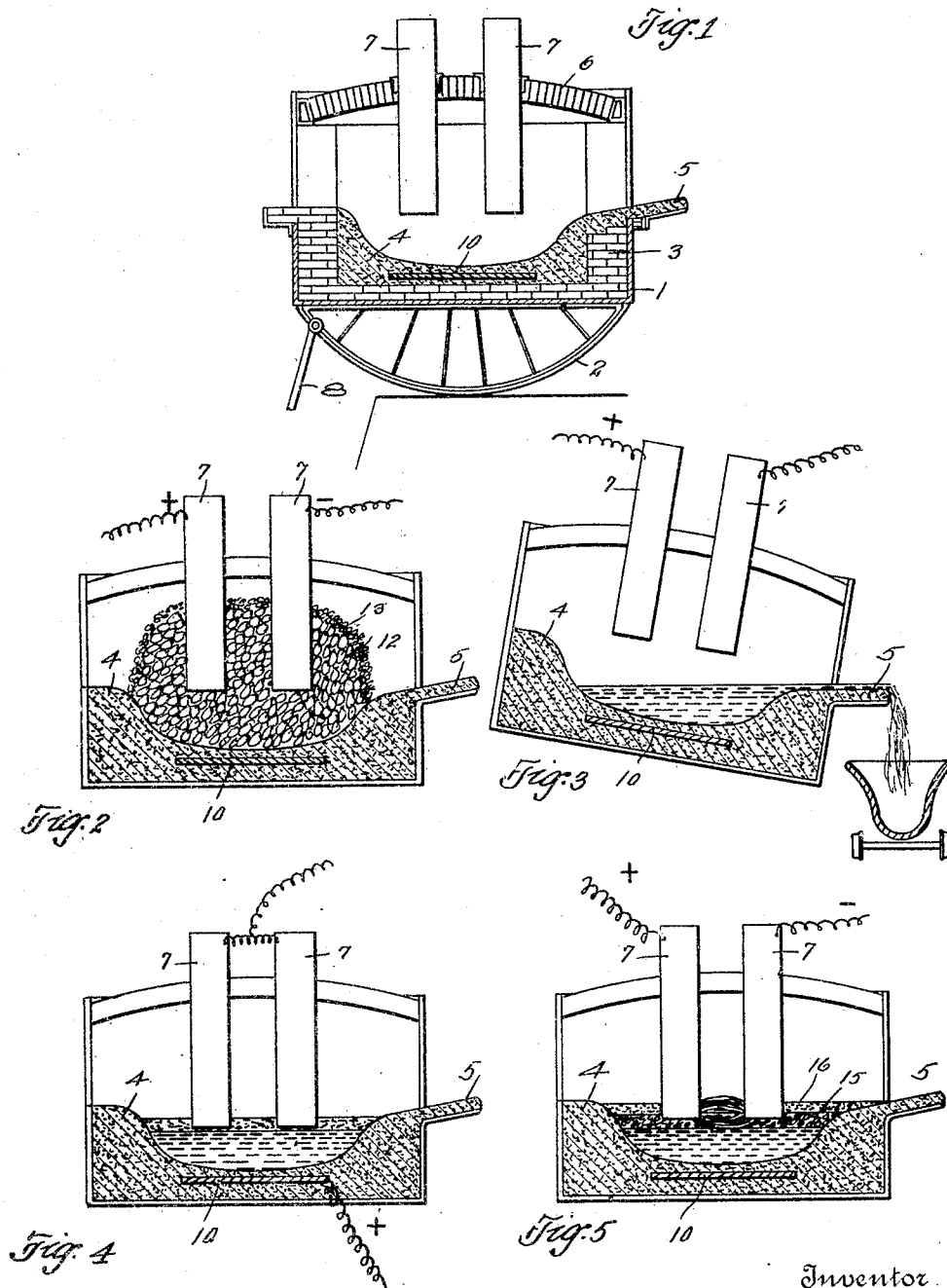


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 ALLOY.  
 APPLICATION FILED MAR. 12, 1917.

1,365,091.

Patented Jan. 11, 1921.



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# UNITED STATES PATENT OFFICE.

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## ALLOY.

1,365,091.

Specification of Letters Patent.

Patented Jan. 11, 1921.

Application filed March 12, 1917. Serial No. 154,119.

*To all whom it may concern:*

Be it known that I, ALVAH W. CLEMENT, a citizen of the United States, residing at East Cleveland, in the county of Cuyahoga and State of Ohio, have invented a certain new and useful Improvement in Alloys, of which the following is a full, clear, and exact description, reference being had to the accompanying drawings.

This invention relates to alloys and has for its object the provision of a composition of this character which shall be susceptible of easy working by commercially cutting, boring, turning and shaping tools and devices; which shall be highly resistant of chemical action, corrosion or oxidation, as by the action of acids, alkalis, or oxidizing atmospheres; the provision of an alloy which shall have a comparatively small coefficient of expansion and which shall be highly resistant to deformation by heat; the provision of an alloy of this nature which shall be cheap to make, and of materials of wide-spread occurrence in nature; the provision of a new and improved process whereby the before-mentioned alloy can be cheaply and expeditiously produced; while further objects and advantages of the invention will become apparent as the description proceeds.

Essentially my improved alloy consists of iron and chromium, the chromium content being equal to at least 10 per cent. of the whole, and the carbon content being not greater than two-tenths of one per cent. of the whole and preferably not over about one-tenth of one per cent. Essentially also the process in question comprises steps of reducing and refining the ingredients mentioned in such wise that the alloy can be made directly from mixed commercial ores in a rapid and expeditious manner, using standard metallurgical equipment and well known practical manipulations.

It should be noted at the outset that my improved alloy is not a chrome steel, the criterion of chrome steel being the possession of a high carbon content which produces a substance of such hardness and brittleness as absolutely to prevent any working or machining operations, this hardness being retained even to a red heat. My researches have shown that if the total carbon content be less than one or two-tenths per cent. this

hardness is entirely absent and the resulting metal possesses exactly the qualities of chemical resistivity combined with mechanical working ability which it is the object of my invention to secure. The resulting alloy can be improved for some purposes without the impairment of these qualities, and sometimes even to their benefit by the addition of certain other metals such as tungsten, vanadium or molybdenum, tantalum, titanium or iridium. Preferably the last named metals, if employed at all, form not more than two per cent. of the alloy mass.

For the commercial production of my improved alloy, the use of the electric furnace appears to be a necessity, owing to the fact that this is the only device now known whereby the necessary elevated temperatures can be secured together with a reducing atmosphere; in addition to which the employment of an electric furnace is practically beneficial by reason of the ability to secure and maintain the desired high-temperature conditions uniformly for extended periods. In the following description I have assumed, illustrated and described the use of an electric furnace, although I do not limit or restrict myself thereto except where I specifically recite the same in my claims, and I have, for the purpose of a practical example, chosen a certain commercial specimen of chromite ore, although it will be understood that the proportions mentioned are not invariable, but that other ores can be employed and other alloys made therefrom within the intent of my invention, merely by following the directions contained in said description, as will be apparent to those skilled in the art.

In the drawings accompanying and forming part of this application Figure 1 illustrates the general construction of the furnace which I prefer to employ; Fig. 2 illustrates the arrangement for the first step; Fig. 3 represents the decantation of the slag following each step; Fig. 4 illustrates the fluxing steps of my improved process; and Fig. 5 represents the step of making the calcium carbide in the furnace on top of the molten charge. Of course it will be understood that other furnaces could be used, and that I illustrate this merely for completeness, and because of the fact that its operation is at-

tended with certain distinct advantages because of the range of connections which it permits.

Chromium ordinarily occurs in the form of an oxid, mixed chiefly with the oxids of iron and secondarily with the oxids of aluminum, magnesium, calcium and silicon. Owing to the comparatively great stability of chromium oxid at high temperatures, it is difficult or impossible to reduce these ores in a common blast surface, since, of the ingredients mentioned, only the iron will become reduced, the silica, alumina, magnesium and lime going to form a slag, and the chromium oxid remaining entangled in the molten iron because of its comparatively great weight, and because it has very little apparent affinity for silica and other slag forming substances. Even though a small portion of the chromium oxid should become reduced in the blast furnace, the metallic chromium almost invariably combines with some of the free carbon present to form a chromium carbid and the product of the reaction is a hard, brittle and unworkable steel.

Assuming the possession of a chromite ore, a typical analysis of which might be as follows:

|    |                                      |       |
|----|--------------------------------------|-------|
| 30 | Cr <sub>2</sub> O <sub>3</sub> ----- | 46.35 |
|    | Fe <sub>2</sub> O <sub>3</sub> ----- | 21.45 |
|    | SiO <sub>2</sub> -----               | 5.48  |
|    | Al <sub>2</sub> O <sub>3</sub> ----- | 12.80 |
| 35 | MgO-----                             | 10.08 |
|    | CaO-----                             | Trace |
|    | P-----                               | .013  |
|    | S-----                               | .45   |

As the first step in my improved process I intimately mix carbon, preferably in the form of coke, with the crushed chromite ore in proportions which will supply an excess of 15 to 18 per cent. of coke over that calculated as theoretically necessary to reduce the chromic oxid to chromium and the iron oxid to iron; thus a charge of one hundred pounds of the foregoing ore would require 16 pounds of carbon for its exact reduction, which is an equivalent to 16.6 pounds of coke having an ash content of four per cent.; and in order to afford the desired excess of coke I employ approximately 20 pounds. The intimately mixed charge is piled around the electrodes of an electric arc furnace and covered with a slagging material composed of crushed lime and fluorspar in the approximate proportions of one hundred parts of lime to twelve parts of fluorspar. The arc furnace now being operated, the reduction of chromium oxid begins when the temperature reaches about 2200 degrees F. and, when complete, the resulting product is a fused mass of more or less impure chromium and iron covered

with a thick viscous slag. A typical analysis of the molten bath is as follows:

|                 |        |    |
|-----------------|--------|----|
| Chromium-----   | 51.80  |    |
| Carbon-----     | 10.05  |    |
| Silicon-----    | .81    | 70 |
| Phosphorus----- | .128   |    |
| Sulfur-----     | .073   |    |
| Iron-----       | 37.139 |    |

The various ingredients of this bath may occur free or mixed and alloyed with each other in any proportions whatever. Thus the carbon may appear as graphite particles scattered through the mixture or in combination with chromium as chromium carbid, or in combination with iron as iron carbid, depending upon the various proportions and the thoroughness of the mixing. This product is known commercially as "ferro-chromium," and has formerly been used to introduce chromium into various steels, usually in quantities so as to make a chromium content in the finished steel of from 0.3% to 3.50%. When cooled and solidified it is extremely hard and brittle and is so permeated with impurities as to be unfit for fabrication into articles of any nature whatever.

It will be understood that my invention consists in the combination of this step with the succeeding steps now to be described whereby this substance is purified and refined and the carbon silicon, phosphorus and sulfur content reduced to the value permissible in the final alloy. The second step of the process follows naturally from the first step, while the charge is still molten and the furnace hot. Of course, however, my inventive idea comprehends the situation in which any impure alloy of iron and chromium is employed.

Referring now to Fig. 1 of the drawings, the furnace which I prefer to employ consists of a metal casing 1 tiltably supported in a suitable manner as by runners 2 and lined with firebrick 3. Inside of the firebrick is a molded hearth 4, preferably of magnesite for the reasons that the same does not react with the metals or slags, that it will withstand the temperatures involved, and that it becomes electrically conducting at high temperatures. At one side of the furnace is formed a pouring lip 5, while the top is bridged by an arch 6 in which are suspended a plurality of vertically movable electrodes 7-7, here shown as two in number. The furnace is maintained in horizontal position or tilted as occasion requires by means of a suitable device 8. Submerged in the material of the hearth 4 is a conducting plate 9, preferably of carbon, since its coefficient of expansion is near that of magnesite. The necessity for its complete submergence rises from the solubility of carbon in the

metals under consideration. The reduction step above described is represented in Fig. 2, mixed ore and carbon being shown at 12 and the slag cover at 13. From this step the electrodes 7—7 are connected to the opposite poles of a suitable current course (either alternating or direct) and the furnace is operated on the arc.

By calculating the amount of chromium and of iron in the above typical analysis of the product it will be seen that it contains chromium and iron in the proportion of 58 to 42 respectively. If it has been predetermined that the final alloy shall contain a percentage of chromium less than this proportion, an excess of iron may be added at any desired stage of the process, either by mixing some iron containing compound such as mill scale ( $\text{Fe}_3\text{O}_4$ ) or iron ore ( $\text{Fe}_2\text{O}_3$ ) with the initial charge in quantities as calculated to increase the iron content; by adding iron scrap in the desired proportion at any stage of the process later than the reduction operation. The temperature maintained in the furnace during the reduction process will vary to some extent with the composition of the ore and the nature of the slag employed as is well understood. The atmosphere of the furnace during this reduction is strongly reducing owing to the formation of carbon monoxid by the reactions and also on account of the electrodes burning in a deficiency of oxygen. All air openings of the furnace are kept closed as tightly as possible.

I now remove the lime slag, containing some chromium oxid and iron oxid (as by decantation, Fig. 3) and proceed with the next step of the process, viz: decarburization. Upon the surface of the molten bath I throw a quantity of crushed lime mixed with an oxygen containing substance, which may be either an oxid of iron if the iron supply is deficient, or an oxid of chromium if the chromium content is meager, or a mixture of these oxids such as the chromite ore. The oxids can, if desired, be introduced directly into the bath of molten metal, and this step is not objectionable in case the decarburizing material be iron oxid, but is unsatisfactory when chromium oxid is employed because of its great weight and the difficulty of mixing it with the metal. There is a definite advantage in introducing these materials by means of the slag and thereafter circulating the molten metal into contact with the slag since by this means there is produced not only the decarburizing effect desired, but also a cleansing of the metal in other respects, such as the removal of sulfur, phosphorus and silicon.

For the purpose of effecting this movement of the molten metal I preferably connect the two electrodes 7—7 in parallel to one pole of the current source, and connect

the other pole to the plate 10, which is now in electric communication with the molten metal owing to the high temperature. The electrodes are depressed so as barely to clear the metal surface, a small gap being preserved so as to prevent the solution of carbon from the same. (See Fig. 4.) The action of the current under these conditions causes the molten metal to be set in motion underneath the surface of the flux, the temperature being meanwhile raised preferably to approximately 3,000 degrees F. so as to render the metal thoroughly liquid and to assist the chemical reactions. These consist of a combination of the oxygen in the oxid with the carbon (both free and combined) in the molten bath with an evolution of carbon monoxid ( $\text{CO}$ ). The function of the lime or slag is to combine with excess silicon, sulfur, phosphorus and aluminum (present in some degree from the electrolytic reduction of alumina contained in the original ore). The amount of oxid employed in the slag should be from 20% to 30% in excess of that chemically required for the reduction of the carbon and the extent of carbon removable from the bath depends on the duration of this period of treatment. In practice this operation is continued until a test piece made from the bath of metal shows less than .2% carbon which I find to be maximum carbon content which will allow easy machining of the metal as cast.

However, upon the completion of this step the product is still unfit for fabrication into articles useful in the arts due to (1) occlusion of oxids of chromium (and to a lesser extent of iron) —(2)— excess of silicon, —(3)— probably excess of aluminum (not yet completely removed by the slag). The most serious defect is the occurrence of the chromium oxid which renders the product heterogeneous, non-coherent, porous and generally worthless, and this oxidized condition is invariably aggravated by the decarburization process since the affinity of chromium for oxygen is rather high, even at the temperatures mentioned, and becomes particularly obnoxious as the carbon content is decreased.

I thereby proceed immediately to the third step of my process, preferably performing the same in the same furnace upon the same charge and without intermediate cooling. This step consists in first carefully removing the slag used in decarburizing (Fig. 3) leaving a bath of metal with a clean surface; a covering of crushed lime (15 Fig. 5) is then thrown upon this bath and the temperature of the furnace raised to a point which will result in melting the lime in about 15 to 20 minutes with the formation of a slag practically excluding the air from the molten metal. This tem-

perature is probably about 3200 degrees to 3400 degrees F. When this lime slag is melted and lies as a complete covering over the bath of metal, I introduce coal or coke dust (16, Fig. 5) in a careful uniform manner upon the top of the slag and around and between the electrodes, care being taken not to distribute the molten slag in any such way as would permit contact of the coke directly with the metal underneath, since such contact would result in an immediate combination between the carbon and the chromium. The upper electrodes are now elevated again and the furnace is operated as an arc furnace at high temperature so as to form calcium carbid by reaction between the lime and carbon. As soon as the coke dust is thoroughly combined with the lime the upper electrodes are again lowered to the position shown in Fig. 4 and the electric connections changed so as to constitute a resistance furnace and set up a flow of the metal beneath the carbid flux, whereupon a strongly deoxidizing effect is produced and the oxids are reduced to the metallic form. During this operation an excess of lime is always preserved, partly to prevent the possibility of any carbon excess which would lead to contamination of the metal, and partly to preserve a basic flux which shall serve to purify the metal of the aluminum and silicon content, thus completing the whole refining process at one operation.

The metal is now ready to pour into suitable molds. It is clean, homogeneous, of good tensile and compressive strength, tough, malleable and ductile. It is soft enough to be easily shaped with ordinary cutting tools, by turning, milling, drilling, filing or shaping. At all temperatures up to a bright red heat (or even above) it shows a resistance to oxidation far superior to that of steel or iron. In addition to the above, my improved alloy, especially when containing tungsten, molybdenum, vanadium, titanium, tantalum or iridium as hereinbefore described, is highly resistant to corrosion by sulfuric acid, either dilute or concentrated, nitric acid, hydrochloric acid, aqua regia, potash, soda or oxidizing atmospheres. In fact the original production of this alloy was occasioned by the demand for pipes and valves of acid resisting material for use in sulfuric and nitric acid plants, and these valves of this material have now been in use for a considerable period with the most remarkable success.

Having thus described my invention, what I claim is:

1. The process of producing an alloy of two or more metals which consists in melting said metals in the presence of carbon, then decarburizing the metals by treatment with oxids of one or more of the metals of the

alloy and afterward deoxidizing the metals without carburizing by a suitable reducing agent.

2. The process of producing an alloy of two or more metals which consists in reducing the ores of said metals by the use of carbon, then decarburizing the metals by treatment with oxids of one or more of the metals of the alloy, and afterward deoxidizing the metals without carburizing by a suitable reducing agent.

3. The process of producing an alloy of iron and chromium substantially free from carbon and oxids which consists in decarburizing an alloy of iron chromium and carbon by treatment with oxids of one or more of the component metals, and afterward deoxidizing the resultant mixture without carburizing by a suitable reducing agent.

4. The process of producing an alloy of iron and chromium substantially free from carbon and oxids which consists in first reducing a combined ore of iron and chromium; second decarburizing the reduced metal by treatment with oxids of one or more of the component metals; third deoxidizing the metal by fluxing with calcium carbid.

5. The process of producing an alloy of iron and chromium substantially free from carbon, oxids and impurities which consists in decarburizing an alloy of iron, chromium and carbon by the action of metallic oxids, and afterward deoxidizing the resulting mixture by the action of an alkali metal carbid.

6. The process of manufacturing an alloy of iron and chromium approximately free from carbon and oxids, which consists in first reducing in an electric furnace a mixture of iron and chromium oxids in the presence of an excess of carbon; second removing the excess of carbon and decarburizing the reduced metal by the addition of oxids of iron or chromium in the presence of a basic slag; third reducing any oxid present in the reduced metal by fluxing the same with an alkali-earth metal carbid.

7. The process of producing an alloy of iron and chromium approximately free from carbon and oxids which consists in fluxing a molten alloy of iron, chromium and carbon in an electric furnace with a limestone flux containing oxids of iron and chromium until the carbon content has been reduced to less than .2 of 1%, and thereafter fluxing the same metal in the same furnace with calcium carbid until the oxids produced by the first fluxing have been reduced.

8. The process of manufacturing an alloy of chromium and iron substantially free from carbon and oxids which consists in fluxing a molten mixture of iron, chromium and carbon in an electric furnace beneath

the surface of molten limestone containing oxids of either or both iron and chromium until the carbon content has been reduced to less than .2%; second, withdrawing the spent  
 5 fluxing material; third, covering the molten metal with a fresh supply of molten limestone; fourth, applying pulverized coke to the upper surface of such limestone; fifth,  
 10 producing calcium carbid from said coke and limestone by the action of the electric arc; and sixth, fluxing the metal with such carbid until the oxids produced therein by the first fluxing have been reduced to the metallic state.

15 9. The process of manufacturing an alloy of chromium and iron substantially free from carbon and oxids which consists in first reducing the mixed oxids of iron and chromium with carbon in an electric furnace;  
 20 second, fluxing the resulting mixture in the same furnace beneath the surface of molten limestone containing oxids of either or both iron and chromium until the carbon content has been reduced to less than .2%;  
 25 third, withdrawing the spent fluxing material; fourth, covering the molten metal with a fresh supply of molten limestone; fifth, applying pulverized coke to the upper surface of such limestone; sixth, producing  
 30 calcium carbid from said coke and limestone; seventh, fluxing the metal with such carbid until the oxids produced therein by the first fluxing have been reduced to the metallic states.

35 10. An alloy containing iron and chro-

mium wherein the chromium constitutes not less than 10% and the carbon less than .2 of 1% of the alloy and substantially free from oxids.

11. An alloy of iron with upward of 10% 40 of chromium which is ductile and malleable when cold and susceptible of machining and substantially free from oxids.

12. An alloy of iron with upward of 20% 45 of chromium which is ductile and malleable when cold and also susceptible of machining and substantially free from oxids.

13. An alloy of iron with more than 20% of chromium and less than .2% of non-metallic substances and substantially free 50 from oxids.

14. An alloy of iron and chromium together with a metal having the properties of molybdenum, and substantially free from 55 oxids.

15. An alloy containing iron, chromium together with a metal having the properties of molybdenum, wherein the chromium constitutes not less than 10% and the third metal not more than about 2% of the whole, 60 the mass containing less than .2 of 1% of carbon and substantially free from oxids.

16. An alloy of iron, chromium and a metal having the properties of molybdenum, the chromium constituting at least 10% of 65 the whole and substantially free from oxids.

In testimony whereof I hereunto affix my signature.

ALVAH W. CLEMENT.