United States Patent Office

3,144,359

Patented Aug. 11, 1964

3,144,359

METHOD FOR SULPHURIZING THE SURFACE OF FERROUS METAL

Rintaro Takahashi, 48 Oyama-machi Tamagawa, Tokyo, Japan

No Drawing. Filed Oct. 23, 1959, Ser. No. 848,191
Claims priority, application Japan Oct. 27, 1958
7 Claims. (Cl. 148—6.11)

The present invention relates to a method for treating carbon-containing iron, steel or alloy steels to penetrate sulphur into the surface thereof or a method for sulphurizing the surface of the said metal or alloys.

One of the main objects of the present invention is to improve the conventional sulphurizing method and to cause sulphur to penetrate uniformly and deeply below the surface of the iron, steel and alloy steels in a short interval of time and to increase the hardness and impart a high corrosion resistance as well as a high surface hardness to the metal surface, in addition to the original characteristics.

Another object of the invention is to sulphurize the surface of iron, steel, cast iron and alloy steels to impart corrosion resistance to their surfaces and simultaneously remarkably increase the surface hardness thereof.

A still further object of this invention is to provide an improved method for treating the surface of iron, steel and alloy steels to create a corrosion resistant surface on the said metal, whereby said metal surface is made abrasion resistant and a given high hardness is imparted thereto, and to exploit novel applications of the product according to the present invention.

Other objects, advantages and features of this invention will be apparent from the following description.

The present invention is characterized by the fact that iron, steel, cast iron and alloy steels are impregnated on the surface thereof with sulphur to provide a special sulphide for remarkably raising the surface hardness of such metals and simultaneously imparting abrasion resistance thereto.

According to the method of the present invention, the surface of metal to be treated is first rendered or made easily wettable to molten sulphur by desorbing gas from the surface, and then immersed in molten sulphur to cause the sulphur to adhere to the surface of metal to be treated, and then said thus preliminarily treated metal surface is heated at a relatively low temperature, for example, of 120° C. to 150° C. for a short interval of time to form a special sulphide layer, thereby remarkably increasing the hardness of the surface of the metal and simultaneously increasing the fatigue strength, improving the friction resistance and imparting excellent abrasion resistance. The process of the present invention is much less expensive than prior methods. The sulphurizing mechanism in the method according to the present invention is entirely different from the mechanism of the usual surface hardening method and sulphurizing method for iron, steel and alloy steels. Namely, in the process of the present invention, the sulphur combines with cementite and ferrite in the surface of said metal to be treated, to form a layer of special sulphide on the metal surface, which distinctly differs in its aspect from the usual sulphurizing mechanism. Particularly, the actual features in the method, which differ from the usual method, lie in the rise in hardness, and the fact that the sulphurized layer firmly adheres to the metal even though thicker than usual .

It is necessary to the sulphurizing method of the present invention that the surface of carbon-containing iron to be treated be made wettable to molten sulphur by a preliminary treatment, which may for example be carried out in any of the following ways:

(1) A method of surface treatment may be used which comprises impressing an electric potential on a sample in molten sulphur, i.e. the sample is put into molten sulphur, said sample is given a positive polarity ⊕ and a voltage of above 10 v., for instance, 30 v. may be impressed thereon, and then said sample is retained at said voltage for 3 to 4 minutes. Thereafter, the voltage is shut off, and after being made wettable to molten sulphur, the sample is put into the molten sulphur as it is and heated, whereby the surface of the sample is impregnated with molten sulphur.

(2) An electrolytic polishing method may be used, in which the electrolytic polishing is carried out by using a mixture, for instance, of 50 cc. of phosphoric acid and 2 grams of gelatine, added with 2 grams of oxalic acid before use; with a current density being at 30 to 200 a./dm.^{2}, for 10 seconds at ordinary temperature and with a cathode, negative pole ⊖ being Pb or stainless steel 18–8. After metal surface to be treated is made wettable to molten sulphur, the sample thus treated is dried and immersed or dipped in molten sulphur.

(3) A chemical polishing method may be used in which 100 grams of H_2SO_4 (d.=1.8), 250 grams of HNO_3 and 150 grams of $CuSO_4$ are added to 1 liter of water, and a sample is put into the resulting mixture, for instance, for 5 to 10 seconds at room temperature. After being made wettable to molten sulphur, the sample is dried and then dipped or immersed in molten sulphur.

(4) A flux method may be employed wherein a sample is immersed for approximately 2 to 3 minutes in a molten flux composing of 28% by weight of NH_4Cl and 72% by weight of $ZnCl_2$ or a molten flux composing of 10% by weight of borax, 30% by weight of $BaCl_2$ and 60% by weight of $CaCl_2$. The sample thus treated is withdrawn from the molten flux and immediately thereafter thrown in molten sulphur and the flux adhered to it is peeled off in the molten sulphur. After being made wettable to the molten sulphur, the sample is heated and sulphurized.

(5) A method may be used wherein the surface of the sample to be sulphurized is covered with a thin sulphide layer by means of H_2S or S_2Cl_2 and then the sample is put into molten sulphur.

(6) A method for electrolysing a sample in molten sulphur may be used wherein, for instance, a metal sulphide, for instance, a small amount of PbS is added to molten sulphur to impart an electric conductivity to the electrolyte (or to produce a solid solution), whereby the sample is made the positive pole ⊕, and electric current, for instance, of 2 to 3 ma. is passed therethrough for about 3 to 4 minutes for electrolysis, after which the sample is put into the molten sulphur as it is.

(7) A method may also be used wherein an iron or steel sample is buffed on the surface and then treated in a stream of hydrogen gas (at 350° C.) and put into a molten sulphur without contact with air.

In the present application the metal surface is first made wettable to molten sulphur by means of any one of the above-mentioned methods which desorb gas from the surface and then the metal thus treated is subjected to the sulphurizing treatment in the molten sulphur.

The method according to the present invention is entirely different from the usual sulphurizing method which has been carried out heretofore in accordance with the reaction of gas with solid material, and in the present invention the surface of metal is made wettable to molten sulphur by the above-mentioned methods. When the surface of iron, steel or alloy steels is treated beforehand, particularly by the preliminary treating methods

(1) to (4) as described above, the surface of said metal can not only be made wettable to molten sulphur, but also the metal surface thus treated can be made in a state richer in cementite (Fe_3C) per unit area, which effects a catalytic action, i.e., the metal surface can be activated. In consequence, the rate of reaction becomes remarkably high. The sulphurization can thus be uniformly effected in a short interval of time. In the conventional method, the thickness of the sulphurized layer on the iron surface, obtained by means of gases, such as H_2S, SO_2, SO_3 and the like is below 0.1 mm. and is liable to be peeled off. Thus, a nonpeeling and uniform thick layer above 0.1 mm. could not be obtained. According to the present invention, however, a homogeneous anti-corrosive, non-peeling and sound sulphurized layer having a hardness of about RA 80 [Rockwell hardness A (RA)] can be obtained in a thickness of the order of 1.0 mm. in a short interval of time. In addition thereto, according to the present invention, metals can be treated at a temperature lower than that in the usual method. Therefore, there is substantially no fear of causing deformation or changes in the structure of the treated metal, due to the treatment. Thus, according to the present invention, it is possible to treat iron, steel or alloy steel products at a low temperature to highly harden the surface thereof and impart abrasion resistance to the finished surface. It is therefore possible to harden the required product safely without deformation due to strain. Furthermore, since no intricate salt bath is required in the present invention, the treating operation is simple and it is also possible to accomplish the increase of hardness and the corrosion resistance, which can not be expected in the usual method. It has been impossible to make molten sulphur to adhere uniformly to ground surfaces of steel or cast iron at a relatively low temperature, for instance, 130 to 250° C. because of the high surface tension of molten sulphur. The method according to the present invention is a simple sulphurizing method, wherein the reaction between molten sulphur and active surface of metal is effected uniformly in a short interval of time, by increasing the reactional affinity between the metal to be treated and sulphur, as compared with the surface tension of molten sulphur, whereby gases adhering to the surface of metal are removed to make the said surface wettable to molten sulphur and simultaneously the cementite in the surface of iron, steel and alloy steels can be utilized as a catalytic agent.

The following examples illustrate the way in which the method according to the present invention may be carried out in practice.

Example 1

One face of a cast iron piece was polished and immersed in a bath of molten borax to have the molten borax to adhere on the outer surface of the said piece, and said piece was then put into a molten bath which was separately prepared beforehand and was a mixed molten flux (180° C.) composing of 50 mol percent of zinc chloride and 50 mol percent of ammonium chloride, having a molten sulphur layer of about 150° C. formed at the upper portion thereof, at which temperature the viscosity of molten sulphur is the lowest. The borax adhering to the aforesaid piece was removed in the molten flux layer at the lower portion of said molten bath and thereafter the cleaned piece was raised to the upper layer of molten sulphur and held for approximately 30 minutes, and then withdrawn from the bath, after which the sulphur attached to the surface of the said piece was wiped off by a solvent for sulphur and if necessary, a thin layer of sulphur may remain adhering to said piece. Thus, a sulphurized layer of approximately 0.6 mm. was obtained in which sulphur penetrates from the thin sulphurized surface towards the interior portion. The original surface hardness of the said piece was at 165 Vickers hardness, but that of the treated surface was found remarkably increased and was at 680 Vickers hardness. Furthermore, the comparative abrasion resistance test was effected on the treated surface, and the surface treated by the method according to this invention was tested under the following conditions: contact pressure (P), 30 kg./cm.^{2}; abrading speed (V), 1.05 m./sec.; oil, paraffin-base 60 Spin oil; oil temperature, 20° C., time, 7 hours, and then was compared with the untreated surface. It was found that the amount of abrasion on the surface treated according to the present invention was one-eighth (1/8) as great as that of the untreated surface.

Furthermore, the sulphurizing treatment could likewise be done with respect to the carbon steel and stainless steel 18–8.

The surface sulphurized by the method according to the present invention was found to be remarkably water repellent, and accordingly, the present invention is remarkably effective as a method for the treatment of the surface of metal material for agricultural, architectural and civil engineering purposes, because the adhesion of earth, cement, concrete and the like is remarkably small as compared with the untreated surface.

On the other hand, the surface of metals treated by means of H_2S, SO_2, SO_3 and the like to form a thin film of sulphide on the surface can also be, in accordance with the present invention, immersed or dipped in the molten sulphur and heated, whereby a sulphurized layer of a considerable thickness as described before can be obtained in a short interval of time.

In the afore-mentioned example, the flux-method was used in order to make the surface of the cast iron piece wettable to molten sulphur. However, the required sulphurizing treatment can likewise be effected also in the case where any one of the methods (1) to (3) and (5) to (7) is used for the purpose of making the surface wettable to the molten surface instead of the said flux-method.

Example 2

The surface of 0.45% C carbon steel plate (Vickers hardness 95) was finished mechanically, degreased and submitted to chemical polishing, for instance, by immersing the said plate for 5 to 10 sec. at room temperature in a solution of 100 grams of H_2SO_4 ($d.=1.8$), 250 grams of HNO_3 and 150 grams of $CuSO_4$ in 1 liter of water or to electrolytic polishing by immersing the aforesaid plate in 50 cc. of phosphoric acid, admixed with 2 grams of gelatine and allowing to stand for about 1 day, the said mixed solution being added with 2 grams of oxalic acid prior to its use, with current density being 30 to 200 amp/dm.^{2} at room temperature for 5 to 10 sec. and stainless steel 18–8 or Pb used as a cathode, or cleaned in the stream of hydrogen gas for 10 minutes at 350° C. Then, the steel plate preliminarily treated as set forth above was immersed in molten sulphur at 150 to 250° C. and sustained for 1 hour, and a hard sulphurized layer of 0.6 to 0.8 mm. thickness was obtained at Vickers hardness 500 to 550 and a corrosion resistant surface of yellowish black luster was produced.

On the other hand, another similar specimen was mechanically finished and degreased and put into molten sulphur at 150° C. and was used as an anode, and a voltage of 10 to 50 volts was impressed thereon for 3 to 4 minutes (no electric current passed), after which the voltage was cut off and retained in molten sulphur for 1 hour as it was. Alternatively another similar specimen was first degreased, and put into molten sulphur, for instance, a molten sulphur admixed with a small proportion of metal or metal sulphide powder and an electric current was passed through the molten sulphur for 3 to 4 minutes, with the specimen using as anode and at a current density of 2 to 3 ma./cm.^{2}, and thereafter the current was cut off and held for 1 hour as it was. In these operations the same results as in the above-mentioned example were obtained respectively.

What I claim is:

1. A method of sulphurizing the surface of ferrous metal, which comprises the steps of desorbing gas from the surface of the metal to make the surface of the metal easily wettable to molten sulphur, and immersing the metal thus preliminarily treated in molten sulphur to sulphurize the surface of the metal.

2. A method as claimed in claim 1, in which the metal is maintained in molten sulphur at about 120° to 445° C. for about one-half to four hours.

3. A method as claimed in claim 2, in which the temperature of the sulphur is about 130° to 250° C.

4. A method as claimed in claim 3, in which the temperature of the sulphur is about 150° C.

5. A method as claimed in claim 1, in which the surface of the metal is rendered easily wettable to molten sulphur by immersion in a molten flux.

6. A method as claimed in claim 5, in which the flux is a molten mixture of NH_4Cl and $ZnCl_2$.

7. A method of sulphurizing the surface of ferrous metal containing cementite, which comprises the steps of desorbing gas from the surface of the metal and increasing the concentration of cementite exposed on the surface of the metal to make the surface of the metal easily wettable to molten sulphur, and immersing the metal thus preliminarily treated in molten sulphur to sulphurize the surface of the metal.

References Cited in the file of this patent

UNITED STATES PATENTS

2,198,843	Ruben	Apr. 30, 1940
2,288,788	Clark et al.	July 7, 1942
2,343,569	Neely et al.	Mar. 7, 1946
2,892,741	Spengler et al.	June 30, 1959

OTHER REFERENCES

Roscoe and Schrolemmer: "Treatise on Chemistry," vol. II, The Metals, pages 1282–1284, 6th edition.