

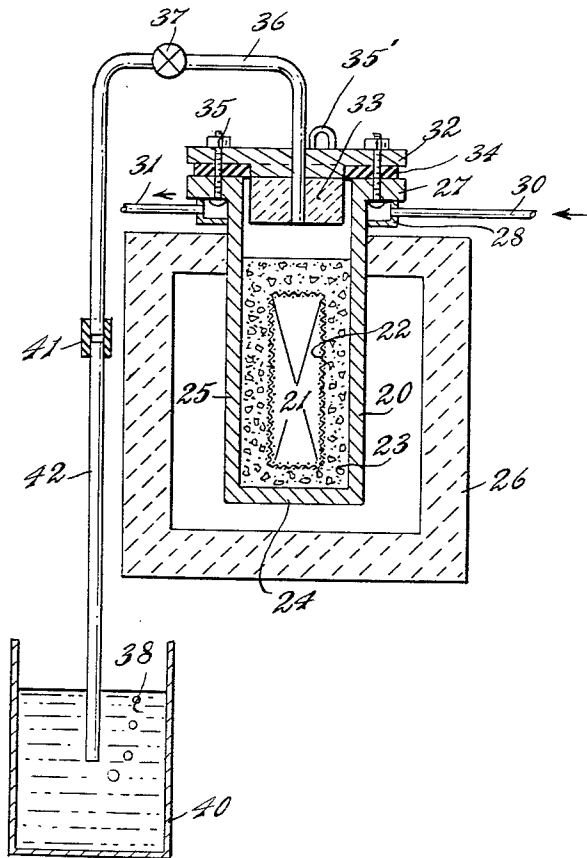
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PROCESS OF CHROMIZING AIR HARDENING TOOL STEEL

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PROCESS OF CHROMIZING AIR HARDENING TOOL STEEL

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The present invention relates to the hardening and chromizing of air hardening tool steels.

A purpose of the invention is to obtain a hard case on air hardening tool steels.

A further purpose is to give adequate support immediately beneath the case in chromizing on air hardening tool steel, so that the case will not only be very hard, but resistant to abrasion.

A further purpose is to reduce or eliminate decarburization of the surface in chromizing air hardening tool steels.

A further purpose is to obtain very effective heat transfer through the chromizing composition and the walls of the retort for the purpose of quenching the air hardening tool steels in the retort.

The drawing illustrates apparatus which may conveniently be applied in performing the process of the invention.

In the prior art, it has been commercially impractical to chromize and then harden air hardening tool steels without largely eliminating the benefit of the chromizing due to oxidation of the chromium rich surface. If, on the other hand, you chromize after hardening, the re-austenitizing of the steel in the chromizing process destroys the effect of the hardening, or the chromizing temperature draws the steel to such an extent that it is too soft.

We have discovered that austenitizing and chromizing can be carried out together in the chromizing retort, and by using a granular source of chromium surrounding the work and extending to the wall of the steel or heat resisting metal retort, the heat conductivity is adequate so that quenching of the entire retort, while still sealed from the atmosphere, in a liquid medium such as water or oil will properly harden the air hardening tool steel. The parts come out bright when the retort is opened up, and the chromizing is of a very superior quality; being very hard and with the case excellently supported by the metal of the core immediately beneath the case.

When reference is made herein to air hardening tool steels, it is intended particularly to refer to the high carbon, high chromium steels which bear AISI designations of D1, D2, D3, D4, D5 and D6, and which nominally contain 12 percent chromium and carbon contents between 1 percent and 2.25 percent, with or without 1 percent of molybdenum, or 1 percent of tungsten, and with or without 3 percent of cobalt, the balance being iron, as set forth for example in Metal Progress, Report of 22 Technical Committees of the American Society for Metals, July 15, 1954, at page 22. It is also intended to include the type known as 44OC, which contain 16 to 18 percent chromium and 1 percent carbon, balance iron. It is also intended to include the air-hardening medium alloy tool steels which are designated AISI A2, A4, A5 and A6, and which have chromium contents of 5 percent or 1 percent, a molybdenum content of 1 percent, carbon content of 0.70 or 1 percent, and in some cases

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a manganese content of 2 percent or 3 percent, the balance being iron.

We also include under the designation of air-hardening tool steels the molybdenum grades of high speed tool steels which bear AISI designations of M1, M2, M3, M4, M6, M8, M10, M30, M34, M35 and M36 and which include 4 percent of chromium, with a carbon content varying between 0.80 and 1 percent, with a vanadium content varying between 1 and 4 percent, a molybdenum content varying between 5 and 8 percent, and in some cases containing between 1.50 and 6 percent of tungsten, in some cases containing between 5 and 12 percent of cobalt, and in one case containing 1.25 percent of columbium, the balance being iron. Each of these air-hardening tool steels has a recognized austenitizing temperature which is in the range between 1600 and 2400 degrees F. and we conduct the chromizing at this austenitizing temperature.

The austenitizing temperature is desirably low within the suitable range, as otherwise the steel might come out relatively soft, because of retained austenite. We also prefer to use the shortest possible time for chromizing in order to avoid excessive grain growth. We prefer not to hold the work at the austenitizing and chromizing temperature much longer than two hours, and good results can be obtained in as little as thirty minutes at the austenitizing and chromizing temperature.

In accordance with the invention, the air hardening tool steel parts to be chromized are placed in a retort surrounded by a source of chromium, which is preferably in granular form. By this we mean that it is larger than 40 mesh per linear inch and preferably not exceeding 3/4 inch diameter, the preferred granular size being in the range between 1/8 inch and 1/4 inch.

The source of chromium may be ferrochrome, which is preferably the low carbon grade having a carbon content of less than 0.04 percent by weight, and having a chromium content higher than 65 percent chromium by weight.

In some cases however, granular electrolytic chromium metal will be used instead of ferrochrome.

It is important that the source of chromium be granular so as to obtain most effective heat transfer from the work through the wall of the retort in quenching.

It is decidedly preferable in the present invention to use a bromide chromizing catalyst, since the bromide chromizing catalysts have the property of producing an extremely hard case which is supported by the metal of the core immediately beneath the case. It is much preferable to use ammonium bromide rather than some other bromide like iron bromide or chromous bromide, because ammonium bromide not only acts very effectively as a catalyst, but it does not etch, and it dissociates to expel air from the retort.

Less desirably, we can also use a chloride chromizing catalyst, preferably ammonium chloride, although permissibly another chloride such as iron chloride or chromous chloride, with another material to expel the air. The chlorides are less desirable because of the tendency to etch.

We can also less desirably use an iodide chromizing catalyst, preferably ammonium iodide, although less desirably ferrous iodide or chromous iodide with another compound to expel the air. Here another difficulty is caused by the tendency to etch.

We can also employ a fluoride chromizing catalyst, such as ammonium chromium fluoride, ammonium bifluoride or ammonium fluoride, but difficulty is encountered through decarburization especially at sharp edges and thin sections, and through the tendency of ammonium bifluoride to etch. Ferrous fluoride and chromous fluoride may also be used with another compound to exclude air,

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The complex ammonium chromium fluoride can conveniently be produced as follows:

Into a solution containing 200 grams of ammonium bifluoride dissolved in 200 cc. of water, metallic chromium powder through 200 mesh per linear inch is introduced until 200 grams have been added. Precautions against a violent reaction or explosion are taken by using remote control techniques, since the reaction generates a tremendous amount of heat and if conducted too rapidly may cause an explosion.

The heat results in drying the product, producing the double fluoride of ammonium and chromium in the form of a dry powder.

Example I

Into a steel retort having an internal volume of about $\frac{1}{3}$ of a cubic foot, we placed a charge of 30 pounds of small air hardening tool steel parts of composition 44OC having a nominal composition of 17 percent chromium and 1 percent carbon, the balance being iron. The tool steel parts were surrounded by a wire screen container of steel screen mesh of the size of mosquito netting. The remainder of the retort, full to the top, and surrounding the work and pressed laterally against the screen wire container and engaging the interior walls of the retort at the bottom and sides, was filled with a source of chromium, in this case, granular ferrochrome, as above described, of a particle size between $\frac{1}{8}$ and $\frac{1}{4}$ inch. The charge in the retort also included 60 grams of ammonium bromide as the chromizing catalyst.

The preferred apparatus of the invention is a steel or heat resisting alloy cylindrical retort 20 containing a charge of air hardening tool steel parts 21 surrounded by a screen wire container 22 which is in turn surrounded by a source of chromium, in this case 30 pounds of granular ferrochrome 23 engaging the bottom retort wall 24 and the side retort wall 25, the retort also containing 60 grams of ammonium bromide.

The retort is surrounded by a muffle furnace 26, suitably electric or gas heated, and extends out through the top where it is flanged at 27, the flange being cooled by a water jacket 28, which has water inlet at 30 and water outlet at 31. The top is closed by a steel cover 32, carrying a refractory plug 33, gasketed at 34 (suitably by silicone rubber or polytetrafluorethylene) and with the gasket clamped by bolts 35 having their heads in the water jacket.

A pipe 36 connects with the interior of the retort through the cover, and has a valve 37 and extends at its outer end beneath the level of water 38 in container 40. The lower end of the pipe is preferably connected by rubber hose 41 to glass tube 42 so that suck-back of water can be noticed.

The work is heated up to temperature while the chromizing catalyst dissociates and expels the air, the chromizing, in this case, being conducted at 1850° F. At about the time the work comes to chromizing temperature a negative pressure in the retort develops and the valve 37 is closed. The work is held at chromizing temperature, in this case for two hours after the interior reaches 1850° F. The retort and its contents, still sealed from the atmosphere, is then taken out of the furnace and quenched in a tub of water within one minute of the time that the retort leaves the furnace.

After the retort and its contents are cooled down, approximately to 300° F., the retort is opened and the work removed.

The work may be subsequently further heat treated, as for example by tempering or deep freezing to remove retained austenite.

A remarkable effect developed. The chromizing case was uniform and free from etching, and extremely hard. The hardness in the case was equivalent to 75 Rockwell C, and the core hardness was equivalent to 63 Rockwell

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C. The core very adequately supported the case and the case was resistant against breaking through. Thus, in testing, it was found that you could not break through the case, even at a corner using a file. You simply dulled the file. The metallographic specimens could not be ground using ordinary techniques, and it was necessary to grind them using diamond dust.

The thickness of the case was between 0.0005 and 0.0007 inch.

Example II

The procedure of Example I was carried on using AISI high carbon, high chromium tool steel B2 having a nominal composition of 12 percent chromium, 1.50 percent carbon and 1 percent molybdenum, balance iron.

The results were similar to those already described, the case hardness being Rockwell C equivalent 75.

Example III

Substituting metallic chromium for ferrochrome, it was found that similar results could be obtained using metallic chromium.

Example IV

The procedure of Example I is carried out using 60 grams of ammonium chromium fluoride as above described instead of ammonium bifluoride. The work is air hardening tool steel parts of composition 44OC. Where the parts are massive, the case is hard, of the order of 75 Rockwell C equivalent, but difficulties are encountered in obtaining hardness in thin sections and sharp edges.

Example V

The procedure of Example I is carried out using ammonium chromium instead of ammonium bifluoride. A hard case is obtained as in Example I, but some difficulty is encountered through etching of machine surfaces.

Example VI

The procedure of Example I is carried out using ammonium iodide instead of ammonium bifluoride. A hard case is obtained as in Example I, but some difficulty is encountered through etching of machine surfaces.

It is desirable, according to the invention, to use bromide activator, particularly rather than fluoride, as the fluoride gives a softer case and a case that is not as well supported in thin sections. Bromide is much preferred also over chloride and iodide because it does not etch.

The quantity of activator used will vary with the volume of the retort, and usually is in the range between 0.06 and 1 percent of the weight of chromium in the source of chromium, preferably about 0.1 percent. In the above examples, a considerable excess of bromide activator was used.

All percentages given herein are by weight.

In view of our invention and disclosure variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of our invention without copying the process shown, and we, therefore, claim all such insofar as they fall within the reasonable spirit and scope of our claims.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The process of chromizing air hardening tool steels, which comprises placing in a metallic retort, air hardening tool steel parts of the class consisting of AISI D1, D2, D3, D4, D5, D6, 44OC, A2, A4, A5, A6, M1, M2, M3, M4, M6, M8, M10, M30, M34, M35 and M36, along with a source of granular metallic chromium and a halogen chromizing catalyst, closing the retort to the atmosphere, heating up the retort and its contents to

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a hardening temperature for said steel in the range between 1600 and 2400 degrees F. and holding said parts at such temperature for at least thirty minutes, and then quenching the retort and its contents in a liquid cooling medium.

2. The process of claim 1, in which the chromizing catalyst is a bromide.

3. The process of claim 2, in which the catalyst is ammonium bromide.

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