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Kanetake

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[45] **May 21, 1974**

[54] **METALLIC CEMENTATION**

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[21] Appl. No.: **120,180**

[30] **Foreign Application Priority Data**

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Mar. 24, 1970	Japan	45-24235

[52] **U.S. Cl.** .... **117/107.2 R,** 148/14, 148/6

[51] **Int. Cl.** **C23c 11/04**

[58] **Field of Search** .... 117/107.2, 106 C, 119.4; 148/6.35, 144

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Attorney, Agent, or Firm—McGlew and Tuttle

[57] **ABSTRACT**

Process for cementation of iron or steel by heat treatment in a chamber with fine particles of chromium, titanium or silicon halide suspended in an inert atmosphere.

5 Claims, 13 Drawing Figures

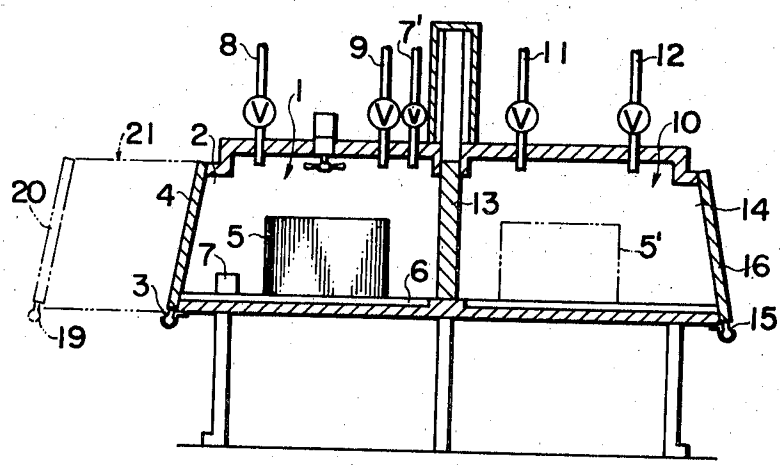

FIG. 1

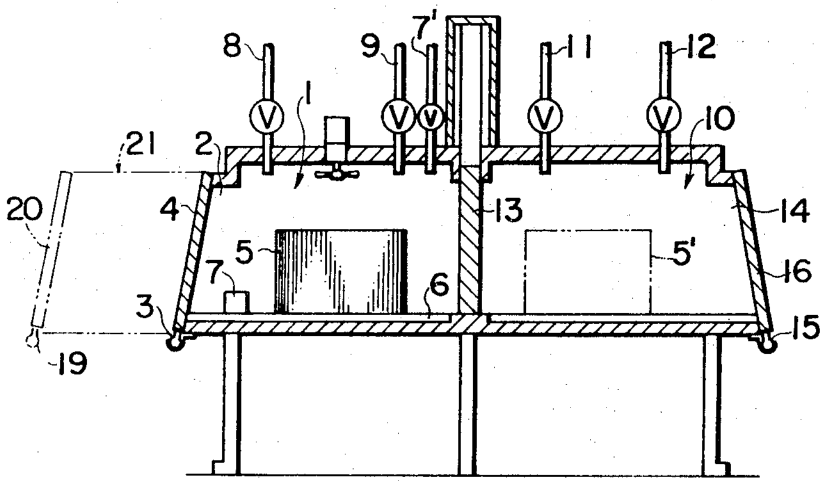

FIG. 2

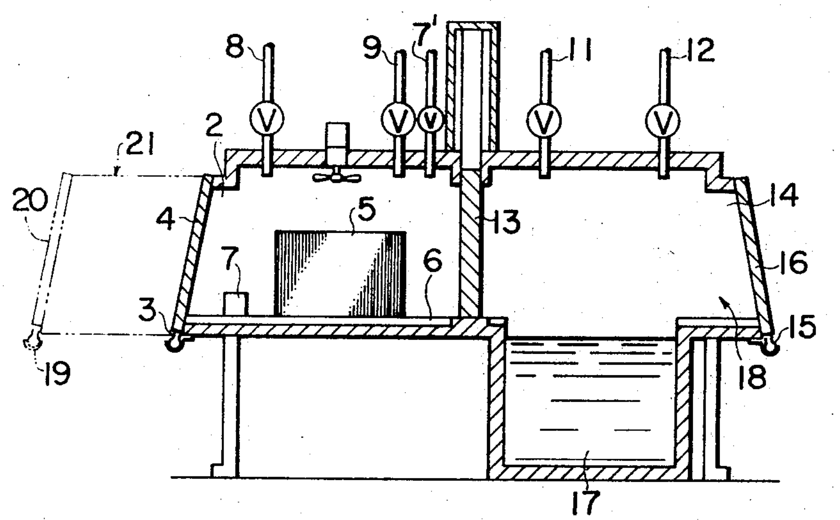

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FIG. 3

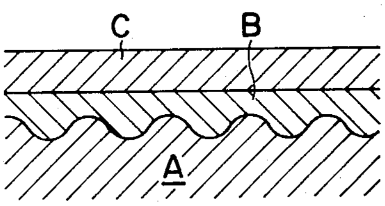

FIG. 4

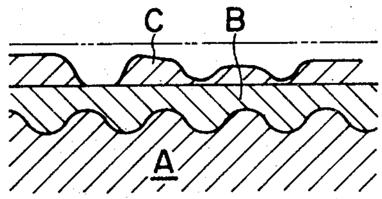

FIG. 5

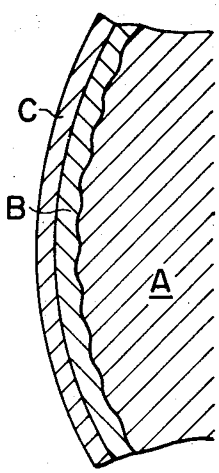

FIG. 6

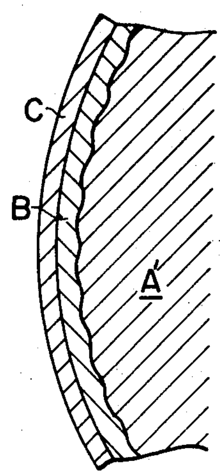

FIG. 7

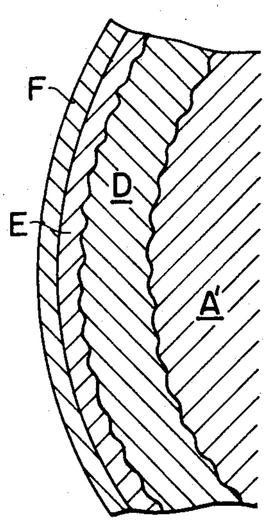

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FIG. 10

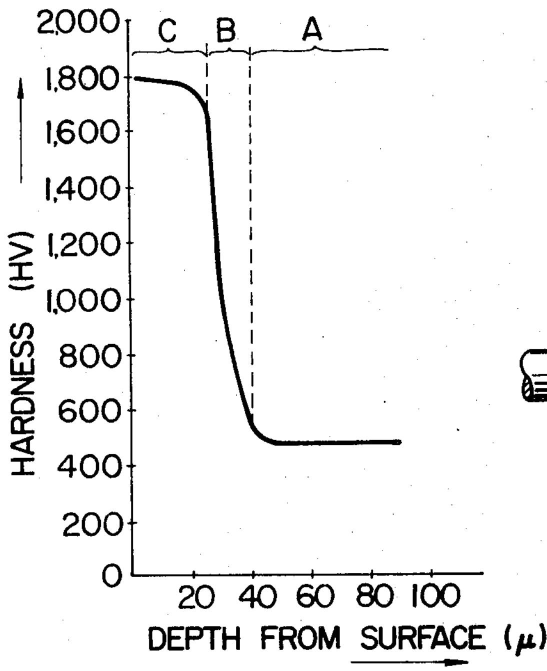

FIG. 8

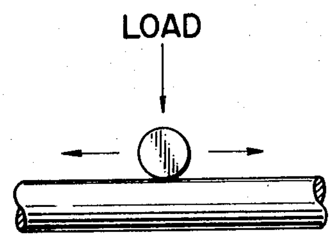

FIG. 9

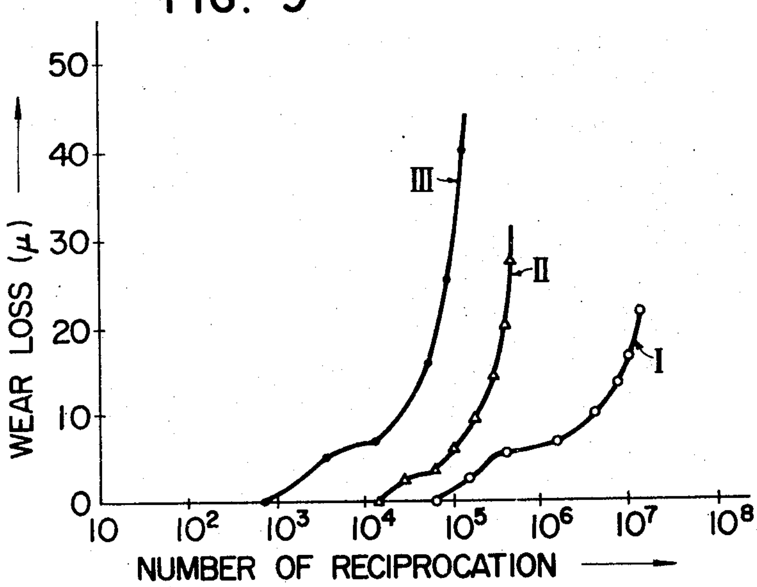

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FIG. 11

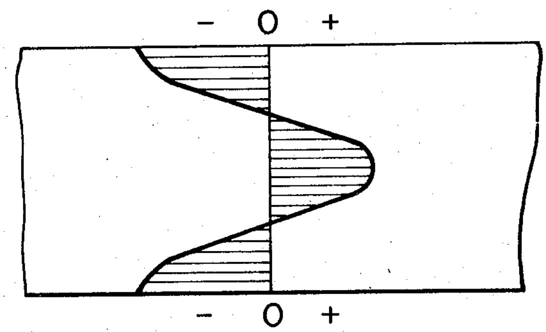


FIG. 12

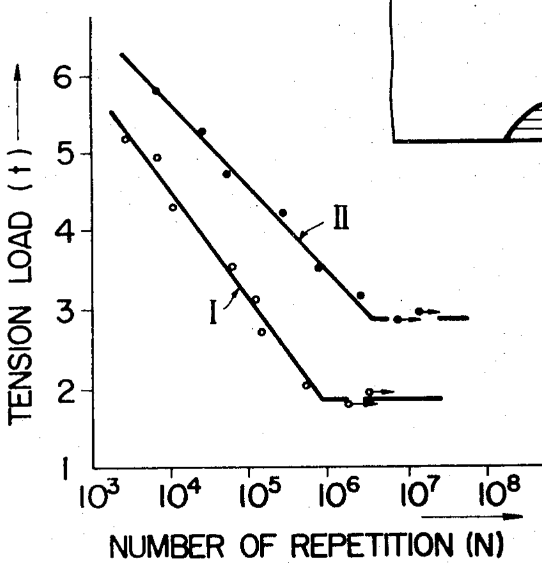
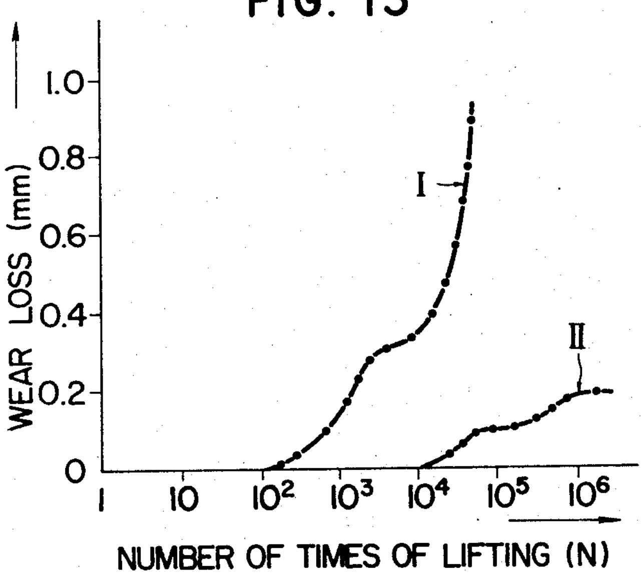


FIG. 13



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METALLIC CEMENTATION

In conventional metal products, there are stainless steels, such as, high alloy steels, material requiring anticorrosion, heat-proof and wear proof properties but these metal products are high-priced. Therefore this invention aims at providing the above-mentioned materials which satisfy these requirements and are low-priced. That is to say, this invention aims at providing iron and steel products whose exterior surface has the desired property of said stainless and high alloy steels and whose interior has the composition of the original material. For example, a stainless steel chain or the like is inferior in weldability, since such a chain is made of a low carbon steel. This invention then is applied to this chain leaving its internal mechanical strength is left intact, while on the surface alone of the chain an alloy layer having anticorrosion, heat-proof properties and wear proof is formed. In this way, are produced metal products, such as iron and steel products, of low price and excellent property. For instance, chains can be manufactured thus.

For a better understanding of the principles of the present invention, reference is made to the following description of a typical embodiment thereof as illustrated in the accompanying drawings, wherein:

FIG. **1** is a longitudinal sectional side view showing an example of a metal cementation apparatus which is used in the case of carrying out this invention;

FIG. **2** is a longitudinal side view of the other example;

FIG. **3** is an enlarged sectional view showing a part of the normally metallic cementation treated product;

FIG. **4** is an enlarged sectional view showing the state in which the cemented metals are partially fallen away;

FIGS. **5** to **9** show a second embodiment of this invention respectively;

FIGS. **5** and **6** are enlarged sectional views showing the surface portion of a specimen whose surface is treated carrying out this invention;

FIG. **7** is an enlarged sectional view showing the surface portion of a sample whose surface is treated by the conventional chromium cementation process;

FIG. **8** is a diagram of a wear test;

FIG. **9** is a diagram showing results of the wear test;

FIGS. **10** to **13** show a third embodiment of this invention respectively;

FIG. **10** is a diagram showing the distribution of hardness of a chain which is treated by the conventional chromium cementation process;

FIG. **11** is a diagram showing the distribution of residual stress in the case of a loaded chain;

FIG. **12** is a diagram showing results of a fatigue test; and

FIG. **13** is a diagram showing a result of the wear test.

This invention is described in greater detail below with reference to the aforementioned drawings.

First, an apparatus for metallic cementation of this invention is described as shown in FIGS. **1** and **2**. In said apparatus, a non-oxidizing gas such as nitrogen, argon or gaseous hydrocarbon is jetted from many jets or air holes in a jet pipe **3** installed at the lower part of a front opening **2** of a treatment chamber **1**, thus forming a gas curtain for the prevention of air invasion. A front door **4** at the front opening **2** is opened and then an iron and steel product **5** to be treated by cementation is moved into treatment chamber **1** through said gas curtain supporting it by rail **6**. A chromium chloride producing material **7** is also moved into the treatment chamber **1**.

Next, when the front door **4** is closed, the jet of a non oxidizing gas from the jet pipe **3** stops. After the air in the treatment chamber **1** is exhausted through an exhaust pipe **8**, the temperature in the treatment chamber is raised to about 1,000°C. By this means the fine particles of chromium chloride which are in a partly fused state throughout, or on the circumference are floated in the treatment chamber. These particles are maintained in that state for 5 hours and in the meantime chromium is cemented on the surface of the iron and steel product **5** and a chromium cementation zone B is formed on the surface of a matrix A. (see FIG. 3)

Further, in the case of practical use of the invention, instead of placing said chromium producing material **7** in the treatment chamber **1**, an opening **7'** is provided in the chamber **1** for supplying the fine particles of metal halide. It is also possible to supply said fine particles into the chamber **1** through the opening **7'**.

Next, in the treatment chamber **1** filled with a gas containing the fine particles of said chromium chloride, a small amount of methane (0.1–5 percent by volume of methane is suitable) methane is added from a feed pipe **9** and the fine particles of carbon are produced by a thermal decomposition of methane in the treatment chamber. Chromium carbide is produced by the reaction of these fine particles and chromium chloride and cementation of this chromium carbide is effected on the surface side of said chromium cementation zone B and thus a chromium zone C is formed on the surface of the iron and steel products in which chromium carbide is dispersed. (See FIG. 3) Propane gas is also useful in place of methane gas.

Next, nonoxidizing gas such as nitrogen, argon, or gaseous hydrocarbon is supplied to the treatment chamber **1** from the feed pipe **9**. The gas containing iron chloride ($FeCl_2$) produced by chromium cementation within the treating chamber is exhausted from the exhaust pipe **8** and thereafter the atmosphere in the treatment chamber **1** is replaced with nonoxidizing gas.

Next, before the chromium cementation work is received in a cooling chamber **10** connected to the treatment chamber **1**, a nonoxidizing gas such as nitrogen, argon, hydrogen or gaseous hydrocarbon is supplied beforehand to the cooling chamber **10** from a feed pipe **11**. Any gas containing iron chloride ($FeCl_2$) which has escaped into the cooling chamber **10** from the treatment chamber **1** is exhausted through an exhaust pipe **12** from the cooling chamber, then the atmosphere in the cooling chamber **10** is replaced with nonoxidizing gas.

Next, an intermediate door **13** is opened between the cooling chamber **10** filled with nonoxidizing gas and the treatment chamber **1**, and the chromium cemented iron and steel product is moved into the cooling chamber **10** supported by the rail **6** as indicated by reference numeral **5'**. Thereafter, the intermediate door **13** is closed and cooling of the chromium cemented iron and steel product takes place in the cooling chamber **10**. Then, nonoxidizing gas is emitted from the jet pipe **3** of the front opening **2**. As a result a gas curtain is formed and the front door 4 is opened and a second iron and steel product to be treated by chromium cementation is moved into the treatment chamber 1 as in the aforesaid case preventing air invasion into the treatment chamber 1 by the air curtain. Then a chromium cementation takes place as in the aforesaid case.

Next, when the chromium cemented iron and steel product in the cooling chamber 10 is cooled below about 300°C, nonoxidizing gas is emitted from a jet pipe 15 located at the lower part of a rear opening 14 of the cooling chamber 10. As a result a gas curtain is formed and then a front door 16 is opened. The chromium cemented iron and steel product is taken out the inside of the cooling chamber 10 and air-cooled up to room temperature. The air invasion into the cooling chamber 1 is prevented by the gas curtain.

As shown in FIG. 3, the structure of section of a the chromium cemented iron and steel product obtained as described above, there are formed, the chromium cementation zone B and the chromium zone C in which chromium carbide is dispersed. These zones B and C are formed in turn on the surface of the matrix A of ferrite and pearlite structures as shown in FIG. 3. The chromium cemented iron and steel product is cooled up to a certain temperature in the cooling chamber without the bad influence of an atmosphere containing iron chloride ($FeCl_2$) produced in the treatment chamber by said chromium cementation. For this reason no dechromium phenomenon takes place such as takes place in the case of cooling in an atmosphere containing iron chloride ($FeCl_2$). Therefore the chromium cemented iron and steel product treated by the process of the invention is rich in brightness.

Further as shown in FIG. 2, a quenching chamber 18 having an oil tank 17 is provided instead of the cooling chamber 10 and the atmosphere of nonoxidizing gas is produced in the treatment chamber 1. Then, the chromium cemented iron and steel product is moved from the treatment chamber 1 to the quenching chamber 18 and is directly thrown into the oil tank 17 where quenching in oil takes place. The section structure of the chromium cementated iron and steel product is obtained by making a tempering successively within the limits of 180°–600°C. The chromium cementation zone and the chromium zone in which chromium carbide is dispersed, are formed in turn on surface of the matrix of the steel products tempered martensite structure yielding a chromium cemented iron and steel product which is rich in brightness without causing a dechromium phenomenon.

Further, in carrying out this invention, a curtain of the nonoxidizing gas may be provided instead of intermediate door 13. After chromium cementation takes place in the treatment chamber 1, the chromium cementation treated work may be moved directly to the cooling chamber 10 or the quenching chamber 18, omitting the supply of methane and nonoxidizing gas into the treatment chamber 1. Chromium iodide or chromium fluoride or the like may be used as chromium halide besides chromium chloride. Further, the same result can be obtained even by the use of titanium halide, for instance, titanium chloride ($TiCl_4$) or silicon halide ($SiCl_4$), instead of chromium halide.

As a means of producing the atmosphere of said halide in the treatment chamber, the material producing halide may be placed beforehand in the treatment chamber as mentioned above. Thereafter, the fine particles of halide are supplied into the treatment chamber 1 from the feed pipe 9. Alternatively those means may concurrently be used.

In a further embodiment of the invention the front part of the treatment chamber is provided with a gas jet pipe 19 for forming a gas curtain and a preheat chamber 21 having a front door 20. When cementation of anticorrosion metal into the desired iron and steel products is taking place in the treatment chamber 1, other iron and steel products can be preheated in the preheat chamber 21 whereby cementation of anticorrosion metal can more efficiently take place.

The following description is set forth below with reference to various embodiments of this invention:

Embodiment 1—(A)

Under the following conditions, there was made a chromium cementation in the gear for a chemical machine made of carbon steel containing a chemical composition of C 0.025 percent, Si 0.25 percent, Mn 0.8 percent, P 0.011 percent and S 0.025 percent.

1. Treatment Amount: 150 Kg (70 pieces) per one time
2. Cementation Temperature: 1,000°C
3. Cementation Time: 5 hours
4. Cooling Time in Cooling Chamber: 2 hours (air-cooled in the atmosphere after the cooling in the cooling chamber)

The chromium cementation work obtained had a chromium zone of 18μ thickness and was rich in brightness without causing a dechromium phenomenon as shown in FIG. 4. Results were also good as regards corrosion resistance in nitric acid solution.

Embodiment 1—(B)

Under the following conditions, there was made a chromium cementation in a gear made of chromium-molybdenum steel containing a chemical composition of C 0.4 percent, Si 0.32 percent, Mn 0.82 percent, P 0.021 percent, S 0.015 percent, Cr 1.02 percent and Mo 0.25 percent.

1. Treatment Amount: 150 Kg (15 pieces) per one time
2. Cementation Temperature: 1,030°C
3. Cementation Time: 5 hours
4. Oil quenching takes place immediately after the cementation.

The chromium cementation work thus obtained had a chromium zone of 20μ thickness and was rich in brightness without causing a dechromium phenomenon as shown in FIG. 4. The resultant work had an HRC (Rochwell hardness) 70 in surface hardness of and HRC 52 in core hardness. As a result this gear was remarkably improved in resistance to corrosion and wear as compared with the ordinary work.

Embodiment 2—(A)

1. Specimen:

A surface smooth round bar of 9.5 mm dia. and 50 mm long having the following chemical composition was treated:

Chemical Composition of Specimen

Kind of Steel	Carbon Steel 1	Low Manganese Steel	Chromium-Molybdenum Steel
C	0.43	0.23	0.22

Chemical Composition of Specimen -Continued

Kind of Steel		Carbon Steel 1	Low Manganese Steel	Chromium-Molybdenum Steel
Chemical Com-position (%)	Si	0.21	0.19	0.21
	Mn	0.68	1.35	0.72
	P	0.021	0.019	0.017
	S	0.016	0.020	0.016
	Cr			1.03
	Mo			0.21

2. Treatment a

In to a furnace whose interior atmospheric gas can be controlled from the outside, specimens and chromium chloride producing material are placed after removing the air inside the furnace, fine particles of chromium chloride ($CrCl_2$) which are in a partially fusing state throughout or on the circumference in the furnace are generated by raising the temperature in the furnace to about 1,000°C. That state is maintained for about 5 hours while in the meantime cementation of chromium is effected on the surface of each specimen in the furnace. Thereupon a chromium cementation zone is formed on said specimens. Then in the furnace filled with the gas containing the fine particles of said chromium chloride, a small amount of methane is added and fine particles of carbon are produced by the thermal decomposition of methane in the furnace. By the reaction of these fine particles of carbon and chromium chloride, chromium carbide is produced. Then, a chromium zone in which chromium carbide is dispersed was formed on the surface of the specimen by the cementation of this chromium carbide on the surface side of said chromium cementation zone. In the foregoing, a volume ratio of 0.1–5 percent of methane to gas is suitable. Also, propane gas may be used in place of methane.

Next, that specimen is cooled in oil immediately after removal from said furnace and quenching is performed preventing oxidation on the surface of the specimen. Tempering is performed within the limits of 180°–600°C corresponding to the mechanical property successively being required.

As shown in FIG. 5, in, the structure sectional of surface treated specimen I obtained as described, there were formed (i) a chromium cementation zone B of about 15μ in average thickness and (ii) a chromium zone C of about 20μ in average thickness in which chromium carbide is dispersed, in turn on the surface of matrix A of the tempered martensite structure.

3. Treatment b:

As shown in FIG. 6, the completion of the foresaid chromium carbide cementation, in another embodiment the specimen is slowly cooled in the furnace omitting the oil quenching in the structure of the surface treated specimen II. On the surface of the steel product matrix of ferrite and pearlighte structure (ii) a chromium zone B of 15μ in average thickness and (ii) a chromium zone C of 20μ in average thickness in which chromium carbide is dispersed.

4. Specimen by the conventional treatment:

As shown in FIG. 7, after treatment was made at 1,000°C for 5 hours by the conventional chromium cementation process, there were formed in turn on the surface of matrix A' of ferrite and pearlite structure in the surface section structure of treated specimen III obtained by the slow cooling of the specimen in the furnace, (i) a decarburizing zone D of ferrite structure of 10μ in average thickness, and (ii) a chromium diffusing zone E of 5μ in average thickness and (iii) chromium zone F of 20μ in average thickness.

5. Wear Test:

Two pieces each of said specimens I, II, III are arranged at right angles to each other as shown in FIG. 8 and machine oil is applied as lubricant to said pieces, which are subjected to a load of 500 Kg and reciprocated. In this manner an amount of change in diameter size was measured to indicate wear loss.

As the result, as compared with a wear resistance of the surface of specimen III treated by the conventional chromium cementation process, the wear resistance is excellent proof of the surface of specimen II treated by process of this invention slowly cooled in the furnace. The wear resistance of the surface of specimen I treated according to the process of this invention by quenching and tempering is much more excellent. These results are seen in FIG. 9.

Embodiment 2—(B)

1. Specimen:

The specimen is the same as in the case of Embodiment 2—(A).

2. Treatment:

Each specimen in this example was treated under the same conditions as described in Embodiment 2—(A) above. After the chromium cementation zone was formed, a small amount of carbon powder in form of fine particles of carbon of a very small diameter is added in the furnace. Then, chromium carbide is produced by the reaction of chromium chloride and carbon, and cementation and dispersion of this chromium carbide were performed in the chromium zone. Thereafter, the specimen was manufactured whose quenching and tempering took place under the same conditions as in Embodiment 2—(A) above and the specimen was manufactured whose slow cooling was performed in the furnace. In this example, about 10 to 200g of carbon powder per 100Kg of work to be treated is suitable. Also, a diameter below about 1mm for such carbon particles is suitable.

The surface treated specimen obtained had the same surface structure and wear resistance as the case of Embodiment 2—(A).

Embodiment 2—(C)

1. Specimen:

The specimen in this example is the same as the specimen described in Embodiment 2—(A).

2. Treatment:

Cementation was performed beforehand in each of said specimen and a cementation zone of 0.03–1.5 mm thickness was formed in the specimens. The resultant specimen and a chromium chloride producing material are placed in the furnace. After the removal of air from the atmosphere in the furnace, the temperature is raised by heating and is maintained at 1,000°C for 5 hours and chromium cementation takes place. Next, the quenching and tempering of the specimen was performed under the same conditions as in the example of Embodiment 2—(A) and the specimen whose slow cooling was performed in the furnace, were manufactured.

In the surface treated specimen so obtained, a cementation zone and a chromium zone in which chromium carbide is dispersed, were formed in turn on the surface of the iron and steel matrix and said speciman had the same wear resistance as described in example of Embodiment 2—(A).

Further, in the case of Embodiment 2—(C), even if a carbonitriding treatment is performed instead of cementation, the same result is obtained. The iron and steel product whose surface treatment is performed by the process of this invention, forms a chromium zone on its surface, so that a rust by corrosion is not produced in the atmosphere as for corrosion resistance to fresh water, sea water, nitric acid, organic acid or the like, this corrosion resistance can be remarkably improved. This is so, since in the chromium zone there exist super hard crystals consisting of chromium and titanium carbide or nitride in the state of dispersion, a wear resistance can be remarkably improved. Further chromium is sufficiently diffused in iron and a metal phase is assumed, so that even if a heavy load partially acts on the so treated iron product, the chromium zone can securely be prevented from its coming off and the iron and steel matrix is made into a tempered martensite structure by quenching and tempering. Therefore, these are the results the iron product increases in a breaking strength, and sufficiently endures a contact pressure and shows further improved wear resistance.

Embodiment 3

A link chain of 7.1 mm in normal size and 20.2 mm in pitch and a link chain of 9.5 mm in normal size and 28.6 mm in pitch are manufactured with the material of low manganese steel (chemical composition: C 0.23 percent, Si 0.21 percent, Mn 1.43 percent, P 0.012 percent, S 0.023 percent). This steel is excellent in weldability and hardenability. When the treatment a of the above described Embodiment 2—(A) is applied to those link chains, and a chromium chloride producing material is used to treat the metal section structure of the link chains, as shown in FIGS. **3** and **5**, a chromium cementation zone B (chromium iron alloy layer) of about 17μ in average thickness and a chromium zone C of about 24μ in average thickness in which chromium carbide is dispersed, are formed in turn on the circumference of core A of a tempered martensite structure by quenching and tempering. As shown in FIG. **10**, and in the distribution of hardness of its section, a hardness of the chromium zone C is the highest, while the chromium cementation zone B has a hardness of iron chromium alloy structure and the core has a tempered martensite structure which is high in hardness.

And as mentioned above, when quenching and tempering are performed after the chromium cementation, in the section structure of the link chain, its specific volume varies according to the difference of transformation in each of the chromium zone C, the chromium cementation zone B and the core A. Thus, as shown in FIG. **11**, a residual stress (compression) is produced on the surface side of the rod and a residual stress (tension) is produced on the center side of the rod. On this account, a pre-stress (compression) is given within the straight portion **5** of the link chain and improvement of a fatigue strength was seen.

Next, description is made below with regard to the results of testing the link chain of this invention. The conventional link chain in which chromium cementation is not performed, is also tested and results given below. The link chain manufactured by the treatment of the conventional chromium cementation process is also tested and results given below:

1. Fatigue Test:

A conventional link chain I of 7.1 mm in normal size and 20.2 mm in pitch consisting of low manganese steel having a chemical composition of C 0.23 percent, Si 0.21 percent, Mn 1.43 percent, P 0.012 percent and S 0.023 percent is tested. Also, a link chain II (about 24μ in average thickness of chromium zone C, about 17μ in average thickness of chromium cementation zone) according to this invention is obtained by performing chromium cementation and heat treatment for said conventional link chain by the process of said Embodiment. When each chain was tested for fatigue strength by giving a partial pulsating tension (lowest stress: 5 Kg/mm^2) by Losenhausen fatigue testing machine, the link chain II of this invention was remarkably excellent more than the conventional link chain I as shown in FIG. **12.**

2. Wear Proof Test:

A Specimen I:

A surface treatment by the conventional chromium cementation process was performed for the link chain of 7.1 mm in normal size and 20.2 mm in pitch consisting of low manganese steel having a chemical composition of C 0.23 percent, Si 0.21 percent, Mn 1.43 percent, P 0.012 percent and S 0.023 percent. A decarburizing zone of ferrite structure, a chromium diffusing zone and a chromium zone were formed in turn on the circumference of the core consisting of ferrite and pearlite. The average thickness of each zone is 9 ≈ 48μ, 10 ≈ 17μ and 11 ≈ 24μ respectively.

B Specimen II:

The chromium cementation described in the Embodiment was performed for said link chain. As shown in FIGS. **3** and **5**, a chromium cementation zone B and a chromium zone C in which chromium carbide is dispersed, were formed in turn on the circumference of the core A of tempered martensite structure by quenching and tempering. The average thickness of each zone is 13 ≈ 17μ and 14 ≈ 24μ respectively.

When said specimens I and II, were tested for a wear resistance, the results shown in FIG. **13** were obtained.

Further, in the wear proof test, machine oil was applied to the link chain and a load of 1 ton was given to the link chain and its going up and down was repeated. As a result, a wear loss was measured (difference between the pitch after test and the pitch before test).

Since the link chain treated according to this invention forms a chromium zone on its surface, corrosion by rust is not produced in the atmosphere. Corrosion resistance to fresh water, sea water, nitric acid, organic acid or the like, can be remarkably improved for this chain. Also, in its chromium zone, super hard crystals consisting of carbide or nitride of chromiums and titaniums, exist in the state of dispersion so that wear resistance can be remarkably improved and the core has a tempered martensite structure by quenching and tempering. Therefore breaking strength can be increased and when the link chain is subjected to load, there is sufficient endurance against a contact pressure in the mutual contact portion of links. Further, as is clear from the metal structure and the hardness distribution shown by FIG. **10**, the chromium in the steel is sufficiently diffused and assumes an alloy phase. Also hardness of this chromium diffusing zone does not change to the extreme, so that even if a heavy load acts on the link chain, the effect is that the chromium zone can securely be prevented securely from its coming off.

What is claimed is:

1. Process of metallic cementation of a work, which comprises performing said metallic cementation by coating the work composed of iron or steel heated to cementation temperature in a treatment chamber with volatile metallic halide selected from the group consisting of Cr halide, Ti halide, and Si halide, and maintaining said halide suspended as fine particles in an inert atmosphere in said chamber while maintaining the same mainly in a partially fused state whereby the so-coated work is protected against corrosion, heat and/or wear.

2. Process of metallic cementation of a work, which comprises performing said metallic cementation by coating the work composed of iron or steel heated to cementation temperature in a treatment chamber with volatile metallic halide selected from the group consisting of halides of chromium, titanium and silicon, maintaining said halide suspended as fine particles in an inert atmosphere mainly in a partially fused state, and cooling the so-cemented work in a cooling chamber containing a non-oxidizing gas in which by-products comprising iron halide are removed, whereby said work so coated is protected against corrosion, heat and wear.

3. Process of metallic cementation of a work, which comprises performing said metallic cementation by coating the work composed of iron or steel heated to cementation temperature in a treatment chamber with volatile metallic halide selected from the group consisting of halides of chromium, titanium, and silicon, and maintaining said halide suspended as fine particles in an inert atmosphere mainly in a partially fused state, and successively quenching the so-cemented work and successively utilizing for the quenching the heat produced by the treatment at the required quenching temperature of 180° – 600°C, said quenching being performed in a quenching chamber containing a non-oxidizing gas in which by-products comprising iron halide are removed, whereby said work so coated is protected against corrosion, heat and wear.

4. Process for surface treatment of iron and steel products, which comprises treating and coating the iron and steel products heated to cementation temperature in an inert atmosphere with fine particles of metallic halide selected from the group consisting of chromium, titanium and silicon halides, said particles being suspended in a partially fused state, and forming a metallic diffusing zone on the surface of said iron and steel products' matrix, and then adding fine particles of carbon to said atmosphere, whereby a carbide of said metal is dispersed on the surface of said diffusing zone and said product is protected against corrosion, heat and wear.

5. Process for surface treatment of iron and steel products, which comprises coating said products heated to cementation temperature by forming a carburizing zone or a carbonitriding zone on the surface of said iron and steel products' matrix by carburizing or carbonitriding the iron and steel products beforehand, and then treating those iron and steel products in an inert atmosphere with fine particles of metallic halide, said particles being suspended and being selected from the group consisting of chromium, titanium, and silicon, whereby said particles impart to said products corrosion resistance, heat resistance, and/or wear resistance, and are suspended mainly in a partially fused state, whereby said metal is cemented on the surface of said carburizing zone or carbonitrizing zone and the metallic carbide is dispersed on the surface of a diffusing zone.

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