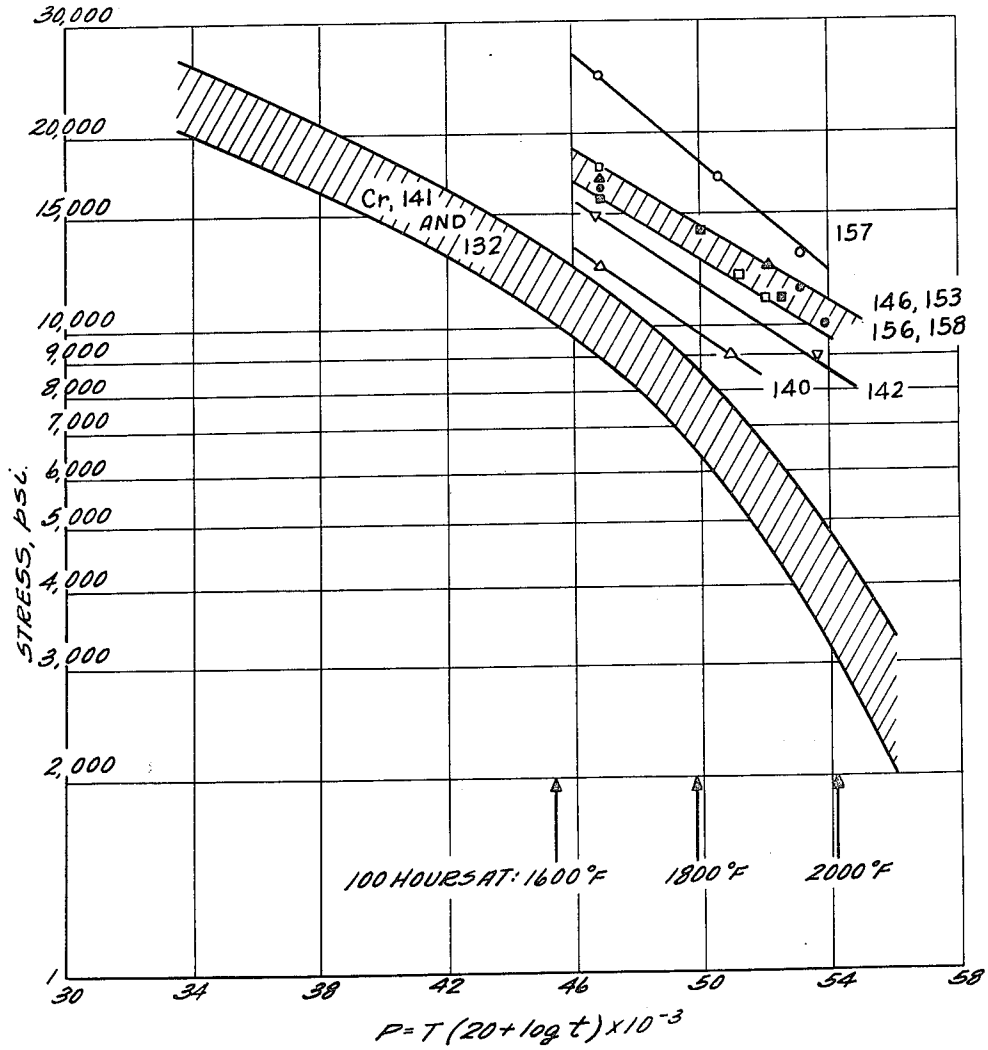
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CHROMIUM BASE ALLOYS

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STRESS-RUPTURE PROPERTIES AT 2000 °F



□ – 146
▣ – 153
△ – 156
◉ – 158

INVENTORS

CHESTER T. SIMS
JACK W. CLARK
EDWARD S. JONES

BY Lee H Sachs

ATTORNEY-

United States Patent Office

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CHROMIUM BASE ALLOYS

Chester T. Sims, Ballston Lake, N.Y., and Jack W. Clark, Milford, and Edward S. Jones, Cincinnati, Ohio, assignors to General Electric Company, a corporation of New York

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This invention relates to chromium base alloys and, more particularly to carbide dispersion strengthened alloys including elements of Group IV–A of the Periodic Table of Elements combined with carbon.

The advance of high temperature metallurgical technology accompanying the development of power producing or propulsion apparatus operating at high temperatures has heretofore concentrated on such elements as molybdenum and columbium more than on chromium for structural materials. Of the metals which melt at temperatures above 1800° C., chromium has superior oxidation resistance to all but the precious metals of the platinum group. Chromium alloy development has been limited because of the lack of alloy ductility at low temperatures, its tendency to become further embrittled by nitrogen absorption during exposure to air at elevated temperatures and its relatively low strength compared with alloys which it might replace.

In United States Patent 2,955,937, McGurty et al. have shown that additions of yttrium are effective in minimizing the absorption of nitrogen during air oxidation of chromium. However, such alloys are relatively weak at high temperatures.

It is a principal object of this invention to provide an improved chromium base alloy having adequate ductility at low temperatures, having good strength characteristics at elevated temperatures accompanied with good resistance to oxidation at elevated temperatures.

Another object is to provide a chromium base alloy including yttrium to which carbon has been added along with particular carbide formers to produce a carbide strengthened chromium base alloy which has good ductility at low temperatures combined with good oxidation resistance and strength at elevated temperatures.

These and other objects and advantages will be more readily recognized from the drawing, and the following detailed description and examples, all of which are meant to be typical of but not limitations on the scope of the invention.

The accompanying drawing is a graphical representation of the stress rupture properties of the alloy of this invention compared with other alloys.

Briefly, the improved chromium base alloy of the present invention consists essentially of 0.1–0.2 weight percent carbon, 0.001–0.5 weight percent yttrium, at least one of the elements titanium, zirconium and hafnium with the total amount of such elements being in the range of about 1–2 weight percent and the total atomic ratio of such elements to carbon being 1–2. to 1, with the balance being chromium.

A potent strengthening mechanism for chromium alloys is the dispersion of stable carbides. According to the present invention, this involves the addition of controlled amounts of at least 1 of the reactive metals of Group IV–A of the Periodic Table of Elements (titanium, zirconium and hafnium), along with carbon.

Because it has been recognized that the addition of yttrium to chromium improved the oxidation resistance of chromium base alloys, a Cr—Y system was selected as a base for most of the alloys although, as will be recognized from the following tables, improved alloys having good oxidation resistance can be obtained with

the retention of some, but not necessarily large amounts, of yttrium.

It is to be understood that the yttrium content referred to herein in connection with final alloy compositions is the yttrium retained in the alloy and not the yttrium added during the melting of the alloy. Frequently there are large variations between the amount of yttrium added and that retained by the alloy because of yttrium's gettering effect.

Although the value of retaining some yttrium was recognized by McGurty et al., yttrium added during melting of the alloy of this invention provides significant scavenging of gaseous interstitials such as oxygen and nitrogen. Furthermore, in addition to its slowing down the absorption of nitrogen at high temperatures, yttrium aids the extrudability and hot workability during fabrication by virtue of such scavenging action. Therefore substantially more yttrium, for example up to about 1 weight percent of the melt, can be added depending on the gaseous interstitial content of the chromium raw material and of the alloying elements, and the variables associated with melting and casting as well as on the amount of yttrium desired to be retained.

The following Table I gives the analysis of some of the alloys melted and studied in connection with the present invention.

Table I

Alloy	Weight percent—balance Cr						Atomic Ratio IV–A (total) to C
	Ti	Zr	C	Y	Hf	Total Gp. IV–A	
141	------	------	.005	.002	------	0	----------
132	------	------	.02	0.5	------	0	----------
140	0.1	0.2	.005	0.3	0.3	0.6	15
153	0.2	0.2	.19	0.6	------	0.4	0.4
156	0.8	0.2	.18	.01	------	1.0	1.3
157	0.2	0.15	.10	.001	0.8	1.15	1.2
158	0.2	0.2	.11	.001	0.6	1.0	1.1
135	2.3	0.3	.32	0.5	------	2.6	1.9
142	2.4	0.3	.30	.001	------	2.6	1.3
146	2.6	0.5	.55	.001	------	3.1	1.3

Although the alloys of Table I which include an atomic ratio of Group IV–A elements to carbon of between 0.4–1.5 to 1 show a strength improvement, it will be shown in connection with subsequent data that those alloys having a Group IV–A (total) to carbon ratio of between about 1–2 to 1, as represented by the last six alloys of Table I, are the preferred range for strength improvement. Alloys **157** and **158** are specifically preferred compositions because of their unusual combination of strength, oxidation resistance and ductility at high and low temperatures.

Table II

Alloy	Properties			
	2,000° F. Tensile			2,000° F. Oxidation
	Ultimate Strength, K p.s.i.	0.2% Yield Str., K p.s.i.	Elong., Percent	Wt. gain (mg./cm.^{2}) 25 hours
Cr	9.3	9.3	104	4.5
141	7.3	2.1	67	3.1
132	9.4	7.7	18	0.9
140	16.9	13.1	47	0.8
153	19.9	15.7	29	0.5
156	22.2	17.6	47	2.5
157	26.9	24.7	25	1.5
158	26.6	16.5	30	1.8
135	----------	----------	----------	5.3
142	18.4	13.8	48	9.4
146	22.4	17.7	59	5.5

In the above Table II, alloys **141** and **132** along with chromium are outside the range of the present invention. A comparison between **141** and **132** shows the affect of improved oxidation resistance through the retention of about 0.5 weight percent yttrium in alloy **132**. Alloys **140** and **153** are at the extremes of the metal to carbon atomic ratio of the alloy of the present invention, and show that even at these relatively low concentrations of Group IV–A elements, improved strength and oxidation resistance can be achieved. The slightly lower strength in alloy **140** is attributed to the lower carbon and higher yttrium retained. Alloys **156**, **157** and **158** have the best overall balance of strength and oxidation resistance, much improved over chromium alone or Cr—Y—C. These latter alloys are within the preferred Group IV–A (total) metal to carbon atomic ratio of about 1–2 to 1 and within the preferred total of Group IV–A elements in the alloy of 0.4–3.1 weight percent. A comparison between alloys **142** and **135** shows the improved oxidation resistance which can be achieved through the retention of additional yttrium in the alloy. Alloy **135**, which was not tested for tensile strength, should have properties similar to but perhaps slightly lower than alloy **142** due to the increased amount of yttrium retained. This is shown from the fact that the 2000° F. Vickers hardness test for alloy **135** was 36 kg./mm.^{2} as compared with 56 for alloy **142** and 12 for alloy **132**. Alloy **140** shows that with a very low amount of carbon (an amount usually included as a residual quantity in the chromium raw material), the inclusion of elements of Group IV–A of the Periodic Table within the range of this invention provides the alloy with improved strength. The higher carbon of alloy **153** provides even higher strength. It is to be noted that alloy **153**, because of its particular combination of elements, achieves high strength along with excellent oxidation resistance with the retention of very little yttrium. However, as will be shown in connection with Table III, its low temperature ductility is not as good as alloys **140**, **157** and **158**.

Although carbon contents up to about 0.55 weight percent will result in alloys of properties improved over Cr alone, it was noted that the higher carbon alloys are more difficult to process than those alloys including about 0.1 weight percent carbon, the preferred range for this invention. The alloys including carbon between about 0.3–0.5 weight percent have a nearly continuous grain-boundary carbide network in the castings. Extrusion of these alloys in the range of about 2600–2700° F. results in fragmentation of the intergranular carbides into massive particles which are detrimental to ductility and would not be expected to contribute significantly to high temperature creep resistance because of their size and distribution. It was recognized that the fine, uniformly dispersed particles provide most of the strengthening for the alloys of the present invention.

Because of the fine, uniformly dispersed particles and their good low temperature properties, as shown in the following Table III, along with good high-temperature strength and oxidation resistance, alloys such as **157** and **158** display an unexpectedly unusual combination of properties.

Table III

LOW TEMPERATURE DUCTILITY

Alloy:	Approximate transition temp. (° F.)
Cr	<50
141	<50
132	100
140	100
157	150
158	50
153	350
142	>400
146	400

In Table III, the approximate transition temperature is that temperature at and above which the alloy behaves in a ductile rather than brittle manner. It is to be noted that alloys including carbon in amounts below about 0.2 weight percent are significantly more ductile than the higher carbon bearing alloys.

The structures of the low-carbon alloys of this invention including those containing, in addition, small amounts of Hf, indicate that maintaining the carbon level within the range of about 0.075–0.15 weight percent minimizes the intergranular carbide network in the castings. These lower carbon alloy forms of the invention were hot and warm-worked more easily than the other compositions.

Referring to the drawing, the stress rupture properties of alloys within and without the scope of the present invention are represented by a comparison of stress with a time-temperature parameter shown at the horizontal coordinate. This parameter, known as the Larson-Miller Parameter, has been calculated from the formula

$$P=T(20+\log t)\times 10^{-3}$$

in which P equals the time-temperature parameter number, T equals absolute temperature in degrees Rankine and t equals time in hours. The curves and bands of the drawing have been prepared from a large number of stress rupture test results some of the representative points for which are shown. Using this type of graph based on actual data, it is possible to predict the stress rupture life of a material under a variety of conditions.

The curves and bands of the drawing show the appreciably greater stress rupture strength of the alloy of this invention over chromium alone or Cr—C—Y alloys.

All of the alloys of the above tables and represented in the drawing were induction melted as 8 to 12 pound ingots in a 20 kilowatt induction furnace. The Cr charges, including additions of elemental yttrium, were pressed into briquettes and heated to about 1800° F. under vacuum. Argon or helium was then introduced and the charge was melted. After holding the melt in a liquid state, the remaining alloy additions of (Ti, Zr, Hf, C) were charged. The melt was held for a short period to promote homogenization and then was cast into a copper chill mold.

Initial breakdown of the cast structure was accomplished by extrusion, the binary alloys being extruded at about 2200° F. and the remainder of the alloys being extruded at temperatures between 2400–2700° F.

In order to accomplish elevated temperature tensile and creep rupture tests, "button-head" specimens were ground from swaged stock to a gage diameter of 0.160" and a gage length of 1.1". High temperature tensile testing was performed in a vacuum of less than 2×10^{-4} mm. Hg, using a crosshead speed of 0.01" per minute. The constant-load creep-rupture tests were conducted in vacuum-purged capsules, back-filled with helium at slight positive pressure.

Although the present invention has been described in connection with specific examples, metallurgists will recognize the variations and modifications of which the invention is capable without departing from its effective scope.

What is claimed is:

1. A chromium base alloy having an improved combination of strength and oxidation resistance consisting essentially of: 0.1–0.2 weight percent carbon; 0.001–0.5 weight percent yttrium; at least one of the elements selected from the group consisting of Ti, Zr and Hf, the total amount of said elements being about 1–2 weight percent, the atomic ratio of the total of Ti+Zr+Hf to carbon being in the range of 1–2 to 1; with the balance chromium.

2. A chromium base alloy having an improved combination of strength and oxidation resistance consisting essentially of, in percent by weight: 0.2–0.8 Ti, 0.15–0.2 Zr, 0.1–0.2 C, .001–0.5 Y, up to 0.8 Hf with the

balance chromium, the total amount of the elements Ti, Zr, and Hf being about 1–2, the atomic ratio of the total of the elements Ti+Zr+Hf to carbon being in the range of 1–2 to 1.

3. A chromium base alloy having an improved combination of strength and oxidation resistance consisting essentially of, in percent by weight: 0.2 Ti, 0.15–0.2 Zr, 0.1 C, .001 Y, 0.6–0.8 Hf with the balance Cr.

4. A chromium base alloy having an improved combination of strength and oxidation resistance consisting essentially of, in percent by weight: 0.8 Ti, 0.2 Zr, 0.2 C, 0.01 Y, with the balance Cr.

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DAVID L. RECK, *Primary Examiner.*

RAY K. WINDHAM, *Examiner.*