METHOD FOR HARDENING CHROMIUM-NICKEL STAINLESS STEEL

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No Drawing. Filed July 31, 1957, Ser. No. 675,282

5 Claims. (Cl. 148—125)

My invention relates to the heat-hardenable chromium-nickel stainless steel, particularly the chromium-nickel-aluminum stainless steels, and more especially to an art of stabilizing the steels for shipment and then subsequently hardening the same for use. As well, it relates to the stabilized steel and to the hardened steel.

One of the objects of my invention is the provision of an art for stabilizing the heat-hardenable chromium-nickel stainless steels, this in such manner as to reliably assure a freedom from unwarranted hardening in shipping, as in cold weather shipments over substantial distances and over prolonged periods of time.

Another object is the provision of a stabilized heat-hardenable stainless steel of the character noted which, following shipment, may be variously formed, stamped, punched, spun, drawn, bent, headed, machined and the like, into various articles and products of use, and then hardened at heat treating temperatures sufficiently low as to minimize the formation of heat- tint or other surface discoloration.

A further object of my invention is the provision of a method for hardening the stabilized heat-hardenable chromium-nickel stainless steels which is simple, effective and thoroughly reliable, and which employs available heat exchange apparatus and equipment.

Other objects of my invention in part will be obvious from a reading of the description which follows and in part particularly pointed out in the course of that description.

My invention, accordingly, resides in the combination of operational steps, in the temperatures and times of treatment employed, and in the relation of each of the same to one or more of the others as described herein, the scope of the useful application of which is set forth in the claims at the end of this specification.

In order to better understand certain features of my invention it is to be noted at this point that the heat-hardenable chromium-nickel stainless steels, and especially the chromium-nickel-aluminum stainless steels, have found great favor in the arts. Attention is drawn to the U.S. Patent 2,506,558 of May 2, 1950, issued to George N. Goller. And more especially, reference is made to the 17–7PH grade of the Armco Steel Corporation, this analyzing approximately 16% to 18% chromium, 6% to 8% nickel, 0.50% to 1.50% aluminum, 0.02% to 0.15% carbon, and remainder substantially all iron. Reference also is made to the Armco PH13–7Mo grade analyzing approximately 14% to 16% chromium, 6% to 8% nickel, 0.50% to 1.50% aluminum, 0.02% to 0.15% carbon, and remainder iron. Additional reference is made to the Armco PH13–7Mo grade which analyzes approximately 12% to 14% chromium, 6% to 8% nickel, 0.50% to 1.50% aluminum, 3% to 6% molybdenum, 0.02% to 0.15% carbon, and remainder iron.

The various heat-hardenable chromium-nickel stainless steels noted above are commonly annealed by suitable heat-treatment at the mill, annealing then cooling in air, oil or water, and then shipped to various customer fabricators. The fabricators work and form the metal into a variety of articles of ultimate use and then transform to give a martensite-like constituent and harden the same by desired heat exchange methods employing cold-treatment, followed by heat-treatment to age-harden, or employing a heating and cooling followed by a reheating to age-harden, all as noted in said Goller patent. I find that the heat-hardenable chromium-nickel-aluminum stainless steels are sensitive to particular analysis differences so that many of them must be stabilized in order to prevent an unwanted transformation in shipment as in water weather over long distances. Unfortunately, however, many of these stabilized steels, and many of the steels which, in absence of a special stabilizing treatment, are sufficiently stable to withstand cold weather shipment without transformation, do not adequately respond to desired transformation and hardening following the working or forming operations.

More particularly, I find that in the 17–7PH stainless steels where chromium is on the low side, or nickel is on the low side, or both chromium and nickel are low, a low annealing temperature makes it difficult to subsequently stabilize the steel. Conversely, where either or both the chromium and nickel contents are high, the steel is stabilized following annealing at low temperature, but, unfortunately, it does not readily respond to cold temperature transformation and hardening following shipment.

Similarly, the 17–7PH steel, irrespective of vagaries in composition, is sensitive to variations in the annealing temperatures as well as in the temperatures of the stabilizing treatment. For with an anneal, that is, anneal at the lower annealing temperatures, there is an inclination to transform in cold weather shipment irrespective of the stabilizing temperatures employed. Moreover, I find that a stabilizing treatment of short duration is ineffective irrespective of the temperature of the stabilizing treatment.

The various problems encountered greatly multiply when the heat-hardenable chromium-nickel-aluminum stainless steel is in the form of sheet, strip and other flatRolled products. Where high annealing temperatures are employed, there is some inclination to develop a rough surface. And although sheet and strip is stabilized by the high temperature annealing treatment followed by the stabilizing treatment I find that it frequently is difficult to transform such sheet and strip through the prior art low temperature transformation treatment, that is, treatment at a temperature of about —100° F.

Accordingly, one of the objects of my invention is the
provision of an art or method of treating the heat-harden-
able chromium-nickel stainless steels, and particularly the chromium-nickel-aluminum stainless steels, to posi-
tively assure freedom from unwanted transformation.

2. Cold weather shipment, irrespective of differences in the chromium and nickel analysis of the various heats of metal being shipped, and yet which fully respond to low

temperature transformation treatment and heat-hardening

treatment to achieve high yield strengths, that is, on the order of 190,000 p.s.i., and ultimate strengths which

may exceed 200,000 p.s.i.

Referring now more particularly to the practice of my invention, I first anneal the heat-hardenable chromium-

nickel stainless steels at a temperature of about 1800° F.

This annealing treatment, however, may be conducted at a

temperature of 1700° to 1850° F. In general, the lower

annealing temperature, that is, on the order of 1700° F,

is employed for the analyses of the greater austenite

stability, that is, chromium on the high side or nickel on

the high side, or both chromium and nickel high.
The higher annealing temperatures, that is, about 1850° F.,

are employed for the steels of the less stability, that is,

with chromium on the low side, or nickel on the low side,

or both chromium and nickel low. And the time of the

annealing treatment which I prefer ranges from a fraction

of a minute up to 30 minutes for sheet, strip, light plate

tubes, and some 15 minutes to 1 hour for bars, heavy

plate and shapes. The annealed steel is cooled in air, oil

or water, as is well known.

I find that the annealing treatment at about 1800° F.
gives the austenite constituent of the steel a medium range

of stability. While some of the steels in the annealed

condition would not transform in cold weather shipment,
I find that many would, particularly where temperatures

as low as —30° F. are reached. In order to assure a

freedom from unwanted transformation at such low

shipping temperatures I stabilize the steel by reheating it to

a temperature of about 900° F. for about 4 hours and

cooling. Actually, I find that the stabilizing treatment

may be conducted at a temperature of 850° to 950° F.

for a period of from 2 hours at the higher temperature

on up to about 12 hours or more at the lower temperature.

This treatment assures a consistent suppression of any

tendency for cold weather transformation. There is

no change in the microstructure of the steel; under the

microscope it looks like austenite.

The annealed and stabilized steel is received by the

customer in the stabilized condition. It has good form-

ing and working properties and readily lends itself to a

variety of operations such as cutting, bending, machining,
punching, stamping, heading and the like. Unfortu-
nately, however, I find that the various worked and

formed products cannot be immediately hardened by

cold-transformation and heat-hardening methods to con-

sistently develop great strength.

In accordance with my invention I find that by re-

heating the steel in the customer plant at a tempera-
ture of about 1100° F. the steel is activated. And by

subsequent heat exchange treatment as by cold treat-

ment followed by further heat treatment great strength

is consistently had. While I do not care to be bound by

the explanation, I feel that there is a precipitation of

some carbides which in some way unknown to me assures

subsequent transformation by cold treatment and heat-

hardening by final heat treatment. Apparently, with the

precipitation of carbides, principally chromium carbides,

there is a depletion of the chromium content of the ma-

trix of the metal. And this lessens the stability; chro-

mium although a well-known ferrite-former, also serves

to stabilize austenite and a lowering of the effective chro-

mium content lessens the stability. Perhaps there is also

some adjustment of the Ms point. In any event, how-

ever, the steel more readily transforms upon subsequent
cold treatment. And it hardens to a greater degree upon

final hardening treatment.

In general, the activation treatment of my invention

may be conducted at a temperature as low as 950° F.,
this for at least one hour, and as high as 1150° F., this

for about 5 minutes or less. At the high temperature I

find that the time of treatment must not exceed 30

minutes for otherwise there is a loss in ductility and other

physical properties. With an activation temperature

of 1000° F. I find that time at such temperature should

be about ½ hour to 4 hours. And at 1100° F. for a

time of 30 minutes to about 30 minutes.

Best results for the under annealed steels (tempera-
tures of about 1775° F.) are had where the activation

treatment is had by heating at 1100° F. for about 10

minutes. This activation treatment also is employed for

the steels where annealed at the higher annealing tem-

peratures.

The activated steel now is subjected to refrigeration

treatment to effect transformation to give a martensite-

like constituent and place the metal in condition for final

hardening. Preferably, the metal is cooled at a tempera-

ture of about —75° F. for a time of 2 hours or more.

Although a temperature of about —75° F. is preferred, I

find that some latitude in treating temperature is per-

missible. In general the temperature may range from

—30° F. down to —150° F. And the time of treatment

from 1 hour to 24 hours.

In the practice of my invention final hardening is

achieved by reheating the steel to a temperature range of

700° to 1150° F. The time for treatment is from a

couple of minutes up to about 24 hours. Best results

are had with a heat-hardening treatment at 900° to

950° F. for about 1 hour. At this narrow hardening tempera-
ture range there is had most rapid ageing and peak

strength is achieved. I find that where a lower harden-

ing temperature is employed the properties are somewhat

less favorable. And so, too, where a higher precipita-

tion temperature is used less favorable results are had.

As specific illustration of the practice of my invention

I have prepared a series of 17—7PH stainless steels of

analyses set forth in Table I below. These various sam-

ples, in the form of sheet, were annealed and box stabil-

ized, then held at winter temperatures for substantial

periods of time to simulate shipping conditions, then

activated, refrigerated and finally precipitation-hardened.

TABLE I

<table>
<thead>
<tr>
<th>Heat</th>
<th>C</th>
<th>Mn</th>
<th>F</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>60800</td>
<td>.074</td>
<td>.77</td>
<td>.024</td>
<td>.006</td>
<td>.21</td>
<td>17.17</td>
<td>7.16</td>
<td>1.31</td>
</tr>
<tr>
<td>60810</td>
<td>.060</td>
<td>.69</td>
<td>.024</td>
<td>.017</td>
<td>.46</td>
<td>17.24</td>
<td>7.25</td>
<td>1.00</td>
</tr>
<tr>
<td>60820</td>
<td>.072</td>
<td>.60</td>
<td>.018</td>
<td>.008</td>
<td>.39</td>
<td>17.10</td>
<td>7.21</td>
<td>1.26</td>
</tr>
<tr>
<td>60830</td>
<td>.065</td>
<td>.60</td>
<td>.019</td>
<td>.008</td>
<td>.39</td>
<td>17.10</td>
<td>7.21</td>
<td>1.18</td>
</tr>
<tr>
<td>60850</td>
<td>.079</td>
<td>.65</td>
<td>.020</td>
<td>.007</td>
<td>.43</td>
<td>17.13</td>
<td>7.20</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Samples, in the form of sheet, of each of the heats of

17—7PH stainless steel of the analyses indicated above

were annealed, some at 1750° F., others at 1775° F. and

still others at 1800° F., all for a period of about ½

minute. Following this they were box stabilized at a

temperature of 900° F. for a period of 4 hours. During

this treatment the samples were slowly heated and

slowly cooled to simulate commercial practice. They

were then maintained at a temperature of 0° F. for 132

hours, in order to simulate winter shipment. Follow-

ing this the various samples were activated at 1100° F.

for 10 minutes, refrigerated at —110° F. for 24 hours

and then hardened by heating at a temperature of 900°

F. for 1 hour. The mechanical properties of the vari-

ous samples both immediately following the simulated

cold weather shipping conditions and after activation,
transformation and hardening, are given in Table II below:

### TABLE II

**Mechanical properties of the under annealed and stabilized samples of 17-7PH stainless steel sheet of analyses of Table I(A) after simulated cold weather shipment and (B) after final hardening**

<table>
<thead>
<tr>
<th>Heat</th>
<th>Anneal. Temp.</th>
<th>(A) After 132 Hrs., 0°F.</th>
<th>(B) After Final Hardening</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.2% Y.S., p.s.i.</td>
<td>T.S., p.s.i.</td>
</tr>
<tr>
<td>2300...</td>
<td>1,770</td>
<td>99,400</td>
<td>128,000</td>
</tr>
<tr>
<td></td>
<td>1,775</td>
<td>71,400</td>
<td>158,200</td>
</tr>
<tr>
<td></td>
<td>1,800</td>
<td>65,200</td>
<td>144,400</td>
</tr>
<tr>
<td>445...</td>
<td>1,770</td>
<td>75,000</td>
<td>142,000</td>
</tr>
<tr>
<td></td>
<td>1,800</td>
<td>65,000</td>
<td>140,000</td>
</tr>
<tr>
<td></td>
<td>1,830</td>
<td>55,000</td>
<td>132,000</td>
</tr>
<tr>
<td>410-...</td>
<td>1,770</td>
<td>65,000</td>
<td>152,300</td>
</tr>
<tr>
<td></td>
<td>1,775</td>
<td>56,000</td>
<td>152,300</td>
</tr>
<tr>
<td></td>
<td>1,800</td>
<td>56,000</td>
<td>154,800</td>
</tr>
<tr>
<td>4685...</td>
<td>1,775</td>
<td>57,000</td>
<td>141,000</td>
</tr>
<tr>
<td></td>
<td>1,800</td>
<td>54,200</td>
<td>137,200</td>
</tr>
<tr>
<td>3289...</td>
<td>1,775</td>
<td>44,000</td>
<td>155,500</td>
</tr>
<tr>
<td></td>
<td>1,780</td>
<td>40,600</td>
<td>152,700</td>
</tr>
<tr>
<td></td>
<td>1,800</td>
<td>41,500</td>
<td>152,000</td>
</tr>
</tbody>
</table>

OG=Sample broke outside gauge marks.

Study of Table II reveals that all of the samples of the 17-7PH stainless steel, whether annealed at 1750°, 1775° or 1800° F., possessed good ductility following cold weather simulated shipment in the annealed and box stabilized condition. The 0.2% yield strength ranges from 62,800 p.s.i. for one of the samples annealed at 1800° F. to 112,500 p.s.i. for a sample annealed at 1750° F., with elongation in 2" for these samples ranging from 21% and hardness Rockwell B94.0 down to 11% and hardness Rockwell C32.0. At the same time it is to be noted that minimum yield and maximum elongation generally are had with the higher annealing temperatures. In all of the samples the mechanical properties suggest reasonably good workability.

After final hardening it will be seen from Table II that there is had great tensile strength, this in every case exceeding 200,000 p.s.i., with 0.2% yield strengths in every case exceeding 190,000 p.s.i. The hardness in every case is Rockwell C44.0 or better.

The activation treatment employed in the art of my invention is rather critical in terms of the treating temperature employed and the time of treatment. I generally find that with low treating temperatures the mechanical properties following transformation and final hardening are somewhat erratic. Samples activated at 1000° and 1100° F., however, consistently responded to the final hardening treatment, the 1000° F. activation treatment being best maintained for a period of 10 minutes to 4 hours, while the 1100° F. treatment being best for a period of 10 minutes or less to about 30 minutes. All of this is rather pointedly shown in tests made on a representative heat of steel of the Table I, as shown in Table III below. The samples of the steel were annealed at 1800° F. for 15 minutes and air cooled, then box stabilized at 900° F. for 4 hours. They were then subjected to simulated cold weather transportation of 336 hours at 0° F., following which they were activated at the temperatures and the times indicated in the table.

### TABLE III

**Effect of activation temperatures and times of activation on the physical properties of the 17-7PH stainless steels**

<table>
<thead>
<tr>
<th>Activation Temp., °F.</th>
<th>Time</th>
<th>0.2% Y.S., p.s.i.</th>
<th>T.S., p.s.i.</th>
<th>Percent R. in 2&quot;</th>
<th>R.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>45 m</td>
<td>125,000</td>
<td>196,000</td>
<td>12 41.0</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>90 m</td>
<td>125,000</td>
<td>196,000</td>
<td>14 45.0</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>120 m</td>
<td>125,000</td>
<td>196,000</td>
<td>12 45.0</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>180 m</td>
<td>125,000</td>
<td>196,000</td>
<td>12 45.0</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>240 m</td>
<td>125,000</td>
<td>196,000</td>
<td>12 45.0</td>
<td></td>
</tr>
</tbody>
</table>

OG=Sample broke outside gauge marks.

Thus it will be seen that I provide in my invention an art for consistently and reliably hardening the chromium-nickel heat-hardenable stainless steels from a fully stabilized condition. Additionally, it will be seen that I provide a steel which is stable, well calculated to resist transformation in winter shipment where sub-zero temperatures are reached and where the time of shipment may run into many days, and yet which by my novel method of treatment may be hardened to develop yield strengths in excess of 190,000 p.s.i. and ultimate strengths in excess of 200,000 p.s.i.

While best results in the art and products of my invention are had in the heat-hardenable chromium-nickel-aluminum stainless steels, I find that many beneficial characteristics are had with the treatment of any heat-hardenable chromium-nickel stainless steel. Benefit notably is had in the heat-hardenable chromium-nickel stain-
In the art and products of my invention there are enjoyed many new and unsuspected beneficial characteristics hereinafter set forth, together with many thoroughly practical advantages. Since many embodiments may be made of the art of my invention and since many changes may be made in the embodiments herein particularly set forth, it is to be understood that all matter described in this specification is to be interpreted as illustrative and not by way of limitation.

I claim as my invention:

1. In the production of heat-hardened chromium-nickel stainless steel products, the art which comprises annealing a heat-hardenable chromium-nickel stainless steel at a temperature of 1700° to 1850° F. and cooling; preheating the steel at a temperature of 850° to 950° F. to stabilize the same forming the steel into products of desired configuration; activating the stabilized steel by reheating at a temperature of 950° to 1150° F. for a time of about 5 minutes or less at the higher temperature to 1 hour or more at the lower temperature; transforming the steel by refrigeration at a temperature of −30° to −150° F.; and then hardening the activated and refrigerated steel by reheating at a temperature of 700° to 1150° F.

2. In the production of heat-hardened chromium-nickel-aluminum stainless steel sheet and strip products, the art which comprises annealing heat-hardenable chromium-nickel-aluminum strip at a temperature of 1700° to 1850° F. for a fraction of 1 minute to 10 minutes and cooling; stabilizing the same by reheating at a temperature of 850° to 950° F.; working or fabricating the sheet or strip into desired products; activating the steel by reheating at a temperature of 950° to 1150° F. for a time of about 5 minutes or less at the higher temperature and 1 hour or more at the lower temperature; transforming the steel by refrigerating the same at a temperature of about −75° F.; and then hardening the same by reheating the products at a temperature of about 900° F.

3. In the production of heat-hardened chromium-nickel-aluminum stainless steel bar products, the art which comprises annealing heat-hardenable chromium-nickel-aluminum stainless steel bar stock at a temperature of 1700° to 1850° F. for about 15 minutes to 1 hour and cooling; stabilizing the same by reheating at a temperature of 850° to 950° F. for 12 hours or more at 850° to about 2 hours for 950° F.; working or forming the steel into desired products; activating the same by heating at a temperature of 950° to 1150° F., the heating at the higher temperature being not over 30 minutes, while that at the lower temperature being at least 1 hour; transforming the same by refrigeration at a temperature of about −75° F.; and hardening the products by reheating at a temperature of about 900° F.

4. In the production of hardened chromium-nickel stainless steel products, the art which comprises activating previously annealed and stabilized heat-hardenable chromium-nickel stainless steel products by heating the same at a temperature of 950° to 1150° F. for a time of about 5 minutes or less at the higher temperature to 1 hour or more at the lower temperature; transforming the same by refrigeration at a temperature of −30° to −150° F.; and hardening the same by reheating at a temperature of 730° to 1150° F.

5. In the production of hardened chromium-nickel-aluminum stainless steel products, the art which comprises activating previously annealed and stabilized heat-hardenable chromium-nickel-aluminum stainless steel products by heating the same at a temperature of about 1100° F. for about 10 to 30 minutes; transforming the same by refrigeration at a temperature of about −75° F.; and hardening the same by reheating at a temperature of about 900° F.

References Cited in the file of this patent

UNITED STATES PATENTS

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