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3,215,510 ALLOY

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This invention relates to cemented carbide compositions combining corrosion resistance with high hardness and strength and to a process for preparing such compositions.

Cemented carbides are well known for their unique combination of hardness, strength and abrasion resistance and are accordingly extensively used in industry as cutting tools, drawing dies and wear parts. They are produced by powder metallurgy techniques from one or more refractory carbides of groups IV, V and VI of the periodic table, bonded or cemented together, by liquid phase sintering, with one or more of the iron group metals.

The binder metal or alloy must possess a number of important properties and must meet a number of demanding requirements, among which are the following. The binder must have, or possess the ability to produce with the carbide through eutectic formation, a reasonable melting point. It must adequately wet the carbide to produce a dense body. The binder should not to any material extent enter into an irreversible reaction with the carbide. Finally, the binder should impart reasonable strength to the cemented carbide alloy.

Of the possible carbide-binder combinations, the best known and most extensively used is the tungsten carbide-cobalt system. A second useful system is titanium carbide in which nickel is the binder. Nickel can also be used in place of cobalt with tungsten carbide but with a

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generation of strength normally observed makes such WC-Ni-Cr₃C₂ alloys of little value.

It is accordingly a principal object of the present invention to provide cemented carbide compositions combining corrosion resistance with high hardness and strength.

It is an additional object of this invention to provide a process for preparing cemented carbide compositions having the foregoing corrosion-resistance, hardness and strength properties. Other objects will become apparent from the description of the invention which follows:

We have now found that the foregoing objects may be achieved in compositions which consist essentially of tungsten carbide and about 10 to about 25%, and not more than 30%, by weight, of a binder of chromium and nickel, the ratio of the weight of chromium to the combined weight of nickel and chromium ranging from about 0.015 to about 0.15. The compositions of the invention are prepared by pressing a powdered mixture of tungsten carbide, chromium and nickel within the foregoing ranges, the chromium being present in chemically uncombined form, and then sintering the pressed mixture in a carbon-free atmosphere.

The compositions of the invention possess outstanding corrosion resistance, particularly to acids and alkalis, combined with hardness and strength comparable, or in some instances superior, to tungsten carbide compositions having a cobalt binder. Moreover, it is superior in corrosion resistance to WC-Ni alloys and is vastly superior to WC-Ni alloys in hardness and strength. In addition, the present compositions can be made non-magnetic, an important advantage over WC-Co alloys in certain applications.

A comparison of the properties of WC-Co and WC-Ni alloys with those of the present WC-Ni-Cr alloys is shown in the following Table I.

TABLE I

Composition	Hardness, RA ¹	Transverse Rupture Strength ²	Corrosion Resistance		Magnetic Susceptibility
			H ₂ SO ₄ ³	NaClO ₄ ⁴ (Clorox)	
WC+16% Co-----	86.5	450,000	Poor-----	Poor-----	Yes.
WC+16% Ni-----	84.0	275,000	Good-----	Fair-----	No.
WC+16% Ni+1% Cr----	87.5	450,000	Very good---	Excellent---	No.
WC+16% Ni+2% Cr----	88.0	400,000	Excellent---	Excellent---	Slight.

¹ Rockwell A.

² P.s.i., 5/8" centers.

³ At pH=1, 40-60° C. for 100 hrs.

⁴ Agitated abrasive, 100 hrs.

decided sacrifice in hardness and strength.

One of the principal disadvantages of tungsten carbide-cobalt systems is their relatively poor corrosion resistance, particularly to acids which readily attack the cobalt binder. The corrosion resistance of WC-Co alloys can be somewhat improved by the addition of small amounts of chromium carbide, but only at the sacrifice of strength and metallurgical soundness. As a result, WC-Co-Cr₃C₂ alloys of sufficient corrosion resistance for most applications are not useful because of low strength. Chromium additions to WC-Co behave similarly to chromium carbide additions and thus have limited usefulness.

Alloys of the WC-Ni system have superior corrosion resistance properties in certain mild acid environments, and are therefore of some limited use. However, as indicated above they do not possess the strength and hardness properties of equivalent WC-Co alloys. Chromium carbide additions to WC-Ni further improve the corrosion resistance of WC-Ni alloys, but the accompanying de-

Compositions of the present invention exhibit superior properties over rather narrow compositional limits of alloy-binder contents. The alloy binder content range should be from 10 to 30%, by weight, of the total weight of the alloy, and preferably from 16-25%, the latter range being that of optimum properties. Compositions containing less than about 10% binder do not provide consistently dense pieces. It is believed that this is due to the poorer wettability of the nickel-chromium alloy binders for tungsten carbide as compared to pure nickel or cobalt binders. This results in the presence of insufficient active liquid phase in the tungsten carbide-nickel-chromium alloy below the 10% binder content.

The upper alloy binder limit of 30% is based upon the sagging characteristics shared by all cemented carbide bodies of high binder content prepared by powder metallurgy. The upper useful binder content limit of the alloys of the invention is thus approximately the same as that of conventional tungsten carbide-cobalt systems.

Tables II and III compare the properties of the present alloy with those of WC-Co over the binder content range of 8-25%, the range most frequently used in known commercially available WC-Co alloys. In Table II, the ratio of the weight of chromium to the combined weight of nickel and chromium was 0.058 in all samples. In Table III, the corresponding ratio was 0.111 for all samples. Strength and hardness were measured as in Table I.

TABLE II

Percent Binder	Type Alloy	Transverse Rupture Strength	Hardness, R _A
8.....	WC-Ni-Cr.....	Not measured. ¹	-----
8.....	WC-Co.....	200-300,000 ²	91
10.....	WC-Ni-Cr.....	310,000.....	89.5
10.....	WC-Co.....	300-400,000.....	90
14.....	WC-Ni-Cr.....	370,000.....	89
14.....	WC-Co.....	325-425,000.....	88
17.....	WC-Ni-Cr.....	420-460,000.....	87.5
16.....	WC-Co.....	375-475,000.....	87
20.....	WC-Ni-Cr.....	430-450,000.....	86
20.....	WC-Co.....	350-450,000.....	86
25.....	WC-Ni-Cr.....	430,000.....	84
25.....	WC-Co.....	325-400,000.....	84

For footnotes see Table III.

TABLE III

Percent Binder	Type Alloy	Transverse Rupture Strength	Hardness, R _A
8.....	WC-Ni-Cr.....	Not measured. ¹	-----
8.....	WC-Co.....	200-300,000 ²	91
10.....	WC-Ni-Cr.....	280,000.....	91
10.....	WC-Co.....	300-400,000.....	90
14.....	WC-Ni-Cr.....	304,000.....	89.5
14.....	WC-Co.....	325-425,000.....	88
18.....	WC-Ni-Cr.....	375-400,000.....	88
18.....	WC-Co.....	375-475,000.....	87
20.....	WC-Ni-Cr.....	420,000.....	87
20.....	WC-Co.....	350-450,000.....	86
25.....	WC-Ni-Cr.....	430,000.....	84
25.....	WC-Co.....	325-400,000.....	84

¹ Satisfactory density not achieved.

² Ranges for WC-Co are those of comparable commercially available alloys.

In all cases, in Tables II and III, the corrosion resistance of the WC-Ni-Cr alloys was either very good or excellent. (Corrosion resistance results cannot be reproduced with sufficient accuracy to warrant the use of quantitative measurements. Corrosion resistance results are therefore indicated herein qualitatively.)

Chromium-nickel contents below approximately 0.015, expressed in terms of Cr/Ni+Cr weight ratio, have been found to offer relatively little improvement in strength and corrosion resistance. Chromium-nickel contents above approximately 0.15, expressed in terms of

Cr/Ni+Cr

weight ratio, have been found to exhibit generally low strength. Examples of the properties of WC-Ni-Cr alloys showing a fixed nickel content and a variable chromium content within the specified limits are given in the following Table IV.

TABLE IV

WC	Ni	Cr	Cr/Ni+Cr	Hardness, R _A	Density	Transverse Rupture Strength
84	16	-----	.00	84.5	13.92	250-300,000
83.75	16	.25	.0153	87.0	13.90	376,000
83.5	16	.50	.0313	87.2	13.93	412,000
83.0	16	1.00	.056	87.5	13.90	420-450,000
82.0	16	2.00	.111	88.0	13.95	375-400,000
81.0	16	3.00	.157	88.5	13.90	260,000

The process of the invention is carried out by first mixing tungsten carbide, nickel and chromium powder

which may be first screened to obtain proper mesh size. The mixing may be carried out in a ball mill while the powder is suspended in a suitable liquid vehicle. After drying, preferably in an inert or reducing atmosphere, a pressing lubricant is usually added and the powder is pressed into a compact. The pressed compact is then preferably presintered in a hydrogen atmosphere, usually between about 400-800° C. Finally, the presintered compact is sintered in a non-carburizing atmosphere, preferably under reduced pressure.

The following examples are illustrative of preferred compositions within the scope of the invention.

Example 1

A cemented carbide alloy containing 16% Ni, 1% Cr and 83% WC was prepared from the following 500 gram charge:

Gm.
Tungsten carbide (1 micron) 415
80/20 Ni/Cr master alloy (-325 mesh) 25
Nickel, carbonyl (-325 mesh) 60

The charge was introduced into a tungsten carbide lined ball mill containing tungsten carbide-cobalt balls and milled in an acetone vehicle for 24 hours. The powder was then dried in a reducing atmosphere and paraffin was added as a pressing lubricant. The powder was pressed into a compact under 20 t.s.i. (tons per square inch) pressure in a carbide lined die and presintered in a hydrogen atmosphere for 3 hours at a peak temperature of 600° C. The presintered compact was then loaded into a vacuum furnace and sintered at 1450° C. for two hours at one to ten microns pressure. The sintered carbide was then cooled in the furnace.

Example 2

The procedure of Example 1 was followed except that an alloy containing 16% Ni, 2% chromium and 82% WC was prepared from the following 500 gram charge:

Gm.
Tungsten carbide (1 micron) 410
Chromium, electrolytic (-325 mesh) 10
Nickel, carbonyl (-325 mesh) 80

The technical explanation for the unique combination of properties obtained with WC-Ni-Cr alloys, within the specified compositional range, appears to be complex. A plausible explanation, supported by the process conditions found necessary to achieve the superior properties is as follows: It is believed that chromium additions to WC-Ni alloys will tend to partition between the metal binder and the refractory carbide phase during sintering. Moreover, chromium is well known to be a strong carbide former as compared to WC and will scavenge carbon to form simple and/or complex carbides. Above the approximate upper Cr/Ni+Cr ratio limit of 0.15, the chromium will enter the refractory-carbide phase in sufficient quantities to form, with the other components of the system, a complex carbide with resulting losses in properties of the final product.

In preparing the composition, steps must accordingly be taken to insure that the chromium is concentrated in the binder phase as a Ni-Cr alloy, and the chromium's carbide forming tendencies must be suppressed. To accomplish this the chromium is introduced in chemically uncombined form as a high purity metal powder or as a nickel-chromium master alloy powder. The addition of chromium as an alloy is preferred but not essential. The tungsten carbide powders used should contain a high combined carbon content and a low free carbon content. Combined carbon contents of 6.10% with free carbon contents of .02% are preferred. Process conditions are chosen to isolate the powdered alloys from outside carbon sources to ensure the ultimate deposition of chromium principally as a nickel-chromium

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alloy. We have found that vacuum sintering does an excellent job of maintaining the neutral or slightly decarburizing atmosphere conditions needed and is preferred over other forms of sintering. However, other forms of sintering, such as hydrogen atmosphere sintering, can be used. It is only essential that a non-carburizing atmosphere be used during sintering. Sintering temperatures of 1350–1500° C. are employed.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A corrosion resistant, cemented carbide alloy consisting essentially of tungsten carbide and about 10 to 30%, by weight, of a binder of an alloy of chromium and nickel, the ratio of the weight of chromium to the combined weight of nickel and chromium ranging from about 0.015 to about 0.15.

2. The alloy of claim 1 containing 16 to 25%, by weight, of a binder.

3. The alloy of claim 2 in which the chromium content is 1 to 2% and the nickel content is 15 to 17%, both by weight, based on the total weight of the alloy.

4. A process for the preparation of a corrosion resistant, cemented carbide alloy comprising

pressing a powder mixture of tungsten carbide, chromium and nickel, said mixture containing about 10 to 30%, by weight, of chromium and nickel and a weight ratio of chromium to combined nickel and chromium of from about 0.015 to about 0.15, said

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chromium being present in chemically uncombined form, and

sintering said pressed mixture in a non-carburizing atmosphere to form a hard, high strength, corrosion resistant alloy.

5. The process of claim 4 in which the chromium is present in the powder mixture as an alloy of nickel and chromium.

6. The process of claim 4 in which said sintering is carried out at subatmospheric pressures.

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