United States Patent

Prill

[15] **3,653,982**

[45] **Apr. 4, 1972**

[54] **TEMPER RESISTANT CHROMIUM-CONTAINING TITANIUM CARBIDE TOOL STEEL**

[72] Inventor: **Arnold Louis Prill,** Suffern, N.Y.

[73] Assignee: **Chromalloy American Corporation,** West Nyack, N.Y.

[22] Filed: **Dec. 18, 1969**

[21] Appl. No.: **886,286**

[52] **U.S. Cl.** **148/31,** 29/182.5, 29/182.7, 29/182.8, 75/203, 75/204, 148/31, 148/126

[51] **Int. Cl.** **C22c 39/14,** B22f 3/24

[58] **Field of Search** 75/126, 128, 203, 204; 148/31, 148/142, 126; 129/182.5, 182.7, 182.8

[56] **References Cited**

UNITED STATES PATENTS

3,416,976	12/1968	Brill-Edwards	148/143 X
2,934,430	4/1960	Klaybor et al.	75/126 C
2,996,376	8/1961	Nehrenberg et al.	75/126 C
3,163,525	12/1964	Fletcher et al.	75/126 C
3,390,967	7/1968	Frehn	29/182.7
2,828,202	3/1958	Goetzel et al.	148/31 X
3,380,861	4/1968	Frehn	148/31 X

OTHER PUBLICATIONS

Metallurgia, August 1950, pages 111- 115

Primary Examiner—Charles N. Lovell
Attorney—Sandoe, Hopgood and Calimafde

[57] **ABSTRACT**

A heat treatable, temper resistant, chromium-containing, carbidic tool steel having a total carbon content of at least about 6 percent by weight is provided comprising about 25 to 75 percent by volume of primary carbide grains of essentially titanium carbide distributed through a heat treatable steel matrix containing by weight about 6 to 12% chromium, about 0.6 to 1.2% carbon, about 0.5 to 5% molybdenum, 0 to 5% tungsten, the total tungsten and molybdenum content not exceeding about 5%, 0 to 2% vanadium, 0 to 3% nickel, 0 to 5% cobalt, 0 to 1.5% silicon, 0 to 2% manganese and the balance essentially iron, the ratio by weight of chromium to carbon in the steel matrix ranging from about 7:1 to 25:1, the steel matrix surrounding the primary carbide grains being characterized by a microstructure comprising an austenitic decomposition product.

4 Claims, 4 Drawing Figures

Patented April 4, 1972 3,653,982

2 Sheets-Sheet 1

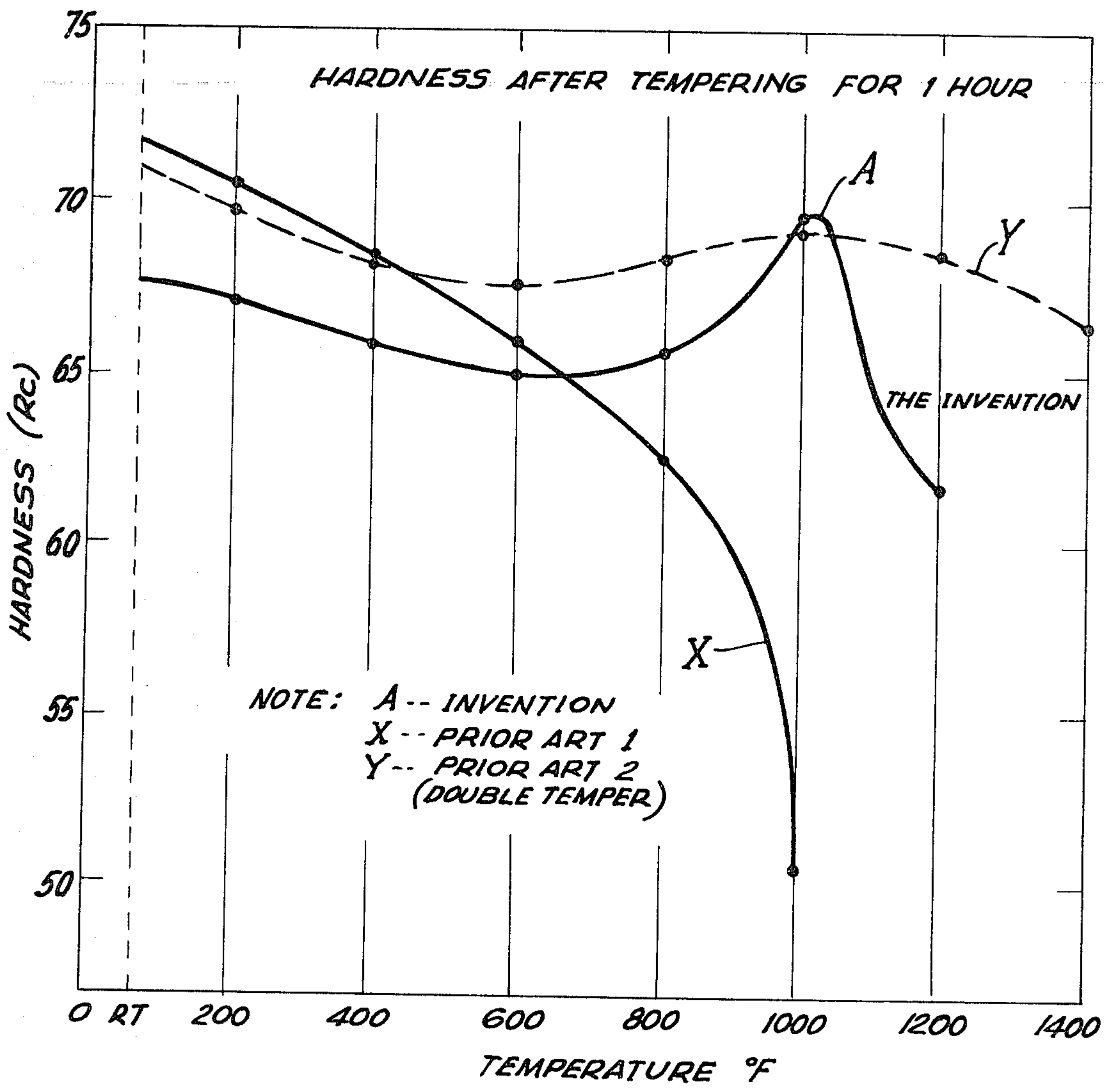

FIG. 1

INVENTOR.
ARNOLD LOUIS PRILL
BY
Sandoe, Hopgood & Calimafde
ATTORNEYS

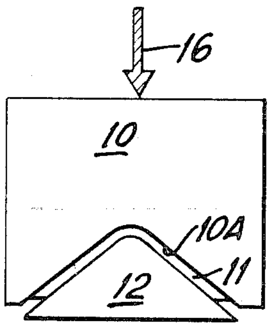

FIG. 3

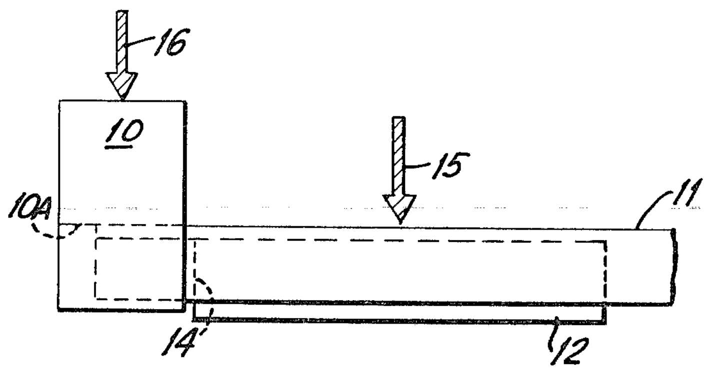

FIG. 2

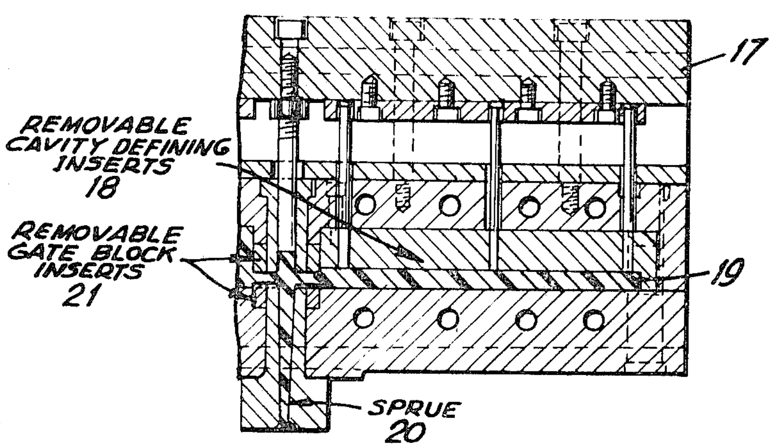

FIG. 4

INVENTOR.
ARNOLD LOUIS PRILL

BY

Sandoe, Hopgood & Calimafde
ATTORNEYS

TEMPER RESISTANT CHROMIUM-CONTAINING TITANIUM CARBIDE TOOL STEEL

This invention relates to a temper resistant, chromium-containing titanium carbide tool steel and bar stock made therefrom and, in particular, to a temper resistant tool steel composition having particular use in wear-resistant cold-heading dies, cold-blanking dies, impact-extrusion dies, heavy cold-forming dies and the like applications, including dies working at temperatures of up to about 1,000° F.

STATE OF THE ART

Titanium carbide tool steel compositions are disclosed in U.S. Pat. No. 2,828,202 (assigned to the same assignee) comprising broadly primary grains of essentially titanium carbide distributed through a heat treatable steel matrix. The steel is preferably produced using powder metallurgy methods which comprise broadly mixing powdered titanium carbide (primary carbide grains) with powdered steel-forming ingredients, forming a compact by pressing the mixture in a mold and then subjecting the compact to liquid phase sintering under non-oxidizing conditions, such as in a vacuum. The term "primary carbide" employed herein is meant to cover the titanium carbide grains per se added directly in making up the composition and which grains are substantially unaffected by heat treatment.

In producing a titanium carbide tool steel composition containing, for example, about 33 percent by weight of TiC (approximately 45 volume percent) and substantially the balance a steel matrix, about 500 grams of TiC (of about 5 to 7 microns in size) are mixed with 1,000 grams of steel-forming ingredients in a mill half filled with stainless steel balls. To the powder ingredients is added one gram of paraffin wax for each 100 grams of mix. The milling is conducted for about 40 hours, using hexane as a vehicle.

After completion of the milling, the mix is removed and dried and compacts of a desired shape pressed at about 15 t.s.i. and the compacts then subjected to liquid phase sintering in vacuum at a temperature of about 2,640° F. (1,450° C.) for about ½ hour at a vacuum corresponding to 20 microns of mercury or better. After completion of the sintering, the compacts are cooled and then annealed by heating to about 1,650° F. (900° C.) for 2 hours followed by cooling at a rate of about 60° F. (15° C.) per hour to about 212° F. (100° C.) and thereafter furnace cooled to room temperature to produce an annealed microstructure containing spheroidite. The annealed hardness is in the neighborhood of about 45 R_c and the high carbon tool steel is capable of being machined and/or ground into any desired tool shape or machine part prior to hardening.

The hardening treatment comprises heating the machined piece to an austenitizing temperature of about 1,750° F. for about one-quarter hour followed by quenching in oil or water to produce a hardness in the neighborhood of about 70 R_c.

A composition which has been found to enjoy particular commercial success is one containing about 45 percent by volume of titanium carbide distributed substantially uniformly through a steel matrix making up the balance, the steel containing by weight about 0.6 percent carbon, about 3 percent chromium, about 3 percent molybdenum and the balance substantially iron. However, a disadvantage of the foregoing composition is that, when used as a die material under conditions in which heat is generated due to friction, or where the metal being worked upon is preheated, over-tempering tended to occur, leading to softening of the die steel. When a die steel of the foregoing type softens to a hardness in the range of about 62 R_c to 65 R_c, it loses much of its resistance to wear, whereby the die must accordingly be replaced with a more dimensionally precise one.

One approach made to overcome the aforementioned difficulty was to provide a heat treatable carbidic tool steel capable of secondary hardening at elevated temperatures, e.g. 1,000° to 1,200° F., such that when the carbidic tool steel was

hardened at such temperatures, it resisted tempering or softening at lower temperatures when employed, for example, as a blanking die. One such material is disclosed in U.S. Pat. No. 3,053,706 (assigned to the same assignee) comprising primary carbide grains of a saturated solid solution of tungsten carbide and titanium carbide (WC-TiC) distributed through a steel matrix containing dissolved tungsten in equilibrium with the saturated solid solution of the primary carbide. While the foregoing composition is satisfactory in providing the necessary secondary hardening effect by the precipitation of secondary carbide to resist tempering at warm die-working temperatures, these compositions tended to be porous. For example, as pointed out in column 4 of the patent, lines 4 to 9, the composition was satisfactory in producing a sintered slug one-half inch thick. However, it was subsequently found that in producing large sizes for use in dies, for example, sizes of about 1½ inches square and larger, the finally sintered produce tended to be porous.

I have now found that the foregoing difficulties can be overcome by employing a titanium carbide tool steel composition in which the steel matrix is characterized by a relatively high chromium content and further characterized by a particular ratio of chromium to carbon in the steel matrix to assure a composition having a secondary hardening effect and which resists tempering at die-working temperatures.

OBJECTS OF THE INVENTION

It is thus the object of the invention to provide a temper resistant, chromium-containing carbidic tool steel composition having particular utility in cold and warm-working dies, and cold and blank forming dies in which heat is generated through friction and deformation.

Another object is to provide a temper resistant, chromium-containing, titanium carbide tool steel characterized by a high degree of resistance to wear, particularly when employed as a die under conditions in which heat is generated during working, where the die is preheated and/or where the workpiece is presented to the die at above ambient temperatures.

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

FIG. 1 depicts curves comparing the tempering hardness after 1 hour of heating at various tempering temperatures of the composition of the invention with compositions outside the invention;

FIGS. 2 and 3 illustrate the use of the composition as a die element in a die wiping operation; and

FIG. 4 illustrates the use of the composition as a gate insert in injection molds.

STATEMENT OF THE INVENTION

Stating it broadly, the invention provides a heat treatable, temper resistant, chromium-containing carbidic tool steel having a total carbon content of at least about 6 percent by weight and comprising about 25 to 75 percent by volume, and more preferably about 30 to 65 percent of primary carbide grains of essentially titanium carbide distributed through a heat treatable steel matrix making up the balance, the steel matrix containing by weight about 6 to 12 percent (e.g., about 8 to 12 percent) chromium, about 0.6 to 1.2 percent carbon (for example, about 0.7 to 1 percent carbon), about 0.5 to 5 percent molybdenum (e.g., about 2 to 5 percent), 0 to about 5 percent tungsten, the total tungsten and molybdenum content not exceeding about 5 percent, 0 to about 2 percent vanadium, 0 to about 3 percent nickel, 0 to about 5 percent cobalt, 0 to about 1.5 percent silicon, 0 to about 2 percent manganese and the balance essentially iron. It is desirable in obtaining the results of the invention that the ratio by weight of chromium to carbon in the steel matrix ranges from about 7:1 to 25:1 and, more advantageously, from about 9:1 to 18:1, the steel matrix being characterized by a microstructure comprising an austenitic decomposition produce, for example, any one of the structures pearlite (spheroidite), bainite and martensite.

DETAILS OF THE INVENTION

By working over the range of composition stated hereinabove, and particularly at the chromium to carbon ratios defined, highly wear resistant carbidic die steels are provided characterized by good secondary hardening response enabling the use of such carbidic steels at temperatures up to 1,000° F. at which excessive temperature softening normally occurs, while maintaining adequate wear resistance. In addition, the compositions within the range defined are characterized by minimum retained austenite. Preferably, by controlling the carbon content in the matrix within the range of about 0.7 to 1 percent by weight and, more advantageously, over 0.8 percent and nearer to 1 percent, gross austenite retention is substantially eliminated, although carbon contents within the range of 0.6 to 1.2 percent have been found adequate in achieving the broad objects of the invention.

In producing alloy compositions in accordance with the invention, the following procedure is employed:

Titanium carbide tool steel compositions with steel matrices of various chromium, molybdenum and carbon contents were produced in which the titanium carbide comprised about **50%** by volume, with the steel matrix making up the balance. Thus, 1,000 grams of titanium carbide of about 5 to 7 microns average size are mixed in a steel ball mill (stainless steel balls) with 1,500 grams of steel-forming ingredients comprising carbonyl iron powder of 20 microns average size and various amounts of chromium, molybdenum and carbon, with or without vanadium to provide the compositions given in Table 1 set forth hereinafter. In adding carbon to the matrix steel, any free carbon in the titanium carbide raw material is taken into account. To the mix is added one gram of paraffin wax for each 100 grams of mix. The milling is conducted for about 40 hours with the mill half full of steel balls of about one-half inch in diameter, using hexane as the vehicle.

After completion of the milling, the mix is removed and vacuum dried. A proportion of the mixed product is compressed in a die at about 15 tons per square inch to the desired shape. The shape is liquid phase sintered, that is, sintered above the melting point of the matrix composition, at a temperature of about 1,435° C. for one-half hour in vacuum, e.g., a vacuum corresponding to 20 microns of mercury or better. After completion of the sintering, the shape is cooled and then annealed by heating to 900° C. for 2 hours followed by cooling at a rate of about 15° C. per hour to about 100° C. to produce an annealed microstructure containing spheroidite, the annealed hardness of the compositions ranging from about 40 R_c to 50 R_c. Examples of compositions produced within the range provided by the invention are as follows:

TABLE 1

No.	% Cr	% Mo	% V	% C	Ratio Cr:C
1	10	3	1	1.0	10 :1
2	10	3	1	0.8	12.5:1
3	10	3	1	0.6	16.7:1
4	10	3	—	0.8	12.5:1
5	8	3	—	0.8	10 :1
6	6	3	—	0.8	7.5:1

Alloys which were found particularly useful from a commercial viewpoint are No. 2 and No. 4, the only difference residing in the vanadium content which is not essential. The presence of vanadium provides additional red hardness at temperatures slightly above 1,000° F. However, the amount of vanadium should preferably not exceed 2 percent as vanadium tends to decrease strength and toughness and, moreover, alloys containing vanadium are more difficult to sinter. With regard to tool steel compositions No. 2 and No. 4, the following comparison is made:

TABLE 2

No.	2000°F 30 min. oil quench	1000°F—1 hr. air quench (twice)	TRS (ksi) *	Impact (inch-lbs.)
2	71 R_c	69 R_c	225–300	2–3
4	70 R_c	68 R_c	250–350	4–7

Note:---* Transverse rupture × 10^6 lbs. per square inch

As will be noted, the No. 4 composition without vanadium has better impact strength (tougher) than the No. 2 composition containing vanadium.

The response of a composition of the invention similar to composition No. 4 to the secondary hardening effect is compared to two prior art compositions X (Prior Art 1) and Y (Prior Art 2) in the accompanying drawing in which it will be noted that the composition of the invention peaks to a relatively high hardness at "A" of about 69 to 70 R_c when subjected to secondary hardening for 1 hour at 1,000° F., the room temperature hardness prior to tempering being about 67 to 68 R_c. Having once been secondary hardened to produce secondary carbides in the matrix, the alloy steel of the invention will resist softening at working temperatures below 1,000° F.

The titanium carbide steel of alloy "X," a commercially successful steel composition having a matrix containing 3 percent Cr, 3 percent Mo, 0.6 percent carbon and the balance essentially iron showed no secondary hardening effect whatever but, on the contrary, shows a substantial drop in hardness at temering temperatures above 600° F. The carbide tool steel "Y," on the other hand, is a composition comprising approximately **50%** by volume of a saturated solid solution of primary carbide grains of WC-TiC (35 percent WC–15 percent TiC) distributed through a steel matrix making up the balance, the steel matrix being a high speed steel type comprising about 18 percent W, 5 percent Cr, 0.8 percent C and the balance essentially iron. As will be noted from the curve "Y" of the drawing, this entirely different composition shows secondary hardening but has the disadvantage of being difficult to make in large sections because of which the product produced tends to be porous which adversely affects its toughness.

The titanium carbide tool steel composition is similar in its ease of manufacture to composition "X," except for its surprisingly good response to secondary hardening. Like "X," it can be produced in large sizes and, therefore, has particular applicability to the making of dies for the blanking, forming and trimming of metals, particularly where die temperature becomes a factor due to working friction, or as die inserts for gates in injection molds, where heat of the plastic being molded tends to adversely affect the metal employed at the gate-forming section of the mold.

The importance of the composition ranges defined hereinabove in achieving the results of the invention will be apparent from secondary hardening test results obtained on compositions outside the invention containing about 50 percent by volume of the steel matrix. When the steel matrix contained 5 percent Cr and 1.5 percent carbon, the annealed hardness of the total composition was 43.6 R_c and the quenched hardness (2,000° F. - oil) was 67.5 R_c, while the hardness after tempering at 1,000° F. for 1 hour dropped to 64.9, thus indicating no secondary hardening response. A composition outside the invention in which the steel matrix contained 5 percent Cr, 1.4 percent Mo, 1 percent V and 0.5 percent carbon, the annealed hardness was 46.5 R_c, the quenched hardness (2,000° F. - oil) was 71.2 R_c, while double tempering of one hour each at 1,000° F. exhibited hardnesses of 65.8 and 63.8 R_c, respectively, again showing no secondary hardening response. A similar result was obtained with the last mentioned composition, except that the composition was quenched in oil from 1,875° F. to provide a hardness of 70.3 R_c. Double tempering at 1,000° F., that is, tempering of 1 hour each, resulted in hardnesses of 64.6 and 61.4 R_c, respectively, again showing no secondary hardening response.

As stated hereinbefore, the chromium-containing, titanium carbide tool steel is particularly useful as a temper resistant die element, whether used for contacting metals during metal working (e.g., metal forming, deep drawing, blanking, etc.) or metal trimming operations, or for contacting hot plastic in injection molding operations. In metal contacting operations, the composition of the invention has shown particular use in die wiping applications where considerable heat is generated by friction on the die.

An example of such an operation is shown in FIGS. **2** and **3**, wherein die element **10** is shown made of the composition of the invention comprising about 45 percent by volume of titanium carbide and about 55 percent by volume of the chromium-containing steel matrix, the steel containing by weight about 10 percent chromium, about 3 percent molybdenum, about 0.8 to 1 percent carbon and the balance essentially iron. The die element **10** is employed in wiping down or forming the end of a stainless steel angle trim **11** employed as trimming on automobile bodies, the trimming being supported or nested on a triangularly shaped anvil or die block **12** as shown by the end view of FIG. **3**. The angle **11** overhangs an end face **14** of the anvil (FIG. **2**) and the grooved wiping die **10** is brought down upon the overhanging portion so that its groove portion **10A** which conforms in contour to the cross-sectional profile of the angle deforms the overhang of the angle to produce a flat end face on the angle trim. The angle **11** is held fast to the anvil by a pressure pad (not shown) which is represented by an arrow **15**, and the die element **10** is carried by a force-applying shaft (not shown), the application of force being represented by arrow **16**.

In the foregoing operation, there is considerable crowding of metal at the end face of the angle, whereupon heat of friction is developed which, under normal conditions, tends to temper other die steels and leads to metal pick-up on the die. As will be noted, die element **10** is spaced a short distance from end face **14** of the anvil to allow sufficient room for metal deformation as the die moves downward to effect complete wiping and hence deformation of the overhang to close off the end of the angle trim. Excess metal resulting from the deformation is later trimmed off.

A die, similar to FIGS. **2** and **3**, which was subjected to secondary hardening to provide a hardness of 68 R_c, deformed 1,276 pieces of cold rolled steel angle with no sign of metal pick-up on the die face. On the other hand, a die steel designated as SAE-W110 showed metal pick-up after only 55 pieces; a die steel designated as SAE-D2 showed metal pick-up after 25 pieces; while a die steel referred to as SAE-D7 showed metal pick-up after 208 pieces. In other words, the die of the invention resisted tempering during the deforming operation, retained its hardness and avoided metal pick-up while deforming 1,276 pieces of cold rolled steel angle.

The composition of the invention has particular use as insert material at the gate portion of plastic injection molds. A portion of an injection mold assembly **17** is shown in FIG. **4**, the main portion of the mold comprising inserts **18** in the form of removable cavity-defining inserts into which cavity **19** plastic is injected via sprue **20**, the plastic then flowing through gates defined by removable gate block inserts **21**. The plastic is generally injected at elevated temperatures and the gate block inserts should be made of temper resistant material and be resistant to erosion. For example, a plastic blended with asbestos which is injected at a temperature of about 500° to 600° F. can erode the gate insert material, unless it is able to retain its hardness under the foregoing temperature. The composition of the invention finds use in such applications.

Thus, as a preferred embodiment, the invention provides a temper resistant die element for use in environments where there is a tendency for the die to heat up due to frictional heat in the forming, blanking or trimming of metals or where the material contacting the die has sensible heat which is absorbed by the die element during operation.

As stated hereinbefore, other elements may be present in the steel matrix. For example, up to 5 percent by weight of cobalt and/or up to 2 percent vanadium may be added to the matrix to promote red hardness, and up to about 1.5 percent silicon or 2 percent manganese and/or up to about 3 percent nickel may be added to impart added toughness. Tungsten, which behaves similarly to molybdenum, may be added up to about 5 percent, the total tungsten and molybdenum content not exceeding about 5 percent.

The titanium carbide tool steel has advantages other than heat treatment. For example, final grinding on the tool steel composition "X," unless carefully done, can produce over-tempering of the working surfaces of the die tool being ground. This may lead to premature failure of the tool. However, tests have indicated that the composition of the invention is essentially insensitive or greatly less sensitive to final grinding damage, particularly when it is plunge ground. Moreover, vacuum heat treatment of fairly heavy sections of the novel composition (e.g., 2 inches by 2 inches cross section) is possible, provided the usual precautions are taken to avoid decarburization.

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. As an article of manufacture, a hardened wear resistant element comprising a hardened chromium-containing titanium carbide tool steel containing about 25 to 75 percent by volume of primary carbide grains of essentially titanium carbide distributed through a hardened steel matrix consisting essentially by weight of about 8 to 12 percent chromium, about 0.6 to 1.2 percent carbon, about 0.5 to 5 percent molybdenum, 0 to 5 percent tungsten, the total molybdenum and tungsten content not exceeding about 5 percent, 0 to about 2 percent vanadium, 0 to about 3 percent nickel, 0 to about 5 percent cobalt, 0 to about 1.5 percent silicon, 0 to about 2 percent manganese and the balance essentially iron, the ratio by weight of chromium to carbon in the steel matrix ranging from over 7:1 to 25:1, the steel matrix surrounding the primary carbide grains being characterized by a microstructure of essentially martensite and being further characterized such that when the hardened tool steel is tempered at 1,000° F., it exhibits improved response to secondary hardening.

2. The wear resistant element of claim **1**, wherein the carbon content of the composition of the wear resistant element ranges from about 0.7 to 1 percent, and wherein the chromium to carbon ratio in the steel matrix ranges from about 9:1 to 18:1.

3. The wear resistant element of claim **2**, wherein the primary titanium carbide grains of the composition range in amount from about 30 to 65 percent by volume of the total composition.

4. The wear resistant element of claim **2**, wherein the molybdenum content of the steel matrix ranges from about 2 to 5 percent by weight.

* * * * *