April 15, 1941. P. H. ROYSTER 2,238,078

PRODUCTION OF FERROCHROMIUM

Filed Jan. 23, 1939 2 Sheets-Sheet 1

Fig. 1.

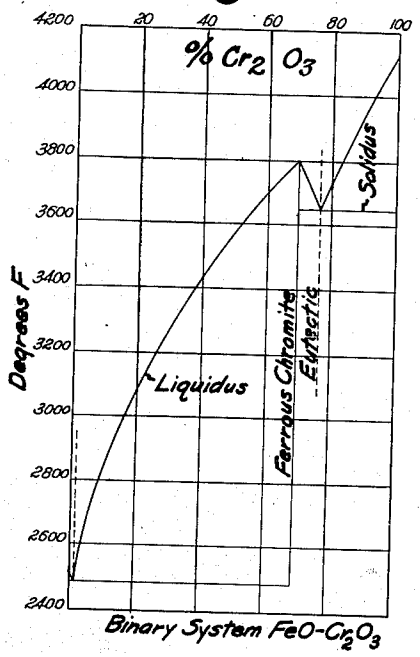


Fig. 2.

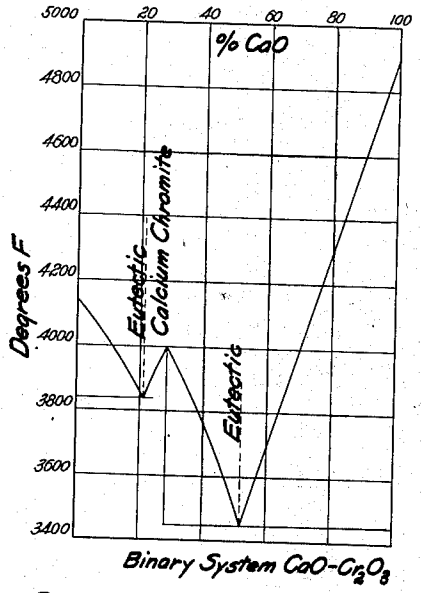
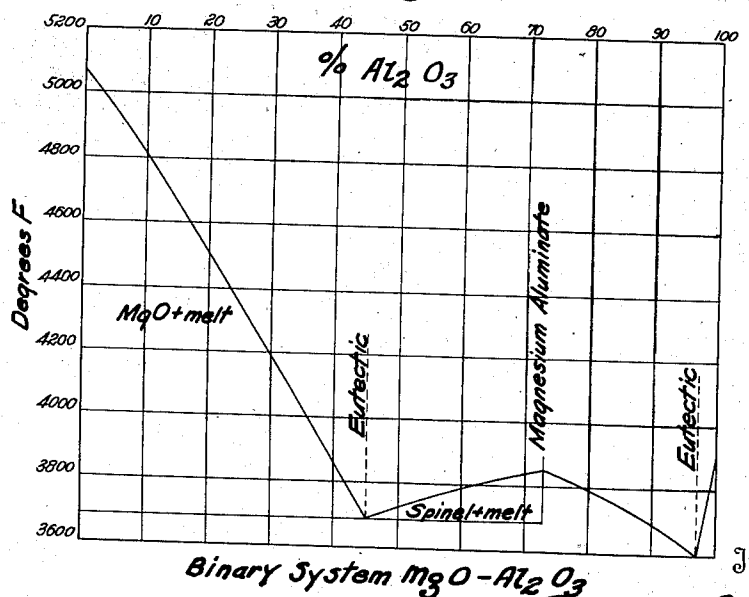


Fig. 3.



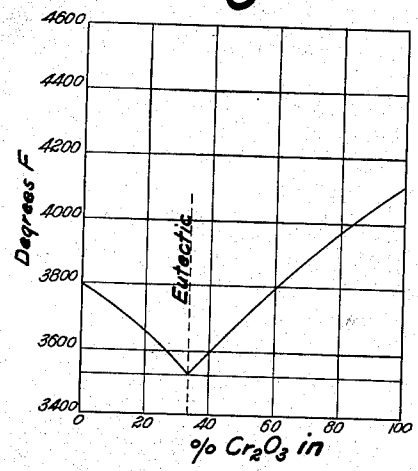
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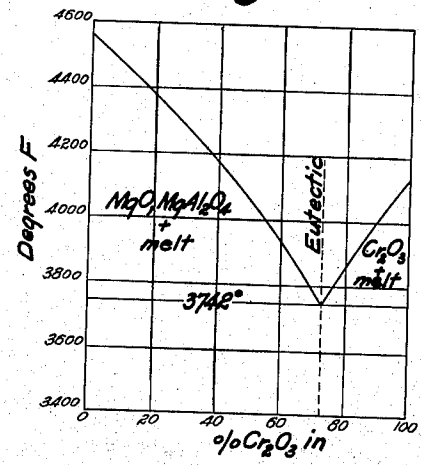
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Fig. 4.



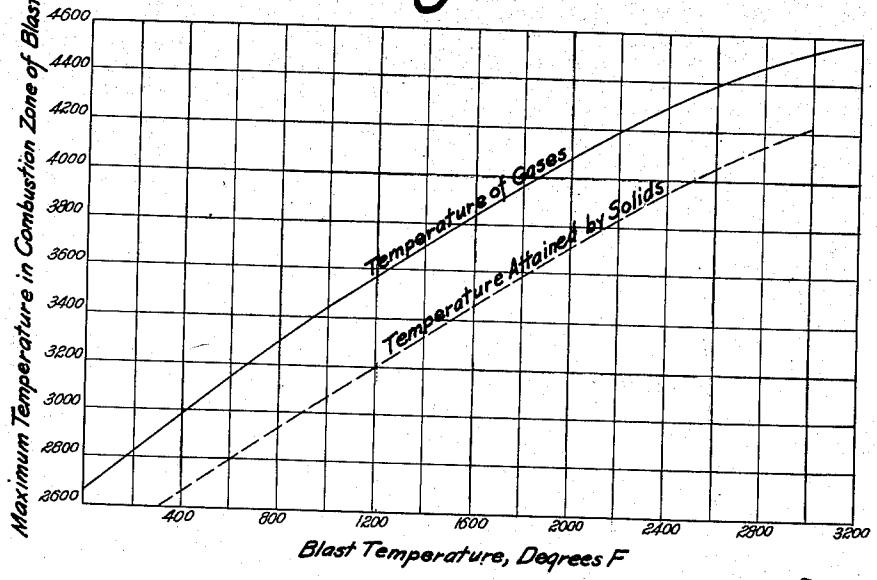
Binary System
Cr_2O_3 - 42 MgO - 58 Al_2O_3

Fig. 5.



Binary System
Cr_2O_3 - 81 MgO - 19 Al_2O_3

Fig. 6.



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UNITED STATES PATENT OFFICE

2,238,078

PRODUCTION OF FERROCHROMIUM

Percy H. Royster, Bethesda, Md.

Application January 23, 1939, Serial No. 252,448

4 Claims. (Cl. 75—127)

This invention relates to the pyrometallurgy of ores containing chromium, and is concerned with the production of alloys containing chromium—e. g., an alloy of chromium, iron and carbon of relatively high (i. e., 30% or more) chromium content—by smelting, in the blast furnace, an ore (or metallurgical equivalent thereof) containing chromium and another metal.

Heretofore ferro-chromium and other alloys containing chromium have been produced exclusively in the electric furnace. It had been thought that the conversion of chromium oxide to chromium carbide is chemically very difficult. Moreover, it had been thought by metallurgists that the conversion of chrome ores into chromium alloys could not, with any practical success, be carried out in the blast furnace because of a supposed necessity for employment of smelting temperatures of a higher order than were attainable in a blast furnace in order that conditions of thermodynamic equilibrium would be favorable to the reduction of the oxide, i. e., favorable for causing the reaction expressed by the equation

$$Cr_2O_3+3C\rightleftarrows 2Cr+3CO \quad \text{----------(1)}$$

to progress from left to right.

The reason for the above-recited openions is not clear. The reaction of the above equation takes place at about 2137° F., or, at one atmosphere pressure, at a temperature of only about 1969° F. The standard enthalpy change, $\Delta H°$, of Equation 1 is 155,760 calories per mol, and the standard change of entropy, $\Delta S°$, is 113.90 entropy units ("e. u.") per mol. From the publication by Kelley (Bur. Mines Bulletin #394, 1936) it is possible to calculate thermodynamically that at one atmosphere, equilibrium in Equation 1 is established at 2032° F. (the temperature at one atmosphere being the ratio of enthalpy change to entropy change), the enthalpy change, $\Delta H°$, being 177,850 calories per mol and the entropy change, $\Delta S°$, being 126.25 e. u. per mol. As reduction takes place according to Equation 1, carburization of the metallic chromium takes place according to the equation

$$5Cr+2C=Cr_5C_2 \quad \text{----------(2)}$$

and the actual mechanism of the reaction between Cr_2O_3 and carbon is a reduction of the oxide and a carburization of the metallic chromium. The effect of this carburization—Equation 2—is to decrease $\Delta H°$ of Equation 1 by 1.5% and to increase $\Delta S°$ by 3.4%. For simplicity, Equation 2 is omitted from the following exposition, and the terms "metallization", "reduction" and "deoxidization" of Cr_2O_3 are used to mean the conversion of chromium oxide into its thermodynamic equilibrium reduction product, which latter is hereinafter indiscriminately called "metal," "metallic product," "carbide," and/or "alloy."

In the accompanying drawings Figs. 1 to 5 inclusive are phase diagrams of binary systems hereinafter referred to, and Fig. 6 is a diagram illustrating the relationship between maximum temperature of the furnace gases at the combustion zone of a blast furnace and blast temperature.

In ores containing iron and sufficient chromium to produce an alloy of iron and chromium of high enough chromium content to warrant the designation "ferro-chromium", the mineral most frequently encountered is "chromite" or ferrous chromite, $FeCr_2O_4$ or $FeO.Cr_2O_3$. Pure chromite melts at 3800° F. The ratio of FeO to Cr_2O_3 varies widely in chromite ores from different sources. The binary system $FeO.Cr_2O_3$ shown in Figure 1 of the accompanying drawings exhibits no low temperature points on the liquidus, the eutectic between $FeCr_2O_4$ and Cr_2O_3, the lowest melting temperature on the right hand half of Figure 1 being 3640° F. The eutectic between FeO and $FeCr_2O_4$ is not of any practical importance, since its composition is about 98% FeO and only about 2% Cr_2O_3 (i. e., a composition not encountered in the production of ferro-chromium).

When ores containing chromite, of whatever ratio of FeO to Cr_2O_3, are charged into a blast furnace they encounter, during their descent through the furnace shaft, ascending furnace gases which are rich in CO and poor in CO_2. During such descent the greater part of whatever FeO may initially have been present in the ore is converted to metal (Fe, or Fe_3C, or both), which event leaves the oxide phase substantially free from FeO although the metallic iron may still be retained mechanically in position in the original lump of ore. As reduction of the FeO content progresses, the Cr_2O_3 content of the ore particle or lump moves from left to right, in the diagram shown in Figure 1 approaching the composition of iron-free Cr_2O_3 with its high melting point of 4,130° F.

Usual efforts to flux these refractory ores fail to produce a low melting mineral particle. This may be illustrated in the binary system CaO—Cr_2O_3 by the phase diagram shown in Figure 2.

From this latter it will be seen that calcium chromite ($CaCr_2O_4$ or $CaO.Cr_2O_3$), long called "infusible," has a melting point of 4,000° F. and that the binary system exhibits a minimum liquidus temperature of 3430° F. (51% CaO and 49% Cr_2O_3, by weight). In practice the amount of CaO which would be added to the Cr_2O_3 would be less than pound per pound, so that the "effective" minimum liquidus temperature in the system is about 3830° F. (for the eutectic between lime and calcium chromite at 21 parts of CaO to 79 parts of Cr_2O_3). Further increase of CaO, such as the suggested scheme for "replacement" of FeO by CaO would call for—i. e., one mol of CaO to each one mol of Cr_2O_3 to form calcium chromite—raises the liquidus temperature to 4,000° F. None of the temperatures in Figures 1 and 2 are within the range of the blast furnace as the same is now known.

Commercial chromite ores are not simply combinations of FeO and Cr_2O_3; in such ores the sum of these two oxides usually amounts to from 70 to 75% by weight of the ore, with gangue oxides (i. e., accompanying impurities) usually amounting to from 25 to 30%. The three important gangue oxides normally encountered in chromite ore are MgO, Al_2O_3 and SiO_2, the relative amounts being in the order given. Magnesia does not act to flux the Cr_2O_3 of the ore. The binary system $MgO.Cr_2O_3$ shows no compound or eutectic but only complete solid solution, with a minimum liquidus temperature of 4130° F. (Cr_2O_3 itself). The same phenomenon (i. e., absence of compounds and eutectics, and a complete series of solid solutions) is found in the binary system $Al_2O_3.Cr_2O_3$, the minimum liquidus temperature of this latter system being 3722° F. (i. e., the melting point of Al_2O_3). SiO_2, the third of the important gangue oxides, does not even form a "system" with Cr_2O_3. Mixtures of SiO_2 and Cr_2O_3 have been found to show no solubility of either oxide in the other at as high as 3852° F. and above. When both oxides are molten together they appear in the melt as immiscible liquids.

The Cr_2O_3 content of chromite ores is readily reducible, but the reaction between carbon and Cr_2O_3 can take place only when chemically reactive contact is established—i. e., only when the carbon atom and the Cr_2O_3 molecule are brought within a distance of 10^{-7} centimeters, which means that the Cr_2O_3 material must be sufficiently liquefied to flow across the surface of the carbon particle.

The above facts probably account for the general opinion that chrome ores could not be smelted in the blast furnace to produce ferro-chromium. They show that the gangue oxides present in chrome ore do not flux Cr_2O_3; also, that FeO and Cr_2O_3 do not produce a compound of low enough melting point to come within the blast furnace range. In the blast furnace shaft the FeO is reduced early in the ore's descent.

The average temperature of coke lumps arriving at the combustion zone of the blast furnace is only 3085° F., ranging between 2993° and 3189° F. (Bur. Mines Technical papers 391 and 393; Iron Trade Review, No. 1919, p. 1452; Blast Furnace & Steel Plant, vol. 12, p. 154), and the average "hearth temperature" (i. e., average of the temperatures of metal and of slag as measured by an optical pyrometer corrected for emissivity) is only 2725° F. These observed temperatures agree very well with the calculated temperatures shown in Figure 6, wherein the lower dotted line indicates the temperature of coke lumps at their arrival at the blast entrance and the solid line indicates the temperature of the gaseous combustion products leaving the combustion zone (i. e., the highest temperature attained in the blast furnace). The blast temperatures given in the references above range between 1030° F. and 1250° F., with about 1450° F. as a maximum. The highest blast temperature known to have been employed in blast furnace practice is about 1600° F. to possibly 1700° F., but use of such a high temperature blast has not been customary or regular. At the more frequently employed 1450° F. hot blast, the tuyère temperature is, according to Figure 6, about 3340° F.

The problem of smelting chrome ores, and of producing ferro-chromium therefrom, in the blast furnace is seen, from the above, to be difficult not because of any property of irreducibility of the Cr_2O_3 but purely because of the mechanical difficulty of liquefying the chromium-bearing material in order that the Cr_2O_3 molecule may be brought into chemically reactive contact with solid carbon.

I have found that for practical operation of the blast furnace as a means for smelting many chrome ores to ferro-chromium blast temperatures materially in excess of those customarily used in blast furnace practice should be employed. The process of the present invention is one of smelting a chrome ore, having a substantially high content of chromium to yield a chromium alloy containing more than 35% chromium, in a blast furnace blown with natural atmospheric air preheated sufficiently high to raise the temperature of the solids in the combustion zone (e. g. tuyère zone) to an extent such that liquefaction of the ore particles is effected and a sufficient superheat above the solidus is attained to cause the fused ore to flow into chemically reactive contact with the solid carbon and thereby to effect reduction of the Cr_2O_3 content of the ore at a rate consistent with the rate of descent of the ore particles into he combustion zone.

While it is impossible to assign any fixed combustion zone temperature to be maintained in the blast furnace smelting of chrome ores—since varying amounts of gangue oxides change this temperature over many hundred degrees—the liquefying temperature of any particular ore can be ascertained (as by experiment): with the liquefying temperature ascertained one can, by consultation of the diagram in Figure 6, readily determine the blast temperature necessary for a furnace charge including that particular chrome ore.

The invention will now be described with greater particularity in the following illustrations:

Illustration 1

A chromite, or chrome, ore from New Caledonia has the analysis: Cr_2O_3—54.5%; FeO—17.7%; MgO—8.0%; Al_2O_3—11.1%; SiO_2—3.1%; with metallics; Cr—37.3%, and Fe—13.8%. When charged into the blast furnace, the CO in the furnace gases reduces the FeO content before the ore particles reach the combustion zone, thus eliminating iron from the oxide phase, and producing a mineral of composition: Cr_2O_3—71.1%; MgO—10.3%; Al_2O_3—14.5%; and SiO_2—4.1%. Considering at the start SiO_2 as a minor diluent and omitting it from instant consideration, the oxide combination lies in the ternary system $MgO—Cr_2O_3—Al_2O_3$, and its composition projected from the ternary system onto the $MgO—Al_2O_3$ binary boundary exhibits an $MgO—Al_2O_3$ com-

position of 42 parts of MgO to 58 parts of Al_2O_3. The phase diagram for MgO—Al_2O_3 is shown in Figure 3. The liquidus temperature is 3805° F. and the solidus is 3680° F., the melt at 3805° having about one-third of its weight as primary crystals of spinel ($MgAl_2O_4$) suspended in the spinel-magnesia melt. Drawing a line from the 42MgO—58Al_2O_3 point on the MgO—Al_2O_3 binary across the ternary system to the Cr_2O_3 apex gives a pseudo-binary system consisting of Cr_2O_3 as one component and the MgO—Al_2O_3 combination as the second. The liquidus of this pseudo-binary is shown in Figure 4, with a minimum temperature (marked "eutectic") at 3510° F. occurring at 34% Cr_2O_3 (by weight. This is not a true ternary eutectic (i. e., quintuple point), but a phase boundary of spinel in the ternary system. The ternary composition is: MgO—10.7%; Cr_2O_3—74.2%; Al_2O_3—15.1%; and its liquidus temperature is 3950° F., and its solidus 3510° (pseudo-binary eutectic). At 3510° F. the ternary system consists of about 60 per cent primary crystals of Cr_2O_3 suspended in the ternary melt. The effect of the 8.54 molar per cent of SiO_2 (ignored until now) is to lower the solidus temperature by 138° F., since the entropy of fusion of the ternary melt is 10.92 e. u. per mol. The minimum point of liquefaction of the ore particle is thus 3372° F. Reference to Figure 6 shows that a blast temperature of 1500° F. is just sufficient to attain a solid particle temperature in the combustion zone of 3372° F. and it is true that some trifling liquefaction of the New Caledonian ore will take place in a blast furnace blown with air preheated to 1500° F. In actual engineering practice, where rates of descent of the charge column of three-eighths of an inch per minute to one inch per minute are employed, the total length of time at which the ore particle remains at the elevated temperature is limited. The minimum temperature given above represents a sextuple point in the quaternary system MgO—Cr_2O_3—Al_2O_3—SiO_3, and the viscosity of the liquid itself is very high. Although it is true, scientifically, that liquefaction begins at 3373°, I have found in actual furnace practice that a superheat of 100° to 200° F. above the solidus is desirable for satisfactory furnace operation in order that the liquefied ore particles have a "free flowing" property. At 100° F. superheat, viz., 3473° F. combustion zone temperature, a blast temperature of 1650° F. is required according to Figure 6 and at 200° superheat, viz., 3573° F. combustion zone temperature, a blast temperature of 1800° F. is required. I prefer to operate with the higher superheat whenever the blast heating equipment (stoves, etc.) are capable of delivering the required blast temperature.

The above-recited principles are further explained in the illustrative specific furnace data of the paragraphs immediately following:

A blast furnace with a 10 foot hearth, blown with 7650 cu. ft./min. of atmospheric air (measured at 60° F., 30 inches Hg, 60% humidity) at 4.5 lbs. pressure (gauge), preheated to 1800° F., was charged at 20 minutes intervals with rounds comprising 3000 lbs. of coke (91.5% fixed carbon; 5.5% ash; 0.5% S) carrying a burden of 4210 lbs. of the above-described New Caledonia ore, 160 lbs. of sintered flue dust, 214 lbs. of slag (i. e., dust and slag from a prior operation of the furnace), 695 lbs. of limestone, 430 lbs. of quartzite rock (essentially, SiO_2), and 32 gallons of water. The furnace discharged 28,000 cu. ft./min. of "top gas" at 920° F., actual volume (10,300 cu. ft./min. dry basis, measured at 60° F. and 30" Hg), which analyzed: CO_2—2.23% by volume; CO—38.50%; H_2—1.61%; N_2—57.66%. The furnace cast 39,600 lbs. of metal at 6-hour intervals, and flushed 6,950 lbs. of slag at hourly intervals. The metal analysis was: Cr—63.64%; Fe—27.35%; Si—1.35%; C—7.37%; S—0.05%; P—0.24%. The slag analysis was: SiO_2—27.94%; Al_2O_3—24.00%; MgO—16.28%; CaO—20.80%; Cr_2O_3—10.34%; FeO—0.27%; S—0.78%. Optical pyrometer readings (corrected for emissivity) on the metal cast (2840°–2880° F.) and on the slag at flush (2880°–2950° F.) indicated a mean "hearth temperature" of 2887° F.

When the blast temperature was raised to 2200° F. each item of the above burden was increased 31%, and metal production became 52,500 lbs. every 6 hours: hourly slag production became 8600 lbs. Under these conditions the quality of the metal improved slightly, the metal analyzing: Cr—64.90%; Fe—26.18%; C—7.45%; Si—1.25%; S—0.04%; P—0.21%. The slag, then, carried away somewhat less chromium values, analyzing: SiO_2—28.78%; Al_2O_3—25.24%; MgO—17.40%; CaO—22.18%; Cr_2O_3—5.58%; FeO—0.32%; S—0.68%. The 400° increase in blast temperature increased the tonnage of metal from 77 to 105 net tons/day, decreased the coke consumption from 2800 to 2050, and—of greater practical importance—improved the handling of the furnace and made operation of the furnace less difficult to maintain.

A similar improvement in operation and economy results from a further 400° increase in hot blast temperature to 2600° F.—a temperature which I have been able to attain for short periods and which will become a metallurgical commonplace when improvements in blast heating equipment, now in development, are realized.

Continued operation "of sorts" with the New Caledonia ore can be attained in the furnace with blast temperatures as low as 1500° F. or even 1400° F.: but, the coke consumption becomes high, the daily tonnage is decreased, furnace irregularities become frequent and distressing, the loss of chromium in the slag is excessive, the grade of metal is adversely affected, and the fluidity of the slag is difficult to control, with unfused unfluxed lumps of ore discharging into the hearth. Even under adverse conditions such as those concomitant with the lower ranges of blast temperature, the economy of the whole process is an improvement over the heretofore exclusive electric furnace production of ferro-chromium.

Illustration 2

A Russian chromite from the Urals shows an analysis Cr_2O_3 55.8; FeO 21.6; MgO 13.9; Al_2O_3 3.3; SiO_2 5.4. After elimination of FeO by CO reduction in the shaft the oxide phase composition is: Cr_2O_3 71.1; MgO 17.7; Al_2O_3 42; and SiO_2 7.0. The MgO—Cr_2O_3—Al_2O_3 ternary composition is Cr_2O_3 76.4; MgO 19.1; Al_2O_3 4.5; and the projection on the MgO—Al_2O_3 binary boundary at the composition 19 parts Al_2O_3, 81 parts MgO. The liquidus on the MgO—Al_2O_3 binary is 4570° F. (Figure 5). The phase diagram for the line drawn across the ternary system from the projected point on the MgO—Al_2O_3 boundary to the Cr_2O_3 apex is shown in Figure 5, where the minimum temperature of the liquidus is 3742° F. occurring at 72% Cr_2O_3; the actual Cr_2O_3 content is 76.4, displaced to the right in Figure 5, 4.4% from the pseudo-eutectic (actually a phase boundary in the ternary system) with a liquidus

of 3800° F. The entropy of fusion of the ternary melt is 14.62 e. u. per mol and the effect of the silica, present as 29 molar per cent of Forsterite (Mg_2SiO_4) depresses the solidus 195° F., producing a minimum solidus in the quaternary system $MgO—Cr_2O_3—Al_2O_3—SiO_2$ of 3547° F., which may be termed the temperature of initial liquefaction. It required (Figure 6) a blast temperature of 1710° F. to just reach this combustion zone temperature. For a desired 200° F. superheat a blast temperature of 2100° F. is required.

The two illustrations of the determination of the liquefying temperature of chrome ores are sufficient to describe the principles used in determining the blast temperature required for the proper production of ferro-chromium in the blast furnace.

My invention, as defined herein, is the process of smelting ores containing a substantially high chromium content (i. e., of sufficient chromium content that the burden contains at least 15% of Cr as Cr_2O_3), in a blast furnace blown with natural atmospheric air (20.97% O_2) with the specific restriction that the blast temperature is sufficiently high to raise the temperature of the solids in the combustion zone to an extent that substantial liquefaction of the ore particles is effected and a sufficient superheat above the solidus is attained to permit fused ore to flow across the surfaces of the solid carbonaceous reducing agent particles or lumps, and hence to effect reduction of Cr_2O_3 of the ore to metallic chromium. In most of the ores available in practical work, the ratio of Cr_2O_3 to MgO, and of MgO to Al_2O_3, is such that the ore particle's oxide composition is very high melting, and I realize that temperatures higher than those heretofore employed in blast furnace practice are necessary in such cases. The necessary increase in combustion zone temperature might possibly be obtained by increasing the oxygen content of the blast as was described by Johnson. My present invention is confined to a blast furnace operation in which a blast of natural atmospheric air (freed from moisture, whenever the same can be done cheaply enough) is employed and in which the temperature of the blast preheat is sufficient to effect the desired elevated temperature in the combustion zone.

It should be noted that in supplying the blast furnace with the highly preheated blasts recommended above, the complete blast line from stove to tuyère nose must be insulated with refractory material since otherwise the usual iron or steel blow pipe is rapidly oxidized.

By the expression "burden" occurring in the appended claims I mean the total charge of the blast furnace (minus the carbon contained in the charge).

I claim:

1. Process of producing a chromium alloy containing more than 35% chromium, which comprises charging into a blast furnace carbonaceous fuel and a material containing chromic oxide and a reducible oxygen compound of another metal, said material containing at least 15% of chromic oxide and at least as much chromic oxide as reducible oxygen compound of the other metal; blasting the furnace with atmospheric air preheated before entrance into the furnace to a temperature, not below 1800° F., controlled with respect to the ratio of carbonaceous fuel to said material, the temperature of preheat being increased as the ratio of carbonaceous fuel to said material is decreased, to maintain in the furnace hearth a temperature sufficiently elevated to effect liquefaction of the material and reduction of chromic oxide by solid carbon, whereby the greater part of the chromium content of the material is deoxidized and chromium alloy is produced; and removing the resulting liquid slag and liquid alloy from the furnace.

2. Process of producing a chromium-iron alloy containing more than 35% chromium, which comprises charging into a blast furnace carbonaceous fuel and a material containing chromic oxide and a reducible oxygen compound of iron, said material containing at least 15% of chromic oxide and less oxygen compound of iron than chromic oxide; blasting the furnace with atmospheric air preheated before entrance into the furnace to a temperature, not below 1800° F., controlled with respect to the ratio of carbonaceous fuel to said material, the temperature of preheat being increased as the ratio of carbonaceous fuel to said material is decreased, to maintain in the furnace hearth a temperature sufficiently elevated to effect liquefaction of the material and reduction of chromic oxide by solid carbon, whereby the greater part of the chromium content of the material is deoxidized and chromium alloy is produced; and removing the resulting slag and liquid alloy from the furnace.

3. Process of metallizing chrome ore, which comprises charging the ore into a blast furnace with carbonaceous fuel and a flux; blasting the charge with air, containing less than 30% oxygen, preheated to an elevated temperature, at least equal to 1800° F., controlled with respect to the ratio of ore to fuel employed in the charge, the temperature of preheat being increased as the ratio of carbonaceous fuel to said material is decreased, whereby the hearth of the furnace is maintained at an elevated temperature greater than the blast temperature and sufficiently high with respect to the compositions of the metal and the slag produced therein to maintain metal and slag fluid; and removing from the hearth a slag containing less than 20% Cr_2O_3 and a metallic product containing more than 35% chromium.

4. Process of preparing ferro-chromium from a material containing chromic oxide, ferrous oxide, magnesia, alumina and silica, wherein the ratio of Cr_2O_3 to FeO exceeds unity and wherein the sum of the metals chromium plus iron exceeds one-fourth of the total material, which comprises heating the material in a blast furnace in chemically reactive contact with a solid carbonaceous reducing agent by means of a blast of atmospheric air preheated to a temperature of at least about 1800° F., whereby reduction of the greater part of the Cr_2O_3 by carbon is effected to produce a fluid product containing more than 35% chromium in a deoxidized condition.

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