

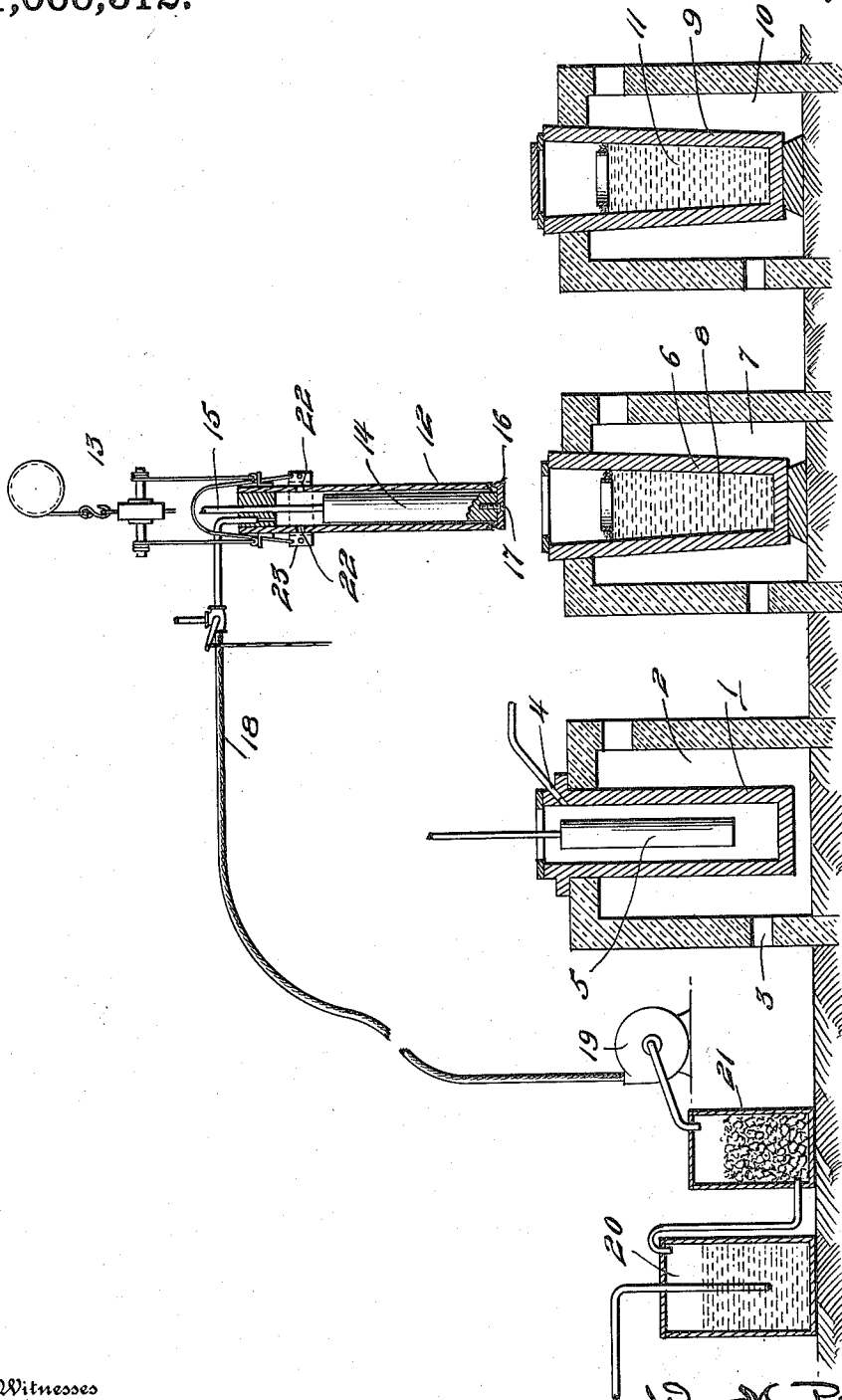
W. M. PAGE.

PROCESS OF PRODUCING CLAD METALS.

APPLICATION FILED DEC. 15, 1908. RENEWED DEC. 11, 1912.

1,066,312.

Patented July 1, 1913.



Witnesses

W. M. Page
A. M. Houghton

By

W. M. Page,
Marble & McElroy
Attorney

Inventor

UNITED STATES PATENT OFFICE.

WILLIAM MARSHALL PAGE, OF PHILADELPHIA, PENNSYLVANIA.

PROCESS OF PRODUCING CLAD METALS.

1,066,312.

Specification of Letters Patent.

Patented July 1, 1913.

Application filed December 15, 1908, Serial No. 467,651. Renewed December 11, 1912. Serial No. 736,233.

To all whom it may concern:

Be it known that I, WILLIAM MARSHALL PAGE, a citizen of the United States, residing at Philadelphia, in the county of Philadelphia and State of Pennsylvania, have invented certain new and useful Improvements in Processes of Producing Clad Metals, of which the following is a specification.

10 This invention relates to processes of producing clad metals; and it comprises a method of making clad metals wherein a billet or ingot of steel containing carbon is treated to remove the carbon superficially and a film or layer of copper or copperlike metal is thereafter weld-united to the treated surface; and it also comprises certain improvements in processes of weld-coating metals; all as more fully hereinafter set forth and as claimed.

15 In a patent to John F. Monnot, No. 853,716, is described and claimed a method of producing clad metals wherein a ferrous metal and an unlike, non-ferrous metal, such as copper, are brought into contact at an extremely high temperature; a temperature exceeding the melting point or the ordinary casting temperature of such unlike metals. Under these circumstances, the ferrous metal and the non-ferrous metal become 20 firmly and permanently united together, the joined metals after cooling being inseparable by heating and quenching, mechanical force or the action of cleaving tools, such as a cold chisel. In copper-clad steel, a cold chisel veers off into the softer metal, refusing to follow the line of union. The joined metals can be drawn, rolled, spun, stamped and otherwise worked like objects 25 of one metal. In the present invention, I have produced a like product by a somewhat different process.

30 In practising the described Monnot process, it is found that high-carbon steel does not form the weld union as easily as low-carbon steel; and in the present invention I therefore convert such steel superficially into iron or a lower-carbon steel prior to applying the coating metal. This decarboni-

zation is also advantageous with commercial 50 low-carbon steels since it promotes the ease of union of the two metals. The decarbonization may be effected in a number of ways. One is to superficially oxidize the steel or iron and then re-reduce, as by heating in producer gas or hydrogen. In the 55 oxidation of the steel, the superficial carbon is also oxidized and on reduction of the iron oxid, the metal formed is nearly free of carbon and in a better condition, both physical and chemical, for welding or uniting to copper and like metals, forming the desired type of union at a lower temperature. In such re-reduction, furthermore, the carbon in the layer of metal next below the 60 oxid layer takes its part in the reduction of such oxid, so that in the re-reduced article or object comparatively pure iron occurs both in the reduced metal and in the next underlying layer of the original metal. In 70 the oxidation, the manner of performing the operation is not a matter of indifference, it being desirable that the iron oxid formed should be a closely cohering layer, and a treatment with superheated steam gives particularly good results. 75

Before oxidation, the steel should be brought to a good metallic surface by mechanical cleansing, such as sand blasting, followed by a pickling, which is best done 80 with an acid capable of forming volatile iron compounds, such as hydrochloric acid or hydrofluoric acid. These treatments are desirable to remove sand, scale, cinder, slag, etc., as well as ordinary rust, since of course 85 the ultimate union must be produced between two purely metallic surfaces free from non-metallic bodies in order to secure a molecular or weld union between the metals, and cinder and the like interfere 90 with a metallic contact, while ordinary rust does not reduce to form a desirable type of spongy, well-cohering iron.

In cleaned steel, carefully oxidized and then re-reduced, the reduced, pure iron forms 95 an excessively thin, porous layer, which unites readily with copper and copperlike metals, such as silver, gold, brass, bronze,

etc.; probably or possibly by forming an alloy therewith; and unions may be effected at comparatively low temperatures, even at the ordinary casting temperature of copper, etc.

5 This desirable superficial layer of pure iron on steel objects may be directly produced in making copper-clad metal by using copper in the coating bath which is somewhat "underpoled" and therefore contains cuprous oxid. The mechanically cleansed and pickled steel billet is first heated and is then dipped into or otherwise contacted with, the underpoled copper, contact being maintained until evolution of gas ceases. The carbon

10 in the superficial layers of the steel and the oxygen in the copper unite to form gaseous products while the iron formed from the superficially purified steel and the copper (which is also purified by this action) form the desired type of molecular or weld union. On removing the steel object from contact with the body of copper, it will be found to carry a cohering (as distinguished from adhering) film of copper, firmly weld-united

15 or molecularly joined thereto, and against a surface thus filmed, another body of copper can afterward be cast or otherwise contacted in a liquid state, this second body welding firmly and permanently to the filmed surface. Since, however, in repeatedly using such an oxygenated bath of copper for dipping steel objects it is difficult to cause it to retain sufficient oxygen and to remain in a proper condition, I preferably use some of

20 the carbon-removing oxygen in the form of an iron oxid. To this end, I first preferably mechanically cleanse the steel billet or other object, pickle and dry. The billet may, for instance, be first sand-blasted, then dipped

25 in hot hydrochloric pickle liquor, dipped in hot water, again dipped in hot pickle and once more dipped in hot water. These operations heat it somewhat and in removing from the final bath, the surface dries, and the billet will be found to have an absolute metallic surface, free from dirt, oxid, scale, etc. Before this surface has a chance to re-oxidize by any long exposure to air, the billet is next preferably treated with super-

30 heated, streaming steam, as by placing it in a heated casing through which steam is streaming. This produces a delicate, thin, firmly cohering coating of oxid; probably mostly magnetic oxid. From the steam bath,

35 the oxidized billet is next best withdrawn into a neutral atmosphere pending further operations, it being undesirable to permit any further and aerial oxidation. It may be withdrawn into a bottomless casing filled with producer gas, for instance. Using producer gas, it is a desirable precaution to

40 preliminarily treat such gas with a substance or solution capable of removing oxygen and carbon dioxid, both of which are usual impurities in producer gas and both of which are capable of oxidizing hot steel. This preliminary purification is not absolutely necessary, but with most grades of gas is quite desirable. From the atmosphere

45 of indifferent gas, the billet is next removed into contact with melted copper, which need not be so hot as in the stated Monnot process, though high heat is advantageous. Under the influence of the heat of the molten copper, the superficial layer or film of iron oxid produced as described and the carbon of the layer of steel next beneath (with which such oxid layer is in absolute contact) react and form pure iron, both from such oxid film and from the steel layer next beneath, and

50 also form carbon monoxid or dioxid which bubbles up through the copper and escapes. With this pure iron, the copper readily combines, physically or chemically, or, and probably, in both ways, giving a cohering coating layer united to the main body of steel by the desired type of union. If the copper be underpoled, the contained oxygen cooperates with the iron oxid in removing carbon from the underlying steel layer. The oxidation of the carbon gives rise to gaseous oxids which escape in the form of bubbles. When bubbling substantially ceases, the desired union is complete.

55 Though the entire amount of copper desired for the coating may be applied from the same copper bath, as by the general methods and with the apparatus described and shown in said Monnot Patent, No. 853,716, yet it is in general desirable to apply merely a film coating in a preliminary operation, applying the main body of copper in a second treatment; this being particularly the case where a high-conductivity coating is desired as in making clad metal for electrical purposes. Underpoled copper where such is used, is not desirable for use in coatings of any thickness; and even with pure copper baths, where the steel is decarbonized in the manner described, the copper quickly becomes contaminated with dissolved iron in a manner which while not making it undesirable for many purposes, does cut down its conductivity for the electric current. By film-coating in the one bath

60 in the manner described and applying a substantial coating by a second bath of pure copper, the main coating layer is of such pure copper. It is therefore desirable where the clad metal is to be used for electrical purposes, that the double operation be employed, though for other purposes the whole coating may be affixed in one bath.

In making high-conductivity clad metal by uniting pure metal with a filmed steel surface, I find it a useful precaution to heat

the mold or other vessel wherein the coating is produced to a temperature just below the melting point of the coating metal and to introduce the molten metal near the wall of the mold so that the first portions entering next such wall solidify thereon, the molten metal used being of course at a suitable temperature. The film produced on the steel article in making copper-clad steel, and especially if produced from a bath of metal which has been repeatedly used, usually contains considerable iron alloyed therewith and if the whole mass of copper surrounding the filmed core in the second operation be liquid, this iron is apt to diffuse therethrough whereas if the external portions of the main copper coating be instantly set, diffusion is confined to the still liquid layers next the filmed core. Other high-melting, ductile metals of a copperlike nature, such as silver and gold may be applied in the same manner as copper. Silver may contain dissolved oxygen, but in the case of gold it is better to rely on the described superficial oxidation of the steel billet. In forming coatings of lower melting metals and alloys like the various brasses and bronzes, copper or the like, a higher melting metal may be applied as the described film and then the low melting metal cast into contact therewith.

In practical operation using the described process, a billet of carbon steel which may contain 0.25 or more of carbon, and generally contains more, is sandblasted, pickled and washed. After these operations it is warm and adhering moisture from the washing bath quickly dries off, leaving a true metallic surface, such surface being composed of crystals of the various crystalline iron and iron-carbon compounds which together form steel. If this surface be now oxidized to form a thin superficial coating of closely adhering oxid the carbon of the oxidized portion disappears as gas and when the billet is reheated, the carbon in the underlying metal reacts with the oxid to form carbon monoxid and pure iron, part of the pure iron coming from the reduced oxid and part from the steel layer which yields the carbon for the reaction. The coating of oxid formed by treatment with superheated steam is particularly suited for this purpose since it is quite thin and closely cohering, so that oxid and carbonaceous iron come into actual contact. An ordinary rusted surface is much less suitable. The heat of molten copper is quite sufficient to perform this reaction where the oxid is closely adhering. Nor need the molten copper be very hot. If the original sandblasted and pickled billet be directly plunged into underpoled copper without preliminarily steaming, the contained oxygen is frequently sufficient to oxi-

dize the superficial carbon and produce pure iron without the preliminary oxidation. In either case, the billet is given a surface of very pure iron of a spongy texture capable of uniting chemically or physically, or perhaps in both ways, with copper and like metals to form the desired type of union at temperatures which are comparatively low; being often as low as the ordinary casting temperature of the copper or the copperlike metal. Higher temperatures are not disadvantageous.

With comparatively thick coatings of ordinary oxid or scale, the carbon in the underlying steel cannot generally exercise the desired reducing action throughout such layer with sufficient speed and thoroughness to secure good and uniform unions. For the present purposes, the coating of oxid must be thin and molecularly contacting with the carboniferous steel layers to secure reduction in the coating bath. Where the coating of oxid is reduced prior to contacting with copper as by heating in producer gas, it is not necessary that it be so thin or so well united. Even where preliminarily oxidized, it is desirable that the manipulation of the billet be performed in a producer gas atmosphere which has been perfectly freed from oxygen and carbon dioxid as these gases have a tendency to form undesirable types of oxid; and where a true metallic surface has been formed, as in oxidizing and reducing prior to coating, or in the ordinary Monnot process, this purified producer gas is still more desirable. While the carbon dioxid in ordinary producer gas will not oxidize the surface of copper, the oxygen of such producer gas will so oxidize it, and this treated producer gas is therefore also advantageous for use with a copper-filmed billet. Even with great care in running a gas producer, the resultant gas cannot ordinarily be produced perfectly free from oxygen and dioxid, a half per cent. or so of each being ordinarily the minimum possible. An alkaline solution of pyrogallol, that is, ordinary pyrogallic acid dissolved in an excess of caustic soda or potash solution, is very efficient in removing both oxygen and carbon dioxid and is convenient to use since the producer gas can be bubbled therethrough without much load on the fan running the producer. Other reagents may however of course be used in lieu of this, such as ferrous sulfate treated with lime or alkali; hot iron chips or filings followed or preceded by lime or alkali, etc.

In the accompanying illustration I have shown, more or less diagrammatically certain apparatus adapted for use in the described method.

In this showing: Element 1 is a heating

casing in furnace chamber 2, heated by an oil flame or the like through orifice 3. Entering the upper part of the casing is a steam inlet 4.

5 Element 5 is a steel billet undergoing treatment therein.

6 is a crucible of suitable material contained in furnace 7 and containing a mass of copper 8, and 9 is a similar crucible in
10 another furnace 10 carrying a mass of purer copper 11.

12 is a mold casing suspended above the crucibles by suitable hoisting means 13 and as shown containing billet 14 carried by
15 porter-bar 15. The hoisting means are adapted to give differential movement to the billet and casing. At its base the billet carries a cap 16, secured by screw 17 and adapted to make joint with the bottom of
20 the casing, joint making means being carried by either cap or casing. Pipe 18 for producer gas enters the casing at its top. The top of this casing is, as shown, preferably made heavy and massive to aid in sub-
25 mergence of the casing in molten metal in the course of the operation. This pipe 18 is supplied with gas by means of fan or pump 19. Purified gas is supplied to the fan from a producer (not shown) through
30 washer 20 and drier 21. Just below the top of the casing and at a suitable distance above the head of the billet are orifices 22 which can be closed by the diagrammatically shown sealing band 23 which may be
35 of asbestos or metal.

The use of the described apparatus is obvious from the foregoing. In a typical process under the present invention for making high-conductivity copper-clad met-
40 als for electric wires and the like, a billet of strong ferrous metal such as ordinary steel, carrying a reasonable per cent. of carbon is preliminarily sandblasted to rid it of oxid, scale, cinder and other mechanical impuri-
45 ties, and is then pickled in dilute hydrochloric acid and washed. It is then introduced into casing 1 where it is subjected to heat and the influence of superheated streaming steam whereby there is formed
50 a thin, cohering coat of oxid upon the surface of the steel. Producer gas which has been purified in washer 20 containing alkaline pyrogallic acid and dried in 21, is sent into the casing 12 through fan 19 and the
55 casing is transferred to a point over the heating casing, whereupon the billet is raised into the casing by the hoisting means and the porter-bar. Cap 16 is attached preferably at this time. Casing and billet
60 are next transferred over crucible 6 and the billet protruded from the casing and lowered into the molten copper where it is allowed to remain until bubbling ceases, the

cap remaining in place on the end of the billet. This bubbling is due to the forma- 65
tion of oxids of carbon by the reaction of the iron oxid on underlying carbon. The time required in this operation is very short. The billet is next raised from the copper into the casing, and is now found to be cov- 70
ered with a thin, cohering film of copper. Where this copper bath has been used for a number of dippings, the copper film is generally rather impure and contains considerable iron. During these operations the 75
flow of purified producer gas into the casing is maintained at such a rate that there is a slight outflow at the bottom of the casing, the outflowing gas burning harmlessly. Cap 16, if not previously so attached as is 80
preferable, is next attached to the base of the billet and the casing lowered to make a good joint with this cap. Billet and casing are next transferred above crucible 9, the flow of producer gas being cut off and 85
lowered thereinto together. Sealing band 23 is next removed or displaced, and the pure copper 11 allowed to flow into the casing and along its walls, displacing the contained gas. This gas prevents oxidation of 90
the inflowing copper. The casing and the copper 11 are preferably of such temperature that the copper so flowing downward along the walls will solidify at once while later entering copper will remain fluid some- 95
what longer and close the space between the solidified copper and the film on the billet. The mold and the contained coated billet are next cooled somewhat to allow all the copper to solidify, and the billet and coat- 100
ing are pushed out of the casing by a ram or other suitable apparatus. The coated billet is then worked in any desired manner either with or without re-heating.

The described process is of course appli- 105
cable to any ferrous metal containing carbon such as the ordinary carbon steels and carboniferous "alloy steels," such as the steels produced with vanadium, chromium, manganese, titanium, tungsten, tantalum, etc. 110

The described process of producing pure coatings by causing a portion of fluid metal for a given coating to solidify next the mold walls prior to allowing such fluid metal to contact with the filmed base is of course ap- 115
plicable also to filmed billets produced in other ways, as in those produced in the acknowledged Monnot process.

In rolling, drawing or otherwise working clad metals thus produced, even with a 120
slight degree of coextension of the joined metals, the quality of the coating is much improved. The relatively soft coating metal being compressed in coextension between the tool and the stiffer base metal 125
while held against lateral yielding by a weld

union to such base metal, assumes throughout a texture comparable with the surface texture of hard drawn wire. This improvement in extension is particularly important where the outer portion of the coating is set prior to making the union while an intervening layer is still liquid since such outer portion often needs compacting as well as the described hardening of texture.

10. What I claim is:—

1. The process of producing clad metals having a ferrous metal base containing carbon which comprises removing carbon from a superficial layer of such base to produce a layer of purer ferrous metal and uniting a layer of a high-melting ductile non-ferrous metal thereto.

2. The process of producing clad metals having a ferrous metal base containing carbon which comprises removing carbon from a superficial layer of such base to produce a layer of purer ferrous metal and uniting a layer of copper thereto.

3. The process of producing clad metals having a ferrous metal base containing carbon which comprises oxidizing out the carbon from a superficial layer of such base to produce a layer of purer ferrous metal and uniting a layer of high-melting ductile non-ferrous metal thereto.

4. The process of producing clad metals having a ferrous metal base containing carbon which comprises oxidizing out carbon from a superficial layer of such base to produce a layer of purer ferrous metal and uniting a layer of copper thereto.

5. The process of producing clad metals having a ferrous metal base containing carbon which comprises producing a thin superficial layer of oxid on such base, causing the oxid to react with the carbon in an underlying layer of such base to produce a purer ferrous metal and uniting a layer of a high-melting ductile non-ferrous metal to such purer ferrous metal.

6. The process of producing clad metals having a ferrous metal base comprising carbon which comprises producing a thin superficial layer of oxid on such base, causing the oxid to react with the carbon in an underlying layer of such base to produce a purer ferrous metal and uniting a layer of copper to such purer ferrous metal.

7. The process of producing clad metals having a ferrous metal base containing carbon which comprises producing a metallic surface on the base, exposing such surface to steam to produce a thin coating of oxid thereon, causing such oxid to react with the carbon in an underlying layer and uniting a high-melting, ductile non-ferrous metal to the treated surface.

8. The process of producing clad metals

having a ferrous metal base containing carbon which comprises producing a metallic surface on the base, exposing such surface to steam to produce a thin coating of oxid thereon, causing such oxid to react with the carbon in an underlying layer and uniting a layer of copper to the treated surface.

9. The process of producing clad metals having a ferrous metal base containing carbon which comprises removing carbon from a superficial layer of such base to produce a purer ferrous metal, uniting a film of ductile, high melting non-ferrous metal to the treated surface and subsequently attaching a further quantity of high-melting, ductile, non-ferrous metal to the treated and filmed surface.

10. The process of producing clad metals having a ferrous metal base containing carbon which comprises removing carbon from a superficial layer of such base to produce a purer ferrous metal, uniting a film of copper to the treated surface and subsequently attaching a further quantity of high-melting, ductile non-ferrous metal to the treated and filmed surface.

11. The process of producing clad metals having a ferrous metal base containing carbon which comprises removing carbon from a superficial layer of such base to produce a purer ferrous metal, uniting a film of copper to the treated surface and subsequently attaching a further quantity of copper to the treated and filmed surface.

12. In the manufacture of clad metals, the process which comprises producing a ferrous metal billet filmed with a high-melting, ductile, non-ferrous metal, placing the same in a mold and adding a further quantity of molten high-melting ductile non-ferrous metal, the manner of addition and the temperature of the molten metal and of the mold walls being so mutually regulated that a setting of the molten metal along the mold walls is produced prior to molten metal contacting with such filmed billet.

13. In the manufacture of clad metals, the process which comprises producing a ferrous metal billet filmed with copper, placing the same in a mold and adding a further quantity of a molten high-melting ductile non-ferrous metal, the manner of addition and the temperature of the molten metal and of the mold walls being so mutually regulated that a setting of the molten metal along the mold walls is produced prior to molten metal contacting with such filmed billet.

14. In the manufacture of clad metals the process which comprises producing a ferrous metal billet filmed with copper, placing the same in a mold and adding a

further quantity of molten copper, the manner of addition and the temperature of the molten metal and of the mold walls being so mutually regulated that a setting of the
5 molten metal along the mold walls is produced prior to molten metal contacting with such filmed billet.

15. The process of producing clad metals having a ferrous base comprising carbon
10 which comprises producing a metallic surface on a billet of said metal, heating in steam to produce a thin layer of oxid, dipping in molten copper to cause such oxid and underlying carbon to react to produce
15 pure ferrous metal with which such copper can unite, and removing the billet covered with a cohering film of copper, said billet between such manipulations being main-

tained in an atmosphere of producer gas freed from carbon dioxide and oxygen.

20 16. In the production of clad metals, the process which comprises producing a clean surface on a ferrous metal base and heating said base, transferring the heated clean base
25 into an atmosphere of producer gas freed from carbon dioxide and oxygen, filming the base by contacting with molten copper and withdrawing the copper filmed base from
30 contact with the molten copper into said producer gas atmosphere.

In testimony whereof, I affix my signature in the presence of witnesses.

WILLIAM MARSHALL PAGE.

Witnesses:

HARRY J. TURTON,
D. P. MILLER.