UNITED STATES PATENT OFFICE.

PERCY A. E. ARMSTRONG, OF LOUDONVILLE, NEW YORK.

STABLE-SURFACE ALLOY STEEL.

1,322,511. Specification of Letters Patent. Patented Nov. 25, 1919.

No Drawing. Application filed May 24, 1919. Serial No. 299,636.

To all whom it may concern:

Be it known that I, PERCY A. E. ARMSTRONG, a subject of the King of Great Britain, and residing at Loudonville, in the county of Albany, State of New York, have invented certain new and useful Improvements in Stable-Surface Alloy Steel, of which the following is a specification.

My invention relates to an alloy steel containing iron, silicon, chromium and carbon, and of a highly stable character, that is to say, highly resistant to change or deterioration, such as produced in ordinary steel, for example, by staining, oxidizing, corroding and the like agents.

The base or principal portion of the alloy steel is iron, on which the material is largely dependent for strength and for cheapness.

One of the effects of chromium when alloyed with iron is, as has long been known, in the direction of making the material more stable, or resistant to deterioration, such as surface corrosion, but chromium, used substantially or entirely alone as an alloying material with iron, has several disadvantages. Chromium and iron do not alloy well together and a streaky and irregular effect is likely to be produced, articles made from the same melt often differing widely in their qualities. Iron-chromium alloys have a tendency toward red shortness with resulting cracks, blemishes and fissures, and scale badly when heated to temperatures required for hot mechanical working during commercial operations. The quantity of carbon which can be present in iron-chromium alloys without causing very substantial loss of surface stability or resistance to deterioration is quite limited. With my improved alloy steel, difficulties of this character are either absent or are reduced to the minimum.

Without being limited to any particular theory of the action of silicon in the alloy, I believe that the very excellent character of the material obtained by my invention may be accounted for by the formation of a silicid or silicids of iron, and of a silicid or silicids of chromium, which iron and chromium silicids are miscible with one another when molten. In any event, the silicon acts as a third alloy material which is highly beneficial in bringing about the formation of a substantially homogeneous alloy, free from troublesome streaks and irregularities, of high surface stability and readily workable. This beneficial action of silicon is not appreciable where it is present only in small proportions, say up to .30–.40%. To get such beneficial effects at least .50% of silicon must be present and more silicon is desirable. With the use of silicon as described herein, it becomes possible to have the ground mass of the material substantially solid solution. The more the ground mass is solid solution, the greater appears to be the stability of the alloy steel produced. With the silicon in the alloy steel, greater amounts of carbon can be used than would be available for production of stable surface material without a substantial proportion of silicon.

I believe that the action of carbon is one of fixing or, in other words, one of setting up a lag or retardation to change in the alloy steel during cooling, and further that the carbon enters into combination with the iron and chromium, which combinations, however, are modified by the action of the silicon present.

With my new alloy steel large numbers of small areas, of appearance similar to carbids in straight carbon steel, may be distinguished under the microscope and, while I have been unable to isolate same, I am inclined to consider them to be chromium carbids, though they may be mere concentrations of the ground mass fixed in their condition by carbon, or may be accounted for in yet other ways. They are not points of local attack, for on etching with *aqua regia* they are etched less than the ground mass, and no intensity of etching is discernible on the boundaries of these small areas. When present in the material either in the as cast or as rolled state, or subjected to prolonged heating and slow cooling, they do not adversely affect its surface stability.

Proportions given herein are by weight and it is to be noted that the atomic weight of silicon being only about half of that of chromium or iron, the percentages of this component, if stated by volume, would be about twice the figures given herein.

For production of stable surface material to be subjected to mechanical working, the silicon content may be from about .50% to 8%, and the chromium from about 3% to

about 50%, and chromium and silicon, taken together, from about 5% to about 58%. Mechanical workability becomes very slight as the extreme upper limits stated are approached, but with up to about 25–30% of chromium and about 5–6% of silicon the material can be hot forged reasonably well. The material just described may be cast, in fact, it usually is cast into ingots before being worked mechanically, and castings may be made therefrom if desired. For making castings, however, which are not to be mechanically worked, more silicon may be used up to about 30%, and chromium up to about 60%, or even higher.

The alloy steel having over about 5% and under about 13% silicon and chromium, taken together, is practically stainless and is resistant to corrosion and the like, when the ground mass is fixed solid solution by heat-treatment, but is more or less readily attacked by corroding and the like agents when not in such state. Heat-treatment is necessary with this material in order to obtain solid solution ground mass. For production of such material the silicon may be from .5% to 7%, and chromium 3% to 10%, the proportions being distributed between the two so as to keep the totals between 5% and 13%. With such low proportions of silicon and chromium, taken together, the carbon should be kept low to get good results. Carbon as low as .05% may be used. Preferably the carbon should be kept under one-tenth of silicon and chromium, taken together. With an alloy steel containing silicon 2.5% and chromium 3%, for example, the carbon should preferably be under .55%, since, with such material, further increase of carbon, to say 1%, results in a considerable reduction of the desired surface stability in the alloy steel. Carbon .30%, for example, gives good results with these proportions of silicon and chromium, provided the ground mass is fixed solid solution by heat-treatment.

With chromium and silicon, taken together, over 13%, and chromium over 10%, the material is substantially solid solution in the ground mass and has high surface stability whether heat-treated or not. With such chromium and silicon, the carbon content may be increased, without substantially reducing the desirable qualities of the material, as, for example, with chromium about 10 to 20%, and silicon about 2% to 7%, it is sufficient, so long as a maximum of 3.5% carbon is not exceeded, to keep the carbon below one-sixth of silicon and chromium, taken together. For example, one very good alloy steel contains chromium 13.7%, silicon 3.2%, and carbon 2.56%. If more readily workable material is desired, low carbon down to about .05% may be used and in such case the silicon may be less, down to about .5%.

With chromium above about 20%, the presence of any considerable amount of carbon tends to make the material brittle and difficult to work, if the silicon is low. Such material is readily workable, however, if the silicon is more than twice the carbon, up to about 8% of silicon. For example, an alloy steel having chromium 22%, silicon 4.5%, and carbon 2.1% has high service stability and works well. As before, 3.5% carbon is about the maximum for mechanically workable material. Considerable relative reduction in carbon is permissible, if desired, as, for example, another good alloy steel contains chromium 31%, silicon 6.12%, and carbon .68%.

As already stated the alloy steel, when used for making castings not mechanically worked, may contain up to about 60% chromium, and up to about 30% silicon. The carbon in such cast material should preferably be less than one-half the silicon.

With the silicon-chromium content about 13% or over, the alloy is highly resistant to change or deterioration in the hot state. Cast into ingots it forges and rolls with very noticeable absence of mill scale, and when rolled down has practically nothing but a sort of brownish "rouge" on the surface, of extreme thinness. When exposed to an oxidizing atmosphere at about 1800° F. for over a month, a specimen containing about 12% chromium, 5% silicon and .45% carbon, showed no more than surface darkening. Alloy steel of this composition does not melt until heated to about 2600° F., and this specimen had a specific resistance of 115 microhms per cubic centimeter. Such material, and material having still higher silicon-chromium content is well adapted for electrical heating elements, particularly where run at high temperatures, which may be as great as 1800–2000° F. or even higher, the temperatures permissible depending to some extent, at least, upon the times they are maintained. For electrical heating elements where lower temperatures are sufficient, say 1300° F. or so, the material may have less silicon-chromium content, so long as silicon and chromium, taken together, are over 5%. The specific resistance of an alloy steel of about this proportion is about 65 microhms. The specific resistance increases much more rapidly with increase of silicon than with increase of chromium. The cast material as well as the mechanically worked material may be made use of for electrical heating elements. When the production of electrical heating elements involves a drawing or bending operation the carbon should be kept low, for example, under 13% of chromium and silicon taken together, carbon may desirably be about .40% and for over 13% silicon-chromium content, carbon about 1% gives good results. Higher carbon may

be used where heating elements are produced by casting or like operation or material cold bending is not involved.

In the production of my improved alloy steel, great practical advantage can be taken of the fact that silicon is present to a substantial extent in the alloy, along with chromium. The production of alloys containing chromium with little or no silicon requires ferro-chromium of high purity, which is expensive to produce. I have found that silicon may be used as a good and inexpensive reducing agent in preparing the ferro-chromium for my alloy steel. Silicon, when used as a reducing agent, enters to a considerable extent into the molten metal as an alloy component, and in this way a ferro-chromium-silicon alloy may be cheaply and conveniently produced. The ferrous alloy so obtained, may be made use of directly in the melting furnace, with, of course, the addition of other materials for obtaining the proper proportions of the various alloy components, and various grades of ferro-chromium-silicon may be utilized by proper choice of other materials. In this way the process of manufacture is simplified and a considerable saving effected of valuable materials, including chromium and silicon. From 80% to nearly 100% of the silicon and practically all the chromium used in the melt can be gotten in the finished product, particularly when the melting is done in the electric furnace, which I consider the desirable apparatus for the purpose, though other systems of melting may be used, if desired, and materials from other sources may, of course, be used.

The known silicids, especially the chromium silicids, can be used to advantage as a ready guide to the production of good quality alloy steel and the nearer the composition is to that of the known silicids the better appears to be its surface stability.

My new material has quite distinctive cooling and heating curves, showing two marked transformation points or stages, the upper one of which tends to rise with increase of silicon and chromium content, or with increase of silicon content alone.

The material has a long plastic stage when melted and cast into an ingot or other mold; with small molds it readily solidifies into coherent ingots which can be worked to good advantage. When cast into larger molds the period of solidification is quite long unless provision is made for withdrawing the heat fairly rapidly. When means are not resorted to to keep down the time for solidification, the casting may be done by top pouring of the metal from the ladle with a considerable proportion of slag which forms a protecting envelop all around and over the molten metal, and can be readily knocked off when the ingot has been removed from the mold. Pouring rapidly as, for example, through a large nozzle, has been found to be of advantage in casting operations.

As an instance of the abnormal plastic stage or undercooling of my alloy, one batch of 5 tons containing about 17% chromium, about 4.5% silicon and about .80% carbon which did not melt until it reached a temperature of about 2600° F., remained molten for considerably over an hour, and was still molten even when the temperature had fallen to below 2000° F. This long plastic stage has the valuable property of eliminating pipe in properly cast ingots or other castings to a very large degree and it is useful, particularly in making small castings, for readily producing castings of great soundness. The plastic stage is likewise quite long upon heating. This long plastic stage can be utilized to good advantage in making various articles and shapes from my new alloy steel, as, for example, it may be extruded or press or drop formed into pipes, bars and shapes of various kinds.

An important property of my new alloy steel is its high resistance to rapid heating or cooling. Placed in a furnace with a piece of ordinary carbon steel, for example, of like dimensions, it remains black for some time after the ordinary steel has been heated to a yellow heat. When made use of for gun linings and the like, where the surface is subjected to the action of nitrous vapors at extremely high temperatures for short periods, highly destructive of materials which heat and cool rapidly, this material gives extremely good results and is highly resistant to erosion. By reason of this same characteristic it is well adapted for a variety of important uses, such as annealing tubes, boxes and articles which are subjected to varying temperatures over long periods. This valuable property of slow heating enables the charge in the annealing boxes and the like to be more uniformly heated than is possible with the alloys or metals at present employed for such purposes.

My improved alloy has the important property of not being readily permeable to gases at high temperatures and is, therefore, well adapted for apparatus such as containers for highly heated gases being subjected to chemical reaction, and for use in tubes for protecting thermo couples of pyrometers, and the like, where it is important to shield highly heated metallic material from being corroded by attacking gases.

The new alloy material, especially when it contains above 13% silicon and chromium taken together, is not attacked or stained to any perceptible extent by nitric acid, nor by acetic or other organic acids, fruit juices and the like. It is attacked to some extent, however, by hydrochloric acid, sulfuric acid,

and hydrofluoric acid, particularly when diluted.

My improved alloy steel, containing substantial proportions of silicon, has greater surface stability, that is to say, is much more resistant to stain, oxidation, corrosion and the like, than similar materials not containing a substantial proportion of silicon. Ingots and billets made from my alloy are worked with practically no formation of mill scale whatever, whereas material of analysis similar to my alloy steel, but containing no silicon more than a very small percentage, for instance. 3%, when heated for hot mechanical working, will scale very badly. So extremely resistant is my alloy steel to oxidation that when carbon analysis is being run, by passing oxygen thereover in presence of high heat, it has been found impossible to get the carbon out by combustion without the addition of oxid, such as lead oxid, so as to set up a chemical action upon the carbon, whereas with an alloy containing the same amount of chromium as my material, but with little or no silicon, an accurate determination of carbon by oxygen can be readily made without resort to use of foreign oxids or the like.

The alloy steel of my invention, within the ranges given for mechanical working above, can be readily worked and is not red short, and is remarkably free from troublesome cracks, fissures, blemishes, and the like. As an instance of its remarkable freedom from surface seams, a 7 inch ingot heated to the necessary temperature for rolling, was cogged down in an 18 inch mill in the billet form, then reheated and rolled in a 9 inch bar mill down to a $\frac{1}{2}$ inch round bar, and was entirely free from cracks, and seams of any sort. A 12 inch square ingot, cast with an envelop of slag, and containing chromium about 17%, silicon about 4.5% and carbon about .8% was forged under a steam hammer, cut into billets and rolled down to a $\frac{5}{16}$ inch square bar, with similarly good results. Such good results are very difficult to obtain, even from low carbon steel free from alloys, and impossible to obtain from steel containing any such percentage of chromium, with no more than .30% of silicon and with such high carbon.

Some of the uses of my improved alloy material have already been referred to, including electrical heating units, castings, cutlery and tools, gun linings, annealing tubes, etc. My alloy steel is eminently suitable for a variety of other uses, including flat iron bases, laundry machinery, propellers, water pipes and pumps for fresh and salt water, for refrigerator pipes and fittings, and generally for apparatus, fittings, etc., which are exposed to heat, moisture, steam or intense cold; for apparatus and articles exposed to action of alkalis to which the alloy steel is highly resistant, also for objects exposed to the atmosphere, such as hinges, latches, and outside hardware generally, for electrical fittings, for power transmission, electric trolley or railroad service, particularly those parts that have to withstand electrolysis, balls for water valves, ball bearing balls and races for ball bearings which have to work under water, ship fittings, surgical instruments, dental tools, steel rules, articles for personal wear, such as jewelry settings, coins and medals, automatic stoker bars which have to withstand high temperatures, and very many other purposes where high resistance to stain, oxidation and corrosion are required. The alloy steel has low magnetic hysteresis and by suitable heat-treatment can be made substantially non magnetic. These qualities make it available for many additional uses, such as in scientific instruments, electrical meters and the like.

My improved alloy steel, of course, contains small percentages of metalloids, such as sulfur, prosphorous, arsenic, etc., and may contain variable percentages of metallic elements, substantially all of which can be employed, to some extent, at least. If the chromium-silicon content is high the quantity of metallic elements which may be present without substantial detriment to the surface stability of the alloy steel may be correspondingly increased. It is undesirable, ordinarily, to include any of these metallic elements in percentages over 1%, when the total chromium and silicon used is as low as 5%, but when 13% or more of chromium and silicon is used, other metallic elements can be incorporated up to a total of about 2% to 5% without substantial detriment to the valuable properties of my alloy steel. I may, for example, incorporate with the alloy steel having chromium-silicon content of 13% or over, as much as 4% of cobalt or nickel, 1% of manganese, molybdenum, tungsten vanadium, titanium, zirconium, or other metals which form silicids or compounds or alloys with the iron, or chromium or both, or which do not materially effect the solid solution ground mass, with no considerable detriment resulting from their use.

I claim:

1. An alloy steel of high surface stability containing chromium 3% to 50%, carbon .05% to 3.5% but not more than $\frac{1}{10}$ of chromium and silicon taken together up to about 13% thereof and not more than 1/6 thereof above about 13%, silicon under 8%, over .5% and also over twice the carbon, silicon and chromium together 5% to 58%, and the principal portion of the remainder iron.

2. An alloy steel of high surface stability

containing chromium over 10%, carbon over .05% silicon over .5% chromium and silicon together over 13%, and the principal portion of the remainder iron.

3. An alloy steel of high surface stability containing chromium over 10%, carbon over .05%, silicon over .5% and also over twice the carbon, chromium and silicon together over 13%, and the principal portion of the remainder iron.

4. An alloy steel of high surface stability, containing chromium 10% to 20%, silicon .5% to 8%, chromium and silicon together 13% to 28%, carbon over .05%, under 3.5%, and also under 1/6 of chromium and silicon taken together, and the principal portion of the remainder iron.

5. An alloy steel of high surface stability, containing chromium over 10%, carbon over .05%, and more than twice as much silicon as carbon, and the principal portion of the remainder iron.

6. An alloy steel of high surface stability, containing chromium 3% to 50%, carbon .05% to 3.5%, silicon .5% to 8% and over twice the carbon, and the principal portion of the remainder iron.

7. A cast article of high surface stability composed of an alloy steel containing chromium 3% to 60%, carbon over .05% silicon .5% to 30% and more than twice the carbon, and the principal portion of the remainder iron.

In testimony that I claim the foregoing I hereto set my hand, this 22nd day of May, 1919.

PERCY A. E. ARMSTRONG.

Correction in Letters Patent No. 1,322,511.

It is hereby certified that in Letters Patent No. 1,322,511, granted November 25, 1919, upon the application of Percy A. E. Armstrong, of Loudonville, New York, for an improvement in "Stable-Surface Alloy Steel," an error appears in the printed specification requiring correction as follows: Page 4, line 14, for "for instance. 3%" read *for instance .3%*, the space occurring between the word "instance" and the period; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of January, A. D., 1920.

[SE

M. H. COULSTON,

Acting Commissioner of Patents.

Cl. 75—1.

DISCLAIMER.

1,322,511.—*Percy A. E. Armstrong*, Loudonville, N. Y. STABLE-SURFACE ALLOY STEEL. Patent dated November 25, 1919. Disclaimer filed January 3, 1928, by the patentee and the assignee, *Ludlum Steel Company*.

Hereby enter this disclaimer to such parts of the thing patented as they do not choose to claim or to hold by virtue of the patent and assignment, to wit, such parts of the specification and of each claim of the patent except claim 4 as include materials or articles containing over 20% of chromium or over 8% of silicon.

[*Official Gazette January 17, 1928.*]