July 9, 1968 W. OLDFIELD 3,392,013

CAST IRON COMPOSITION AND PROCESS FOR MAKING

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FIG. 1.

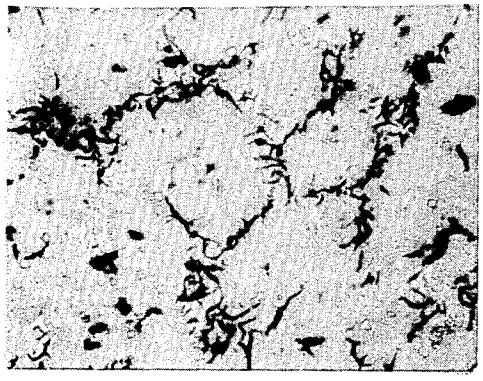


FIG. 3.

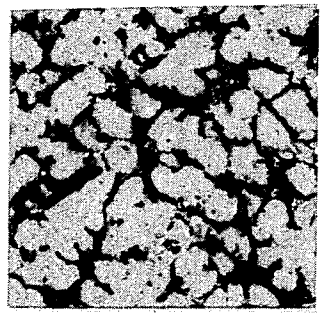


FIG. 2.



FIG. 4.

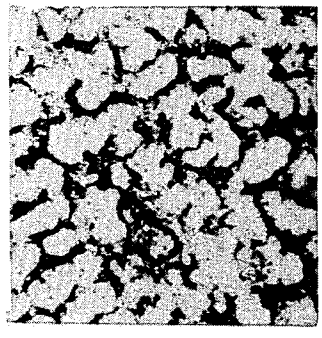


FIG. 5.



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FIG. 6.

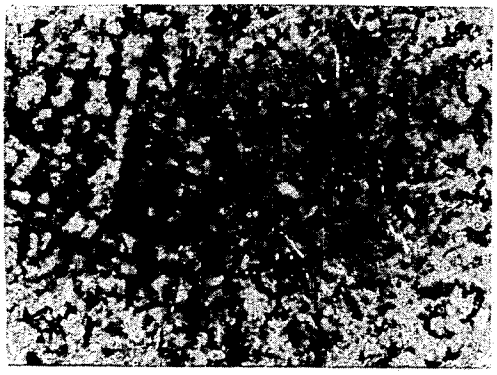


FIG. 7.



FIG. 8.

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United States Patent Office

3,392,013
Patented July 9, 1968

3,392,013

CAST IRON COMPOSITION AND PROCESS FOR MAKING

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Filed Mar. 14, 1966, Ser. No. 545,182
10 Claims. (Cl. 75—124)

This invention relates to a cast iron composition and a process for making the same. More specifically, this invention relates to a cast iron which contains aluminum and chromium and is characterized by a fine Type D graphite. The invention also specifically relates to a process for the preparation of an alloy cast iron which incorporates Type D graphite.

As is mentioned above, the cast iron of this invention is characterized by a final structure which incorporates Type D graphite. Type D graphite is also known as undercooled graphite, compact graphite or is technically described as ASTM A247–47 (Type D) graphite.

Cast iron always incorporates substantial percentages of carbon. The distribution and form which this carbon takes is a primary factor in the determination of the ultimate properties of the resulting cast iron. This carbon can take many forms such as nodular, flake, fine Type D, etc. It is known that the physical properties of cast iron, particularly the tensile strength, elongation, machineability, etc., are effected by reducing the size and distribution of the graphite flakes and by introducing a specified pattern of distribution in said graphite. For some purposes, it is desirable for cast iron to incorporate fine, evenly distributed graphite.

Likewise, cast iron is generally susceptible to high temperature oxidation and has a tendency to fire crack when utilized at higher temperatures. Traditionally, gray cast iron has been utilized for the manufacture of glass mold equipment since it is relatively cheap. However, gray cast iron in an unalloyed condition, is undesirable as a glass mold material because when utilized at high temperatures it tends to scale and fire crack.

Likewise, the oxides of carbon are gaseous and thus permanently damage the scale during their escape from the metal oxide interface. When the graphite is present as extremely fine flakes such as Type D graphite and is evenly distributed, there is greater resistance to fire cracking and better polishability. Therefore, it is imperative that any cast iron which is to be utilized as a glass mold material must have this graphite structure.

Various alloying elements can be added to cast iron to increase its oxidation resistance. These alloying elements tend to cause the formation of an adherent oxide scale on the surface of the mold.

Chromium is known to improve the oxidation resistance of cast iron. The scale formed during the utilization of a chromium alloy cast iron at high temperature is thin and adherent. In addition, chromium alloys are extremely advantageous in that substantial improvements are imparted to the tensile strength, and hardness, of the resulting cast iron. Accordingly, chromium alloy cast iron is extremely desirable for use as a high temperature mold material in that it simultaneously improves the mechanical properties, the thermal fatigue life and oxidation resistance of the glass mold.

The above mentioned advantages of chromium are outweighed by its tendency to form massive, complex carbides with the carbon present in cast iron. Ordinarily, if a cast iron contains more than one percent chromium, the carbides formed make the casting unmachineable. The tendency to form these massive carbides is minimized by the presence of suitable graphitizers such as aluminum. Aluminum is also a desirable alloying element for cast iron which is to be subjected to high temperature use in that it tends to make the alloy more oxidation resistant.

The subject invention relates to a chromium alloy cast iron wherein the carbides are minimal due to the presence of aluminum and wherein the carbon is present not as coarse flake graphite, but as extremely fine Type D graphite. The cast irons of this inventioin also contain other alloy components which enhance the properties of the resulting cast iron.

When glass molds are formed from the cast irons of this invention, the mold blanks are machineable and can be highly polished. The resulting molds likewise have exceptional oxidation resistance and a minimal tendency to fire crack during use.

Generally, prior art discloses several methods wherein cast irons having Type D graphite can be produced. Among these methods are the chill castings of the cast iron, the addition of inoculants such as titanium and purging of the molten cast irons with various gases such as helium and argon. However, alloy cast irons containing significant amounts of aluminum and chromium having Type D graphite are not known in the prior art. The applicant has found that alloy cast iron having Type D graphite can be readily produced by the critical addition of cerium or a cerium containing material just prior to the casting of the alloy cast iron.

The primary object of this invention is the preparation of an alloy cast iron which contains Type D graphite. More specifically, an object of this invention is the preparation of an alloy cast iron which contains aluminum and chromium having Type D graphite. The objects of this invention also include a process for the preparation of an alloy cast iron which incorporates its carbon as Type D graphite.

Cerium has long been utilized as a cast iron inoculant for the formation of nodular cast iron. In nodular cast iron, the graphite is present as spheroid balls which are of a relatively large size. Due to the relatively large size and uneven distribution of the spherical graphite particles, nodular cast iron is undesirable as a glass mold material. By the processes of the subject invention, an extremely fine Type D graphite having a very even distribution is formed. Due to the fact that the graphite particles are very fine and evenly distributed, the cast iron of this invention is extremely desirable as a glass mold material for high temperature use.

Photomicrographs of the chromium-aluminum cast iron of this invention and related alloys are represented in FIGURES 1 through 8. In all cases, the samples were cut, polished, lapped and etched with Nital. The magnification of these photomicrographs is 250×, except FIGS. 3 and 4 which are 125×.

FIGURE 1 is ap hotomicrograph of the chromium-aluminum cast iron of this invention which is produced by the critical cerium addition. It is to be noted that the carbon is present as Type D graphite. This Type D graphite is characterized by extremely fine particles of

graphite which are intermixed with the iron matrix in a spaghetti-like fashion and are evenly distributed throughout the iron matrix. Due to this fine graphite distribution, this material is machineable, very oxidation resistant and it will take a high polish.

FIGURE 2 is a photomicrograph of an alloy which is identical in composition to the alloy as shown in FIGURE 1. This alloy was produced by the same processes except that the critical cerium addition was not made just prior to casting. An examination of this photomicrograph will reveal that the graphite is in the form of relatively coarse flakes. Due to the presence of this flake graphite, mold blanks formed from this alloy are less oxidation resistant, they will not take a high polish and they have a greater tendency to fire crack.

The alloy of this invention has the general chemistry as is represented in Table I.

TABLE I

Ingredients:	Percent
Total carbon as Type D graphite	2–4.
Silicon	1–3.5.
Aluminum	1–5.
Chromium	1–5.
Manganese	.2–2.
Phosphorus	0–.25
Sulfur	0–.25
Titanium	.1–1.
Cerium	Trace.
Iron	Balance.

A more preferred range for the various constituents of the cast iron of this invention is as represented in Table II.

TABLE II

Ingredients:	Percent
Total carbon as Type D graphite	2.5–4.
Silicon	1.5–3.
Aluminum	1–3.5.
Chromium	1–3.5.
Manganese	.5–1.
Phosphorus	.0–.15.
Sulfur	.0–.15.
Titanium	.2–.8.
Cerium	Trace.
Iron	Balance.

Finally, a preferred cast iron in accordance with the invention has the chemistry as is represented by Table III.

TABLE III

Ingredients:	Percent
Total carbon as Type D graphite	2.5–4.
Silicon	1.5–3.
Aluminum	2.5–3.5.
Chromium	2.5–3.5.
Manganese	.5–1.
Phosphorus	.0–.15.
Sulfur	.0–.15.
Titanium	.2–.8.
Cerium	Trace.
Iron	Balance.

It is to be noted that the compositions as represented in Tables I–III, incorporate only a trace quantity of cerimum. However, larger quantities of elemental cerium or a cerium alloy are added to the cast iron melt just prior to casting. While the applicant is not sure of the processes whereby the added cerium is expended, said cerium while refining the graphite structure is expelled from the cast iron as a vapor and as insoluble oxides and sulfides.

As based on the weight of the melt, the critical cerium additions can range from about .02 to about .05%. With a more preferred range being from about .03 to about .04%, and a most preferred addition being .035%. The resulting concentration of cerium is defined in Tables I–III above. If the critical cerium addition falls outside the above specified ranges a uniform distribution of Type D graphite is not achieved. This point is exemplified by the below listed Examples 3–6. The above specified range for the cerium addition is applicable to cast iron melts of normal sulfur content. It is obvious to one skilled in the art that if cast irons of high sulfur content are utilized an appropriate modification of the cerium addition must be made.

It is also to be noted that larger quantities of titanium are added to the melt than appear in the final analysis. However, some of the titanium vaporizes after its addition and hence is lost in a fashion that is somewhat analogous to the loss of the cerium additive.

As is mentioned above, the cerium addition can be made in the form of elemental cerium or in the form of an alloy of cerium. An extremely convenient and economic method for adding cerium is by the addition of misch metal which has a typical composition of

	Percent
Cerium	52
Neodymium	18
Praseodymium	5
Samarium	1
Other rare earth metals	24

While it is convenient to utilize either elemental cerium or misch metal, the applicant does not restrict himself to the use of any form of cerium in the practice of this invention.

The cerium addition can be made when the cast iron melt is at any temperature between the range of from about 2400 to about 2750° F. A more preferred operating range is from about 2400 to about 2550° F. with a more preferred addition temperature being 2500° F. It is obvious to one skilled in the art that the addition and casting temperature must be balanced to achieve an optimum graphite structure of the Type D variety and the most desirable crystalline structure.

After making the cerium addition, the melt must be held at a temperature of from about 2400 to about 2750° F. wth a more preferred temperature range being 2400 to 2550° F. and a most preferred temperature being 2500° F., for a period of time of from about 5 minutes to about 15 miutes from the cerium addition. A more preferred hold period is 10 minutes. This hold period allows the cerium addition to effect the formation of the desired fine Type D graphite structure upon solidification.

After the cerium addition, the cast iron melt must be poured within from about 15 minutes to about 30 minutes. A more preferred pouring time is from about 15 to about 20 minutes from the time of the cerium addition. If the pour is not made within this period, the effect of the cerium addition is lost and a product having an undesirable graphite structure results. It is obvious to one skilled in the art that the optimum hold and cast period are related to the size of the melt. That is the rate of loss of the cerium addition is a function of the surface area. The relative surface area of a melt varies with the size of the melt. Accordingly, the vaporization of the cerium addition is controlled by the size of the melt and hence the hold and cast periods for a melt vary with its size.

The following examples will illustrate the subject invention. These examples are given for the purpose of illustration and not for purposes of limiting this invention.

Example I

A 3% chromium-3% aluminum alloy was prepared. A charge of 50 lb. cast iron with appropriate ferrosilicon and ferrochrome additions was melted. Theoretical analysis was 3.2% total carbon, 3.3% Si, 3.2% cr. The aluminum was added as a .5% cerium-aluminum alloy to a charge of 50 pounds of chromium containing cast iron.

Ferrotitanium was then added to give a .5% theoretical titanium content. The metal was superheated to 2732° F., and 1% theoretical (.5% actual cerium content) cerium-aluminum was added to give 3.4% aluminum addition. The furnace charge was held at temperature for 15 minutes under an inert atmosphere (argon) cover, then tapped into the ladle. Castings were poured at 2462–2552° F. After polishing and etching examination revealed that the sample had a completely refined graphite structure which was of the ASTM Type D classification. The photomicrograph for this run is as represented in FIGURE 3.

Example II

A 3% chromium, 3% aluminum alloy was made by melting a 50 pound charge of cast iron. 50 gm. silicon magnesium was added after melt down to remove sulfur. The theoretical analysis was the same as in Example I. Titanium was added as ferrotitanium after the magnesium addition to give a .5% theoretical titanium content, and later, the aluminum was charged to give a 3.6% theoretical addition. The melt was superheated to 2732° F., and held for 15 minutes. It was then allowed to cool to 2552° F. An addition of 15 gm. misch metal was made, by adding it to the metal stream while metal was poured into the ladle. After 7 minutes while the furnace was held at 2552° F., a five inch long keel block was cast. The block was then machined to yield a 1" square bar.

An analysis of the microstructure of the sample revealed a completely fine graphite structure falling into the ASTM Type D classification. The photomicrograph is illustrated in FIGURE 4.

Example III

A 110 pound induction furnace melt was carried out using a mixture of heamatite pig iron and steel scrap. The heamatite pig iron had the following chemical composition: T.C. 4.30%; Si 2.25%; Mn 0.83%; S 0.013%; P 0.028%; Ti 0.13%.

When the metal temperature reached 2570° F., 0.4% titanium metal was added to the furnace. The melt was then superheated to 2730° F. The aluminum was added to the furnace as an aluminum/cerium alloy containing 1.05 percent cerium by analysis. After the addition of the aluminum/cerium alloy the melt was held at 2730° F. for 10 minutes. The metal was tapped and blown with argon, in the ladle, for about five minutes until the metal temperature had fallen to 2550° F. Three 1.2 in. diameter bars, 12 in. long, were cast into dry sand molds containing 6 percent sea coal.

Micro-examination of the 1.2 in. bars revealed a fine flake graphite structure and this is shown in FIGURE 5.

Example IV

The melt of Example III, was repeated using an exactly similar melting procedure but with a supplementary addition of 40 g. of cerium misch metal added with the 1 percent cerium/aluminum alloy. Micro-examination revealed a pseudo-nodular graphite structure which is illustrated in FIGURE 6.

Example V

Using the procedure of Example III, a melt was carried out with the cerium misch metal addition reduced to 20 g. This resulted in a mixed structure of normal flake graphite and undercooled graphite as shown in FIGURE 7.

Example VI

With the procedure of Example III, a melt was prepared with a supplementary addition of 30 g. of cerium misch metal and this produced a uniform undercooled graphite structure, as shown in FIGURE 8.

The chemical compositions of the irons produced in the above series of melts are given below:

CHEMICAL COMPOSITION

Example	T.C., Percent	Si, Percent	Mn, Percent	S, Percent	P, Percent	Cr, Percent	Al, Percent	Ti, Percent
3	2.95	3.19	0.51	0.012	0.028	2.75	3.10	0.36
4	3.03	3.18	0.53	0.003	0.028	2.91	2.76	0.34
5	3.00	3.12	0.50	0 010	0.026	2.89	2.73	0.37
6	3.00	3.12	0.55	0.006	0.028	3.00	2.85	0.37

What is claimed is:

1. A casting formed from a ferrous alloy having the folowing chemistry:

Ingredients:	Percent
Total carbon	2–4
Silicon	1–3.5
Aluminum	1–5
Chromium	1–5
Manganese	.2–2
Phosphorus	0–.25
Sulfur	0–.25
Titanium	.1–1
Cerium	Trace
Iron	Balance

wherein the total carbon is present as Type D graphite throughout the casting.

2. The casting of claim 1 wherein the ferrous alloy has the following chemistry:

	Percent
Carbon	2.5–4
Silicon	1.5–3
Aluminum	1–3.5
Chromium	1–3.5
Manganese	.5–1
Phosphorus	.0–.15
Sulfur	.0–.15
Titanium	.2–.8
Cerium	Trace
Iron	Balance

3. The casting of claim 1 wherein the ferrous alloy has the following chemistry:

Ingredients:	Percent
Total carbon as Type D graphite	2.5–4
Silicon	1.5–3
Aluminum	2.5–3.5
Chromium	2.5–3.5
Manganese	.5–1
Phosphorus	.0–.15
Sulfur	.0–.15
Titanium	.2–.8
Cerium	Trace
Iron	Balance

4. A process for forming Type D graphite in a ferrous alloy as set forth in claim 1 which comprises adding cerium to a melt of said alloy.

5. The process of claim 4 wherein the melt of said alloy is heated to a temperature of from about 2400 to about 2650° F., the cerium additive is elemental cerium or a cerium alloy, the molten melt is then held at a temperature of from about 2400 to about 2650° F. for a period of time of from about five minutes to about 30 minutes from the cerium addition and said melt is cast within a period of time of from about 10 to about 60 minutes from the cerium addition.

6. The process of claim 5 wherein the cerium addition is made by the addition of elemental cerium.

7. The process of claim 5 wherein the cerium addition is made by the addition of misch metal.

8. The process of claim 4 wherein the melt of said alloy is heated to a temperature of from about 2450 to

about 2550° F., the cerium additive is elemental cerium or a cerium alloy, the molten melt is then held at a temperature of from about 2450 to about 2550° F. for a period of time of from about five to about 15 minutes from the cerium addition and said melt is cast within a period of time of from about 15 minutes to about 30 minutes from the cerium addition.

9. The process of claim **4** wherein the melt of said alloy containing all components except cerium is heated to a temperature of about 2500° F., the cerium is added as a cerium alloy, the molten melt is then held at a temperature of about 2500° F. for 10 minutes from the cerium addition and said melt is cast in about 20 minutes from the cerium addition.

10. The ferrous alloy of claim **3** which is produced by

heating a melt to a temperature of about 2500° F., adding thereto .035 percent cerium as misch metal, holding the melt at a temperature of about 2500° F. for 10 minutes from the cerium addition and pouring said melt in about 20 minutes from the cerium addition.

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HYLAND BIZOT, *Primary Examiner.*