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HEAT TREATABLE TOOL STEEL OF HIGH CARBIDE CONTENT

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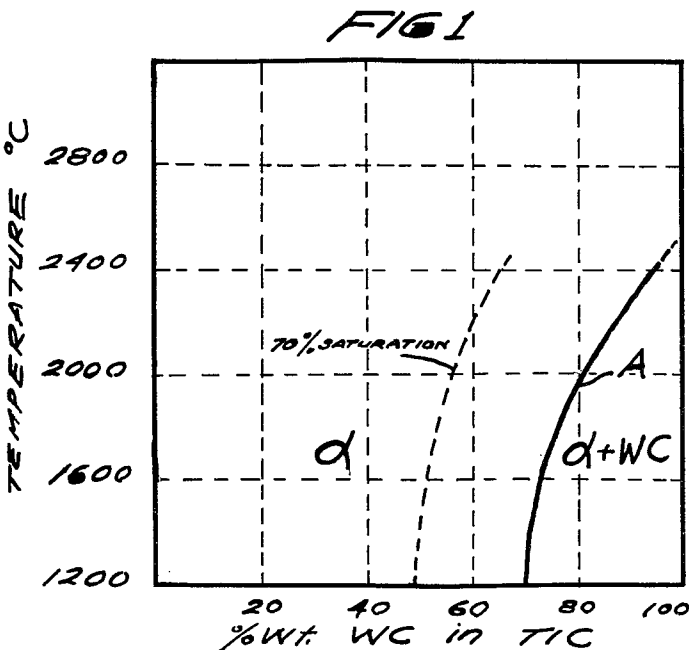


FIG. 2



FIG. 3

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3,053,706 HEAT TREATABLE TOOL STEEL OF HIGH CARBIDE CONTENT

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This invention relates to carbide steels and more particularly to a machinable titanium carbide containing tool steel composition capable of being heat treated to high hardness.

In U.S. Patent No. 2,828,202, dated March 25, 1958, and issued to the same assignee, a tool steel of high carbon content based on titanium carbide is disclosed in which the amount of titanium employed is at least 10% by weight substantially all combined in the form of a primary carbide. The titanium carbide is uniformly distributed through a heat treatable ferrous matrix comprising either carbon steel, medium alloy steel or high alloy steel.

As pointed out in the aforementioned patent, the composition is formed by employing titanium and carbon together in a combined form as titanium carbide as an alloying ingredient together with a steel matrix which cooperates with said carbide in producing the desired composition. The steel employed in forming the matrix contains iron as the major alloying element which generally comprises at least about 60% by weight of the steel matrix composition. The amount of titanium may range from about 10% to 70% by weight (about 20% to 90% by volume of titanium carbide) and preferably about 20% to 58% by weight of titanium (about 40% to 80% by volume of titanium carbide), substantially the balance being formed of the steel matrix. According to the patent, the titanium carbide may be replaced in part, preferably as a solid solution, by up to about 35% by weight of tungsten carbide, up to about 35% vanadium carbide, up to about 25% zirconium carbide, up to about 10% columbium carbide, up to 10% tantalum carbide, etc., the total amount of such carbides not exceeding 50% by weight of the carbides present.

Powder metallurgy is employed as the preferred method of producing the desired composition which comprises broadly mixing powdered titanium carbide with powdered steel-forming ingredients and forming a slug by pressing the mixture in a mold, followed by subjecting the slug to liquid phase sintering under non-oxidizing conditions such as in a vacuum. The method is also applicable to solid solution titanium carbides such as for example a primary carbide comprising tungsten carbide dissolved in titanium carbide to form an alpha solid solution of WC in TiC having a face centered cubic structure.

More complex alloys based on titanium carbide solid solution carbides, e.g. WC in TiC, are desirable for some tool applications, particularly where high alloy steel matrix alloys are employed to produce compositions having improved resistance to tempering, improved properties at elevated temperatures, improved hot hardness and controlled grain size of the primary carbide. In dealing with such complex alloy systems, we have observed certain anomalies in the compounding of certain alloy compositions. For example, in producing a heat treatable steel containing primary carbide grains comprised substantially of titanium carbide, to the matrix of which tungsten and carbon have been added to improve certain properties of the matrix surrounding the primary carbide grains, such as improved resistance to tempering, the expected improvement is not always obtained. For one thing, the matrix does not appear to achieve the full

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benefits of the alloying additions of such elements as tungsten. For another, the primary titanium carbide phase tends to grow at the expense of tungsten added to the matrix whereby the matrix does not achieve full benefit of the tungsten added.

According to our observations, it appeared that where substantially all of the primary carbide was composed of TiC or an unsaturated TiC solid solution, e.g. a solid solution carbide containing by weight 75% TiC and 25% WC, a large portion of the tungsten and carbon added to improve the matrix would be absorbed by the primary carbide at the expense of the matrix. The extent to which this occurred seemed to vary in accordance with the composition of the primary carbide.

For the purposes of this invention, by "primary carbide" is meant that carbide which is substantially unaffected by normal steel heat treating practices. By "secondary carbide" is meant that carbide which may be substantially dissolved by a normal tool steel austenitizing heat treatment.

We have now found that the aforementioned difficulty can be overcome by starting with a particular solid solution carbide composition and by considering this composition in determining the addition of an alloying metal such as tungsten to the matrix.

It is the object of this invention to provide a method for preparing a heat treatable carbide steel comprising a primary carbide containing titanium carbide and a tungsten group metal carbide in solid solution therewith distributed through an alloy steel matrix containing a secondary carbide which contains said tungsten group metal.

Another object is to provide a method for producing a heat treatable ferrous alloy containing a primary solid solution carbide of tungsten carbide in titanium carbide distributed through an alloy steel matrix containing a secondary carbide which contains tungsten.

A further object is to provide a carbide steel composition comprising a primary solid solution carbide of titanium and a tungsten group metal distributed through an alloy steel matrix having a secondary carbide containing said tungsten group metal.

These and other objects will more clearly appear from the following disclosure taken in conjunction with the accompanying drawing, wherein:

FIG. 1 shows the solid solution relationship between WC and TiC;

FIG. 2 is a representation of a photomicrograph of a heat treatable alloy of the invention taken at 1000 magnification comprising a substantially saturated primary solid solution carbide grains of WC—TiC in an alloy steel matrix having dispersed therethrough a spheroidized secondary carbide; and

FIG. 3 is a representation of a photomicrograph as in FIG. 2 excepting that the matrix is martensitic.

Broadly stated, one aspect of the invention provides a method of forming a heat treatable ferrous alloy containing a primary solid solution carbide of titanium carbide having in solid solution therewith at least one tungsten group metal carbide preferably selected from the group consisting of tungsten carbide, molybdenum carbide and chromium carbide in an amount corresponding to substantially the solid solution saturation amount, said primary carbide being distributed through heat treatable ferrous matrix having dispersed therethrough secondary carbide containing at least one of said tungsten group metals. The primary carbide solid solution should be as saturated as possible in order to obtain the desired composition in the alloy matrix.

For example, in producing a heat treatable alloy containing a primary carbide, based on the WC—TiC solid solution and containing tungsten as a secondary carbide

in the matrix, we find that we can start with a solid solution primary carbide in which the tungsten carbide is at least about 70% of its saturation value and to add an amount of tungsten and carbon to the steel-forming ingredients of the matrix sufficient to saturate the solid solution of the primary carbide as well as an excess to make available sufficient tungsten for solution into the steel matrix and form secondary carbide with carbon and other elements present in the matrix. An advantage in having tungsten in the matrix as a secondary carbide is to have available a source of tungsten for solution into the matrix by decomposition during heat treatment in order to improve elevated temperature properties of the matrix.

In order to get a better understanding of the method of the invention, reference is made to FIG. 1 of the drawing showing an equilibrium diagram of the solid solution between TiC and WC. It will be noted that at 1200° C., WC goes into solid solution with TiC up to an equilibrium value determined by line "A" to be about 70% by weight. At 2000° C., line "A" shows the solid solution to be saturated at about 80% WC. Between 1200 to 1600° C., the saturation is fairly constant at about 70% WC. At 50% saturation at the foregoing temperature range the solid solution would contain about 35% WC. If the foregoing solid solution primary carbide containing 35% WC were employed as a starting material in forming a steel alloy in which the starting matrix ingredient is an 18-4-1 high speed steel composition, the full benefit of the 18-4-1 composition would not be realized in view of the presence of the unsaturated solid solution carbide which, because of the relatively high free energy of formation thereof, would selectively remove WC from the matrix until the primary carbide becomes substantially saturated with WC, assuming enough is available to saturate it. Thus, the original primary carbide would grow at the expense of the tungsten and carbon in the matrix thus rendering the matrix deficient in the desired tungsten content. Under such conditions, the primary carbide may grow to undesirable sizes and adversely affect the physical properties of the resulting alloy.

To overcome the foregoing disadvantages, we would employ as a starting material a solid solution carbide of the TiC-WC at least about 70% saturated, preferably as saturated a solid solution of TiC-WC as is possible. It will be appreciated that equilibrium line "A" of FIG. 1 may shift slightly depending upon the composition of the steel matrix in contact with the solid solution primary carbide crystals. In any event, we have found that we can achieve our desired results starting with a primary solid solution carbide of TiC which is at least 70% saturated with respect to the tungsten metal group carbide.

As illustrative of the method aspect of the invention the following example is given:

An alloy useful for hot swaging dies has the following composition by weight:

About 35% WC	Substantially a saturated solid solution of TiC-WC.	In the matrix.
About 15% TiC		
About 9% W		
About 2.5% Cr		
About 0.4% C		
About 38.1% Fe		
100.0%		

In producing this composition, 1000 grams of a substantially saturated solid solution of TiC-WC (30% TiC-70% WC) of about 3 microns average size is mixed with 1000 grams of steel-forming ingredients, containing 18% tungsten, 5% chromium, 0.8% carbon and the balance carbonyl iron of about 20 micron average particle size by milling in a steel mill. The powdered ingredients contain 1 gram of paraffin wax for each 100

grams of mix. The milling is conducted for about 40 hours, the mill being half filled with stainless steel balls. Hexane is used as a vehicle. After completion of the milling, the material is removed and vacuum dried. The mixed product is then pressed to form a slug 5 inches long by 1½ inches wide by ½ inch thick. The slug is then subjected to liquid phase sintering at a temperature of about 1450° C. for about ½ hour in a vacuum of about 20 microns of mercury or better. After completion of the sintering the slug is cooled and then annealed by heating to 1675° F. for 2 hours followed by cooling at a rate of 25°/hour to 1300° F. and thereafter furnace cooled to room temperature to produce a microstructure comprising primary solid solution carbide of TiC-WC distributed through a steel matrix characterized by a dispersion of secondary carbide in spheroidite form (note FIG. 2). The annealed slug is then machined to the desired shape and hardened by austenitizing at a temperature of about 2300° F. for a time sufficient, e.g. 15 minutes at temperature, to austenitize the matrix and dissolve the secondary carbides. The slug is then oil quenched to yield a hardness of about 72R_C.

The ferrous alloy produced in the foregoing manner is characterized by a microstructure comprising approximately 50% by weight of the saturated solid solution TiC-WC as a primary carbide distributed uniformly throughout a martensitic steel matrix (note FIG. 3).

Should the TiC-WC solid solution be about 80% saturated with WC, then the amount of tungsten and carbon added to the matrix should be sufficient to saturate the primary solution carbide and leave enough for the matrix. For example, assuming an alloy is desired containing about 50% by weight of a primary solid solution carbide of TiC-WC and the balance a matrix of steel, and the starting solid solution carbide is about 80% saturated, allowance for the 80% saturation can be made as follows in determining the amount of tungsten to go into the matrix to form a steel matrix containing 18% W and about 5% Cr.

The primary carbide at 80% saturation will according to FIG. 1 (assuming no substantial shifting of line "A") comprise about 44% TiC and 56% WC (70% WC being saturation). Assuming that 2000 grams of the final alloy is desired, then the amounts of the constituents necessary to produce a steel matrix containing about 18% W and between 4 to 5% Cr having a saturated primary carbide distributed therethrough are as follows:

	Grams
80% saturated TiC-WC	682
Steel-forming ingredients	1318
Total	2000

The steel-forming ingredients contain the following:

(A) 318 grams of W and C to form WC	Gms.
W	298.5
C	19.5

Total 318

(B) 1000 grams of steel-forming ingredients	Gms.
W	180
C	8.0
Cr	50.0
Fe	762

Total 1000

Approximately 318 grams of W and C of (A) above will go to combine with approximately 682 grams of the TiC-WC solid solution to form 1000 grams of saturated primary carbide grains of TiC-WC, while the remaining 1000 grams of the steel-forming ingredients form the matrix which will have secondary carbides containing tungsten and carbon from the matrix.

The powdered ingredients are mixed together as de-

scribed in the previous example by ball milling and the mixed product then pressed to form a slug of desired dimension. The slug is subjected to liquid phase sintering at a temperature of about 1450° C. for about ½ hour in a vacuum of about 20 microns of mercury or better to homogenize the composition and after completion, the slug is treated similarly as described hereinbefore to produce either an annealed or hardened structure.

Similar procedures are followed in producing heat treatable ferrous alloys containing primary carbides based on saturated solid solution carbides of titanium carbide-chromium carbide or titanium carbide-molybdenum carbide. In producing such alloys we prefer to start with the saturated solid solution carbide, although as stated hereinbefore we can start with solid solution carbides at least 70% saturated and take this in account in preparing the composition.

In producing sintered compositions in accordance with the invention, the powder mixture is first formed into the desired shape. For example, the mixture may be compacted at a pressure sufficient to yield a density at least 50% of true density. Such pressure may range from about 10 t.s.i. to 75 t.s.i., preferably 15 t.s.i. to 50 t.s.i.

The pressed compact is then subjected to sintering at preferably above the melting point of the matrix composition, that is liquid phase sintered, generally at a temperature ranging from about 1300° C. to about 1575° C. under non-oxidizing conditions, preferably vacuum. Such vacuum may include sub-atmospheric pressures not exceeding about 300 microns of mercury column. The sintering time at temperature should be sufficient to obtain substantially complete densification and may range from about one minute to 6 hours, shorter times being used the higher the temperature.

Upon completion of the sintering, the sintered compact is furnace cooled to room temperature.

In producing an annealed structure, the sintered alloy is heated to a temperature range of 650° C. to 975° C. for about ½ to 4 hours and then cooled at a rate of 10° C./hour to below 600° C. and then furnace cooled.

In producing a hardened structure, the alloy is heated to an austenitizing temperature range of about 870° C. to 1315° C. for a time sufficient to obtain substantial conversion to austenite, for example about one minute to 3 hours, and then quenched in air, oil or water depending on the composition of the alloy to produce a matrix having martensitic structure.

The composition of the ferrous alloy to which the invention may be applied comprises about 22% to 90% by weight of the solid solution carbide and the balance the steel matrix. Preferably the composition should range from about 25% to 75% of the primary solid solution carbide and the balance the steel matrix. Examples of steels which may be employed include low, medium and high alloy steels. Such steels may comprise about 0.8% chromium, 0.2% molybdenum, about 0.30% carbon, and iron substantially the balance; about 5% chromium, 1.4% molybdenum, 1.4% tungsten, 0.45% vanadium, 0.35% carbon, and iron substantially the balance; about 8% molybdenum, 4% chromium, 2% vanadium, 0.85% carbon, and iron substantially the balance; about 18% tungsten, 4% chromium, 1% vanadium, 0.75% carbon, and iron substantially the balance; about 20% tungsten, 12% cobalt, 2% chromium, 2% vanadium, 0.80% carbon, and iron substantially the balance; and generally other types of steels characterized crystallographically by a body centered cubic structure at ordinary temperatures and by being transformable to a face centered cubic structure at an elevated temperature below the melting point of the steel.

The invention provides a high tungsten, high carbon ferrous alloy which in the form of bar stock, rounds, squares, blocks, ingots and other shapes can be utilized in the fabrication of cutting tools, blanking dies, forming dies, drawing dies, rolls, hot extrusion dies, forging dies, upsetting dies, broaching tools, and in general all types of wear and/or heat resisting elements, tools or machine parts.

Generally, as heat treated, the alloy of the invention will have a microstructure comprising any one of the austenitic decomposition products pearlite, bainite and martensite.

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 appended claims.

What is claimed is:

1. A heat treatable ferrous alloy formed of a primary solid solution carbide, and the balance of the alloy being formed of a heat treatable steel matrix, said primary carbide comprising substantially a solid solution of a tungsten group metal carbide selected from the group consisting of tungsten carbide, molybdenum carbide and chromium carbide in titanium carbide at substantially the saturation limit of the solid solution composition in equilibrium with said steel matrix, said steel matrix having dispersed therethrough a secondary carbide comprised substantially of a carbide selected from the group consisting of tungsten carbide, molybdenum carbide and chromium carbide.

2. The ferrous alloy defined in claim 1 wherein the steel matrix is pearlitic.

3. The ferrous alloy defined in claim 1 wherein the steel matrix is martensitic.

4. A heat treatable ferrous alloy formed of a primary solid solution carbide, the balance of the alloy being formed of a heat treatable steel matrix, said primary carbide comprising substantially a solid solution of tungsten carbide in titanium carbide at substantially the saturation limit of the solid solution composition in equilibrium with said steel matrix, said steel matrix having dispersed therethrough a secondary carbide containing tungsten and carbon.

5. The ferrous alloy defined in claim 4 wherein the steel matrix is pearlitic.

6. The ferrous alloy defined in claim 4 wherein the steel matrix is martensitic.

7. A heat treatable ferrous alloy containing 22% to 90% by weight of a primary carbide, the balance of the alloy being formed of a heat treatable steel matrix, said primary carbide comprising substantially a solid solution of tungsten carbide in titanium carbide at substantially the saturation limit of the solid solution composition in equilibrium with said steel matrix, said steel matrix having dispersed therethrough a secondary carbide containing tungsten and carbon.

8. The ferrous alloy defined in claim 7 wherein the steel matrix is pearlitic.

9. The ferrous alloy defined in claim 7 wherein the steel matrix is martensitic.

References Cited in the file of this patent

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