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1

3,183,127 HEAT TREATABLE TOOL STEEL OF HIGH CARBIDE CONTENT

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- Original application Apr. 27, 1959, Ser. No. 809,217. Divided and this application Apr. 30, 1963, Ser. No. 276,895

5 Claims. (Cl. 148-31)

This application is a division of our U.S. application Serial No. 809,217, filed April 27, 1959, now abandoned.

This invention relates to carbidic steels and in particular to a heat treated tool steel containing as a primary 15 carbide at least one carbide selected from the group consisting of VC, CbC and TaC.

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 20 which the amount of titanium employed is at least 10% 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. 25

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 30 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 35 90% by volume of titanium carbide or 12.5% to 87% by weight) and preferably about 20% to 58% by weight of titanium (about 40% to 80% by volume of titanium carbide or 25% to 75% by weight), substantially the balance being formed of the steel matrix. 40

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 4 to liquid phase sintering under non-oxidizing conditions such as in a vacuum.

We find the foregoing method best adapted to produce the tool steel of the invention, particularly where the amount of primary carbide is of the order of about 30 50 to 60% by weight of the total composition, for the reason that the formation of large dendritic carbides are prevented which otherwise would occur if the elements V. Cb or Ta and carbon were added to a molten bath of iron such as is done in the addition of tungsten and chromium in the making of high speed steel. 55

It would be desirable to have a product with substantially large amounts of the primary carbide and yet be capable of being heat treated over a wide range of hardnesses without change in shape of the primary carbide grain. By "primary carbide" is meant that carbide which is substantially unaffected by normal steel heat treating practices. Of particular importance would be a highly carbidic product capable of being annealed to relatively low hardnesses for machining and other purposes. 65

We have found that tool steel compositions containing substantial amounts of CbC or TaC, e.g. as high as 45 weight percent of the carbide are capable of being annealed to as low as 30 to 35 Rockwell "C" and hardened to as high as 65 to 70 Rockwell "C." This decrease in annealed hardness, compared to 40 R_c obtained with cer2

tain of the titanium carbide tool steel compositions, is important as it greatly improves the machinability of the steel alloy and extends its use to the manufacture of complicated shapes where high hardness in the heat treated condition is an essential requirement.

It is the object of the present invention to provide a new tool steel composition containing substantial amounts of a primary carbide and yet which can be heat treated, e.g. annealed and hardened similar to conventional tool 10 steels.

Another object is to provide as an article of manufacture a tool steel bar stock containing substantially large amounts of carbon and a metal from the group consisting of V, Cb and Ta in the form of sharply cornered primary carbide grains distributed uniformly through a heat treatable steel matrix.

A still further object is to provide a carbidic steel which in the hardened condition has to a large extent the attributes of cemented carbides.

These and other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing wherein:

FIG. 1 depicts a representation of a photograph taken at 1000 diameters showing a microstructure comprising 25 primary grains of columbium carbide distributed through a pearlitic steel matrix;

FIG. 2 is similar to FIG. 1 but shows primary grains of tantalum carbide distributed through a pearlitic steel matrix; and

FIG. 3 depicts a representation of a photomicrograph taken at 1000 diameters showing primary columbium carbide grains distributed through a martensitic steel matrix.

In producing the carbidic tool steel of the invention, the primary carbide selected from the group consisting of VC, CbC and TaC may range from about 15% to 90% by weight (about 20% to 90% by volume), substantially the balance being the steel matrix. Preferably, the carbide composition may range from about 20% to 75% by weight (about 35% to 85% by volume) and the balance steel.

The steel employed in the invention as the ferrous matrix contains iron as the major alloying element, which generally comprises at least about 60% by weight of the matrix composition. Thus, in carrying out the invention, the steel may be an alloy steel, a carbon steel or may comprise pure iron to which carbon is added to form the required steel composition. The carbon present, exclusive of that in the primary carbide, should be sufficient to confer heat treatability to the ferrous matrix.

The expressions "ferrous matrix" or "steel matrix" as employed herein is one which crystallographically at ordinary temperatures is characterized in the annealed state by a substantially ferritic or body centered cubic structure and which at an elevated temperature below the melting point of the ferrous alloy is transferred to a substantially austenitic or face-centered cubic structure.

As illustrative of the useful compositions provided by the invention, the following examples are given:

Example 1

A heat treatable steel containing substantial amounts of CbC was formed by using the following ingredients:

Columbium carbide:

5	Percent Cb	About 8	36.0
	Percent Ta	About	2.0
	Percent Ti	About	0.6
	Percent total Carbon	About 1	0.72
	Percent free carbon	About	0.05
	Percent Fe	About	0.1
	Percent Si	About	0.03
	Percent Ca	About	0.03

5

This powder had an average particle size based on the Fisher sub-sieve sizer of about 8.71 microns,

The iron powder employed in producing the steel matrix comprised carbonyl iron powder containing the following:

Percent Fe	99.6 to 99.9
Percent C	0.01 to 0.06
Percent O	0.10 to 0.30
Percent N	0.00 to 0.05
	0.00 10 0.00

The average particle size was 20 microns.

In producing the steel composition, a mixture containing by weight 45% CbC, 54.72% Fe and 0.28% C was prepared with one gram of paraffin wax for each 100 grams of mix by ball milling the ingredients for 60 hours in a stainless steel ball mill half filled with stainless steel balls using hexane as a vehicle. After milling, the mixture was dried on a hot plate at 150° F. until all the hexane was driven off. The dry powder was pressed into briquettes or slugs at 15 tons per square inch. 20

The briquettes were then subjected to sintering by heating them to 1450° C. in 21/2 hours in vacuum, holding at temperature for three-quarters of an hour, followed by cooling to 1300° C. in 30 minutes and then from 1300 to room temperature by furnace cooling. The sintering 25 was carried out on a ceramic plate of previously fired "Magnorite" (a commercial MgO refractory). The sintered briquettes were then annealed by heating at 1575° F. for 2 hours followed by cooling from 1575° F. to 1300° F. at the rate of 20°/hour in hydrogen and then allowed 30 thereafter to furnace cool to room temperature. The as-sintered hardness of the steel was 39.1 Rc which dropped to 34.7 R_c after annealing. In the as-sintered condition, the steel had a modulus of rupture of about 226,000 p.s.i. 35

The annealed steel is then hardened by austenitizing at 950° C. for one quarter hour and quenched in oil or water. When oil quenched the hardness was 67.4 R_c, while water quenching gave a value of 69.0 R_c. The steel had a density of 7.81 grams per cubic centimeter. 40

The microstructure of the foregoing composition in the annealed condition is shown in FIG. 1 as comprising primary carbide grains of CbC distributed through a steel matrix containing pearlite.

FIG. 2 shows a microstructure of the steel of Example 1 in the hardened state as comprising primary carbide grains of CbC distributed through a steel matrix containing martensite.

Example 2

A heat treatable steel based on a primary carbide of 50 TaC was produced from the following ingredients:

Tantalum carbide:

Percent free carbon About 05.2. 55	Percent Ta and Cb	About 93.3 to 93.7.	
	Percent total carbon	Up to I (included above).	55
Percent SiO_2 (max.) 0.05.	Percent SiO ₂ (max.)	0.05.	
Percent Ti (max.) 0.2.			
Percent CaO (max.) 0.2.	Percent CaO (max.)	0.2.	

The particle size based on the Fisher sub-sizer was 4.18 microns. The iron used in forming the matrix was the same as that used in preparing the steel alloy of Example 1.

In producing the steel composition, a mixture containing by weight 56.2% TaC, 43.58% Fe and 0.22% C as carbon black was prepared in the same manner as described in Example 1. The same technique was used in pressing and sintering the composition. The as-sintered hardness was of the order of about 29.1 R_c and asannealed was slightly higher at 30.4 R_c. The oil quenched hardness using the same heat treatment desribed in Example 1 was about 65.0 while the water quenched hardness was 66.4 R_c. The transverse rupture in the as-sintered state was 207,000 p.s.i., the density being 10.46 grams/cc. 75 4

It will be noted that with as much as 56.2% by weight of TaC (about 45% by volume), even lower annealed hardnesses are obtainable than steels based on CbC accompanied by further improvement in machinability. The microstructure of the foregoing TaC steel composition is shown in FIG. 2 as comprising primary carbide grains of TaC distributed through a steel matrix containing pearlite.

As illustrative of other compositions provided by the invention, the following are given:

	3	4	5	6	7	8
Percent VC. Percent CbC	45	20		35	.70	
Percent Fe Percent Fe Percent C	54.72 0.28	79.6 0.4	25 74.63 0.37	64.68 0.32	29.85 0.15	80 19.9 0.1

It will be noted that assuming no carbon leaves the steel matrix the carbon content of the matrix will calculate to about 0.5%.

As has been stated, generally the composition will comprise about 15% to 90% by weight of a carbide selected from the group consisting of VC, CbC, and TaC with the balance being made up of a steel matrix. Preferably, the composition will comprise about 20 to 75% by weight of the primary carbide.

While steel alloys 3 to 8 above are substantially based on a matrix of 0.5 carbon steel, it is understood that a wide range of steel compositions may be employed. These include SAE 1010 steel, SAE 1020 steel, SAE 1030 steel, SAE 1040 steel, SAE 1080 steel, etc. Pure iron may be used since it combines with carbon to form a steel during the process of producing the ferrous alloy of the invention. Low, medium and high alloy steels may also be employed, including the following: 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, 4% 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.

One of the main advantages of the carbidic steel provided by the invention is that it is possible to produce a heat treatable product containing large amounts of a primary carbide in the form of isolated, sharply angled grains distributed through a steel matrix without form-ing massive carbide dendrites. This is achieved by utilizing powder metallurgy as described hereinabove. Another method that can be employed comprises coalescing primary carbide grains into a coherent porous body by briquetting followed by firing at an elevated temperature, generally from about 1000° C. to 1600° C. for about one half hour to six hours, preferably at a vacuum or a subatmospheric pressure not exceeding about 300 microns of mercury. As an alternative method, the coalescing may be achieved by simultaneously briquetting and firing at the indicated temperature range under non-oxidizing conditions for about ten minutes to about two hours. The first porous body is then prepared for the casting process by encasing it in a mold of refractory material substantially inert to the ferrous alloy, for example stabilized zirconia, with provisions made for the molten steel to enter the mold and contact the porous carbide structure. The mold of refractory material and the porous carbide structure supported therein is then placed

1

into a suitable casting furnace. Sufficient amount of steel to produce the casting is placed at the mold opening and the whole brought to a temperature of generally up to about 100° C. above the melting point of the steel so that the molten steel flows interstitially into the porous 5 body, completely filling it and providing excess feed for shrinkage cavities, pipes, etc. The casting is achieved in vacuum or at a sub-atmospheric pressure generally not exceeding about 300 microns of mercury. After the steel has interstitially filled all of the voids in the porous pri- 10 mary carbide structure, and then allowed to reach equilibrium with it, the carbide is modified by partial solution in the liquid phase, whereby it is disrupted into discrete and uniformly distributed grains. The interstitially cast ferrous alloy body is cooled in vacuum, is re- 15 moved from the furnace and is finally separated from the refractory mold. Thereafter the product is subjected to annealing and heat treatment.

We prefer to use the method of mixing the ingredients together, forming a shape thereof and sintering the shape 20 at an elevated temperature for a time sufficient to obtain substantially full densification. Broadly this method comprises mixing the appropriate amount of steel-forming ingredients with the appropriate amount of the primary carbide, using a small amount of wax to give sufficient 25 green strength to the resulting pressed compact, for example one gram of wax for each 100 grams of mixture. The mixture may be shaped a variety of ways. We prefer to press the mixture to a density at least 50% of true. density by pressing over the range of about 10 t.s.i. to 30 75 t.s.i., preferably 15 t.s.i. to 50 t.s.i., followed by sintering in a vacuum, preferably below 300 microns of mercury, preferably at a temperature above the melting point of the steel matrix, depending on the alloying ingredients present, ranging from about 1300° C. to 1575° C. for a 35 time sufficient for the primary carbide and the matrix to reach equilibrium and to obtain substantially complete densification, for example for about one minute to six hours.

When the liquid phase sintering is completed, the product is allowed to furnace cool to room temperature. If necessary, the as-sintered product is subject to any mechanical cleaning and then annealed at a temperature in the range of about 650° C. to 975° C. for about $\frac{1}{2}$ hour to 4 hours and then cooled at a rate of 10° C./hour to $\frac{45}{500}$ below 600° C., and thereafter furnace cooled.

The annealed structure will generally show a microstructure of primary carbides distributed substantially uniformly through a steel matrix comprising an austentitic decomposition product such as pearlite and ferrite, or, 50 depending on the heating cycle, spheroidite and ferrite. The hardening is achieved by heating to an austenitiz-

The hardening is achieved by heating to an austenitizing temperature, e.g. in the range of about 870° C. to 1315° C. for a time sufficient to convert substantially the matrix to a face centered cubic structure, e.g. one 55 minute to three hours, and then subsequently quenched by cooling in air, oil or water, depending upon the composition of the ferrous alloy, thus decomposing austenite to martensite. The austenite may also be transformed into bainite by isothermally quenching to a bainite formation temperature from the aforementioned austenitizing temperature.

The primary carbides of the group VC, CbC and TaC may include limited amounts by weight of other carbides, such as up to about 50% tungsten carbide, up to about 50% molybdenum carbide, up to about 10% chromium carbide, up to about 25% zirconium carbide, up to about 25% titanium carbide, and the like. The total amounts of other carbides will generally range up to 50% by weight of the primary carbides present. 70

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.

The invention provides a carbidic heat treatable 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 elments, tools or machine parts.

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 hardened, wear resistant, high carbon tool steel consisting essentially of about 15% to 90% by weight of primary carbide based on at least one carbide selected from the group consisting of VC, CbC and TaC distributed substantially uniformly through a ferrous matrix consisting essentially of the balance, said ferrous matrix containing iron as the major alloying constituent and containing combined carbon and consisting essentially of a microstructure selected from the group consisting of martensite and bainite.

2. A hardened, wear-resistant, high carbon tool steel consisting essentially of about 15% to 90% by weight of a primary carbide based on at least one carbide selected from the group consisting of VC, CbC and TaC distributed substantially uniformly through a ferrous matrix consisting essentially of the balance, said ferrous matrix containing iron as the major alloying constituent and containing combined carbon and consisting essentially of a microstructure of martensite.

3. A hardened, wear-resistant, high carbon tool steel consisting essentially of about 20% to 75% by weight of a primary carbide selected from the group consisting of VC, CbC and TaC distributed substantially uniformly as sharply cornered grains through a ferrous matrix consisting essentially of the balance, said ferrous matrix containing iron as the major alloying constituent and containing combined carbon and consisting essentially of a microstructure of martensite.

4. A hardened, wear-resistant, high carbon tool steel consisting essentially of about 15% to 90% by weight of a primary carbide selected from the group consisting of VC, CbC and TaC distributed substantially uniformly through a ferrous matrix consisting essentially of the balance, said ferrous matrix containing iron as the major alloying constituent and containing combined carbon and consisting essentially of a microstructure of bainite.

5. A hardened, wear-resistant, high carbon tool steel consisting essentially of about 20% to 75% by weight of a primary carbide selected from the group consisting of VC, CbC and TaC distributed substantially uniformly as sharply cornered grains through a ferrous matrix consisting essentially of the balance, said ferrous matrix containing iron as the major alloying constituent and containing combined carbon and consisting essentially of a microstructure of bainite.

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DAVID L. RECK, Primary Examiner.