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OXIDATION RESISTANT CHROMIUM ALLOY

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This invention relates in general to high temperature oxidation resistant alloys and specifically to chromium base alloys possessing good high temperature oxidation resistance.

It is an object of this invention to provide alloys with superior resistance to oxidation at temperatures in excess of 1800° F.

A further object of this invention is to provide alloys with superior corrosion resistance, and good strength and ductility characteristics at temperatures in excess of 1800° F.

Yet another object of this invention is to provide chromium base alloys which will resist oxidation and corrosion at temperatures in excess of 1800° F., and which will retain good strength and ductility characteristics at such elevated temperatures.

For applications in air, the field of high temperature metallurgy is for most practical purposes limited to the utilization of iron, cobalt and nickel base alloys, and the use of even these materials under stress is limited to temperatures not in excess of 2000° F. The only other readily available metals which might be expected to have useful strength and oxidation resistance above 2000° F. are chromium base alloys. Now, it is known that high temperature, high strength structural chromium base alloys do exist, but the usefulness of such chromium base alloys has been limited by the fact that the oxide film formed on the surface of such an alloy does not afford the alloy much protection against further oxidation at high temperatures. The chromium oxide film formed when the metal is heated in air does afford some useful protection at temperatures up to 1700° F., however, above this temperature attack is sufficiently rapid to discourage use of the metal at such elevated temperatures. Certainly, the oxidation resistance of chromium at 2000° F. can not be compared favorably to that of iron or nickel alloys containing major additions of chromium or aluminum. To make the situation even worse, unlike iron, cobalt and nickel, chromium also reacts with the nitrogen in air, even at temperatures below 1700° F. The mechanism of this reaction is such that nitrogen contamination is not limited to a surface attack on the alloy, but extends deeply into the chromium because of a rather rapid penetration of nitrogen into the metal by diffusion. The effect of such a nitrogen attack is the conversion of the chromium alloy from a ductile high strength structural metal to a brittle substance of practically no useful ductility. Prior to the research which resulted in the discovery which is the subject of this application, all of the known alloying metals which could be added to chromium without impairing its useful metallic properties were studied with the object of producing chromium base alloys that would be resistant to oxygen and nitrogen attack in air at elevated temperatures; but no useful alloys were discovered. Elements such as beryllium, boron, aluminum, titanium, zirconium and silicon which tend to improve the oxidation resistance of iron, cobalt, or nickel base alloys were wholly in-

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effective for improving the high temperature stability of chromium.

Since aluminum proved to be ineffective for improving the oxidation resistance of chromium there was little reason to suspect that scandium, yttrium, or the rare elements, which also belong to the group III of the periodic table would be effective. From what little was known of chromium-base alloys containing the rare earths, it appeared that the solid solubility of such elements in chromium would not be large and therefore would not be too effective. Furthermore, from previously reported work on chromium base alloys containing cerium, one of the rare earths, it was known that cerium was not effective for preventing nitrogen absorption of the metal at high temperatures.

The effect of small amounts of yttrium, and certain other rare earths, on chromium is therefore extraordinary, for although the solubility of yttrium in chromium is not over 1 percent, additions in this amount are sufficient to provide alloys which are stable in air to temperatures well above 2000° F. and even above 2200° F. and in addition, these alloys are much stronger than iron, cobalt, or nickel base alloys and also have excellent ductility for structural applications.

During the research which led to the discovery of these oxidation resistant chromium alloys, a series of small arc melted chromium-yttrium buttons were prepared. These alloy buttons, containing from 0.2 to 10 percent yttrium, were heated in air at 2200° F. for 100 hours. The specimens were then examined metallographically, weight changes measured, and nitrogen contamination measured by chemical analysis. The data tabulated in Table I shows the excellent stability of the chromium alloys containing yttrium as compared to pure chromium and some other chromium base alloys. The unique stability of the chromium-yttrium alloys is apparent.

TABLE I

Oxidation resistance of chromium base alloys

[100 hrs., air, 2,200° F.]

Additions, w/o	Hard- ness, RA	Nature of Oxidized Surface	Wt. Gain, percent	Nitrogen Pickup, p.p.m.
100% Cr.....	43	Heavy scale.....	2.7	2,470
0.2 Y.....	41	Medium scale.....	0.4	370
0.5 Y.....	42	Mild scale.....	0.1	550
1.0 Y.....	43	Thin film.....	0.1	860
1.5 Y.....	43	Mild scale.....	0.1	290
2.5 Y.....	40	Thin film.....	0.3	660
5 Y.....	42	do.....	0.7	4,100
10 Y.....	42	Irreg. scale.....	3.0	7,460
2 Al.....	55	Mild scale.....	0.9	720
5 Al.....	65	Heavy scale.....	2.1	970
7.5 Al.....	68	Thin film.....	1.1	1,210
10 Al.....	78	do.....	1.0	430
5 Th-5 Al.....	63	do.....	1.1	5,960
5 Ti-5 Al.....	70	Completely oxidized.....	3.7	-----
5 Zr-5 Al.....	65	do.....	2.3	-----
10 Ti.....	70	do.....	5.3	-----

From this data it was found that as little as 0.2 weight percent yttrium is effective for improving the oxidation resistance of chromium, although from 1 to 1.5 weight percent yttrium appears to be the optimum amount of yttrium addition. As the yttrium content is increased beyond 1.5 percent, the oxidation stability of the alloy is adversely affected. While we do not wish to be restricted by theory, we believe that the explanation for this loss of oxidation stability lies in the fact that the maximum solid solubility of yttrium in chromium is not much over 1 percent. As a result, alloys containing more than 1.5 percent yttrium actually contain a second phase of the yttrium metal solid solution and this second phase is probably not stable in air at elevated temperatures. Hence, the decrease in oxidation resistance of

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chromium alloys containing more than 1.5 percent yttrium appears to be due to oxygen and nitrogen attack on this second phase.

Although the exact mechanism by which the yttrium additions affords protection to chromium base alloys is not known, and although, again, applicants do not wish to be limited by theory, we are of the opinion that yttrium in combination with chromium is preferentially oxidized to form Y_2O_3 which may or may not react with chromium oxide and that the resultant film formed on the chromium probably is impervious to oxygen or nitrogen. Chromium also appears unable to diffuse through this film.

Chromium base alloys containing yttrium when alloyed with other elements such as molybdenum, columbium, tungsten, etc., retain the good oxidation resistance characteristics of the binary chromium-yttrium alloy. Some of the rare earth elements which are very similar to yttrium in metallurgical properties also afford oxidation resistance to chromium. The rare earths differ greatly among themselves, with regard to their metallurgical properties. Some, such as cerium and lanthanum, have very low melting points and very low boiling points, and readily corrode in air, while others, such as lutecium and ytterbium, have very high melting points, and are

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monvolatile and stable in air. The latter metals, along with scandium and other rare earths which are similar to yttrium may also be employed to provide high temperature oxidation resistant chromium base alloys.

While this invention has been described with reference to specific embodiments thereof, it is not intended to limit the invention in any way, except by the scope of the appended claims.

We claim:

1. A binary alloy of chromium and yttrium consisting of from about 0.2 weight percent to about 2.5 weight percent yttrium, the balance being chromium.
2. A binary alloy of chromium and yttrium consisting of from about 1.0 weight percent to about 1.5 weight percent yttrium, the balance being chromium.

References Cited in the file of this patent

- Hampel: Rare Metals Handbook, Reinhold Publ. Co., N.Y., 1954, p. 334.
- Gilbert et al.: Malleable Chromium and Its Alloys, Bureau of Mines, Report of Investigations 4905, 1952, pp. 12, 14.