Nov. 1, 1966 T. E. PERRY ET AL 3,282,676

PROCESS FOR PRODUCTION OF ULTRA-CLEAN STEEL

Filed May 14, 1962 2 Sheets-Sheet 1

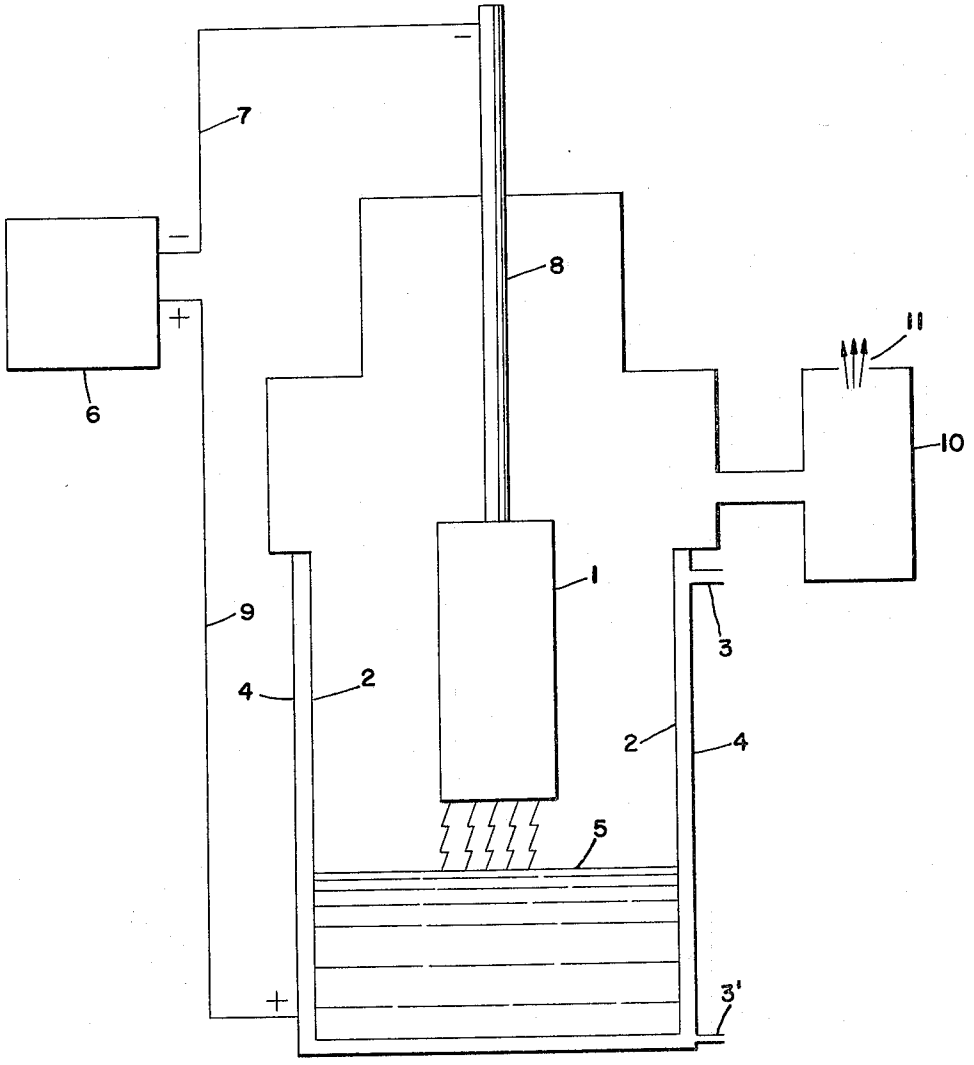


Fig. 1

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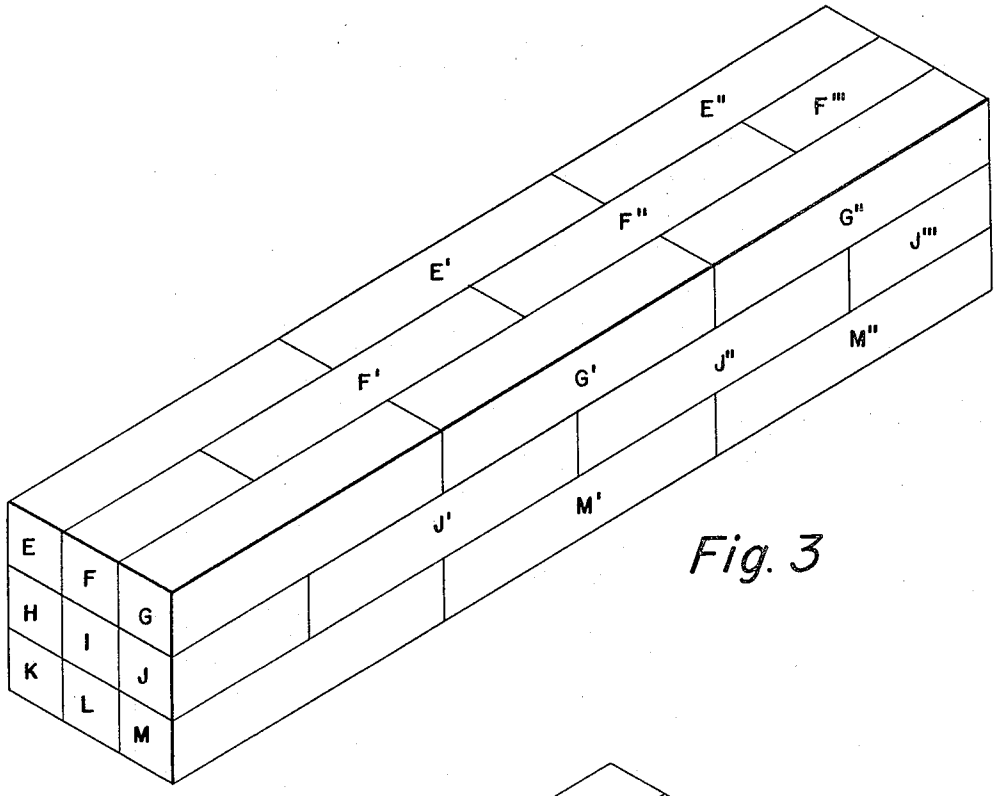


Fig. 3

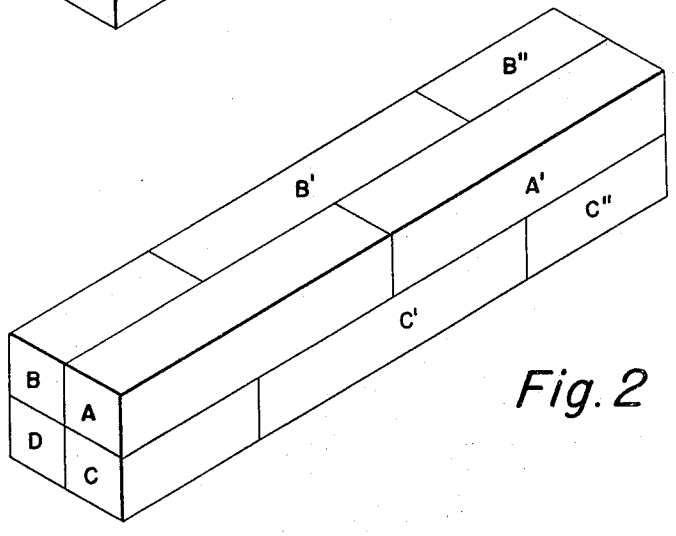


Fig. 2

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PROCESS FOR PRODUCTION OF ULTRA-CLEAN STEEL

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Filed May 14, 1962, Ser. No. 194,446
12 Claims. (Cl. 75—12)

This invention relates to a process for the production of ultra-clean steel. More specifically it relates to a process for the production of ultra-clean steel from steel powder of high purity by vacuum melting of the steel in the form of consumable electrodes.

Ordinarily the production of steel having carbon contents in the range of 0.15 to 1 percent results in various inclusions due to conditions required in preparing such steel. When alloying elements, such as manganese, silicon and aluminum are added, they form inclusions of corresponding oxides if the oxygen has not been completely removed before the addition of these alloying elements. In cases where sulfur has not been completely removed, inclusions will also be formed by reaction of manganese with the sulfur.

In various types of steel to be heat-treated to high hardness and strength levels, such as ball-bearing steel, missile steel, etc., cleanliness of the steel, that is freedom from inclusions, is essential. Inclusions cause weak spots, e.g. internal notches, in the steel. For example, when the steel is used in ball-bearings, cleanliness of the steel is most critical. Inclusions cannot be tolerated in such steel since considerable pressures are exerted on very small areas on which the ball-bearings must rest or on which they must support considerable weight.

When inclusions are present in the steel, the resistance to propagation of cracks or notches is lowered. In steels used for missile production, weight is an important factor. Therefore, the ordinary practice of using excess steel as a safety factor to provide for contingencies where a piece of steel may be weakened by inclusions cannot be tolerated. Steels of high strength-to-weight ratios are required. Consequently, it is essential that a steel of extreme cleanliness or freedom from inclusions be used for this purpose to insure good notch properties in the steel.

In missile and jet engine steels it is also essential to have toughness and ductility as well as high tensile strength. High tensile strength can be obtained by increasing the carbon content. However, this generally means a sacrifice in the toughness and ductility. Therefore, it is necessary to have good notch properties by avoiding inclusions in the steel, and to have optimum tensile strength without increasing the carbon content. These properties are effected, together with good toughness and ductility, by the process of this invention for the production of an ultra-clean steel.

Whereas consumable electrode vacuum remelting has been used in the production of steel, it has been found that the process used in making the first melt results in introducing new impurities or in failure to remove sufficiently the original impurities. For example, steel has been made by induction vacuum melting of the steel composition and then tapping the heat into electrode form which is subsequently remelted by consumable electrode melting. This technique does not give satisfactory results since impurities, such as refractories, are introduced in the induction melting step and conditions are such that the original oxygen content of the charge is not as effectively removed as desired.

Copending application Serial No. 153,650, filed November 20, 1961, now Patent No. 3,235,373, is directed to a two-step process involving the vacuum-electric arc

melting of consumable electrodes made from a blend of finely divided carbon with finely divided iron powder of high purity, shaped as electrodes, and then the remelting of the resultant ingot as a consumable electrode in an electric-arc furnace, the first melting being conducted at a pressure of less than 1000 microns of mercury, and the second melting being conducted at a second pressure of less than 100 microns of mercury. This two-step process has been found to produce ultra-clean steels of improved toughness, ductility, notch properties, etc., which improvements as indicated above are highly desirable.

In accordance with the present invention, it has now been found that similar superior results can be obtained with a single melting of such a consumable electrode pressed or otherwise shaped from highly purified iron powder and finely divided carbon provided that the pressure in this single vacuum melting step is maintained below 100 microns of mercury throughout the melting operation.

By the practice of this invention it has been found that such a single melting step is capable of substantially completely removing the oxygen from this composition and substantially completely avoiding the gassy condition of the ingot previously obtained when such a consumable electrode was melted under conditions which allowed the pressure to rise as high as 1000 microns. It has now been found that if the pressure is maintained below the 100 micron level, it is possible to avoid this gassy condition of the resultant ingot. This avoids the necessity of performing the two-step process described in the above-mentioned application. It likewise avoids the various disadvantages of other prior art methods wherein a first melt has been conducted in an induction furnace with the result that the initial ingot has been contaminated by refractory from the induction furnace, and which contamination remains even after the ingot is remelted in a consumable electrode vacuum remelting operation.

It is found that the combination of the powder condition of the starting material, the maintenance of the extremely low pressure, the high temperature effected in the vacuum consumable electrode furnace, and freedom from contamination from refractories all combine to give an ultra-clean steel with resultant improvements in freedom from inclusions, notch properties, toughness and ductility.

In accordance with the practice of this invention, an ultra-clean steel is produced from iron powder of high purity such as electrolytic iron, etc., by blending the iron powder of high purity with an appropriate amount of carbon, with or without alloying metals, briquetting or otherwise forming the resultant mixture into a consumable electrode, and vacuum arc melting the resultant consumable electrode while maintaining a reduced pressure at no greater than 100 microns of mercury. By conducting the vacuum melting step in a copper crucible, contamination by refractory is thereby avoided.

FIG. 1 of the accompanying drawings illustrates a schematic arrangement of a typical consumable electrode vacuum furnace.

FIGS. 2 and 3 illustrate the assembly of a consumable electrode assembled from a number of smaller linear shapes or rods, pressed or otherwise formed, from the iron powder-carbon powder blends.

In preparing ultra-clean steel according to the practice of this invention, it is desirable to start with highly pure iron powder having as little sulfur, phosphorus, and oxygen as possible. It is desirable that there be no more than about 0.01, preferably no more than 0.005, percent by weight of sulfur, and no more than about 0.01, preferably no more than about 0.005, percent by weight of phosphorus.

While it is generally desirable to have no more than

about 0.06 percent by weight of oxygen, as much as 0.2 percent oxygen can be present provided a compensating greater amount of carbon is used in the first melting. Where sulfur is present and hydrogen reduction is effected for removal of the sulfur, the hydrogen reduction will remove oxygen simultaneously with the removal of sulfur. However, if such hydrogen reduction is not effected for the removal of sulfur, as much as 0.2 percent oxygen can be present in the iron powder and compensated for by an additional amount of carbon added for removal thereof.

Moreover, while it is generally desirable to have no more than about 1 percent by weight of carbon in the powder, it is also possible to have higher amounts of carbon in the starting material and to compensate for such higher amount by adding a calculated amount of iron oxide for carbon removal.

Iron powder of such sufficient purity can be prepared in accordance with prior practice used in the hydrogen reduction of electrolytic iron. For example satisfactory removal of sulfur from electrolytic iron is effected with wet hydrogen at 1500–1700° F. for 2–4 hours. The resultant product, after grinding, is blended with finely divided carbon and, when desired, with specified amounts of alloying metals, such as nickel, chromium, molybdenum, vanadium, etc., and formed or briquetted into desired consumable electrode sections, for example, at about 50,000 pounds per square inch. The electrode sections can be vacuum sintered at about 1750° F. or can be sintered in an inert gas, such as argon, at temperatures up to 2200° F.

It is generally preferred to form briquettes of the same length, with each having a cross section one quarter of that of the ultimate electrodes and then to weld four quarters into one electrode.

High pressure hydrostatic pressing of electrodes with a cylindrical configuration can also be used utilizing pressure conditions which will give an equivalent amount of binding effect.

In operating the furnace, the atmosphere is exhausted preferably to a pressure of 1–2 microns. Then as the electrode is taken to a temperature at which melting starts, the pressure rises as high as 100 microns (0.1 mm.), care being taken that the pumping equipment has sufficient capacity to remove the gases given off. The electrode is thus arc-melted into a copper crucible while maintaining a pressure of less than 100 microns, preferably as low as possible.

An important feature of this invention is the manner in which the oxygen content is reduced in this electrode melting. The amount of carbon added to the iron powder is based on the amount required for reducing the oxygen plus the amount needed to give the desired carbon content in the ultimate product.

In the vacuum melting operation, the vacuum can be effected by a mechanical pump in the early stages for preliminary removal of the atmosphere and then by an oil diffusion pump to more completely exhaust gases and produce the desired vacuum. In order to maintain the vacuum at the desired level, it may be necessary to have two or more oil diffusion pumps to supply sufficient capacity to completely exhaust gases and maintain the desired vacuum.

The type of equipment and method of effecting vacuum arc melting can be of various types normally used for such purposes. Typical of a type of apparatus suitable for this purpose is that shown in Patents Nos. 2,727,936, issued December 20, 1955; 2,818,461, issued December 31, 1957; and in copending application Serial No. 698,256, filed by Robert J. Garmy on November 22, 1957, now Patent No. 2,973,452, issued February 28, 1961.

While the various preliminary steps of preparing fine powder of high purity, mixing the same with carbon and with whatever alloy metals are to be used, briquetting the same, sintering, etc. can be varied somewhat in accordance with well known methods for performing such steps, the following procedures have been found satisfactory for such purposes in preparing the consumable electrodes used in the practice of this invention.

As indicated above, high purity fine powder is preferably used, such as electrolytic iron. Where the sulfur and oxygen content need to be reduced to the low value indicated above, a preliminary hydrogen treatment is given. If alloying metals are to be used which are also hydrogen reducible, such as nickel, molybdenum, cobalt, etc., such powders are also added and blended with the iron powder for this preliminary treatment. The resultant powder is treated advantageously with wet hydrogen at temperatures of 1500 to 1800° F. for a period of from 2 to 4 hours which is generally sufficient to drop the sulfur to the desired low value. The hydrogen used for this purpose is saturated with water vapor at approximately 150° F. After this treatment, the wet hydrogen is removed and the powdered metal treated with dry hydrogen at the same temperature for approximately 15 minutes to effect optimum oxide removal. The powder mixture is then cooled in dry hydrogen.

The foregoing treatment produces a loosely sintered cake which is then ground, such as by a standard single disc attrition mill of the usual type. While the particle size is not critical, a mesh size of approximately —40 is generally satisfactory.

The resultant product is then mixed with finely divided carbon such as graphite, and at the same time can be mixed with any non-hydrogen reducible metals, in powder form, such as chromium, vanadium and columbium, which are desired in the ultimate steel product. The amount of carbon added is calculated roughly on the basis of approximately 135–300% of the theoretical amount required to convert the oxygen present in the powder as oxides to carbon monoxide. The excess is to compensate for physical losses incurred during melting probably due to the fact that the gas emanating from the reaction mass sweeps out some of the finely divided carbon from the system. The required amount should also include any amount desired to be present in the resultant steel, referred to as the carbon "aim." The amount of carbon added should also take into account the carbon that is already present in the iron powder. Therefore, the amount of carbon to be added to the iron powder can be calculated roughly as the carbon "aim" plus 1.35–2 times the stoichiometric amount required to reduce the oxygen present to carbon monoxide, minus the amount of carbon already present in the iron powder.

Then the mixed powder is formed by compression into the electrode shapes or segments which will make up the final electrode. Generally pressures of 40,000 to 50,000 p.s.i. are adequate to form such electrodes or electrode segments. These electrodes or electrode segments are advantageously vacuum sintered for approximately 2 hours at about 1750° F. This sintering operation effects a cohesion of the metal particles and also eliminates some amount of oxygen. While other methods, such as hydrostatic pressing, etc. can directly effect sufficient cohesion of the particles to give the electrodes the required strength for subsequent use, subsequent vacuum sintering has been found to be advantageous in many cases. Where electrode segments are used in the sintering operation, the segments can be welded together by means of inert gas welding. Various other methods of pressing and assembling electrodes can be used in the practice of this invention.

In the melting operation, standard consumable electrode vacuum melting equipment can be used in the practice of this invention. FIG. 1 illustrates a general schematic arrangement of such equipment. Since such equipment is well known and used for various other purposes, such as titanium and zirconium melting, details are omit-

ted and only the relative arrangements of various parts of the equipment as are helpful in the discussion of this invention are shown.

Consumable electrode 1 is held in position by supporting means (not shown) but positioned in a region above copper crucible 2. The copper crucible is cooled by water flowing in water inlet 3 and out water outlet 3' and circulating between the copper crucible and the outer supporting shell 4. This copper crucible acts as a receptacle for the melt 5. Power supply 6 feeds current through conductor 7 and through power tube 8 to electrode 1, and through conductor 9 to the copper crucible. The arcing effect between the melt in the crucible and the consumable electrode is shown by the jagged lines connecting the electrode 1 and the melt 5. The position of the consumable electrode is adjusted upward gradually to control the arcing as the level of 5 is raised by additional melt. Vacuum pump 10 creates and maintains a vacuum on the furnace and exhaust gases are forced out through outlet 11.

The resultant ingot is found to be dense and substantially completely free from pores or the cellular structure which results when the pressure is allowed to go substantially above 100 microns of mercury.

Due to the fact that the oxygen content is reduced to levels below which manganese acts as deoxidizer, it is possible to have manganese present without suffering any loss thereof due to oxidation to the corresponding oxides. Moreover, due to the higher temperatures effected on the melting operation as well as the vacuum conditions existent therein, the mass action effect of the carbon reaction with oxygen for conversion to carbon monoxide results in much more effective and complete removal of the oxygen. Whereas such conditions do not exist in prior melt operations, the advantages of this lower oxygen content are now effected earlier and more completely than in other processes.

It has been found possible by the process of this invention to reduce the oxygen content to levels below 10 parts per million. This level is so low that there is no need for oxygen removal in a second melting operation. This melting operation effects the removal of entrapped carbon monoxide gas and also effects the production of a sound, dense ingot suitable for many purposes which require an extremely clean steel having high strength, ductility and notch toughness. Such steels can have as low as 0.08 percent carbon therein.

It has also been found, apparently because of the violent reaction between the carbon and the oxides in the metal powder and the accompanying sweeping effect of the resultant carbon monoxide, that there is an effective removal of gases such as nitrogen and hydrogen that may be originally present in the iron.

The particular effectiveness of this invention in producing ultra-clean steel is demonstrated by results obtained when steels produced according to this invention are tested according to the J.K. inclusion rating described in "Tentative Recommended Practice for Determining the Inclusion Content of Steel," Designation E45–60T which appears in part 3, pages 105–118, of the 1960 Supplement for the American Society for Testing Materials Standards. As illustrated hereinafter in the examples, the values for the chart or table of page 112 of the above supplement do not exceed a value of 1 for any type of inclusion and in most cases there are no inclusions or they have a value no greater than 0.5 when steels are produced according to the practice of this invention.

The "J.K." designation for this inclusion rating is derived from "Jern Kontoret" which is the designation for a test developed by the Swedish iron and steel makers and adopted by the American Society for Testing Materials. In the tabulated results shown below for the ingots produced in Examples I and II, the values under column A are sulfide type of inclusions up to 4 microns in size and also those of 6 microns or more. In column B the alumina inclusions are indicated for inclusions up to 9 microns in size and 15 microns or more. Column C indicates the silicate inclusions in one case up to 5 microns in size and in the other case, 9 microns. In column D the inclusions having a globular shape are reported with those having up to 8 microns in size and 12 microns in size.

The following examples illustrate various modifications for practicing the process of this invention. These examples are intended merely as illustration and are not to be interpreted as limiting the scope of the invention or the manner in which the invention can be practiced. Unless specifically indicated otherwise, parts and percentages are given as parts and percentages by weight.

EXAMPLE I

A finely divided iron powder produced by electrolytic means and reduced by hydrogen as described above with a resultant analysis of 0.02% carbon, 0.05% oxygen, 0.006% sulfur and 0.005% phosphorus, was mixed with finely divided carbon, manganese, chromium and ferro-silicon powders to give a blend containing 1.10% by weight of added carbon, 0.32% manganese, 1.40% chromium and 0.28% of a ferro-silicon alloy containing 85% silicon. This blend was pressed under 50,000 pounds per square inch pressure to give rods having a cross-section 1.5 inches square and approximately 15 inches long. These rods were vacuum sintered at about 1–500 microns at 1750° F. Two of these rods were weld-assembled by inert gas shielded welding ("Heliarc") to give an assembled electrode 1.5 inches square and 29 inches long having a weight of 16 pounds. This electrode was vacuum melted in a consumable electrode electric arc furnace under a vacuum initially at 1–2 microns and maintained at less than 100 microns throughout the melting operation which was conducted at 1250 amperes for 11 minutes. The resultant ingot had a diameter of 3.5 inches, a length of 5 inches, and weighed 15 pounds.

An average analysis of samples taken from the ingot ¾ inch from the top and 1¼ inches from the bottom, had the following average analyses: 0.827% carbon, 0.215% Mn, 0.006% phosphorus, 0.006% sulfur, 0.228% silicon, 0.05% nickel, 1.37% chromium, and 0.0010% oxygen.

For ¾ inch forged bars of metal taken from the top and bottom of this ingot, the inclusion ratings (J.K. chart) was as follows:

	Sulfide A		Alumina B		Silicate C		Globular D	
Sample	4m	6m	9m	15m	5m	9m	8m	12m
Top			0.5				0.5	
Bottom		1.0	0.5				1.0	

(m=microns.)

EXAMPLE II

Finely divided electrolytic iron powder having .017% carbon, 0.005% phosphorus, 0.008% sulfur, and 0.075% oxygen, was mixed with finely divided carbon, nickel, chromium and molybdenum powders to give a blend having 0.77% C, 2.1% Ni, 1.4% Cr, and 0.48% Mo. This blend was shaped as in Example I into rods having a cross-section 1.5 inches square and a length of 15 inches. These were vacuum sintered at 1750° F. at 1–500 microns for 2 hours. After vacuum sintering the carbon content was 0.634%.

An electrode was assembled from eight of these rods with an assembled cross-section 3 inches square and length of 30 inches. In assembling the electrode, the square cross-section was made by putting together the four cross-sections of 4 rods each having cross-sections 1.5 inches square. To avoid having a structural weakness at the

linear midpoint of the assembly, the length of the rods were staggered so that the diagonally opposite rods had the same length. In one case, the diagonally opposite sections were made by two full lengths of the original rods. The other two sections were made by cutting two rods to half lengths, using half lengths as the end portions for these other two diagonally opposite sections and using a full length as the middle section. In this way the rods were staggered from each other so as not to have the intermediate ends all appear at the same section. This staggered arrangement is illustrated in FIG. 2 wherein rods A and A' are full length rods in diagonally opposite relationship to rod D and to another rod D' which is not shown but which is in the same linear relationship to D as A' is to A. Half-sections B and B'' are in diagonally opposite relationship to half-sections C and C'' and likewise B' and C' are full length rods in diagonally opposite relationship to each other so as to give strength to the assembled eelctrode. As in Example I, the rods are welded to each other in this relationship.

The welded electrode is melted in a consumable electrode vacuum melting electric furnace at an amperage of 1000–2800 for about 20 minutes at a reduced pressure of 7.5–100 microns of mercury. The resultant ingot is 6.5 inches in diameter and 6.5 inches long and weighs 54 pounds. Analyses of a sample taken from the bottom center and the top center of the ingot has the following average values: 0.501% C, 0.01% Mn, 0.004% P, 0.10% S, 0.01% Si, 2.00% Ni, 1.49% Cr, 0.44% Mo and 0.00095% O.

Various tests results from samples taken from this ingot are summarized in the following tables which give the inclusion rating, notched tensile strengths, ratio of notched to unnotched tensile strengths and Charpy V-notched impact tests. The notched tensile strengths are given for various temperatures of double draw in thousands of pounds per sq. in. (K s.i.). The Charpy V-notched impact tests are given in foot-pounds (ft. lbs.).

Inclusion rating and grain size—J.–K. inclusion rating

[m=microns]

Test No.	A		B		C		D		McQuaid-Ehns grain size
	4m	6m	9m	15m	5m	9m	8m	12m	
31-A	------	1.0	.5	------	------	1.0	.5	------	6–5 occasional 4.
31-B	.5	------	.5	------	1.0	------	1.0	------	6–5 occasional 4.
31-C	.5	------	------	------	1.0	------	------	0.5	6–5 occasional 4.

Notched Tensile Tests—.252" diam./.178" diam., .005" radius, 60° VK_t=4.0

Test No.	Oil Quenched	Double Draw	TS, K s.i.
31-B	1,550 F	300 F	344.6
31-B5	1,550 F	350 F	333.4
31-B4	1,550 F	400 F	336.7
31-C2	1,550 F	600 F	321.2
31-A3	1,550 F	800 F	317.6

Notched/unnotched TS:
300 F.—31-B/31-B=344,600/281,000=1.23
350 F.—31-B5/31-B5=333,400/318,000=1.05
600 F.—31-C2/31-A2=312,200/263,000=1.22
800 F.—31-A3/31-A3=317,600/237,500=1.33

Charpy [1] Test No.	Temp. F.	Draw Temp. F.	R_c	C, Percent	Ft.-lb.
31-C2	R.T	350 F	55/56	.501/.505	19.1
31-C3	R.T	350 F	55/56	.502/.505	19.3
31-C1	−40	350 F	55/56	.502/.506	16.8
31-C4	−40	350 F	55/56	.501/.504	13.7

[1] Charpy V-Notch Impact Tests: 1,500 F.—OQ—Double Draw.

EXAMPLE III

Cylindrical rods 2 inches in diameter and 5 inches long were produced using the same powder composition as used in Example II and putting the powder blend in a cylindrical polyethylene bag surrounded by a perforated metal cylinder and placing this under hydrostatic pressure of 50,000 p.s.i. according to a method used commercially for producing molybdenum electrode ingots from molybdenum powder. Two of these rods were welded together in a linear arrangement to give an electrode of 2 inches diameter and 10 inches length.

Similar advantageous results were obtained according to the procedure of Example II when this electrode was used in place of the electrode used in Example II but omitting the vacuum sintering treatment.

The efficacy of the practice of the present invention involving the use of powdered iron as a starting material and using the low vacuum described herein is shown by making a comparative run using a vacuum of 50 mm. of mercury in a first melt of a typical composition as shown above in Example II. Analysis of the resultant ingot shows that the oxygen reduction is very inefficient. It might be expected, however, that if this ingot is used as the electrode in a second melt conducted at a very low vacuum such as used in the practice of this invention, then the resultant deoxidation might be similar to that produced according to the single melt of the present invention. Nevertheless, when such a second melt is performed at less than 0.1 mm. (100 microns) of mercury, the deoxidation is nowhere near as effectively accomplished as in the single melt of the present invention. These results show that starting with the iron in the powder form and at the lower vacuum permits the deoxidation reaction to be effectively accomplished. Apparently once the iron has been melted, this deoxidation is more difficult to effect.

The process of this invention is desirably applied to the production steels and ferrous alloys containing at least 50% iron therein, preferably at least 75% iron.

Although the above examples illustrate the use of relatively small electrodes, the size of the electrode and the size of ingot produced in any particular melt is governed merely by the manner as assembling the electrode and the size of the furnace used. Thus it is possible to assemble electrodes in the manner described and by various other means to accommodate the largest size consumable-

electrode, vacuum furnaces that are in commercial use.

FIG. 3 illustrates an assembly of larger electrodes, in this case using 9 rods of square cross-section to make up the cross-section of the assembled electrode and using the equivalent of 3 lengths of the rods to make up the assembled length of the electrode. As shown in the drawing, the top layer at the left end is made up of rods E, F, and G. The rows in which E and G appear are assembled of rods having the normal rod length. F is a rod of half-length, as is the rod F‴, in the same top row, whereas rods F′ and F″ are of the normal rod length. In this way the rods are staggered so that the ends of the rods do not meet in the same cross-sectional area of the assembled electrode.

In the second or middle layer of rods where the ends are labeled H, I and J, the series of rods J, J′, J″ and J‴ have the same arrangement of lengths as described above for F, F′, F″ and F‴. Likewise, series of rods in linear arrangement with H and L have similar arrangements. The series of rods M, M′ and M″, as well as the series of rods in the line having K as the end rod has a similar linear arrangement as shown for G, G′ and G″. In this way the various rods are staggered with adjacent rods and therefore have greater resistance to shearing in the ultimate welded assembly. Greater numbers of rods can be similarly assembled to make larger electrodes.

However, as indicated above, the consumable electrode can be assembled in various manners either by being pressed in a unitary assembly or by being pressed into a number of smaller pieces which are united in various manners in an electrode assembly.

While the use of carbon powder has been described above for effecting deoxidation, it is also possible to use a powdered iron in which the carbon content contained in the iron is appropriate to give the amount of carbon required for deoxidation and to supply the carbon aim. Since the selection of particular iron powder having the appropriate amount of carbon therein is rather difficult, this method can be more easily practiced by using a blend of two or more iron powders with the proportions adjusted to give the total desired carbon content. This particular method is more suited to the use of iron powders having very low oxygen content and for the production of steels in which the carbon aim is low. Otherwise, it is generally preferable to supply the carbon in powdered form for the purpose of this invention. In most cases it is generally preferable to use at least 0.02% carbon powder in the powdered iron blend used in making the consumable electrode, depending on the amount of carbon already in the iron, the amount of oxygen to be removed and the carbon aim for the ultimate steel.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. A process for the preparation of an ultra-clean steel consisting of the steps of

(a) blending finely divided carbon with a finely divided iron powder having no more than 0.01 percent by weight of sulfur and no more than 0.01 percent by weight of phosphorus therein, the amount of said carbon being such that the combined weight of carbon in the iron powder and of the added carbon powder is sufficient to supply the carbon aim for the ultimate steel product and to react with the oxygen contained in said iron powder for conversion to carbon monoxide,

(b) forming the resultant mixture into a shape and of sufficient cohesive character to be adapted for ultimate use as an electrode in a consumable electrode vacuum electric arc furnace,

(c) applying said shaped iron electrode as the electrode in a consumable electrode vacuum electric arc furnace adapted to apply and maintain a vacuum in the melting region of said furnace and adapted to receive the melt from said electrode in a water-cooled metal crucible,

(d) thereafter reducing the pressure in the electrode region of said furnace to a pressure of less than 100 microns of mercury,

(e) passing current through said electrode and thereby heating said electrode and maintaining a pressure of less than 100 microns of mercury until said electrode is completely melted and collected in said metal crucible, and

(f) cooling and removing the resultant melt ingot from said crucible, and

(g) thereafter shaping said ingot for its ultimate use without any further consumable electrode vacuum melting.

2. A process of claim 1 in which said iron powder has been given a preliminary reduction with wet hydrogen at approximately 1500–1800° F. and subsequently a reduction with dry hydrogen at approximately 1500–1800° F.

3. A process of claim 1 in which the resultant powder mixture has been pressed into said shape under a pressure of at least 40,000 p.s.i.

4. A process of claim 3 in which said electrode has also been sintered in an inert atmosphere at a temperature of approximately 1750° F. for at least 1.5 hours.

5. A process of claim 3 in which said electrode has also been vacuum-sintered at a temperature of approximately 1750° F. for at least 1.5 hours.

6. A process of claim 1 in which said iron powder is an iron produced by electrolytic refinement which has been treated with wet hydrogen at approximately 1500–1800° F. and subsequently treated with dry hydrogen at approximately 1500–1800° F., said powder thereafter being pressed into said electrode shape under a pressure of at least 40,000 p.s.i. and subsequently vacuum-sintered at a temperature of approximately 1750° F. for at least 1.5 hours.

7. A process of claim 1 in which said iron powder is pressed under a pressure of at least 40,000 p.s.i. into a number of long narrow shapes smaller than the desired electrode size, said shapes are sintered in an inert atmosphere, and said sintered shapes are assembled and joined into the desired electrode shape.

8. A process of claim 1 in which said iron powder is an iron produced by electrolytic refinement and which has been treated with wet hydrogen at approximately 1500–1800° F. and subsequently treated with dry hydrogen at approximately 1500–1800° F., said powder thereafter being pressed under a pressure of at least 40,000 p.s.i. into a number of long, narrow shapes, smaller than the desired ultimate electrode size, said pressed shapes are sintered in an inert atmosphere, and said sintered shapes are assembled and joined into an electrode.

9. A process for the preparation of an ultra-clean steel consisting of the steps of

(a) forming a finely divided iron powder, having no more than 0.01 percent by weight of sulfur and no more than 0.01 percent by weight of phosphorus therein, into a shape and of sufficient cohesive character to be adapted for ultimate use as an electrode in a consumable electrode vacuum electric arc furnace, said shaped electrode having a carbon content therein sufficient to supply the carbon aim of the ultimate steel product and to convert the oxygen content of said electrode to carbon monoxide,

(b) applying said shaped iron electrode as the electrode in a consumable electrode vacuum electric arc furnace adapted to supply and maintain a vacuum in

the melting region of said furnace and adapted to receive the melt from said electrode in a water-cooled metal crucible,

(c) thereafter reducing the pressure in the electrode region of said furnace to a pressure of less than 100 microns of mercury,

(d) passing current through said electrode and thereby heating said electrode and maintaining a pressure of less than 100 microns of mercury until said electrode is completely melted and collected in said metal crucible, and

(e) cooling and removing the resultant melt ingot from said crucible, and

(f) thereafter shaping said ingot for its ultimate use without any further consumable electrode vacuum melting.

10. A process of claim **9** whereby the desired carbon content is achieved by blending at least two grades of said finely divided iron powder varying in the carbon content thereof and using appropriate proportions of each of said grades of iron powder to give the desired amount of carbon.

11. A process of claim **9** in which carbon content is equivalent to the amount to supply said carbon aim plus 135–200 percent of the theoretical stoichiometric amount necessary to convert the oxygen content of said electrode to carbon monoxide.

12. A process of claim **1** in which carbon content is equivalent to the amount to supply said carbon aim plus 135–200 percent of the theoretical stoichiometric amount necessary to convert the oxygen content of said electrode to carbon monoxide.

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