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METHOD FOR TREATING STEEL BY ELECTROLYSIS IN A MOLTEN THIOCYANATE

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4 Claims

ABSTRACT OF THE DISCLOSURE

Frictional properties of steel are improved by electrolytic treatment in a bath of molten thiocyanates at a temperature not to exceed about 350°C, and with the treated part anodically connected. A superficial introduction of sulfur results. The thiocyanates may be potassium, sodium, ammonium, etc., in a concentration of 20–100% by weight of the bath, preferably 30–100% by weight of the bath. The inclusion of chlorides such as zinc and/or potassium produces a reducing bath which ensures deoxidization of the steel piece.

This application is a continuation-in-part of copending application Ser. No. 450,223 now abandoned, filed Apr. 22, 1965.

The present invention has for its object a method of treatment of steel surfaces with the object of improving their frictional characteristics.

It is known that the seizure of metal parts in contact is frequently caused by microcracks on the rough parts of the surfaces in contact. These microcracks are caused by very high localized pressures on the said roughnesses, and by very high temperatures over small surfaces.

It is advantageous to make these microcracks as fragile as possible in order to reduce the force required to break them, that is to say, to reduce the coefficient of friction. It has been found that the substances which are most easily broken mechanically are ionic compounds. It is therefore possible to make the microcracks fragile by introducing, at the surface of one or both of the two metal parts, a nonmetal capable of forming these ionic compounds. This nonmetal can form with one or both of the two metals a preexisting ionic compound or, alternatively, it may combine with the metals in order to produce the ionic compounds when the microcrack junctions occur.

Researches carried out by the applicant have shown that, in order to obtain the introduction of a nonmetal, it is advantageous to treat the metal part by electrolysis in a bath of molten salts, the treated part serving as the anode. Applicant has discovered that a considerable improvement in these frictional characteristics is obtained when the nonmetal which is introduced by electrolysis in a bath of molten salts is sulphur.

The bath of molten salts comprises a thiocyanate or a mixture of thiocyanates in a concentration of 20–100% by weight of the bath, preferably 30–100% by weight of the bath. Any remainder of the bath, in addition to the thiocyanates, may be harmless diluents such as chlorides, for example zinc and/or potassium chlorides. The chlorides produce a reducing bath which ensures the oxidization of the steel piece prior to introduction of the sulphur.

With this bath, the introduction of the sulphur by electrolysis is effected at relatively low temperatures, considerably lower than the temperatures of prior treatments, without electrolysis, the phenomenon being accelerated by the electrical effect. Such low-temperature operation, at a temperature not to exceed about 350°C, is especially valuable for steels which usually lose their desired characteristics when they are heated to higher temperatures. Examples of such steels with which the present invention is particularly useful are tempered case-hardened steels; roller-bearing steels, such as tempered 100C6 steel; so-called "rapid" steels such as those containing 18% tungsten or 6% cobalt for cutting tools; and bainitic steels.

According to the invention, the superficial layer resulting from the treatment forms an integral part of the metal piece.

As shown in FIG. 1 of the accompanying drawing, the metal piece 10 to be treated is immersed in a tank 11 containing the molten salt 12. The piece 10 is connected to the positive pole 13 of a source of current 14. The tank 11 is connected to the negative pole 15 of this same source of current.

There are given below examples of surface treatment according to the invention, improving the frictional behavior and resistance to wear of a piece of a given metal. These examples are of course in no way limiting; they simply illustrate some of the fields of application of the invention, in the case of a given nonmetal and a given metal treated.

In the examples which follow, the performances noted have been obtained on a friction-testing machine of the so-called "Paville-Leval" type. As shown in FIG. 2, this machine comprises two jaws 16 and 17 cut to the shape of a V, between which the test piece 10A to be treated is rotated and gripped.

The clamping effect applied by the jaws on the test sample is hereinafter termed the "grip of the jaws."

At the beginning of each test, there is applied to the jaws a load of 200 kg. Thereafter the grip increases with time, this increase being 8 kg per second.

The friction test is stopped, either when seizure occurs or at the moment when the creep of the test sample, which heats up, compensates for the movement together of the jaws.

The quality index is given by the value

\[
\int_0^t f(t)\,dt
\]

in which \( t \) represents the duration of the test.

EXAMPLE 1

A test sample of semi-hard annealed carbon steel XC32f was immersed in a bath of molten potassium thiocyanate at 200–250°C, and was subjected to electrolysis as the anode with a current density of 3 amperes per square decimeter for 20 minutes.

An untreated but otherwise identical test sample seized during the first seconds of the friction test at a load of 200 kg; but the treated test sample creeps without seizure after 60 seconds of test, the gripping load on the jaws having then reached 500 kg. The quality index is 24,000 kg per second.

EXAMPLE 2

A test sample of carbon steel identical with that of Example 1 is immersed in a bath consisting of a mixture by weight of:

| Percent |
|------------------|-----|
| Potassium thiocyanate KSCN | 50  |
| Ammonium thiocyanate NH₄SCN | 50  |

This bath is brought up to 175°C.
The test sample serves as the anode, the cathode being a steel cylinder arranged around the test sample and having an internal diameter of 35 mm.

The density of the direct current employed for the electrolysis is 10 amperes per square decimeter.

After a treatment of 10 minutes, it is found that the test sample creeps at a load of 450 kg. The quality index is 22,000 kg per second.

**EXAMPLE 3**

A test sample of steel of the grade 16NC6, case-hardened and tempered, was treated in a bath of:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium thiocyanate</td>
<td>70</td>
</tr>
<tr>
<td>Sodium thiocyanate</td>
<td>20</td>
</tr>
<tr>
<td>Ammonium thiocyanate</td>
<td>10</td>
</tr>
<tr>
<td>Melted at a temperature of 160° to 280° C.</td>
<td></td>
</tr>
</tbody>
</table>

This treatment is carried out with a current density of 5 amperes per square decimeter for 15 minutes.

Whereas an identical untreated test sample seizes in the first second of the test, the sample treated as indicated above creeps after 50 seconds under a load of 520 kg. The quality index is 29,000 kg per second.

**EXAMPLE 4**

A steel sample is immersed in a bath containing:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium thiocyanate KSCN</td>
<td>40</td>
</tr>
<tr>
<td>Zinc chloride ZnCl₂</td>
<td>30</td>
</tr>
<tr>
<td>Potassium chloride KCl</td>
<td>30</td>
</tr>
<tr>
<td>Melted at 280°-350° C.</td>
<td></td>
</tr>
</tbody>
</table>

The electrolysis is carried out with a current density comprised between 7 and 15 amperes per square decimeter for 20 minutes.

**EXAMPLE 5**

A steel test sample of the grade 16NC6, case-hardened and tempered, is immersed in a bath containing, by weight:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium thiocyanate NaSCN</td>
<td>25</td>
</tr>
<tr>
<td>Potassium thiocyanate KSCN</td>
<td>75</td>
</tr>
<tr>
<td>Melted and kept at 190° C.</td>
<td></td>
</tr>
</tbody>
</table>

The electrolysis is carried out with a current density of 3.2 amperes per square decimeter for 15 minutes.

Whereas an untreated test sample seizes in the first few seconds of the test, the sample treated as above described creeps without seizure after 75 seconds. The quality index exceeds 30,000 kg per second.

Having described my invention, I claim:

1. A method of improving the frictional properties of steel, comprising introducing a piece of steel into a bath of molten salts containing 20–100% by weight of thiocyanate, passing an electric current through the steel piece and the bath with the steel piece anodically connected thereby to introduce sulphur into the surface of the steel piece, and maintaining the temperature of the bath no higher than about 350° C.

2. A method as claimed in claim 1, in which said bath contains less than 100% by weight thiocyanate, balance essentially a chloride selected from the class consisting of a zinc chloride and potassium chloride and mixtures thereof.

3. A method as claimed in claim 1, said thiocyanate being present in an amount about 30–100% by weight.

4. A method as claimed in claim 1, said thiocyanate being present in an amount about 100% by weight.

**References Cited**

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