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NICKEL-CHROMIUM-COBALT ALLOYS FOR USE AT RELATIVELY HIGH TEMPERATURES
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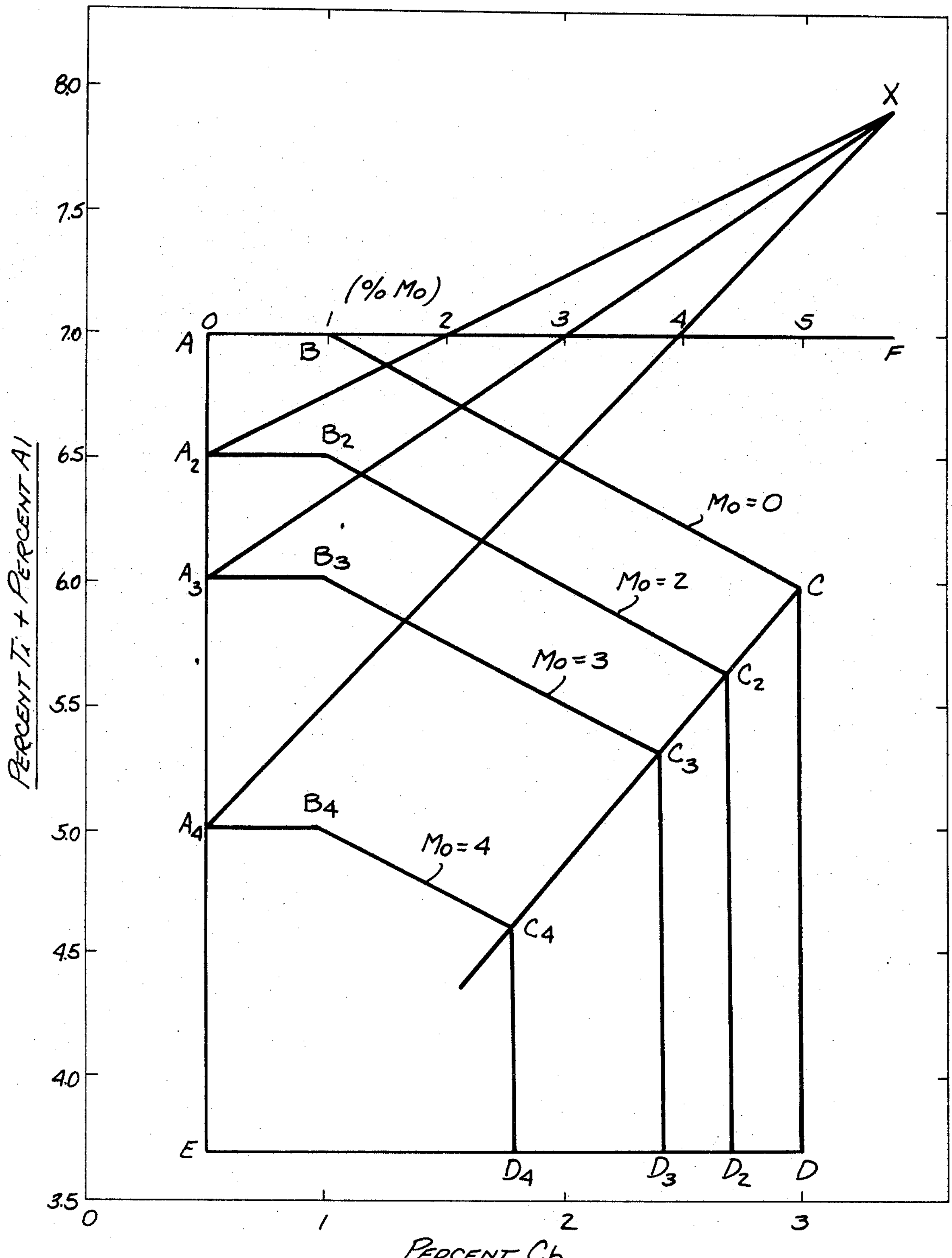

Fig. 1.

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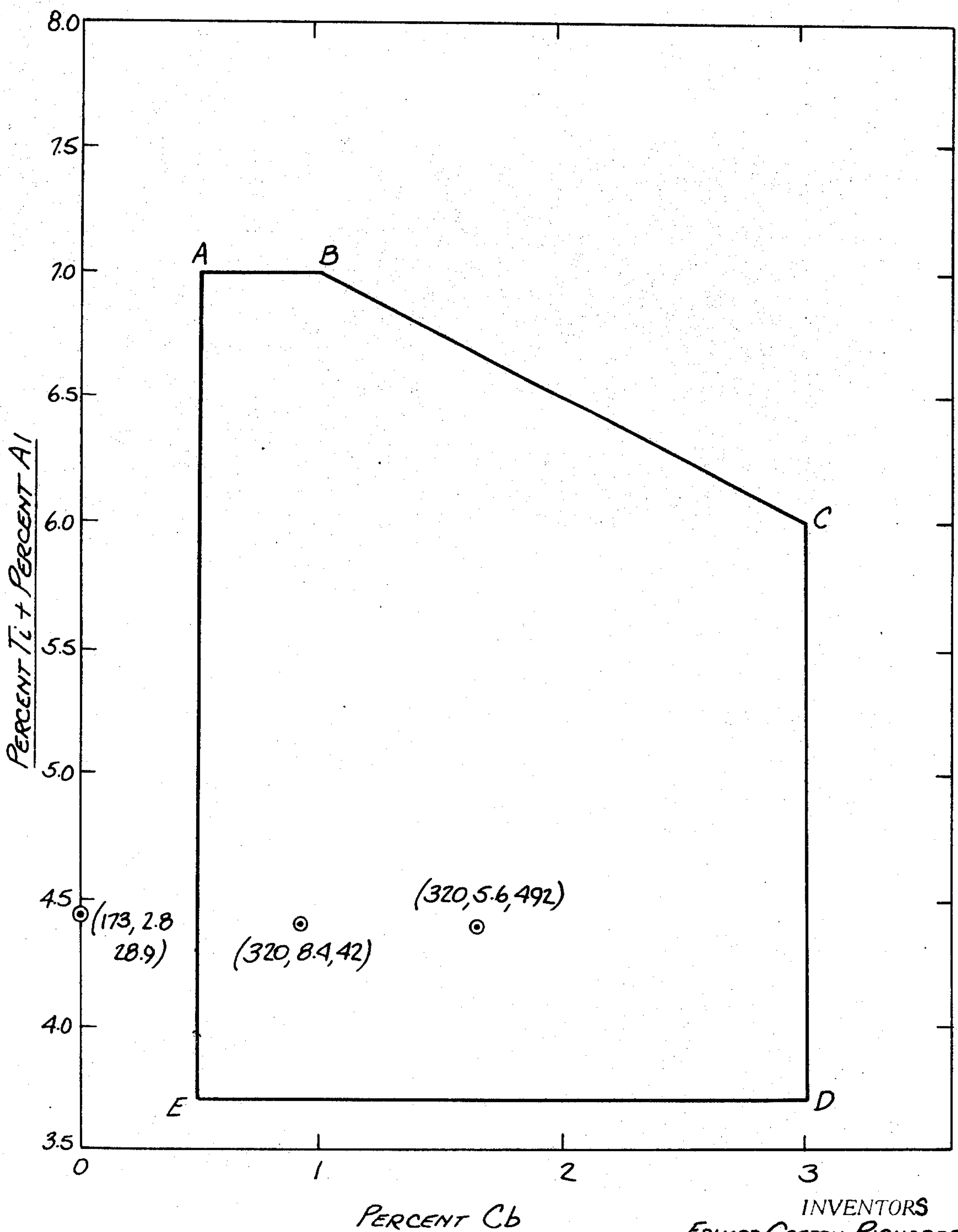

Fig. 2.

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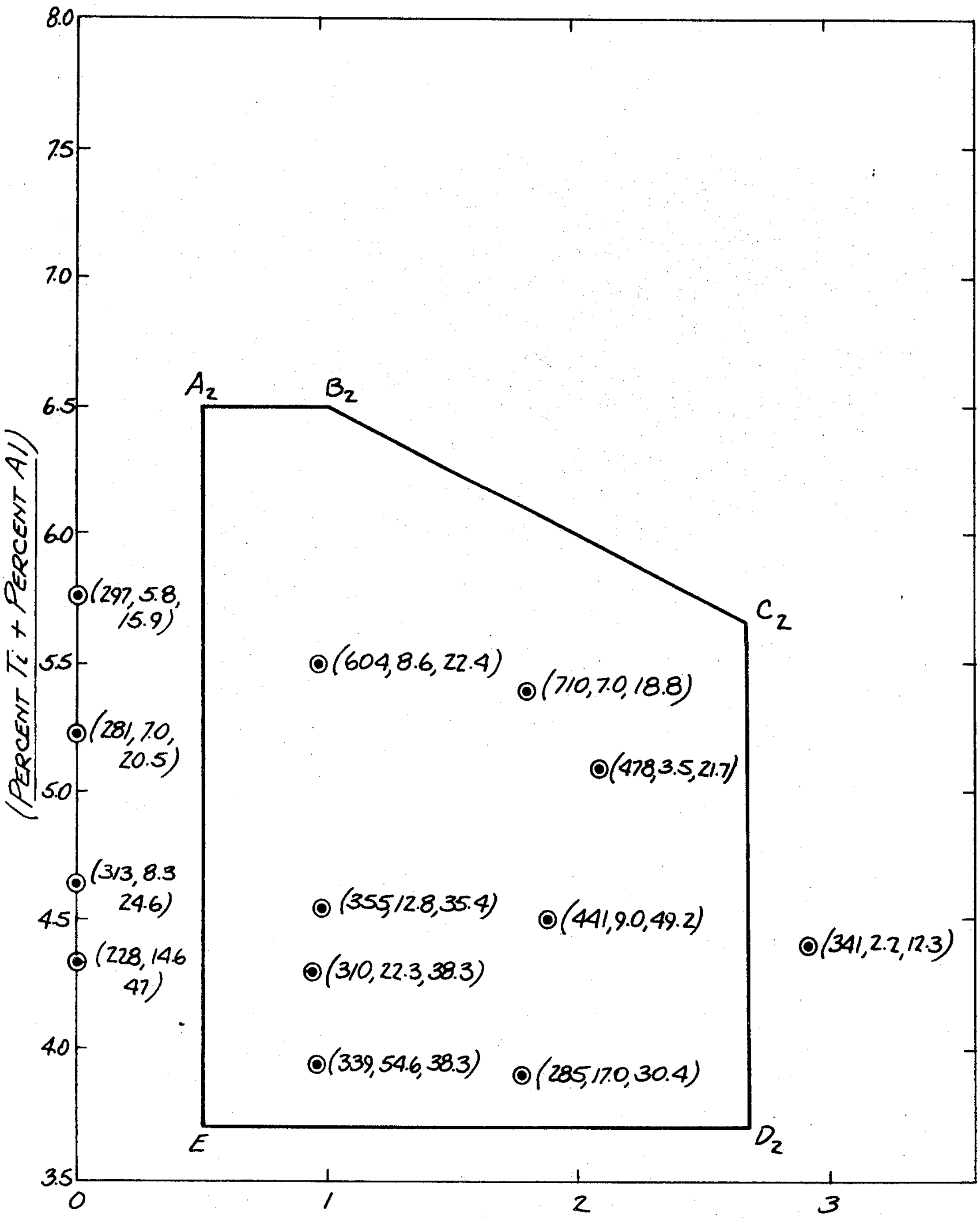

FIG. 3.

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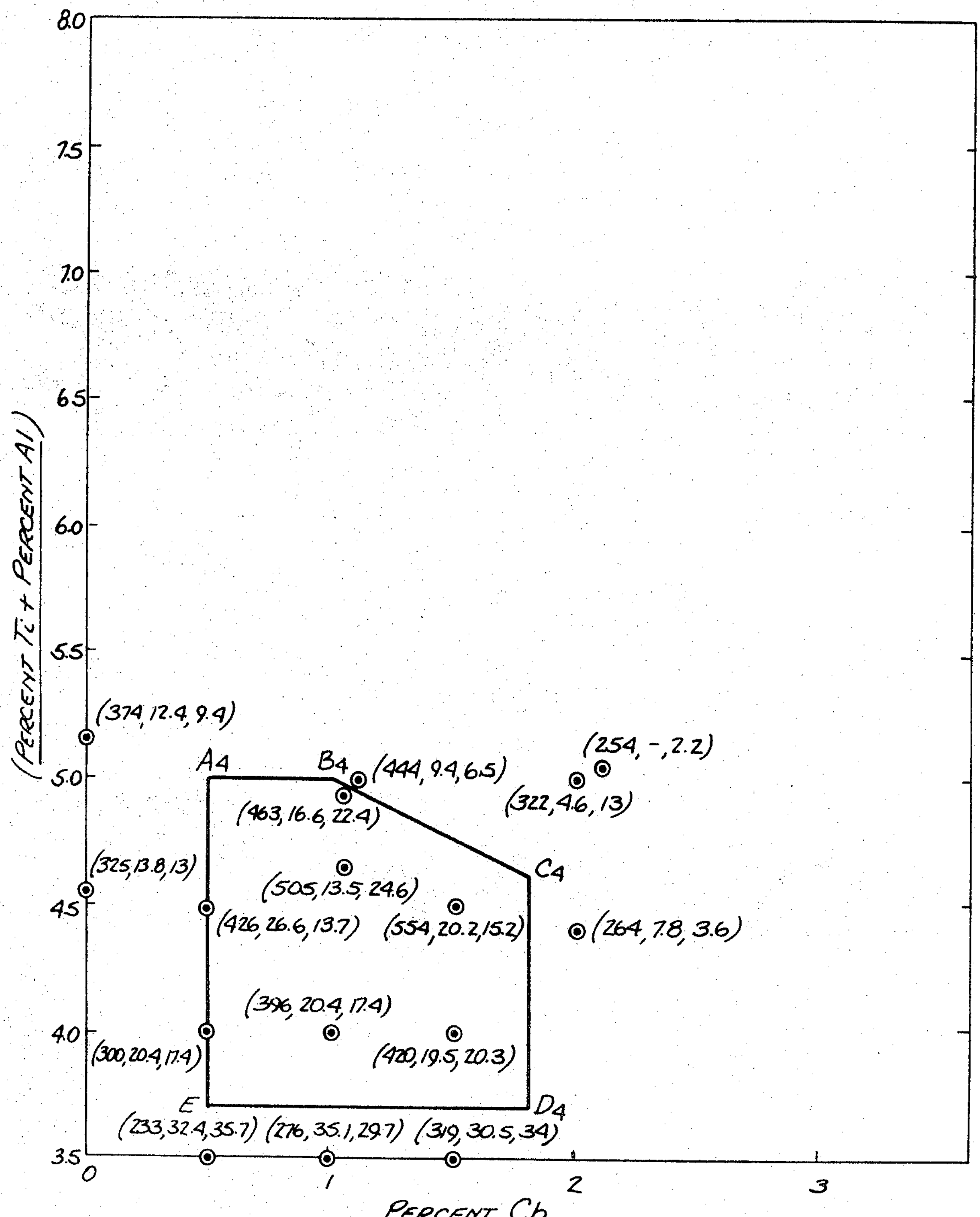

Fig. 4.

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NICKEL-CHROMIUM-COBALT ALLOYS FOR USE AT RELATIVELY HIGH TEMPERATURES

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Claims priority, application Great Britain, Mar. 7, 1969, 12,261/69
Int. Cl. C22c *19/00*
U.S. Cl. 75—171 **2 Claims**

ABSTRACT OF THE DISCLOSURE

Nickel-chromium-cobalt-base alloys containing correlated amounts of titanium, aluminum, columbium and, when present, molybdenum, as well as carbon and other constituents offer a combination of high temperature stress-rupture strength, ductility and impact resistance together with good corrosion resistance of such magnitude as to render the materials suitable for various gas turbine engine components.

As those skilled in the art are aware, research efforts have been endless in the quest of alloys capable of delivering in use certain metallurgical properties. Usually such alloys have been of the nickel-chromium or cobalt-chromium-base variety (rather exotically termed "superalloys") and have found extensive utility in a number of high temperature applications. Commonly these alloys contain one or more such elements as titanium, aluminum, columbium (niobium), molybdenum, etc., primarily for the purpose of imparting strength and hardness properties.

However, such characteristics as strength and hardness, including elevated temperature stress-rupture strength, are by no means all encompassing in respect of the properties such alloys might be called upon to exhibit. Resistance to high temperature corrosion, for example, is often an indispensible necessity, depending, of course, upon the intended application. And this aspect plus other considerations, e.g., tensile ductility, the ability to absorb impact energy upon prolonged exposure, etc., focus attention on the objectives of the subject invention since such properties usually do not go hand in hand.

It has been demonstrated, for example, that with increasing chromium content the ability of various nickel-chromium-cobalt-base alloys to resist corrosion at high temperatures, in, say, sulfur-containing environments is significantly improved. But it has also been shown that increasing the chromium level is not without its drawbacks. For example, in such alloys high percentages of chromium have been known to induce loss in stress-rupture life. Another adverse effect can be a decrease in the amount of the hardening and strengthening elements titanium, aluminum, columbium and molybdenum that may be present without causing alloy embrittlement upon prolonged exposure to high temperatures. Accordingly, the present invention is directed in the main to minimizing these conflicting effects.

In any case, it has now been discovered that an excellent combination of high temperature stress-rupture strength, ductility and impact strength can be attained together with good corrosion resistance, illustratively in respect of hydrocarbon fuels containing sulfur or in marine environments in which chlorides might be injected into, say, gas turbine engines, with high chromium, nickel-base alloys containing special amounts of titanium, aluminum, columbium, and other elements as described herein, including, under certain compositional limitations, molybdenum.

Generally speaking and in accordance with the present invention, alloys contemplated herein contain (in weight percent) from 19.5% to 23% chromium, about 0.01% to 0.2% carbon, about 10% to 24% cobalt, from 3% to 7% in total of titanium plus aluminum, the ratio of titanium to aluminum being from about 1:1 to 4:1, from about 0.5% to 2% columbium, with the proviso that the total percentage of titanium plus aluminum is so related to the percentage of columbium that it is represented by a point in the area ABCDEA of the accompanying drawing, up to 4.5% molybdenum, from 0.001% to 0.05% boron, e.g. 0.01% to 0.01% or 0.02%, up to 0.15% zirconium, with the further proviso that ten times the percentage of boron plus the percentage of zirconium is at least 0.02%, up to about 0.1% hafnium, up to about 0.04% magnesium, up to about 0.3% rare earth metal, up to about 2% yttrium, and the balance, apart from impurities, being essentially nickel.

In carrying the invention into practice, the minimum chromium content of 19.5% is dictated by the need for the greatest corrosion-resistance, but more than 23%, having in mind the relatively high total percentage of titanium, aluminum, columbium and molybdenum that can be employed, leads to embrittlement or loss of stress-rupture strength or both. In striving for the best combination of results the chromium should be from 20.5% to 22.5%.

If the percentage of carbon is below 0.01%, stress-rupture strength is reduced. On the other hand, too much carbon renders the alloys susceptible to embrittlement, and it should therefore not exceed 0.2%. A range of 0.015% to 0.08% is most beneficial.

Cobalt strengthens the alloys and at least 10%, preferably at least 14%, is required for this purpose. Should the cobalt exceed 24% the alloys tend to undesirably embrittle on prolonged heating and advantageously it does not exceed 22%.

The alloys are further and principally strengthened by titanium, aluminum, columbium and, provided certain conditions are observed, the presence of molybdenum is also most advantageous. Within the composition ranges set forth herein, the percentages of columbium and molybdenum and the sum of the contents of titanium and aluminum must also be interrelated in a manner that will be described with reference to FIG. 1 of the accompanying drawing. Prefacing this however, it should be emphasized that stress-rupture life is generally improved by columbium, and the alloys must contain at least 0.5% and preferably at least 1.0% thereof. Should the columbium exceed 3% the alloys have inadequate stress-rupture lives and may tend to embrittle. Moreover, subject to what is set forth hereinafter, as the molybdenum content increases stress-rupture life increases, and it is most beneficial that the alloys contain at least about 2% molybdenum.

Turning to FIG. 1, when the alloys are molybdenum-free, the (Ti+Al) and Cb contents must be represented by a point in the area ABCDEA, where the point C is 6% (Ti+Al) and 3% Cb. When the alloys contain 2% molybdenum, the amounts of (Ti+Al) and Cb must be represented by a point in the area $A_2B_2C_2D_2EA_2$, where the point C_2 is 5.65% (Ti+Al) and 2.7% Cb, and when the alloys contain 4% molybdenum, the (Ti+Al) and Cb percentages must be represented by a point in the area $A_4B_4C_4D_4EA_4$, where the point C_4 is 4.6% (Ti+Al) and 1.8% Cb. Corresponding areas defining the relationship between (Ti+Al) and Cb for other contents of molybdenum between 0 and 4.5% are obtained by the following geometrical construction. A line is drawn from the point X (7.9% Ti+Al and 3.4% Cb) through the point of the line AF corresponding to the molybdenum content (*n* percent) of the alloy, and extended to intersect the line AE in the point A_n, which represents the maximum (Ti+Al) content of the alloy. The point B_n is given by this (Ti+Al) content and Cb=1%. The point C_n is the intercept of the line CC_4 and a line through B_n parallel to the line BC, and the point D_n is the point on the line DE (Ti+Al=3.7%) at the same Cb content as C_n. In this way the area $A_3B_3C_3D_3EA$ is obtained for molybdenum contents of 3%.

For a given molybdenum content, if the (Ti+Al) and Cb contents corespond to a point above or to the right of the area defined in this way, one or generally both of the impact strength and stress-rupture ductility (elongation) of the alloy is impaired.

The effects imparted by titanium, aluminum, columbium and molybdenum, are illustrated by the results of tests on a series of alloys having the analyzed compositions set forth in Table I, and nominally also 0.003% boron and 0.05% zirconium, the balance being nickel and impurities. After vacuum-melting an addition of 0.03% magnesium was made as a Ni-15% Mg alloy, giving a residual magnesium content of 0.02%, and the alloys were vacuum-cast. The ingots were hot-worked to bar from which stress-rupture test-pieces were machined and given a heat treatment consisting of solution heating for 4 hours at 1150° C., air cooling, aging for 16 hours at 850° C., and again air cooling. The stress-rupture life and elongation to rupture were determined on specimens of each alloy under a stress of 17 ton-f./in.^{2} at 815° C. Further test-pieces were solution heated for 4 hours at 1150° C., air cooled, and then heated for 1000 hours at 850° C., and again air cooled, the Charpy V-notch impact strength being thereafter determined at room temperature. The results are set forth in the last three columns of Table I. Alloys identified by a numeral are within the invention, the others being outside the scope thereof.

were generally inferior in respect of one or other property to the alloys according to the invention having compositions within the area. Within the areas, the stress-rupture life increases with the (Ti+Al) content. It is to be pointed out in this regard that if the percentage of molybdenum does not exceed 2% it is of considerable benefit if the total amount of Ti+Al is at least 4.5%.

It should also be mentioned in terms of the respective amounts of titanium and aluminum, that at ratios of titanium to aluminum less than 1:1, stress-rupture ductility and impact strength are reduced, while if the ratio exceeds 4:1 the stress-rupture strength is inadequate. In consistently achieving good results the ratio should be from 1:1 to 2.5:1.

The resistance of alloys according to the invention to corrosion by the combustion products of impure hydrocarbon fuels and by marine salts has been determined by tests in which specimens of the alloys were exposed to a molten mixture of 25% by weight of sodium chloride and 75% sodium sulfate at 900° C. The corrosion damage was assessed by comparing the weight of each specimen, after removing the corrosion products by cathodic descaling in molten sodium hydroxide, with the initial weight before exposure. The more resistant materials are those that show the least loss in weight.

The tests were performed in two ways:

Test A: Samples of each alloy were half-immersed in the salt mixture while heated in air.

Test B: Samples of each alloy were heated in a vertical open-top furnace into which the salt mixture was continuously fed as a fine dispersion at a rate of 5 g./hour.

The results obtained for Alloy 14 are set forth in Table II, the results being generally representative of alloys in accordance herewith.

TABLE I

Alloy No.	Composition (percent by weight)								Stress-rupture		Impact strength (ft.-lbs.)
	C	Al	Ti	Ti+Al	Cr	Co	Cb	Mo	Life (hrs.)	Elong. (percent)	
A	0.048	1.55	2.9	4.45	21.7	19.8			173	2.8	28.9
1	0.049	1.5	2.9	4.4	21.2	19.6	0.92		320	8.4	42
2	0.051	1.45	2.95	4.4	20.7	19.5	1.65		320	5.6	49.2
B	0.049	1.35	3.0	4.35	22.65	19.3		2.1	228	14.6	47
C	0.065	1.7	2.95	4.65	20.7	20.3		2.15	313	8.3	24.6
D	0.042	1.85	3.4	5.25	21.65	20		2.15	281	7.0	20.5
E	0.042	1.95	3.8	5.75	22.5	19.6		2.05	297	5.8	15.9
3	0.046	1.35	2.6	3.95	21.1	19	0.98	2.1	339	54.6	38.3
4	0.049	1.3	3.0	4.3	22.05	19.7	0.94	2.1	310	22.3	38.3
5	0.066	1.55	3.0	4.55	20.5	20.4	1.0	2.15	355	12.8	35.4
6	0.044	1.8	3.7	5.5	21	19.4	0.97	2.05	604	8.6	22.4
7	0.045	1.3	2.6	3.9	20.7	19	1.8	2.1	285	17.0	30.4
8	0.066	1.5	3.0	4.5	20	20	1.9	2.05	441	9.0	49.2
9	0.019	1.80	3.3	5.1	21.5	22	2.1	2.0	478	3.5	21.7
10	0.043	1.75	3.65	5.4	20.45	19	1.8	2.05	710	7.0	18.8
F	0.068	1.5	2.9	4.4	19.5	19.9	2.75	2.05	341	2.2	12.3
G	0.041	1.55	3.1	4.66	22.2	20		3.95	325	13.8	13.0
H	0.041	1.75	3.4	5.15	22.4	20		3.95	374	12.4	9.4
J	0.040	1.2	2.3	3.5	22	20	0.5	4.0	233	32.4	35.7
11	0.040	1.3	2.7	4.0	22	20	0.5	4.0	300	17.8	16
12	0.040	1.5	3.0	4.5	22	20	0.5	4.0	426	26.6	13.7
K	0.040	1.2	2 3	3.5	22	20	1.0	4.0	276	35.1	29.7
13	0.040	1.3	2.7	4.0	22	20	1.0	4.0	396	20.4	17.4
14	0.036	1.55	3.1	4.65	21.2	20.4	1.05	4.0	505	13.5	24.6
15	0.043	1.6	3.3	4.9	20.2	20.4	1.05	3.9	463	16.6	22.4
L	0.044	1.6	3.4	5.0	21.8	19.9	1.1	3.95	444	9.4	6.5
M	0.040	1.2	2.3	3.5	22	20	1.5	4.0	319	30.5	34
16	0.040	1.3	2.7	4.0	22	20	1.5	4.0	420	19.5	20.3
17	0.010	1.5	3.0	4.5	22	20	1.5	4.0	554	20.2	15.2
N	0.023	1.5	2.9	4.4	21.9	19.9	2.0	3.95	264	7.8	3.6
P	0.049	1.8	3.25	5.05	21.7	20.2	2.1	4.0	254		2.2

Points corresponding to the composition of each alloy in Table I are plotted on FIGS. 2 to 4 of the accompanying drawing, which represent the areas from FIG. 1 corresponding to molybdenum contents of 0%, 2% and 4%, respectively. The first figure in parentheses for each alloy is the stress-rupture life in hours, the second figure the elongation in percent, and the third figure the impact strength. It will readily be seen that the alloys, whose composition fell outside the areas

$$ABCDEA,\ A_2B_2C_2D_2EA_2 \text{ and } A_4B_4C_4D_4EA_4$$

TABLE III

Alloy No. 14

Composition:	Wt. percent [1]
C	0.036
Cr	21.2
Co	20.4
Mo	4.0
Ti	3.1
Al	1.55
Cb	1.05

[1] Balance nickel, impurities and nominally 0.05% Zr and 0.003% B.

TABLE III—Continued

Weight loss (mg./cm.^{2}):	
Test A:	
300 hr.	24.3
Test B:	
73 hr.	72
120 hr.	250

As to other alloying constituents, boron and to a lesser extent zirconium, both improve the stress-rupture strength, and the alloys must contain at least 0.001% but not more than 0.05% boron, since amounts larger than 0.05% boron impair the forgeability of the alloys. Zirconium may be present in amounts up to 0.15%, and the combined amount of boron and zirconium, as expressed by 10×percent B+percent Zr should be at least 0.02%.

Hafnium can be present in amounts up to 0.1%, for example, from 0.02% to 0.07%, to improve weldability, especially those containing both boron and zirconium. Magnesium is advantageously added in amounts up to 0.04% to improve workability, but larger amounts have the opposite effect and make working more difficult. Most suitably the magnesium content is from 0.01% to 0.03%.

The resistance of the alloys to oxidation and scaling is improved by the presence of rare earth metals, and one or more of these metals may be added, for example, in the form of Mischmetall. Advantageously from 0.01% to 0.3% of rare earth metal, e.g., from 0.03% to 0.08%, is added.

We find the yttrium additions also improve the oxidation and scaling resistance of the alloys and their resistance to sulfidation, and yttrium can advantageously be added in amounts from 0.2% to 2%, for example, from 0.5% to 10%. As an example of an yttrium-containing alloy, Alloy No. 18, which contains 0.04% C, 22% Cr, 20% Co, 4% Mo, 3.1% Ti, 1.6% Al, 1% Cb, 0.05% Zr, 0.003% B and 1% Y, the balance, apart from impurities, being nickel, had after heat treating as for the alloys in Table I, a stress-rupture life at 17 ton-f./in.^{2} at 815° C. of 403 hours with an elongation of 8.6% and a Charpy V-notch impact strength at room temperature, after heating at 850° C. for 1000 hours, of 12.2 ft. lb.

Of the elements that may be present as impurities, silicon has a deleterious effect on corrosion-resistance and should therefore be kept below 1% and preferably below 0.5%. Other impurities may include manganese in amounts up to 1% and iron in amounts up to 2%. Tantalum may be introduced incidentally with the columbium in an amount up to about one-tenth of the columbium content. For the purposes of the present invention, such amounts of tantalum are to be regarded as part of the columbium content.

A particularly advantageous combination of properties is exhibited by alloys containing from 20.5% to 22.5% chromium, 15% to 22% cobalt, from 0.015%, e.g., from 0.03% or 0.035%, to 0.08% carbon, 4% to 5% titanium plus aluminum with a Ti:Al ratio of from 1:1 to 2.5:1 or 3:1, 1.0% to 1.7% columbium, 3.5% to 4.2% molybdenum, 0.001% to 0.006% boron, 0.03% to 0.06% zirconium, up to 0.03% magnesium, up to 0.07% hafnium, up to 0.3% rare earth metal and up to 1% yttrium, the balance, apart from impurities, being nickel.

To develop the full stress-rupture properties of the alloys in wrought form they must be subjected to a heat treatment comprising solution heating and subsequent aging. The solution treatment may consist of heating from 1 to 8 hours in the temperature range of 1050° C. to 1250° C., and the alloys may then be aged by heating for 1 to 24 hours in the temperature range of 600° C. to 950° C. An intermediate aging treatment consisting of heating for 1 to 16 hours at 800° C. to 1050° C., may be interposed between the solution treatment and the final aging stages. The alloys may be cooled at any convenient rate after each heat treatment stage, e.g., by air cooling

(generally to room temperature) or by direct transfer from a furnace at one temperature to one at a lower temperature.

The alloys can be air-melted, but to ensure the best creep properties they are preferably melted and cast under vacuum. They can be readily processed by conventional means such as extrusion, forging, or rolling. Although they are primarily intended for use in the wrought form as gas turbine blades they are suitable for use in other applications where a combination of good stress-rupture strength and resistance to corrosion is required, particularly for articles and parts that are subject in use to stress at high temperatures while exposed to the combustion products of impure hydrocarbon fuels or to salt or both. They may also be used to make cast articles and parts, which may also require heat treatments to develop their strength properties.

The alloys of the invention are also useful as matrix materials for alloys dispersion-hardened by the presence of finely divided refractory particles such as thoria, yttria, lanthana, ceria, or rare earth oxide mixtures, such as didimia. The refractory compound may suitably be present in an amount of at least 0.2%, preferably 0.5 to 5%, by volume and the particles should preferably be maintained as fine as possible, for example below 0.5 micron, most suitably from 10 angstroms to 1000 angstroms (0.001 to 0.1 micron). The present invention includes the use of the alloys as matrix materials in dispersion-hardened alloys.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A nickel-chromium alloy characterized by a combination of good stress-rupture strength, tensile ductility and the ability to absorb impact energy together with good resistance to various corrosive media, the stress rupture strength being at least about 300 hours at a temperature of about 815° C. under a stress of 17 ton-f./in.^{2}, said alloy consisting of from 19.5% to 23% chromium, about 0.01% to about 0.2% carbon, from 10% to 24% cobalt, about 3.7% to 7% in total of titanium plus aluminum, the ratio of titanium to aluminum being from 1:1 to 4:1, from 0.5% to 3% columbium, up to 4.5% molybdenum, with the proviso that the total percentage of titanium plus aluminum is correlated with the columbium and molybdenum so as to represent a point within the area ABCDEA of FIG. 1 of the accompanying drawing, from 0.001% to 0.05% boron, up to 0.15% zirconium, the sum of 10×percent B+percent Zr being at least 0.02%, up to 2% iron, up to 1% silicon, up to 1% manganese, and the balance essentially nickel.

2. An alloy in accordance with claim **1** containing from 20.5% to 22.5% chromium, from 0.015% to 0.08% carbon, 15% to 22% cobalt, 4% to 5% titanium plus aluminum, the ratio of titanium to aluminum being up to 3:1, 1.0% to 1.7% columbium, 3.5% to 4.2% molybdenum, 0.001% to 0.006% boron, 0.03% to 0.06% zirconium, up to 0.03% magnesium, up to 0.07% hafnium, up to 0.3% rare earth metal, and up to 1% yttrium.

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RICHARD O. DEAN, Primary Examiner

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,723,107 Dated March 27, 1973

Inventor(s) Edward Gordon Richards, Paul Isidore Fontaine & Michael John Fleetwooc

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 12, for "0.01%" first occurrence, read "0.001%";

Table I, Alloy No. K, column "Ti", for "23" read "2.3";

Column 5, line 43, for "12.2" read "15.2";

Signed and sealed this 22nd day of January 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents