STAINLESS STEELS AND PRODUCTS THEREOF
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No Drawing. Filed Nov. 21, 1961, Ser. No. 154,046
4 Claims. (Cl. 75—125)

This invention relates to stainless steels and in particular it concerns such steels that are formed and used in decorative applications in which corrosive conditions are encountered.

A major object of the present invention is to provide novel stainless steel alloys and product forms thereof including strip and sheet that are characterized by the capability of being drawn or formed to various shapes for decorative applications and in that form being free from roping or ridging and particularly resistant to corrosion.

Stainless steels of the type exemplified by the American Iron and Steel Institute classification Type 430 have been widely used in the automobile, appliance, and utensil industries for applications that combine utility with decorativeness. Generally such steels are drawn or formed to the desired shape and then polished to a high degree.

In forming such articles as automobile wheel covers, body trim, sink rims, pans, mixing bowls, and the like from regular Type 430, the resulting product frequently exhibits a phenomenon called roping or ridging. This roping or ridging appears as a plurality of directional lines or bands on the surface of the article after the forming operation. These lines are unsightly and must be removed to obtain an acceptable article. Where only moderate roping occurs, polishing is effective for removing it, but manufacturers object to this additional operation and the time and expense involved in performing it.

Recent developments in the use of small additions of certain chemical elements have practically overcome the roping problem. However, with the use of the straight chromium stainless Type 430, another major problem has presented itself especially where the material is used for exterior automobile applications. This is the lack of required corrosion-resistance in Type 430.

Exterior automobile parts are constantly exposed to severe corrosive conditions. During summer months this may be moisture or rain which has absorbed corrosive agents from the atmosphere. This type of corrosive attack occurs in industrial and coastal regions. However, by far the most severe corrosive conditions occur in the winter months due, more recently, to the widespread use of various salts combined with other materials which are applied to road surfaces to reduce hazardous driving conditions, such as snow and ice.

Since such salts and the like are always present with moisture, they are continuously splashed on the exterior automobile parts. The composition of the salt used varies in different localities. In addition, the salt is mixed with ashes, slag, sand, and like substances so that the actual corrosive agent can be of quite varying compositions. The combination is especially corrosive and the industry had the problem of finding a material resistant to these corrosive conditions and which also possesses minimum roping characteristics without appreciable increase in its cost.

The present invention relates to steels as well as products formed therefrom, and it is the primary object to provide such steels and products that are particularly suited for the foregoing purposes in that they are both free from roping upon being deep drawn or formed by other severe forming methods, are corrosion resistant and yet are not unduly more expensive than competitive alloys. The resulting products can be used in the same manner as Type 430 and analogous stainless steels are now used, but with the advantages just specified.

The stainless steels that comprise the present invention are substantially straight chrome steels. For example, and except for the variations hereinafter noted, the AISI Type 430 steels are representative of one particular analysis within the invention.

The straight chrome stainless ferritic steels embodying the present invention and by which its stated objects are attained contain, by weight, about 14 to 25 percent of chromium, up to a maximum of about 0.30 percent of carbon, up to about 1.25 percent of manganese, a maximum of 1 percent of silicon, at least one member selected from the group consisting of 0.01 to 0.75 percent of vanadium and 0.01 to 1 percent of columbium, 0.25 to 1.25 percent of molybdenum, 0.25 to 1.25 percent of copper, with the remainder iron and incidental impurities. Where such elements as phosphorus and sulfur are present, they do not exceed about 0.04 to 0.03 respectively. In addition, alloying constituents can be included to develop special characteristics as desired provided they do not detract from the non-roping and corrosion resistant characteristics of the resulting products.

Within the foregoing broad range, intermediate ranges are definitive of steels that are of particular interest, usually as a consequence of an intended application. A suitable intermediate range of straight chrome ferritic stainless steel compositions in accordance with this invention includes, by weight, 14 to 19 percent of chromium, 0.15 percent maximum of carbon, a maximum of 1 percent of manganese, a maximum of 1 percent of silicon, a maximum of 0.04 percent of phosphorus, a maximum of 0.03 percent of sulfur, one member from the group consisting of 0.1 to 0.6 percent of vanadium and 0.1 to 0.7 percent of columbium, 0.40 to 1.10 percent of molybdenum, 0.40 to 1.10 percent of copper, and the remainder iron and incidental impurities. A particularly preferred range is one which has molybdenum present in the range of 0.5 to 1.0 percent, copper in the range of 0.5 to 1.0 percent, and columbium in the range of 0.2 to 0.7 percent. An additional preference is that the combined columbium and/or vanadium, copper, and molybdenum contents should exceed 1.25 percent.

It will be evident that all alloys within the foregoing ranges are not equivalent for all purposes. The particular analysis chosen is usually indicated by known conditions of the end use. Thus, one product may require outstanding corrosion resistance but only moderate roping resistance, while those considerations may be of reverse order of importance for some other application.

The steels of the present invention are prepared in the same general manner that Type 430 steels and its variations are now prepared. Similarly, the manner of forming shapes from the resulting products that are presently used is satisfactory in producing products in accordance with this invention.

The invention will be described in conjunction with the following examples in which the details are given by way of illustration and not by way of limitation. A batch of stainless steel in accordance with the invention was prepared by melting in an electric furnace used for the commercial production of steel. The heat, as cast, weighed 10,000 pounds. Ingots were poured from the heat and, when solidified, were cooled, hot worked, and subsequently were cold worked to strip and
annealed in accordance with standard practices for Type 430 steel. The analysis of this heat was as follows, in weight percent:

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.062</td>
</tr>
<tr>
<td>Mn</td>
<td>0.56</td>
</tr>
<tr>
<td>Si</td>
<td>0.33</td>
</tr>
<tr>
<td>S</td>
<td>0.010</td>
</tr>
<tr>
<td>P</td>
<td>0.018</td>
</tr>
<tr>
<td>Cr</td>
<td>17.81</td>
</tr>
<tr>
<td>Mo</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu</td>
<td>0.06</td>
</tr>
<tr>
<td>Nb</td>
<td>0.40</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Strip of this material was tested by commercial procedures for roping characteristics. Visual inspection of the test specimens showed them to have good non-roping characteristics.

This steel was subjected to corrosion tests used in the automobile manufacturing industry for evaluating the resistance to corrosion of various materials and especially of steels used for the purpose for which the steel of this invention was developed. In addition, other tests to determine resistance to corrosion were made.

One such test used in the automobile industry is commonly known as the Cass test. Specimens of 0.019 inch strip, having the surface in the "mill finished" condition, were subjected to a spray of the Cass solution in a cabinet maintained at a temperature of 120° F. The Cass solution consisted of 4.2 pounds of sodium chloride, 10 grams of cupric chloride, and 10 gallons of distilled water. The pH of the solution was adjusted to 2.8 to 3.0 with glacial acetic acid. After 16 hours of exposure in the spray cabinet, the specimens were removed, visually examined, and rated according to a procedure established by an automobile manufacturing company in which a rating of 3 or higher indicates failure due to surface corrosive attack. The specimens of this material had the best possible rating of 1 and, therefore, are considered particularly resistant to corrosive conditions to which automobile parts are subjected.

Another test, used to determine resistance to corrosion of automobile materials, is called the Dip-Dri test. This test was devised to simulate corrosive conditions encountered in certain districts where slag, salt, and calcium chloride are used for winter road delcing. The solution used consisted of specified quantities of sodium sulfate, sodium thiosulfate, sodium chloride, calcium chloride, and distilled water. An automatic cycle timer and elevating mechanism raised and lowered the test samples into the solution, adjusted to a pH of 9.3±0.05 for an 8-hour period. One complete cycle required from 98–102 seconds. This involved immersion for 1 to 2 seconds and a drying period of 98–102 seconds. The samples were dried and maintained during the dry period at a temperature of 110° to 130° F, by means of a heat lamp. After the test was completed, the samples were cleaned, dried, and visually examined for pits and rust products. Specimens from the heat, having a size of 1 x 6 x .019 inch were subjected to this test and upon examination after completion of the test, were found to be entirely free of pitting or corrosive attack, indicative of the quite satisfactory corrosion resistant characteristics of the alloy.

Another test, used for determining resistance to corrosion, is the total immersion test using a chloride solution. The procedures followed were those specified in ASTM standard A279-44T. The solution used consisted of 10 grams of ferric chloride, 5 grams of sodium chloride, 2.5 ml of hydrochloric acid (concentrated), and 200 ml of distilled water. Using separate beakers, individual specimens were immersed in 250 ml of the solution at room temperature. The specimens were weighed before and after each 48-hour period of immersion. The corrosion rate in inches penetration per year was calculated for each testing period and for the total number of periods. This alloy, tested for three 48-hour periods, had a corrosion rate of 0.243 inch penetration per year.

The mechanical properties of this steel were determined on annealed and pickled strip 0.019 inch thick that had been subjected to a temper pass. The ultimate tensile strength was 83,000 p.s.i., the 0.2 percent offset yield strength was 57,000 p.s.i., and the elongation was 23 percent in a 2 inch gauge length. These properties are representative of the properties for all steels within the invention, for they exhibit an ultimate tensile strength of at least 70,000 p.s.i., the 0.2 percent offset yield strength of at least 45,000 p.s.i., and a 15 percent minimum elongation in two inches.

In addition to the heat mentioned above, other steels of the invention were prepared in the same manner. Specimens were then tested for corrosion resistance by several procedures, including those established by automobile manufacturing companies.

Specimens of these steels were subjected to the Cass test as previously described. Upon visual examination after completion of the test, all specimens were found to have a rating of 1, indicative of very good resistance to corrosion.

In addition, specimens of these steels were also subjected to the Dip-Dri, total immersion with sulfate solution, and total immersion with chloride solution tests for corrosion. The Dip-Dri and the total immersion with chloride solution tests were previously described. The total immersion test with sulfate solution also uses the procedures as set forth in ASTM standard A279-44T. The solution used was composed of 0.50 gram of anhydrous sodium sulfate, 0.25 gram of anhydrous sodium sulfate, 0.10 gram of anhydrous sodium thiosulfate, 5.5 grams of sodium chloride (CP), 5.5 grams of hydrated calcium chloride (CaCl₂·2H₂O), and 1050 ml of distilled water. Using a flask containing 500 ml of this solution maintained at the boiling point, duplicate specimens were immersed in the solution. The specimens were weighed before and after each 48-hour period of immersion. The corrosion rate in inches penetration per year was calculated for each testing period and for the total number of periods. Specimens from these steels were tested for five 48-hour periods and the corrosion rate calculated. Specimens of regular Type 430 were tested at the same time and under the same conditions. The analyses of these steels and the resistance to corrosion data obtained are given in Table I.

### Table I

<table>
<thead>
<tr>
<th>Heat</th>
<th>&quot;C&quot;</th>
<th>&quot;Mn&quot;</th>
<th>&quot;Si&quot;</th>
<th>&quot;Cr&quot;</th>
<th>&quot;Mo&quot;</th>
<th>&quot;Cu&quot;</th>
<th>Dip-Dri I, percent</th>
<th>Total Immersion Sulfate Solution 1</th>
<th>Total Immersion Chloride Solution 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.039</td>
<td>0.44</td>
<td>0.16</td>
<td>16.74</td>
<td>0.83</td>
<td>0.38</td>
<td>1.00</td>
<td>0.07</td>
<td>0.0391</td>
</tr>
<tr>
<td>2</td>
<td>0.065</td>
<td>0.44</td>
<td>0.25</td>
<td>16.80</td>
<td>0.55</td>
<td>0.41</td>
<td>0.52</td>
<td>0.05</td>
<td>0.0324</td>
</tr>
<tr>
<td>3</td>
<td>0.067</td>
<td>0.62</td>
<td>0.27</td>
<td>16.28</td>
<td>0.03</td>
<td>0.54</td>
<td>None</td>
<td>None</td>
<td>0.0303</td>
</tr>
<tr>
<td>4</td>
<td>0.067</td>
<td>0.53</td>
<td>0.23</td>
<td>16.44</td>
<td>0.03</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>0.0610</td>
</tr>
</tbody>
</table>

1 Rated in percent area showing pits.
2 Rated in inches penetration per year for five 48-hour test periods.
3 Rated in inches penetration per year for three 48-hour test periods.
Heats identified as 1 and 2 are alloys of this invention while heats 3 and 4 are regular Type 430 compositions. The improvement in resistance to corrosion of alloys of this invention is apparent from a comparison of these data.

From the foregoing, it is evident that the present invention constitutes a significant advance in providing straight chrome ferritic stainless steels that are free from roping and highly corrosive resistant. The invention marks a clear improvement in the art, and it is evident that it will enjoy marked commercial acceptance. These unique results are further advantageous in that normal production and utilization practices can be carried out in achieving them with skills presently available in the art.

In accordance with the provisions of the patent statutes, the invention has been explained with what is now considered to be its best embodiment. However, within the scope of the appended claims, it should be understood that the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A corrosion resistant straight chrome ferritic stainless steel consisting essentially, by weight, of about 14 to 25 percent of chromium, up to a maximum of about 0.30 percent of carbon, up to about 1.25 percent of manganese, a maximum of 1 percent of silicon, about .001 up to 1 percent of columbium, 0.25 to 1.25 percent of molybdenum, 0.25 to 1.25 percent of copper, with the remainder iron and incidental impurities, which steel is free from roping upon being formed and has an ultimate tensile strength of at least 70,000 p.s.i., a 0.2 percent offset yield strength of at least 45,000 p.s.i. and an elongation of at least 15 percent.

2. A corrosion resistant straight chrome ferritic stainless steel consisting essentially, by weight, of 14 to 19 percent of chromium, 0.15 percent maximum of carbon, a maximum of 1 percent of manganese, a maximum of 1 percent of silicon, a maximum of 0.04 percent of phosphorus, a maximum of 0.03 percent of sulfur, about 0.40 to 1.10 percent of molybdenum, about 0.1 to 0.7 percent of columbium, about 0.40 to 1.10 percent of copper and the remainder iron and incidental impurities and alloying constituents, said molybdenum, columbium, and copper totaling a minimum of 1.25 percent, which steel is free from roping upon being formed.

3. A decorative article for use on an automobile and which is free from roping and is corrosion resistant, said article having a composition in accordance with claim 1.

4. A formed article free from roping and corrosion resistant having a composition according to claim 2.

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DAVID L. RECK, Primary Examiner.

RAY K. WINDHAM, Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,183,080

Norman R. Harpster

May 11, 1965

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 28, for ".001" read -- 0.01 --.

Signed and sealed this 28th day of September 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents