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PROCESS FOR IMPROVING THE PHYSICAL PROPERTIES OF CHROMIZED ARTICLES

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The invention relates to a process of improving the properties, more especially the physical properties, of articles plated by the chromium diffusion (chromizing) process. It is known to be of particular advantage to produce such articles with the aid of halogen compounds, more particularly the chlorides and fluorides of chromium, which are made to act at elevated temperatures and in the gaseous condition on the steel surface. A surface zone of an alloy enriched with chromium is produced. This chromizing method is applied with advantage to articles made of steel whose carbon content does not exceed 0.1%, since a higher carbon content impairs the chromized zone owing to countercurrent migration between the diffused-in chromium and the diffused-out carbon. However steels may be used which have a higher carbon content if the carbon is bound in a stable fashion by carbide-forming substances such as titanium, tantalum and niobium, so that the aforesaid countercurrent migration does not take place during chromizing.

Although chromized zones of adequate strength have been hitherto produced on steel articles, it has been observed that the mechanical properties of the carrier material are impaired to a certain extent more especially if carbide-forming agents are not employed. The chromized zone may also have unsatisfactory physical properties especially with respect to tenacity, although the reason therefor is not clear and also often accompanied by a reduced chemical stability. This is apparently independent of whether use is made of a steel with a low total carbon content or a steel having a carbon content bound in stable manner by carbide-forming substances.

It is understandable that the physical properties of a chromized article of this kind are not entirely satisfactory. The chromizing operation takes place at temperatures of 1000° C. and more, and the articles have to be subjected to this temperature for several hours. A layer is produced which is enriched with chromium and which in the outermost regions may have a chromium content of 50% or more, the chromium content decreasing steadily inwards towards the core or carrier material. Consequently, through the cross-section of the article there is a continually varying structure with differing physical properties, the difference being particularly great between the properties of the outermost boundary zone and the core zone.

We have found that by a single uniform heat treatment, the physical properties of both the chromized zone and the core or carrier material may be improved, and more especially the tenacity of both. According to the invention this heat treatment consists in cooling the articles rapidly from temperatures above 900° C. subsequent to the chromizing operation. It has been found particularly advantageous to carry out the rapid cooling operation from 950° C. Best results are obtained when the articles are quenched in oil or water from the aforesaid temperatures. Other methods of rapid cooling can also be effective according to the size of the work piece; thus for example the articles can be cooled in a protective gas in a

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passage which is strongly externally cooled, for example by water circulation.

The process can be carried into effect most simply if the articles are cooled directly from the chromizing furnace. In this case, it is not particularly important how long the period is during which the work pieces are cooled from the chromizing temperature of, for example, 1050° C. to 950° C., provided that during this period oxygen is excluded as far as possible. However, this process can only be employed if chromizing is carried out without the articles being packed in a special carrier material, viz., in a ceramic material enriched with chromium chloride. If the articles are packed in such carrier materials which in known manner facilitate the transfer of the chromium to the surface of the articles, it is of advantage to allow the articles to cool to room temperature in the carrier material, to unpack them and, after re-heating to 950° C. for example, to cool or quench them rapidly.

Whether or not re-heating is employed, the result of the heat treatment is an increase in the tenacity of the steel core or carrier material. Whereas in the absence of the heat treatment according to the present invention there is a risk that breaks will occur more particularly at sudden changes in cross-section, it is possible after using the present process, for example, to bend a screw or bolt through at least 90° without the occurrence of fractures or cracks. This is not only of importance in itself in the use of the chromized articles but also in the trueing of the articles which may be necessary if they have become distorted at the chromizing temperature. The increase in ductility is all the more surprising since it is accompanied by an increase in strength values and independently of whether or not the steel used as carrier material has the carbon content bound by carbide-forming substances. The strength, which without the use of the heat treatment according to the present invention may be approximately 40 kg./mm.², is increased by the treatment to a value of 50 kg./mm.² or more, and even above 60 kg./mm.² when using a steel containing titanium, the value which is actually achieved being of course dependent on the quenching temperature chosen and on the composition of the carrier or core material. In the above-mentioned bending test it was found, moreover, that the layer where the chromium is concentrated neither cracks nor flakes off and therefore the tenacity of this zone is distinctly improved.

It has been found particularly advantageous that where the way of carrying out the process involves reheating and quenching, it should be carried out in a protective atmosphere which should, however, contain a certain quantity of oxygen so as to bring about a controlled oxidation of the chromized surface of the article and to form a green chromium oxide skin. It has been found that this green chromium oxide skin provides additional chemical protection. The skin is resistant to corrosive substances and has greater hardness than, for example, a brightly chromized surface. The conditions under which the green oxide skin is produced can be ascertained by a few sample tests with known protective gases. It has been found particularly advantageous to operate in an atmosphere of incompletely burned illuminating gas, which is already used in industry for producing desired surface effects. It is not difficult to establish the correct amount of oxygen content in the gas mixture for each individual case of treatment.

Two specific embodiments of the process are as follows:

Example 1.—A steel article containing 0.06% carbon is chromized with the aid of a chromium halogen compound acting at a temperature of about 1030° C. and in the gaseous state, the treatment at this temperature lasting for 6 hours. The chromized articles are then cooled at any desired rate to 950° C. whilst oxygen is excluded

as far as possible and thereafter they are quenched in oil or water and thereby rapidly cooled from the said temperature of 950° C. The resulting articles had a strength of 50 kg./mm.².

Example II.—A steel article containing 0.12% carbon 0.65% titanium is packed in a ceramic material enriched with chromium chloride and is chromized by the chromizing compound being brought to the gaseous condition a chromizing temperature of about 1030° C. being reached, this treatment lasting for 6 hours. The chromized articles are then allowed to cool at any desired rate to room temperature. The articles are then unpacked from the packing material and re-heated to 950° C. and thereafter are quenched in oil or water and rapidly cooled thereby from the said temperature, the re-heating and immersion taking place in the atmosphere of a protective gas, viz., an incompletely burned illuminating gas in which a sufficient quantity of oxygen is present to bring about a controlled oxidising of the chromized surface of the article and to form a green chromium oxide skin. The resulting articles had a strength of 65 kg./mm.².

Good results are obtained if the steel mentioned in Example II contains 1.25% niobium or 1.80% tantalum in place of the titanium or if suitable quantities of two or more of the elements titanium, niobium and tantalum are present.

To completely bind the carbon stably, the titanium should be present in an amount at least five times the amount of the carbon content, niobium in an amount at least ten times the carbon content or tantalum in an amount at least fifteen times the carbon content, but it is preferred to keep the titanium content below 1%, the niobium content below 2% and the tantalum content below 2.2%.

It is to be understood that where reference is made in the claims hereof to a "chromized article," an article is

meant which is made of steel having a carbon content not exceeding 0.1%, or alternatively having the carbon content stably bound by at least one carbide-forming substance such as titanium, tantalum and/or niobium (in which case the carbon content may exceed 0.1%), and which has been acted upon to produce a substantially carbon-free chromized surface by subjection to the action of a chromium compound or compounds such as chloride or fluoride of chromium in the gaseous state or by packing in powdered chromium material (sometimes containing other constituents) and heating.

What we claim is:

1. Process for improving the physical properties of a chromized article which comprises the step of quenching the article, after the chromizing operation and without previous mechanical deformation from a temperature above 900° C.
2. Process according to claim 1 which comprises cooling the article to room temperature after this has been chromized by embedment in a chromizing agent and heating, and then re-heating the article to a temperature of above 900° C. and quenching it in a cold medium selected from the group of media consisting of water and oil.
3. Process according to claim 1 in which the temperature from which the chromized article is quenched is approximately 950° C.

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