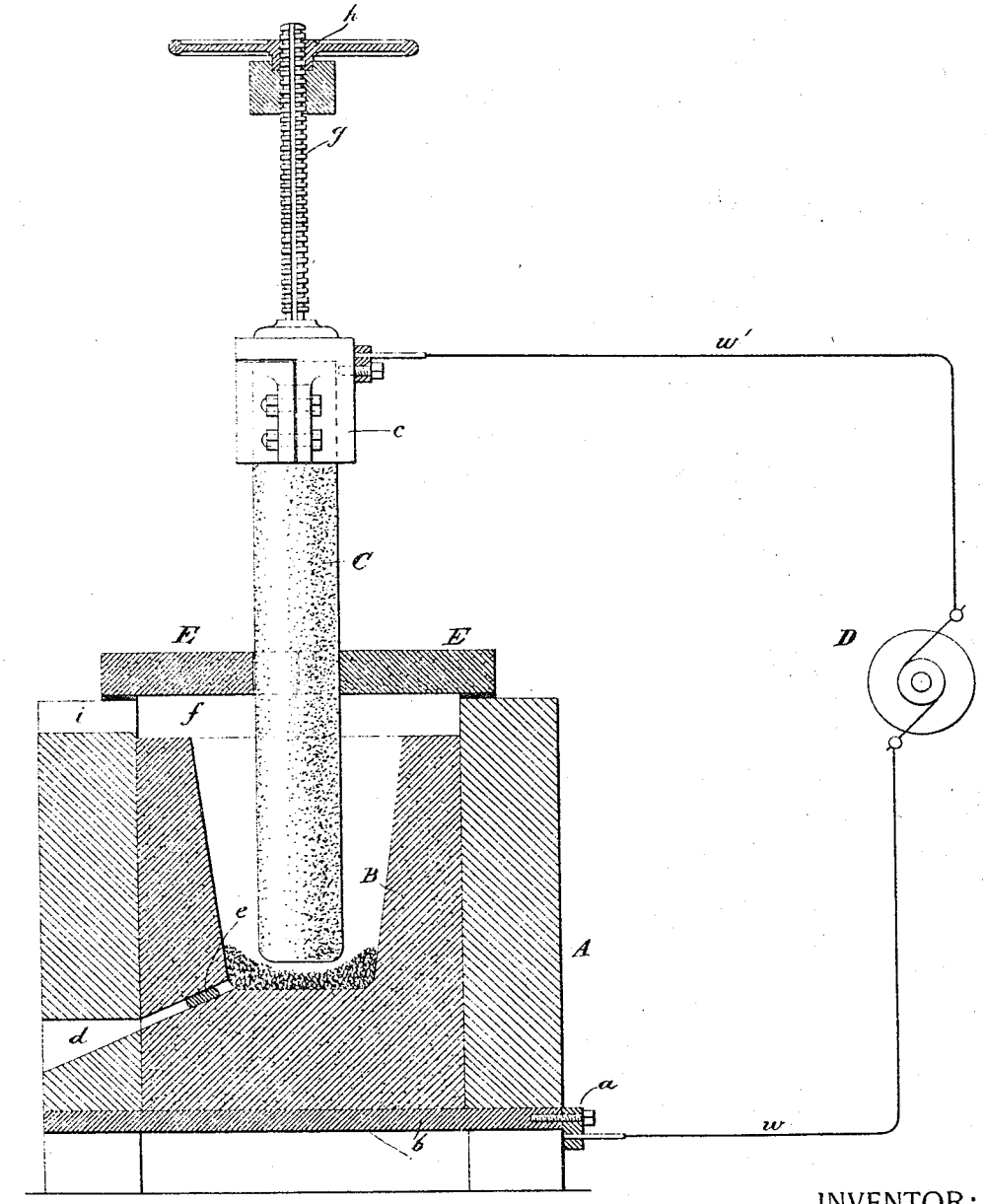
(No Model.)

T. L. WILLSON.

ELECTRIC REDUCTION OF REFRACTORY METALLIC COMPOUNDS.

No. 492,377. Patented Feb. 21, 1893.



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ELECTRIC REDUCTION OF REFRACTORY METALLIC COMPOUNDS.

SPECIFICATION forming part of Letters Patent No. 492,377, dated February 21, 1893.

Application filed August 9, 1892. Serial No. 442,601. (No model.)

To all whom it may concern:

Be it known that I, THOMAS L. WILLSON, a citizen of the United States, residing at Leaksville, in the county of Rockingham and State of North Carolina, have invented certain new and useful Improvements in the Electric Reduction of Refractory Metallic Compounds, of which the following is a specification.

This invention relates to the reduction of aluminium and other difficultly reducible metals from refractory ores or compounds thereof by means of electric smelting. Electric smelting, or metallurgical reduction by means of electrically generated heat, has heretofore been performed in two ways, namely, by an incandescent furnace heated by the passage of an electric current through a mass of broken carbon, the heat being generated by the resistance which this poor conductor presents to the passage of the electric current; and in an arc furnace wherein the heat is generated by the passage of an electric current across an arc between two separated electrodes. In the former or incandescent furnace, the current is passed horizontally between two carbon bars or electrodes, the space between them being filled with a mixture of broken carbon and the ore to be reduced, and with a base metal, as copper. Such furnaces are subject to the practical disadvantage that as the base metal fuses a pool or bath is formed extending between the electrodes and serving to short-circuit them around the mass of material to be reduced, which necessitates the continual drawing apart of the electrodes in order to maintain the necessary resistance in the furnace. This difficulty is in great measure overcome by the use of an arc furnace in which the current passes vertically between two electrodes, one of which consists of a carbon or graphite crucible or hearth, and the other a carbon bar or pencil above and entering the hollow of the crucible or hearth. The pencil being lowered into contact with the crucible or an intervening conducting material, is raised out of contact therewith to produce an arc, the heat of which performs the reduction of the material placed in the crucible. As reduction in an arc furnace has been practiced prior to my invention, the alumina or other refractory ore is fused by the heat of the arc and covers the bottom of the crucible in a molten pool or bath. In the direct manufacture of bronzes or other alloys the base metal thereof forms a pool at the bottom of the crucible, and the molten alumina or other ore lies in a bath superposed thereupon. The carbon pencil is kept elevated above the surface of the bath of alumina in order to maintain the arc. A reducing agent being present in the furnace, either by introducing a reducing atmosphere therein, or by the utilization of the carbon of the electrodes as such agent, the reduction of the alumina or other metallic compound is effected by the combined action of the electric arc and the reducing agent. When a base metal is present it combines with the reduced metal, forming an alloy.

In the operation of such an electric arc furnace, considerable practical difficulty is experienced by reason of the sudden and violent fluctuations in the resistance of the furnace, which occur by reason of the ebullition of the fused bath. The fused alumina or other ore or metallic compound, being a much better electrical conductor than the vaporous medium of the arc, must be kept out of contact with the carbon pencil in order to maintain an arc. By the ebullition of this fused bath, the liquid alumina or other ore is caused to spatter, or spout, or foam, upwardly at frequent irregular intervals, into contact with the carbon pencil, thereby to a great extent short-circuiting the arc and lowering the resistance of the furnace. In practice, it is found that this boiling up of the alumina produces a short-circuit of such very low resistance as to seriously affect the operation of the dynamo by which the current is generated. Whenever such a short-circuit is formed, the quantity of the current is increased in proportion as the resistance is lowered, thereby throwing a greatly increased load or work upon the dynamo, the practical effect of which is to tend to instantly stop its rotation, thereby subjecting the dynamo and the motive power which drives it, as well as the belt or other intermediary through which the power is transmitted, to a severe shock, these shocks following each other in such rapid and irregular succession as to be extremely injurious and detrimental to the machinery. There is furthermore great liability of burning out the armature of the dy-

namo by reason of the excessive current, even in the case of dynamos whose armatures are constructed to carry currents of extraordinary volume such as must be used for electro-metallurgical work. This short-circuiting of the arc is perhaps partly due to the boiling up of the copper or other base metal through the bath of alumina or other ore when, as in the making of aluminium bronze, such a base metal is present in the furnace; but the same difficulty is experienced, and to nearly or quite the same degree, when no base metal is present in the furnace, and when consequently the only fluid bath is that of the alumina or other ore under treatment.

The object of my present invention is to overcome the practical difficulties arising from the presence in the furnace of a fused bath of the ore or compound under treatment. In the course of numerous experiments that I have made, and the use of various reducing agents, I have discovered that subdivided or pulverized carbon when commingled with the alumina or other metallic compound to be reduced, and in sufficient proportions, has the effect of preventing the formation of a bath of the fused metallic compound.

My present invention therefore consists as an improvement in electric smelting in an arc or vertical furnace in subjecting alumina or other refractory metallic compound to the continued heat of an electric arc while commingled with subdivided carbon in sufficient proportion to prevent the formation of a bath of the fused compound. The violent fluctuations in the resistance of the arc due to the ebullition of such a bath are consequently avoided, and the resistance of the arc is rendered so nearly uniform as to render the smelting process of practical operation in connection with existing means for generating the requisite heavy electrical currents. Such fluctuations as occur are so trifling in extent, and so gradual, that the machinery is subjected to no injurious strains. The smelting process is also rendered more economical because it is conducted more regularly and progressively, is subject to less interruption by reason of the slowing down of the dynamo, such as results from the occurrence of a serious short-circuit, and is consequently effected by the maximum current that the dynamo can generate under the requisite resistance of the furnace.

In the practice of my present invention I employ by preference an electric furnace of the construction and proportions shown in the accompanying drawing, which shows the furnace in vertical mid-section, the electric circuit and the dynamo being shown diagrammatically.

Referring to the drawings, let A designate the outer masonry shell or bench of the furnace, B the carbon or graphite crucible or hearth, C the carbon bar or pencil constituting the movable electrode, and D the dynamo for generating the currents. From the terminal brushes of this dynamo, one wire w leads to and communicates with the crucible B, while the other wire w' leads to and communicates with the carbon pencil C. The connections are preferably made in the manner shown, the wire w being connected through a fastening bar a to an iron plate b underlying the crucible B, and the wire w' being connected to a metal socket c embracing the upper end of the carbon pencil C. The bench A is made preferably of firebrick, which is a non-conductor of electricity, and the furnace is covered over with a plate, or preferably two plates E E of carbon, having a central hole through which the carbon pencil C projects down into the crucible.

For tapping out the resulting product, a tap-hole d is formed which in operation is closed by a plug e of alumina, clay, or other suitable refractory material. The carbon plates E E rest on the top of the firebrick walls A, which project above the top of the crucible, forming an intervening space f for insulating purposes to prevent the short-circuiting of the furnace between B and E.

For the vertical adjustment of the carbon pencil, a screw-threaded shaft g is provided which may be propelled up and down by the engagement therewith of a suitably mounted rotative nut h. The details shown, however, are not essential to my invention, which may be applied in connection with furnaces widely different from that shown. The dynamo being in operation and the electrical connections properly made, the carbon pencil C is thrust down until its end touches the bottom or hearth of the crucible, thereby closing the circuit. The pencil is thereupon slightly elevated in order to cause an arc to spring between the crucible and the pencil. This arc is preferably permitted to play for a minute or more before putting any material into the furnace, in order to first thoroughly heat up the furnace. Thereupon some alumina or other refractory metallic compound, preferably thoroughly commingled or intermixed with finely divided carbon, is introduced into the furnace, which may be done by shoveling the charge through a top opening i formed as a notch in the brickwork A. The granular material thus introduced falls around the lower end of the carbon pencil, and if it comes in contact therewith, and is itself sufficiently conductive, it may extinguish the arc, in which case the attendant will lift the carbon pencil somewhat higher in order to re-establish the arc. The reduction then proceeds, either gradually or violently by a series of explosions according to the nature of the materials introduced. No fused bath is formed, and consequently no ebullition occurs within the crucible. The presence of the subdivided carbon appears to have the effect of maintaining the subdivision of the alumina as the latter becomes fused, and perhaps to some extent of absorbing it, the alumina being thus held by the carbon until the intense

heat of the arc effects the dissociation of its oxygen, which is taken up by the carbon, forming carbon monoxide or dioxide, which flows out of the furnace, leaving the aluminium free. Upon the interruption of the process while the reduction is at its height, and the immediate cooling down of the furnace, no cake of solidified alumina is found such as would result from the presence of a molten bath; but on the contrary the material in the furnace is found in apparently the same condition as before its introduction into the furnace, being a powdered or granulated alumina intermixed or impregnated with carbon, and ordinarily not even agglomerated by the heat. In the reduction of aluminium by this method, the aluminium freed within the furnace must be recovered in some way before it can escape into contact with the air and be oxidized. The particular means for recovering the aluminium forms no essential part of my present invention, but there are two methods which as I believe may be used for this purpose. Of these, the first is to introduce a base metal into the furnace to instantly alloy with the nascent aluminium as it is freed, this being the method commonly heretofore employed. The second method is to have an excess of carbon in the crucible sufficient to combine with the nascent aluminium, forming an aluminium carbide, from which the metal may be subsequently extracted. The result of suppressing the fused bath and consequent ebullition will not be attained unless the carbon commingled with the ore or compound under treatment be in sufficient proportion. The proportion required will vary according to the condition of the ore and carbon, varying with their fineness and the degree of intimacy of their admixture. When alumina is used in the form of a fine powder, and the carbon is combined with it with the utmost intimacy by impregnating the alumina with the carbon, I have found that an amount of carbon equal by weight to fifteen per cent. of the mixture, is sufficient to prevent the formation of a fused bath. If the material is in coarser form, and less intimately commingled, a larger percentage of carbon may be required. I prefer to use alumina or other ore or compound impregnated with coal tar or other heavy suitable hydro-carbon, by stirring powdered or granulated alumina or other metallic compound into the tar or other hydro-carbon while the latter is maintained in the liquid state, preferably by being heated, until the alumina &c. is thoroughly impregnated with the hydro-carbon, and thereupon driving off the hydrogen and lighter hydro-carbons by heat until the whole is reduced to a dry powder. This tar-impregnated alumina is claimed in my application for patent filed April 20, 1892, Serial No. 429,923. In lieu thereof, however, comminuted alumina or other metallic compound to be reduced, and powdered or comminuted carbon may be mechanically mixed and introduced together into the furnace.

The precise method of commingling subdivided carbon with the material to be reduced is not essential to my present invention, it being only essential thereto that while the material under treatment is being subjected to the continued heat of the electric arc, subdivided carbon in sufficient proportion shall be commingled with it. Thus the actual intermixture of the two may first take place in the arc itself.

I have found that by first introducing alumina and fusing it in the furnace so that it is brought into the condition of a molten bath, and when it reaches such a state of ebullition as to cause serious fluctuations in the resistance of the furnace, the introduction into the crucible of the requisite proportion of comminuted or subdivided carbon will quickly suppress the ebullition and bring the resistance of the furnace to substantial uniformity. In this case the carbon is commingled with the alumina by reason of the violent circulation of the latter due to its ebullition, the suppression of the ebullition occurring apparently immediately upon the thorough commingling of the introduced carbon with the alumina.

In practicing my process for the production of aluminium bronze, I find it preferable after initially heating up the furnace, to first introduce the copper, which instantly fuses and forms a pool of molten base metal in the bottom of the crucible, and thereafter to introduce the tar-impregnated alumina, or intermixed alumina and powdered carbon as the case may be, lifting the carbon pencil sufficiently to maintain the arc. The copper, and the alumina and carbon, are preferably introduced in small quantities or charges and at frequent intervals, and preferably in alternation. As the reduction proceeds, the pool of copper at the bottom of the crucible is converted into aluminium bronze, the quantity of which gradually increases, until after a run of several hours it is tapped out of the crucible without cooling down the furnace, whereupon the carbon pencil is readjusted and the operation proceeded with with only momentary interruption. The pool or bath of molten aluminium bronze is not subject to any material degree of ebullition, since it is heated only from above, so that what vaporization occurs is only at its upper surface, and consequently no bubbles of vapor rise up through it. The current passing through it generates practically no heat, since the molten metal is in excellent conductor. It is only in the case of a superposed bath of molten ore that difficulty is experienced in the short-circuiting of the arc, since this ore being a somewhat poor conductor, is heated by the passage of the current through it, as well as by the heat of the arc immediately above it, and is kept in violent ebullition. But by my invention the ebullition of the molten ore is wholly pre-

vented, since as it is fused it does not form a bath, but constitutes with its inter-commingled carbon a quiescent mass floating upon the top of the bath of molten bronze beneath.

In practicing my invention, the positive terminal of the dynamo may be connected to the crucible B and the negative terminal to the carbon pencil C, thereby passing the current upwardly through the furnace, or the reverse arrangement may be made, thereby passing the current downwardly through the furnace. I prefer the upward passage of the current because I find that it involves much less wasting away of the electrodes B C by oxidation. The crucible B is so thoroughly protected by the presence of the material being acted upon, that it is but slightly oxidized in any event, and by making the carbon pencil C the negative electrode, it is caused to waste away much less rapidly than if it were made the positive. Furthermore, the presence of the inter-commingled carbon which serves as a reducing agent almost wholly prevents the oxidation of the electrodes, since the oxygen which is dissociated from the alumina is instantly taken up by the inter-commingled carbon, which is in closer proximity to the points of evolution of the oxygen than are the surfaces of the electrodes, and consequently the oxygen is almost wholly reduced to carbon monoxide or dioxide before it comes in contact with the electrodes.

My present invention is not applicable to incandescent furnaces, that is to say, those in which the heat is generated by passing a current through a broken resistance material, such as retort carbon, and I specifically disclaim its application to such furnaces. My invention is applicable only where the heat is derived from the electric arc. The conditions essential to the maintenance of such an arc in an electric furnace are well understood in the art. The arc is caused by the separation of the electrodes, thereby forming an interruption in the circuit, and to maintain the arc, at least one of the electrodes must be maintained out of contact with any conducting material in the furnace of such low resistance as to shunt sufficient current around the arc to extinguish the arc. In any case the arc is formed and maintained close over the material under treatment, or at least close over such portion of the material as is immediately under treatment.

The best arrangement for producing an arc is that shown, wherein the current passes in vertical direction through a furnace, the crucible constituting one electrode, and a carbon pencil thrust into it constituting the other. Other arrangements, however, are admissible, although believed to be inferior. For example, two carbon pencils may be connected to the respective terminals of the circuit and thrust into a crucible or arranged close over a hearth (which might be non-conducting), being separated to form an arc between them, which arc is brought down into close contact with the material under treatment, or, they may be so arranged that the arc shall pass from one pencil into the material and out therefrom to the other pencil, thus forming a double arc.

I contemplate applying my invention in connection with the reduction of other metals than aluminium. I believe it to be applicable to the reduction of the following metals among others, namely, barium, calcium, manganese, strontium, magnesium, titanium, tungsten, and zirconium. In the manufacture of bronzes, I propose to apply it to the manufacture of bronzes containing silicon and boron.

My invention is applicable to other chemical reactions than those included by the word "reduction" used merely in its metallurgical sense; for example, I propose to apply it for the treatment of refractory compounds or ores of metals, not necessarily for the production of the metals themselves, but for the production of other compounds thereof. For example, I have already employed it for reducing calcium oxide and producing calcium carbide.

I claim as my invention the following defined novel features, substantially as hereinbefore specified, namely:

1. The process of decomposing refractory compounds which consists in subjecting the compound, while commingled with subdivided carbon in sufficient proportion to prevent the formation of a bath of fused compound, to the continued heat of an electric arc between separated electrodes, one (at least) of which is arranged close above the material immediately under treatment, so that the arc is close above such material, whereby during the operation the fluctuations in the resistance of the arc which would be due to the presence and ebullition of such bath are avoided.

2. The process of deoxidizing refractory metallic compounds which consists in subjecting the compound, while commingled with subdivided carbon in sufficient proportion to prevent the formation of a bath of fused compound, to the continued heat of an electric arc between separated electrodes one above the other, such arc being close to the material immediately under treatment, whereby during the operation the fluctuations in the resistance of the arc which would be due to the presence and ebullition of such bath are avoided.

3. The process of reducing refractory metallic compounds which consists in subjecting the compound, while commingled with subdivided carbon in sufficient proportion to prevent the formation of a bath of fused compound, to the continued heat of an electric arc produced by passing a current in approximately vertical direction between separated electrodes, so that the arc is maintained close above the material immediately under treatment whereby during the reduction the fluctuations in the resistance of the arc which would be due to the presence and ebullition of such bath are avoided.

4. The process of reducing alumina which consists in subjecting it, while commingled with subdivided carbon in sufficient proportion to prevent the formation of a bath of fused alumina, to the continued heat of an electric arc between separated electrodes one above the other, so that the arc is maintained close above the material immediately under treatment whereby during the reduction the fluctuations in the resistance of the arc which would be due to the presence of such bath are avoided.

5. The process of reducing a refractory metallic compound which consists in commingling therewith a sufficient proportion of finely subdivided carbon as described, feeding the mixture into an electric arc, maintained between vertically separated electrodes, and maintaining it subject to the continued heat of such arc, and so that the arc is maintained close above the material immediately under treatment whereby the formation of a bath of the fused compound is avoided.

In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.

THOMAS L. WILLSON.

Witnesses:
ARTHUR C. FRASER,
CHARLES K. FRASER.