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CEMENTED CARBIDE COMPOSITION AND METHOD OF PREPARATION

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ABSTRACT OF THE DISCLOSURE

This invention relates generally to improved cemented carbide compositions and more particularly to modified tungsten carbide-cobalt compositions which in a single cemented alloy possess improved strength and hardness characteristics that make them particularly useful in applications requiring resistance to wear and impact. This invention also concerns the method of making the improved compositions of this invention.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of copending application Ser. No. 738,401, entitled "Cemented Carbide Composition and Method of Preparation," filed June 20, 1968 now abandoned.

BACKGROUND OF THE INVENTION

Hardness and strength are generally accepted to be the most important characteristics of cemented carbide compositions since both are required in some degree for success in all of the varied applications in which cemented carbides are employed. Throughout the years since cemented carbides were first discovered and as the result of widespread commercial use and research it has become generally accepted, with respect to tungsten carbide-cobalt systems, that modifications which increase hardness normally decrease strength and vice versa. It is known that the transverse rupture strength of a tungsten carbide-cobalt composition can be increased by increasing the cobalt content to some value within the range of 2 to 25 weight percent cobalt, but at the expense of reducing the hardness. Those skilled in the art also know that for any given WC-Co composition, transverse rupture strength is partially a function of the WC grain size, which WC grain size has a tendency to increase during sintering; this tendency increases as the cobalt content of the composition increases. It is also generally believed that transverse rupture strength is improved, at any given cobalt concentration, by coarsening the tungsten carbide grain structure. On the other hand, it is known that hardness is increased as the WC grain size decreases; thus, intentionally insuring the presence of large WC grains to improve strength does so at the expense of hardness, and when hardness is maximized by employing only small grain size WC and a cobalt binder the strength of the material suffers. This general understanding in the art appears in British Pat. 1,077,921, published Aug. 2, 1967, most particularly at lines 23–31 and 45–58.

Many attempts have been made in the past to increase hardness in cemented carbide compositions while maintaining strength but little success has been attained. One such approach to the problem is represented by Schwartzkopf Pats. 2,091,017, Aug. 24, 1937, Re. 21,520, July 30, 1940, and Re. 22,207, Oct. 20, 1942, which formed mixed carbide crystals of two or more of the refractory metals, tungsten, molybdenum, titanium, vanadium, etc. at temperatures up to about 2000° C. and thereafter added

a binder metal from the iron group, i.e., iron, cobalt and nickel, to the mixed crystals and sintered. Another approach is represented by Dawihl et al. U.S. Pat. 2,169,090, Aug. 8, 1939 and Ohlsson et al. U.S. Pat. 3,245,763, Apr. 12, 1966, wherein tungsten carbide was mixed with titanium carbide and an iron group metal binder and that mixture modified to include vanadium and molybdenum carbide in Dawihl et al., or tantalum, niobium, vanadium, chromium, zirconium, hafnium and molybdenum carbide in Ohlsson et al. Others have modified the iron group binder metal by allowing it to binary or ternary form, such as: Wiley U.S. Pat. 2,147,329, Feb. 14, 1939, which discloses a ternary binder alloy of nickel, molybdenum and chromium; Ollier U.S. Pat. 2,349,052, May 16, 1944, which discloses alloying iron and iron alloys with cobalt and nickel as binder; Kelly et al. U.S. Pat. 3,215,510, Nov. 2, 1965 which discloses nickel-chromium binders; Boeckeler U.S. Pat. 3,147,542, Sept. 8, 1964, which discloses cobalt, nickel, molybdenum, iron, chromium, tungsten, manganese and mixtures thereof as binders; Goetzel et al. U.S. Pat. 2,752,666, July 3, 1966, which discloses the use of titanium carbide and a binder alloy comprising iron, cobalt, and nickel alloyed with one or more of chromium, molybdenum, tungsten, columbium, tantalum and vanadium; Corbett U.S. Pat. 3,322,513, May 30, 1967, which discloses nickel and cobalt base high temperature alloys which are precipitation hardenable as binders for sintered carbides; British Pat. 459,854, Jan. 13, 1937, which discloses tungsten carbide and a binder of cobalt, together with one of nickel or molybdenum, or silver, or gold, or platinum or copper; and British Pat. 1,077,921, Aug. 2, 1967 which discloses a heavy metal carbide of Groups IV and VI of the Periodic System and an iron group metal binder alloyed with a rare earth metal or mixtures thereof, particularly binders containing Ce or Y.

As far as it is known at this time, those skilled in the art have heretofore been unable to provide a tungsten carbide-cobalt cemented alloy having values of maximum hardness and maximum strength or approximately those maximums. The expressions maximum hardness and maximum strength refer to the hardness and the strength value which has been separately achieved in a single commercially available tungsten carbide-cobalt sintered alloy made from tungsten carbide and 2–25 weight percent cobalt. For such commercial alloys the hardness range is from about 93–84 Rockwell A, and the transverse rupture strength ranges from about 175,000 to about 475,000 p.s.i. Heretofore, specific tungsten carbide-cobalt cemented alloys that have been made having a hardness approaching the maximum of 93, Rockwell A, have a transverse rupture strength approaching the minimum of 175,000 p.s.i. Conversely, specific tungsten carbide-cobalt cemented alloys that have been made, prior to this invention, that possessed a transverse rupture strength approaching the conventional maximum of about 475,000 p.s.i. have a hardness approaching the minimum of 84, Rockwell A.

It is the primary objection of this invention to provide a family of modified tungsten carbide base-cobalt compositions, each of which in hard cemented carbide alloy form is characterized by having high hardness and high strength.

Another object of this invention is to provide a method for making the compositions of this invention.

SUMMARY OF THE INVENTION

This invention is based on the discovery that tungsten-carbide-cobalt cemented alloys can be fabricated to possess concurrently high strength and high hardness by using cobalt in an amount in the range of about 2% to about 20% by weight of the total composition, small particle

size starting tungsten carbide material, and an amount of molybdenum in the range of about 5% to about 50% by weight of the cobalt binder. The starting materials, in powder form, are blended and sintered, or hot-pressed, under conditions such that the hard carbide alloy product is substantially free of large areas of intermetallic phases and has a Rockwell A hardness in the range of about 87.5 to about 94.0 and a transverse rupture strength in the range of about 240,000 to about 600,000 p.s.i. determined in accordance with the procedure of A.S.T.M B 406–63T.

It has been found that for tungsten-carbide cemented alloys the highest concurrent hardness and transverse rupture strength in any specific alloy is achieved by using tungsten carbide powder having an average particle size below about 5 microns, and a mixture of cobalt and molybdenum or a mixture of cobalt and dimolybdenum carbide powders in the amounts previously stated. In order to achieve the improvement of concurrent high hardness and high transverse rupture strength which characterizes this invention in any given alloy having a composition within the limits of proportions amove stated, it is necessary that the molybdenum, or at least a portion thereof, is present as molybdenum metal during at least a portion of the period while the tungsten carbide is being cemented into cemented alloy form, that is, during sintering or hot-pressing, and that the elemental molybdenum content in the hard cemented alloy is less than about 12% of the total binder, as determined by carbon analysis of that alloy.

The function of molybdenum in the alloys of this invention is complex but is now believed that molybdenum acts to reduce the solubility of tungsten carbide in the binder phase during sintering and concurrently provides improved bonding between the tungsten carbide grains. It has been found that the degree of inhibition of grain growth of the tungsten carbide grains in the alloys of this invention is a function of the amount of elemental molybdenum present in the binder phase during sintering with inhibition increasing with increasing quantities of molybdenum in elemental form. Further, it has been found that the molybdenum tends to form, during sintering, a solid solution of molybdenum monocarbide in tungsten monocarbide at the interface between the tungsten carbide and binder, and the degree to which this occurs is dependent upon the availability of carbon in excess of that associated with the WC phase.

Although the improvement in hardness which is obtained is associated with the decreased solubility of tungsten carbide in the binder during sintering, it is not known for certain what causes the concurrent improvement in strength of the alloys of this invention. It is believed, however, that the improvement in strength in the hard cemented alloys of this invention is due to the extremely small grain size of the carbide phase, the uniformity of that small grain size, the improved dispersion of those grains and the improved uniformity of the binder coating in the WC grain boundaries through the alloy; all of these improvements are believed to combine to improve the metallurgical soundness of structure of the cemented carbide alloys of this invention. The size of the grains of the tungsten carbide phase of the alloys of this invention is an average below about 5 microns and preferably is an average below about 1 micron.

The numerical limits on grain size, as used in this specification and the appended claims, refer to sizes determined by visual microscopic inspection of portions of the alloy at 1500 magnification and it is to be appreciated that they represent an approximation rather than an exact numerical limit.

It has been found that specific cemented alloys of this invention that have the highest hardness and concurrently the highest transverse rupture strength are those compositions which contain quantities of cobalt approaching 20% by weight, a quantity of molybdenum approaching its maximum and a tungsten carbide grain size less than about 1 micron average.

However, as the quantity of molybdenum which is present approaches its maximum the tendency increases for the formation during sintering of large areas of intermetallic phases which are detrimental to the transverse rupture strength property of the composition. By the expression "large areas of intermetallic phases" as used in this specification and claims is meant an intermetallic phase having an average size from at least about twice up to about 150 times the average size of the tungsten carbide grains in the material. Transverse rupture strength is decreased to the greatest extent when the intermetallic phases are massive in size relative to the average grain size of the tungsten carbide, for example, are twenty to one hundred times or more the average tungsten carbide grain size; in such case the desired improvement in strength is not obtained when even small amounts of such intermetallics are present. Where the size of the intermetallic phase is smaller than about 10 to 20 times the average tungsten carbide grain size the composition can tolerate the presence of a larger amount of that intermetallic phase before losing the unsual improvement in transverse rupture strength which characterizes the compositions of this invention. Thus, the use herein and in the claims of the expression "substantially free of large areas of intermetallic phases" refers to either the complete absence of such large phases or the presence of an insufficient quantity of such phases to nullify the improvement in transverse rupture strength, which characterizes the compositions of this invention.

The elemental constituency, or chemical identity of the large areas of intermetallic phases has not been established but under certain conditions their presence has been detected by microscopic examination, and when present in the sintered product the transverse rupture strength is detrimentally affected.

In order to avoid the intermetallics and obtain the desired increases in hardness and strength it is necessary to control the proportions of elemental molybdenum, cobalt and carbon that are present during sintering. Conditions which result in the formation of intermetallics can be avoided by insuring that no more than about 12% elemental molybdenum is present in the binder phase after sintering, substantially the balance of the molybdenum being in the form of molybdenum monocarbide, (MoC).

Such molybdenum monocarbide can be formed in situ during sintering in a neutral or reducing atmosphere, in vacuum or by hot pressing from carbon initially added or provided in the sintering environment or from a combination of these sources. It is also satisfactory, and even preferred for some alloys to employ dimolybdenum carbide (Mo_2C) as a partial or entire source of the elemental molybdenum needed during sintering and desired in the particular alloy of this invention which is being made. In such case, the dimolybdenum carbide changes during sintering to molybdenum carbide and releases the needed elemental molybdenum.

It is also satisfactory to use dimolybdenum carbide and additional carbon, but in this case the quantity of carbon in the powdered ingredients and any carbon available for pick-up from the sintering atmosphere should be less than the amount required to convert the liberated elemental molybdenum to molybdenum carbide.

In any case, sufficient carbon must be present in the original powder mixture or provided by pick-up during sintering to insure that any carbon deficiency in the starting tungsten carbide powder, or oxygen content in those powders, is offset and the final cemented alloy contains in the binder no more than about 12 weight percent elemental molybdenum and preferably no more than about 2% to about 7% of elemental molybdenum.

It is to be understood further that when a carburizing atmosphere is employed, during sintering and at least a part of the molybdenum in the starting powders is in ele-

mental form, or is converted to elemental form during the early stages of sintering, the final cemented carbide alloy may have all of its molybdenum content in the form of molybdenum monocarbide. In this case, the elemental molybdenum which is present during at least a portion of the cementing operation performs its sintering function and the final alloy possesses the improved hardness and strength which are desired.

The method of this invention comprises the steps of mixing the tungsten carbide, cobalt and molybdenum ingredients in powder form in conventional carbide manufacturing equipment using conventional safeguards to avoid oxidation or contamination. The tungsten carbide powder, after ball milling, should have an average particle size below about 3 microns and preferably has an average particle size below about 1 micron. The cobalt and molybdenum or dimolybdenum carbide should be finely powdered and cobalt and elemental molybdenum powders having a particle size less than about 10 microns average have been found to be satisfactory. After mixing, or ball milling, the mixed powder is conventionally pressed, may be presintered in a hydrogen atmosphere at a conventional temperature between about 400° C.–800° C. and formed, and then is final sintered, in a hydrogen atmosphere or under reduced pressure or hot pressed to the cemented alloy form usually at a temperature in the range of 1350° C.–1550° C. Sintering in a hydrogen atmosphere furnace with a carburizing atmosphere has been satisfactorily used and offers a simple procedure for controlling, and insuring, the presence of the needed quantity of carbon during sintering to avoid the formation of the large areas of intermetallic phases in the sintered product.

DESCRIPTION OF PREFERRED EMBODIMENTS

When the above described starting materials are employed in amounts within the ranges specified, and processed through final sintering under the specified conditions, the resulting cemented carbide alloys possess improvements in both hardness and strength. The improvement, in each case, is measurable and significant in terms of improved performance, particularly impact resistance and wear resistance. It is to be understood, however, that each of the specific cemented carbide compositions of this invention which may be made by selecting proportions of the components within the ranges specified above will not necessarily have a hardness, a transverse rupture strength, or both, which is higher than a hardness or a strength heretofore attained separately in some cemented carbide composition. On the other hand, each specific composition of this invention is improved in the hardness and strength in the same composition relative to a tungsten carbide-cobalt composition containing the same quantity of cobalt and made from identical procedures. Moreover, when the proportions of cobalt and molybdenum approach the maximums set forth in the above given ranges, the specific alloys possess concurrently higher hardness and strength than any heretofore known in a single cemented carbide alloy.

The benefits of this invention may be obtained even though certain modifications which would readily occur to one skilled in this art were made in the above described starting materials, proportions thereof, or handling procedures therefor. To illustrate, a portion of the tungsten carbide can be replaced with another hard metal carbide which is known to confer other desired properties on tungsten carbide such as titanium, columbium, or tantalum carbide, and in alloys of this invention can improve hardness or strength or both, or a portion of the cobalt can be replaced with nickel or iron or both, or a portion of the molybdenum can be replaced with chromium, columbium, thorium, hafnium, vanadium, etc., or the necessary carbon supplied during presintering, etc., or the numerical end limits on cobalt or molybdenum, or both, are slightly changed, but it is to be understood that any and all such modifications are intended to be encompassed by this description and to be a part thereof to the extent that such changes do not destroy the beneficial effects herein specifically described.

The following examples are representative of preferred compositions and procedures of this invention and contain the best known composition and procedure for making the same which has been discovered and used to this time.

EXAMPLE I

A cemented carbide alloy containing 19.5% cobalt, 3.5% molybdenum and 76.9% tungsten carbide, by weight, was prepared from the following charge into a steel ball mill 4" diameter and 4" long:

	Grams
Tungsten carbide	663
Cobalt (400 mesh)	169
Elemental molybdenum powder (average about 5 microns)	30.2

The tungsten carbide powder had a chemical analysis of 6.12% total carbide, 0.03% free carbon, 0.05% iron, 0.02% molybdenum, and a Fisher Sub-Sieve particle size of 1.46 microns. The Fisher Sub-Sieve size method, abbreviated F.S.S., is a determination in accordance with ASTM Test B–330–64. The molybdenum powder was made from ammonium molybdate and meets Climax Molybdenum Company Specification CMX–MMP–4 and is 99.95% pure molybdenum; the cobalt was obtained from African Metals Corporation and is 99.5% pure.

The charge was milled in an acetone vehicle in the presence of 2540 grams of tungsten carbide balls and 1¾% of a wax pressing lubricant at 120 r.p.m. for 24 hours. After ball milling and sieving to remove the balls and agglomerates, the average tungsten carbide particle size was about 0.7–0.8 micron. The material was pressed into transverse rupture specimens of the approximate size for use in transverse rupture strength determination in accordance with ASTM designation B 406–63T, and after dewaxing the bars were packed in graphite boats in aluminum oxide sand containing approximately 0.05% carbon distributed therethrough and sintered in a hydrogen atmosphere furnace at 1415° C., at a ⅜" per minute stoking rate, which sintering required approximately 4 hours total time. The first and second test set of 6 bars each were dewaxed in a neutral atmosphere at about 580° F., while the third set of 6 bars was dewaxed in a very slightly oxidizing atmosphere which slightly reduced the carbon content of this set of bars relative to the first and second sets.

After sintering, the Rockwell A hardness and transverse rupture strength of the six bars in each set was determined; the transverse rupture test employed the conditions of ASTM Test B 406–63–T, and the hardness determination was in accordance with ASTM Test B—294–64.

The first set of bars had an average Rockwell A hardness of 8.6 and an average transverse rupture strength of 505,000 p.s.i. The second set of bars had a Rockwell A hardness of 88.3 and an average transverse rupture strength of 489,000. The third set of bars had an average Rockwell A hardness of 89.2 and an average transverse rupture strength of 229,000. Microscopic examinations of sections of the bars from the first and second set showed a typical regular tungsten carbide pattern of fine WC grains still averaging less than about 1 micron in size and free of large areas of intermetallic phases; in the third set of bars the tungsten carbide grain size appeared to be slightly smaller than that of the first and second set of bars but large areas of intermetallic phases were readily seen in the structure.

EXAMPLE II

The procedures specified in Example I for sets 1 and 2, and the starting materials used in Example I were employed to prepare a series of transverse rupture test bars to enable evaluation of comparative sets of molybdenum-

containing and molybdenum-free compositions. The results of these comparative sets are set forth below, the values being average values.

TABLE 1

WC	Co	Mo, percent	Hardness, R_A	Transverse rupture strength, p.s.i.
87	13	----	90.1	363,000
85.55	13	1.45	90.2	390,000
82	18	----	88.2	416,000
80	18	2	88.6	440,000
84	16	----	89.1	349,000
81.18	16	2.82	90.1	392,000

EXAMPLE III

Using the same starting materials and the same processing procedures of Example II, the following compositions were made and tested for average hardness and transverse rupture strength with the results set forth below in Table 2.

TABLE 2

Alloy	WC	Co	Mo, percent	Hardness R_A	Transverse rupture strength, p.s.i.
1	77.5	18	4.5	90.0	[1] 536,000
2	78.2	19.6	2.2	87.8	478,000
3	75.5	19.6	4.9	89.2	332,000

[1] Average value of 5 bars with individual high strength of 585,000 p.s.i.

In Alloy 1 the total carbon content of the starting materials was 4.76%, whereas the total carbon in the sintered alloy was 5.07%, showing an increase during sintering of 0.31%. In Alloy 2, the carbon content of the starting materials was 4.79% while the sintered alloy contained the 5.02% carbon, thus showing an increase of 0.23% during sintering. Microscopic examination of Alloys 1 and 2 showed substantial freedom from large areas of intermetallic phases, whereas Alloy 3 contained visible large areas of intermetallic phases.

EXAMPLE IV

Using the starting materials of Example I and the handling procedures specified in Example I for Sets 1 and 2, a further series of low cobalt content alloys was prepared and the average hardness and strength properties of these alloys are set forth below in Table 3.

TABLE 3

WC	Co, percent	Mo, percent	Hardness, R_A	Transverse rupture strength, p.s.i.
88.9	10	1.1	91.1	329,000
87.5	10	2.5	91.7	370,000
86.7	12.0	1.3	90.6	391,000

EXAMPLE V

Using the cobalt and molybdenum starting materials described above in Example I and a tungsten carbide material having the chemical analysis of the tungsten carbide material of Example I but having an average particle size of about 7 microns (F.S.S. method) before ball milling, a series of samples were prepared using the procedures specified in Example I. The results of the testing for average hardness and strength of those samples is as follows:

TABLE 4

WC	Co, percent	Mo, percent	Hardness, R_A	Transverse rupture strength, p.s.i.
84	16	----	86.9	322,000
82.2	16	1.8	87.1	426,000
90	10	----	88.6	341,000
88.9	10	1.1	89.2	407,000

Microscopic inspection of the sintered alloys of Table 4 established that the average tungsten carbide grain size was about 3 microns.

For applications requiring maximized impact resistance and concurrent hardness and based on the strength and hardness data set forth in Examples I–IV inclusive and other data developed to date, the preferred cemented carbide alloys of this invention are those which contain about 15 to about 20 weight percent cobalt and about 10% to about 33% molybdenum by weight of the cobalt. For applications involving metal cutting, boring, broaching and the like, preferred cemented carbide alloys of this invention are those which contain between about 6 and about 10 weight percent cobalt and about 10% to about 50% molybdenum by weight of the cobalt. Preferred compositions for use in mining applications are those which contain about 10 to about 15 weight percent cobalt and about 10% to about 40% molybdenum by weight of the cobalt.

EXAMPLE VI

A series of transverse rupture bars were prepared using the procedures and the cobalt, molybdenum and tungsten carbide starting materials specified above in Example I to illustrate the effect of the carbon content of the starting materials and in the final sintered alloys. The compositions and the results of the testing, reporting average values are as follows:

TABLE 5

Alloy	WC	Co	Mo	C	C.F.	Hardness, R_A	Transverse rupture strength	Carbon content,[1] percent
1	84.44	14	1.56	----	183	90.1	454,000	5.29
2	84.40	14	1.56	.04	179	89.9	447,000	5.31
3	84.27	14	1.56	.17	156	89.2	394,000	5.36
4	82.88	14	3.12	----	221	90.2	220,000	5.16
5	82.68	14	3.12	.20	227	90.2	463,000	5.28

[1] Total carbon content measured after sintering by direct combustion method.

The column headed "C" (Carbon), includes those quantities of carbon added to the powders and is in addition to the carbon found in the tungsten carbide.

The column headed "C.F." represents the coercive force, in oersteds, of each of the samples. Coercive force is defined as the field strength required to demagnetize a fully magnetized ferro-magnetic substance. Since cobalt is known to exhibit ferro-magnetic tendencies, those skilled in the cemented carbide alloy art have employed the measurement of coercive force of cemented tungsten carbide-cobalt alloys as a measure of carbide particle size variations in such alloys. According to H. Krainer, in an article in Arch. Eisenhuttenw. 21, 119, 1950, the coercive force of cemented carbides depends greatly on the degree of distribution of the carbide phase and, thus, coercive force measurements can be utilized for grain-size determinations. It is known that low coercive force values indicate large tungsten carbide particles and higher coercive force values indicate smaller tungsten carbide particles.

From Table 5, it can be observed with respect to Alloys 1, 2 and 3 that as the carbon content of the starting materials was increased, the resultant sintered alloys decreased

in coercive force and, thus, Alloy 3 contained larger tungsten carbide particles than Alloy 2 and Alloy 2 contained larger tungsten carbide particles than Alloy 1. Moreover, the transverse rupture strength and hardness of Alloys 2 and 3 decreased with increasing carbon concentration. While the molybdenum content of the powdered starting materials represents 10% of the binder, when the carbon content of the sintered alloys is considered, the calculated elemental molybdenum content in the binder of the sintered alloys are, for Alloy 1, 4.9%; for Alloy 2, 3.9% and for Alloy 3, 1.1%.

Microscopic examination of the Alloys 1–5 reveals that Alloy 4 contained substantial areas of large-size intermetallics, whereas, Alloys 1, 2, 3 and 5 did not show areas. By comparing Alloy 5 with Alloy 4, it is apparent that the additional carbon in Alloy 5 did not substantially affect the tungsten carbide particle size since the coercive force values are approximately the same, but that carbon did prevent the formation of undesirable large-size intermetallics and markedly increased the transverse rupture strength of Alloy 5 relative to Alloy 4.

Taking the carbon content of the sintered alloys 4 and 5 into consideration, the quantity of elemental molybdenum present in Alloy 4 is calculated to be 15.2%, while the elemental molybdenum content of Alloy 5 is 10.1%.

EXAMPLE VII

Using the tungsten carbide, cobalt and molybdenum starting materials described in Example I and a dimolybdenum carbide material of 99.9% purity and of about 3 micron particle size, a series of samples were prepared to enable evaluation of comparative sets of molybdenum containing compositions. The results are set forth below in Table 6.

TABLE 6

Alloy	WC	Co	Mo	Mo_2C	C	C.F.	Hardness, R_A	Transverse rupture strength
A	82.54	14	3.12	----	.340	221	90.1	461,000
B	82.54	14	----	3.315	.145	215	90.2	445,000
C	86.00	14	----	----	----	120	89.1	416,000

It will be observed from Table 6 that Alloys A and B contain the same quantity of molybdenum and carbon and that the alloys have substantially similar tungsten carbide particle size, hardness and transverse rupture strengths irrespective of whether the molybdenum and carbon are supplied in the starting material as elemental molybdenum and carbon powder or as dimolybdenum carbide and carbon powder. By comparing Alloy C with Alloys A and B, it can be seen that the presence of molybdenum and carbon substantially reduces the tungsten carbide particle size, in Alloys A and B relative to Alloy C, and concurrently increases their hardness and transverse rupture strength relative to Alloy C.

EXAMPLE VIII

Using the cobalt starting material described in Example I and a tungsten carbide starting material similar to that of Example I but having an average particle size of about 0.85 micron, Alloy D was prepared using the procedures specified in Example I with the exception that the sintering temperature was 1465° C. This composition contained 96% tungsten carbide, 4% cobalt and after sintering was tested and found to have a coercive force of 225, a Rockwell A hardness of 92.2 and a transverse rupture strength of 286,000.

Using the same cobalt, the same tungsten carbide material, except that it was ball milled to an average of about 0.3–0.6 micron, a dimolybdenum carbide material of 99.9% purity and of about 3.5 micron particle size and a high purity carbon powder, Alloy E was prepared using the procedures of Example I except that the sintering temperature was 1465° C. The fine particle size tungsten carbide is obtainable by ball milling for longer than conventional times, or by using small milling balls or mixtures of various sizes of milling balls until the desired particle size is achieved. This sample contained 94.91% WC, 4% cobalt, 1.06% Mo_2C and 0.03% carbon, and after sintering, the properties of the sintered alloy were found to be a coercive force of 376, a Rockwell A hardness of 93.7 and a transverse rupture strength of 288,000.

By comparing Alloy E with Alloy D, it may be seen that the smaller particle size tungsten carbide in the starting materials was substantially maintained during sintering and the higher coercive force of Alloy E shows that the alloy contained substantially smaller tungsten carbide grains than Alloy D, the Rockwell A hardness is substantially increased, while the transverse rupture strength is also improved.

EXAMPLE IX

Using the cobalt starting material described in Example I and a tungsten carbide starting material similar to that of Example I but having an average particle size of about 0.85 micron. Alloy F was prepared using the procedures specified in Example I with the exception that the sintering temperature was 1465° C. This composition contained 98% tungsten carbide, 2% cobalt and after sintering was tested and found to have a coercive force of 295, a Rockwell A hardness of 93.0 and a transverse rupture strength of 237,000.

Using the same cobalt, the same tungsten carbide material, except that it was ball milled to an average of about 0.3–0.6 micron, a dimolybdenum carbide material of 99.9% purity and of about 3.5 micron particle size and a high purity carbon powder, Alloy G was prepared using the procedures of Example I except that the sintering temperature was 1465° C. This sample contained 97.46% WC, 2% cobalt, 0.53 Mo_2C and .01 carbon, and after sintering, the properties of the sintered alloy were found to be a coercive force of 460, a Rockwell A hardness of 94.0 and a transverse rupture strength of 251,000.

By comparing Alloy G with Alloy F, it may be seen that the smaller particle size tungsten carbide in the starting materials was substantially maintained during sintering and the higher coercive force of Alloy G shows that the alloy contained substantially smaller tungsten carbide grains than Alloy F, the Rockwell A hardness is substantially increased, while the transverse rupture strength is also improved.

What is claimed is:

1. A cement carbide alloy consisting essentially of, in weight percent,
   (A) cobalt in an amount of about 2 to about 20 percent of the total composition,
   (B) molybdenum in an amount of about 5 to about 50% of said cobalt,
   (C) balance tungsten carbide having an average particle size below about 5 microns,

said alloy being substantially free of intermetallic phases having an average size larger than about 2 times the average size of the said tungsten carbide grains, and having
   a Rockwell A hardness in the range of about 87.5 to about 94, and
   a transverse rupture strength in the range of about 240,000 to about 600,000 p.s.i.

2. A composition in accordance with claim 1, wherein the grain size of said tungsten carbide is an average of about 3 microns or less.

3. A composition in accordance with claim 1, wherein cobalt is present in an amount of about 6 to about 10%

and said molybdenum is present in an amount of about 10% to about 50% of said cobalt and said average tungsten carbide grain size is about 3 microns or less.

4. A composition in accordance with claim 1 wherein cobalt is present in an amount of about 10 to about 15%, and said molybdenum is present in an amount of about 10 to about 40% of said cobalt, and said average tungsten carbide grain size is about 3 microns or less.

5. A composition in accordance with claim 1 wherein cobalt is present in an amount of about 15 to about 20%, and said molybdenum is present in an amount of about 10 to about 33% of said cobalt, and said average tungsten carbide grain size is about 3 microns or less.

6. A composition in accordance with claim 1, wherein the grain size of said tungsten carbide is an average of about 1 micron or less.

7. A composition in accordance with claim 1, wherein cobalt is present in an amount of about 6 to about 10% and said molybdenum is present in an amount of about 10% to about 50% of said cobalt and said average tungsten carbide grain size is about 1 micron or less.

8. A composition in accordance with claim 1 wherein cobalt is present in an amount of about 10 to about 15%, and said molybdenum is present in an amount of about 10 to about 40% of said cobalt, and said average tungsten carbide grain size is about 1 micron or less.

9. A composition in accordance with claim 1, wherein cobalt is present in an amount of about 15 to about 20%, and said molybdenum is present in an amount of about 10 to about 33% of said cobalt, and said average tungsten carbide grain size is about 1 micron or less.

10. A cemented carbide alloy consisting essentially of, in weight percent,

(A) cobalt in an amount of about 10 to about 20 percent of the total composition,

(B) molybdenum in an amount of about 10 to about 33% of said cobalt,

(C) balance tungsten carbide having an average particle size below about 5 microns,

said alloy being substantially free of intermetallic phases having an average size larger than about 2 times the average size of the said tungsten carbide grains, and having

a Rockwell A hardness in the range of about 87.5 to about 92.5, and

a transverse rupture strength in the range of about 325,000 to about 600,000 p.s.i.

11. A composition in accordance with claim 10, wherein the grain size of said tungsten carbide is less than about 1 micron average.

References Cited

UNITED STATES PATENTS

3,451,791	6/1969	Meadows	29—182.8
3,525,610	8/1970	Meadows	75—204
2,057,786	10/1936	Mills	75—204
3,514,818	6/1970	Meadows	29—182.8

OTHER REFERENCES

Hansen, M.; Constitution of Binary Alloys, 2d ed., McGraw-Hill, 1958.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,677,722 Dated July 18, 1972

Inventor(s) Frank Rymas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Line 22, "amove" should read --- above ---

Column 3, Line 58, "through" should read --- throughout ---

Column 4, Line 23, "unsual" should read --- usual ---

Column 6, Line 56, "8.6" should read --- 88.6 ---

Column 9, Line 13, "show areas" should read --- show such areas ---

Claim 1, Line 1, "cement" should read --- cemented ---

Signed and sealed this 3rd day of April 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

PO-1050
(5/69)

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