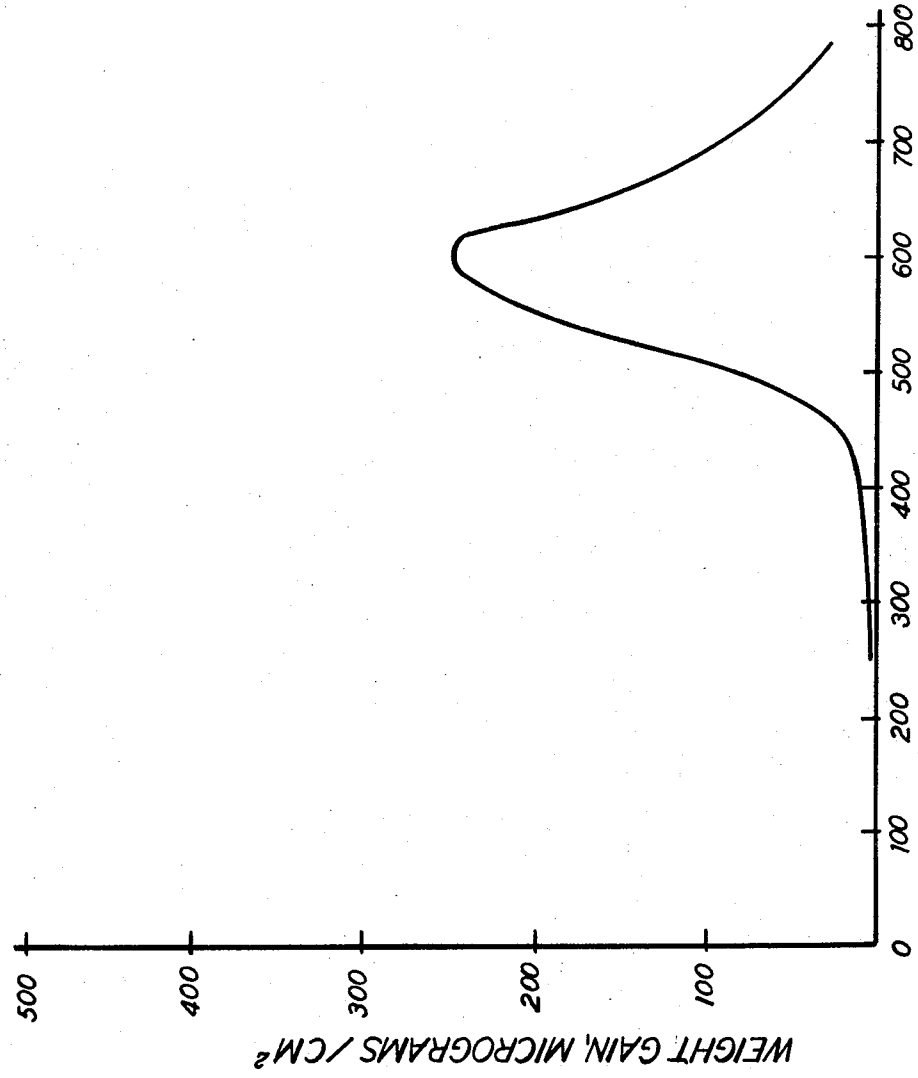


FIG - 1

INVENTORS.
ELMER J. CAULE
PHILIP R. SPERRY
MICHAEL J. PRYOR
JAMES A. FORD
BY Robert W. Beckmann
ATTORNEY

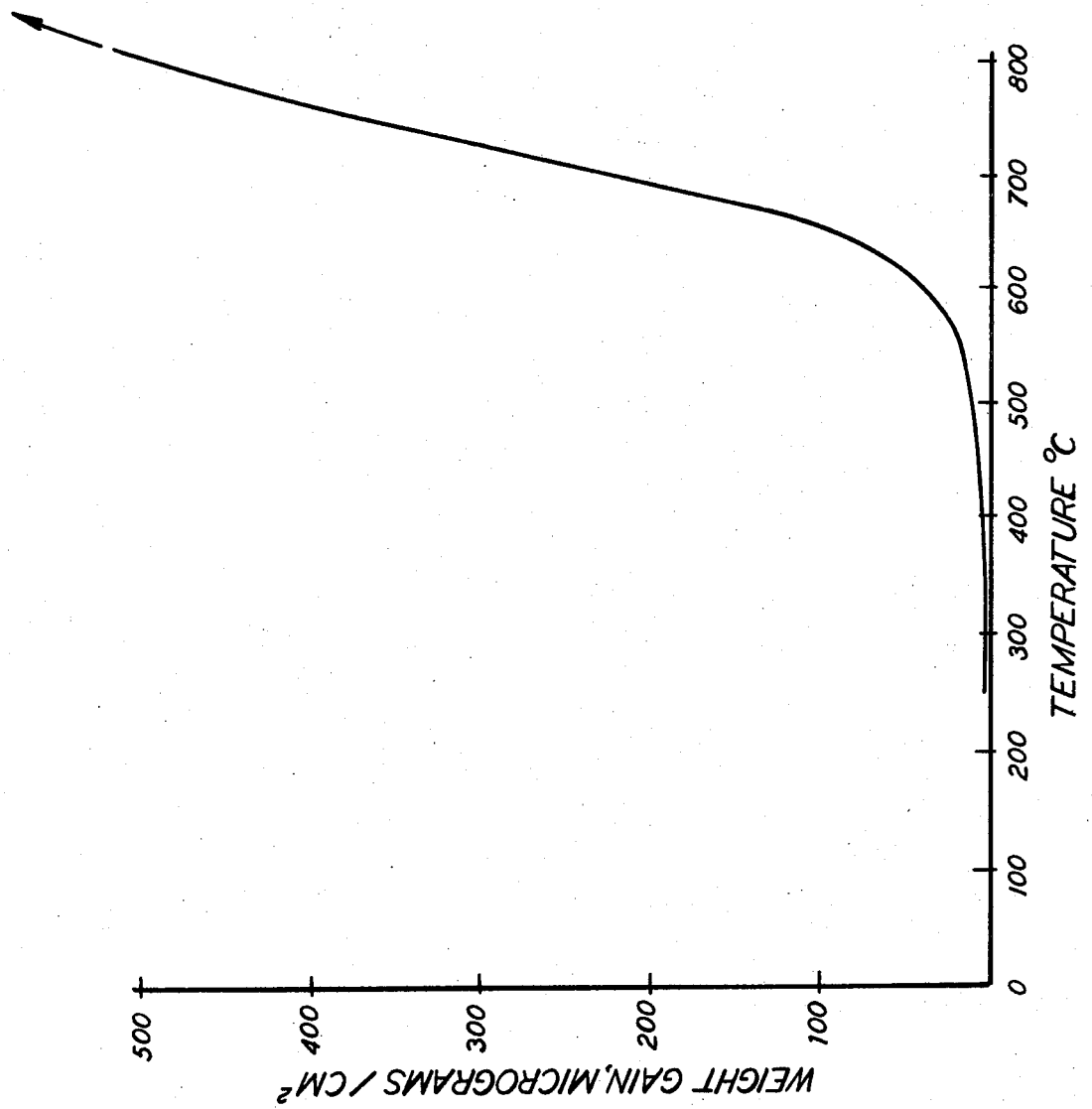


FIG-2

INVENTORS
ELMER J. CAULE
PHILIP R. SPERRY
MICHAEL J. PRYOR
JAMES A. FORD
BY Robert W. Barlow
ATTORNEY

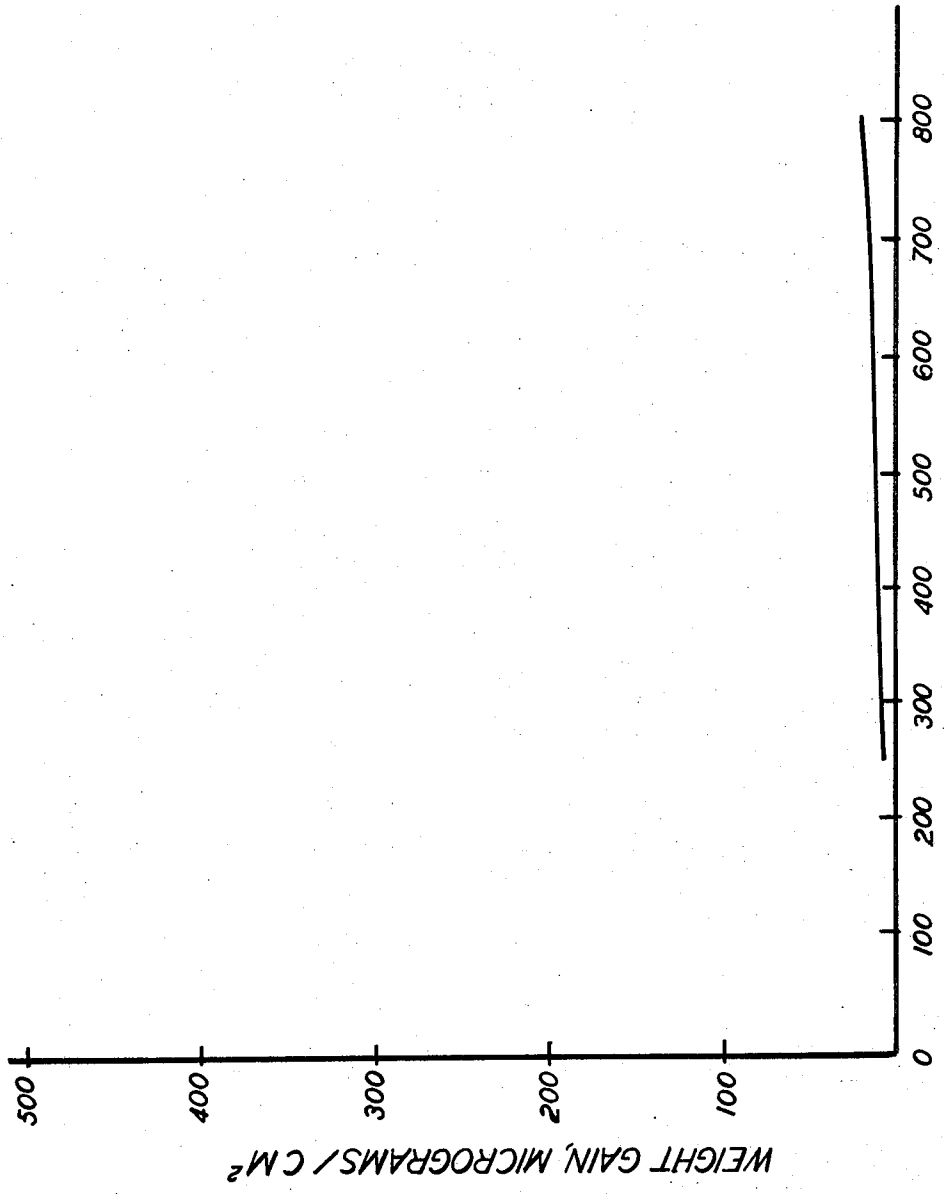


FIG-3

INVENTORS
ELMER J. CAULE
PHILIP R. SPERRY
MICHAEL J. PRYOR
JAMES A. FORD
BY Robert W. Bachman
ATTORNEY

United States Patent Office 3,698,964 Patented Oct. 17, 1972

3,698,964

OXIDATION-RESISTANT ARTICLES OF AN IRON BASE ALLOY CONTAINING CHROMIUM AND ALUMINUM AND/OR SILICON

Elmer J. Caule, New Haven, Philip R. Sperry, North Haven, Michael J. Pryor, Woodbridge, and James A. Ford, North Haven, Conn., assignors to Olin Corporation

Original application Aug. 8, 1968, Ser. No. 751,311. Divided and this application Nov. 4, 1970, Ser. No. 86,768

Int. Cl. C22c *39/06, 39/14*

U.S. Cl. 148—31.5 6 Claims

ABSTRACT OF THE DISCLOSURE

Iron base alloys with alloying additions of chromium and aluminum and/or silicon are described which exhibit unique and unexpectedly low weight gains when exposed to oxidizing environments. One of the major advantages of the group of alloys described herein lies in their moderate cost, especially as compared to other oxidation resistant Fe-base alloys such as the various grades of stainless steel containing at least 11% chromium. The oxidation resistance is imparted to these alloys through the formation of a tenacious compact oxide film consisting essentially of oxides of the alloying additions.

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of copending application Ser. No. 751,311, filed Aug. 8, 1968, for "Oxidation Resistant Iron Base Alloy Containing Chromium and Aluminum and/or Silicon," by Elmer J. Caule, Philip R. Sperry, Michael J. Pryor and James A. Ford, now abandoned.

BACKGROUND OF THE INVENTION

It has long been an objective of the art to achieve a low cost Fe-base alloy with oxidation resistance superior to that exhibited by the stainless steels containing more than 11% chromium. Presently, the only known method for providing such oxidation resistance relies in the formation of an adherent Cr_2O_3 surface layer; this requires large amounts of Cr in solid solution; in fact, it has been shown that a minimum of about 11 weight percent Cr is necessary to provide the very excellent oxidation resistance characteristics of stainless steels.

It is an object of the present invention to provide alloys which are less expensive than stainless steels.

It is another object of the present invention to provide alloys which give equal, or superior, oxidation and corrosion resistance when compared to stainless steels in the 500 to 1000° C. temperature range.

It is another object of the present invention to provide alloys which do not require special processing techniques or equipment.

Other objects and advantages will become apparent to those skilled in the art as a detailed description of a particular embodiment proceeds and with reference to the drawings which form a part hereof.

SUMMARY OF THE INVENTION

A class of alloys is described in this invention which are essentially low alloys of Fe and which have oxidation resistance significantly greater than achieved by the stainless steels in the temperature range from 500 to 1000° C.

This unusual oxidation resistance is achieved through

the addition of combinations of chromium and aluminum and/or silicon alloying elements. Specifically, extensive research has shown that the combination of Al and/or Si in a high purity Fe-base provides unusual and unexpected oxidation behavior in a high temperature air environment when used with 1 to 5% chromium. It has been shown that over the composition range of 1–5% Cr and 1–4% Si and/or 1–4%. Al, oxidation weight gain of the alloys of this invention is on the order of 20 times less than that experienced by stainless steels.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIG. 1 is a plot of weight gain in micrograms per square centimeters observed having 2% chromium-3% aluminum alloy exposed to temperatures of 250–800° C. for two hours;

FIG. 2 is a plot of weight gain in micrograms per square centimeter for type 301 stainless steel (17 chromium, 7 nickel) against temperatures in degrees C also after exposure to these temperatures for a period of two hours; and

FIG. 3 is a plot of weight gain in micrograms per square centimeter against temperatures after exposure of a 3% chromium-2% silicon alloy to temperatures from 250–800° C. for two hours.

DETAILED DESCRIPTION

As shown in FIG. 1, the combination of 3% Al and 2% Cr produces a unique and unusual reversal in oxidation weight gain in the temperature range of 600 to 900° C. Weight gains below 100 micrograms per square centimeter are obtained at temperatures of 700 to 800° C. This is in distinct contrast to the oxidation weight gain exhibited by stainless steel (type 301–17 chromium, 7 nickel) shown in FIG. 2 over the same temperature range.

The oxide films produced in this temperature range are nearly colorless and adherent. On the other hand, certain (type 301) stainless steels begin to form non-adherent scales at the higher temperatures, i.e., 900° C. This unique and distinct reversal in oxidation weight gain occurs over the range of chemistry given above, for 1–5% Cr and Al and/or Si at 1–4%.

FIG. 3 is a plot for the iron-chromium-silicon alloy of the present invention showing weight gains in micrograms per square centimeter against temperature after the alloy having the composition 3.0% chromium, 2.0% silicon shown was heated for two hours in the temperature range of 250 to 800° C. It is apparent that the alloy had much lower weight gains than the type 301 stainless steels shown in FIG. 2 in the 500 to 800° C. temperature range. In fact, from this data, it is apparent that weight gains below 50 micrograms per square centimeter are assured for the entire temperature range.

The decrease in the weight gain with temperature is believed to result from the formation of alumina, Al_2O_3, together with complexes such as $FeO.Al_2O_3$. When silicon is present in addition to aluminum, the silicon appears to stimulate the formation of these compounds in a manner not clearly understood.

In the case of silicon alloyed with chromium, the silicon stimulates the formation of chromium oxide compounds in a manner not clearly understood.

It will be apparent that the alloys of the present invention are considerably less expensive than alloys containing chromium in amounts of at least 11%; for example, 18 chromium-8 nickel is commonly used.

The Fe-base alloys of the present invention may be processed according to ordinary Fe-base melting, casting, and hot and cold working procedures. The alloys of the

present invention do not require specialized equipment or technology.

For example, the alloys of the present invention may be vacuum cast, homogenized, for example, at 1800° F., hot rolled to approximately 0.200 inch, with a reheat to 1800° F., if desired, scalped, and cold rolled without interannealing from 0.20 gage to 0.015.

The steel to be used in the present invention does not, however, require vacuum casting. Ordinary steel making procedures may be used such as blast furnace treatment with either open hearth or LD process reduction of the carbon content, as is well known in the art. The resulting composition of the alloys may be as follows: phosphorus and sulfur, 0.04 max. each, manganese may be up to 1.5%, preferably up to 0.2%, copper may be present as high as 2%, but preferably not more than 0.5%, others, including nickel, molybdenum, vanadium, and other alloying elements commonly present in low alloy steels may be present up to 0.20%. The carbon content may range as high as 2%, for some applications requiring very high wear resistance. However, the carbon content is preferably not more than about 1%. Furthermore, the most preferred range of carbon is from 0.01 to 0.25%. It is expected that the latter range will have the most general application.

As a further superior feature of these alloys, it has been found that the alloys of the present invention are highly resistant to atmospheric oxidation and tarnishing after first being exposed to high temperature air oxidation for 5 minutes to 100 hours at 400 to 1000° C., preferably 600 to 1000° C. For example, two hours at 800° C. has been found to be very satisfactory.

It has also been found that these alloys are resistant to contaminated atmospheres containing sulfur and/or water vapor and/or carbon monoxide-dioxide combinations. These atmospheres are representative of most hydrocarbon combustion gases.

It is to be understood that the invention is not limited to the illustrations described and shown herein which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modifications of form, size, arrangement of parts and detail of operation, but rather is intended to encompass

all such modifications which are within the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. An oxidation and tarnish resistant article consisting essentially of an iron base alloy consisting of chromium from 1 to 5%, a material selected from the group consisting of aluminum from 1 to 4%, silicon from 1 to 4% and mixtures thereof, phosphorus 0.04% max., sulfur 0.04% max., manganese up to 1.5%, copper up to 2%, carbon up to 2%, others up to 0.20%, balance iron, said alloy of said article having a substantially colorless and adherent oxide film and having significantly greater oxidation resistance than stainless steels in the 500 to 1000° C. temperature range.

2. An article according to claim 1 wherein said material is aluminum and wherein a reversal occurs in the plot of oxidation weight gain against temperature in the 600 to 1000° C. range.

3. An article according to claim 1 wherein said material is silicon.

4. An article according to claim 1 containing manganese in an amount up to 0.2%.

5. An article according to claim 1 containing copper in an amount up to 0.5%.

6. An article according to claim 1 containing carbon in an amount up to 1%.

References Cited

UNITED STATES PATENTS

1,166,342	12/1915	Field	75—128 A
3,144,362	8/1964	Bradd	75—124 X
2,763,544	9/1956	Wagner	75—124 X
2,770,563	11/1956	Herzog	75—124 X
2,941,883	6/1960	Ida	75—124
3,031,392	4/1962	Ida	75—124 X

L. DEWAYNE RUTLEDGE, Primary Examiner

J. E. LEGRU, Assistant Examiner

U.S. Cl. X.R.

75—126 A, 126 B, 126 Q, 124, 125; 148—36