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[54] **ABRASION RESISTANT CEMENTED TUNGSTEN CARBIDE BONDED WITH Fe-C-Ni-Co**

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[58] Field of Search 29/182.7, 182.8; 75/203, 75/204

[56] **References Cited**
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FOREIGN PATENTS OR APPLICATIONS

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[57]   **ABSTRACT**

The use of between 3 percent and 9 percent by weight of an alloy of iron, nickel and cobalt as the bonding agent for fine-particle (1 micron or less) tungsten carbide compact provides a material having enhanced abrasion resistance without incurring significant changes in transverse rupture strength.

3 Claims, No Drawings

ABRASION RESISTANT CEMENTED TUNGSTEN CARBIDE BONDED WITH Fe-C-Ni-Co

BACKGROUND OF THE INVENTION

Cemented carbides are well known for their unique combination of hardness, strength and abrasion resistance and are, accordingly, extensively used for such industrial applications as cutting tools, drawing dies, wear parts, and other applications requiring these properties. They are produced by powder metallurgy techniques involving the liquid phase sintering of one or more refractory carbides of Groups IV, V and VI of the Periodic Table with one or more of the iron group metals. The iron group metal exists as a matrix or binder in the sintered alloy and acts to bond or cement the refractory carbide particles together.

For ferrous alloy metal-cutting applications either mixed carbides of WC-TiC-TaC(NbC) or pure TiC are used since the presence of TiC and TaC enhance wear and deformation resistance for this type of application. For most other applications either pure tungsten carbide or tungsten carbide with minor additions of TaC, NbC, or Cr is used since tungsten carbide imparts superior abrasion resistance and strength to cemented carbides.

When the carbide is based upon pure WC, with or without minor additions of TaC, NbC, or Cr, the matrix or binder metal is almost exclusively cobalt since the use of cobalt results in lower porosity and superior strength and hardness compared with results obtained when nickel or iron is used, especially when the matrix metal content is relatively low, such as 10 volume percent or less. One notable exception is the use of an iron-nickel-carbon alloy as disclosed in Humenik et al., U.S. Pat. No. 3,384,465. When properly composed and treated in accordance with Humenik et al., an iron-nickel-carbon alloy can produce a WC based cemented carbide with enhanced strength and toughness.

In applications where maximum abrasion resistance is desired and imposed stresses are low to medium, such as grit blast nozzles or wear protection plates, WC-Co compositions having 5 to 10 percent matrix content and a fine carbide grain size are used. Usually a small amount (0.1 to 1.0 wt. percent) of one of several additions known to minimize grain growth during sintering (TaC, NbC, or Cr) is added. While it is known that an even finer WC grain structure would produce higher abrasion resistance, this is very difficult to achieve in practice since grain growth does occur and the rate of grain growth during sintering is higher for finer starting grain sizes.

It is a principal object of this invention to provide cemented carbide compositions having unusually high abrasion resistance. It is an additional object of this invention to provide cemented carbide compositions having unusual resistance to grain growth during sintering. It is an additional object of this invention to provide a process for producing such compositions.

SUMMARY OF THE INVENTION

This invention is based upon the unexpected finding that grain growth of the WC phase during sintering is substantially less when the matrix phase is an iron-based alloy present in low concentration. In accordance with the invention a cemented carbide alloy composed of tungsten carbide with a minor addition (0.5–1.0 percent) of tantalum carbide and a matrix consisting of 3 to 9 percent by weight of the total of an alloy of 8 to 20 percent nickel, 5 to 15 percent cobalt, 0.8 to 1.4 percent carbon and the balance iron is prepared. The starting tungsten carbide powder should be very fine, with an average particle size of no more than one micron and preferably in the 0.5 to 0.8 micron range. The other ingredient powders shoud also be fairly fine, preferably in the 1 to 5 micron average particle size range. It is necessary to add carbon in an amount in sufficient excess of the desired final amount to allow for carbon losses sustained through subsequent processing, especially the sintering step. The finally desired carbon content can be best characterized as that amount which is just large enough to prevent formation of the eta phase, a compound of nominal composition W_3Fe_3C. Larger amounts of carbon are undesirable since this causes some grain growth to occur. The proper final carbon content for the preferred compositions of this invention lies in the range of 0.8 to 1.4 percent of the matrix portion of the total composition. The amount of excess carbon necessary to obtain the desired final amount depends upon the particular processing techniques employed.

DESCRIPTION OF PREFERRED EMBODIMENTS

Useful articles within the scope of this invention can be made without the addition of nickel and cobalt. However, these alloying elements are preferred because they provide enhanced abrasion resistance and strength over and above that obtained through the use of a straight iron-carbon matrix. To be useful, the nickel content should be sufficient to allow the matrix phase to partially or fully transform from its high temperature austenitic form to its low temperature martensitic form at moderately fast cooling rates (comparable to air cooling) rather than allowing the formation of Fe_3C to occur, since the formation of Fe_3C causes some reduction in strength. The useful range of nickel content is from about 8 to about 20 percent by weight of the matrix portion and the preferred range is from 10 to 14 percent of the matrix phase portion.

The presence of cobalt is important for its ability to aid the sintering of the cemented carbide alloy to a low porosity state with resulting beneficial effects upon abrasion resistance and strength. For this purpose, cobalt additions of 5 to 15 wt. percent of the matrix portion are effective.

The properly composed starting powders are wet ball milled using a WC-Co lined mill and WC-Co balls and a fluid such as acetone for a period sufficient to grind the powder to a very fine size and produce an intimate mixture of the constituent powders. For these purposes a milling period of 2 to 4 days is necessary for the starting ingredients and milling conditions employed. The milled slurry is then dried in a hydrogen atmosphere oven and a pressing lubricant such as paraffin wax is added in an amount of about 1.5 percent of the weight of the powder. The powder is then pressed in molds to the desired shape using a pressure of about 30,000 psi and the paraffin is removed by firing the parts in a dry hydrogen or vacuum atmosphere at a temperature of 500° to 600°C.

The pressed and dewaxed parts are then sintered in a hydrogen or, preferably, a vacuum furnace to a temperature of 1,350° to 1,450°C and held at that temperature for 15 to 30 minutes.

In the as-sintered state, the matrix phase usually contains large amounts of Fe_3C and, sometimes, graphite flakes. This is due to the slow cooling rate from sintering which occurs when large production scale furnaces are used, especially when the parts are vacuum sintered. To transform the matrix phase into the more desirable austenite or austenite plus martensite form, it is necessary to reheat the parts briefly to a temperature sufficiently high (1,200°–1,300°C) to dissolve the Fe_3C and graphite and then cool at a fairly fast rate (1 to 5 minutes from 1,000° to about 200°C). In this solution-treated condition, nearly maximum abrasion resistance and strength are obtained, as will be illustrated in one of the following examples. Slight additional gains can be obtained by low-temperature treating followed by a tempering treatment. The low-temperature treatment causes the formation of additional amounts of martens-

disk submerged in a slurry of the grit and water. The periphery of the rotating disk was forced against a flat pad of the cemented carbide to be tested using a force of 40 pounds. The test duration consisted of 1,500 revolutions of the disk at a speed of 100 rpm. Fresh slurry was used for each test. The volume of material abraded away was then determined by measuring the weight loss of the pad. The results obtained are shown in Table I. The abrasion test results are reported as the reciprocal of the volume loss since the number so obtained is of convenient size and is directly proportional to the abrasion resistance of the material being tested. Included in Table I are test results for a 93.5% WC—0.5% TaC—6% Co cemented carbide composed of the same starting particle sizes used for the iron-based matrix composition and subjected to comparable processing conditions.

TABLE I

Composition	Processing Stage	Hardness R_A	Abrasion Resistance l/vol loss (cc)	Transverse Rupture Strength
94% wC–1% TaC–5% (74% Fe–15% Ni–10% Co–1C%)	As sintered	93.5	92	257,000
do.	Above + solution treated	93.5	111	187,000
do.	Above + liq. N2 treated	93.7	100	190,000
do.	Above + 300°F tempered	93.7	113	204,000
93.5% WC–0.5% TaC–6% Co	As sintered	92.9	55	260,000

ite and the tempering treatment provides some stress relief of the highly strained martensite phase.

The superior hardness and abrasion resistance that can be obtained through the use of iron-based alloy-bonded tungsten carbide will be demonstrated in the following examples:

EXAMPLE 1

A composition was prepared consisting of 4,000 grams total of a powder mixture containing 94% WC of about 1.0 micron average particle size, 1% TaC and 5 percent of a matrix portion composed of 75 percent carbonyl iron containing 0.8 percent carbon, 15 percent nickel and 10 percent cobalt. Nine grams of carbon were added to this mixture to establish the desired final carbon content. The powder mixture was then ball-milled 3 days in a 7-inch diameter mill lined with WC-Co and containing 12 kg. of ¼-inch diameter WC-Co balls and 2,000 cc. of acetone. The ball-mill charge was then dried, paraffinized, pressed into compacts, preheated at 500°C in H_2 to remove the paraffin and sintered 30 minutes at 1,400°C in vacuum.

Subsequent to sintering, some of the parts were then solution-treated 5 minutes at 1,300°C followed by fast cooling, then cooled to liquid nitrogen temperature, and then tempered by heating one hour at 300°F in air. Tests of hardness, abrasion resistance, and transverse rupture strength were made at each stage of processing after sintering to determine the effect of the thermal treatments. The abrasion test apparatus consisted of a rotating 6½ inch diameter, ½-inch wide steel disk which contained on its periphery particles of aluminum oxide grit obtained by having the lower portion of the

It can be observed that at any stage of processing the WC-iron alloy composition has higher hardness and abrasion resistance than does the comparable WC-Co material. It is also evident that a significant increase in abrasion resistance is obtained by solution-treating the WC-iron alloy material, although this is accompanied by a strength reduction. The additional thermal treatments provide slight additional benefit in the form of optimizing the combination of strength and abrasion resistance.

When the microstructures of the two compositions were viewed at 1,500 power it was observed that the WC-iron alloy material had a noticeably finer WC grain structure, apparently caused by the superior ability of the iron alloy to inhibit WC grain growth during sintering.

EXAMPLE 2

A composition consisting of 94% WC—1% TaC—5% (74% Fe—15% Ni—10% Co—1C) was prepared as in Example 1 above with the exception that the starting WC powder particle size was somewhat finer, averaging about 0.85 microns. Abrasion test pads and transverse rupture strength test bars were prepared and processed through the full thermal treatment sequence shown in Example 1 above. For comparison purposes a composition consisting of 93 % WC—1% TaC—6% Co was prepared using the same WC powder. It should be noted that the matrix phase contents of these two compositions are equal on a volume basis. They differ on a weight basis because of their differing densities. The resulting properties are shown in Table II.

TABLE II

Composition	Hardness R_A	Abrasion Resistance 1/vol. loss (cc)	Transverse Rupture Strength
94% WC–1% TaC–5% (74% Fe–15% Ni–10% Co–1C%)	94.1	191	185,000
93% WC–1% TaC–6% Co	93.4	70	192,000

In this case the abrasion resistance of both compositions is higher than their counterparts in Table I, apparently due to the use of finer WC powder. The iron-alloy matrix composition, however, made much more effective use of the finer starting WC powder than did the cobalt matrix composition, resulting in a nearly doubled abrasion resistance compared with about a 30 percent increase for the cobalt-matrix composition. This

ance Fe ranging in matrix content from 3 to 9 weight percent were prepared and processed as in Example 1 above. The resulting hardness, strength and abrasion resistance were then determined for each composition in order to establish the useful range of matrix content. The results are shown in Table III along with results obtained for a comparably prepared composition consisting of 93% WC—1% TaC—6% Co.

TABLE III

Composition	Hardness R_A	Abrasion Resistance 1/vol. loss	Transverse Rupture Strength
96% WC–1% TaC–3% (74% Fe–15% Ni–10% Co–1C%)	94.0	135	175,000
94% WC–1% TaC–5% (74% Fe–15% Ni–10% Co–1C%)	94.0	175	180,000
92% WC–1% TaC–7% (74% Fe–15% Ni–10% Co–1C%)	93.2	95	190,000
90% WC–1% TaC–9% (74% Fe–15% Ni–10% Co–1C%)	93.0	60	240,000
93% WC–1% Tac–6% Co	93.4	70	190,000

even more clearly demonstrates the superior ability of the iron-alloy matrix to inhibit grain growth during sintering.

EXAMPLE 3

A 4,000-gram batch of a composition consisting of 94% WC of about 0.85 micron average particle size and 5 percent iron containing 1 percent carbon was prepared and processed as in Example 1 above. The resulting hardness and abrasion resistance were 93.3 and 118, respectively, and the transverse rupture strength was 160,000 psi. While not as good as the comparable composition containing nickel and cobalt in the matrix phase, the straight iron-carbon matrix alloy composition has utility since its abrasion resistance is significantly higher than can be easily obtained using a cobalt matrix.

EXAMPLE 4

For 4,000-gram batches of compositions consisting of WC of about 0.85 micron average particle size and varying amounts of matrix powders to compose a matrix composition 15% Ni—10% Co—1% C and the bal-

It can be seen that as a function of the amount of matrix phase present, the abrasion resistance is optimized at about the 5 weight percent level and that there is no advantage in increasing the matrix content to above 9 percent since the abrasion resistance drops to a level below that which can be obtained using a conventional cobalt matrix.

What I claim as new and desire to secure by letters patent in the United States is:

1. A hard, sintered compact consisting of 91 to 97 percent by weight of tungsten carbide base particles bonded by an alloy consisting of 8 to 20 percent by weight of nickel, 5 percent to 15 percent by weight of cobalt, 0.8 to 1.4 percent by weight of carbon, and the balance iron.

2. A hard, sintered compact as claimed in claim 1 wherein the carbide contains between 0.5 and 1.0 percent by weight of tantalum carbide.

3. A hard, sintered compact as claimed in claim 1 wherein the bonding alloy consists of about 15 percent by weight of nickel, about 10 percent by weight of cobalt, and about 0.8 percent by weight of carbon.

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