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NICKEL-CHROMIUM-ALUMINUM HEAT RESISTING ALLOY

Filed Sept. 16, 1959

2 Sheets-Sheet 1

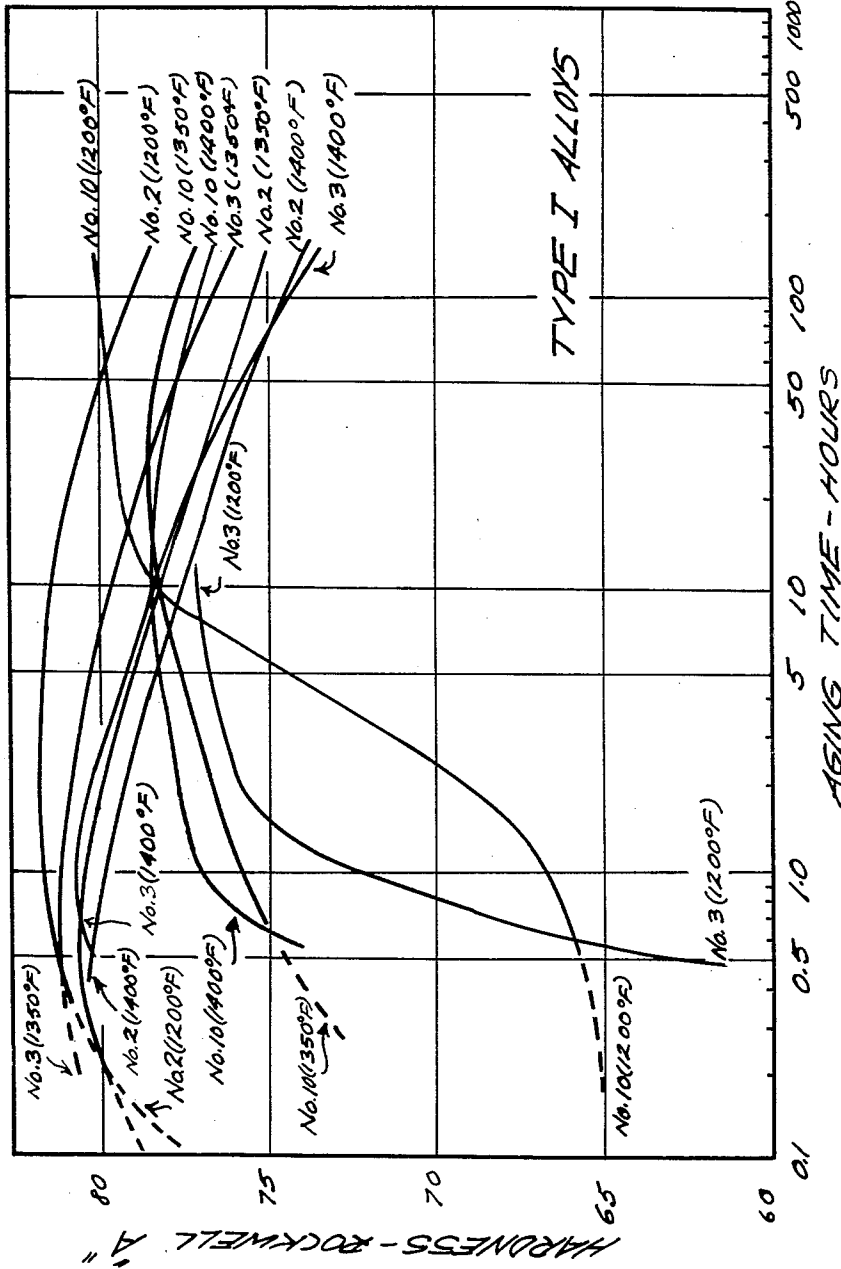


FIG. 1

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2 Sheets-Sheet 2

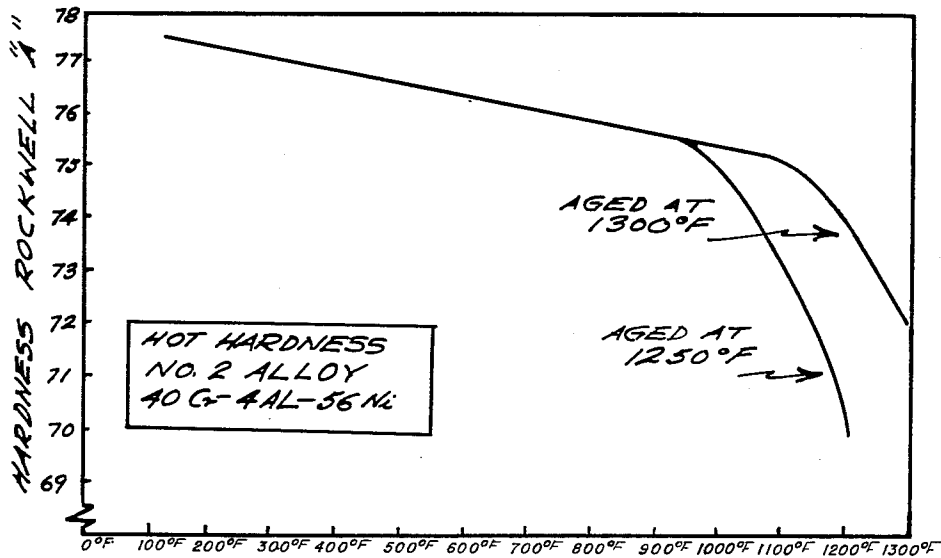


FIG. 2

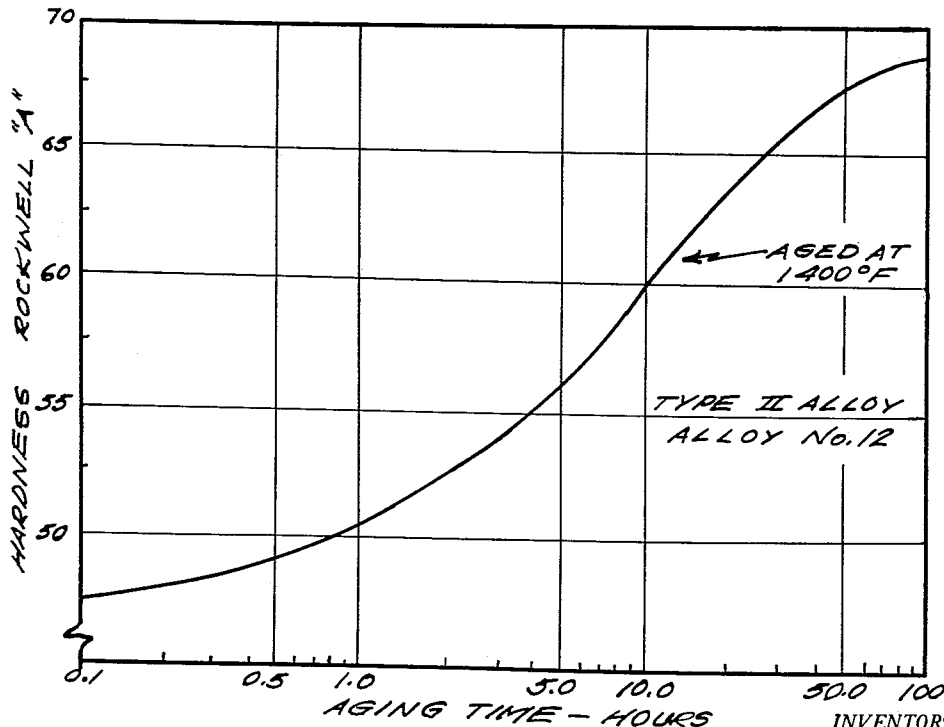


FIG. 3

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**NICKEL-CHROMIUM-ALUMINUM HEAT
RESISTING ALLOY**

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11 Claims. (Cl. 75-171)

This invention relates to heat resistant alloys characterized by improved physical properties at elevated temperatures and in particular to age-hardenable, aluminum-containing, high chromium nickel alloys.

In recent years the art has been earnestly endeavoring to obtain heat and stress-resisting alloys either in the cast or wrought condition capable of withstanding working stresses, corrosive oxidizing atmospheres and the like at elevated temperatures ranging up to 1800° F. and above for prolonged periods of time. In such endeavors the art has been seeking a composition range whereby, through judicious proportioning of essential elements over the range, alloys with various types of metallurgical properties are obtainable, depending upon the use to which the alloys are to be put. For example, it would be desirable if such a composition range would make available a non-ferrous heat resistant alloy of high hardenability through age hardening heat treatment, particularly a composition for use in high temperature bearings, gears and the like capable of sustaining high hot hardness, i.e. resist softening, at elevated temperatures ranging up to about 1200° F. Or in the alternative it would be desirable if an alloy could be made available from the composition range characterized by delayed age hardening but which is easily fabricated into sheets and other shapes for use at elevated temperatures ranging up to 1800° F. under applied stress.

We have discovered a novel alloy composition capable of fulfilling the above desirable attributes by employing nickel alloys containing a judicious proportioning of nickel, chromium and aluminum as essential elements.

It is the object of this invention to provide an age-hardenable, aluminum-containing, high chromium nickel alloy characterized by improved physical properties at elevated temperatures.

Another object is to provide a heat resistant nickel alloy capable of being quickly age hardened to relatively high hardnesses at temperatures in the range of 1000° F. to 1600° F., particularly at temperatures within the range of 1000° F. to 1400° F.

A further object is to provide an age-hardened composition characterized by resistance to softening at temperatures ranging up to about 1200° F.

Still another object is to provide a hot workable, aluminum-containing, high chromium nickel alloy with delayed aging characteristics and capable of being fabricated into a high strength sheet metal product.

It is moreover the object of the invention to provide an aluminum-containing, high chromium nickel alloy containing complex alloy additions for use in shaped articles subjected to temperatures ranging up to about 1800° F.

These and other objects will more clearly appear to those skilled in the art from the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 contains age hardening curves showing the effect of time and temperature on the age hardening response of Type I alloy compositions;

FIG. 2 depicts curves showing the resistance of an age hardened Type I alloy to softening at temperatures ranging up to about 1200° F.; and

FIG. 3 is illustrative of an age hardening curve for a Type II alloy showing delayed aging at 1400° F.

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This invention is based on the discovery by us that heat resistant nickel alloys of improved combination of physical properties at room and elevated temperatures can be produced by controlling in combination the essential elements nickel, chromium and aluminum. In order to achieve the desired results it is essential, unlike other age-hardenable nickel-chromium alloys, that the chromium content range from about 28% to 45%, aluminum from about 1% to 6%, and the balance substantially nickel by weight, the sum of the nickel and chromium content being at least about 70%, the ratio of nickel to chromium being maintained at least about 1 to 1, and being particularly maintained at a ratio ranging from about 1 to 1 to about 2.25 to 1.

Other ingredients may be present in the alloy in optional amounts provided the foregoing conditions with respect to the nickel and chromium contents are maintained. As illustrative of other alloying ingredients are the following by weight: up to about 20% iron, up to about 10% molybdenum, up to about 15% cobalt, up to about 3% titanium, up to about 2% columbium and/or tantalum, up to 4% silicon, up to about 2% manganese and up to 2% tin.

In carrying the invention into practice, we prefer a composition containing about 30 to 40% chromium, about 2 to 5% aluminum and the balance substantially nickel, the sum of the nickel and chromium content being at least about 80% at a ratio of nickel to chromium of at least about 1.3 to 1. Optional ingredients may likewise be present in the amounts as stated above. However, we prefer when the sum of the nickel and chromium content is above 80%, for example above 85%, to employ optional ingredients in the following amounts: up to about 5% iron, up to about 5% molybdenum, up to about 10% cobalt, up to about 2% titanium, up to about 2% columbium and/or tantalum and up to about 4% silicon.

In connection with the foregoing broad and preferred ranges certain other optional elemental additions may be made, such as carbon, nitrogen and certain of the de-oxidizers such as boron, magnesium, cerium, zirconium, etc. With respect to carbon and nitrogen, they may each be present singly or together in amounts ranging up to about 0.4%. Boron may be added in small amounts up to about 0.1%, calcium or magnesium in amounts up to about 0.2% and rare earth elements in amounts up to about 0.2%. Zirconium may be employed over a range starting with a small but effective amount (e.g. 0.002%) and range up to about 0.3%. The foregoing additional optional ingredients are mentioned by way of illustration and not by way of limitation, it being understood that other small additions may be made in accordance with the existing knowledge of the art concerning heat resistant alloys without substantially affecting the desirable characteristics of the alloys provided by the invention.

We have found in working over the broadly stated range of composition that it is possible to provide several types of alloys depending upon the use to which the alloys are to be put. We have found in particular three types of alloys: (I) those exhibiting fast aging response over a low range of aging temperatures leading to very high hardness, the alloys having particular use in bearings and gears at elevated temperatures and for hard, corrosion resistant applications at lower temperatures; (II) those with delayed aging characteristics and moderate hardness but which can be fabricated into high strength sheet with good resistance to corrosion; and (III) complex alloys which are more sluggish with respect to aging but which are capable of being hardened at higher aging temperatures and which alloys are useful for sheet products and other shapes subjected in use under high stress at elevated temperatures ranging up to about 1800° F.

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TYPE I ALLOYS

These alloys exhibit quick aging response and in the hardened condition resist softening at elevated temperatures ranging up to about 1200° F. The composition may range from about 30 to 45% chromium, from about 3 to 6% aluminum and the balance substantially nickel, the sum of nickel and chromium being at least 85% of the total composition at a nickel to chromium ratio ranging from about 1 to 1 to about 2.25 to 1.

For consistently high age-hardening response we prefer a composition containing about 30% to 40% chromium, about 3% to 5% aluminum and the balance substantially nickel, the sum of the nickel and chromium content being at least 90% by weight of the total composition at a nickel to chromium ratio of about 1.3 to 1 to about 1.75 to 1. We have found that 4% aluminum employed over a range of 30% to 40% chromium to be particularly effective in producing an alloy having quick age hardening response and yet hot workable in the annealed condition.

Examples of Type I alloys are given in the following Table:

Table I

Alloy No.	Percent Cr	Percent Ni	Percent Al	Percent Others	Ni and Cr	Ni/Cr
1	45	51	4		96	1.13
2	40	56	4		96	1.4
3	38	56	4	2% Ti	94	1.47
4	40	54	4	2% Si	94	1.35
5	40	54	4	2% Sn	94	1.35
6	35	59	4	2% Ti	94	1.69
7	38	56	6		94	1.47
8	30	64	6		94	2.13
9	35	55	3	2% Ti	90	1.57
10	35	56	4	5% Mo	91	1.6
11	30	64	4	2% Si	94	2.13

A method for producing the foregoing alloys comprises melting the nickel and chromium together in a high frequency induction furnace in air but, preferably, in an inert gas cover. The aluminum or other elements are added after the usual deoxidation treatment. These alloys have also been melted as non-consumable or consumable electrode ingots under sub-atmospheric pressure (about 100-400 mm. Hg) of argon. After the ingot has cooled to room temperature, it is removed from its mold and surface imperfections removed from the ingot by grinding before being subjected to hot working.

The resulting ingot is then hot worked by hammer forging, press forging, or extrusion using a maximum of about 2300° F. As the ingot structure is refined, it is possible to work the alloy at progressively lower temperatures to refine the grain size; however, working below 1600° F. should be avoided to prevent hardening due to aging.

As an example, alloy No. 2 which was cast as a ten pound ingot two and one half inches square by five inches high, was hot forged at a temperature of about 2300° F. to a one inch square bar. The bar was then solution treated at a temperature of about 2250° F. for about one half hour, water quenched and then cold rolled to one half inch square and again solution treated as above.

In determining hardening response through aging heat treatments, samples of the various alloys were subjected to solution heat treatment followed by aging at various times at temperatures of from 1000° F. to 1800° F. in approximately 100° F. intervals. The solution treatment comprised heating the alloy at about 2250° F. for about two

hours followed by water quenching. The aging results obtained are given in Table II as follows:

Table II

Temp., ° F.	Time, Hrs.	Alloys No. 1 to 11												
		Hardness, Rockwell "A"												
		1	2	3	4	5	6	7	8	9	10	11		
10	2,250	water	64	57	---	60	68	---	67	56	---	57	---	
		quench	81	81	62	80	68	78	---	68	---	66	---	
15	1,200	1	81	81	72	80	78	79	---	76	---	69	---	
		2	81	81	---	76	80	78	79	---	79	---	75	---
20	1,200	3	81	81	76	80	78	78	---	80	---	79	---	
		6	81	81	76	80	78	78	---	80	---	79	---	
25	1,200	9	80	---	---	---	---	---	---	---	---	79	---	
		12	80	---	---	---	---	---	---	---	---	79	---	
30	1,200	18	80	---	---	---	---	---	---	---	---	79	---	
		100	80	79	---	---	---	---	---	---	---	77	---	
35	1,300	1/2	80	81	77	82	76	81	---	76	71	67	74	
		1	80	79	81	76	79	81	80	72	62	---	---	
40	1,300	3	80	80	79	80	76	79	81	80	---	76	76	
		4 1/2	---	---	78	79	77	79	81	80	---	76	76	
45	1,300	6	---	---	80	79	77	79	81	80	---	78	78	
		9	---	---	80	80	78	76	79	81	---	78	78	
50	1,300	10	82	---	---	---	---	---	---	---	---	78	78	
		25	82	---	---	---	---	---	---	---	---	---	78	80
55	1,300	67	82	78	---	---	---	---	79	78	---	78	80	
		75	---	---	---	---	---	---	---	79	78	---	74	---
60	1,350	145	80	80	81	81	78	80	---	78	---	78	---	
		1/2	80	80	81	81	80	78	80	---	78	---	77	---
65	1,350	1	78	80	---	---	---	---	---	---	---	---	---	
		2	78	80	---	---	---	---	---	---	---	---	---	---
70	1,350	3	---	---	80	80	78	80	---	80	---	79	78	
		6	78	79	80	78	78	80	---	79	---	78	---	
75	1,350	9	---	---	80	77	76	79	---	79	---	78	---	
		12	77	---	---	---	---	---	---	---	---	78	---	
80	1,350	18	77	---	---	---	---	---	---	---	---	79	---	
		23	---	---	---	---	---	---	---	---	---	---	78	---
85	1,350	45	---	---	---	---	---	---	---	---	---	---	77	---
		75	---	---	---	---	---	---	---	---	---	---	---	77
90	1,350	135	74	76	76	74	74	77	---	76	---	---	---	
		145	---	---	---	---	---	---	---	---	---	---	---	---
95	1,400	1/2	79	80	80	80	80	80	---	80	76	72	---	
		1	78	80	80	80	80	80	---	80	78	77	---	
100	1,400	3	78	78	79	78	80	79	---	79	80	78	---	
		6	77	78	79	78	78	79	---	79	80	78	---	
105	1,400	9	77	78	79	78	78	79	---	79	80	78	---	
		16	76	---	---	---	---	---	---	---	---	---	---	
110	1,400	57	75	75	74	76	75	---	76	---	---	---		
		121	74	74	74	72	74	75	---	75	---	---	---	
115	1,500	1/2	74	---	80	72	---	---	80	78	---	---	---	
		2	76	---	---	---	---	---	---	---	77	76	70	
120	1,500	3	75	75	78	78	72	---	78	78	---	---	---	
		5	75	75	---	76	71	---	---	78	76	77	77	
125	1,500	9	74	74	---	74	70	---	---	78	76	79	76	
		15	74	74	74	72	---	---	---	76	76	---	72	
130	1,500	21	73	73	70	---	---	---	75	74	---	77	75	
		28	73	---	---	---	---	---	---	75	74	---	71	
135	1,500	46	73	73	70	---	---	---	---	76	75	---	---	
		52	71	---	---	---	---	---	---	74	74	---	70	
140	1,530	73	73	73	70	---	---	---	74	74	---	---	70	
		97	72	72	68	---	---	---	74	73	---	---	69	
145	1,500	119	70	---	---	---	---	---	75	74	---	---		

As illustrative of the age hardening response of some of the alloys, reference is made to FIG. 1 which shows the effect of time and temperature on the aging of alloy Nos. 2, 3 and 10. It will be noted that No. 2 responds more rapidly at 1200° F. (in less than half an hour at temperature) as compared to Nos. 3 and 10 which takes several hours before the age hardening becomes appreciably effective. However, at 1350° F. it will be noted that Nos. 3 and 10 gain rapidly in hardness and harden almost as fast as alloy No. 2 at 1400° F.

With increasing temperatures, however, at and above 1400° F., hardness falls off more rapidly with increasing time at temperature. In any event, the alloys are age hardenable broadly over the temperature range of about 1000° to 1600° F., but preferably over the range of about 1000° to 1400° F., the preferred time and temperature depending on the aggregate properties desired for any alloy.

As a further illustration of the response of alloy No. 2 to low temperature age hardening, the following was obtained at 1100° F., starting with the alloy in the solution treated condition:

Temp., ° F.	Time, Hours	Hardness, R _A
1,100.....	1	52
1,100.....	5	67
1,100.....	10	75
1,100.....	24	78

Additions of other elements such as titanium, iron and molybdenum tend to have a slight delaying effect on the response to age hardening. We prefer, where hardness is the prime consideration, to control the chromium content over the range of 30% to 40% with the aluminum content in the neighborhood of about 3.5% (e.g. 3 to 5%) provided the amount of nickel present is sufficient to yield a Ni plus Cr content of at least about 94% at a ratio of Ni to Cr of at least 1.3.

It will be noted from Table I that the Ni to Cr ratios vary from 1.13 to 2.13 which falls within the desired range of about 1.1 to 2.25. It is preferred, where the ratio exceeds 1.6, to employ aluminum at the higher range (above 4%) in order to achieve full benefit of the hardening effect.

By controlling the conditions of hardening, a wide range of hardnesses is possible ranging from about 60 to over 80 Rockwell "A" (corresponding to 20 to 60 R_C) and preferably ranging from 70 to 80 R_A (corresponding to 40 to 60 R_C).

We have found that the foregoing alloys lend themselves to use as bearing materials and gears for use at elevated temperatures. These alloys also find use in hot pressing dies where resistance to oxidation and abrasion are important considerations. Bearing tests at 1000° F. showed that high hot hardness was accompanied by very low friction, apparently due to the presence of high amounts of chromium and aluminum.

Hot hardness tests showed the Type I alloy particularly to resist softening at temperatures up to 1200° F. This is illustrated by FIG. 2 which shows the hot hardness of alloy No. 2 (40% Cr, 4% Al and 56% Ni) up to 1200° F. It will be noted that while the initial hardness values (aged at 1250 and 1300° F.) were in the neighborhood of about 78 Rockwell "A," alloy No. 2 maintained its hardness to above 74 Rockwell "A" at about 1000° F., the hardness falling off more rapidly between 1050° F. and 1300° F.

The foregoing alloy (No. 2) also exhibited rather high tensile strength at elevated temperatures after being subjected to solution and aging treatments as will be apparent from Table III. The results were obtained on specimens having a diameter of 0.250" and a gage length of 1.25".

Table III

Solution Temp.	Aging Temp. and Time	R _A	Temp. of Test, ° F.	(p.s.i.) Ultimate Strength	Percent Elong.
2,250° F.....	1,600° F.—2 hrs.....	74	1,000	198,300	12
2,250° F.....	1,500° F.—2 hrs.....	76	1,350	118,300	6
2,250° F.....	1,600° F.—2 hrs.....	75	1,500	63,800	16
2,300° F.....	1,500° F.—2 hrs.....	77	1,000	190,600	4
2,300° F.....	1,500° F.—2 hrs.....	76	1,350	112,600	4
2,300° F.....	1,600° F.—2 hrs.....	74	1,500	65,100	16

Of particular importance is the low solution treated hardness which is in the order of 10 R_C. This permits easy fabrication and machining operations. These alloys can be readily cold worked to achieve high strength and hardness values, which can be further increased by ap-

propriate aging, up to values as high as 63 to 66 R_C (83 to 84.5 R_A).

TYPE II ALLOYS

As previously stated, the Type II alloys are characterized generally by delayed aging and are capable of being easily fabricated into high strength sheet having good resistance to corrosion. The composition of such alloys ranges from about 30 to 40% chromium, about 1% to 2.5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 90% of the total composition at a ratio of nickel to chromium of about 1.3 to 1 to 1.75 to 1. We prefer a composition containing aluminum in the neighborhood of about 2% as shown in Table IV.

Table IV

Alloy No.	Percent Cr	Percent Ni	Percent Al	Percent Others	Ni and Cr	Ni/Cr
12.....	40	58	2		98	1.45
13.....	40	54	2	4% Si	94	1.35

The method employed in producing the foregoing alloys was similar to that described in the production of Type I alloys. Hardness data was similarly obtained as follows:

Table V

Temp., ° F.	Time, Hrs.	Alloy Nos. 12—13	
		Hardness R _A	
		12	13
2,250.....	Water Quench	49	57
1,200.....	1/2	50	58
1,200.....	1	52	58
1,200.....	3	52	63
1,200.....	6	52	70
1,300.....	1/2	50	61
1,300.....	1	50	67
1,300.....	3	51	75
1,300.....	6	52	77
1,300.....	9	54	79
1,300.....	23	60	69
1,300.....	45	59	69
1,300.....	145	62	72
1,350.....	1/2	50	68
1,350.....	1	50	73
1,350.....	3	52	77
1,350.....	6	56	76
1,350.....	9	56	76
1,350.....	15	62	77
1,350.....	145	69	74
1,400.....	1/2	50	64
1,400.....	1	50	66
1,400.....	3	53	74
1,400.....	6	57	74
1,400.....	9	58	76
1,400.....	15	62	75
1,400.....	57	68	73
1,400.....	121	68	73
1,500.....	1/2	51	60
1,500.....	1	52	62
1,500.....	3	55	62
1,500.....	6	61	68
1,500.....	9	66	70
1,500.....	15	65	70
1,500.....	21	64	70
1,500.....	46	64	69
1,500.....	73	65	68
1,500.....	97	65	66

It will be apparent from the foregoing data that the age hardening response of alloy No. 12 is delayed and depressed and tends to yield maximum values when heated for 50 or more hours at 1400° F. (note FIG. 3). Such delayed response has its advantages in connection with welding operations where one would not want the aging to proceed in the heat effected zone too rapidly as this might result in embrittlement. Alloy No. 13 which is

similar to No. 12 but differs in containing 4% Si indicates a faster hardenability response. Generally the alloys will exhibit hardnesses in the age hardened condition ranging from 50 to 77 R_A.

Alloy No. 12 exhibited a rather high tensile strength at room temperature in the cold swaged condition of 210,000 p.s.i. with 11% elongation (0.250" diameter and gage length of 1.25"). The alloy also exhibited a modulus of elasticity in the neighborhood of about 30 to 33 × 10⁶ p.s.i. In producing the cold swaged alloy, the method employed comprised taking a casting of alloy No. 12 about 6 inches long and 1 inch in diameter and forging it at 2250° F. to 1900° F. to a one half inch square. This was followed by machining to a 7/16 inch round to remove surface defects and swaging at room temperature to a 1/4 inch round without annealing. Swaging is conducted in small steps to avoid overheating and any age hardening which may occur as a consequence of heating developed by cold working in large steps.

Material produced from the Type II alloy is particularly useful in aircraft gas turbine combustion liners and after burners; high temperature, high pressure piping and other parts subjected in use to erosive and/or corrosive conditions at elevated temperatures. These alloys couple outstanding oxidation resistance with great formability, yet offer very high strength at temperatures up to about 1200° F. for other parts.

TYPE III ALLOYS

The Type III alloys find particular use in the production of sheet material or thermal elements subjected in use to high stresses at elevated temperature ranging up to about 1800° F. Generally, the Type III alloys will contain from about 28% to 35% Cr, 1% to 4% Al and the balance substantially nickel, the sum of the chromium and nickel being at least about 70% of the total composition, with the nickel to chromium ratio ranging from about 1.3 to 1 to about 1.75 to 1. It is desirable that the aluminum content not substantially exceed 3% nor chromium exceed 35% as aluminum and chromium together above these amounts render hot working more difficult.

It is preferred, however, that other alloying ingredients be used provided the foregoing compositions are maintained, the other ingredients comprising up to about 20% iron (preferably up to 10% Fe), up to about 10% molybdenum (preferably up to 5% Mo), up to about 15% cobalt (preferably up to 10% Co), up to about 3% titanium (preferably up to 1% Ti), up to about 2% columbium and/or tantalum (preferably up to 1%), up to about 4% silicon, and up to about 2% manganese.

Examples of alloys falling in the foregoing composition range are given as follows:

Table VI

Alloy No.	Per-cent Cr	Per-cent Ni	Per-cent Al	Percent Others	Ni and Cr	Ni/Cr
14	35	46	4	15 Fe	81	1.32
15	35	54	3	2 Ti, 3 Mo, 3 W	89	1.54
16	35	53	3	2 Ti, 3 Mo, 3 W, 1 Cb.	88	1.54
17	30	50	3	2 Ti, 5 Mo, 10 Fe	80	1.66
18	28	47	3	2 Ti, 5 Mo, 15 Co	75	1.67
19	28	48	3	1 Ti, 3 Mo, 5 Fe, 2 Mn, 5 Co, 2 Si, 2 W, 1 Cb.	76	1.71
20	30	50	3	1 Ti, 5 Mo, 5 Fe, 5 Co, 1 Cb.	80	1.66

The method in producing the foregoing alloys was similar to that described in the production of Type I alloys. Hardness data were similarly obtained on alloys Nos. 14, 17, 19, 20 as follows:

Table VII

Temp., ° F.	Time, Hrs.	Alloy No.			
		Hardness R _A			
		14	17	19	20
2,250	water quench	57	57	---	---
1,200	1/2	63	62	---	---
1,200	2	70	67	---	---
1,200	6	72	70	---	---
1,200	12	72	72	---	---
1,200	18	78	73	---	---
1,200	1/2	65	68	---	---
1,300	1 1/2	70	70	---	---
1,300	4 1/2	76	74	---	---
1,300	10	76	77	---	---
1,300	25	76	80	---	---
1,300	67	75	81	---	---
1,300	135	75	80	---	---
1,300	1/2	71	65	---	---
1,370	2	74	74	---	---
1,370	6	75	76	---	---
1,370	12	77	77	---	---
1,370	18	78	78	---	---
1,370	23	---	---	---	62
1,370	45	---	---	---	62
1,370	67	74	---	---	---
1,370	75	---	---	---	64
1,370	135	74	78	---	---
1,370	1/2	70	69	---	62
1,400	1	72	73	---	64
1,400	3	74	76	---	---
1,400	9	75	78	---	---
1,400	16	74	78	---	---
1,400	17	---	---	---	75
1,400	49	---	---	---	78
1,400	57	73	78	---	---
1,400	121	72	72	---	---
1,500	1/2	74	75	---	---
1,500	1	75	76	68	68
1,500	2	---	---	75	---
1,500	3	75	77	76	---
1,500	5	75	77	77	---
1,500	9	75	77	77	---
1,500	18	71	---	---	74
1,500	21	---	---	---	75
1,500	24	---	75	77	---
1,500	28	---	75	75	---
1,500	52	71	---	---	---
1,500	73	---	---	---	76
1,500	89	---	---	---	---
1,500	119	74	76	---	---

Alloy No. 20 was also age hardened at about 1620° F. for 1, 2, 18 and 90 hours to give hardness values of about 73, 74, 75 and 75 Rockwell "A," respectively. Fairly high hardness values were obtained for most of the alloys, longer aging times at higher temperatures being required for the more complex alloys.

Alloy No. 20 also exhibited high ultimate tensile strength at elevated temperatures. For example, after solution quenching at 2250° F. followed by aging at 1600° F., the alloy exhibited an ultimate strength of about 132,500 p.s.i. at 1300° F., a value of 109,500 p.s.i. at 1500° F., and 69,200 p.s.i. at 1700° F. Tests based on specimens of 0.250" diameter and gage length of 1.25" indicated that the alloy was also capable of withstanding applied loads at temperatures from 1800 to 2000° F. for prolonged periods of time as follows:

Table VIII

Temp., ° F.	Stress p.s.i.	Time, Hrs.	Percent Elong.
1,800	8,000	23	4
1,900	4,000	17	---
2,000	2,000	76	---

An advantage of complex alloys of Type III is that the alloys are capable of being softened to as low as 70 Rockwell "B" (44 Rockwell "A") for fabrication purposes and thereafter hardened to any desired hardness ranging up to as high as 75 Rockwell "A" and higher.

It is apparent from the foregoing that the invention provides a number of different types of alloys falling within the broad range of composition defined herein. Various properties are obtainable depending upon the composition and the particular heat treatment employed

in optimizing the desired properties. The properties are developed by employing a high temperature heat treatment followed by an aging treatment at lower temperatures.

Broadly speaking, the high temperature treatment is conducted at temperatures far exceeding the temperature at which precipitable phases which impart age hardenability go into complete solution. The high temperature treatment comprises heating the alloy to a solution temperature of at least about 1950° F. for a time sufficient to effect substantially complete solution, preferably for at least about 2 hours and more preferably within the range of about 2050° F. to 2250° F. usually between 1 to 4 hours followed by sufficiently rapid cooling to preserve the solid solution. Such rapid cooling may be effected by water or oil quenching or in some instances by air cooling. Generally, the cooling rate should be such that the alloy will cool to below 1300° F. in a relatively short time, for example within 3 minutes. If desired the cooling can be interrupted at the desired aging temperature and held there for the required time.

Upon completion of the high temperature treatment, the cooled alloys are then subjected to aging comprising heating the alloys at a temperature from about 1000° F. to 1600° F. for a time at least sufficient to obtain substantial hardening, preferably for at least 4 hours, and more preferably from about 12 hours to 48 hours. The aging treatment imparts high temperature strength and hardness to the alloys. If desired, the aging treatment may be conducted in several steps, for example at 1500° F. for 4 hours, then at 1400° F. for 4 hours, and finish up at 1300° F. for 4 hours or any other combination of aging steps between the temperature ranges of 1000° F. to 1600° F.

In the case of Type I alloys, we prefer aging at temperatures within the range of about 1000° F. to 1400° F. because of the particularly fast response of such alloys to aging at lower temperatures. For the more complex alloys of Type III, the aging temperature will generally range from 1200° F. to 1600° F.; but we prefer aging temperatures in the range of 1400° F. to 1600° F. to insure high resistance to high loads at elevated temperatures for prolonged periods of time.

In the age hardened condition the structure of these alloys comprises a gamma, face centered cubic matrix in which there are present two other precipitated phases which are responsible for the high hardness and high strength of the alloys. These phases are the ordered face centered cubic gamma prime phase basically of the formula Ni_3Al into which titanium, cobalt and some chromium may be substituted without changing the lattice structure except for changes in the size of the lattice.

A second precipitated phase which differentiates these alloys from conventional nickel-chromium-aluminum-titanium alloys of the super alloy classification is the alpha, body centered cubic chromium rich phase. The precipitation of this phase results in the observed higher hardness values compared to those reported in the past for the conventional Ni—Cr—Ti—Al super alloys. Examination of solution treated alloy No. 7 showed a structure comprised of gamma nickel solid solution with small islands of alpha chromium solid solution. In the aged condition the alloy showed a structure comprising a fine precipitate of essentially unresolvable gamma prime phase (Ni_3Al) and alpha chromium in gamma.

Different dispersions and particle size of the precipitates can be achieved by variations in composition, aging time and aging temperature.

X-ray diffraction studies appear to substantiate the observed phases noted in the microstructure.

If carbon or nitrogen is present in relatively small amounts it is to be expected that carbides and nitrides or carbonitrides can appear in the structure without material-

ly affecting the aging processes or the resultant properties. The gamma nickel solid solution would however be stable or more prevalent to higher chromium contents and correction for this change in chromium content of the matrix would have to be made.

The softness of the more highly alloyed materials will depend on the solution treatment temperature. Higher solution temperatures will increase the softness due to greater solution of the complex structure in the single phase gamma field. Thus, by using higher solution temperatures, it is possible to achieve greater age hardening after the aging treatment.

The alloys of the invention may be employed as cast alloys or as wrought products. Where hot working is resorted to in the production of shapes, precaution must be taken when the aluminum content exceeds about 4%. Where the aluminum is on the high side, we prefer to keep chromium on the lower end of the range so as to maintain the Ni to Cr ratio above 1.5 or preferably above 1.75. The alloys are particularly adapted to precision casting in the production of precise shapes such as turbine blades and the like. Other articles for which the alloy may be employed include valves, valve seats, extrusion dies, furnace parts, supports and elements in vacuum tubes, brick mold linings and the like.

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, and such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. An age-hardenable, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening in the aged condition at elevated temperatures ranging up to about 1200° F. which comprises by weight about 30% to 40% chromium, about 2% to 5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 85% of the total composition at a ratio of nickel to chromium of about 1.3 to 1 to about 1.75 to 1.

2. An age-hardenable, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening in the aged condition at elevated temperatures ranging up to about 1200° F. which comprises by weight about 30% to 40% chromium, about 2% to 5% aluminum and nickel in an amount such that the sum of the chromium and nickel content is at least about 80% of the total composition at a ratio of nickel to chromium of about 1.3 to 1 to about 1.75 to 1 and the balance up to 5% iron, up to 5% molybdenum, up to 10% cobalt, up to 2% titanium, up to 2% columbium and up to 4% silicon.

3. An age-hardenable, aluminum-containing, heat-resistant, high chromium nickel alloy characterized by improved resistance to softening at elevated temperatures ranging up to about 1200° F. which comprises by weight about 30% to 45% chromium, about 3% to 6% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 85% at a ratio of nickel to chromium of about 1 to 1 to about 1.75 to 1.

4. An age-hardenable, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening at elevated temperatures ranging up to about 1200° F. which comprises by weight about 30% to 40% chromium, about 3% to 5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 90% at a ratio of nickel to chromium of about 1.3 to 1 to about 1.75 to 1.

5. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by im-

proved physical properties at elevated temperatures, said alloy comprising by weight about 30% to 45% chromium, about 2% to 5% aluminum, nickel in an amount such that the sum of the chromium and nickel content is at least about 70% of the total composition at a ratio of nickel to chromium of about 1 to 1 to about 1.75 to 1 and the balance up to about 20% iron, up to about 10% molybdenum, up to 15% cobalt, up to 3% titanium, up to 2% columbium, up to 4% silicon, up to 2% manganese and up to 2% tin, said alloy being further characterized by a microstructure comprising a gamma nickel solid solution containing precipitated alpha chromium phase and a face centered gamma prime phase of the type Ni_3Al .

6. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening in the aged condition at elevated temperatures ranging up to about 1200° F., said alloy comprising by weight about 30% to 40% chromium, about 2% to 5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 80% of the total composition at a ratio of nickel to chromium of at least about 1.3 to 1 to about 1.75 to 1, said alloy being further characterized by a microstructure comprising a gamma nickel solid solution containing precipitated alpha chromium phase and a face centered gamma prime phase of the type Ni_3Al .

7. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening in the aged condition at elevated temperatures ranging up to about 1200° F., said alloy comprising by weight about 30% to 40% chromium, about 2% to 5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 85% of the total composition at a ratio of nickel to chromium of about 1.3 to 1 to about 1.75 to 1, said alloy being further characterized by a microstructure comprising a gamma nickel solid solution containing precipitated alpha chromium phase and a face centered gamma prime phase of the type Ni_3Al .

8. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening in the aged condition at elevated temperatures ranging up to about 1200° F., said alloy comprising by weight about 30% to 40% chromium, about 2% to 5% aluminum and nickel in an amount such that the sum of the chromium and nickel content is at least about 80% of the total composition at a ratio of nickel to chromium of at least about 1.3 to 1 to about 1.75 to 1 and the balance up to 5% iron, up to 5% molybdenum, up to 10% cobalt, up to 2%

titanium, up to 2% columbium and up to 4% silicon, said alloy being further characterized by a microstructure comprising a gamma nickel solid solution containing precipitated alpha chromium phase and a face centered gamma prime phase of the type Ni_3Al .

9. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening at elevated temperatures ranging up to about 1200° F., said alloy comprising by weight about 30% to 45% chromium, about 3% to 6% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 85% at a ratio of nickel to chromium of about 1 to 1 to about 1.75 to 1, said alloy being further characterized by a microstructure comprising a gamma nickel solid solution containing precipitated alpha chromium phase and a face centered gamma prime phase of the type Ni_3Al .

10. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved resistance to softening at elevated temperatures ranging up to about 1200° F., said alloy comprising by weight about 30% to 40% chromium, about 3% to 5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 90% at a ratio of nickel to chromium of about 1.3 to 1 to about 1.75 to 1, said alloy being further characterized by a microstructure comprising a gamma nickel solid solution containing precipitated alpha chromium phase and a face centered gamma prime phase of the type Ni_3Al .

11. An age-hardened, aluminum-containing, heat resistant, high chromium nickel alloy characterized by improved physical properties at elevated temperatures which comprises by weight about 30% to 45% chromium, about 2% to 5% aluminum and the balance substantially nickel, the sum of the chromium and nickel content being at least about 70% of the total composition at a ratio of nickel to chromium of at least about 1 to 1 but not exceeding about 1.75 to 1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,015,558

January 2, 1962

Nicholas J. Grant et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 12, line 31, for "age-hardened" read -- age-harden-able --.

Signed and sealed this 8th day of May 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

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Commissioner of Patents