

[54] **POWDER METALLURGY SINTERED
CORROSION AND HEAT-RESISTANT,
AGE HARDENABLE NICKEL-
CHROMIUM REFRACTORY CARBIDE
ALLOY**

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[57] **ABSTRACT**

An age hardenable, corrosion and heat resistant nickel-chromium, refractory carbide alloy is provided by powder metallurgy for use at elevated temperatures as high as 2000°F (1090°C) comprising primary grains of at least one refractory carbide selected from the group consisting of TiC, CbC, VC and TaC dispersed through a matrix of an age hardenable, corrosion and heat resistant nickel-chromium alloy consisting essentially by weight of about 5 to 30 percent chromium, up to about 15 percent iron, about 0.5 to 5 percent titanium, about 0.2 to 5 percent aluminum, up to about 25 percent cobalt, up to about 0.25 percent carbon and the balance essentially nickel.

8 Claims, No Drawings

POWDER METALLURGY SINTERED CORROSION AND HEAT-RESISTANT, AGE HARDENABLE NICKEL-CHROMIUM REFRACTORY CARBIDE ALLOY

This invention relates to a powder metallurgy sintered age-hardenable, corrosion, wear and heat resistant nickel-chromium refractory carbide alloy and also to articles of manufacture of the class including heat resistant dies and machine parts made thereof.

The invention also relates to a method for producing said alloy.

BACKGROUND OF THE INVENTION

Refractory carbide alloys are known comprising a non-ferrous matrix metal, such as nickel, having dispersed therethrough primary grains of refractory carbide, such as titanium carbide. While such alloys have been very useful in the manufacture of wear resisting elements, e.g. dies, machine parts, and the like, they generally have been limited in their application to normal environments in which heat and corrosion resistance is a secondary consideration. Nickel, as a matrix, is relatively soft compared to the refractory carbide dispersed therein and tends to be selectively removed or eroded from between the carbide grains in wear applications involving the rubbing of one metal surface against another. When this occurs, the carbide particles at the surface lose their support and fall out, thus accelerating wear. Another disadvantage is that the matrix tends to oxidize easily at elevated temperatures of up to about 2000°F. While adding chromium to the nickel improved the heat and corrosion resistance to a large extent, the matrix was still soft relative to the carbide grains, such that it was not sufficiently hard to resist selective wearing between the carbide grains.

It would be desirable to provide a heat, corrosion and wear resistant refractory carbide alloy capable of withstanding high temperature oxidation up to 2000°F (1090°C) and higher while sustaining adequate resistance to wear and corrosion.

OBJECTS OF THE INVENTION

It is thus the object of this invention to provide a powder metallurgy sintered heat, corrosion and wear resistant refractory carbide alloy characterized by improved resistance to oxidation and wear at elevated temperatures of up to about 2000°F (1090°C) and higher.

Another object is to provide, as an article of manufacture, a hardened sintered heat, corrosion and wear resistant element of the class including heat resistant dies and machine parts.

Still another object is to provide a method for producing said refractory carbide alloy.

These and other objects will more clearly appear from the following disclosure and the appended claims.

STATEMENT OF INVENTION

Stating it broadly, the invention resides in the production of a powder metallurgy sintered age hardenable corrosion and heat resistant nickel-chromium refractory carbide alloy comprising primary grains of at least one refractory carbide selected from the group consisting of TiC, CbC, VC and TaC dispersed

through a nickel-chromium matrix alloy consisting essentially by weight of about 5 to 30 percent chromium, up to about 15 percent iron, about 0.5 to 5 percent titanium, about 0.2 to 5 percent aluminum, up to about 25 percent cobalt, up to about 0.5 percent carbon and the balance essentially at least about 40 percent nickel.

A composition range which is particularly advantageous is one in which the amount of refractory carbide by volume ranges from about 30 to 75 percent and the balance essentially the matrix alloy.

A more advantageous composition is one in which the refractory carbide (e.g. TiC) ranges by volume from about 35 to 55 percent, and wherein the matrix alloy making up substantially the balance consists essentially by weight of about 10 to 25 percent chromium, about 2 to 12 percent iron, about 1 to 3 percent titanium, about 0.5 to 2 percent aluminum, up to about 15 percent cobalt, up to about 0.25 percent carbon and the balance essentially at least about 50 percent nickel.

The foregoing refractory carbide alloy is capable of being solution annealed to a hardness as low as 46 R_c and age hardened to a level of about 54 R_c. The alloy resists oxidation at elevated temperatures as high as 2000°F (1090°C) and is particularly resistant to acid corrosion as evidenced by substantially low rates of corrosion in 10 percent concentrated H₂SO₄, in 50 percent concentrated H₂SO₄ and in pure concentrated H₂SO₄. In addition, the alloy exhibits high strength at elevated temperatures. The alloy is easily machinable in the annealed state and can be precisely machined or ground to any desired shape and thereafter hardened by age hardening without affecting the precise dimensions.

DETAIL ASPECTS OF THE INVENTION

As illustrative of the various embodiments of the invention, the following examples are given.

EXAMPLE 1

An age hardenable, nickel-chromium refractory carbide alloy comprised of titanium carbide and a non-ferrous nickel-base chromium containing matrix was produced as follows:

Primary carbide	about 45 vol.% TiC
Alloy Matrix	about 55 vol.%

The matrix had the following nominal composition by weight:

	Percent
Chromium	18
Iron	8
Titanium	2
Aluminum	1
Nickel*	essentially the balance

*The balance nickel may include optionally other ingredients in amounts which do not adversely affect the basic characteristics of the alloy.

In producing the composition, 500 grams of TiC powder (about 45 vol. percent) of average particle size of about 5 to 7 microns are mixed with 1000 grams of powdered alloy-forming ingredients which include 180 grams of minus 100 mesh high purity electrolytic chromium powder, 80 grams of iron powder of approx-

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imately 20 microns average size, 20 grams of titanium added as TiH_2 powder, 31.8 grams of NiAl powder (contains 10 grams aluminum) and the balance (688.2 grams) carbonyl nickel powder of about 5 to 8 microns average size. The aluminum is added as NiAl in order to assure take-up of the aluminum by the liquid melt, otherwise, the aluminum added alone tends to be lost by vaporization in vacuum. The powder mixture also contains 1 gram of paraffin (1 percent) for each 100 grams of mix. The mix is placed in a stainless steel ball mill half filled with stainless steel balls, using hexane as the vehicle. The milling is conducted for about 40 hours.

After completion of the milling, the mix is removed and vacuum dried. A proportion of the mixed product is compressed in a die at 15 tons/sq. in. to the desired shape. The shape is liquid phase sintered at a temperature of about 1350°C for one-half hour (after reaching the temperature) at a vacuum corresponding to 20 microns or better. After completion of sintering, the shape is cooled at a rate through the liquidus solidus region such as to prevent hot tearing during solidification from the liquid phase. Such a rate should not exceed 35°C per hour as the liquidus-solidus region is quite narrow and should not be traversed too quickly during solidification. For example, a compact of 2 inches in diameter and 2 inches high is cooled at a rate not exceeding about 25°C per hour. The sintered compact is subjected to a solution heat treatment by heating to 1232°C for 30 minutes to provide a hardness of about 46 R_c. The sintered shape is machined and/or ground into a tool element, e.g. a hot extrusion die, and thereafter age hardened in a two-step hardening treatment by heating at 900°C (1600°F) for 8 hours, followed by heating at 800°C (1400°F) for 4 hours and then air cooled. The hardness obtained is in the neighborhood of about 54 R_c.

EXAMPLE 2

Primary carbide about 30 vol.% CbC
Alloy Matrix about 70 vol.%

The nominal composition by weight of the matrix is as follows:

	Percent
Chromium	5
Iron	12
Cobalt	10
Titanium	3
Aluminum*	2
Nickel	essentially the balance

*Aluminum is added in the form of NiAl

The method of formulation, the sintering procedure and the heat treatment are similar to those described for Example 1.

Similar procedures are employed in the following examples:

EXAMPLE 3

Primary carbide about 40 vol.% VC
Alloy Matrix about 60 vol.%

The nominal composition of the matrix by weight is as follows:

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	Percent
Chromium	10
Cobalt	15
Titanium	4
Aluminum	1.5
Nickel	essentially the balance

EXAMPLE 4

Primary carbide about 55 vol.% TaC
Alloy Matrix about 45 vol.%

The nominal composition of the matrix by weight is as follows:

	Percent
Chromium	10
Titanium	1
Aluminum	0.5
Nickel	essentially the balance

EXAMPLE 5

Primary Carbide about 65 vol.% TiC
Alloy Matrix about 35 vol.%

The nominal composition of the matrix by weight is as follows:

	Percent
Chromium	25
Iron	6
Cobalt	5
Titanium	4.5
Aluminum	3
Nickel	essentially the balance

EXAMPLE 6

Primary Carbide about 70 vol.% TiC
Alloy Matrix about 30 vol.%

The nominal composition of the matrix by weight is as follows:

	Percent
Chromium	15
Molybdenum	5
Cobalt	10
Titanium	2
Aluminum	1
Nickel	essentially the balance

As stated hereinabove, the non-ferrous alloy matrix should contain at least about 40 percent and, more preferably, at least about 50 percent nickel by weight. Other elements may be present in the alloy matrix, such as up to about 10 percent molybdenum, up to about 6 percent tungsten, up to about 5 percent columbium and/or tantalum, up to about 2 percent zirconium, up to about 2 percent hafnium, up to about 2 percent manganese, up to about 2 percent silicon, and the like, the total amount of the other elements not exceeding about 15 percent by weight of the total composition of the alloy matrix.

Broadly, in producing the various compositions by powder metallurgy, the appropriate amount of alloy-forming ingredients is mixed with an appropriate amount of primary carbide in a ball mill. The mixture may be shaped a variety of ways. It is preferred to press the mixture to a density of at least about 50 percent of true density by pressing over the range of about 10 t.s.i. to 75 t.s.i., preferably 15 t.s.i. to 50 t.s.i., followed by sintering under substantially inert conditions, e.g. in a vacuum or an inert atmosphere. Advantageously, the temperature employed is above the melting point of the

chromium steel matrix, for example, at a temperature up to about 100°C above the melting point for a time sufficient for the primary carbide and the matrix to reach equilibrium and to obtain substantially complete densification, for example, for about 1 minute to 6 hours.

When the liquid phase sintering is completed, the product is allowed to furnace cool to room temperature, the rate through the liquidus phase not exceeding about 35°C per hour. If necessary, the as-sintered product is subjected to mechanical cleaning. If the as-sintered product requires solution annealing, it is heated to a temperature of about 1900°F (1038°C) to 2300°F (1260°C) for about 30 minutes to 5 hours followed by air cooling.

For age hardening, the temperature may range in a first hardening step from about 1350°F (732°C) to 1800°F (982°C) for about 4 to 30 hours followed by air cooling, and then further age hardened at a temperature ranging from about 1200°F (649°C) to 1650°F (899°C) for about 2 to 25 hours. For the compositions given hereinbefore, the hardness after aging may range from about 49 R_c to 66 R_c.

Corrosion studies have indicated that the alloy compositions of the invention exhibit good resistance to corrosion in such acid media as sulfuric acid, nitric acid and hydrochloric acid (boiling).

Examples of heat resistant dies and machine parts are hot pressing dies, hot extrusion punches, rolls for ironing welded tubing to flatten out the weld bead, hot forging dies, corrosion resistant rotating seals, mold inserts for aluminum and zinc die casting molds, 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. 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. A powder metallurgy sintered age hardenable corrosion and heat resistant nickel-chromium refractory carbide alloy comprising by volume about 30 to 75 percent of primary grains of at least one refractory carbide selected from the group consisting of TiC, CbC, VC and TaC dispersed through a nickel-chromium matrix alloy making up the balance, said matrix alloy consisting essentially by weight of about 5 to 30 percent chromium, up to about 15 percent iron, about 0.5 to 5 percent titanium, about 0.2 to 5 percent aluminum, up to about 25 percent cobalt, up to about 0.5 percent carbon and the balance essentially at least about 40 percent nickel.

2. The sintered and age hardenable, corrosion and heat resistant nickel-chromium refractory carbide alloy of claim 1, wherein the refractory carbide ranges by volume from about 35 to 55 percent TiC, and wherein the matrix alloy making up substantially the balance consists essentially by weight of about 10 to 25 percent chromium, about 2 to 12 percent iron, about 1 to 3 percent titanium, about 0.5 to 2 percent aluminum, up to about 15 percent cobalt, up to about 0.25 percent carbon and the balance essentially at least about 50 percent nickel.

3. The sintered and age hardenable corrosion and heat resistant nickel-chromium alloy of claim 2, wherein the TiC by volume is about 45 percent and the balance is essentially the matrix alloy consisting essentially by weight of about 18 percent chromium, about 8 percent iron, about 2 percent titanium, about 1 percent aluminum and the balance essentially nickel.

4. As an article of manufacture, a heat resistant element of the class including heat resistant dies and machine parts formed of an age hardened powder metallurgy sintered corrosion and heat resistant nickel-chromium refractory carbide alloy comprising by volume about 30 to 75 percent of primary grains of at least one refractory carbide selected from the group consisting of TiC, CbC, VC and TaC dispersed through an age hardened nickel-chromium matrix alloy making up the balance, the matrix alloy consisting essentially by weight about 5 to 30 percent chromium, up to about 15 percent iron, about 0.5 to 5 percent titanium, about 0.2 to 5 percent aluminum, up to about 25 percent cobalt, up to about 0.5 percent carbon and the balance essentially at least about 40 percent nickel.

5. The age hardened sintered refractory carbide article of manufacture of claim 4, wherein the refractory carbide ranges by volume from about 35 to 55 percent TiC, and wherein the matrix alloy making up substantially the balance consists essentially by weight of about 10 to 25 percent chromium, about 2 to 12 percent iron, about 1 to 3 percent titanium, about 0.5 to 2 percent aluminum, up to about 15 percent cobalt, up to about 0.25 percent carbon, and the balance essentially about 50 percent nickel.

6. The age hardened sintered refractory carbide article of manufacture of claim 5, wherein the TiC by volume is 45 percent and the balance is essentially the matrix alloy consisting essentially by weight of about 18 percent chromium, about 8 percent iron, about 2 percent titanium, about 1 percent aluminum and the balance essentially nickel.

7. A method of producing by powder metallurgy a sintered, age hardenable, corrosion and heat resistant nickel-chromium refractory carbide alloy which comprises, providing a powder composition containing about 30 to 75 percent by volume of at least one refractory carbide selected from the group consisting of TiC, CbC, VC and TaC mixed with a powder formulation of alloy-forming ingredients to form an alloy matrix making up the balance containing about 5 to 30 percent chromium, up to about 15 percent iron, about 0.5 to 5 percent titanium, about 0.2 to 5 percent aluminum, up to about 25 percent cobalt, up to about 0.5 percent carbon and the balance essentially at least about 40 percent nickel, the aluminum in the powder mixture being in the form of NiAl to assure recovery of the aluminum in the alloy matrix, forming the powder mixture into a compact, heating said compact to a liquid phase sintering temperature in vacuum ranging up to about 100° C above the melting point of the alloy matrix, cooling said sintered refractory carbide alloy through the liquidus-solidus region of the alloy at a rate not exceeding 35°C per hour, and thereafter cooling to room temperature at a rate not exceeding about 100°C.

8. The method of claim 7, wherein the refractory carbide ranges by volume from about 35 to 55 percent TiC and wherein the alloy matrix making up substantially the balance consists essentially by weight of about 10 to

25 percent chromium, about 2 to 12 percent iron, about 1 to 3 percent titanium, about 0.5 to 2 percent aluminum, up to about 15 percent cobalt, up to about 0.25 percent carbon and the balance at least about 50 percent nickel.

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