

UNITED STATES PATENT OFFICE

2,458,655

PROCESS OF CASE-HARDENING METALS

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No Drawing. Application February 4, 1944,
Serial No. 521,123

5 Claims. (Cl. 148—14)

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This invention relates in general to the case hardening of metals and in particular to the case hardening and impregnation of metals with silicon.

As heretofore practiced the case hardening of steel and other iron alloys has comprised heating the metal to a temperature just above its critical temperature, about 900° C., in contact with carbon until carburizing or cementation had extended to the desired depth from the surface and then quenching the treated metal with or without an intermediate cooling and reheating step. The effects or results desired in ideal case hardening are (a) to harden surface without adversely embrittling the metal (b) to toughen so that the metal becomes more or less malleable, (c) to increase the resistance of the surface to attrition and abrasion. However, the carburizing step in conventional methods of case hardening is slow and disadvantages arise when an attempt is made to extend the cementation to a greater depth by lengthening the period of heating. Also, such prior methods do not provide any method of increasing the amount of silicon in the surface layers of the metal although it has long been recognized that this would improve certain properties of the metal.

Steel containing substantial amounts of e. g. above 7% of silicon is highly resistant to corrosion especially by acids. However, cast silicon steels containing 7% silicon throughout the piece are so brittle that wrought articles can not be made from them and the cast articles break easily. Moreover such silicon steels cannot be machined readily so that their use is greatly restricted.

Again, it would be desirable for some purposes to use high-silicon ferrous base alloys for welding, or for metallizing by metal spraying processes. This has not been feasible heretofore, however, because commonly the metal used has been in the form of rod or wire, and high-silicon irons and steels could not be obtained in those forms.

Prior attempts to siliconize metals have not been able to overcome the difficulties mentioned nor to increase the silicon content in the surface layers to the desired amount. Attempts to use inorganic silicon compounds, such as silicates, silicon carbide or silicon dioxide have failed to obtain the uniformity or depth of impregnation required

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by the trade because all of these inorganic substances are solid and do not decompose readily or at all at the critical temperature of the metal.

Therefore, it is a general object of the present invention to provide a method for case hardening metals in a rapid and economical manner.

A major object of this invention is to provide a method of siliconizing metallic, especially ferrous, articles which is rapid, relatively cheap, controllable to vary not only the depth of silicon penetration but also the concentration of silicon in the case, provided coherent and adherent siliconized cases possessing the desirable corrosion resistant properties of the high-silicon steels referred to hereinabove, by which the article may be impregnated throughout its structure, if desired, which is applicable to articles fabricated to completed form and size prior to cementation, whether cast or wrought, which is readily practiced in simple apparatus, and which does not cause any objectionable change in size of the article.

Another general object is to provide a rapid and simple method of increasing the amount both of silicon and carbon in the surface.

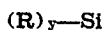
It is another object to provide means for increasing the speed of migration of carbon during carburization. A further object is to provide an iron alloy having a case hardened surface in which the percentage of both silicon and carbon in the surface layers is greater than in the interior of the metal.

Other objects of the invention will be obvious or will appear hereinafter.

According to the present invention the case hardening of metals is accomplished in a simple and rapid manner by subjecting the metal heated to a carburizing temperature to the action of the thermal decomposition products of an organo-silicon compound by which the ratio of carbon to silicon in the carburizing atmosphere as well as in the metal surface layers may be varied over a wide range and the migration of carbon into the metal greatly increased in both speed and depth. In general, the process of case hardening according to the present invention comprises heating the metal to an elevated temperature in which carbon and silicon impregnation will occur and contacting the heated metal with the thermo-decomposition products

of an organic silicon compound which contains at least one carbon directly united to silicon. Both free carbon and free silicon are absorbed in and react with the metal to bring about a carburizing and silicizing of the surface layers.

The organo-silicon compounds used may be any compound containing both silicon and an organic radical and in which at least one of the carbon atoms is united direct to the silicon, that is, a compound having the general formula



in which R is an organic radical, either aliphatic, aromatic, alicyclic or heterocyclic and "y" is an integer from 1 to 4. The radical R may occupy one or more of the silicon valences, or each valence may be occupied by the same or a different organic radical, but at least one R radical is linked direct to silicon. When the organic radicals do not occupy all the valences of silicon the remaining valences may be occupied by inorganic atoms or radicals such for example as oxygen, hydrogen, hydroxyl, carboxyl, chlorine and the like.

By way of illustrating but not by way of limiting the invention, there will be given several examples of different classes of organo-silicon compounds which are suitable for use in the invention:

- (1) Organo-silicon oxides: $(R)_ySiO$
- (2) Silicylethers: $R_ySi-O-R$
- (3) Di-silicylethers: $R_ySi-O-SiR_z$
- (4) Silicols: R_ySi-OH
- (5) Organo silicon hydrides: R_ySi-H_z
- (6) Organo silicon chlorides: R_ySi-Cl_z
- (7) Polymeric silicenes: R_ySi-R_z
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- (8) Chlorine-substituted silicenes: ClR_ySiX_z

The numerous examples above given are to indicate not only what organo-silicon compounds may be employed, but also that by suitably selecting the compound the ratio of carbon to silicon can be varied from 1 to 1 to other ratios or integers over a wide range.

Various methods may be employed for bringing the organo-silicon compound into the reaction zone used in the case hardening. For example, if the silicon compound is a solid it may be comminuted and dusted on the metal surface; or if the compound is liquid it may be applied to the metal by dipping, coating or spraying, or atomized and injected into the reaction zone. Upon heating the metal to the carburizing temperature the liquid or solid compounds will be decomposed. If the silicon compound is a gas or is readily vaporized the vapor or gas is passed into contact with the hot metal whereupon the gas decomposes. Finally, the organo-silicon compound may be thermally decomposed and the hot decomposition products in the form of a gaseous dispersion passed into contact with the heated metal surface.

It has been found that as a class organo-silicon compounds having at least one carbon linked direct to silicon are decomposed when subjected to temperatures normally employed in case hardening of steel and iron alloys, usually a temperature of 900° C. or above. Under such conditions the thermal decomposition products comprise free carbon, free silicon and some hydrocarbon gases, such as methane and the like and intermediate decomposition products. Thus the carbon and silicon are formed in situ in contact

with the hot metal surface so that absorption and combination of such elements with the metal takes place rapidly. It has now been found that the silicon greatly increases both the rate and depth of penetration of the carbon.

In general it has been found preferable to carry out the case hardening in the presence of reducing gases such for example as, hydrogen, ammonia, carbon monoxide, ethylene and the like since they assist in the decomposition of the organic radical of the silicon compound to elemental carbon. However, other chemically inert gases such as nitrogen, helium, carbon dioxide and the like may be employed in the case hardening atmosphere to increase gas pressure and promote decomposition. When the organo-silicon compound is a liquid any of the above mentioned gases may be used to assist in atomizing or vaporizing the liquid and carrying it to the reaction zone.

The temperature employed in case hardening metals and alloys according to the present invention will depend largely on the particular metal or alloy, and in general the carburizing temperature employed should be just slightly above the critical temperature of the metal or alloy being treated. For most ferrous alloys this temperature lies between about 880° C. and 1000° C. In general the lowest possible temperature should be employed to avoid embrittlement by the production of too much "cementite" (iron carbide).

The time required for case hardening at the temperatures indicated above will depend upon the depth of cementation desired. In general, a time of treatment from 2 to 10 hours will result in case hardening to a depth of from 10 to 30 mm. in steel at 900° C.

The time will be shortened if the case hardening is carried out while the thermal decomposition products of the organic silicon compound are maintained under an elevated pressure. The depth of hardening also increases with increase in the pressure of the contacting gases.

The results of the present process include (a) carburizing of the surface layers to a greater depth and more rapidly than when the cementation is carried out in the absence of silicon as herein applied, (b) penetration of free silicon into the surface layers and with the formation of ferro-silicon (c) when the silicon content of the applied gases is high, some free silicon may be deposited on the surface of the metal so that a more or less ceramic coating is formed thereon, and (d) the formation on the surface and within the surface layers of some silicon carbide. By merely selecting a particular organo-silicon compound having the desired ratio of carbon to silicon one may readily increase or decrease one or more of the results above outlined.

It is possible, under the present process, to raise the silicon content of the surface layers to 7% or above by weight of the metal, and to raise the carbon content up to about 3%. However, when the carbon content exceeds about 2.2% by weight the surface layers may be unduly embrittled so that for most metal articles a carburizing to a carbon content of less than 2% is indicated. The silicon content of the surface layers should not be substantially below 1.5% by weight. If the surface is to be machined the silicon content of the surface layers should be preferably between 1.5% and 2% by weight. It is observed, therefore, that the silicon plays an important role in the present process, for not

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only does it act as a carburizing catalyst (increasing both the rate and depth of cementation) but the silicon also reacts with the carbon and the iron to impart other important characteristics to the metal and extend its uses.

After the carburizing and siliconizing treatments have been completed the metal article, with or without preliminary cooling and reheating, is preferably suddenly cooled as by quenching in cold water or oil to produce the desired hard structure in the metal. By way of illustrating but not by way of limiting the invention there will be given the following specific examples:

I. A low carbon soft steel containing from 0.1 to 0.2% carbon is heated in an electric furnace to 900° C. and a stream of gas comprising nitrogen and tetra ethyl or tetra methyl silicane is passed into contact with the hot metal. The silicane decomposes to give a mixture of free carbon, free silicon and some low molecular weight hydrocarbon. After 6 hours the metal is slowly cooled in air, reheated to just above its critical temperature and then quenched suddenly in cold water. Products were obtainable with the carbon content of the surface layers to about .9% and to a silicon content in the surface layers of 2.5% by weight.

II. A nickel alloy steel containing 0.15% carbon and 1% nickel coated with a thin layer of triethylsilical and heated in a closed electric furnace to a temperature of 890° C. for mm. 8 hours. The article is allowed to cool in air, reheated to 760° C. and then suddenly quenched in cold water. An analysis of the surface layers showed a substantial increase in the carbon content to a depth of 15 mm. and a silicon content of over 3%.

It is to be understood that the process of the present invention is applicable to iron, and its alloys such for example as alloys of iron with carbon, silicon, manganese, nickel, molybdenum, chromium and the like; also to non-ferrous metals and non-ferrous alloys such for example as Monel metal, nickel alloys, Phosphor bronze, "Stettite," manganese, magnesium and aluminum and their alloys.

Both of the articles produced according to the examples given above were characterized by relatively soft tough cores and hard surface layers, the article showing a substantial increase in tensile strength and a high resistance to attrition and surface abrasion. Further the samples exhibited in increased resistance to sealing when heated for long periods at elevated temperatures, and an increased electrical resistance without embrittlement. Moreover, when the silicon content is increased to 7% or above in the surface layers, the article shows a marked resistance to corrosion particularly by acids.

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In view of the above mentioned new properties and characteristics which are imparted thereto, the articles produced find a wide variety of uses, such for example as corrosion-resistant containers and pipes for acids, electrical wiring for heating elements, welding rods, rods used for metal spraying; needles, punches, drills and other pointed tools, cutting tools of all kinds, articles where high abrasion resistance and strength are required such as tractor treads, shovel lips, wheel rims, bearings and the like; files and rasps; shell and torpedo nose casings, armor plate, trench helmets and other articles requiring toughness with hard surface.

I claim:

1. A process of case-hardening an article formed from a metal capable of cementation by carbon and silicon, comprising heating the metal to an elevated temperature at which carbon and silicon impregnation will occur and contacting the heated metal with the thermodecomposition products of an organo-silicon compound containing at least one organic radical selected from the group consisting of aliphatic, aromatic, alicyclic and heterocyclic radicals, at least one carbon atom of the radical being united directly to silicon.

2. A process of case-hardening an article formed from a metal capable of cementation by carbon and silicon, comprising heating the metal to an elevated temperature at which carbon and silicon impregnation will occur and passing into contact with the heated metal a stream of gas containing the vapor of an organo-silicon compound so that the compound is decomposed while in contact with the metal, said organo-silicon compound containing at least one organic radical selected from the group consisting of aliphatic, aromatic, alicyclic and heterocyclic radicals, at least one carbon atom of the radical being united directly to silicon.

3. A process according to claim 2 in which the gas stream comprises a reducing gas.

4. A process according to claim 1 in which the metal is a ferrous alloy.

5. A process according to claim 1 in which the metal is a non-ferrous alloy.

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