Jan. 7, 1969 D. J. HANSEN **3,420,657**

OXYGEN TREATMENT OF CHROMIUM ALLOYS

Filed Feb. 14, 1966

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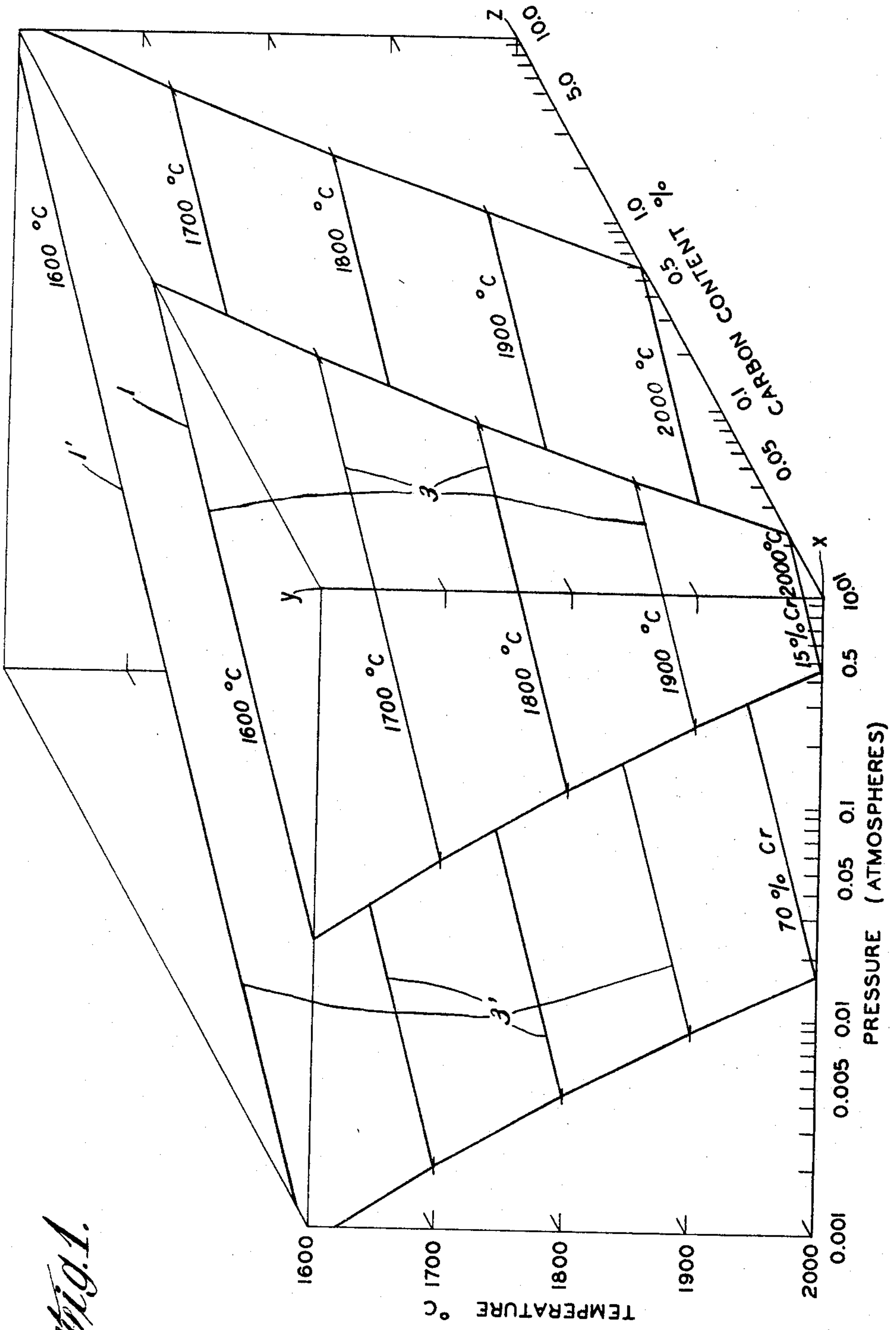

Fig. 1.

INVENTOR
DONALD J. HANSEN
BY

ATTORNEY

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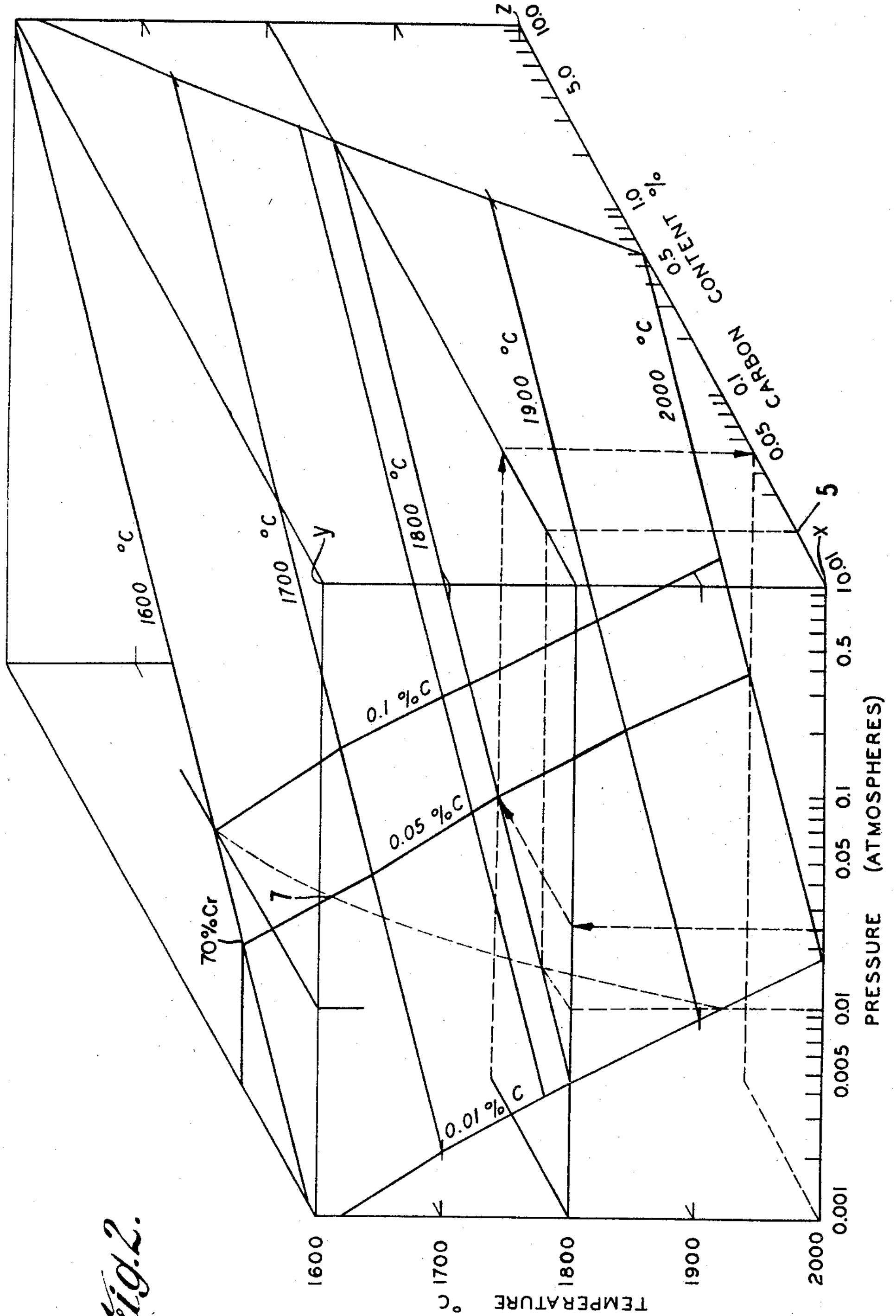

Fig. 2.

INVENTOR.
DONALD J. HANSEN
BY
ATTORNEY

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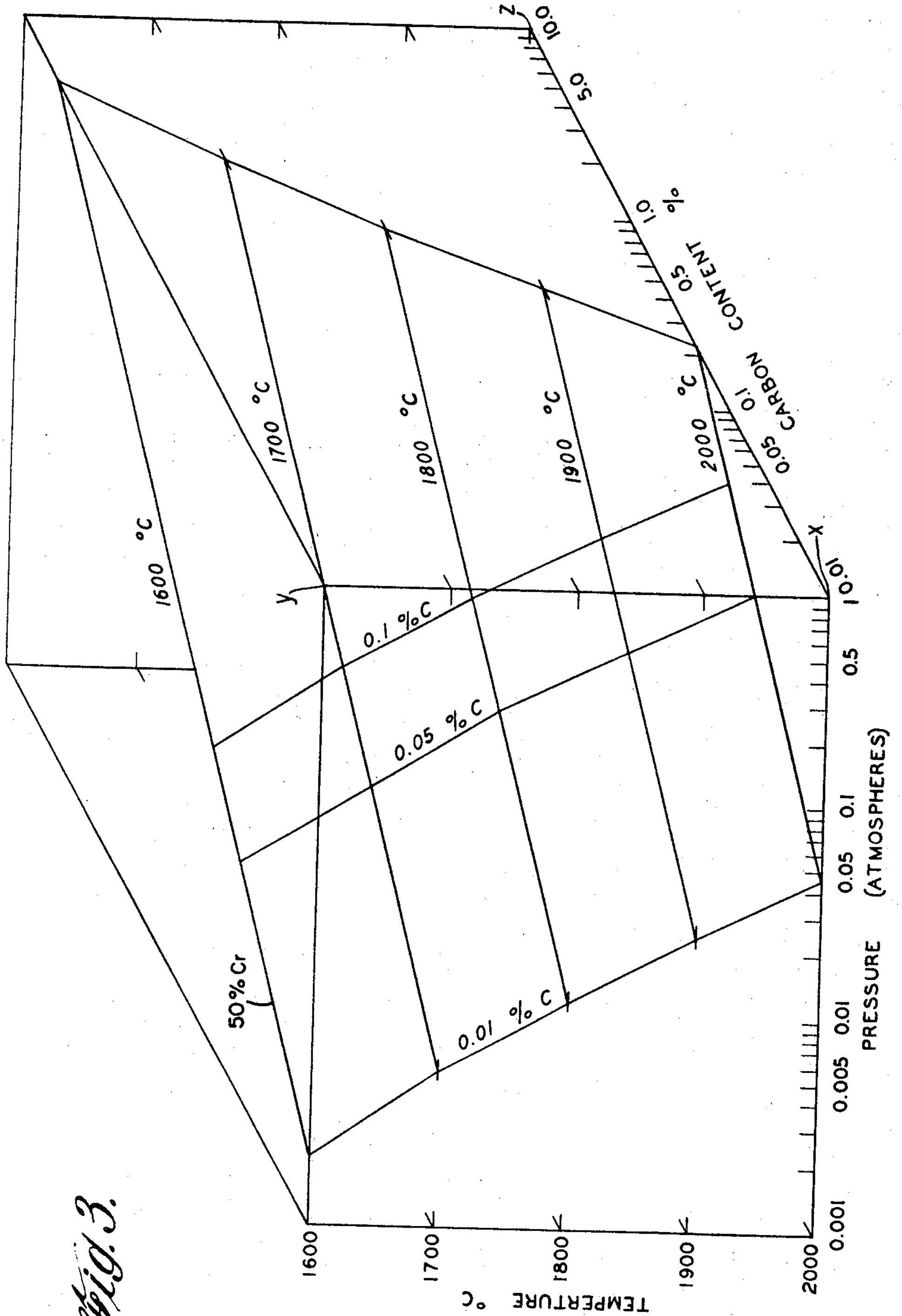

Fig. 3.

INVENTOR.
DONALD J. HANSEN
BY
ATTORNEY

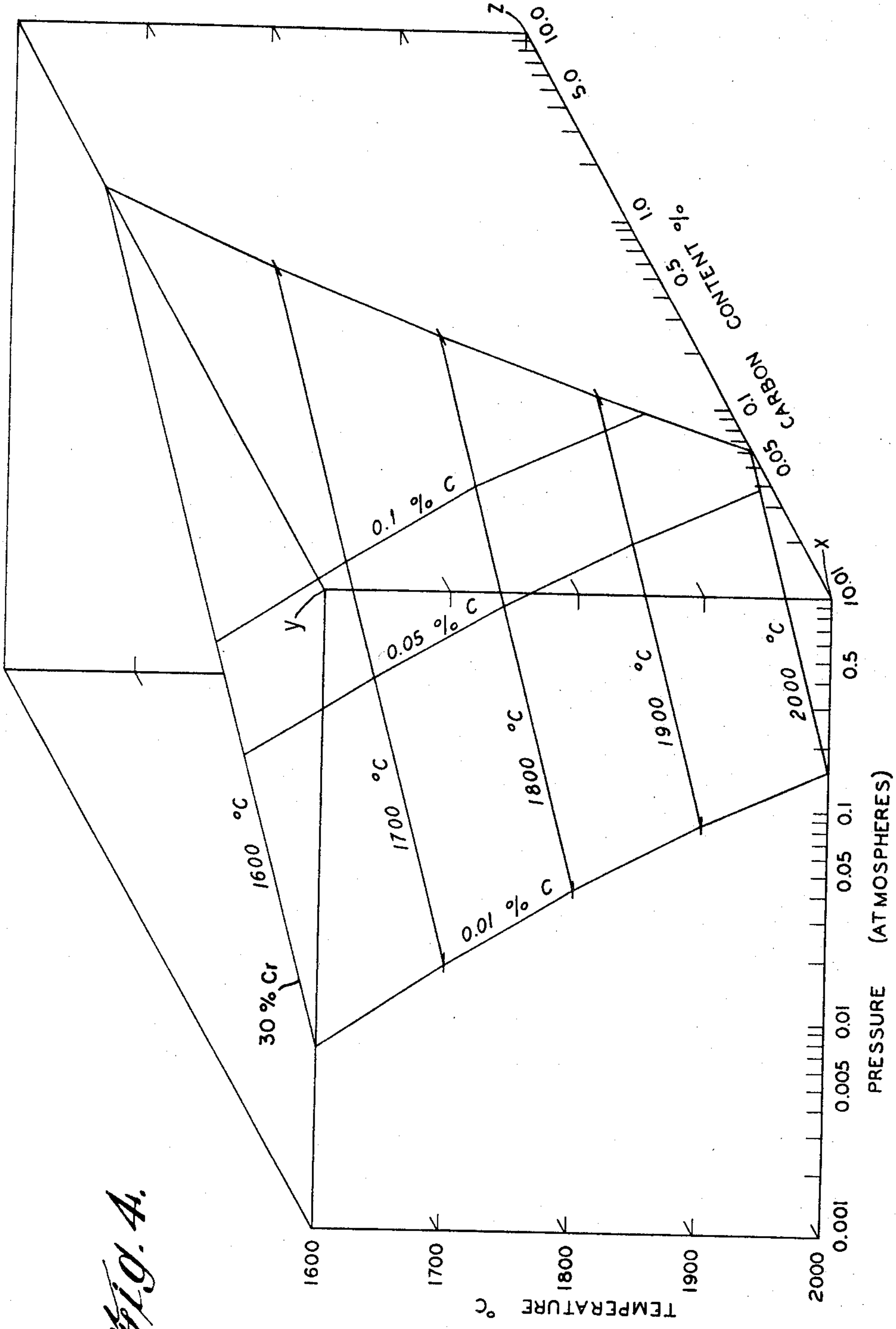

Fig. 4.

INVENTOR.
DONALD J. HANSEN
BY
ATTORNEY

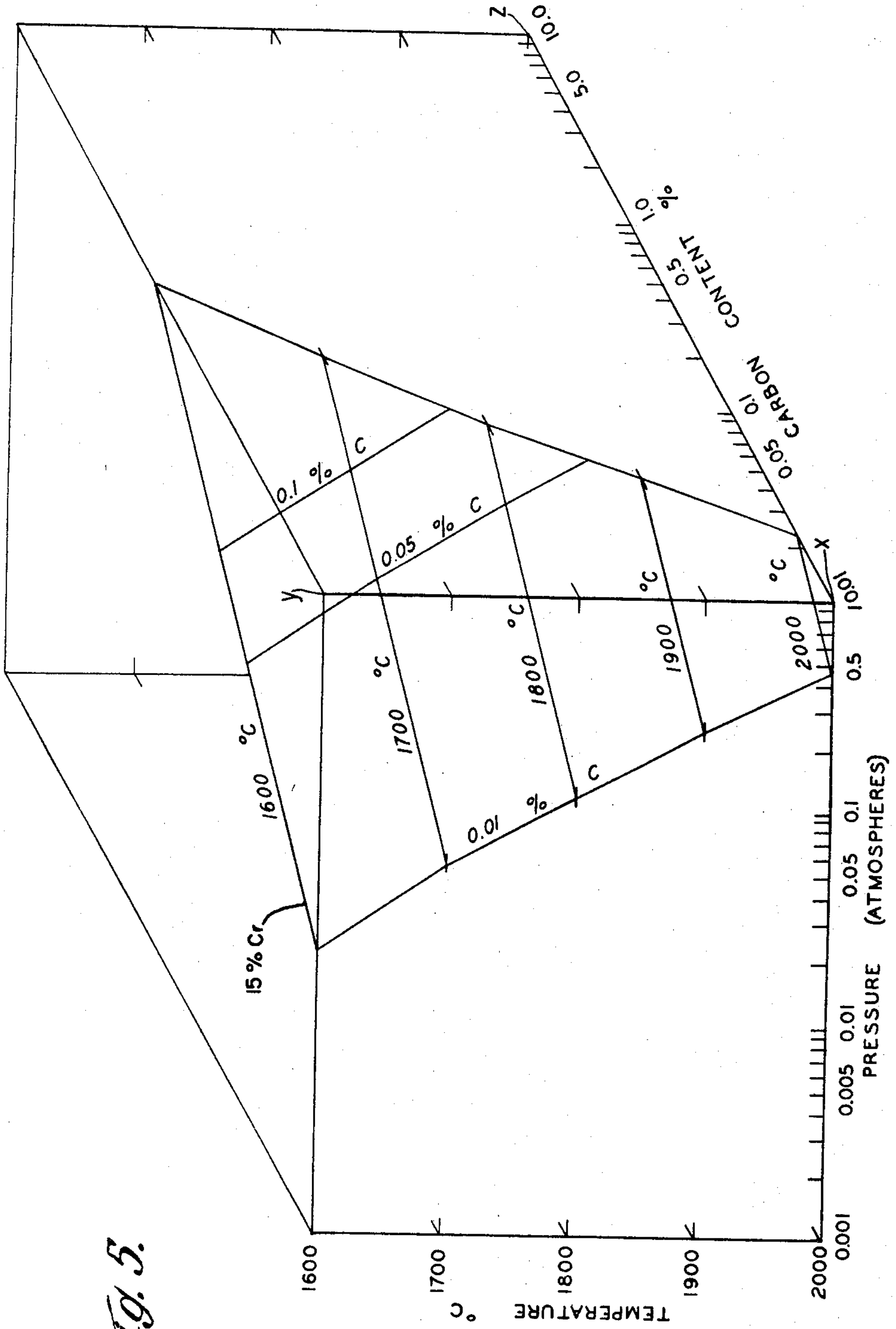

Fig. 5.

INVENTOR.
DONALD J. HANSEN
BY Donald J. McCarthy
ATTORNEY

United States Patent Office
3,420,657
Patented Jan. 7, 1969

3,420,657

OXYGEN TREATMENT OF CHROMIUM ALLOYS

Donald J. Hansen, Lewiston, N.Y., assignor to Union Carbide Corporation, a corporation of New York

Filed Feb. 14, 1966, Ser. No. 527,214
U.S. Cl. 75—60 2 Claims
Int. Cl. C22c 3/00

ABSTRACT OF THE DISCLOSURE

A process for removing carbon from iron-chromium-carbon alloys without substantial loss of chromium which comprises: providing a substantially slag-free molten mass of iron-chromium-carbon alloy, adjusting the starting composition of the alloy to provide between 75% and 15% chromium and a silicon content of less than about 3% and treating the molten alloy by blowing oxygen on the surface of said alloy, the pressure conditions at all times during oxygen treatment, for a particular metal temperature, being in the volume of the graph of the drawing which extends to the left of the plane corresponding to the chromium content of the alloy and in front of the plane corresponding to the desired final carbon content of the alloy.

The present invention relates to the oxygen treatment of chromium allows. More particularly, the present invention relates to the oxygen treatment of chromium-iron-carbon alloys to provide such alloys with a predetermined chromium-carbon content.

The oxygen treatment of iron-chromium-carbon alloys at pressures below atmospheric to remove carbon from the alloys has been known for some time. However, the presently known techniques suffer from disadvantages which include the substantial undesirable loss of chromium, particularly when the effort is to achieve very low carbon levels. Moreover, using presently known oxygen techniques, control of the chromium-carbon ratio in the final alloy, and the production of high chromium, low carbon alloys has been found to be unpredictable at best.

It is therefore an object of the present invention to provide a process for the oxygen treatment of chromium-iron-carbon alloys whereby the chromium-carbon ratio in the final alloy can be closely controlled.

It is another object of the present invention to provide an oxygen treatment for chromium-iron-carbon alloys whereby high chromium, low carbon alloys can be provided.

It is a further object of the present invention to provide an oxygen-treatment process for chromium-iron-carbon alloys whereby undesirable chromium losses are avoided.

Other objects will be apparent from the following description and claims taken in conjunction with the drawing which illustrates in FIGURES 1 through 5 temperatures and pressure conditions which are suitable for the practice of the present invention.

A process in accordance with the present invention for adjusting the chromium-carbon content of iron-chromium-carbon alloys to provide at least a predetermined minimum chromium-to-carbon ratio in the final alloy comprises providing a substantially slag-free molten mass of iron-chromium-carbon alloy at a temperature of at least about 50° C. above its melting point; adjusting the composition of the alloy to the extent necessary to provide a chromium content in the range of about 15 to 75% and a silicon content of not more than 3%; treating the molten alloy by blowing oxygen on the surface of said alloy and reducing the ambient pressure below atmospheric pressure to cause reaction of the oxygen and alloy, and

the evolution of reaction gases from the surface of the alloy the temperature and pressure conditions being in accordance with the schedules more fully described hereinafter.

In the present invention, the alloys which can be effectively treated range from about 15 to 75% Cr, up to 10% C balance iron and incidental amounts of other elements such as Mn, S, Si, P, Ni, Cb, Ta, and Mo.

It is very important in the present invention that the silicon content, if any, of the alloy to be treated be less than about 3% by weight. If necessary, the silicon content can be adjusted by the addition of suitable amounts of chromium, iron, or low-silicon iron-chromium alloy when the alloy is in the molten state and prior to oxygen treatment.

The broad reason for maintaining the silicon content below the aforesaid value is to substantially avoid the formation of slag on the surface of the alloy during oxygen treatment. By operating essentially without slag on the surface of the alloy during oxygen treatment several significant advantages are obtained. For eaxmple, recovery of chromium is improved because any chromium that is inadvertently oxidized will not be dissolved in a slag with resultant loss in activity. In a slagless process any chromium oxide formed can be readily redissolved with liberation of CO by suitable pressure reduction. A further increase in chromium recovery can be realized since no fine metal droplets will be lost as suspended particles in a slag. Also for obtaining very low carbon alloys, the absence of a slag allows the surface of the molten metal to be completely exposed to the reduced pressure which promotes escape of CO gas with resultant lowering of the carbon content. On the other hand, with a slag present, CO gas can be trapped between the metal-slag interface resulting in a higher CO partial pressure and less effective decarburization. Another important consideration favoring a slagless operation is the effect on maximum temperature of operation. The maximum temperature of an oxygen blowing operation is usually limited by the vessel refractories. When a slag cover is present, eutectics form between slag and the refractory lining lowering the maximum temperature of operation. The complete failure of a refractory-lined vacuum blowing vessel has been demonstrated when a slag cover was used under conditions that were completely satisfactory for a slagless operation. A still further advantage is higher efficiency of oxygen since with a slag some of the oxygen will be deflected before it comes in contact with the metal to be processed. Moreover the formation of a silicate slag requires addition of lime or some other material as a flux to make the slag fluid.

Most importantly, however, the avoidance of a silica slag permits the use of particular processing schedules which enables the economical and accurate compositional adjustment of iron-chromium-carbon alloy.

The figures of the drawing represent relationships between chromium and carbon content for various temperature and pressure conditions during oxygen treatment which have been found to be effective only when the silicon content of the alloy being treated is below 3%.

With higher silicon contents, the illustrated relationships are not meaningful due to the silica slag cover which develops and processing becomes unpredictable.

With reference to the drawing, FIGURE 1 shows an orthogonal, three dimensional graph in which the surfaces indicated as **1** and **1'** correspond to the chromium contents desired in the final product and are referred to herein as chromium planes. The two chromium planes illustrated in FIGURE 1 represent 70% Cr and 15% Cr which substantially covers the range of alloys suitably treated in accordance with the present invention. The

x, y, and z ordinates represent, respectively, ambient pressure during oxygen treatment, the temperature of the molten alloy being treated and the carbon content of the alloy. FIGURE 1 also shows at **3** and **3'** the intersection of temperature planes with the chromium planes for various temperatures from 1600° C. to 2000° C.

FIGURE 2 shows the 70% chromium plane of FIGURE 1 and the intersection therewith of carbon planes corresponding to carbon contents of 0.01%, 0.05% and 0.1% and exemplary temperature planes. The remaining FIGURES 3–5 show the chromium planes for 50%, 30% and 15% chromium and the relationships therewith of carbon content, temperature, and pressure. Chromium planes for other Cr values can be readily obtained by interpolation or extrapolation. In the practice of the present invention, a molten chromium-iron-carbon alloy is heated to initially provide a temperature about 50° C. or more above its melting point. The metal is transferred to a suitable vessel, for example a magnesia lined reactor which is placed within a vacuum chamber and fitted with a vacuum cover and oxygen is blown onto the surface of the molten metal for example using 20 to 70 s.c.f.m. per sq. ft. of molten metal surface. During the oxygen treatment, the pressure is reduced to below atmospheric and controlled, together with the temperature of the molten metal surface as hereinafter described.

The ambient pressure over the metal bath can be adjusted by controlling the rate at which gases are exhausted from the system, using conventional vacuum equipment, preferably steam ejectors. The temperature of the metal surface is adjusted by altering the rate at which oxygen is reacted with the surface of the metal knowing the initial temperature and the heat transfer characteristics of the reactor. The temperature can be suitably measured by an immersion type thermocouple or by a suitably adapted optical pyrometer.

By way of example, in the practice of the present invention, starting for example with an iron-chromium-carbon alloy containing 70% Cr and 1% C, to obtain a final alloy for 70% Cr and not more than 0.05% carbon, suitable pressure conditions employed during oxygen treatment lie in the volume of the graph of the drawing which is to the left of the 70% chromium plane at a particular operating temperature and in front of the carbon plane corresponding to 0.05% carbon.

Operating conditions to the right of the chromium plane will cause oxidation of chromium in pereference to carbon before the desired carbon level is reached.

More specifically, and with reference to FIGURE 2, and the dotted arrows shown therein, oxygen treatment of a 70% Cr alloy at a metal temperature of 1800° C., and a pressure of 0.022 atmospheres provides the selective oxidation and removal of carbon to 0.05% without significant oxidation of chromium i.e., not more than 5% of the chromium is oxidized. Operation at a lower pressure, e.g. 0.01 atmospheres can provide an even lower carbon content, as indicated at **5**, before chromium is significantly oxidized, or permit the use of a lower temperature, as indicated at **7**, to obtain a carbon content of 0.05% without chromium oxidation. Similarly, operation at a higher temperature will permit the use of a higher pressure. In any event, throughout the practice of the present invention, for the operating temperature employed, the pressure should be to the left of the intersection of the chromium plane and in front of the carbon plane corresponding to the carbon content of the alloy. This means that initial pressure can be higher than the final pressure, but that under such circumstances, as the carbon content is decreased, the pressure must be decreased in accordance with the relationship shown in the drawing.

The beginning of chromium oxidation, in preference to carbon oxidation can be detected by a sharp decrease in the evolution of CO and CO_2 from the surface of the molten alloy, regardless of the oxygen flow rate. For example, with oxygen flow rate held constant, when chromium begins to oxidize in preference to carbon, the decreased amount of reaction gases will cause a sudden noticeable decrease in pressure, and this phenomena may be used in conjunction with the diagrams to control the composition of the desired alloy.

In accordance with the preferred embodiments of the present invention, the conditions of temperature and pressure are controlled so that they coincide with the intersection of the desired final carbon and chromium planes, and oxygen treatment is terminated when a sudden pressure drop is observed since further oxygen treatment would lead to additional oxidation of chromium.

The FIGURES 3 through 5 as previously noted illustrate chromium planes for 50%, 30% and 15% chromium respectively. Also shown in FIGURES 3–5 are carbon plane intersections for 0.1%, 0.05% carbon and 0.01% carbon. The graphs of these figures, and FIGURE 2, can be used following the aforedescribed procedure to define oxygen treatment operating conditions for other alloys merely by interpolating or extrapolating when the chromium contents or intended operating temperatures do not correspond to the particular values illustrated.

In another embodiment of the present invention, the chromium/carbon ratio of an iron-chromium-carbon alloy can be adjusted by the oxidation of chromium.

By way of example, the starting alloy can contain 16% chromium and 0.05% carbon, and the desired alloy is one containing 15% chromium and 0.05% maximum carbon. Molten alloy is provided at an initial temperature of about 1600° C., the pressure above the molten metal surface is reduced to below atmospheric, and oxygen is blown onto the surface of the alloy. As a result of the oxygen treatment, the temperature of the surface of the metal rises. Since it is desired to reduce the chromium content of the alloy, the temperature and ambient pressure are controlled in accordance with the present invention so as to be to the right of a 16% chromium plane and substantially coincident with the intersection of the 15% chromium plane and the 0.05% carbon plane. It has been found that under such operating conditions, chromium is oxidized and removed from the alloy in preference to carbon. That is to say, the chromium will be preferentially oxidized until the chromium content of the alloy is about 15%, then chromium oxidation will abruptly cease and carbon will be oxidized. The commencement of carbon oxidation will be evidenced by the evolution of CO and CO_2 from the surface of the molten alloy.

The following examples will further illustrate the present invention.

EXAMPLE 1

Two thousand six hundred twenty pounds of molten iron-chromium-carbon alloy at 1710° C. contained in a magnesia-lined reactor were positioned in a vacuum shell. The analysis of the alloy was 66.8% chromium, 4.4% carbon, less than 0.5% silicon, balance iron. The pressure in the vessel was reduced to 0.44 atmosphere by means of steam ejectors, and 600 cubic feet of oxygen were introduced to the surface (3.40 sq. ft.) of the molten alloy through a water-cooled lance at a rate of 105 c.f.m. causing the temperature of the alloy to increase. The pressure was reduced during the oxygen blow from 0.44 atmosphere to 0.21 atmosphere, after which the vacuum vessel was backfilled with air and the product sampled. The product analysis was 67.6% chromium, 2.7% carbon, less than 0.5% silicon, balance iron. Not more than 1.3% of the original chromium was lost through oxidation.

EXAMPLE 2

Molten iron-carbon-chromium alloy weighing 4270 pounds at a temperature of 1600° C. and contained in a magnesia-lined reactor was provided in a vacuum shell. The analysis of the alloy was 0.38% carbon, 19.4% chromium, less than 0.1% silicon, balance iron. The pressure in the vessel was reduced to 0.275 atmosphere and 1250 cubic feet of oxygen were introduced to the surface at 250 s.c.f.m. During the 5-minute oxygen blowing period, the pressure was reduced to 0.01 atmosphere. After the oxygen was turned off, the alloy was held for an additional 5 minutes at this pressure. The shell was backfilled with air, and the product analyzed 0.06% carbon, 18.4% chromium, balance iron.

EXAMPLE 3

Into a magnesia-lined reactor was poured 2100 pounds of slag-free high-carbon ferrochrome analyzing 8.9% carbon, 63.5% chromium, less than 1% silicon, balance iron. The shell was closed and evacuated to 500 mm. Hg pressure using steam ejectors. Approximately 400 cubic feet of oxygen were introduced to the surface of the metal through a water-cooled lance according to the following schedule which was selected first to keep the pressure of the shell to the left of the chromium plane in FIGURE 2, second to reduce the amount of gases being evolved at lower pressures to minimize splashing, and third to provide an oxygen rate to bring the temperature of the alloy to about 1800° C.

O_2 rate	Time, min.	Shell pressure	
		mm. of Hg	Atmospheres
175	13.3	550–500	(.724–.658)
140	6.1	500–335	(.658–.441)
105	5.4	335–145	(.441–.191)
80	4.2	145– 40	(.191–.053)

At this point in the oxygen blow, the pressure of the system dropped suddenly from 40 to 36 mm., indicating the beginning of chromium oxidation. According to the graphs of the drawing 1800° C. and 0.05 atmosphere pressure would begin at a carbon level of 0.2%. Since a lower carbon was desired, an additional 500 cubic feet of oxygen at 80 c.f.m. were introduced to the surface of the alloy, resulting in oxidation of chromium with formation of chromium oxide. The oxygen was then turned off and the pressure was reduced to 5 mm. which, according to the graphs of the drawing was below that necessary to obtain a 0.05% carbon alloy at 1800° C. The chromium oxide reacted with the carbon in the alloy causing evolution of CO. When gas evolution had essentially ceased (13 minutes), the shell was backfilled with air and the resulting product analyzed 0.04% carbon, 68.4% chromium. The chromium oxidation was calculated to be 5%.

What is claimed is:

1. A process for removing carbon from iron-chromium-carbon alloys without substantial loss of chromium which comprises:

(1) providing a substantially slag-free molten mass of iron-chromium-carbon alloy at a temperature of at least about 50° C. above its melting point

(2) adjusting the starting composition of the alloy to the extent necessary to provide between about 75% and 15% chromium and a silicon content of less than about 3%

(3) treating the molten alloy by blowing oxygen on the surface of said alloy and reducing the ambient pressure below atmospheric pressure to cause reaction of the oxygen and carbon in the alloy and the evolution of reaction gases from the surface of said alloy, the pressure conditions at all times during oxygen treatment, for a particular metal temperature, being in the volume of the graph of the drawing which extends to the left of the plane corresponding to the chromium content of the alloy and in front of the plane corresponding to the desired final carbon content of the alloy.

2. A process in accordance with claim **1** wherein the oxygen blowing is terminated when the amount of gas evolved from the surface of the alloy being treated suddenly decreases independently of the amount of oxygen being used in the oxygen blowing.

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RICHARD O. DEAN, *Primary Examiner.*

U.S. Cl. X.R.

75—49, 130.5