Feb. 23, 1932. S. R. KEITH 1,846,114

METHOD AND COMPOSITION FOR DEOXIDIZING ALLOYS

Filed July 3, 1930

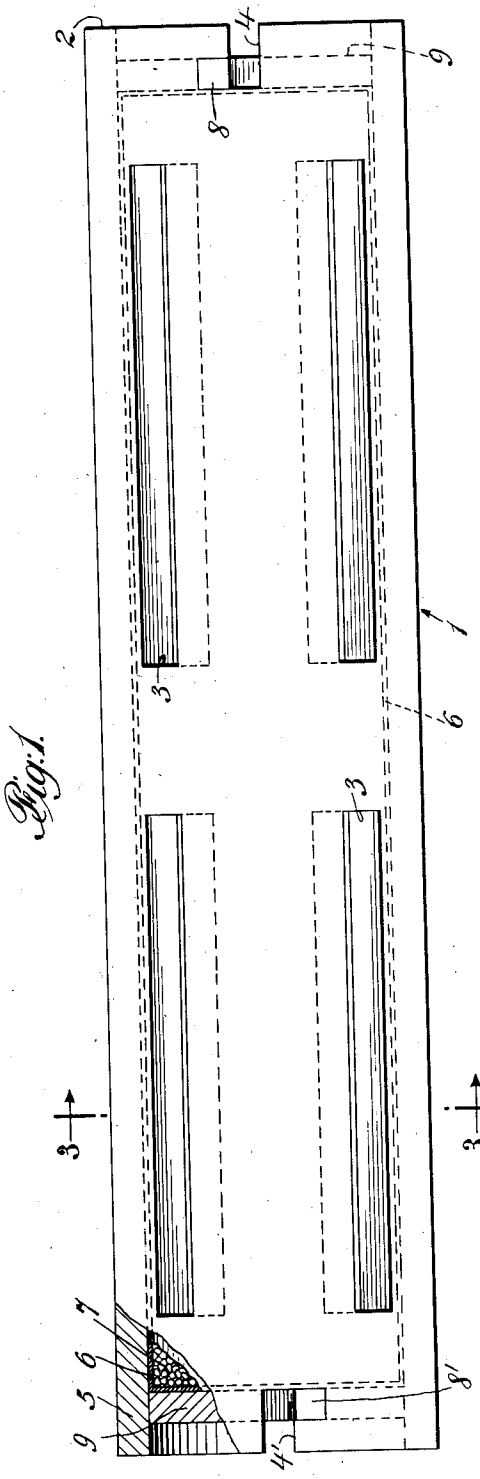


Fig. 1.

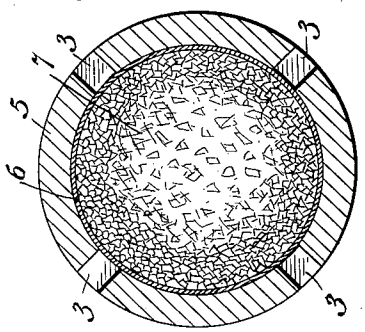


Fig. 3.

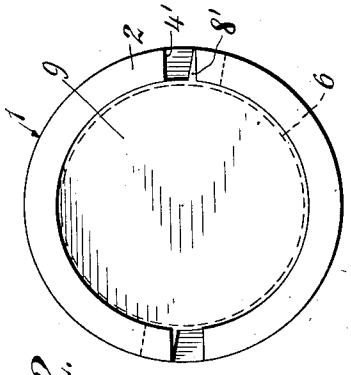


Fig. 2.

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UNITED STATES PATENT OFFICE

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METHOD AND COMPOSITION FOR DEOXIDIZING ALLOYS

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This invention relates to a deoxidizing compound and method of deoxidizing metallic alloys.

In alloying metals many conditions arise such as "gassy heats", "wild metal", brittle metal, or an alloy which cannot be cast in forms or ingots, as well as lack of uniformity in the alloys. This is due to the variables which are difficult to control and reduce to constant factors. Even steel will sometimes have a "wild" heat. Various elements have been used to correct and control metallic alloys. Aluminum has been added to the moulds when casting ingots. It has been somewhat effective in steel but in the case of nickel-chromium-alloys it is harmful. The aluminum areas in a nickel-chromium casting operating at 1800° F., frequently initiates a localized thermic reaction resulting in the burning through of the container prematurely. Other elements such as manganese, magnesium, boron, titanium, etc., have also been used but have only been partially successful. Sometimes they give rise to a thermic reaction in the furnace that burns up the entire heat probably due to improper balance. Others, like magnesium when used alone, are treacherous, tending to make the alloy brittle by reason of the by-products and the rapid oxidation and voluminous volatilization. So that, for instance, although aluminum hinders gassing it has ill effects and although magnesium deoxidizes, it has ill effects. The securing of a deoxidizer therefore is difficult because upon each addition of an element to an alloy various reactions take place. It therefore becomes necessary to use more than one element forming a composition which must be so sequenced as to react in the definite order named and required.

The objects of this invention are to provide a composition which acts in consecutive elapsed periods, with supplementary reaction one to another to produce degasification, deoxidation, altered sulfidation, grain reduction, more uniform density through the decreased solidification range, cleansing from preceding by-products of oxidation in the production of alloys and the method and apparatus whereby the composition can be added to the bath.

Referring to the drawings:

Figure 1 is a view in longitudinal elevation, parts broken off, of device embodying the principles of my invention.

Figure 2 is an end view of Figure 1.

Figure 3 is a sectional view of Figure 1 looking in the direction of the arrows.

In carrying out my invention I add to a properly worked and refined heat of nickel-chromium-iron or other alloy, a composition comprising a series of five additional alloys, four of which are simple and the fifth complex. This composition must be added to the bath in such a manner as to be completely submerged therein and held in the bath for the successive melting of the constituents of the composition as they rise to perform the work intended in the order of their arrangement. I have found that the most efficient method is to pack the composition 7 within a cylinder 1 filled with plugs 9 at both ends. Plugs 9 are locked in position by bayonet locks 8, 8′, in slots and grooves 4, 4′, in walls 5. The walls 5 of cylinder 1 have slots 3 longitudinally thereof and a paper cylinder 6 is inserted within the container prior to packing in order to retain the composition 7 therein. The filled container is plunged by means of an iron rod, which encircles it, or in any other convenient way, into the bath and in the vicinity of the bottom or the greatest practicable depth where it is held until all reactions have ceased. These reactions are noticeable to the trained eye of an operator. The container walls 5 are preferably made of the same composition as the bath so that the melting of the container will not affect the alloy in process of manufacture. The container walls must be of sufficient thickness to permit of

the successive melting and passing into the bath of the contents of the container prior to the entire melting of the container itself and I have found that such wall thickness should at least be one-quarter of an inch.

The composition which I have found effective, and the formula of which, is as follows:

4½ lbs. manganese.
3½ lbs. low carbon ferro-titanium (25% titanium).
2 lbs. ferro-vanadium (35% to 40% vanadium).
10 lbs. calcium (silico-natric).
1 lb. magnesium.

Two pounds of the composition together with an additional pound of magnesium are used in each container and are sufficient generally for a 1200 lb. heat or less in a one-half ton furnace. When the heats approach 1500 lbs., it is advisable to use two containers. The elements of the composition have sequenced melting points, for instance, magnesium melts at 651° C., then calcium (silico-natric) melts at below 810° C., then follows the melting of ferro-vanadium and carbon free ferro-titanium, and lastly manganese at 1230° C. The magnesium combines with the oxygen in the alloys with great avidity to form magnesium oxides. The oxides of magnesium must be removed as they are harmful to the alloy causing brittleness and other difficulties. The calcium (silico-natric) following the magnesium, also functions as a deoxidizer and as a flux to remove the oxides of magnesium by the formation of a double silicate, since these oxides are infusible at the normal temperatures of the bath. The ferro-vanadium also functions as a deoxidizer but primarily acts to reduce the size of the grain and thereby refine the micro structure of the alloy which improves the mechanical properties of the alloy. The carbon free ferro-titanium decreases the solidification range and provides a more uniform density likewise improving the physical properties of the alloy. The ferro-titanium and ferro-vanadium are used in the composition in small quantities and primarily for their affect upon the grain structure and not for the purpose of the addition of the characteristics of the metals themselves. Manganese, the last of the composition to melt, is also a useful deoxidizer and is of importance in changing the nickel sulphide to sulphide of mangenese. The nickel sulphide surrounds the grains of the alloy in a film which is brittle and the sulphide of nickel melts at about 1200° F. The manganese sulphide has a higher melting point and does not surround the crystals or grains of the alloy but occurs as an occluded sonim evenly distributed in the grain. The silicate manganese which is formed acts as a flux for any of the remaining oxides of the composition not previously fused. The manganese can remain in the nickel-chromium alloy, for instance, without injury and therefore a slight excess of manganese is used in the composition whereby the harmful oxides can be all removed with a factor of safety in the excess manganese.

Although it may be possible to secure the proper form of calcium (silico-natric) on the open market I have found that the substance is most satisfactory when prepared as follows:

The crucible is first heated to 1500° Fahrenheit in a hydrogen atmosphere electric furnace, to which silicon is added gradually raising the temperature and adding sodium. When completely melted the calcium is added by stirring in calcium rods of approximately one-half inch diameter. This latter must be done carefully as the repeated shutting off of the hydrogen and the turning on of carbon dioxide to avoid explosion is dangerous. When thoroughly alloyed the heat is turned off and the metal cooled in the crucible under a hydrogen pressure of about one pound. The product is easily ground. The composition of the calcium (silico-natric) is 25 to 30% calcium, 30 to 50% sodium, and 25 to 30% silicon.

It will thus be seen that I have invented a composition wherein the desired results in accomplishing the alloying of metal particularly alloys having a nickel base, or an iron base with chromium, is had by the addition of elements of such a nature that the reactions take place in sequence thereby furnishing a control of the variables and whereby as the reactions take place the subsequent elements remove the harmful by-products of the previous reactions. In the practicable operation of my composition I have found that the composition was a complete success in the accomplishment of its purposes without a single failure in about 2500 heats.

What I claim is:

1. A composition to be added in the manufacture of alloys comprising manganese, low carbon ferro-titanium, ferro-vanadium, calcium-siliconatric and magnesium.

2. A deoxidizing, degassifying, grain size reducing composition for alloys comprising 25% manganese, 15.91% low carbon ferro-titanium, 9.09% ferro-vanadium, 45.45% calcium-siliconatric and 4.55% magnesium.

3. The method of deoxidizing a metallic alloy which consists in plunging a container packed with manganese, low carbon ferro-titanium, ferro-vanadium, calcium-siliconatric and magnesium to the greatest practicable depth in the alloy bath and allowing said container to melt therein and the reactions to cease.

4. The method of deoxidizing, degassifying and reducing the grain sizes and increasing the density of metallic allows which consists in plunging a composition comprising

manganese, low carbon ferro-titanium, ferro-vanadium, calcium-siliconatric and magnesium in the alloy bath and allowing said container to remain until the reactions are completed.

Signed at New York in the county of New York and State of New York this 24th day of June A. D. 1930.

STANLEY R. KEITH.