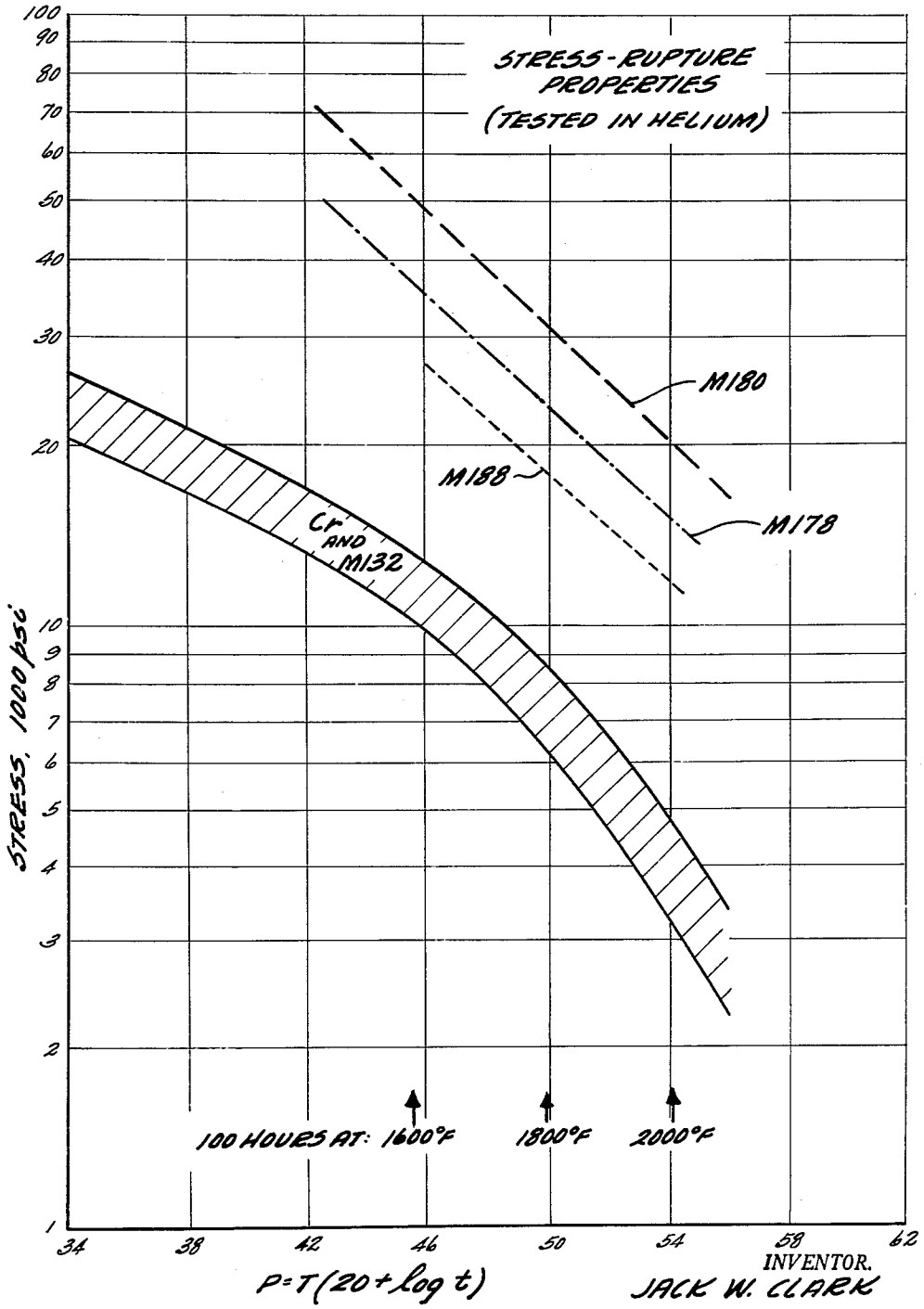
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CHROMIUM BASE ALLOY

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CHROMIUM BASE ALLOY

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This invention relates to chromium base alloys and, more particularly, to chromium base alloys strengthened by a combination of carbide dispersion strengthening and solution strengthening.

In co-pending application Serial No. 179,941, filed March 15, 1962 and assigned to the assignee of the present invention, there is described an improved chromium base alloy strengthened by the dispersion of carbides formed from carbon and Group IV A elements of the Periodic Table of Elements. Although the alloys of that co-pending application achieve good strength and oxidation characteristics at elevated temperatures, it is necessary for use in aircraft or rocket propulsion apparatus that chromium base alloys be developed which have the high temperature characteristics at least equal to the best available nickel base super-alloys.

Therefore, it is an object of this invention to provide a chromium base alloy having high strength characteristics and oxidation resistance at elevated temperatures while at the same time being sufficiently workable to allow its fabrication into useful articles.

This and other objects and advantags will be more readily recognized from the following detailed description and examples, all of which are menat 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 high strength chromium base alloy of the present invention consists of, by weight, 5–15% W; up to about 10% Mo; about 0.4–2% of elements selected from the group consisting of Ti, Zr and Hf; 0.05–0.2% C; up to about 0.7% retained Y; with the balance chromium and incidental impurities.

In a preferred form, the alloy of the present invention consists essentially of, by weight, 5–15% W, 0.4–1.2% Zr, up to 0.4% Ti, 0.05–0.2% C, up to about 0.7% retained Y, with the balance Cr and incidental impurities.

The advantages of additions of yttrium and its gettering effect in reducig the oxygen content of alloy melts, as well as minimizing the oxidation rates and absorption of nitrogen during their working or use in air have been described in the above-identified co-pending application as well as in the United States Patent 2,955,937—McGurty et al. The present invention employs yttrium (1) as a gettering agent and (2) for its value when retained in the alloy. However, it has been found that the addition to the melt of more than about 1.5 weight percent Y results in alloy brittleness (hot-shortness) at elevated temperatures whereas the addition of less than about 0.5 weight percent Y results in the retention of too little yttrium in the alloy for improvement in an oxidation resistance after melting.

It has been recognized that a combination of solution strengthening by the addition of tungsten and the dispersion strengthening by precipitation of a complex carbide system is very effective in increasing the elevated temperature mechanical properties of chromium. It has been discovered that the careful selection of amounts of solution strengthening and dispersion strengthening additions at the same time can result in alloys which have a very desirable combination of fabricability, elevated-temperature strength, low-temperature ductility and resistance to air oxidation.

Typical of example alloys which were studied in the evaluation of the present invention are those included in the following Table I.

TABLE I

Example	Weight percent (balance Cr)						Other	Ti+Zr+Hf
	W	Zr	Ti	C	Y (added)	Y (retained)		
M 132					1.0	0.4		
178	5	0.8	0.2	0.1	0.7	0.15		1.
179	10	0.4	0.4	0.1	0.7	0.02		0.8
180	10	0.8	0.2	0.1	0.7	0.1		1.
183	10				0.7	<20 p.p.m.		
184	10	1.2		0.1	0.7	0.15		1.2
186	10	0.8	0.2		0.7	0.12		1.
187	10	0.4	0.1	0.05	0.7	0.13		0.5
188		0.8	0.2	0.1	0.7	<20 p.p.m.		1.
197	10	1.6	0.4	0.2	0.7	NA		2.
198	15	0.8	0.2	0.1	0.7	NA		1.
199	10	0.8	0.2	0.1	0.7	NA	5 Mo	1.
201	10	0.6		0.1	0.7	NA	1.2 Hf	1.8

NA—Not available.

As a priliminary indication of the strength and workability of alloys in this series, Vickers hardness tests were performed on the example alloys in the cast condition as well as in various worked conditions. The following Table II summarizes these tests.

TABLE II.—Vickers Hardness (kg./mm.²)

Example	Cast	Extruded	Swaged
M 178	210	207	255
179	[a] 275	278	
180	271	263	356
183	262	245	285
184	257	261	313
186	273	280	307
187	265	259	321
197	[b] 325		
198	[b] 354		
199	[b] 374		
201	300	292	308

[a] Extensive solidification cracks in ingot.
[b] Too high hardness to fabricate.

Alloys M 197, M 198 and M 199 in Table II define the practical limits of the present alloy from a fabricability point of view. Although the 800 to 1200 ton extrusion presses employed as ingot breakdown equipment were unable to process alloys M197, M 198 and M 199, they should be amenable to processing by higher capacity presses. The high strength potential of such alloys are indicated by the Vickers hardnesses of from 325 to 374 kg./mm.². It has been found that inclusion of more than about 15 weight percent tungsten or the combination of tungsten and molybdenum provides too much solution strengthening for good fabricability. Similarly, as shown

by M 197, a carbon level of as high as 0.2% with a lower tungsten level results in too much precipitation strengthening for good ingot soundness and fabricability. Thus, with regard to W and C, the two principal elements involved in solution strengthening and precipitation strengthening it has been found that the tungsten level should be maintained at about 15 weight percent or less and the carbon level should be maintained at about 0.2 weight percent or less.

With regard to M 179 which had extensive solidification cracks in the ingot due to the high Ti level as well as M 197 which had high hardness due to the high carbon and Ti level, it has been found that a titanium level of greater than about 0.4 weight percent not only results in adverse fabricability characteristics, but also, as shown in Table III below, decreases the oxidation resistance of the alloy.

The primary carbide formers of the alloy of the present invention are the elements Hf, Zr and Ti. It has been recognized that the total of these elements in the alloy of the present invention should be maintained in the range of about 0.4–2 weight percent. The preferred carbide obtained in the present invention is predominantly the monocarbide ZrC. However, the element titanium can be added to the alloy of the present invention up to about 0.4 weight percent to replace some of the zirconium in the monocarbide thereby to increase the stability of the dispersed phase or phases in the alloy. As was mentioned above, the addition of too great an amount of titanium will result in undesirable characteristics.

A comparison of examples M 180, M 184 and M 201 in Tables I and II shows that Hf can be substituted for Zr or Ti as a carbide former. It is to be noted that on an atomic basis the metal to carbon ratios in Examples M 180, M 184 and M 201 are the same. In Example M 201, titanium has been eliminated because in some applications Ti is slightly harmful from an oxidation point of view. Thus, the same type of strengthening through complexing of carbides is accomplished by simultaneous addition of Hf and Zr without sacrifice of the excellent oxidation resistance of M 184, as shown in Table III. The improvement in cast hardness of M 201 over M 184 shown in Table II suggests that strength improvements would result and limited stress-rupture data presented in Table V shows this to be the case.

TABLE III.—AIR OXIDATION RESISTANCE AT 2000° F, 24 HOURS

Alloy	Weight gain (mg./cm.²)	Depth hardened [a] (mils)
M 132	0.35	0
M 178	1.78	2-3
M 179	2.95	4-5
M 180	2.11	1-2
M 184	0.76	0
M 187	1.06	------
M 188	1.54	------
M 201	0.74	0-1

[a] Depth below surface scale(s) hardened by internal reaction with N^2 and/or O^2.

As mentioned above, the element tungsten is included within the range of this invention for elevated-temperature solid solution strengthening because it is the only metallic element so far identified which increases the melting point of chromium when added in small quantities. Elements such as Mo and Re and particularly Fe, Ni, V, Cb and Ta and the like decrease the melting point, although in some alloy forms up to about 10 weight percent Mo and possibly Re can be added without decreasing the melting point below a useful level.

The following Tables IV and V show tensile and stress-rupture properties of some of the alloys of Table I.

TABLE IV.—TENSILE PROPERTIES

Example	Ultimate (k.s.i.)			0.2% yield (k.s.i.)			Percent elongation		
	1800° F.	2000° F.	2200° F.	1800° F.	2000° F.	2200° F.	1800° F.	2000° F.	2200° F.
M 132	15.5	9.4	------	15.0	7.7	------	28.0	18.1	------
178	49.3	33.1	18.4	47.3	33.1	15.2	12.3	19.8	37.5
180	68.5	49.8	29.5	65.8	45.7	24.1	18.6	31.4	22.8
183	53.8	43.8	------	51.3	39.8	------	13.6	23.6	------
184	55.0	39.8	23.0	52.0	35.3	19.1	17.0	14.5	25.8
187	63.3	43.3	------	61.3	42.8	------	16.2	12.8	------
188	44.8	29.9	------	40.3	25.9	------	12.4	14.9	------

TABLE V.—STRESS RUPTURE PROPERTIES AT 2000° F.

Example	Stress (k.s.i.)	Life (hrs.)
M 178	17.5	20.9
180	17.5	[a]240
183	17.5	38.7
184	17.5	14.4
187	17.5	93.6
201	17.5	46.8
178	20.0	7.9
180	20.0	102.6
184	20.0	4.8
187	20.0	39.6
201	20.0	20.6

[a] Test discontinued, no failure.

Referring to Table IV, it is easily seen that Examples M 180 and M 187 are the strongest of the alloy forms in the series. This is further shown in Table V with regard to stress rupture properties.

In Table IV the comparison of M 132 and M 183 shows the striking effect of the addition of 10 weight percent tungsten to a Cr-Y alloy for solution strengthening purposes. At the same time, comparison of M 188, M 178 and M 180 shows that increasing the tungsten from 0 to 5 to 10 weight percent, in combination with carbon and the proper amounts of strong carbide forming elements, results in a further and significant strength increase. Note the unusual and unexpectedly great difference between the stress rupture properties of M 180 and M 178 in Table V. Thus, in example M180, the inclusion of the proper combination of solution strengthening and precipitation strengthening elements results in an unusually high strength chromium base alloy which is fabricable and which has adequate oxidation resistance. Useful low-temperature ductility of the alloy of this invention can be attained by proper control of processing variables. Tensile elongation of 5 to 10% are measured at 75° F.

The drawing is a graphical representation combining a large amount of data and comparing the stress-rupture properties of the preferred form of the alloy of this invention, M 180, with other alloys such as M 178 and alloys M 188, M 132 and chromium which lie outside of the scope of the present invention. It can be seen from this data that the stress-rupture strength of alloy M 180 is significantly greater than other alloy forms. Although the 100 hour points in the drawing have been indicated, the horizontal coordinate has been represented in the form of the Larson-Miller parameter formula

$$P=T\ (20 + \log t)$$

in which P is the Larson-Miller parameter number, T is the temperature in degree Rankine and t is the time in hours. It is well established in the metallurgical art that the Larson-Miller parameter plots can be used, once the curves are established by actual data, to compare alloys along any point on the curves.

All the alloys of the tables and those represented in the drawing were induction melted as 8 to 12 pound ingots in a 20 kilowatt induction furnace. The chromium and tungsten charges were pressed into briquettes and heated to about 1800° F. in 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, Y or C were charged. The melt was held for a short period to promote homogenization and then was cast. Initial breakdown of the cast structure was accomplished by extrusion at temperatures between 2400 and 2800° F.

In order to accomplish elevated temperature tensile and creep rupture tests, "button-head" speciments 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 about

$$2\times10^{-4} \text{ mm. Hg}$$

using a crosshead speed of about 0.01" per minute. The constant-load creep rupture tests were conducted in vacuum purged capsules, back-filled with helium at a slight positive pressure.

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

What is claimed is:

1. An improved chromium base alloy consisting of, by weight: 5–15% W; up to about 10% Mo; about 0.4–2% of elements selected from the group consisting of Ti, Zr and Hf; 0.05–0.2% C; up to about 0.7% retained Y; with the balance Cr and incidental impurities.

2. An improved chromium base alloy consisting of, by weight: 5–15% W; 0.4–1.2% Zr; up to 0.4% Ti; 0.05–0.2% C; up to about 0.7% Y; with the balance Cr and incidential impurities.

3. An improved chromium base alloy consisting of, by weight: about 10% W; up to about 5% Mo; about 0.4–2% of elements selected from the group consisting of Ti, Zr and Hf; 0.05–0.2% C; up to about 0.7% retained Y; with the balance Cr and incidental impurities.

4. A high strength chromium base alloy consisting of, by weight: about 10% W; 0.4%–0.8% Zr; 0.1–0.2% Ti; 0.05–0.1% C; up to about 0.7% Y with the balance Cr and incidential impurities.

5. A highly oxidation-resistant chromium base alloy consisting of, by weight: about 10% W; 0.6–1.2% Zr; 0.05%–0.1% C; up to about 0.7% Y with the balance Cr and incidental impurities.

6. A strong, oxidation-resistant chromium base alloy consisting of, by weight: about 10% W; 0.6–1.2% Hf; 0.3–0.6% Zr; 0.05–0.1% C; up to about 0.7% Y with the balance Cr and incidental impurities.

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DAVID L. RECK, *Primary Examiner.*