Fig. 1. Vacuum treated Duriron containing cerium. Nodules and extremely small flakes (Type D) result. Transverse strength 1942 pounds. 100X.

Fig. 2. Vacuum treated Duriron containing calcium. Photomicrograph of a 1/4" section showing small graphite flakes (Type A) and little porosity. 100X.

Fig. 3. Vacuum treated Duriron containing calcium. Photomicrograph from a 2" section shows small graphite flakes (Type A) and little porosity. 100X.

Fig. 4. Vacuum treated Duriron with excess calcium produces nodules and fine graphite. Transverse strength 2060. 100X.
VACUUM TREATED HIGH SILICON CAST IRON WITH GRAPHITIZING INCOULANT

Walter A. Luce and Glenn W. Jackson, both of Dayton, Ohio, assignors to The Duriron Company, Inc., Dayton, Ohio, a corporation of New York

Filed Jan. 2, 1964, Ser. No. 335,207

7 Claims. (Cl. 75—123)

This invention relates to high silicon cast iron and particularly to cast iron of this type in which substantial improvement is obtained in respect to mechanical properties.

The conventional high silicon cast irons are generally well known and well publicized. These alloys are characterized by outstanding corrosion resistance and relatively low cost. Unfortunately, however, the advantages of high silicon cast irons from the corrosion and cost standpoint are commonly offset by the disadvantage of low mechanical strength in comparison with other structural metals, which has accordingly greatly restricted their use.

It has long been known that if the strength of the high silicon cast irons could be improved substantially, this could have an important effect on their application, particularly in the chemical industry, since many of the now commonly used more expensive materials might very advantageously be replaced by high silicon cast iron. Numerous private companies and research organizations have been striving for years to enhance the strength of these cast irons, but until applicants' earlier discovery of a method of vacuum melting, as set out in their co-pending application Serial No. 286,676, filed June 10, 1963, now Patent No. 3,222,161, little in the way of substantial improvement had been achieved which found any practical, commercial acceptance.

By way of definition, the term high silicon cast iron used here is consistent with its use in industry and designates cast irons having more than 6% to 8% silicon, where a definite transition occurs in the type of metallurgical structure; usually 12% to 15% silicon is present in the alloys here under consideration.

Work done by the British indicates that a suitable grade of high silicon cast iron is made with about 0.06% carbon and that it should have controlled internal porosity. Under these conditions, tensile strengths of as much as 20,000 p.s.i. have been realized. It has been recognized, however, that this strength is achieved only by tensile testing under very specialized conditions, and that with ordinary test procedures the values are substantially lower.

In the United States, manufacturers of high silicon iron alloys publish tensile properties for their products of about 16,000 p.s.i., which represents the equivalent of the British material under ordinary test procedures. However, in following the latter, great difficulty is encountered in the testing of brittle compositions such as high silicon alloys. Because of this, it is normal in the United States to determine tensile strength from converted transverse tests values and to use transverse test data for purposes of direct comparison. Further explanation of this will appear hereinafter.

Commercial high silicon irons manufactured in the United States generally have higher carbon contents than recommended by the British and in general this ranges around 1.0% to 1.25% for overall application or use. In addition, they contain controlled amounts of porosity in order to help retard those failures in service caused by rapid fluctuations in temperature (thermal shock). The high silicon cast irons are accordingly more widely used in the United States than in Europe, principally because this "cushioning" effect from the graphite and controlled internal porosity helps to minimize breakage. But the limited strength situation is still sufficiently serious to restrict the use of these alloys to the more severe acid media where other metals have limited serviceability from the corrosion standpoint.

Much emphasis has also been given heretofore to "siliconizing" which is a process of impregnating a steel surface with silicon to achieve a combination of corrosion resistance on the surface and ductility underneath. However, this process has serious drawbacks which has limited its usefulness commercially, and it has not yet become a commercial operation. Considerable research has likewise been done in the treatment of high silicon cast iron with nodularizing inoculants, e.g. cerium, and while the strength of the cast iron can be improved, it has remained a most critical and unpredictable process resulting in material of an extreme brittleness and substantially worsened thermal shock resistance. In addition, serious porosity defects are encountered on the cope surface of castings made of cerium inoculated high silicon cast iron, and it has been apparent from this work that graphite in the nodular form does not provide the "cushion" needed for good serviceability. Accordingly such cerium inoculated high silicon cast iron has received only very limited commercial acceptance.

Vacuum treatment has also been tried on a variety of metals and alloy steel while in molten state, especially stainless steels, in attempts to improve their properties. These relatively expensive alloys have been vacuum treated on a commercial basis primarily because certain mechanical properties, such as high temperature strength as contrasted to normal room temperature strength, are somewhat improved by the process. A careful study of the literature indicates that these improvements have not been accompanied by added cleanliness of the melt in these cases and do not involve any change in the alloy microstructure, as such. As a consequence, the improvement on room temperature tensile strength is rarely 25% of the non-vacuum treated value and never over 50%.

Very little work is reported in the literature on vacuum treatment of cast irons specifically, and this is probably explainable on two grounds. First, the initial work in cast irons and other alloys has indicated that no strength benefit, at least none which would be of significant order in the case of the high silicon cast irons, appears likely. Secondly, the economics of vacuum treating a cast iron or any other relatively inexpensive alloy is certainly unfavorable. General purpose high silicon cast iron, having a nominal analysis of 14% to 15% silicon, about 0.9% to 1.1% carbon, 0.65% manganese, the balance substantially all iron, has a transverse load strength of only about 900 to 1250 pounds, with a statistical mean value of around 1075 pounds. The order of improvement desired, if it is to be of significance, is a minimum of 50% of this statistical mean value. As mentioned above, this is beyond anything experienced by vacuum treatment of alloys generally.

Again, by way of definition, the term transverse load strength signifies the load in pounds, needed to fracture a standard test bar of the alloy. This is determined by using a standard cast bar 1" x 1" x 13", supported on 1/2" centers and loaded at the midpoint until fracture occurs. The results can be converted into approximate tensile strengths by multiplying the values thus obtained by a factor of 15. A similar test for ordinary cast iron is covered by ASTM specification A 438—62 and may be used as a guide in the testing of the high silicon cast irons.

In our aforesaid application Serial No. 286,676, now Patent No. 3,222,161, we have disclosed a method of vacuum treatment of high silicon cast iron which has produced a remarkable and unexpected improvement in the mechanical properties of high silicon cast irons when the operating criteria therein disclosed are met. As dis-
3,271,187

It was found that hydrogen and nitrogen gas normally present in high silicon iron must be reduced to very low values on the order of two parts per million and six parts per million, as a maximum, respectively. Oxygen levels were also found to be important, as oxygen should be reduced to about the level of 20 to 30 p.p.m., which appears to be the equilibrium obtained when these gases are held under vacuum in the usual oxide lined furnace. Following such teaching it was found by the present inventors that a transverse load strength of 1600 pounds could usually be obtained in ordinary practice, and values of 2000 pounds and up were sometimes possible. What was also most important, such strengths were achieved without loss of adequate thermal shock resistance in the alloy, and generally this property was improved.

As stated in the aforesaid prior copending application, the increase in strength appeared in the case of cast iron. It was achieved through combination of vacuum degassing and careful treatment with calcium, a compound of calcium, and to some extent by another element of the same type or group as calcium. The combination of these treatments consistently produces a transverse load strength of 1600 pounds and above. The alloy is rendered ductile by this procedure. However, the thermal shock resistance and the ability to withstand sudden temperature fluctuations (thermal shock) are also increased proportionately to the transverse strength which is most significant. Thermal shock characteristics are in fact improved beyond any point previously obtained. What is also quite as important, the mechanical improvements thus afforded are not accompanied by any adverse effect on corrosion resistance which of course remains one of the predominant requirements of the alloy. The new alloys retain all of the properties of the untreated high silicon alloys in this respect, and in some areas even show substantially improved corrosion resistance.

When high silicon cast irons are melted by a conventional process in contact with the atmosphere, the resultant melt will of course vary in the amount of residual nitrogen, oxygen, hydrogen and perhaps other deleterious elements they contain. Such variables, although within narrow limits not previously considered significant, can have a profound effect on the serviceability of castings, especially in the case of a relatively brittle composition such as that here concerned. Vacuum treatment can and does readily hydrogen and nitrogen contents to levels which are certain to provide a "shrink-type" iron, i.e. essentially gas or void-free; but that may not always produce castings having a strength increase of 50% minimum over the conventional untreated alloy, particularly in castings of heavier cross section. This result may be consistently obtained, however, by treatment of the vacuum degassed iron with calcium, or a calcium compound as already mentioned, to provide a fine graphite structure and a refined grain size.

It is currently believed that calcium reacts first with oxygen and certain other deleterious elements and then with carbon to form numerous calcium carbide particles. These calcium carbides act as favorable nucleation points for graphite to precipitate. Thus a large number of graphite flakes can grow, and since none can become excessively large, a uniformly refined structure results. This particular material has a relatively good transverse strength (1942 pounds) but its thermal shock properties are quite poor. It has been determined that residual calcium levels above about 0.05% should be avoided, since they definitely tend toward a nodular graphite structure.

Other elements, in the same group as calcium, notably barium and magnesium, have a corresponding influence on the graphite pattern. Magnesium will readily nodularize the carbon when added in sufficient quantities but is similar to barium in that the effect is quite drastic with slight changes in amount added. Proper control is therefore more difficult to achieve with magnesium, although it is substantially better than calcium in this respect. Quantities of barium up to 0.40% added to vacuum degassed high silicon iron do not provide mechanical properties or structure which approach that of the calcium treated metal. The amount of barium needed to provide minimum mechanical properties appears to be around 1%, or perhaps slightly less, but at the present time this is not economical in comparison with the use of calcium.

The accompanying drawing is illustrative of differences in microstructure of various vacuum treated high silicon cast irons, in which photomicrographs at a magnification of 100X are shown for alloy sections of the same basic high silicon cast iron composition. This basic composition is that previously noted, namely 14% to 15% silicon, 0.9% to 1.1% carbon, 0.65% manganese, the balance essentially all iron, apart from the calcium or cerium inclusion, as mentioned in the respective cases under comparison here.

FIG. 1 illustrates a vacuum treated high silicon alloy of the basic composition to which magnesium has been added. The characteristic nodular form of the graphite is readily apparent, and this is accompanied by extremely small flakes (type D). This particular material has a relatively good transverse strength (1942 pounds) but its thermal
shock resistance is extremely low. FIG. 2 shows a conventional high silicon cast iron of the same composition as in FIG. 1, but in this case calcium was added in place of cerium. The relative uniformity of the graphite which is in small flake (type A) form, and the virtual absence of porosity, characterize the microstructure of this alloy. FIG. 3 illustrates essentially the same composition as in FIG. 2 but the section shown is from a casting of substantially greater thickness, being approximately 2" thick as against 1/4" in FIG. 2. FIG. 4 also shows the microstructure of a vacuum treated high silicon cast iron of the same basic composition as in this case however residual calcium in excess of the recommended level, i.e. over about 0.05%. Here again it is noted that the nodular form of graphite appears, and the microstructure is essentially similar to that of the cerium treated material in FIG. 1. Although the transverse strength is relatively high, thermal shock properties are very poor in this material, roughly only one-fourth as good as that of the material in FIGS. 2 and 3 when thermally shocked from a temperature of around 600° F. Such a test is conducted by heating a standard transverse load test bar to elevated temperature (e.g. 600° F. mentioned above) and immediately lowering the bar onto spaced supports in a continuous circularizing water bath in a vacuum atmosphere of pressures of 65" to 70" F. The supports are placed to dispose the bar horizontally so that the water surface of the bath bisects the bar along its length. When conditions are stabilized, the bar is checked visually for cracks and also is subjected to the standard transverse load test previously described.

It is most significant to note that the microstructure does no vary greatly with section size of the casting as seen by comparison of FIGS. 2 and 3. This differs from the results previously obtained in the use of vacuum treatment alone, without calcium addition, and is most important from a practical standpoint as this provides a consistency of product not previously obtained.

The effect on transverse strength of the calcium addition is shown in Table I. The basic alloy composition in all cases was standard "Duriron" (nominally 14.5% silicon, 1.0% carbon, 0.65% manganese, the balance iron). This was modified by the addition of calcium (in the form of calcium-silicon) to provide the various levels of retained calcium noted in the table.

### Table I: Effect of Retained Calcium on Transverse Strength

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Percent Retained Calcium</th>
<th>Transverse Strength, Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-39497</td>
<td>0.016</td>
<td>1,030</td>
</tr>
<tr>
<td>E-39492</td>
<td>0.018</td>
<td>2,964</td>
</tr>
<tr>
<td>E-39490</td>
<td>0.025</td>
<td>3,688</td>
</tr>
<tr>
<td>E-39499</td>
<td>0.036</td>
<td>1,900</td>
</tr>
<tr>
<td>E-39494</td>
<td>0.040</td>
<td>2,118</td>
</tr>
<tr>
<td>E-39487</td>
<td>0.048</td>
<td>1,818</td>
</tr>
<tr>
<td>E-39503</td>
<td>0.058</td>
<td>1,760</td>
</tr>
<tr>
<td>E-39498</td>
<td>0.060</td>
<td>1,830</td>
</tr>
</tbody>
</table>

The production of the improved alloys permits of considerable leeway in the vacuum treatment without drastically affecting the properties of the resultant material. Good results are obtained when the vacuum operation is conducted for 10 minutes at 2625° F. at a pressure of not over 5 mm. Hg. But temperatures of 2600° to 2800° F., and pressures as high as 50 mm. Hg will give acceptable results in some cases; better practice dictates that the maximum pressure should not exceed about 25 mm. Hg. However, Table II indicates the effect on transverse strength of different times and pressures in the area of the recommended or optimum conditions of vacuum operation.

### Table II: Effect of Pressure and Time in Vacuum Furnace

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Time, min.</th>
<th>Pressure, mm. Hg.</th>
<th>Temp., F.</th>
<th>Before Vacuum</th>
<th>After Vacuum</th>
<th>After Vacuum Plus Calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-39497</td>
<td>12</td>
<td>25</td>
<td>2,620</td>
<td>1,290</td>
<td>1,294</td>
<td>1,765</td>
</tr>
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<td>E-39492</td>
<td>12</td>
<td>48</td>
<td>2,116</td>
<td>1,414</td>
<td>1,749</td>
<td>1,403</td>
</tr>
<tr>
<td>E-39490</td>
<td>20</td>
<td>48</td>
<td>2,610</td>
<td>1,018</td>
<td>1,226</td>
<td>1,003</td>
</tr>
<tr>
<td>E-39494</td>
<td>12</td>
<td>69</td>
<td>2,610</td>
<td>1,179</td>
<td>1,878</td>
<td>1,580</td>
</tr>
<tr>
<td>E-39487</td>
<td>12</td>
<td>75</td>
<td>2,610</td>
<td>1,480</td>
<td>1,487</td>
<td>1,478</td>
</tr>
<tr>
<td>E-39498</td>
<td>12</td>
<td>75</td>
<td>2,620</td>
<td>1,416</td>
<td>1,487</td>
<td>1,487</td>
</tr>
</tbody>
</table>

It appears that the new alloys have more linear shrinkage than conventional high silicon cast iron, and it is reasoned from this that a higher order of residual stress is introduced into the more dense vacuum treated metal during solidification and/or cooling. In castings of a complex, non-symmetrical design, it is accordingly sometimes necessary to remove such castings from the molds while still hot and place them immediately in hot furnaces to permit stress relief treatment. This treatment is not necessary in simple castings or those having substantially symmetrical, e.g. concentric, shapes since these do not develop high residual stresses.

**Corrosion resistance of the calcium inoculated, vacuum degassed metal is fully as high as that of the standard vacuum degassed metal without calcium inoculation previously disclosed.** A definite improvement in corrosion resistance over standard air furnace melted "Duriron" is obtained, as illustrated by the comparison in Table III showing typical results in several severe media.

### Table III: Corrosion Rate, Mils Per Year, Means of 24-Hour Periods

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Boiling 30% HNO₃</th>
<th>30% HCl, 100° F.</th>
<th>Boiling 65% HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>29003 1</td>
<td>44</td>
<td>53</td>
<td>1</td>
</tr>
<tr>
<td>E-20092 2</td>
<td>31</td>
<td>62</td>
<td>1</td>
</tr>
</tbody>
</table>

1 Air furnace melted "Duriron," 1.225 pounds transverse strength.
2 Vacuum treated "Duriron," 1.684 pounds transverse strength.

The inoculation of the melt presents no difficulty or unusual operation. It is conveniently effected by the lade addition of calcium in the form of calcium-silicon (31.5% Ca, 63% Si) to the vacuum treated metal just prior to casting. The amount of inoculant added is dependent on the particular casting and the melt, especially as to the oxygen content, and this will vary in some slight but significant degree from one melt to another. It is not practical to specify a constant amount of calcium (or calcium-silicon) addition, although the addition of 0.050% calcium (0.15% calcium-silicon) is an average figure to arrive at a retained calcium level of 0.025% to 0.035% in the cast material, which level represents the optimum range. In any event, the amount of inoculant to be added is controlled by what is necessary to produce the desired residual calcium level in the cast material.

While as just mentioned, successive melts will vary from one another in some slight respect, the invention permits substantial latitude in the type of charge introduced initially into the melting furnace. In fact the particular type of charge used appears to have no outstanding effect on the final product so long as the proper elements are present within the compositional limits of ordinary high silicon cast irons. At the more usual level of 14% to 15% silicon, carbon may range from as low as around 0.3% (but usually at least 0.6%) to as high as 1.3% (but usually not over 1.1%), with manganese of 0.6% to 0.7% except where carbon is above 1.1%. In the latter case manganese may be increased to about 1% or the normal manganese level retained and titanium of 0.07% to 0.12% used to prevent "kishing" of excess car-
bon. A maximum carbon of about 1.5% cannot be exceeded, however, even with modifying carbide formers present. The balance of the composition, for all significant purposes, is of course iron.

It is most convenient and simple in practical commercial foundry operation to use molten high silicon iron from another furnace as the starting material for the vacuum treating operation, and accordingly this practice is preferred. But it is also entirely possible to melt the initial charge directly in a vacuum furnace. Nor does it make any difference in either procedure whether the initial charge is virgin metal (pig iron, ingot iron and ferrosilicon) or scrap castings from previous operations, or mixtures of both. All have proven to be entirely operative.

The foregoing teaching in respect to vacuum treatment plus calcium inoculation is also applicable to certain modifications of the ordinary high silicon cast iron composition defined above. This applies to alloys of this basic type containing, as modifying elements, molybdenum from about 0.5% to 3% and chromium of from 3% to 6%, as disclosed in a copending application, Serial No. 279,163, filed May 9, 1963, now Patent No. 3,129,095. These modified alloys, which have special corrosion resistance in some of the more severely corrosive media, also show a similar substantial improvement in transverse load strength and thermal shock resistance, while maintaining their high order of corrosion resistance, comparable to the more conventional high silicon cast irons.

What is claimed is:

1. High silicon cast iron having a silicon content of from 12% to 15%, carbon from 0.3% to 1.5%, manganese of from approximately 0.65% to 1.0%, plus retained calcium of from 0.02% to 0.05%, the balance substantially all iron; said alloy as cast having its residual gas content reduced by vacuum furnace treatment to remove hydrogen to not over about 2 p.p.m., nitrogen to not over about 6 p.p.m. and oxygen to not over 20-30 p.p.m.; said alloy having a minimum transverse load strength of 1600 pounds and a microstructure characterized by fine acicular graphite uniformly distributed in a fine grain dendritic iron silicide matrix.

2. High silicon cast iron as defined in claim 1, wherein the silicon ranges from 14% to 15%, and carbon from 0.6% to 1.3%.

3. High silicon cast iron as defined in claim 1, wherein the silicon ranges from 14% to 15%, carbon from 0.9% to 1.1% and manganese of about 0.65%.

4. High silicon cast iron as defined in claim 3 wherein retained calcium is from 0.025% to 0.035%.

5. High silicon cast iron as defined in claim 3, which further includes molybdenum of from about 0.5% to 3%.

6. High silicon cast iron as defined in claim 5, which further includes chromium from 3% to 6%.

7. High silicon cast iron as defined in claim 4, which further includes chromium from 3% to 6%.

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