

UNITED STATES PATENT OFFICE

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METHOD OF IMPROVING THE CORROSION
RESISTANCE OF CHROMIUM ALLOYSHerbert H. Uhlig, Schenectady, N. Y., assignor to
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New YorkNo Drawing. Application September 22, 1944,
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2 Claims. (Cl. 148-6.35)

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The present invention is a method for improving the corrosion resistance of chromium alloys. The oxidation resistance of such alloys improves with increase in the chromium content. Also, the resistance of such alloys to corrosion in aqueous media improves with increase in chromium content although not in the same fashion. Alloyed with iron, 12% chromium in aqueous media is a critical composition. For example, alloys containing less than 12% chromium rust in the manner characteristic of iron while those alloys which contain more than 12% chromium are in the class commonly known as stainless irons and steels. Any method therefore which increases the surface concentration of chromium will improve the corrosion resistance of the alloy regardless of the original surface concentration.

It is one of the objects of the present invention to provide a simple method for increasing the corrosion resistance of alloys containing chromium. It is a further object of the invention to provide an improved method for increasing the surface concentration of chromium in chromium alloys. Other objects will appear hereinafter.

In carrying out my invention I may improve the oxidation resistance of any chromium alloy regardless of its original chromium content. If the alloy, for example, contains less than 12% chromium my improved method may be employed to increase the surface concentration of chromium to a point above 12% which will produce a stainless alloy surface. The increase in surface concentration of a chromium alloy is accomplished by diffusing chromium from the interior of the alloy. The diffusion takes place at elevated temperatures provided an appropriate concentration gradient of chromium can be established and maintained in the alloy. This concentration gradient can be obtained by preferentially reacting the surface chromium so that chromium is continually removed as a compound or a reaction product. The chromium compound can then be reduced to metal leaving an enriched chromium surface. However, if desired, the compound may be employed to protect the underlying metal from corrosion.

Hydrogen containing water vapor will react with iron-chromium alloys in a manner which meets the required conditions for chromium enrichment of the alloy surface. A mixture of hydrogen and water vapor at elevated temperatures reacts easily with chromium in an iron-chromium alloy to form Cr_2O_3 but the iron remains unaffected. The molal ratio of H_2 to H_2O at 1000°C . can be as low as 1.5 before iron is attacked,

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whereas chromium is oxidized when the molal ratio is as high as 32. Consequently, heating a chrome-iron alloy in moist hydrogen produces an adherent green chrome oxide (Cr_2O_3) coating. This oxide coating is adherent and non-porous and protects underlying metal core against further oxidation and to a greater extent than the mixture of iron and chrome oxides which is formed when the iron-chromium alloy is heated directly in air.

A .0508 cm. diameter iron-chromium wire 81.4 cm. long and containing 25% chromium was heated in a mixture of H_2 and H_2O (molal ratio=32) at 1150°C . for 68 minutes with a resultant gain of .003 gm.=0.23 mg./cm.². When wire treated as above was heated in air at 1000°C . for 24 hours it showed a loss of 0.155 mg./cm.² while an untreated wire showed a loss of 3.65 mg./cm.². Similar weight losses occurred in the second 24 hours at 1000°C . in air.

The oxide coat Cr_2O_3 on the treated wire is adherent whereas the mixed oxide coating on the untreated wire flakes off, exposing bare metal underneath. The oxide coating on the treated wire is far more protective in air than that on the untreated wire by a factor

$$\frac{3.65}{.155 + .23} = 9.5$$

The growth of oxide in the hydrogen-water mixture at 1150°C . after 3 minutes obeys the equation:

$$y = 10.85 \log t - 16.4$$

where y =mg. wt. gain/sq. decimeter and t =time in seconds.

The similarly protective value of a Cr_2O_3 coating on a nickel chrome alloy (20 Cr 80 Ni) is shown by the data below. In this case the oxide coat was formed as for the Cr-Fe alloy by heating in hydrogen which bubbles through water, since nickel like iron is not oxidized by a gas mixture of this composition.

A 16 mil wire 41.2 cm. long was heated in $\text{H}_2 + \text{H}_2\text{O}$ (molal ratio=32) at 1150°C . for 76 minutes showed a weight gain of .0007 gm.=0.13 mg./cm.². Wire so treated when heated in air at 1200°C . for 63 minutes showed a weight gain of 0.22 mg./cm.² while untreated wire under the same conditions showed a weight gain of 0.51 mg./cm.².

The above tests indicate clearly that the treated wire which oxidized in air was far superior to the untreated wire. Greater advantage may be secured by increasing the thickness of the preliminary Cr_2O_3 coat. This increase in preliminary

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oxide thickness may be accomplished by increasing the temperature and time of treatment and also by decreasing the H_2/H_2O ratio used as oxidizing atmosphere.

The amount of chromium brought to the surface in each of the above instances is small but appreciable. The enrichment of Cr produced on the 25% Cr-Fe alloy wire by heating in moist H_2 at $1150^\circ C.$ for only one hour and eight minutes is calculated to be equivalent to .01 mil of chromium metal. Commercially it is the practice to protect metal surfaces from corrosion by electrodepositing chromium layers of the order of .01 to 0.1 mil thickness. The amount of chromium diffused to the surface by the present method is therefore of the same order of magnitude as a commercial electroplate.

In producing a stainless surface on low chrome iron alloys by diffusing chromium to the surface by reaction with H_2+H_2O and then reducing the Cr_2O_3 layer with pure dry hydrogen, the chromium during the high temperature reduction has a tendency to diffuse again into the metal interior. In the short time involved however, it diffuses only a short distance and produces thereby a high chrome iron stainless alloy surface which is somewhat thicker than the equivalent .01 mil of pure chromium. Bars $\frac{1}{4}"$ thick 2" long consisting of a 5% chrome-iron alloy were heated in moist hydrogen in a furnace at $1100^\circ C.$ for 24 hours to produce an oxide scale of Cr_2O_3 . This oxide was thereafter completely reduced by heating the oxide coated metal in pure dry hydrogen at $1100^\circ C.$ for 15 minutes thereby producing a stainless or passive surface on the iron chrome alloy.

The improvement in surface properties obtained by forming a protective oxide coating is not limited to iron-chrome and nickel-chrome alloys but applies to copper-aluminum and copper-beryllium alloys and to a wide variety of heat resistant and corrosion resistant alloys. moreover, iron-chromium alloys may contain in addition to chromium and iron one or more of the following elements: Al, Mo, Co, Ni, Cu, Si, Mn and W. In chrome-iron-aluminum alloys, aluminum and chromium are oxidized by H_2 and H_2O to produce a chromium-aluminum oxide protective coating i. e., a protective coating of chromium and aluminum oxides. Iron-chromium wire or nickel-chromium wire which has been given a chrome oxide coating by my improved process is particularly useful in heating

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devices, for example in household appliances such as toasters, electric flat irons and the like which normally operate in air. The life of such heater wires when coated with chrome oxide is greatly increased over that of untreated wire.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A process for improving the corrosion resistance of an alloy containing less than 12% chromium, the remainder being principally metal of the group iron and nickel which comprises heating the alloy in a moist hydrogen atmosphere at a temperature high enough to produce a coating of Cr_2O_3 on the alloy, the ratio of hydrogen and water in said atmosphere being such as to oxidize the chromium but not the principal metal in the surface of said alloy, and thereafter reducing the said Cr_2O_3 coating to chromium metal by heating said coated alloy in an atmosphere of pure dry hydrogen.

2. A process for improving the corrosion resistance of an alloy containing less than 12% chromium, the principal metal being of the group iron and nickel which comprises heating the alloy in a mixture of hydrogen and water vapor at a temperature of about $1,000^\circ C.$ to produce a coating of Cr_2O_3 on the alloy, the molal ratio of hydrogen to water in said mixture being from 1.5 to 32 inclusive, and thereafter heating said alloy in pure dry hydrogen at about $1100^\circ C.$ until the oxide is completely reduced.

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