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METHOD FOR HEAT TREATING CHROMIUM BASE ALLOY

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Fig. 1

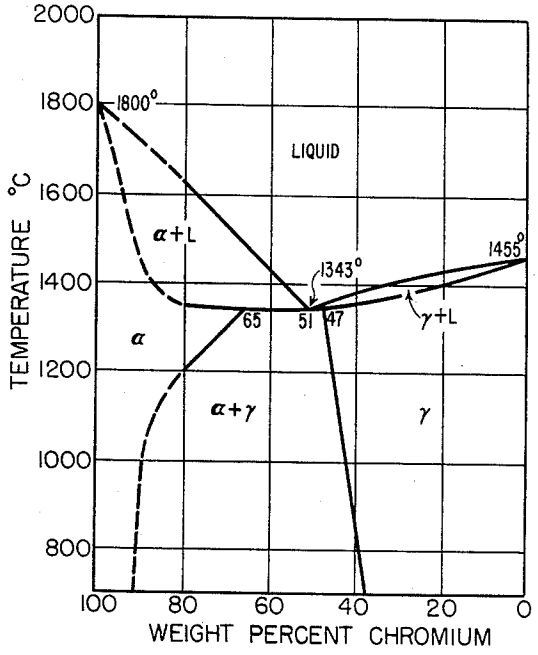
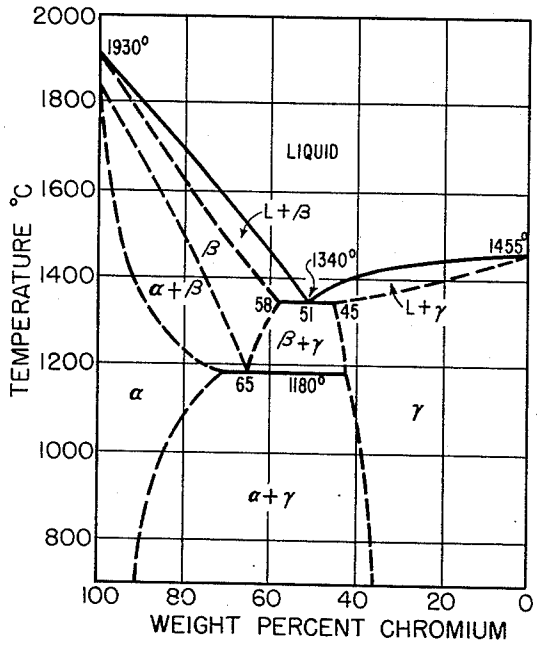


Fig. 2



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METHOD FOR HEAT TREATING CHROMIUM BASE ALLOY

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6 Claims. (Cl. 148—13)

The present invention relates to high temperature alloys, and more particularly to alloys which have a relatively high chromium content but which at the same time have superior mechanical properties, including ductility.

It has long been assumed that high chrome alloys were of necessity brittle because of the inherent highly brittle nature of pure chromium. Furthermore, the phase diagram of the binary chromium-nickel system has long been accepted as a simple eutectic type consisting of two terminal solid solutions and their mixture, which were all stable up to the melting point. It is axiomatic that a system which shows no change in its structure at elevated temperature cannot be heat treated for structure control and for grain refinement, though solution heat treatment and age hardening may be possible. This general knowledge plus the brittle nature of chromium has discouraged attempts to achieve improved high temperature alloys based on the chrome-nickel system despite chromium's well-known heat resisting qualities.

It is the object of this invention to provide a group of heat treatable chrome-nickel and chrome-nickel based alloys having greatly improved mechanical properties at high temperature.

It is also an object of the invention to provide a new group of metal cutting materials performing the function of tool steels but based on the chrome-nickel system. An important aspect of this development is the fact that it becomes possible to provide a new class of heat treatable alloys based on the chrome-nickel system and incorporating conventional alloying elements.

We have discovered that it is possible to bring about a change in the structure of chrome-nickel alloys rich in chromium at high temperatures. The resultant high temperature structure can be preserved and modified by conventional heat treatment either with or without the addition of conventional alloying elements, and the result is a class of high temperature alloys having excellent properties. These properties may be further improved, particularly their ductility, by reducing the oxygen content below the level now common for commercial chromium compounds.

In the drawings illustrating the invention:

Fig. 1 shows a phase diagram of the chromium-nickel system as it was formerly thought to exist.

Fig. 2 shows the revised phase diagram of the chromium-nickel system based on our discovery.

It will be noted in Fig. 1, which is the phase diagram for the chromium-nickel system currently shown in the Metals Handbook and other reference works, that two solid solution structures, one for chromium and one for nickel, exist below approximately 1400° C., and the same structures coexist together with liquid in the transition phase before complete melting. This is a simple binary eutectic phase diagram. Since there is no change in the crystal structure of the metal with increasing temperature, there is no chance of heat treatment and grain refinement as it is conventionally understood or as it is exercised in the presently understood heat treatable systems such as

the iron-carbon system. Accordingly until the present invention it was believed that a chromium-nickel alloy retained a given crystal structure until it melted and regained the same structure when it resolidified.

Our studies have shown that this is not the case but that there is a transformation in the chrome-nickel system which closely parallels that in the iron-carbon system and which makes possible a group of heat treatable alloys based on the chromium-nickel system which have excellent mechanical characteristics. As will be seen by reference to Fig. 2, this new chromium-nickel phase diagram exhibits the face-centered-cubic nickel solid solution phase (gamma), within approximately the same range as it had formerly been understood to exist. It also shows the body-centered-cubic chromium solid solution phase (alpha). There is added, however, a chromium beta phase at high temperature in those compositions containing more than 40% to 45% by weight of chromium. This beta phase is a high temperature chromium structure which is evidenced to be either a face-centered-cubic or a face-centered-tetragonal structure. In the binary chromium-nickel system between the limits of slightly over 40 to 65 percent chromium, the transition of the chromium from the alpha to the beta phase takes place at temperatures in the neighborhood of 1180° C. and between this temperature and about 1340° the structure consists of beta chromium and gamma nickel.

In compositions consisting of more than approximately 65% by weight of chromium there is little or no nickel structure as such above about 1180° C., but the same alpha to beta transformation takes place in the chromium. The alloys in these regions consist of either alpha and beta chromium together, or the pure beta structure, the exact limits of these changes being not precisely determined at this time. Nickel and alloying elements in these regions are contained within the basic chromium crystal structure and may effect the properties of the alloy through their effect on the crystal structure.

This basic and heretofore unknown transition is apparently present in pure chromium at around 1800° C. and will undoubtedly persist into other chromium based systems at this high temperature. At the present state of the metallurgical art, however, working at temperatures such as these is impractical, and much of the value of the present invention lies in providing a heat treatable chromium based system which undergoes transformation within a workable range of temperatures.

There is in addition to the structures shown on the phase diagram, a metastable transition phase which for convenience will be termed alpha prime. The structure of this phase has been tentatively identified as a body centered tetragonal crystal and it is interesting to note that this structure is apparently very significantly ferromagnetic. This is indicated by the fact that if a eutectoid alloy is quenched from above the eutectic temperature and then powdered, portions of the powder exhibit strong ferromagnetism.

The above described system bears resemblance to the iron-carbon phase diagram for amounts of carbon up to 1.2% as well as general resemblance to other heat treatable systems and it is believed possible, therefore, that the similar types of heat treatment which are effective with other transition structures will be effective here. Verification of the heat treatability of simple chrome-nickel alloys is shown in the table below, which gives the Rockwell C hardness readings for various percentage combinations of chromium and nickel after several types of treatment.

The first group represents the results of heat treatments on specimens covered with a ⅛" layer of alundum to retard the effect of any sudden change in temperature. The second, smaller group represents the results obtain-

able with a more rapid quenching made possible by the elimination of the alundum covering.

TABLE I

Hardness data showing heat treatability of Cr-Ni *alloys*

(a) SPECIMENS COATED BY ⅛" ALUNDUM

Compositions	Rockwell "C" Hardness Readings			
	70 Cr–30 Ni	65 Cr–35 Ni	60 Cr–40 Ni	50 Cr–50 Ni
Heat Treated Condition:				
As Cast	47.5	38.0	34.5	16.5
Quenched 1,250° C	61.3	57.5	48.1	13.3
Quenched 1,250° C. and aged 16 hr. 760° C	42.5	40.4	40.9	39.2
Quenched 1,150° C		45.7	38.9	
Annealed 200 hr. 900° C		27		

(b) SPECIMENS HAVING NO ALUNDUM COATING

Heat Treatment	Rockwell "C" Readings	
	70 Cr–30 Ni	68 Cr–32 Ni
Quenched 1,250° C	67–69	59–66
Quenched 1,150° C		49–54

A typical set of results is that shown for the 70% chromium-30% nickel alloy which showed an as-cast hardness of 47½ Rockwell C compared with a high of 69 Rockwell C for the rapidly quenched specimen. Even more conclusive are the comparative effects of quenching from above and below the eutectoid temperatures. This comparison is available for the 65 Cr-35 Ni binary alloy and it is apparent that there is a difference of about 10 Rockwell points achieved as a result of transforming chromium into the beta phase (i. e. quenching from 1250° C. instead of 1150° C.). It should be noted too, that these alloys can be softened by annealing at temperatures in the vicinity of 1000° C. so that machining or other shaping operations can be performed. For example, the 65% chrome 35% nickel specimen showed a hardness of 38 Rockwell as-cast but only 27 Rockwell after annealing for 200 hrs. at a temperature of 900° C.

It has been found that these high chromium alloys, treated in accordance with the invention, exhibit sufficient hardness to compare favorably with tool steels, while possessing certain advantages thereover. Tests of tools formed of 65 and 70 percent chromium (balance essentially nickel) alloys which were water quenched and oil quenched from temperatures of 1100 to 1200° C. compared favorably with high speed tool steel and showed an advantage of lower surface friction. As a result, these new alloys may operate at higher temperatures than conventional tool steels.

A typical 68% chrome 32% nickel alloy tested as a tool steel was initially homogenized at between 1150 and 1280° C. for one hour and thereafter quenched in lead at 500° C. and held 15 minutes. This specimen showed a hardness of 63 Rockwell C, which remained constant after annealing for 3 hours at 520° C. The coefficient of friction of this bar was .41 as against .52 for a typical tool steel. This low coefficient of friction, in addition to being valuable in cutting applications, suggests that these alloys may be quite useful in ball bearings and other wear resistant parts.

It has been consistently true in the past that alloys containing the amount of chromium used here have been extremely brittle (to the complete detriment of utility), and a fundamental difference in the subject alloys, which is to a considerable extent responsible for their success, is the low oxygen content of these alloys. As a test of the ductility of conventional chromium alloys, hot forging was attempted on a 65% chromium-35% nickel ingot made using commercial purity chromium and heated to 1150° C., but the metal could not be moved without cracking. When the temperature was increased to 1227° C. the ingot was found to be hot short, due to incipient intergranular melting. It is estimated that the oxygen content of this alloy was of the order of .3%, based on the fact that the original chromium contained up to .7% free oxygen and this was reduced by alloying with oxygen-free nickel and further reduced by the use of a carbon arc furnace.

In comparison with this experience, it was found possible to hot forge alloys containing up to 70% chromium, where the oxygen content was below .01%. Alloys of this nature having chromium-nickel ratios varying between 80–20 and 10–90 were successfully forged at a temperature of 1250° C. In order to standardize the test a ⅜" specimen cube was struck with a weight of 50 pounds falling from a height of 1 foot. The percentage reduction in length varied from 20 to 30% for alloys containing 60% chromium and under. The 70% chrome alloys showed a sharp decrease in ductility and gave only a 7.8% reduction in length, while the 80% chrome specimen exhibited severe cracking in the course of a 10% reduction in height. Some comparison of this performance with metals whose characteristics are better understood is gained from the fact that for vitallium cubes, tests under the same condition did not crack and gave an average reduction in length of 18.7%.

It is apparent that an increase in nickel content makes forging easier. It is also apparent however that a low oxygen content and high purity with respect to nitrogen, sulfur and other elements are essential to ductility. This is shown by the fact that the 70% high purity specimen was forgeable but the 65% specimen using commercial purity chromium proved to be hot short. No difficulties of the nature of intergranular melting were noted with the high purity specimens and it is our belief that a very low oxygen content is essential to the formation of high chromium alloys which do not show excessive brittleness.

While these binary alloys have many useful and valuable properties, the invention is not limited to such alloys, but in addition comprehends the use of this binary system together with conventional alloying elements to form a new class of heat treatable high temperature alloys. Such alloys are characterized by high oxidation and corrosion resistance and high melting point. The high chrome content, with nickel as the secondary alloying element, when prepared in accordance with the invention, provide substantial shock resistance and ductility, as compared with prior chromium-alloy systems. The suitability of these materials for high temperature use, as well as the improvements which may be obtained by additional alloying can best be seen by reference to the following Table II which lists the results of rupture testing a variety of specimens based on this system at 1500° F. and 20,000 pounds per square inch. Specimens used for rupture testing were all made from commercial raw materials by precision casting from a carbon arc furnace and contain from .15 to .20% carbon with .3% or less oxygen. It should be remembered that these alloys were formed in accordance with the same method used to form the billet of commercially pure chrome nickel alloy which could not be forged. These two specimens are therefore within the range of commercial purity as far as oxygen is concerned, though some reduction techniques were used in their manufacture. A further reduction of oxygen content in accordance with the teachings of this invention would further improve the ductility and shock resistance of these specimens.

TABLE II

Alloy Composition								Rupture Life	Percent El.	Red. Area	Heat Treatment
Cr	Ni	Mo	Fe	Al	Ti	Ta	Mn				
70	25	5	------	------	------	------	------	29.2	6	11	As cast.
65	35	------	------	------	------	------	------	3.4	------	2.8	Do.
65	25	5	5	------	------	------	------	19.3	4	10	Do.
60	40	------	------	------	------	------	------	6.6	4	5	Quenched from 1,150° C. and aged 16 hrs. at 760° C.
60	30	5	5	------	------	------	------	18.8	25	29	As cast.
50	50	------	------	------	------	------	------	1.1	5.8	4	Do.
50	50	------	------	------	------	------	------	13.7	------	10	Quenched 1,250° C.
50	50	------	------	------	------	------	------	3.06	5	.9	Quenched 1,150° C.
50	50	------	------	------	------	------	------	9.05	4	9	Quenched 1,150° C., aged 16 hrs. 760° C.
49	49	2	------	------	------	------	------	1.9	------	------	As cast.
49	49	2	------	------	------	------	------	5.3	------	------	Quenched from 1,250° C.
48	48	4	------	------	------	------	------	3.53	9	2.3	As cast.
50	40	5	5	------	------	------	------	6.6	25	32	Do.
36.4	54.6	4	------	1	1	1	.5	19	------	------	Do.
36.4	54.6	4	------	1	1	1	.5	114	------	------	Quenched 1,038° C., aged 60 hrs. 815° C.

In many instances no heat treatments were given these alloys, since the as cast comparisons are considered to give good evidence of the change brought about through the use of a given alloying element. Certain of the basic alloys were heat treated, as were one or two of the more complex systems, in order to confirm the degree of improvement anticipated after such treatment. When used, these heat treatments have involved one or more of the following stages.

Step 1.—The alloy is heated to a temperature above the eutectoid temperature at which it will consist primarily of the high temperature chromium phase and will have a rather coarse structure (e. g. 1300° C. for two hours).

Step 2.—The alloy is cooled to below the eutectoid and held for a sufficient length of time to remove the coarse structure formed in Step 1 (e. g. cooled to 1100° C. and held for ½ hour).

Step 3.—The alloy is reheated to above the eutectoid temperature and held in order to develop a fine grained high temperature structure (e. g. 1200° C. for ¾ hour).

Step 4.—The alloy is cooled as desired, perhaps with the use of a bath of lead or Woods metal in order to avoid cooling too quickly and producing cracks.

The creep-rupture specimens treated in this manner showed a fine-grained structure indicating that the attempts at grain refinement were successful.

Reference to the creep-rupture data indicates that the characteristics of the binary alloy were not exceptional and ran, for example, for from 1.1 to 3.4 hours in rupture life for specimens which were tested in the "as cast" condition. These values, however, are exceedingly good when compared to other known high temperature binary alloys such as the cobalt-chromium, nickel-chromium and iron-chromium systems. Moderate amounts of various alloying elements, however, gave complex alloys showing improvements of between five and ten times the rupture life of the original specimens. A typical example is the improvement obtained in the 50% chromium-50% nickel specimen which showed a 1.1 hour rupture life with a 4% reduction in area in the as-cast condition, as compared with a 13.7 hour rupture life with a 10% reduction in area when quenched from 1250° C.

The same basic alloy in the as cast condition with an addition of 4% molybdenum showed a rupture life of 3.53 hours with a 2.3% reduction in area and 9% elongation, this being roughly 3 times the rupture life of the binary alloy. When this alloy system was made even more complex, consisting of 50 chrome, 40 nickel, 5 molybdenum, and 5 iron, the rupture life increased to 6.6 hrs., tested as cast. Increase in chromium to 65% (25% Ni, 5% Mo, 5% Fe) increased the life to 19.3 hrs. because of the increase in the amount of the strong chromium structure. A further increase in chromium to 70% chromium, 25% nickel, 5% molybdenum increased the rupture life to 29.2 hours without the use of any iron.

Examination of the micro-structures of these chromium base alloys indicates that it is the chromium phase which exhibits the greatest strength and therefore cracking tends to take place along the inter-face between chromium and nickel phases. There are two possible approaches, through alloying, to correct this deficiency. One procedure which showed good results, as above, is to increase the percentage of chromium so that the alloy consists basically of the heat treatable chromium crystal structure, together with the added alloying elements within that structure. In this instance the weak nickel phase is reduced or eliminated completely.

The other approach is to use alloying elements which result in strengthening the nickel phase and perhaps also in increasing the strength of the chromium crystal. Typical elements which are known to improve the strength of nickel are aluminum and titanium which are traditionally used to improve the age hardening of this material. A test alloy based upon this idea of increasing the strength of the nickel phase was made as follows:

	Percent
Chromium	36.4
Nickel	54.6
Molybdenum	4
Tantalum	1
Titanium	0.5
Aluminum	1
Manganese	0.5

When tested in the as-cast condition this alloy showed a 19 hour rupture life. With the benefit of a heat treatment, which consisted of quenching from 1038° C. (1900° F.) (i. e. below the eutectic) and aging 60 hours at 815° C. (1500° F.), this alloy so treated showed a rupture life of 114 hours.

It is apparent from the above data that appropriate alloying procedures based on the present invention create a new group of high temperature alloys possessing exceptional mechanical properties. It is believed that the following alloying techniques show the most promise.

One group of alloying elements has been found useful in strengthening the lattice matrix of nickel or chromium without the formation of new solid solution phases. It is believed that the following elements will be most effective in achieving this result and should be used in not more than the percentages indicated for this purpose.

	Percent
Iron	10
Molybdenum	20
Tungsten	10
Columbium or tantalium	8
Cobalt	20
Vanadium	6

In addition, aluminum (up to 2%) and titanium (up to 3%) may be used as alloying elements to give an aging reaction with any nickel phases which may be present. This aging reaction results in a considerable increase in strength for these nickel phases.

Certain additives in trace amounts up to 1% may be used to counteract the otherwise detrimental influence of carbon and nitrogen which may be present in these systems as impurities. Carbon and nitrogen up to an amount of about 0.7% for each element can be tolerated in these alloys if other alloying elements are used which have a stronger carbide, nitride or oxide-forming tendency than does chromium. Such alloying elements would be columbium, titanium, zirconium, tantalum, vanadium and hafnium, used for this purpose in amounts up to approximately 1%. All of these elements will have the effect of forming a second phase with the carbon or nitrogen which will strengthen the end product.

It is obvious that not all of these alloying additives would be used in any one alloy, nor will all of the elements that are used be used in the maximum percentages specified above. The chromium and nickel will together comprise at least 70% of these alloys, with sufficient chromium, probably in excess of 30%, to assure the existence of a materially significant amount of beta phase chromium.

These alloys, based as they are on the heat treatable chromium-nickel system, will permit control of grain size and hardness because of the high temperature transition in the chromium structure from a body centered form to the beta phase. Furthermore, because of the crystal structure of this beta form of high temperature chromium, a reduction in oxygen to minimal trace amounts well below 0.3% permits the use of large proportions of chromium in alloys having properties particularly suitable for high temperature applications.

The heat treatments now possible with these high chromium alloys may include quenching to retain the beta structure, treatment to obtain a partial transformation to the hard metastable structure which resembles the martensite structure in steel, or grain refinement which makes no attempt to retain one of the high temperature structures.

We claim as our invention:

1. The method which comprises heating an alloy of the chromium-nickel system containing chromium in an amount sufficient to be transformable in a materially significant proportion to the beta phase, to a temperature above the transition temperature at which a substantial proportion of the chromium present in said alloy is transformed to the beta phase, and thereafter rapidly quenching said alloy to retain a substantial portion of beta phase chromium therein.

2. An alloy produced by the method of claim 1.

3. The method which comprises heating an alloy of the chromium-nickel system containing chromium in an amount sufficient to be transformable in a materially significant proportion to the beta phase and less than 0.1% oxygen, to a temperature above the transition temperature at which a substantial proportion of the chromium present in said alloy is transformed to the beta phase, and thereafter rapidly quenching said alloy to retain a substantial portion of beta phase chromium therein.

4. An alloy produced by the method of claim 3.

5. The method which comprises heating an alloy of the chromium-nickel system containing chromium in an amount sufficient to be transformable in a materially significant proportion to the beta phase, to a temperature above the transition temperature at which a substantial proportion of the chromium present in said alloy is transformed to the beta phase, and thereafter rapidly quenching said alloy to retain a substantial portion of beta phase chromium therein; said alloy containing in addition to chromium and nickel at least one alloying material, present in not more than the following indicated percentages, and selected from the group consisting of: iron 10%, molybdenum 20%, tungsten 10%, columbium 8%, tantalum 8%, cobalt 20%, vanadium 6%, titanium 3%, aluminum 2%, zirconium 1%, hafnium 1%.

6. An alloy produced by the method of claim 5.

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