May 20, 1958 K. D. MILLIS ET AL 2,835,619

METHOD OF HEAT TREATING CAST IRON

Filed Jan. 8, 1954



Fig. 1

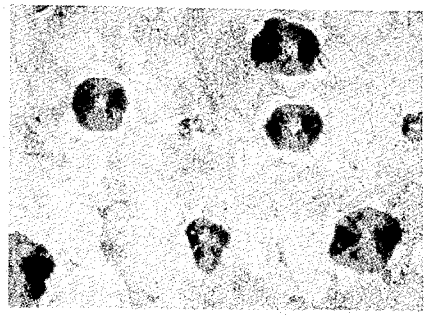


Fig. 2

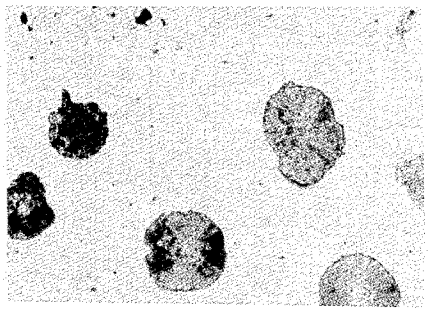


Fig. 3

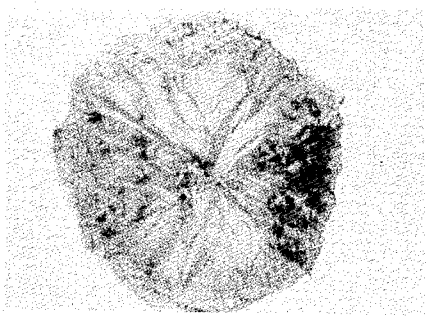


Fig. 4

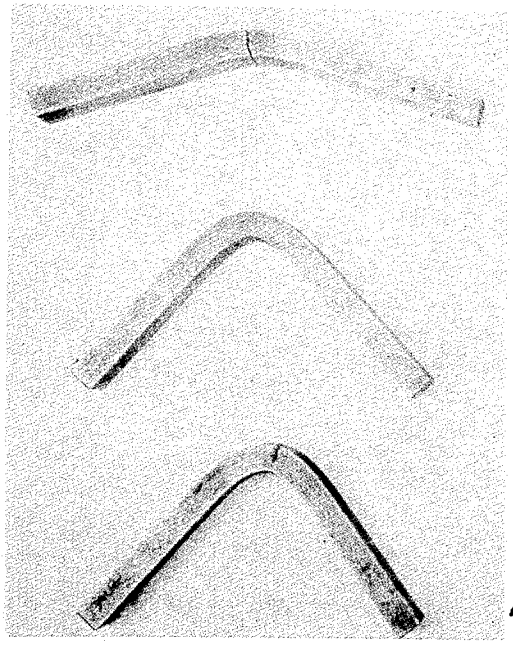


Fig. 5

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METHOD OF HEAT TREATING CAST IRON

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Claims priority, application Great Britain March 22, 1947

4 Claims. (Cl. 148—21.7)

The present invention relates to a process for producing a new ferrous product possessing advantageous features of malleable iron but devoid of defects and shortcomings thereof and, more particularly, to a process for heat treating a special ferrous product to provide therein an improved and unusual combination of mechanical and physical properties.

The present application is a continuation-in-part of our copending U. S. application Serial No. 115,088, filed September 10, 1949 (now U. S. Patent No. 2,749,238, granted June 5, 1956), said copending U. S. application being in turn a continuation-in-part of our earlier U. S. application Serial No. 787,420, filed November 21, 1947 (now U. S. Patent No. 2,485,760, granted October 25, 1949) and copending therewith.

Because malleable iron, which has bene recognized to possess higher ductility than gray cast iron, usually depends for its production upon the sand casting of a hard and less ductile white iron and the heat treatment of this white iron, it possessses numerous disadvantages and limitations. For example, the composition that can be employed in making malleable iron from such castings must be maintained within certain limits so that it is low in graphitizing power, for example, low in carbon and in silicon, in order that it will remain white when cast and will be free from primary graphite in the "as-cast" condition, as required by malleable iron specifications such as A. S. T. M. specifications A47–33, A197–39 and A220–44T. In order that the iron casting cool rapidly and not graphitize, the sand castings which are to be converted by heat treatment to malleable iron are usually limited to relatively thin section sizes, for example, up to about 1 inch in thickness, although sections up to 2 or 2¼ inches have been produced occasionally by employing the greatest refinement in technique. Since increasing the section size increases the graphitization, products having the larger section sizes must have compositions lower in graphitizing power, e. g., lower in carbon and silicon contents, than products having the smaller section sizes. The use of the low carbon and silicon contents required in the white cast iron has the disadvantage that the resultant molten baths have poorer castability and higher melting points than the baths that can be employed to produce ferrous alloys containing uncombined carbon in the "as-cast" condition, e. g., gray cast iron. The higher melting points necessitate the use of higher melting temperatures than are required for the production of gray cast irons. In addition, white iron castings to be utilized for the production of high-grade malleable iron are usually processed in the air furnace, the open hearth furnace, the electric furnace or by duplex operations in such a furnace following cupola melting and are not processed in the cupola furnace alone, although the latter is an inexpensively operated furnace that is commonly and usually preferably employed for the production of gray cast iron. The production of malleable iron requires the use of a high-temperature annealing treatment. One essential purpose of the

heat treatment of the white cast iron is to decompose the combined carbon which is present as free massive carbides (often referred to as cementite). In addition, further heat treatment is often employed to decompose the combined carbon present in the pearlite (as laminations of carbides or cementite). In the white cast iron before heat treatment, the free massive carbides which exist in addition to the combined carbon present in the matrix represent the excess of combined carbon over that required to produce the matrix structure. While these two forms of combined carbon are chemically similar in that they are both carbides, different temperatures are employed during the heat treatment to decompose them. The temperatures employed are related to the temperature at which the alpha-gamma transformation takes place because of the fact that the combined carbon in the matrix is in solution above this transformation temperature (but not below this temperature) while the free massive carbides are substantially undissolved above the transformation temperature. In order to decompose the combined carbon or carbides, they must not be in solution at the particular temperature of treatment. Since the carbides generally decompose more rapidly the higher the treating temperature, the usual heat treatment employed to produce malleable iron involves the use of several temperatures, including at least a high-temperature treatment above the transformation temperature to decompose the free massive carbides which may be followed by a lower temperature treatment below the transformation temperature to decompose the carbides or combined carbon in the matrix (when it is desired to obtain a ferrite matrix rather than a pearlite matrix). Ferritic malleable iron is employed where optimum ductility is desired at the sacrifice of tensile strength, whereas pearlitic malleable iron finds more usefulness where higher tensile strength is desired at the sacrifice of ductility. The heat treatment employed in the commercial production of ferritic malleable iron frequently requires about fifty hours, and in some cases heat treating times of the order of 150 hours are actually employed.

The present invention is based upon the discovery of a method whereby special ferrous alloy castings containing carbon and silicon in the cast iron range can be heat treated without the development of flake graphite forms to produce an unexpectedly high combination of properties in said castings as compared to those of conventional malleable irons.

It is an object of the present invention to provide a process for heat treating a special high-carbon ferrous alloy to produce properties therein equivalent to or higher than those of malleable iron with the same matrix structure and which can be cast in larger sections than can be used in the production of malleable iron.

It is another object of the invention to provide a process for heat treating a special ferrous alloy which can contain larger amounts of carbon, silicon and other graphitizing elements than it is possible to obtain in malleable iron and which has a better combination of properties than malleable iron.

Still another object of the invention is to provide a process for heat treating a special ferrous alloy which can be made from ferrous materials melted in a cupola furnace to provide therein an improved combination of mechanical 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:

Figure 1 is a reproduction of a photomicrograph taken at a magnification of 250 diameters showing the polished and etched structure of a base composition in the as-cast condition;

Fig. 2 is a reproduction of a photomicrograph taken at the same magnification as Fig. 1 showing the polished and etched structure of the same base composition after treatment to convert the uncombined carbon thereof to a spheroidal form;

Fig. 3 is are production of a photomicrograph taken at the same magnification as Figs. 1 and 2 and showing the polished and etched structure of the alloy of Fig. 2 after a heat treatment to "ferritize" the matrix;

Fig. 4 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; and

Fig. 5 is a reproduction of a photograph of three bend-test specimens, one specimen having been tested in the as-cast condition and the other two specimens having been tested after different "ferritizing" treatments contemplated by the present invention.

The present invention provides a method for heat treating special cast ferrous products containing about 87% or 90% or more iron, carbon and silicon within the cast iron range, with the carbon in excess of that required to form the matrix being predominantly in the uncombined form, and containing a small but effective amount of retained magnesium (e. g., as little as about 0.035% or less magnesium) up to about 0.5% of retained magnesium to control the occurrence of uncombined carbon in the form of randomly dispersed, soft, gray-colored, substantially spheroidal or spherical particles or agglomerates of such particles. Such cast iron products are characterized by the alpha-gamma phase transformation on heating and are fully described in our copending U. S. application Serial No. 115,088 (now U. S. Patent No. 2,749,238) and in our U. S. application Serial No. 787,420 (now U. S. Patent No. 2,485,760). These alloys, in general, have a pearlitic matrix. As pointed out in the aforesaid U. S. Patent No. 2,485,760, it was recognized that magnesium determinations of the order involved herein were difficult to make, and the values given herein are based upon analyses by a chemical wet method and were reproductible within about 0.005% or so. It was also pointed out in the aforesaid patent that the accuracy of the values of retained magnesium were complicated by the presence of other elements associated with magnesium in the ferrous product.

The special heat treatment provided by the present invention produces markedly improved ductility in combination with high tensile strength in the aforesaid alloys and comprises heat treating such alloys 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. It is also preferred that the heat treatment at an elevated temperature slightly below the critical temperature to 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 of the present invention, 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 structure of heat treated or ferritized product of the invention is preferably substantially free from flake graphite. Generally, no sulfide particles appear in the matrix, whereas ordinary gray cast irons, white cast irons and malleable irons contain many easily recognized sulfide inclusions embedded in the matrix. The spherulitoid or spheroidal particles in the ferritized product of the invention are soft and gray-colored and are comprised of a large spheroidal or spherical body with a very thin irregular fringe, shell, edging or rim as shown in Figure 4. Under high magnification, e. g., a magnification of 1000 diameters at which the particles are usually about 1 to 2½ inches in average diameter, the spherulitoid or spheroidal particles are characterized by a radiating or radial type of structure in the body portion, which is apparently composed of a plurality of crystals radiating from one or more points near the center of the particle. 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.

The ferritized alloy provided by the present invention usually contains over about 1.7% but less than 5% carbon, over 1% but less than 4% silicon, and magnesium usually within the range of about 0.04% to 0.25% or 0.3%. A feature of the composition is that it can have a high graphitizing power such as cannot be present in compositions employed to produce malleable iron. Compositions having such high graphitizing power that the carbon content plus one-third the silicon content is over 3.5% or 3.7% can be employed to produce the ferritized alloy of the present invention as well as compositions having lower graphitizing power. Many as-cast compositions in which the carbon content plus one-third the silicon content was 4.2% or more have been treated very satisfactorily to produce the heat treated ferritized product of the present invention. In producing the ferritized alloy, it is preferred to maintain the carbon content within the range of 2% to 4.5%, to maintain the silicon content within the range of 1.3% to 3.5%, more preferably within the rang of 1.5% to 3%, and to maintain the magnesium content within the range of about 0.04% or about 0.05% to 0.2%, especially within the range of 0.06% to 0.15%. The fact that silicon contents above 1.5% and/or carbon contents above 3% can be employed in part distinguishes the ferritized product of the present invention from high quality malleable iron which has been restricted to low silicon contents, usually not over 1.2% (e. g., 0.8% to 1.2%), and/or low carbon contents usually not over 2.7% (e. g., 2.0% to 2.7%). Most of the carbon, and often essentially all the carbon, will be uncombined and will be present in the spherulitoid or spheroidal form of uncombined carbon in the ferritized alloy of the present invention. 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. The ferritized alloy may be free from alloying elements or may contain small amounts of alloying elements, particularly nickel. Thus, the alloy to be ferritized may contain the small amounts of nickel, molybdenum, chromium, maganese, etc., that permit obtaining a pearlitic matrix in the as-cast product. The nickel content is preferably less than 4%, e. g., 0.5% to 2.5% or 3%. Molybdenum stabilizes austenite and, in addition, tends to increase the heat treating time required. It is preferred that chromium be absent, although amounts of chromium not exceeding about 0.5% or 0.8% may be present. Manganese preferably does not exceed 0.8% or 1%. Manganese is an austenite stabilizer and, like chromium, interferes to some extent with the ferritizing heat treatment, usually by increasing the heat treating time required, and for this reason is more preferably maintained below 0.4% or 0.3%. It is preferred that copper not be present in large amounts, e. g., in amounts exceeding 2%. While phosphorus may be as high as 0.4% or 0.5%, it preferably should not exceed 0.25% and more preferably not more than about 0.06%, as it has been found that phosphorus tends to lower the properties of the ferritized product, especially the ductility and the tensile strength. Due to the presence of magnesium in the product, the sulfur content is low as magnesium reacts and/or combines with sulfur present in a molten cast iron bath and reduces the sulfur content of castings made therefrom to a low level as pointed out in the aforementioned U. S. Patents No. 2,485,760 and No. 2,749,238. Thus, said patents disclose that the sulfur content of the cast product usually does not exceed about 0.02% and is commonly between about 0.007% or 0.010% and 0.015% unless the process employed in producing the product introduces less sulfur. The product will be substantially devoid of or will contain only very small amounts of the subversive elements arsenic, antimony, tin, bismuth, selenium, tellurium, titanium, etc., as these subversive elements interfere with the formation of the spheroidal form of carbon and/or the attainment of the high properties provided in accordance with the invention. It is obvious from said patents that the lower the content of undesirable elements which tend to combine with and/or counteract the effect of magnesium, for example, sulfur, etc. (and including oxygen, if any be present in the molten cast iron bath as believed by some metallurgists) and the lower the content of subversive, detrimental and/or interfering elements in the molten cast iron bath employed to produce castings for treatment in accordance with this invention, the lower is the amount of magnesium that needs to be introduced and retained in castings produced therefrom to cause the occurrence of spheroidal graphite therein. The balance of the composition is iron except for small amounts of impurities. The iron content, in general, will be at least about 87% and will usually be at least 90% of the total composition. The final heat treated ferritic product made in accordance with the invention and having the foregoing compositions will have the structure described hereinbefore.

The ferritic product produced by the special heat treatment and having the aforementioned composition and micro-structure is distinguished from ferritic malleable iron by an improved combination of founding properties, strength and ductility. Usually, the ferritized castings of the invention possess high ductility which is evidenced by an elongation in tension of over 5% and as high as 20% or more. The high ductility is obtained in conjunction with higher strength than has been obtained in malleable iron and similar alloys. The high ductility combined with high strength can be obtained in compositions containing more carbon and/or silicon than has been employed in 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. For example, it has been recognized that increasing the section size up to about 2 inches considerably lowers the properties of malleable iron and generally increases the heat treating time required to produce the same. In addition, a requirement of malleable iron is that it be made from a cast iron substantially devoid of uncombined carbon in the as-cast condition, i. e., a white cast iron free from primary graphite, whereas the ferritized product of the present invention is made from a magnesium-containing ferrous alloy having a substantial amount of the total carbon content present in the uncombined form in the as-cast condition.

In actual practice, particularly satisfactory results have been obtained in ferritized products containing about 2.8% to about 3.8% carbon, about 1.5% to about 2.7% silicon, about 0.06% to about 0.15% magnesium, about 0.5% to about 3% nickel, about 0.1% to about 1% manganese, and the balance essentially iron, particularly when the manganese content does not exceed about 0.3% and the phosphorus content does not exceed about 0.05%. Ferritized products having compositions within the aforesaid range of compositions 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 I 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 I

Property	As-cast	Ferritized
Percent Elongation (2 in.)	7	20.5
Percent Reduction of area	6.4	17.6
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. As those skilled in the art will appreciate, the casting to be ferritized may contain some free massive carbides due to production variables. 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. This higher temperature treatment which precedes the lower temperature treatment can be effected by holding the casting at one or more temperatures and then cooling at any convenient rate, or by gradually cooling the casting through the range of temperatures. Such a gradual cooling treatment is obtained by furnace cooling, pit cooling, or even cooling in the mold when the mass is sufficiently large to maintain a slow cooling rate. Average cooling rates of about 75° to 200° F. per hour, e. g., about 100° F. per hour, through the range of temperatures down to the critical temperature can be utilized as the higher temperature treatment to produce satisfactory results. The foregoing treatment can be accomplished in a number of ways. For example, in one method which utilizes the heat contained within the hot casting, these hot castings are stripped from their molds at red or black heats, transferred to a preheated pit at 1400° F. to 1800° F., e. g., 1500° F. to 1750° F., and allowed to cool slowly in the pit until the temperature is slightly below the critical temperature, at which point the cooling is interrupted and the castings held at that temperature for the required time. Alternatively, cold pearlitic castings can be placed in the preheated pit and held for the required time to raise the temperature to within the range of 1400° F. to 1800° F. and then treated in the same manner. Cold castings can also be transferred to a furnace or pit and held at a temperature between 1400° F. and 1800° F., e. g., 1550° F. or 1600° F. or 1700° F. or 1750° F., then air cooled or quenched, e. g., to room temperature or to just below the critical temperature, and then treated at a temperature or within the range of temperatures just below the critical temperature. In general, a temperature range (for treating just below the critical temperature) of about 1270° F. to 1310° F. has given satisfactory results in treating most compositions in accordance with the invention. Instead of holding the casting at one temperature or a plurality of temperatures just below the critical temperature and/or instead of interrupting the cooling from above the critical temperature when a temperature just below the critical temperature is reached, satisfactory results can be obtained by slowly cooling the casting through the range of temperatures just below the critical temperature, e. g., furnace cooling, pit cooling, or even by cooling extremely slowly in a mold. Slow cooling rates of 50° F. per hour, more preferably 25° F. or 30° F. per hour, or slower, can be used in cooling through the range of temperatures slightly below the critical temperature without interrupting the cooling or without holding the casting at one or more fixed temperatures. The critical temperature is influenced by many factors, as is well known to those skilled in the art. For example, each composition has its own critical temperature. The temperature range set forth hereinbefore is generally suitable for most compositions but may have to be adjusted under particular conditions. Thus, silicon usually raises the critical temperature while nickel lowers the critical temperature. Accordingly, if the nickel content is high, slightly lower temperatures should be employed while if the silicon content is high, slightly higher temperatures should be employed. Nickel and/or silicon may occasionally be present in the composition in amounts which may require an adjustment in the treating temperature in order to maintain said treating temperature just below the critical temperature as described hereinbefore.

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. 1 to 3. Fig. 1 shows the polished and etched as-cast structure at a magnification of 250 diameters of an inoculated base composition melted in a cupola and containing about 3.6% carbon and 2.3% silicon. Fig. 2 shows the as-cast structure in the polished and etched condition at 250 diameters of the base composition after the introduction of magnesium and inoculation with ferro-silicon to provide the required amount of retained magnesium and the spheroidal form of carbon in the as-cast condition. Fig. 3 shows the effect on the matrix structure shown in Fig. 2 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. 3 (taken at a magnification of 250 diameters), the pearlite in the matrix has been converted by the heat treatment to ferrite. As previously indicated, Fig. 4 shows at a magnification of 1000 diameters a carbon particle in a ferritized product produced in accordance with the present invention.

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 the properties that can be obtained in the ferritized product, data have been set forth in Tables II, III, and IV 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 speroidal form of carbon in the as-cast condition.

Table II

Alloy No.	Percent C	Percent Si	Percent Mg	Percent Mn	Percent P	Percent 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	[1] 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

[1] N. D.=not determined, low.

Table III

No.	Heat Treatment
0	As cast (no heat treatment).
5	Cold castings heated to about 1,750° F., held 5 hrs., furnace cooled to room temperature, reheated to about 1,300° F., held 5 hrs.
6	Cold castings heated to about 1,700° F., held 15 min., furnace or pit cooled to about 1,280° F., held 5 hrs.
7	Red hot castings (stripped from mold) furnace or pit cooled from about 1,700° F. to about 1,275° F., held 2 hrs.
8	Red hot castings (stripped from mold) furnace or pit cooled from about 1,700° F., to about 1,275° F., held 5 hrs.
9	Cold castings normalized by holding for 1 hr. at about 1,550° F. and air cooling to room temperature, reheated to about 1,300° F., held for 5 hrs.
10	Cold castings heated to about 1,550° F. and held for 1 hr., quenched in oil, reheated to about 1,300° F., held for 5 hrs.

Table IV

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

El.=Percent elongation in 2 inches.
R. A.=Percent reduction of area.
VHN=Vickers hardness number.
Y. S.=Yield Strength (0.2% offset) in pounds per square inch.
T. S.=Tensile strength in pounds per square inch.

The improvement in ductility obtained by the ferritizing heat treatment is illustrated in Fig. 5 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 alloys 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 V 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 V.

Table V

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

As indicated by the foregoing data in Table V and by the data in Tables III and IV, a high combination of properties, particularly high ductility, can be obtained by a ferritizing heat treatment in which the total time of treatment required is short. The data presented herein illustrate the satisfactory results that can be obtained by the ferritizing heat treatment of the present invention in a total time, including a high temperature treatment, of about 5 to 17 hours. In many cases, particularly those in which the more preferred maximum amounts of manganese, chromium and other stabilizing elements are not exceeded (and in which other carbide stabilizing factors are not dominant), a satisfactory combination of properties can be obtained by treating hot castings for about two hours at 1275° F. to 1300° F. When a partially pearlitic or spheroidized matrix structure is required, as, for example, where somewhat higher strength with a moderate increase in ductility is desired, the total time of treatment can be shortened. For practical purposes, the pit cooling treatment referred to hereinbefore, e. g., in Table III, is a particularly satisfactory treatment because it can be carried out in the simplest equipment.

It has been indicated hereinbefore that the phosphorus content of the ferritized casting is preferably maintained low. 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 VI which gives the properties of alloy 30 containing 0.015% phosphorus and alloys 20C and 30E to 30G, which are similar alloys containing increasing amounts of phosphorus in the order given and in the amounts indicated in Table VI, after having been given ferritizing heat treatments 5 or 6 described hereinbefore.

Table VI

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	[1] 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

[1] 0.1— offset; specimen fractured before 0.2% offset was reached.

As indicated hereinbefore, it is 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%.

It has been found that any free massive carbides existing, as a result of production variables, in the pearlitic castings can be removed by the treatment above the critical temperature. Magnesium-containing alloys which are carbidic as cast but in which the excess carbon is predominantly in the uncombined form and which contain uncombined carbon in the spheroidal form, 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 production of a ferritized product from such a carbidic casting by this method will usually require a longer time, particularly in the high temperature treatment, e. g., at least 2 hours in the high temperature treatment and at least 2 hours in the treatment just below the critical temperature.

The ferritizing heat treatment provided by the present invention 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.

It will be appreciated from the foregoing that carbides in the as-cast structure of the casting can be decomposed at a temperature at least as high as about 75° F. below the critical temperature, e. g., over a range extending from the aforementioned temperature slightly below the critical temperature up to about 1800° F. When the carbides are massive primary carbides, the temperature employed to decompose the carbides should exceed the critical temperature; and when the carbides are a component of the matrix, the temperature should be within 75° F. below the critical temperature.

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 alloy of 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. The spheroidal form of carbon resembles a form of natural graphite having a radial structure which is referred to by Dana, as indicated hereinbefore. 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.

The ferritized magnesium-containing alloy of the invention is particularly applicable in articles requiring high ductility, including articles made heretofore of ferritic malleable iron. In the production of such articles, the alloy of the invention has better founding properties, is not encumbered by section size limitations or compositional limitations imposed on malleable iron, etc., and provides greater flexibility in design than malleable iron. Innumerable other applications utilizing the improved combination of properties provided by 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 appended claims.

We claim:

1. A method for producing a ferrous alloy having improved ductility in combination with substantial strength properties, which comprises subjecting a casting made of a ferrous alloy having a matrix containing combined carbon and having iron in the alpha form and said alloy containing carbon in excess of that required to form said matrix predominantly in the uncombined form and containing magnesium in at least a small but effective amount up to less than 0.5% to cause the occurrence of said uncombined carbon in the form of spheroidal particles dispersed in said matrix, the balance of said alloy being a gray cast iron composition, to a heat treatment for at least about one hour at an elevated temperature within about 75° F. below the alpha-gamma transformation temperature for said alloy to decompose said combined carbon and to provide an increase in the ductility of said alloy.

2. A method for producing a ferrous alloy having improved ductility in combination with substantial strength properties which comprises subjecting a casting made of a ferrous alloy containing at least about 87% iron, carbon and silicon within the cast iron range, having a matrix containing combined carbon and having the carbon in excess of that required to form the matrix present predominantly in the uncombined form and containing magnesium in at least a small but effective amount up to less than 0.5% to cause the occurrence of uncombined carbon in the form of spheroidal particles, to a heat treatment for at least about two hours at an elevated temperature within about 75° F. below the alpha-gamma transformation temperature for said alloy to decompose said combined carbon and to provide an increase in the ductility of said alloy.

3. A method for producing a ferrous alloy having improved ductility in combination with substantial strength properties, which comprises subjecting a casting made of a ferrous alloy having a ferrous matrix containing a constituent from the group consisting of pearlite, martensite and bainite and said alloy containing about

1.7% to 5% carbon, about 1% to 3.5% silicon, magnesium in at least a small but effective amount up to less than about 0.5% to control the excess carbon not required to form said matrix predominantly in the form of said spheroidal particles, and the balance essentially iron, to a heat treatment for at least about two hours at a temperature within about 50° F. below the alpha-gamma transformation temperaure for said alloy to decompose said matrix constituents and to provide a ferrous casting having improved ductility.

4. A method for producing a ferrous alloy having improved ductility in combination with substantial strength properties, which comprises subjecting a casting made of a ferrous alloy having a pearlitic matrix and containing carbon in excess of that required to form said matrix predominantly in the uncombined form and containing magnesium in at least a small but effective amount up to less than 0.5% to cause the occurrence of said uncombined carbon in the form of spheroidal particles dispersed in said matrix, the balance of said alloy being a gray cast iron composition, to a heat treatment for at least about one hour within the range of about 1270° F. to about 1310° F. to decompose combined carbon contained in said matrix and to provide an increase in the ductility of said alloy.

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U. S. DEPARTMENT OF COMMERCE

PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,835,619 Keith Dwight Millis et al. May 20, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 30, for "bene" read -- been --; column 3, line 6, for "are production" read -- a reproduction --; line 43, for "reproductible" read -- reproducible --; line 63, after "temperature" strike out "to"; column 4, line 55, for "rang" read -- range --; column 10, line 39, for "20C" read -- 30C --; line 58, in the footnote to Table VI, for "0.1- offset" read -- 0.1% offset --; column 13, line 8, for "temperaure" read -- temperature --; column 14, line 18, list of references cited, under "FOREIGN PATENTS, for

678,487 Great Britain - - - Sept.13, 1952

read

678,487 Great Britain - - - Sept. 3, 1952

(SEAL) Signed and sealed this 12th day of August 1958.

Attest:

KARL H. AXLINE

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Commissioner of Patents