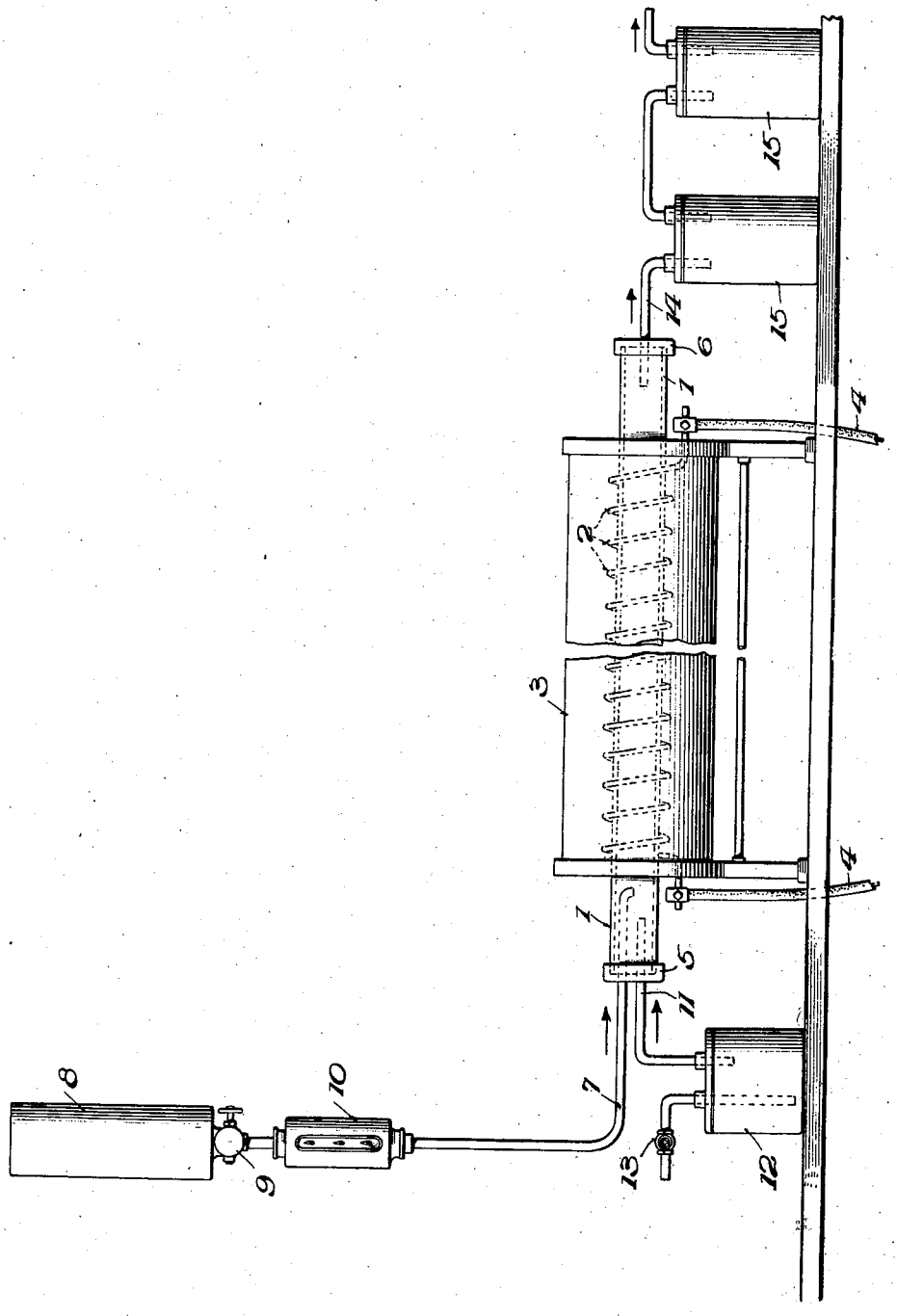
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CEMENTATION PROCESS OF TREATING METAL

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CEMENTATION PROCESS OF TREATING METAL

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This invention relates to cementation processes of treating metal; and it relates more particularly to novel processes of modifying the surface of metal articles, by causing a suitable modifying agent to diffuse or penetrate thereinto, in such manner as to form a protective case or layer having desired properties such, for example, as resistance to chemical corrosion or mechanical wear, wherein the diffusion or penetration of the modifying agent into such surface is aided and expedited by the action of an applied magnetic field.

For many industrial purposes it is desirable, as is well known, to provide shaped metal articles with certain exposed or working surface portions distinctly differing from underlying portions in respect to composition and properties. This is notably so in the chemical industries where apparatus and equipment parts often are not only subjected to heavy mechanical stress but must also be highly resistant to acids or other corroding agents. Again, tubes in oil-cracking plants, for example, commonly have to conduct oil in liquid or vapor form under high pressure while subjected externally to contact in a furnace chamber with intensely hot flame and combustion gases which, because of their oxidizing or other characteristics, exercise a relatively rapid corroding and weakening action on the metal of the tubes. To provide at reasonable cost tubes capable of satisfactorily withstanding such action and at the same time possessing the requisite great strength and toughness is merely one typical form in which the general problem indicated presents itself.

It is very commonly impossible or impracticable to solve the problem by fabricating the article or part as a whole, that is, with uniform or homogeneous composition throughout, from a metal or alloy having the desired high degree of resistance to corrosion or wear. Such a metal or alloy may be and in notable instances (e. g. a high silicon-iron alloy) is inherently brittle and relatively weak or lacking in toughness; so that an article made wholly of it, although sufficiently resistant to acids and other corroding agents, has a comparatively limited field of utility at best because of its inability to withstand substantial mechanical shock or stress. Difficulty or practical impossibility of machining the material, prohibitively high cost thereof, as well as other considerations, are sometimes additional reasons why its use as the sole material in making the article is impractical.

Attempts to solve the problem thus presented have therefore usually had in view, as an ideal objective, the production of an article having a hard resistant surface and a strong tough core, by fabricating the required article or part in desired final form from a metal having the desired mechanical properties, this metal ordinarily being ferrous almost wholly or in large part; and then modifying the surface of the article or some selected portion thereof by causing a modifying agent to penetrate or diffuse into the metal to a sufficient depth to produce the desired protective skin, layer or case of an alloy resistant to corrosion or wear, or both. In other words, it was sought thereby to produce, in a typical instance, an article consisting primarily of a tough and ductile base, e. g. a casting, forging or wrought shape, to which base was to be securely bonded a relatively thin, brittle case of lower strength but having the desired resistant properties.

The methods most commonly proposed for producing such articles have been of the type coming under the general head of cementation in the limited sense of "case hardening" more especially. This involves bringing the modifying agent or material, e. g. a metal or a metalloid, into intimate contact with the surface of the casting, forging or the like which is to be provided with the protective case or coating, at temperatures and under other operating conditions such that the modifying material will diffuse or penetrate into the metal of the base and become intimately associated therewith and united thereto as by alloying, to a depth sufficient to give the required protective effect. This type of method is subject to limitations which have heretofore very narrowly restricted its practical use; with the result that, outside of the case hardening of iron and steel by carbon cementation, the provision of zinc coatings by sherardizing or by the Cowper-Cowles process, and to a much less extent the surface impregnation of ferrous articles with chromium and aluminum by the so-called chromizing and calorizing methods, respectively, the cementation type of treatment has found little practical application industrially as a means of attaining the objective under discussion.

Of the aforesaid limitations, that imposed by the necessity for conducting the operation within a somewhat restricted temperature range is of primary importance. The temperature must be high enough to enable the modifying material to penetrate or diffuse into the base metal to the required depth and to become intimately associated or alloyed therewith, at a sufficiently rapid rate to render the method commercially feas-

ible; yet the temperature must not be so high as to soften the metal of the base and cause deformation of the casing, forging or other shaped article. Nor, especially in the case of an article that has been machined to size, should a protective layer be built up substantially beyond the original finished surface, thus altering the desired dimensions; and this consideration further restricts the permissible operating temperature range. But it so happens that, under the conditions of operation heretofore proposed, the temperature range permissible for cementing a ferrous or other metal base with some of the most important modifying agents is not such as to bring about rapid and effective penetration or diffusion of the modifying agent into, and its union or alloying with, the base metal. That is, the degree of reactivity between the modifying agent and the metal of the base is insufficiently high, normally, within such permissible temperature range. To this is mainly due the failure of prior proposals to cement iron or steel with a modifying agent or material, such as silicon, for example, in order to provide it with a corrosion and wear resistant surface.

It has now been found that if the cementing operation is carried on in a magnetic field of substantial strength or density, cementation of a metal base, e. g. a ferrous metal base, with modifying agents of the character here in question is in general favored and expedited; and that certain cementations formerly regarded as impossible or quite impractical commercially, notably that of iron or steel with silicon, are rendered practical and industrially useful. It is upon this discovery that the present invention is essentially based. While the invention rests upon observed and demonstrated facts, independently of any theory or explanation, it is believed that the surprisingly favorable effect of an applied magnetic field upon the progress of cementation may be due to its serving, during the period of application, to so control or modify in some manner the properties of the metal base and also, perhaps, those of the modifying agent, as to increase the reactivity between them considerably beyond what is normal for temperatures within said permissible range.

In order that the underlying principles of the invention may be made further evident, but without limitation or restriction of its scope, the application of the new process to the cementation of iron and steel with silicon, specifically, will now be described by way of illustrative example.

The possibility of producing high-silicon iron cases or sheaths high in silicon on low-silicon iron or steel has been of considerable interest to engineers and metallurgists for many years. As is well known, a silicon-iron alloy containing upwards of 12 per cent silicon is highly resistant to acids and other corrosive agents and has been extensively employed heretofore in many connections. But such alloys are not sufficiently strong and tough to make it practical to fabricate from them parts that must withstand mechanical stresses of great magnitude in addition to being corrosion-resisting. Consequently the field of practical utility for corrosion-resistant silicon-iron alloys has heretofore been rather narrowly circumscribed. It has long been recognized that this field of utility could be enormously extended to meet many industrial needs heretofore unfulfilled, if it were possible to construct apparatus, apparatus parts and equipment in which a protective case or layer of the relatively brittle high-silicon iron alloy is securely bonded to a tough and ductile core or body portion, in the general form of a casting, forging, or other fabricated shape. Thus it would be possible to combine in an integral metal unit a high degree of mechanical strength and toughness with a high degree of surface resistance both to corrosion and to wear and abrasion. Many unsuccessful attempts have been made heretofore to accomplish this highly desirable result.

The literature of the art shows that more than forty years ago Moissan attempted to cement soft iron cylinders with silicon by heating the former in contact with the latter at sub-melting temperature. He obtained a surface coating containing as much as 2 per cent silicon; but such a low-silicon alloy is of little value for either corrosion or wear resistance. Later attempts to duplicate even Moissan's results were unsuccessful, and some investigators concluded that silicon would not diffuse into iron under conditions characterizing cementation procedures. It was subsequently reported by other investigators, however, that while no appreciable results could be obtained at temperatures below 1100° C. (2010° F.), some diffusion of silicon into iron occurred at higher temperatures up to 1350° C. (2460° F.), the depth of penetration being to some extent proportional to the time the material was held at these higher temperatures. Still other experimenters found that by heating at such higher temperatures and for long periods of time of the order of from 50 to 100 hours, some penetration was obtainable, but to a depth rarely exceeding 0.020 inch, the resultant coating being, moreover, pitted and non-uniform, as well as too low in percentage of silicon to be useful. Furthermore, the coating was in many cases built-up on the surface, that is, outwardly or beyond the original surface, thus undesirably changing the dimensions of the finished article. But at the extremely high temperatures which it was found necessary to use in obtaining even these unsatisfactory and impractical results, the tendency to produce distortion and even fusion of articles undergoing cementation, especially when they are at all intricate in shape, is so great as to bar the method from practical use for that reason alone if for no other.

Most of the investigators thus far mentioned employed powdered silicon or ferro-silicon, with or without other materials such as silica, as a packing in which the article was embedded while undergoing the prolonged heating operation. A still later investigator employed silicon tetrachloride gas as the silicon-carrying agent, instead of packing the article with solid materials supplying available silicon. This led to no results of practical value, however; and during the past decade no further progress toward a satisfactory solution of the problem appears to have been reported.

As a result of the present invention, however, it now becomes possible to cause relatively very rapid diffusion or penetration of silicon into pure iron, steel, cast iron or other ferrous products, with production of a highly satisfactory protective case or layer of silicon-iron alloy, of any desired thickness and of high silicon content (e. g. as high as 20 per cent or more), and to accomplish this while employing cementation temperatures sufficiently low to avoid all danger of distorting or fusing the articles undergoing treatment, however intricate their shape or pattern. An essential feature of the new method is to

maintain the work (i. e. articles being treated) in a magnetic field of substantial strength during the heating operation; and the maintenance of such field by means of alternating electric current is especially recommended as most desirable and effective. Much latitude is permissible as to the particular way of supplying available silicon to the surface of the articles undergoing treatment. The article may sometimes be packed in silicon-carrying mixtures of any of the various types heretofore proposed; or, with decidedly greater advantage, silicon may be supplied in the form of a volatile or gaseous compound thereof, such as silicon tetrachloride, employed as such or produced by reaction in situ; or a combination of the packing and gassing methods may be resorted to. The important point is that subjecting the articles or work to the action of a strong magnetic field, more especially an alternating current field, during the cementing operation is so remarkably effective in expediting diffusion or penetration of silicon into the ferrous articles, that a layer of highly resistant silicon-iron alloy of the desired thickness, firmly bonded to the underlying tough and strong ferrous body or core, may be produced in a comparatively brief period of time, notwithstanding the employment of temperatures far below the minimum previously supposed to be essential to secure any appreciable penetration or diffusion of silicon into iron. It has been found, moreover, that by far the most effective and satisfactory results are obtained when the magnetic field is produced by means of an alternating current of relatively low frequency, the frequencies ordinarily available commercially, such as 60-cycle, being particularly well adapted for the purposes of the invention. Current of very much higher frequencies, on the order of 20,000 to 30,000 cycles, has been found far less desirable to employ, and in some cases to lead to negative or useless results.

In the best mode of practicing the invention, another important point is the maintenance of non-oxidizing conditions in the reaction chamber or zone where the cementing reaction or operation is going on; and most desirably the atmosphere in said zone should be kept more or less strongly reducing in character. This may be most conveniently accomplished by introducing a suitable reducing gas, such as hydrogen, into the reaction zone or chamber while the cementation is progressing. Not only is the character of the protective case or layer formed on the articles being treated more uniform and otherwise satisfactory in character, but greater smoothness of operation is attained and there is less liability to obstruction or stoppage of gas and vapor flow through the reaction zone by deposits of reaction products. Thus, in cementing iron or steel with silicon in accordance with the novel process, employing silicon tetrachloride as the source of availabel silicon, the iron displaced in the course of the cementing action is oxidized to ferric oxide, unless precaution is taken to prevent this, forming deposits in the treating apparatus which sometimes causes trouble through clogging the passage or passages for gas and vapor outflow from the reaction chamber. By introducing hydrogen gas along with the silicon tetrachloride, iron chloride is obtained as a by-product which is readily carried out of the system by outflowing gas and causes no trouble. At the same time, the resulting protective case or layer of silicon-iron alloy produced on the work being silicided or siliconized is more uniform and otherwise satisfactory than where introduction of hydrogen is omitted.

Applicants have found that by a special control of the atmosphere in contact with the ferrous article to be siliconized, remarkably efficient results are obtained. Of course, in all work the furnace is supposed to be sealed air-tight, and steps are taken to remove all moisture from any gas, such as hydrogen, supplied to the furnace; but actual practice has shown that, notwithstanding all efforts, the exclusion of absolutely all moisture is often an unattainable ideal. But it has been discovered that where the amount of moisture is kept very small, that is, to a practical minimum, and where hydrogen as dry as practical is supplied, so as to maintain as nearly as possible a hydrogen silicon atmosphere around the article to be siliconized, an equilibrium can be obtained and maintained between the iron of the ferrous article, the water vapor, and the hydrogen. In other words, water vapor is oxidizing, hydrogen is reducing and these two along with the iron to be silicided may be held in equilibrium for any given temperature, so that, notwithstanding the presence of a small amount of water vapor, there is no oxidation of the iron and a strongly adherent and satisfactory coating of silicon uncontaminated by iron oxide is obtained. In fact it has been discovered that where there is such an equilibrium in the atmosphere good coatings are sometimes obtainable even when the magnetic field is reduced.

Experience with the new process as applied to the cementation of a ferrous metal base with silicon shows a tendency toward formation, in the resultant silicided case or layer, of the intermetallic compound, Fe_3Si (14.3% Si). That such a compound is produced is further indicated by the fact, shown by analysis of many specimens, that the average composition appears automatically to adjust itself more or less approximately to this formula or proportioning regardless of the thickness of the cemented or silicided layer. This is not to be understood as meaning that silicon-iron combinations containing more than 14.3 per cent silicon are not obtainable in the practice of the present process. On the contrary, as stated above, products of this type can be made by the process containing as much as 20 per cent or more silicon. Assuming the essential conditions of operation, such as temperature, area of article exposed, amount of volatilized silicon tetrachloride in contact with the article, strength and distribution of the magnetic field, and time of treatment, to remain the same, the thickness of the silicided layer obtained on different ferrous metal articles to be treated or processed seems generally to be inversely proportional to the mass of the different articles.

Practice of the new process is not confined to employment of any specific type of apparatus in order to achieve successful results, except that there must be adequate provision for maintaining the work in a suitable magnetic field of sufficient strength to substantially accelerate the otherwise very slow rate at which diffusion or penetration of the alloying or modifying agent into the metal to be cemented therewith would normally occur at the temperatures employed. The accompanying drawing illustrates more or less diagrammatically one type of apparatus practical to employ in practicing the invention, but this is to be understood as merely by way of

example and in no sense restrictive. The drawing shows an electric furnace of the muffle type, having a tube 1 of suitable refractory material, such as alundum, supporting the resistance heating coil 2 of heavy nichrome wire, for example, the whole surrounded by heavy heat insulation, such as asbestos packing, enclosed in the cylindrical casing or jacket 3. The coiled heating resistance is designed for operation at relatively low voltage and high amperage in maintaining the required elevated working temperature in the reaction or treating chamber or zone provided within the refractory tube 1; and because of such design, said coil or soleniod also functions to provide a magnetic field of the requisite strength or intensity for carrying out the process of the invention. The ends of the coil are connected by leads 4 to suitable mains supplying current at the proper voltage.

The projecting ends of the tube 1 are provided with suitable closures 5 and 6. Closure 5 is apertured to accommodate tube 7 through which liquid silicon tetrachloride, for example, may be supplied from a container 8 at a rate adjustable and controllable by means of a valve 9, a sight feed device 10 being desirably provided to enable direct observation of the rate of supply, by drops per minute or otherwise.

Through tube 11, a reducing gas, such as hydrogen, may also be introduced into the processing zone along with the silicon tetrachloride. In order to avoid introducing moisture along with the hydrogen, the hydrogen must first be thoroughly dried by bubbling through concentrated sulphuric acid, contained in a drying device 12 of conventional type. The rate of hydrogen introduction can be controlled by adjustment of valve 13. Through outlet tube 14 extending through closure 6, gaseous and vaporous materials may leave the reaction chamber or zone, one or more traps 15 being desirably provided wherein excess silicon tetrachloride vapors may be condensed and collected, as well as other products such as iron chloride, for example. To this end the traps may advantageously be cooled.

In a typical instance the solenoid 2 may be approximately 12 inches along by 1⅜ inches in diameter and consist of 26 turns, taking 30 amperes at full load from supply mains furnishing 60-cycle alternating current at 16 to 17 volts. The magnetizing force, H, of such a solenoid, calculated from the data given above, will be about 65 gausses. Where an article such as an iron or steel pipe, rod, or the like is to be cemented with silicon, the article is placed inside the tube 1 so as to form the core of the solenoid and thus be subjected most effectively to the influence of the magnetic field produced when the solenoid is energized. The reaction zone having been heated up to the desired working temperature, most desirably between 1800° and 1900° F. or slightly higher, approximately 1900° F. being usually about an optimum, introduction of silicon tetrachloride and hydrogen is begun and continued throughout the cementing operation, the temperature being maintained substantially constant meanwhile. Upon being fed into the reaction chamber or zone, the liquid silicon tetrachloride immediately volatilizes, the resultant gas or vapor in mixture with the hydrogen bathing all exposed surfaces of the pipe or rod to be siliconized. The silicon tetrachloride should be fed in at a sufficiently rapid rate to ensure at all times a liberal supply of the vapors within the reaction zone, with some excess passing out to be caught in the traps or receivers 15. Almost immediately, chloride of iron begins to appear in the first receiver, indicating that substitution of iron by silicon is taking place; and iron products continue thus to be carried out of the reaction zone during the operation.

The work (e. g. pipe or rod) may desirably be supported approximately in the axis of the tube 1 by pieces of refractory material spacing it away from the bottom of the chamber. This not only affords opportunity for more uniform contacting of the silicon tetrachloride with all portions of the exposed surface of the work but also centers the work in the applied magnetic field. In typical instances, when treating iron or steel rod or pipe in the manner described, a penetration of silicon to a depth of about one thirty-second to three thirty-seconds of an inch may be obtained in from four to six hours, or even considerably more rapidly, depending upon the specific temperature and other operating conditions employed. The protective case or layer of silicon-iron alloy, commonly analyzing somewhere in the neighborhood of 14 per cent silicon, is usually remarkably uniform in character and is so firmly bonded or united to the residual underlying tough and strong ferrous metal base that it withstands severe hammering or similar drastic treatment without separating therefrom. Where pipe is treated, such protective layers or cases can be produced on both the inside and outside of the pipe, if desired. It is feasible to produce considerably thicker silicon-iron cases than those mentioned above by way of example, but ordinarily it is not necessary to do this in most commercial work in order to get a satisfactorily high degree of resistance to corrosion and wear.

As affording additional instances of resistance heating coils or solenoids operating at relatively low voltage and high amperage and producing magnetic fields of an intensity suitable to employ in practicing the present process, reference may be made here to further typical examples. Thus, excellent results are obtainable with a furnace having a heating solenoid 18 inches long by 4 inches in diameter, consisting of 28 turns of heavy nichrome wire, this coil being designed to take 83 amperes at full load when energized from current mains supplying 60-cycle alternating current at 16 to 17 volts. The magnetizing force, H, of this solenoid will be about 129 gausses. In another instance, using the same current supply, the solenoid may be 36 inches long by 2¼ inches in diameter and consist of 28 turns, taking 100 amperes at full load. The magnetizing force, H of this solenoid will be about 77 to 78 gausses. It is to be understood that these are merely typical examples illustrating how electromagnetic fields of strength suitable for the practice of the new process may be obtained and applied. The invention is of course not restricted to these typical examples either in respect to strength of field or particular manner of obtaining it. By way of contrast, however, it may be pointed out that relatively weak fields are substantially without useful effect and are therefore to be understood as not included within the scope of the invention. For example, if it be attempted to cement iron or steel with silicon, using an electric furnace heated by a resistance solenoid 12 inches long and 1⅜ inches in diameter, designed to operate at 110 volts and taking 5 amperes at full load, the coil having 33 turns.

unless the special control of atmosphere maintenance of equilibrium conditions hereinabove referred to are rigidly observed, no useful result is obtained, only a very slight penetration by silicon into the iron or steel article being obtained even after many hours in the furnace. In this unsuccessful solenoid the magnetizing force, H, calculated from the data given, falls between 13 and 14 and, as shown by the unsuccessful results, such a low magnetizing force is without useful effect. In practicing the invention, it is ordinarily desirable to employ a magnetic field whose magnetizing force H is not less than 65.

It is of course not essential in the practice of the invention that both the function of heating the reaction chamber and the function of providing a magnetic field of proper intensity shall be performed by one and the same means. Thus, the heating may be accomplished in any other appropriate and practical manner whether electrically or otherwise; while the proper magnetic field can be provided and maintained by entirely distinct electric means of suitable character. In still another specific embodiment of the invention, the article, such as a rod or bar, which is to be cemented with a modifying agent may be heated to the necessary temperature by passage of a heavy alternating current directly therethrough during the cementation treatment, a magnetic field of requisite strength being at the same time thus provided to facilitate the cementation.

In practice, 1500° to 1600° F. may be regarded as virtually the lower limit of the temperature range within which useful results are obtainable in cementing iron or steel with silicon in accordance with the invention; and as a general rule the best results are obtainable at temperatures ranging from about 1800° F. upwards to 1900° or 1950° F. Ordinarily, a maximum of 2000° F. should never be exceeded, and it is usually better to keep somewhat below that maximum. It is to be noted that this maximum is below the lowest temperature previously thought necessary to employ in order to obtain any appreciable penetration of silicon into iron or steel.

This application is a continuation in part of our application filed March 17, 1936, Serial No. 69,383, for Cementation processes of treating metals.

What is claimed is:

1. The process of cementing a ferrous metal article with silicon which comprises subjecting such an article to the action of a suitable cementing agent comprising available silicon, at a temperature above 1500° F. and below 2000° F., while maintaining the article in a magnetic field whose magnetizing force, H, is not less than 65.

2. The process of cementing a ferrous metal article with silicon which comprises subjecting such an article to the action of a suitable cementing agent comprising available silicon, at a temperature above 1500° F. and below 2000° F., while maintaining the article in an alternating current magnetic field whose magnetizing force, H, is not less than 65.

3. The process of cementing a ferrous metal article with silicon which comprises subjecting such an article to the action of a suitable cementing agent comprising available silicon, at a temperature above 1500° F. and below 2000° F., while maintaining the article in a low frequency alternating current magnetic field whose magnetizing force, H, is not less than 65, the frequency of said alternating current being materially below radio frequencies.

4. The process of cementing a ferrous metal article with silicon which comprises subjecting such an article to the action of a suitable cementing agent comprising available silicon, at a temperature within the approximate range of 1800° F. to 1900° F., while maintaining the article in a low frequency alternating current magnetic field whose magnetizing force, H, is not less than 65, the frequency of said alternating current being materially below radio frequencies.

5. The process of cementing a ferrous metal article with silicon which comprises subjecting such an article to the action of a suitable cementing agent comprising available silicon, at an elevated temperature but below that at which substantial deformation of the article would occur, while maintaining the article in a magnetic field whose magnetizing force, H, is not less than 65, and also maintaining non-oxidizing conditions in the treating zone.

6. The process of cementing a ferrous metal article with silicon which comprises subjecting such an article to the action of a suitable cementing agent comprising available silicon, at an elevated temperature but below that at which substantial deformation of the article would occur, while maintaining the article in a magnetic field of sufficient strength to expedite the cementing action substantially, and also introducing hydrogen into the treating zone.

7. The process as defined in claim 2, further characterized by the fact that a volatile compound of silicon is employed as the source of available silicon.

8. The process as defined in claim 3, further characterized by the fact that a volatile compound of silicon is employed as the source of available silicon.

9. The process as defined in claim 4, further characterized by the fact that a volatile compound of silicon is employed as the source of available silicon.

10. The process as defined in claim 5, further characterized by the fact that a volatile compound of silicon is employed as the source of available silicon.

11. The process as defined in claim 6, further characterized by the fact that a volatile compound of silicon is employed as the source of available silicon.

12. In a process of cementing a ferrous metal article with silicon, comprising heating said article in a container to a temperature above 1500° F. and below 2000° F., the steps which include flowing gaseous silicon tetrachloride and hydrogen gas into contact with the heated ferrous metal article in said container, while maintaining in said container a minimum of water vapor, and allowing the resultant gaseous products to flow out from said container, the supply of hydrogen being such as to maintain the water vapor, hydrogen and iron to be silicided in equilibrium in the container at the temperature of operation, whereby decomposition of the water vapor and oxidation of the iron are prevented, and simultaneously subjecting the iron to be silicided to the action of a magnetic field whose magnetizing force, H, is not less than 65.

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