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ALLOYS

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This invention relates to alloys containing both beryllium and boron which alloys have among their properties an inherent resistance to softening at elevated temperatures. This property is of extreme importance when the alloys are used as nozzles for ejection of hot gases, parts for furnaces and other heat-generating and heat transfer devices, and as parts of engines and turbines which must retain high strength at elevated temperature for a considerable period of time. It also is of importance in cutting tools which may be required to operate at red heat. While the alloys are of particular importance for uses involving high strength at elevated temperature, they have a combination of physical properties including resistance to corrosion and oxidation which render them valuable for many industrial purposes at temperatures from below zero up to about 2000° F.

The alloys of our invention contain from 5 to 40% chromium, preferably from 20 to 35% chromium. They contain one or more of tungsten, molybdenum, or uranium, these metals sometimes being referred to as "tungsten-type" metals. Where the alloy contains tungsten alone or molybdenum alone or uranium alone, the tungsten-type metal is from 1 to 40%, the tungsten preferably being from 10 to 30%, the molybdenum from 2 to 20% and the uranium from 2 to 20%. Where the alloy contains two of the tungsten-type metals, the preferred ranges of these metals in any combination are 3 to 25% tungsten, 1 to 15% molybdenum and 2 to 15% uranium. Where the alloy contains three of the tungsten-type metals, the preferred ranges of these metals are 3 to 15% tungsten, 1 to 10% molybdenum and 2 to 15% uranium. Molybdenum appears to be considerably more potent than tungsten. The addition of 3% molybdenum to chromium-nickel-cobalt-beryllium-boron base alloys gives the same hot hardness as the addition of about 11 to 13% tungsten. 6% molybdenum gives the same hot hardness as about 14 to 16% tungsten. 9% molybdenum gives the same hot hardness as about 16 to 18% tungsten. Uranium appears to have somewhat higher potency than tungsten. The ratio of molybdenum to tungsten in any replacement of tungsten by molybdenum varies from 1:6 to 1:1.5, each per cent of molybdenum becoming less effective as a replacement for tungsten as the percentage of molybdenum increases. The alloys also contain one or more of the matrix metals cobalt, nickel or iron in total amount between 25% and 65% of the alloy. The total per cent of the matrix metals preferably is about 25

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to 52% and much better results for many purposes are attained if this total per cent is not over about 44%.

In our alloys, beryllium is employed in amounts between 0.05 and 7%, preferably between 0.15 and 2%. The alloys contain 0.25 to 7% boron, preferably 0.50 to 2% boron. The carbon is generally between 0.01 and 3%, usually between 0.10 and 1% and preferably between 0.15 and .60%. For alloys which are to be used in applications requiring high hardness at elevated temperatures, it is preferred to keep the carbon on the low side of the range and to obtain the required hardness by the use of beryllium and boron. For other applications not requiring such high hardness at elevated temperatures, the major hardening effect may be obtained from carbon so that the alloy is derived by employing carbon in the high side of the range together with beryllium and boron in the low side of these ranges. Where cutting qualities or abrasion resistance may be most important and high temperature strength less important, the alloy may contain carbon up to about 4 or 5 per cent.

Where the alloy contains tungsten as the only tungsten-type metal, a preferred composition range of our alloys is

	Per cent
Chromium -----	20 to 35
30 Tungsten -----	10 to 35
Cobalt -----	20 to 28
Nickel -----	20 to 28
Beryllium -----	0.15 to 2
Boron -----	0.50 to 2
35 Carbon -----	0.10 to 1

Uranium may be substituted for part or all of the tungsten in somewhat lower percentages than tungsten. Molybdenum may be substituted for part or all of the tungsten, but due to the greater potency of molybdenum as previously pointed out, the amount of molybdenum required to give the same hot hardness is less than would be required for tungsten.

It has been observed that elements of small atomic diameter exert a powerful influence as hardeners in some alloys. Since it is possible for elements of small atomic diameter to occupy the interstices between atoms of much larger atomic diameter, carbon (atomic diameter 1.5 Å.), boron (atomic diameter 1.9 Å.) and beryllium (2.25 Å.) may form interstitial solid solutions with chromium (2.71 Å.), tungsten (2.82 Å.), molybdenum (2.80 Å.), uranium (2.83 Å.), iron (2.52 Å.), cobalt (2.50 Å.) and nickel (2.49 Å.). Also possible is

the formation of intermetallic compounds of the elements carbon and/or beryllium and/or boron with chromium, tungsten, molybdenum, uranium, cobalt, nickel and iron. Examination of the micro-structures of our alloys suggest that both solid solutions and intermetallic compound phases are present.

Although the small size of the atoms of beryllium, boron and carbon makes them useful as hardening elements, a small atom also diffuses readily within the alloy structure at high temperature. This diffusion, exemplified by the coalescence of carbides in steel, may be a cause of softening which is undesirable for parts which must retain high hardness for long periods of time at elevated temperature. Beryllium and boron, having larger atomic diameters than carbon, appear to be more effective hardeners than carbon, due at least in part to their slower diffusion at high temperature.

Alloys containing chromium, tungsten and matrix metal, such as cobalt, nickel or iron contain a substantial amount of carbon to serve as a hardener when used as cutting tools or hard surfacing materials. The presence of a large amount of carbon is beneficial in a cutting tool since abrasion resistance is required and in the usual service the tool is not at extremely high temperature for any great length of time. We have found, however, that where the alloys are to be subjected to high temperature for long periods of time, the substitution of beryllium and boron for much of the carbon results in a material which is more resistant to softening at high temperature. However, where high hardness at elevated temperatures is not a dominant consideration, our alloys may contain carbon on the high side of the range together with beryllium and boron within the ranges specified.

The influence of combinations of beryllium and boron in causing alloy hardness and hardness retention at elevated temperature is shown in Table 1.

Table 1

Alloy No.	Chemical Composition							Brinell Hardness	
	W	Cr	Ni	Co	B	Be	C	Room Temp. WC-Ball	1500° F. WC-Ball
1.	17.93	30.33	26.66	25.28	none	none	0.23	260	151
2.	16.70	31.09	24.13	23.73	0.62	0.63	0.23	412	207
3.	17.47	30.30	22.73	24.43	0.65	0.89	0.25	430	228
4.	15.88	30.20	23.86	22.94	1.33	0.87	0.24	451	219
5.	16.52	28.83	24.78	23.14	1.99	0.75	0.34	477	255
6.	29.43	30.01	19.05	18.78	none	none	0.19	404	243
7.	27.55	28.75	17.18	18.66	1.16	0.17	0.39	522	372

It will be seen from the table that the combination of beryllium and boron, even when used in small amounts, is an effective hardener for alloys of the type contemplated by our invention at both room temperature and at elevated temperature.

The most effective tungsten addition falls within the range of 10 to 35% tungsten and more specifically between 15 and 30% tungsten. For many applications, alloys containing less than 10% tungsten do not have sufficient strength and hardness at high temperature. For many applications, alloys containing above 35 or 40% tungsten are too brittle at room temperature to be satisfactory. Alloys containing from 10 to 35% tungsten or preferably from 15 to 21% tungsten have good hardness and strength at elevated

temperatures while retaining adequate toughness at room temperature.

In our alloys, increasing the chromium content up to 40% causes progressively higher hot hardness while the room temperature hardness passes through a minimum in the region of about 25% chromium. It is highly desirable to have the room temperature hardness of these alloys as low as possible in order to avoid the glass-like brittleness usually associated with alloys having high hardness at elevated temperature. Accordingly, alloys containing about 20 to 30 or 35% chromium are especially valuable in that they have lower room temperature hardness and higher high temperature hardness than alloys containing less than this amount of chromium.

In addition to the effect of chromium on the room temperature and high temperature hardness of the alloy it contributes greatly to resistance of the alloy to corrosion and oxidation. For instance, in tests carried out at high temperature a tungsten-nickel-cobalt-iron alloy containing no chromium developed a red powdery rust-like coating on its surface in one hour at 1500° F. As little as 10% chromium caused the red powder to be displaced by a thin grey scale. Increasing the amount of chromium to 20%, 30% or 40% sufficiently increases the resistance to oxidation at 1500° F. that only a light bluish discoloration results. Accordingly, alloys containing chromium in the range of about 20 to 30 or 35% have the very desirable combination of properties of good resistance to oxidation and corrosion, low room temperature hardness and high hardness at elevated temperature.

The metals cobalt, nickel and iron constitute a matrix for the hard borides, beryllides and carbides and serve as a valuable adjunct to the control of the final hardness of the alloy. Although the individual matrix metals all serve the common function of providing a matrix for the hard borides, beryllides and carbides and have somewhat similar characteristics in this respect, they

differ somewhat in their individual characteristics. Generally speaking, the use of cobalt in place of nickel tends to harden and strengthen the alloy while the substitution of nickel for cobalt tends to soften and toughen the alloy. The addition of iron to an alloy containing cobalt and nickel increases the hardness slightly at room temperature and at elevated temperature as the percentage of iron is increased from zero to about 3 or 4%. Further increase in iron beyond this point tends to soften the alloy both at room temperature and at high temperature. The alloys which we have used most frequently and very successfully have contained little iron, usually less than 2%.

The following table gives examples of some alloys according to our invention:

Table 2

Example No.	C	W	Mo	U	Cr	Ni	Co	Fe	Be	B
1	2.5	3			40	23	19	5	5.00	0.50
2	0.90	12			32	18	31		0.25	4.50
3	0.55	19			29	25	23		1.00	0.75
4	0.30	32			25	15	22		1.40	2.50
5	0.75	40			17	20	18		0.90	1.50
6	1.80		1		40	14	35		0.20	6.25
7	0.60		6		32	30	26		1.30	2.50
8	0.15		14		30	26	25		2.00	0.80
9	0.35		22		20	39	15		1.75	0.50
10	1.00	3	2		25	25	40		1.25	0.75
11	0.65	6	4		29	29	27		0.90	1.50
12	1.00	8	11		40	20	16		1.80	0.65
13	0.35	3	15		35	27	15		1.25	1.50
14	0.10	12	6		27	20	26	3.0	0.40	4.00
15	0.50	19	7		32	22	15		1.10	1.75
16	3.00	25	3		20	26	18		3.00	0.55
17	1.25			14	35	22	24		1.25	0.70
18	0.50			26	30	20	19		0.80	1.60
19	0.90		4	10	35	20	25		1.25	2.00
20	0.40	12		9	25	22	27		2.25	0.50
21	0.05	8		6	33	24	22		0.80	1.75
22	0.50	14			30		52		0.75	1.25
23	0.60	27			34	35			1.00	0.90

In our alloys in addition to chromium, the tungsten-type metals, the matrix metals, beryllium and boron, there may be present small amounts of other elements such as silicon, manganese, aluminum, magnesium, calcium, barium, strontium, titanium, zirconium, vanadium, etc., depending upon (1) the purity of the metals and alloys used in making the heats, (2) the method of melting and the refractories used, and (3) deoxidation and degasifying practices, or (4) small percentages intentionally added to improve casting or fabricating properties, to control as-cast grain size or to contribute to strength, toughness, etc. The amount of each such element should be restricted to percentages which do not adversely affect the desired properties of the alloy; in many cases the additional element will not exceed about 1%.

As used herein, the term "tungsten-type metal" is intended to include tungsten, molybdenum or uranium or any combination thereof. This term does not include chromium.

The method of forming the alloys into shape may be varied somewhat depending upon the specific composition selected and the intended use of the article. Both sand molds and cast iron or other permanent or semi-permanent molds are satisfactory for casting ingots and other forms which may be rolled, machined or ground into final shape. Centrifugal or pressure casting is preferred for thin or complex sections. For parts to be forged into shape, the alloys toward the low side in tungsten, cobalt and beryllium are preferred. While the alloys may be used in the cast condition, they are also responsive to heat treatment. A solution heat treatment consisting of heating any of these alloys to a temperature somewhat below its softening range followed by rapid cooling, for example, cooling in water, oil or air, results in a more homogenous alloy with uniform structure as revealed by micro-examination. Subsequent aging at temperatures from 1000° F. to 1800° F. for fifteen minutes to 24 hours produces stabilized alloys of extremely uniform hardness.

The invention is not limited to the preferred embodiments which have been given merely for purposes of illustration but may be otherwise embodied within the scope of the following claims.

We claim:

1. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% of at least one tungsten-type metal of the group consisting of tungsten, molybdenum and uranium, 0.05 to 7% beryllium

0.25 to 7% boron, 0.01 to 3% carbon, an effective amount of cobalt and an effective amount of nickel, the sum of the cobalt and nickel constituting 25 to 65% of the alloy, the tungsten-type metals not exceeding 40% of the alloy.

2. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% of at least one tungsten-type metal of the group consisting of tungsten, molybdenum and uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, at least 15% cobalt and at least 15% nickel, the sum of the cobalt and nickel constituting 30 to 52% of the alloy.

3. An alloy containing 5 to 40% chromium, 1 to 40% of at least one tungsten-type metal of the group consisting of tungsten, molybdenum and uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, not over about 5% iron, the balance being substantially all nickel and cobalt, the nickel comprising from 15 to 39% of the alloy, the cobalt comprising from 15 to 40% of the alloy, the sum of the nickel, cobalt and iron being not over 65% of the alloy, the tungsten-type metals not exceeding 40% of the alloy.

4. An alloy containing 5 to 40% chromium, 1 to 40% of at least one tungsten-type metal of the group consisting of tungsten, molybdenum and uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, not over about 5% iron, the balance being substantially all nickel and cobalt, the nickel constituting at least 15% of the alloy, the cobalt constituting at least 15% of the alloy, the sum of the nickel, cobalt and iron being not over 52% of the alloy, the tungsten-type metals not exceeding 40% of the alloy.

5. An alloy containing 5 to 40% chromium, 1 to 40% of at least one tungsten-type metal of the group consisting of tungsten, molybdenum and uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, not over about 5% iron, the balance being substantially all nickel and cobalt, the nickel constituting at least 15% of the alloy, the cobalt constituting at least 15% of the alloy, the sum of the nickel, cobalt and iron being not over 44% of the alloy, the tungsten-type metals not exceeding 40% of the alloy.

6. An alloy containing 5 to 40% chromium, 1 to 40% tungsten, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, not over about 5% iron, the balance being substantially all nickel and cobalt, the nickel comprising from 15 to 39% of the alloy, the cobalt comprising from 15 to 40% of the alloy, the sum of the nickel, cobalt and iron being not over 65% of the alloy.

7. An alloy consisting essentially of 20 to 35% chromium, 10 to 35% tungsten, 20 to 28% cobalt, 20 to 28% nickel, 0.15 to 2% beryllium, 0.50 to 2% boron, and 0.10 to 1% carbon.

8. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% of at least one tungsten-type metal of the group consisting of tungsten, molybdenum and uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, an effective amount of cobalt and an effective amount of nickel, the sum of the cobalt and nickel constituting 25 to 52% of the alloy, the tungsten-type metals not exceeding 40% of the alloy.

9. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% molybdenum, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, an effective amount of cobalt and an effective amount of nickel, the sum of the cobalt and nickel constituting 25 to 65% of the alloy.

10. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% molybdenum, 0.05 to 7%

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beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, at least 15% cobalt and at least 15% nickel, the sum of the cobalt and nickel constituting 30 to 52% of the alloy.

11. An alloy containing 5 to 40% chromium, 1 to 40% molybdenum, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, not over about 5% iron, the balance being substantially all nickel and cobalt, the nickel comprising from 15 to 39% of the alloy, the cobalt comprising from 15 to 40% of the alloy, the sum of the nickel, cobalt and iron being not over 65% of the alloy.

12. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, an effective amount of cobalt and an effective amount of nickel, the sum of the cobalt and nickel constituting 25 to 65% of the alloy.

13. An alloy consisting essentially of 5 to 40% chromium, 1 to 40% uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, at least 15% cobalt and at least 15% nickel, the sum of the cobalt and nickel constituting 30 to 52% of the alloy.

14. An alloy containing 5 to 40% chromium, 25

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1 to 40% uranium, 0.05 to 7% beryllium, 0.25 to 7% boron, 0.01 to 3% carbon, not over about 5% iron, the balance being substantially all nickel and cobalt, the nickel comprising from 15 to 39% of the alloy, the cobalt comprising from 15 to 40% of the alloy, the sum of the nickel, cobalt and iron being not over 65% of the alloy.

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