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[54] **WEAR RESISTANT ALLOY STEELS CONTAINING Cb AND ONE OF Ti, Hf OR Zr.**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 142,229, May 11, 1971, abandoned.

[52] **U.S. Cl.** .... **75/123 H;** 75/123 J; 75/123 M; 75/123 N; 75/124; 75/125; 75/126 A; 75/126 B; 75/126 C; 75/126 D; 75/126 E; 75/126 F; 75/126 H; 75/128 G; 75/128 Z; 75/128 T

[51] **Int. Cl.** **C22c 39/54**

[58] **Field of Search** .... 75/128 G, 128 T, 128 V, 75/128 Z, 128 A, 128 B, 128 C, 128 D, 128 N, 128 W, 128 P, 124, 125, 126 A, 126 B, 126 C, 126 D, 126 E, 126 F, 126 H, 126 J, 126 Q, 126 L, 126 M, 123 J, 123 M, 123 H

[56] **References Cited**

UNITED STATES PATENTS

2,140,237	12/1938	Leitner	75/128 G
2,513,471	7/1950	Franks	75/128 G
2,751,291	6/1956	Carter	75/128 G
2,801,916	8/1957	Harris	75/128 T
3,165,400	6/1961	Roy	75/128 G
3,250,612	5/1966	Roy	75/126 I
3,649,252	3/1972	Kirkby	75/128 G
3,795,509	1/1971	Mimino	75/128 G

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[57] **ABSTRACT**

Alloy steels are provided with improved resistance to abrasive wear, without significantly detracting from other desired properties, by the addition of columbium and carbon to form CbC and at least one of the elements titanium, zirconium and hafnium so that an effective amount of the columbium carbide formed is idiomorphic. Specific examples are given of A.I.S.I. type H12 and type A6, and a high speed steel modified in accordance with the invention.

28 Claims, 5 Drawing Figures

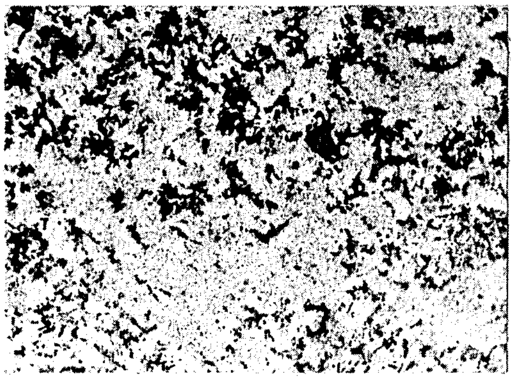

FIG.1

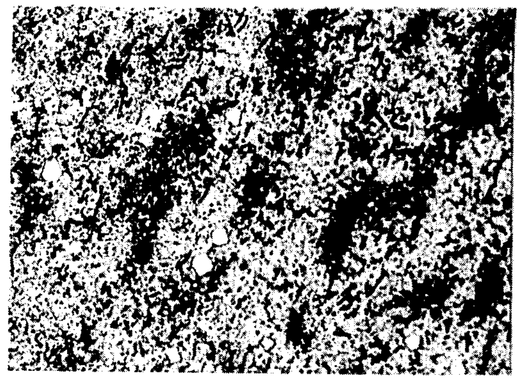

FIG.2

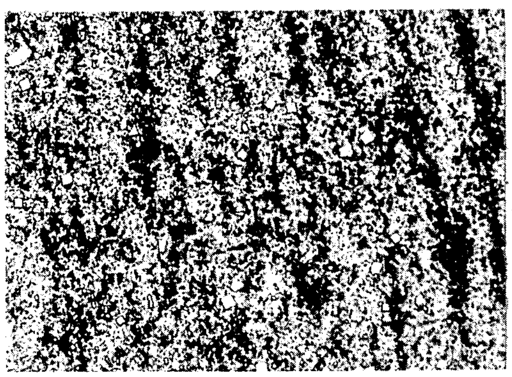

FIG.3

FIG. 4

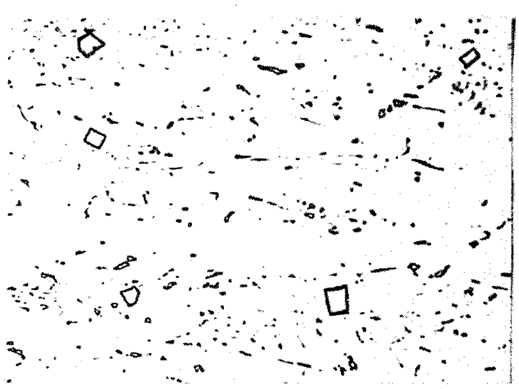

FIG.5

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WEAR RESISTANT ALLOY STEELS CONTAINING CB AND ONE OF TI, HF OR ZR

This application is a continuation-in-part of our copending application filed May 11, 1971, Ser. No. 142,229, and now abandoned.

This invention relates to alloy steel containing at least about 65% iron and, more particularly, to such steel containing columbium carbide having improved resistance to abrasive wear.

In Fetzer and Post U.S. Pat. No. 2,450,888, granted Oct. 12, 1948 and assigned to the assignee of the present application, there is disclosed alloy steel containing columbium carbide characterized by improved abrasive wear resistance. In accordance with the invention of that patent, the alloy steels (generally understood to include a wide variety of steels such as hot-work steels, quench-hardenable steels, shock-resistant steels and others) are improved as to resistance to abrasive wear by the presence of columbium carbide therein. U.S. Pat. No. 2,450,888 teaches utilizing varying amounts of columbium carbide depending upon the amount of carbon present in the alloy matrix uncombined as columbium carbide; the amount of columbium carbide is to range from about 1.5% to 2.0% for a matrix carbon content of about 1.50%, and as the amount of matrix carbon present decreases to about 0.30%, the range of the amount of columbium carbide to be incorporated in the steel increases to from 3.6% to 4.5%. However, for reasons which were not fully understood, consistent results could not always be obtained and, particularly in the case of when the larger amounts of columbium carbide were used, the alloy tended to become objectionably brittle.

A discovery we have made which has inspired the present invention is that of two possible forms of columbium carbide that can be formed when columbium and carbon in the proper proportions are incorporated in the steel, only idiomorphic columbium carbide seems to improve resistance to abrasive wear. And, also in accordance with the present invention, it has been found that the presence of a small but critical amount of at least one of the elements titanium, zirconium or hafnium serves to insure that at least an effective amount of the idiomorphic type of columbium carbide is formed during solidification of the steel.

It is therefore a principal object of this invention to provide alloy steel having consistently improved resistance to abrasive wear without objectionably affecting other desired properties of such steel.

A more specific object is to provide such steel having improved resistance to abrasive wear due to idiomorphic columbium carbide distributed throughout the steel and formed in situ in the presence of carefully controlled additions of at least one of the elements titanium, zirconium or hafnium.

The foregoing as well as additional objects and advantages of this invention will be apparent from the following detailed description of preferred embodiments thereof and the accompanying drawing in which

FIGS. 1–3 are micrographs showing A.I.S.I. type H12 alloy at 250 magnification modified by the addition of carbon and columbium and with 0.01%, 0.05% and 0.09% titanium respectively; and

FIGS. 4 and 5 are micrographs showing A.I.S.I. type A6 at 250 magnification similarly modified with carbon and columbium, and with residual titanium and with 0.05% titanium, respectively.

The present invention stems from the discovery that columbium carbide serves to enhance the abrasive wear resistance of steel only when it is present in the steel in the idiomorphic form. Generally stated, in accordance with the present invention effective amounts of columbium and carbon together with at least one element selected from the group of 0.04–0.3% titanium, 0.05–0.5% zirconium, and 0.03–0.5% hafnium are added to plain carbon steels and alloy steels so that effective amounts of idiomorphic columbium carbide are formed in the steel as it solidifies from the molten state to provide improved resistance to abrasive wear. The preferred range for titanium is 0.05% to 0.15%, for zirconium 0.05% to 0.2%, and for hafnium 0.1% to 0.25%. Here and elsewhere throughout this application, proportions in percent are intended as weight percent.

By plain carbon steels is meant those steels whose properties are determined primarily by the carbon content thereof which may range from about 0.1% to 2%. Various elements may be present incidental to the steelmaking process, usually small amounts of manganese up to about 0.4%, aluminum when used as a deoxidizer usually less than about 0.25%, and silicon less than about 0.4%. Certain plain carbon steels may contain as much as 1.65% manganese though not considered an alloy steel. Other elements may be present in residual or incidental amounts, as for example, up to about 0.04% phosphorus, up to about 0.05% sulfur, up to about 0.2% chromium, up to about 0.25% nickel, up to about 0.1% molybdenum, up to about 0.15% tungsten, up to about 0.1% vanadium, up to about 0.15% cobalt, and up to about 0.3% copper.

When additional amounts of those elements, other than carbon, are included in steel so as to affect its properties, then the steel is termed an alloy steel which, in addition to a minimum of about 65% iron, 0.07% to 2.5% carbon and the nominal amounts of manganese and silicon present in such steels, may contain up to about 2.5% manganese, up to about 2.5% silicon, and aluminum up to about 1.5%, and, depending upon the properties desired, one or more of up to about 19% chromium, up to about 5% nickel, up to about 10.5% molybdenum, up to about 20% tungsten, up to about 6% vanadium, up to about 15% cobalt, up to about 0.1% nitrogen, and up to about 4% copper.

Columbium is an essential constituent of the present composition and is present from about 1.1% to less than 3%. Above about 3% columbium and with the corresponding amount of carbon, the results tend to be inconsistent while above about 3.25% embrittlement as a result of carbide segregation may result. Therefore, it is preferred to use no more than about 2.99% and better yet no more than about 2.85% columbium. In addition to columbium, there is added carbon in the approximate stoichiometric proportions required to form columbium carbide (CbC) in the steel. That amount of carbon is in addition to the carbon typically present in the particular steel, but the total is no more than the maximum amounts previously stated of about 2.5% for wrought steels and 3% for castings. When free machining properties are desired, the usual free machining additives may be included such as, for example, one or more of sulfur, selenium, lead, or tellurium, up to a total of 0.5%. Normally sulfur and also phosphorus are present in no more than incidental amounts, that is less than about 0.025% although, in certain steels, as much as about 0.25% phosphorus may be included.

No special procedures or precautions need be observed in producing the steels of the present invention characterized by improved resistance to abrasive wear. It is sufficient that the steel be made and processed as would be customary for the same composition absent the columbium plus carbon addition and the addition of titanium, zirconium or hafnium but, as is well known, deoxidation should be completed before such elements as Ti, Zr or Hf are added. As was noted, columbium and carbon are added substantially in stoichiometric proportions with the amount of carbon thus added being in addition to that usually present in the steel. In practice, to avoid increasing the matrix carbon, that is the amount of carbon not tied up by the columbium, it is best to maintain the proportion of columbium somewhat in excess of the amount required to combine stoichiometrically with the additional carbon. In practice, about 0.12% carbon for each 1% of columbium seems to give best results, but as little as 0.10% carbon for each 1% of columbium can also be used. In other words, the ratio of the amount of columbium to the amount of carbon added to a given steel can vary from about 7.75 to 1 to about 10. to 1.

From the foregoing, it is apparent that the minimum amount of carbon present in the steel of this invention is about 0.07% plus the amount of carbon required to combine with 1.1% columbium, the minimum of columbium. Using the preferred proportions of 0.12% carbon for each 1% of columbium, the minimum carbon content is seen to be about 0.2%. Since the amount of columbium added to the steel does not exceed about 2.99%, and preferably no more than about 2.85%, the compositions are not embrittled.

As a more specific illustration of the present invention, four experimental vacuum induction heats (about 17 pounds each) were prepared and cast as split heats into 2 ingots each weighing about 7.5 pounds and having the following analysis:

TABLE I

	Example No.							
	1	2	3	4	5	6	7	8
C	.79	—	80	—	.78	—	.80	—
Mn	.51	.47	.50	.47	.49	.46	.49	.46
Si	1.00	—	.98	—	.99	—	.95	—
P	.003	—	.003	—	.003	—	.002	—
S	.006	—	.003	—	.004	—	.002	—
Cr	4.98	4.96	4.98	4.97	4.97	4.96	4.96	4.95
Ni	.03	—	.02	—	.01	—	.02	—
Mo	1.51	1.50	1.51	1.49	1.52	1.55	1.52	1.50
W	1.41	1.35	1.44	1.43	1.42	1.42	1.45	1.39
V	.25	.25	.26	.26	.26	.26	.26	.26
Cb	2.56	2.52	2.55	2.57	2.56	2.55	2.54	2.49
Al*	.02	.02	.02	.03	.02	.02	.01	.01
Ti	.01	.03	.05	.09	.17	.28	.35	.40

*About 0.07% aluminum was added to ensure complete deoxidation before Ti was added to the melt.

In each of Examples 1–8, the balance was iron and incidental impurities. The dashes in the even-numbered examples indicate that it was not considered necessary to make a second analysis for C, Si, P, S and Ni in the second half of each of the split heats.

Each of the ingots of Examples 1–8 was 2¼ inch sq. They were each forged from a furnace temperature of 2150°F to 1 inch square bars and then buried in vermiculite and cooled. The forged bars were packed an-

nealed at 1600°F for 4 hours and then cooled 20°F per hour to 1100°F followed by cooling in air. The hardness of the bars in this condition was measured and found to be between Rockwell B94–95.

Cylindrical wear test specimens having a 0.875 in. diameter and a 1.5 in. length were prepared and heat treated to the hardness indicated in Table II. The opposite-end surfaces of each specimen were ground parallel. In carrying out these and the other abrasive wear tests referred to herein, unless otherwise indicated, each specimen was mounted in the test apparatus so as to be held fixed in a holder against the surface of an abrasive paper under a constant load of 5 pounds, the paper being mounted on a circular disc. While the abrasive paper is rotated, the holder carrying the specimen is traversed back and forth across the surface of the paper so that substantially the entire available surface of the paper is utilized. In order to help standardize the results, each specimen was subjected to an initial break-in period of at least 1,000 revolutions, whereupon the specimen was weighed, remounted in the holder and brought up to a fresh abrasive paper. Throughout these procedures, the abrasive disc was rotated at 24 revolutions per minute, and the abrasive paper utilized was a carefully calibrated 120 grit alumina paper. The test itself consisted of 250 revolutions of the paper against the end of the specimen under the conditions stated. Following this, the specimen was reweighed to determine the weight loss. The average of what was considered to be a sufficient number of tests on one or more samples was determined and is reported in Table II.

The specimens of Exs. 1 and 2 were heat treated by heating to 1850°F, quenching in oil followed by heating at 1125°F for 2 hours, cooling in air, and then heating for 2 hours at 1100°F and cooling in air. The specimens of Exs. 3–5, 7 and 8 were also quenched in oil from 1850°F, but were subjected to two 2-hour periods at 1100°F each followed by cooling in air. In the case of Ex. 6 after quenching in oil from 1850°F, three 2-hour periods at 1100°F each followed by cooling in air were used.

TABLE II

Ex. No.	% Ti	Hardness (R_c)	Average Wt. Loss, Grams	No. of Tests
1	.01	47.5	.457	10

TABLE II-Continued

Ex. No.	% Ti	Hardness (R_c)	Average Wt. Loss, Grams	No. of Tests
2	.03	47.5	.442	21
3	.05	47.5	.207	20
4	.09	47.5	.231	15
5	.17	47.0	.373	10
6	.28	46.5	.356	7
7	.35	47.0	.328	10
8	.40	46.5	.327	10

Except for the added carbon and columbium, Ex. 1 corresponds to the well-known A.I.S.I. type H12 alloy, a hot work tool and die steel. The nominal carbon content of type H12 is usually 0.35%. Thus, the carbon content of about 0.8% in Exs. 1–8 is seen to be about 0.15% more than the 0.65% preferable for the columbium content of approximately 2.5% present in these examples. For the amount of columbium, the stoichiometric proportion of carbon to be added to react with the columbium would be close to 0.3%. However, except for the increase in the hardness level, the added carbon had no significant effect as is apparent from the deviation in hardness of only plus or minus 0.5 R_c, and the abrasive wear resistance test data of the various examples given in Table II can be directly compared. The data in Table II clearly demonstrates the sharp criticallity of a small amount of titanium. With 0.01% and 0.03% titanium, there was no apparent effect on the abrasive wear resistance. FIG. 1 is a micrograph prepared from a specimen of Ex. 1. Except for the columbium carbides in the form of more or less rod-shaped or lamellar allotriomorphic crystals, the microstructure is believed to be typical of and not significantly different from what would be expected of such a composition after forging. While the microstructure of Ex. 2 with 0.03% titanium is not illustrated in the drawing, it does not differ significantly from that shown in FIG. 1 and contained only a few widely scattered idiomorphic columbium carbides. With 0.05% titanium, Ex. 3 shows a sharp average reduction in weight loss down to 0.207 grams as an average of 20 tests and with the same hardness, R_c47.5 as Exs. 1 and 2. Numerous tests and studies have demonstrated that the small but effective amount of titanium, about 0.04% preferably 0.05%, radically affects the morphology of the columbium carbide crystals in a way which is not fully understood. But the apparent effect is the formation of the angular, idiomorphic columbium carbides, several of which are visible near the center of FIG. 2. An even larger number of idiomorphic columbium carbides is visible in the micrograph of FIG. 3. At about 0.2% titanium and above all the columbium carbide present in the compositions tested appears to be in the form of idiomorphic carbides. It has also been found that in each of the Exs. 2–8 the number of idiomorphic columbium carbides increased as the titanium content was increased with the individual carbides decreasing in size and becoming more uniformly distributed. It is therefore hypothesized that the titanium was precipitated probably as titanium carbide and caused nucleation of the columbium carbides early enough in the solidification of the melt so that, being free to grow unrestrained, the idiomorphic crystals were formed.

From the data in Table II, it is apparent that in each of the Exs. 3–8 there was a substantial improvement in resistance to abrasive wear as measured by the test described. However, as will be seen, with 0.35% and 0.40% titanium respectively, Exs. 7 and 8 showed embrittlement due to carbide segregation. For this reason, titanium is limited to about 0.3% and preferably to about 0.15%.

It may be well to note that the idomorphic columbium carbides are generally cubic in form; much of the differences in the idiomorphic columbium carbides apparent in the drawing are primarily the result of variations in orientation of the carbides with respect to the plane of the micrographs.

Standard room temperature tensile test specimens were prepared having a gauge diameter of 0.252 in. and a gauge length 4 times the gauge diameter. They were heat treated as was previously described for each example except that the specimens of Ex. 6 received the same heat treatment as Exs. 3–5, 7 and 8. The results of these tests together with the hardness of the specimen as tested are set forth in Table III as the average of two tests except for Exs. 1, 7 and 8. In the case of Ex. 1, only one test specimen was available. In the case of Exs. 7 and 8, two specimens were tested, but one specimen of each pair failed with low ductility, less than 4% elongation and less than 11% reduction in area because of columbium carbide segregation. In Table III, the 0.2% yield strength (0.2% YS) and the ultimate tensile strength (UTS) are given in units of 1,000 pounds per square inch (ksi) as indicated. Percent elongation (% El) and percent reduction in area (% Ra) are also given.

TABLE III

Ex. No.	% Ti	Hardness (R_c)	.2% YS (ksi)	UTS (ksi)	% El (4D)	% Ra
1	.01	48.0	201	245	8.2	19
2	.03	47.5	192	234	7.8	23
3	.05	47.5	204	238	7.9	21
4	.09	48.0	199	238	8.1	22
5	.17	47.5	199	235	7.3	22
6	.28	48.5	204	238	6.8	20
7	.35	47.0	—	239	8.4	26
8	.40	46.5	—	228	7.6	24

These results indicate that the tensile properties are not significantly affected by the presence of idiomorphic carbides and with columbium at the level of about 2.5% tested, tensile ductility is improved as compared to the tensile ductility of such a composition but with as much as 3.5% columbium. It should also be observed that with no more than about 0.3% titanium, the tensile properties were adequate for most, if not all, customary uses A.I.S.I. type H12.

Thus, one preferred composition of the present invention consists essentially of of about 0.45% to 0.9% carbon (the total of matrix carbon and that in the form of carbides), a maximum of 0.6% manganese, about 0.75% to 1.25% silicon, about 4% to 5.5% chromium, about 1% to 1.7% molybdenum, about 1% to 1.7% tungsten, about 0.2% to 0.6% vanadium, about 2% to 2.75% columbium, at least one element selected from the group of 0.04% to 0.15%, preferably 0.05% to 0.15%, titanium, 0.05% to 0.2% zirconium, and 0.03% to 0.5%, preferably 0.1% to 0.2%, hafnium, and the balance essentially iron and incidental impurities. This will be recognized as A.I.S.I. type H12 modified in accordance with the present invention. This composition, like H12, is suited for use as a hot work die steel and because of its substantially greater resistance to abrasive wear is better suited for such uses as well as others. It is particularly well suited for use in making crimping tools, hot-work extrusion dies, and hot-work forging dies.

As a further illustration of this invention, two 5-pound experimental air induction heats were melted to the analysis indicated in Table IV, the balance in each case being iron and incidental impurities. To ensure complete deoxidation before the addition of the titanium, 0.10% aluminum was added to each heat.

TABLE IV

Ex. No.	C	Mn	Si	Cr	Mo	Cb	Ti
9	1.01	1.97	.46	1.06	1.27	2.58	.05
10	1.00	2.00	.42	1.05	1.26	2.65	≤ .01

Example 9 will be recognized as A.I.S.I. type A6 alloy modified in accordance with the present invention.

The heats were cast as 1⅞ in. sq. ingots which were forged to 1⅛ in. sq. billets from a furnace temperature of 2050°F and then buried in vermiculite to cool. The billets were pack annealed at 1400°F for 4 hours, cooled 20°F per hour to 1000°F and then air cooled. The annealed hardnesses obtained were R_b98.5–99.5. Wear test specimens of the type described in connection with Exs. 1–8 were prepared from the billets of Exs. 9 and 10, and the specimens were then heated at 1550°F for 3 minutes, air cooled and then tempered at 350°F for 1 hour. Because of the hardness of these specimens, the abrasive wear test was modified to ensure that the abrasive paper was not worn out prematurely and would continue to abrade each specimen throughout each test. The modified test consisted of determining the weight loss in grams after 500 revolutions with a fresh abrasive paper being used after each 100 revolutions. The other conditions of the test were the same as those previously noted. The average weight loss from 3 tests, the titanium content and the hardness of the specimens are given in Table V.

TABLE V

Ex. No.	% Ti	Hardness (R_c)	Average Weight loss, Grams
9	.05	61.0	.154
10	≤.01	61.0	.376

Example 9 containing 0.05% titanium in accordance with the present invention lost an average of only 0.154 grams as compared to an average weight loss for Ex. 10 of 0.376 grams from essentially the same analysis as Ex. 9 but with only residual titanium. Referring to FIGS. 4 and 5, the very great difference in the form of the columbium carbides can be clearly seen. The few small idiomorphic carbides that can be seen in the micrograph of FIG. 4 prepared from Ex. 10 reflect the fact that there was not an effective amount of titanium present. In the case of the micrograph of Ex. 9 shown in FIG. 5, the more numerous and larger idiomorphic carbides are clearly seen which provide the improved resistance to abrasive wear. As in the case of Exs. 1–8, the sharp difference between Exs. 9 and 10 clearly demonstrates the criticallity of the small but effective

amount of titanium which, with the columbium and carbon, provides a synergistic effect.

Thus, another preferred composition of the present invention consists essentially of about 0.4% to 1.2% carbon (matrix carbon plus carbides), about 0.5% to 2.5% manganese, about 0.5% to 1.5% chromium, about 0.25% to 1.75% molybdenum, about 1.1% to 2.99%, preferably 2.5% to 2.85%, columbium, at least one element selected from the group of 0.04% to 0.3% preferably 0.05% to 0.15% titanium, 0.05% to 0.5% preferably 0.05% to 0.2% zirconium, and 0.03% to 0.5% preferably 0.1% to 0.25% hafnium, and the balance essentially iron and incidental impurities.

Referring once again to FIGS. 4 and 5, it is apparent that, even in the absence of a titanium addition, some idiomorphic columbium carbides too small to be effective are formed. As the columbium is increased to 3% in the composition of Ex. 10, more larger idiomorphic carbides are formed, but the addition of titanium with columbium less than 3% affects the morphology of the columbium carbide sufficiently to provide a small but definite improvement in abrasive wear resistance.

A.I.S.I. type A6 alloy modified in accordance with this invention, Example 9, is a deep air-hardening alloy steel suitable for a wide variety of cold-work uses such as in blanking and coining and for use as thread rolling dies and trimming dies. It is well suited for such uses and others because of its improved resistance to abrasive wear without a significant loss in ductility.

Other modifications will be apparent to those skilled in this art. For example, in the case of A.I.S.I. type H12 as modified in accordance with the present invention, reduction of the tungsten content to no more than a residual amount of less than about 0.15% gives A.I.S.I. type H11 modified according to this invention. Further, when about 0.85% to 1.25% vanadium is included in the thus modified type H11, the result is A.I.S.I. type H13 modified in accordance with this invention.

As an additional illustration of this invention, two 5-pound experimental air induction heats of a high-speed steel were melted to the analyses indicated in Table VI, the balance in each case being iron and incidental impurities. To ensure complete deoxidation before the addition of the titanium, 0.10% aluminum was added to each heat, as in Examples 9 and 10.

TABLE VI

	Ex 11	Ex 12
Carbon	0.89	0.86
Manganese	<0.01	<0.01
Silicon	0.10	0.19
Chromium	3.97	4.23
Nickel	0.10	0.08
Molybdenum	5.13	5.13
Cobalt	8.09	8.20
Tungsten	1.02	1.00
Vanadium	0.88	1.02
Columbium	2.34	2.44
Aluminum	0.02	0.05
Titanium	0.07	0.01

The heats were cast as 1⅞ in. sq. ingots which were forged from a furnace temperature of 2000°F to 1⅛ in. sq. billets and cooled in vermiculite. The billets were pack annealed at 1550°F for 4 hours, cooled 20°F per hour to 1100°F and then air cooled. Wear-test specimens of the type described in connection with Examples 1–8 were prepared from the billets of Examples 11 and 12. The specimens were heat treated by heating at 2200°F for 5 minutes, quenching in oil, followed by heating for 2 hours at about 1050°F, cooling in air, and then heating again for 2 hours at about 1050°F. The abrasive wear tests were the same as those described for Examples 1–8. The average weight loss from 5 tests, the titanium content, and the hardness of the specimens are given in Table VII.

TABLE VII

Ex. No.	% Ti	Hardness (R_c)	Average Weight Loss, Grams
11	0.07	62.5	0.0324
12	0.01	63.0	0.0797

Example 11 containing 0.07% titanium, in accordance with the present invention, lost an average of only 0.0324 grams. Example 12, from essentially the same analysis as Example 11, but with only 0.01% titanium, had a much larger average weight loss of 0.0797 grams. Examination of the microstructure of Examples 11 and 12 showed that Example 11 has more numerous and larger idiomorphic carbide crystals than Example 12. Examples 11 and 12 clearly show, as did Examples 1–10, the synergistic effect of a small but critical amount of titanium which, when added with the columbium and carbon, provides improved resistance to abrasive wear.

Thus, another preferred composition of the present invention consists essentially of about 0.5% to 2.0% carbon (matrix carbon plus carbides), less than about 0.5%, preferably about 0.15% to 0.4% manganese, less than about 0.5%, preferably about 0.15% to 0.4% silicon, about 3.5% to 4.5% chromium, a maximum of about 0.5% nickel, up to about 19% tungsten, up to about 10% molybdenum, a maximum of about 0.5% copper, 0.75% to 5.5% vanadium, about 3% to 12% cobalt, a maximum of about 0.1% nitrogen, about 1.1% to 2.99%, preferably 2.5% to 2.85%, columbium, at least one element selected from the group of 0.04% to 0.3%, preferably 0.05% to 0.15%, titanium, 0.05% to 0.5%, preferably 0.05% to 0.2%, zirconium, and 0.03% to 0.5%, preferably 0.1% to 0.25%, hafnium, and the balànce essentially iron and incidental impurities.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

We claim:

1. Alloy steel consisting essentially by weight of about 0.2% to 2.5% carbon, up to about 2.5% manganese, up to about 2.5% silicon, up to about 1.5% aluminum, up to about 19% chromium, up to about 5% nickel, up to about 10.5% molybdenum, up to about 20% tungsten, up to about 6% vanadium, up to about 15% cobalt, up to about 4% copper, up to about 0.1% nitrogen, about 1.1% to 2.99% columbium, at least one element selected from the group consisting of 0.04% to 0.3% titanium, 0.05% to 0.5% zirconium and 0.03% to 0.5% hafnium, the balance iron and incidental impurities, the iron content being at least 65%, the amount of carbon being at least about 0.07% plus the amount required to combine with the columbium to form columbium carbide, and said one element being effective to increase the amount of idiomorphic columbium carbide formed whereby said steel has improved resistance to abrasive wear.

2. The steel set forth in claim **1** further containing up to about 0.5% of at least one additive selected from the group consisting of sulfur, selenium, lead and tellurium.

3. The steel set forth in claim **1** in which said one element is about 0.04% to 0.15% titanium.

4. The steel set forth in claim **1** in which said one element is about 0.05% to 0.2% zirconium.

5. The steel set forth in claim **1** in which said one element is about 0.1 to 0.25% hafnium.

6. The steel set forth in claim **3** which contains about 1.1% to 2.85% columbium.

7. The steel set forth in claim **4** which contains about 1.1% to 2.85% columbium.

8. The steel set forth in claim **5** which contains about 1.1% to 2.85% columbium.

9. Abrasive wear resistant hot work steel consisting essentially by weight of about 0.45% to 0.9% carbon, no more than about 0.6% manganese, about 0.75% to 1.25% silicon, about 4% to 5.5% chromium, about 1% to 1.7% molybdenum, up to about 1.7% tungsten, about 0.2% to 1.25% vanadium, up to about 0.1% nitrogen, about 2% to 2.75% columbium at least one element selected from the group consisting of 0.04% to 0.15% titanium, 0.05% to 0.2% zirconium, and 0.03% to 0.5% hafnium, the balance consisting essentially of iron and incidental impurities, the amount of carbon being at least about 0.07% plus the amount required to combine with the columbium to form columbium carbide, and said one element being effective to increase substantially the amount of idiomorphic columbium carbide formed whereby said steel has improved resistance to abrasive wear.

10. The abrasive wear resistant hot work steel set forth in claim **9** in which said one element is about 0.05% to 0.15% titanium.

11. The abrasive wear resistant hot work steel set forth in claim **9** which said one element is about 0.1% to 0.25% hafnium.

12. Abrasive wear resistant deep air-hardening steel consisting essentially by weight of 0.4% to 1.2% carbon, about 0.5% to 2.5% manganese, about 0.5% to 1.5% chromium, about 0.25% to 1.75% molybdenum, up to about 0.1% nitrogen, about 1.1% to 2.99 columbium, at least one element selected from the group consisting of 0.04% to 0.3% titanium, 0.05% to 0.5% zirconium, and 0.03% to 0.5% hafnium, the balance consisting essentially of iron and incidental impurities, the amount of carbon being at least about 0.07% plus the amount required to combine with the columbium to form columbium carbide, and said one element being effective to increase the amount of idiomorphic columbium carbide formed whereby said steel has improved resistance to abrasive wear.

13. The abrasive wear resistant deep air-hardening steel set forth in claim **12** which contains about 1.1% to 2.85% columbium.

14. The abrasive wear resistant deep air-hardneing steel set forth in claim **13** in which said one element is 0.05% to 0.15% titanium.

15. The abrasive wear resistant deep air-hardening steel set forth in claim **13** in which said one element is 0.05% to 0.2% zirconium.

16. The abrasive wear resistant deep air-hardening steel set forth in claim **13** in which said one element is 0.1% to 0.25% hafnium.

17. The abrasive wear resistant deep air-hardening steel set forth in claim **14** which contains about 2.5% to 2.85% columbium.

18. The abrasive wear resistant deep air-hardening steel set forth in claim **15** which contains about 2.5% to 2.85% columbium.

19. The abrasive wear resistant deep air-hardening steel set forth in claim **16** which contains about 2.5% to 2.85% columbium.

20. Abrasive wear resistant high speed steel consisting essentially by weight of about 0.5% to 2.0% carbon, less than about 0.5% manganese, less than about 0.5% silicon, about 3.5% to 4.5% chromium, up to about 0.5% nickel, up to about 10.5% molybdenum, up to about 19% tungsten, about 0.75% to 5.5% vanadium, about 3% to 12% cobalt, up to about 0.5% copper, about 1.1% to 2.99% columbium, up to about 0.1% nitrogen, at least one element selected from the group consisting of 0.04% to 0.3% titanium, 0.05% to 0.5% zirconium and 0.03% to 0.5% hafnium, the balance consisting essentially of iron and incidental impurities, the columbium and some of the carbon forming columbium carbide, and said one element being effective to increase the amount of idiomorphic columbium carbide formed whereby said steel has improved resistance to abrasive wear.

21. The abrasive wear resistant high speed steel set forth in claim **20** which contains about 0.15% to 0.4% manganese and about 0.15% to 0.4% silicon.

22. The abrasive wear resistant high speed steel set forth in claim **20** which contains 1.1% to 2.85% columbium.

23. The abrasive wear resistant high speed steel set forth in claim **22** in which said one element is about 0.05% to 0.15% titanium.

24. The abrasive wear resistant high speed steel set forth in claim **22** in which said one element is about 0.05% to 0.2% zirconium.

25. The abrasive wear resistant high speed steel set forth in claim **22** in which said one element is about 0.1% to 0.25% hafnium.

26. The abrasive wear resistant high speed steel set forth in claim **23** which contains about 2.5% to 2.85% columbium.

27. The abrasive wear resistant high speed steel set forth in claim **24** which contains about 2.5% to 2.85% columbium.

28. The abrasive wear resistant high speed steel set forth in claim **25** which contains about 2.5% to 2.85% columbium.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,901,690

DATED : August 26, 1975

INVENTOR(S) : Thoni V. Philip and Douglas W. Dietrich

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, Table I, in line "C", under the subheading "3", for "80" read -- .80 --;
line 68, for "packed" read -- pack --.
Col. 5, line 19, after "For", for "the" read -- that --.
Col. 6, line 52, after "uses" insert -- of --;
line 54, delete the second occurrence of "of".
Col. 7, line 31, for "3" read -- 30 --.
Col. 10, line 27, after "columbium", insert -- , --;
line 48, for "2.99" read -- 2.99% --.

Signed and Sealed this

thirtieth Day of *March 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks