possessed by graphite. It is also soft like graphite. It behaves in the same manner as graphite under chemical tests. Thus, in the chemical analysis of the as-cast alloy provided by the invention for uncombined carbon, it is obtained as a residue after treatment with acids in the same manner as a graphite residue is obtained in the chemical analysis of gray cast iron and in the same proportion to the total carbon as if the spheroidal form of carbon were graphite. Like graphite, the spheroidal form of gray-colored carbon behaves anisotropically under polarized, reflected light. It has a greasy feel similar to that exhibited by graphite. No evidence has been found to indicate that the spheroidal form of carbon is not graphite. In describing the present invention, the carbon in the spheroidal form has been referred to as "uncombined carbon" in view of its close resemblance in behavior, color and properties to the uncombined carbon obtained as a residue after treatment with acids, as in the chemical analysis of gray cast iron, and in view of the fact that, like the graphite residue, it is combustible to a gaseous compound of carbon and oxygen. The term "uncombined carbon" is employed in the conventional metallurgical sense as applied to ferrous alloys such as gray cast iron and refers to the presence of the carbon in a substantially uncombined condition. Thus, while the flake graphite of gray cast iron is conventionally referred to as uncombined carbon, it is known that this flake graphite often contains small amounts of other elements, particularly iron.

MECHANISM OF INVENTION

While the mechanism involved in the present invention is not fully understood theoretically, the conditions which need to be met in the production of the as-cast product containing the spheroidal form of uncombined carbon are believed to comprise (1) establishing a molten ferrous composition which strongly tends to freeze as a white cast iron, yet the carbides of which are at the same time relatively unstable; and (2) providing a graphitizing tendency opposing the whitening tendency of the molten composition, such as by providing high graphitizing power in the primitive melt or by effective inoculation whereby uncombined carbon is stimulated to start crystallizing from the melt at a temperature sufficiently high to allow its free growth as spheroids or spheres, largely in liquid surroundings. This delicate relationship between opposing tendencies may be approached variously, provided sufficient control is exercised. The metallurgical relations of magnesium to iron, including the power it possesses to whiten iron and its limited solubility in molten iron, provide a very practical means for the dependable accomplishment of this balance.

The microstructure containing uncombined carbon in the form of numerous spheroidal bodies or particles having a radiating and polycrystalline appearance which is obtained in the product provided by the present invention in the as-cast condition is not to be confused with microstructures containing uncombined carbon in the form of particles which are referred to as "nodular," "nodules," "granular," "temper carbon," etc., and which do not have a radiating and polycrystalline appearance and/or did not exist in the as-cast microstructure.

APPLICATIONS

The present invention may be applied to the manufacture of a wide variety of ferrous products and articles which will be apparent to those skilled in the art from the properties and structure of the ferrous alloy provided by the invention. These products and articles include those made heretofore of ferrous alloys such as gray cast iron, pearlitic malleable iron, ferritic or standard malleable iron, and even certain grades of cast steels. Illustrative examples of such products and articles include engine crank shafts, dies, car wheels, beds for machine tools, understructures of large steel mill and railroad weighing scales, machinery parts such as roll mill housings and run-out tables for steel mill equipment, rolls such as paper machinery rolls and steel mill rolls, gyratory crusher housings and shells, castings for railroad equipment, for ships, for agricultural implements and machinery and for earth-moving and conveying machinery, pressure castings for valves and pumps such as are used in power stations, in the oil industry and in the mining industry, furnace parts, melting and heat treating pots, manifolds and other articles subjected to heat, composite products in which the material provided by the invention forms one or more components, e. g., steel mill rolls with machinable necks in combination with a non-machinable martensitic body, car wheels having a steel rim with the material provided by the invention forming the hub and web, composite rolls having roll shells made of the material provided by the invention, and centrifugally cast products having one metallic material in the outer portion and another metallic material in the inner portion. Innumerable other applications utilizing the improved combination of properties provided by the product embodying the present invention will be apparent to those skilled in the art.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such variations and modifications apparent to those skilled in the art are considered to be within the purview and scope of the invention and the appended claims.

We claim:

1. As a new article of manufacture, an iron casting containing 0.04% to about 0.3% magnesium, and the balance a gray cast iron composition, said casting being characterized in the as-cast condition by a microstructure comprised of soft, gray-colored, substantially spheroidal particles having a radiating structure, said particles being dispersed in a ferrous matrix.

2. A ductile cast iron having the characteristic in the as-cast condition of a microstructure containing substantially spheroidal particles of uncombined carbon dispersed in a ferrous matrix and comprised of about 0.05% to about 0.2% magnesium with the balance a cast iron composition devoid of elements materially subversive to the aforesaid characteristic.

3. A cast iron containing uncombined carbon and a small but effective amount up to less than about 0.4% of magnesium sufficient to control the occurrence of uncombined carbon as substantially spheroidal particles, the cast iron without magnesium having the composition of a gray cast iron normally containing uncombined carbon in the form of flakes.

4. As a new article of manufacture, an iron casting with included sections exceeding three-eighths of an inch in thickness made of cast iron containing about 0.04% to 0.3% magnesium, less than about 1.2% combined carbon, about 2.5% to about 4.5% total carbon, and more than about 1% up to about 4% silicon, the silicon content being related to the carbon content such that the sum of the percentage of silicon divided by 3.1 plus the percentage of carbon divided by 4.5 exceeds 1.00, said casting containing at least about 87% iron, being substantially devoid of tellurium and bismuth, and being characterized by an uncombined carbon content predominantly in the form of dispersed spheroids having a radiating and polycrystalline appearance and by being substantially free from flake graphite.

5. As a new article of manufacture, a casting comprised of an alloy containing about 0.05% to 0.2% magnesium, about 2.5% to about 4.5% total carbon, about 1.3% to about 3.5% silicon and at least 87% iron and characterized in the as-cast condition by a combined carbon content less than about 1.2% and by a microstructure containing uncombined carbon predominantly in the form of radiating and polycrystalline-appearing spheroids, said alloy being substantially free from flake graphite.

6. As a new article of manufacture, a ductile cast iron having a microstructure comprising in the as-cast condition a matrix containing pearlite and having uncombined carbon in the form of spheroids dispersed in said matrix, said cast iron being comprised of a small but effective amount up to about 0.4% magnesium to control the occurrence of at least some of the uncombined carbon in the form of said dispersed spheroids, and the balance being essentially a pearlitic gray cast iron composition devoid of subersive amounts of elements which materially interfere with the effect of magnesium, said ductile cast iron having a higher combination of properties, including tensile strength and ductility, as compared with those of the same gray cast iron but devoid of retained magnesium.

7. As a new article of manufacture, a ductile cast iron having a microstructure comprising a pearlite-ferrite matrix and uncombined carbon in the form of spheroidal particles dispersed in said matrix, said cast iron being comprised of about 0.05 to about 0.2% magnesium to control the occurrence of at least some of the uncombined carbon in the form of said dispersed spheroidal particles, and the balance being essentially a gray cast iron composition having about 2% to about 4.5% carbon and about 1.5% to about 4.5% silicon, said ductile cast iron having a higher combination of properties, including tensile strength and ductility, as compared with those of the same gray cast iron composition but devoid of magnesium.

8. As a new article of manufacture, a ductile cast iron having a microstructure comprising a pearlitic matrix having uncombined carbon in the form of spheroidal particles dispersed in said matrix, said cast iron being comprised of about 0.06% to about 0.15% magnesium to control the occurrence of at least some of the uncombined carbon in the form of said dispersed spheroidal particles, and the balance being essentially a gray cast iron composition having about 2.8% to about 3.8% carbon, about 1.5% to about 2.7% silicon, about 0.5% to about 3% nickel, and about 0.1% to about 1% manganese, said ductile cast iron having a higher combination of properties, including tensile strength and ductility, as compared with those of the same gray cast iron but devoid of magnesium and said ductile cast iron having the uncombined carbon predominantly in the form of spheroidal particles as compared with a similar gray cast iron which is devoid of magnesium and which contains the uncombined carbon principally in the form of flakes.

9. A casting comprised of a ferrous alloy having a matrix with iron mainly in the alpha form and containing uncombined carbon and a small but effective amount up to about 0.5% magnesium to effect the occurrence of uncombined carbon as substantially spheroidal particles dispersed in a ferrous matrix having iron mainly in the alpha form, the balance of the alloy being a gray cast iron composition having iron mainly in the alpha form and devoid of subversive amounts of elements materially interferring with the aforesaid effect of the magnesium content.

10. As a new article of manufacture, an iron casting with included sections exceeding three-eighths of an inch in thickness made of cast iron containing less than about 1.2% combined carbon, about 2.5% to about 4.5% total carbon, and more than about 1% to about 4% silicon, the

silicon content being related to the carbon content such that the sum of the percentage of silicon divided by 3.1 plus the percentage of carbon divided by 4.5 exceeds 1.00, and a small but effective amount up to about 0.3% magnesium to control the occurrence of uncombined carbon in the form of spheroids, said cast iron containing more than about 50% iron, being characterized by a microstructure containing spheroids of uncombined carbon and being devoid of subversive amounts of elements materially interfering with said characteristic.

11. As a new article of manufacture, an iron casting having a microstructure containing in the as-cast condition spheroids of uncombined carbon, having increased tensile strength and being made of cast iron containing 1.7% to 5% carbon with less than about 1.2% combined carbon in the as-cast condition, 1% to 6% silicon, a small but effective amount up to about 0.5% magnesium to increase the as-cast tensile strength of the cast iron at least about 100%, and the balance except for alloying elements being essentially iron with the iron content over about 87%, said cast iron being devoid of subversive amounts of elements materially interfering with the effect of magnesium in increasing the tensile strength.

12. An improved cast iron having increased ductility and having a microstructure containing in the as-cast condition uncombined carbon in the form of spheroids dispersed in a matrix having iron mainly in the alpha form, said cast iron being comprised of a small but effective amount up to about 0.2% magnesium to promote the occurrence of uncombined carbon in the form of said dispersed spheroids with the balance essentially a gray cast iron composition having about 2% to about 4.5% carbon and about 1.5% to about 4.5% silicon and said cast iron having a higher combination of tensile strength and ductility than the same gray cast iron devoid of magnesium.

13. An iron casting having a microstructure containing in the as-cast condition uncombined carbon in the form of substantially spheroidal particles dispersed in a matrix with iron mainly in the alpha form and said casting comprising about 0.04% to about 0.3% magnesium with the balance a gray cast iron composition having iron mainly in the alpha form and being devoid of subversive amounts of elements materially interfering with the occurrence of the aforesaid form of uncombined carbon.

14. As a new article of manufacture, a casting characterized by a microstructure containing spheroids of uncombined carbon and comprised of a ferrous alloy containing a small but effective amount up to 0.5% magnesium, about 1.7% to about 5% total carbon, up to about 6% silicon, and over 50% iron, said ferrous alloy being devoid of subversive amounts of elements materially interfering with the aforesaid characteristic.

15. An improved cast iron having a microstructure containing soft, gray-colored, substantially spheroidal particles of uncombined carbon dispersed in a ferrous matrix and comprising about 0.04% to about 0.5% magnesium to promote the

occurrence of uncombined carbon in the form of substantially spheroidal particles in the as-cast condition with the balance a cast iron composition containing about 2.5% to about 4.5% total carbon with less than about 1.2% carbon in the combined form and about 1% to about 4% silicon, the silicon content being related to the carbon content such that the sum of the percentage of silicon divided by 3.1 plus the percentage of carbon divided by 4.5 exceeds 1.00, and said cast iron composition being devoid of subversive amounts of elements materially interfering with the occurrence of said spheroidal particles.

16. A cast iron characterized in the as-cast condition by a microstructure in which uncombined carbon occurs in the form of substantially spheroidal particles dispersed in the matrix and containing more than about 2% and up to about 5% carbon, the excess carbon not required to form the matrix being predominantly uncombined, more than about 1% and up to about 6% silicon, up to about 36% nickel, about 0.04% to about 0.3% magnesium and, except for elements in minor amounts not subversive to the aforesaid microstructural characteristic, the balance being essentially iron to provide the matrix in which said spheroidal particles are dispersed.

17. As a new article of manufacture, a ferrous casting having a microstructure comprising a matrix containing iron mainly in the alpha form and having uncombined carbon in the form of substantially spheroidal particles dispersed in said matrix, said ferrous casting being comprised of about 1.7% to about 5% carbon, about 1% to about 6% silicon, about 0.04% to about 0.3% magnesium to promote the occurrence of at least some of the uncombined carbon in the form of dispersed spheroidal particles, and at least 87% iron, and said ferrous casting being devoid of subversive amounts of elements which materially interfere with the aforesaid occurrence of uncombined carbon.

KEITH DWIGHT MILLIS.
ALBERT PAUL GAGNEBIN.
NORMAN BODEN PILLING.

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Certificate of Correction

Patent No. 2,485,760 October 25, 1949

KEITH DWIGHT MILLIS ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 65, for "sulfied" read *sulfide*; column 4, line 53, for "representive" read *representative*; column 5, line 19, for "ac-cast" read *as-cast*; lines 45 and 46, after the word "example" insert a comma; line 64, for "leser" read *lesser*; column 6, line 30, for "of spherical" read *or spherical*; column 7, line 74, for "matric" read *matrix*; column 10, line 1, for "magesium-containing" read *magnesium-containing*; column 12, line 24, for "aded" read *added*; line 35, for "magesium" read *magnesium*; column 14, line 23, for "shunken" read *shrunken*; line 47, for "casting" read *castings*; column 17, Table V, for that portion of the heading to the sixth column reading "Nu" read *Mn*; column 18, Table VI, sixth column thereof, for "2,150" read *2.150*; column 19, line 1, for "possess" read *possesses*; column 20, lines 18 and 19, for "65 respectively" read *65, respectively*); line 57, for "(alloy 65)" read (*alloy 63*); column 21, line 32, for "Table VII." read *Table XII.*; line 73, for "Tables VIII and XIV" read *Tables XIII and XIV*; column 22, line 27, for "produced" read *produces*; column 23, Table XV, under the heading "Ferritized" for the numeral "20.6" read *20.5*; same column, for "17.5" read *17.6*; column 30, line 13, for "subersive" read *subversive*; line 25, for "0.05" read *0.05%*; line 68, for "interferring" read *interfering*; column 32, line 55, list of references cited, for "Veazley" read *Veazey*; line 58, for "Oct. 15, 1939" read *Oct. 15, 1929*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of April, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.