

1

3,698,878

SINTERED TUNGSTEN CARBIDE-BASE ALLOYS

Thomas E. Hale, Warren, Mich., assignor to
General Electric Company

No Drawing. Filed Dec. 29, 1969, Ser. No. 888,860

Int. Cl. B22f 3/24

U.S. Cl. 29—182.7

4 Claims

ABSTRACT OF THE DISCLOSURE

Sintered tungsten carbide-base alloys containing from 40–80% by weight of an iron-base binder alloy which in turn contains from about 5–25% by weight nickel and an amount of carbon ranging from about 0.5–2% by weight of the binder. The alloys of the invention are prepared by sintering a pressed mixture of the tungsten carbide and binder, which may then be machined or otherwise shaped in the soft as-sintered state and subsequently hardened by heat treatment to form a fully dense, strong and hard cemented carbide compact.

This invention relates to a sintered cemented tungsten carbide composition.

Certain steel compositions undergo a phase transformation when heat-treated from austenite to martensite, such that they may be machined or otherwise shaped in the soft austenitic state and then hardened to form martensite or tempered martensite. It would be desirable to impart this property of phase transformation to cemented tungsten carbides which, because of their extremely high hardness, cannot be machined or can be machined only with great difficulty. However, virtually all commercially available cemented tungsten carbides contain a cobalt binder and are not subject to this hardening transformation. It is possible that such phase transformation could occur if the cobalt binder were replaced with steel or other iron-base alloy. The use of iron-nickel binders for tungsten carbide-base alloys is suggested, for example, by Schwarzkopf & Kieffer in "Cemented Carbides," MacMillan Co., 1960, at pp. 188–190. However, cemented tungsten carbides, even with such a steel binder, would normally be too hard—even with the binder phase in the soft austenitic state—to be machined.

Titanium carbide-base alloys or composites of titanium carbide with tantalum-, columbium-, or hafnium-carbide, containing steel binders, are known and have been fairly extensively used. They generally have high binder levels (40–60 volume percent) and are capable of the aforementioned phase transformation, permitting machining while the steel binder is in a soft condition. However, tungsten carbide-base composites are stronger than those with a titanium carbide base and it would be highly desirable to produce these characteristics in a tungsten carbide-base alloy.

The present invention has as its chief object the provision of a sintered tungsten carbide-base composition capable of being significantly hardened by heat treatment. It is an additional object of the invention to provide such a composition having the ability to be shaped to its desired final configuration while in a soft condition and then to be hardened by phase transformation to produce a fully dense, fine-grained strong and hard cemented carbide compact.

These and other objects of the invention are accomplished by using as a matrix or binder for tungsten carbide-base alloys relatively large percentages of a binder of an alloy of iron and nickel containing sufficient carbon to suppress the formation of eta phase. The amount of binder used with the present alloys is higher

2

than it has been heretofore been thought desirable to use in cemented tungsten carbides and still obtain a usable sintered product. More specifically, the present invention is directed to a sintered cemented carbide composition containing from 40–80% by weight of an iron-base alloy binder containing from 5–25% by weight of nickel and from 0.50–2.0% and preferably 0.75–1.5% by weight of carbon. The use of this specific binder in these proportions permits the sintered tungsten carbide-base alloy to be machined or otherwise shaped to the desired final configuration while it is still in a relatively soft state and subsequently hardened by heat treatment to a high-wear resistance, high-strength condition.

The presence of nickel in the binder within the ranges indicated lowers the critical temperature for the hardening transformation of the steel binder. If nickel is present in sufficient amounts, the critical temperature is below room temperature. The latter permits the sintered alloy to be cooled, at any rate desired, down to room temperature, at which point the binder is in a machinable austenitic condition. This cool sintered composite may then be machined to the desired shape, after which it is cooled to below room temperature to transform most of the austenitic binder to hard, wear-resistant martensite. This technique of cold-treating to achieve the hardening transformation imposes less severe thermal stresses on the part than would occur by use of the more usual hardening technique of heating to 760°–1100° C. and then rapid cooling. It also minimizes cracking and distortion and eliminates the need to have the finished part go through a solution-treating furnace operation. However, both hardening techniques may be used with the compositions of the invention.

Steels are generally considered to be "machinable" when the hardness is no more than about 50–55 on the Rockwell C scale (Rc). The compositions of the invention possess a hardness either in this range or lower, in the soft state. The lower the content of the hard WC phase, of course, the lower the hardness of the alloy. To retain its ability to be machinable in the soft condition, the alloy should contain no more than 60% by weight carbide, or stated conversely, no less than 40% by weight binder. For purposes of both convenience and consistency, relative amounts of carbide and binder phase are here expressed in terms of weight percent because weight percent is more conventionally used to identify proportions of alloy constituents. It should be noted, however, that tungsten carbide has a considerably higher density than steel, so that volume ratios of the two phases of the present alloy would perhaps be more meaningful than weight ratios. By volume, the binder content of the present alloy ranges from 55–90% of the total volume of the alloy, illustrating their unusually high binder content as contrasted with known cemented tungsten carbide compositions which normally contain a maximum of 40% by volume binder.

The conditions of heating and cooling required to obtain the desired hardening transformation of the matrix phase from the austenitic or coarse pearlitic soft states to the mostly martensitic hard state are dependent upon composition of the matrix, being strongly affected by the content of the carbon and nickel. Since the carbon content of the compositions of this invention has been held at fairly constant values (in order to prevent formation of eta phase and excess carbon), the primary variable affecting the transformation conditions of the compositions is the nickel content.

When the nickel content of these compositions exceeds about 10 weight percent of the matrix, the temperatures at which the hardening transformation begins (Ms temperature) is depressed to below room temperature. The matrix phase of such compositions is thus soft austenite at room

temperature so long as the compact is cooled from sintering temperature at a moderately rapid rate (approximating air cooling conditions) to prevent the formation of iron carbide (Fe_3C). These compacts are subsequently hardened by cooling to below the M_s temperature, preferably to liquid nitrogen temperature to achieve more complete transformation. As the nickel content of the matrix is increased to values above 10%, the M_s temperature is depressed to lower values and it becomes increasingly difficult to obtain sufficiently complete transformation. When the nickel content exceeds 25–30% of the matrix, the M_s temperature is depressed to such a low value that no hardening is obtained at liquid nitrogen temperature. It is possible to improve the degree of transformation of compositions with higher nickel contents (12–25%) by heating them to 800° C. and holding for a sufficient period of time ($\frac{1}{2}$ to 4 hours) to precipitate dissolved tungsten and carbon from the matrix. This effectively increases to M_s temperature and the amount of martensite that will form at liquid nitrogen temperature.

When the nickel content of the matrix is less than about 10%, the M_s temperature is above room temperature and the matrix can no longer be placed in the soft austenitic form by moderately fast cooling to room temperature. In order to obtain the softest condition with such compositions, they must be very slowly cooled (5–15° per hour) through the temperature range 600–900° C. in order to place the matrix in a coarse perlite condition. Such compositions are subsequently hardened by heating to a temperature above which the matrix becomes fully austenitic (about 800° C.) and then rapidly cooling (oil or water quench) to room temperature to obtain the martensitic transformation. Further hardening can be achieved by liquid N_2 cooling to achieve more complete transformation. The degree of transformation obtained for compositions having less than 10% Ni in the matrix is strongly influenced by the specific Ni content and the time and temperature of the austenitizing treatment. Thus for each nickel content there is an optimum austenitizing condition required to obtain maximum hardness. For example, with a composition having a matrix consisting of 1% C, 5% Ni, balance Fe, maximum hardness is obtained by austenitizing 30 minutes at 1025° C., oil quenching, and liquid nitrogen cooling. When the Ni content is increased to 7%, the optimum conditions are 30 minutes at 800° C., oil quenching and liquid nitrogen cooling. For nickel contents less than about 5%, extremely rapid cooling rates, such as those obtained by quenching into a well-stirred cold-water bath, are needed to obtain maximum hardness.

The following examples illustrate the practice of the present invention. All parts and percentages are by weight.

EXAMPLE I

A sintered compact was prepared from a composition consisting of 50% WC, 50% of an iron-base matrix alloy containing 12% nickel, 1% carbon, balance iron. The starting materials, consisting of 2–4 micron tungsten carbide powder, 2–5 micron carbonyl iron powder, 2–3 micron carbonyl nickel powder, and fine graphite powder to bring the total charge to 400 grams, were ball-milled 24 hours in a 4-inch diameter cemented-carbide-lined mill containing 1000 gms. of cemented carbide balls and 250 cc. of acetone. One percent of paraffin was then added and the compact was pressed at a pressure of 30,000 p.s.i. The paraffin was then removed by presintering at a temperature of 500° C. in a hydrogen atmosphere. It was then sintered to full density by heating to 1300° C., holding 15 minutes at 1300° C. in a hydrogen atmosphere and cooled at a rate approximating air cooling to room temperature. At this point the steel matrix was in the soft austenitic condition (Rc 45) and could be machined to the desired shape. The finished compact was then hardened to about Rc 66 by cooling to liquid nitrogen temperature and holding for about 30 minutes. Even higher hardness (about Rc 68) was obtained by heating the compact to

800° C., holding 1 to 3 hours, air cooling to room temperature, and then liquid nitrogen cooling.

EXAMPLE II

A sintered compact of 50% WC, 50% of an iron-base matrix alloy containing 6% nickel, 1% carbon, balance iron, was prepared by ball-milling, pressing, and sintering as in Example I above. Due to the lower nickel content of this composition compared with the composition in Example I, the softening and hardening procedures were quite different. Softening of the composition was accomplished by very slowly cooling to room temperature from a temperature of 800–1000° C. The compact was softened by reheating to 1000° C. in a vacuum furnace having an inside diameter of 14 inches and then cooling to room temperature at the natural cooling rate of the furnace. After this treatment the matrix was in a coarse pearlitic condition and the compact had a hardness of Rc 44. After machining to the required final shape, the compact was hardened to Rc 68 by heating to 1025° C., holding 30 minutes, oil quenching, and tempering 15 minutes at 150° C.

The following table shows the hardness in both the soft and hard condition and the transverse rupture strength in the hard condition of a series of compositions within the scope of the invention. For purposes of comparison, steel binder compositions within the scope of the invention—compositions 1 thru 5—are compared with a known tungsten carbide-cobalt sample, composition 6, having a cobalt content of 25% by weight. This particular tungsten carbide-cobalt composition, known commercially as Carboloy cemented carbide grade 190, is selected because it represents one of the highest binder content, highest toughness, commercially available tungsten carbide-base alloys, and further because machining operations are sometimes performed on this grade of material even though its hardness (Rc 65) is outside the machinable range.

	Composition ¹	Hardness ²		Transverse rupture strength ³
		Soft	Hard	
1-----	WC Ni, 5 C, 1.5 Fe, bal	60 Ra 78.5 40 Rc 55	Ra 87.6 Rc 72	410,000
2-----	WC Ni, 12 C, 1 Fe, bal	60 Ra 76.5 40 Rc 51	Ra 87 Rc 71	
3-----	WC Ni, 11 C, 1.5 Fe, bal	51 Ra 75 49 Rc 48.5	Ra 86 Rc 69	540,000
4-----	WC Ni, 11 C, 1.5 Fe, bal	33 Ra 68.5 67 Rc 35	Ra 83.5 Rc 63.4	
5-----	WC Ni, 11 C, 1.5 Fe, bal	18 Ra 61.5 82 Rc 20	Ra 82.2 Rc 62	450,000
6-----	WC Co	75 ----- 25 -----	Ra 84 Rc 65	

¹ All compositions are percent by weight.

² Ra is Rockwell A and Rc is Rockwell C.

³ Pounds/square inch—hardened composition.

Abrasion resistance tests on the above samples established that abrasion resistance followed the normal correlation of this property in cemented tungsten carbides with the hardness results given above. Impact strength tests similarly correlated well with the transverse rupture strengths given above.

In addition to the properties set forth in the above table, a machining test was run on a 0.75" diameter x 2.5" long cylinder of the composition identified as composition 3 above, along with a similar test on a cylinder of the standard tungsten carbide-cobalt sample identified above as composition 6. Using cutting conditions that produced a minimum amount of wear on the cutting tool, it took only 0.5 minute to develop a 0.022 wear land when machining the tungsten carbide-cobalt (composition 6). Using the same conditions, the wear land

5

was only 0.0065" after one minute of machining composition 3 in the soft condition, and a much better surface finish was obtained. The steel binder material of the invention was thus rated to be at least four times more machinable than the standard tungsten carbide-cobalt grade (composition 6). This demonstrates the very desirable combination of machinability and physical properties, subsequent to hardening, available with the compositions of the invention.

The term "tungsten carbide base" cemented carbides, as used herein, does not exclude the presence of other well-known carbide constituents in the carbide phase of the composition, such as titanium and tantalum carbide. Tungsten carbide has a very large solubility, for example, in titanium carbide, and the term "tungsten carbide base" is intended to exclude sintered compositions which do not contain a free tungsten carbide phase. It also excludes compositions which are not more than 50% tungsten carbide by weight of the refractory carbide.

The steel alloy binder must be an iron-base alloy in the sense that over 50% by weight of the binder alloy is iron. It is possible to have small amounts of other metals present in the steel binder alloy, as for example molybdenum, vanadium, chromium or cobalt, as long as the foregoing parameters are satisfied with respect to the chemistry of the alloy. For example, small amounts of cobalt may be present in the binder as long as the hardening temperature is not significantly raised. Normally, cobalt raises the hardening temperature while nickel lowers the hardening temperature, so that suitable additions of nickel may compensate for the presence of cobalt. In addition, within the ranges set forth, the percentages of nickel and carbon must be suitably adjusted

6

so that the transformation temperature is not changed. If more carbon is used within the stated range, normally less nickel will be used and vice versa.

What is claimed is:

1. A sintered cemented carbide composition capable of being machined in the as-sintered condition and then hardened by phase transformation, said sintered composition consisting essentially of a tungsten carbide-base refractory carbide and from 40-80% by weight of an iron-base binder alloy containing by weight of the binder from 5-25% nickel and from 0.5-2% carbon.

2. The sintered composition of claim 1 containing from 50-70% by weight of the iron-base binder alloy.

3. The sintered composition of claim 1 in which the iron-base binder alloy contains from 10-25% nickel and from 0.7-1.5% carbon.

4. The sintered composition of claim 1 in which the tungsten carbide-base refractory carbide consists of tungsten carbide.

References Cited

UNITED STATES PATENTS

3,303,066	2/1967	McGee	148—126
2,637,671	5/1953	Pavitt	148—126
3,183,127	5/1965	Gregory et al.	148—126
3,053,706	9/1962	Gregory et al.	148—126
3,384,465	5/1968	Humenik, Jr. et al.	29—182.8

CARL D. QUARFORTH, Primary Examiner

B. H. HUNT, Assistant Examiner

U.S. Cl. X.R.

29—182.8; 148—126