Patented May 14, 1940 2,201,072

UNITED STATES PATENT OFFICE

2,201,072

ALLOY STEEL

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No Drawing. Application November 11, 1937, Serial No. 174,009

14 Claims. (Cl. 75—128)

The present invention relates to molybdenum-chromium-tungsten steels of the type adapted for dies such as hot or cold forging dies, wire drawing dies and casting dies, and for cutting tools, especially red hard cutting tools, such as turning tools, milling cutters, punches and the like.

The invention has for an object to provide an improved steel of this type and one which can be economically manufactured.

Another object is to provide a steel of this type which will be substantially immune to decarburization and demolybdenization at its hot working and hardening temperature.

Another object is to provide a steel of this type having a low hardening temperature.

Another object is to provide a high quality steel having effective red hardness at unusually high temperatures.

It has been discovered in accordance with the invention that if molybdenum and chromium are combined in the steel in relatively high proportions and in proportions such that the proportion of chromium and that of molybdenum are not too widely different then a desired toughness and hardness, together with the property of hardening at a relatively low hardening temperature is given to the steel. It has also been discovered that in such steels the tendency to decarburize and/or demolybdenize at high temperatures is substantially eliminated or very much reduced. The chromium appears to serve as a carrier for the molybdenum and possibly causes a thin film of chromium or mixed oxide on the surface which inhibits decarburization and demolybdenization. For a die steel the proportion of chromium should preferably be substantially equal to or greater than but not more than about 25% or perhaps 50% greater than the proportion of molybdenum and for a tool steel the proportion of molybdenum should preferably be substantially equal to the proportion of chromium or between the proportion 3:2 and 2:3 and probably between the proportions 5:4 and 4:5.

Molybdenum and tungsten have been used heretofore in steels as alloying ingredients and have even been combined with chromium with varying success. However, the steels produced have been of other types than that of the present invention or the proportions and quantities of molybdenum and chromium necessary to obtain the results of the present invention have not been maintained. In fact, experiments heretofore made have indicated that a steel of the type produced by the present invention must not contain so large a proportion of chromium and of molybdenum as has now been found highly effective. High tungsten steels are rendered brittle by high percentages of chromium and metallurgists have heretofore believed that in high speed steels generally it was necessary to avoid the presence of more than about 5% of chromium when good forgeability was required. It is an important discovery of the present invention that with the higher percentages of molybdenum and low percentages of tungsten, high percentages of chromium do not render the steel brittle, but on the other hand give a surprisingly better forgeable steel having the remarkable quality of resisting decarburization and demolybdenization. Applicant's experiments indicate that chromium in proper percentages has a pronounced effect in bringing out the hardening and heat resisting properties induced by molybdenum and tungsten in these alloys, and that when large percentages of chromium, as 8, or better 9, to 17% are combined with large percentages of molybdenum, as 8, or better 9, to about 15% and small percentages of tungsten as up to 2 or 5%, the full effect of these elements and particularly of the molybdenum is brought out and intensified and better cutting and heat resisting, that is to say, scale resisting and red hardness, properties are given to the steel. It is believed that the addition of chromium with the molybdenum and tungsten and especially with the addition of chromium in a proportion not greatly different from that of the molybdenum has the effect of increasing the solubility of the molybdenum in iron and for this reason improves the quality of the alloy. The solubility of the molybdenum carbide, tungsten carbide, mixed carbides and iron carbide is believed also to be improved and in any event it is found that the steel can be properly hardened at lower temperatures, (below 2200° F.) as for example at temperatures between 1800 and 2100° F.

Cobalt when combined with large percentages of chromium and of molybdenum in the steel of the present invention adds toughness, increases the resistance to checking at high temperatures and improves the cutting qualities.

It is one of the peculiar developments of the invention that the cobalt appears to reduce the hardening temperature or at least does not increase it. The herein described chromium-molybdenum-tungsten steels containing, for example, 3 to 12% cobalt with less than 2% tungsten are found to develop the amazing property of hardening at comparative low temperatures (about 1800 to 2050° F.). This is very striking when compared to the tungsten series such as the 18—4—1 high speed steels in which when increasing quantities of cobalt are added we find a tendency for hardening temperatures to increase. For example, for 18—4—1 steel the recommended hardening temperature for best results is 2300 to 2350° F., but when 12% cobalt is added to this steel the recommended hardening temperature is 2400 to 2500° F. The high cobalt, molybdenum, chromium steels of this se-

ries with tungsten will become increasingly austenitic and the temperature required to produce this condition appears to be progressively lowered as the percentage of cobalt is increased, provided the tungsten content is low, and at the same time if a steel having initially an austenitic condition is desired, it may be hardened at a comparatively low temperature without sacrificing its property of developing a secondary hardness with increased minerological hardness at unusually high drawing temperatures. When the steels described are quenched from the higher hardening temperatures as about 2000 to 2100° F. austenitic structure results. A secondary hardening or precipitation hardening of steels so hardened, as also steels hardened at lower temperatures, can be obtained by drawing at temperatures of about 1000 to 1200° F. or even higher. A hardness of about C–60 to C–65 for steels herein described can be obtained if the hardening temperature is well chosen for this result. When the austenitic structure is obtained the hardness may be below C–50 or even below C–40 but a high secondary hardness, for example about C–55 may be obtained by re-heating to the temperatures above indicated and especially by holding the steel at such temperatures for several hours. A little experimenting with sample pieces of the steel enables one to determine the optimum reheating temperatures. The steels of the invention, especially steels having the higher percentages of cobalt, hardened and reheated as above indicated, are surprisingly durable for hot work. For certain work it is advantageous to draw hardened tools at temperatures of 1000 to 1300 or 1400° F. for 5 to 35 hours depending upon the degree of precipitation and hardness desired.

Certain other alloying ingredients commonly used in die steels and in high speed steels may also be added for their usual effects without impairing the effect of the molybdenum and chromium or losing the advantages thereof. It is particularly desirable to add a small proportion of vanadium for example 0.1 to 3% or even 5% to increase the toughness.

The improved steel may contain, for example:

	Per cent by weight
Molybdenum	8 –15
Tungsten	0 – 5
Chromium	8 –17
Vanadium	0 – 5
Carbon	0.20– 1.50
Silicon	0 – 1.50
Manganese	0 – 1.50
Cobalt	0 –15
Iron	The remainder

The steel of the present invention is particularly suitable for dies and for high speed hot-hard tools. If the steel is to be used for dies a composition such as the following may be used:

	Effective composition	Preferred composition
	Percent	*Percent*
Molybdenum	8 –12	8 –11
Tungsten	0 – 2	0.20– 2
Chromium	8 –15	8 –12.50
Vanadium	0 – 2.50	0.50– 2
Carbon	0.20– 0.80	0.20– 0.65
Silicon	0.15– 1.50	0.75– 1.25
Manganese	0.15– 1.50	0.30– 0.75
Cobalt	0 –15	0.50–13
Iron	The remainder	The remainder

More specifically, for certain types of dies a steel of this composition having a chromium content of 8.5 to 10% with 8 to 10% molybdenum and not more than 1% of tungsten provides especially satisfactory durability. If the die is more of the nature of a cutting tool, the carbon should be raised. The following illustrate representative steels—

	Percent	Percent	Percent
Molybdenum	8.50–9	9.50–11	9.50–10.50
Tungsten	0.25–2	0.25–1	0.25–1
Chromium	8 –8.50	8 –8.50	9.50–10.50
Vanadium	0.50–1	0.50–2.50	0.50– 2.50
Carbon	0.30–0.50	0.25–0.60	0.20– 0.70
Silicon	0.75–1.10	0.75–1.10	0.75– 1.10
Manganese	0.40–0.70	0.35–0.75	0.35– 0.75
Cobalt	0.50–1	0.50–7	11.50–12.50
Iron	The remainder	The remainder	The remainder

	Per-cent	Per-cent	Per-cent
Molybdenum	8.50	9.25	8.50
Tungsten	1	2	0.25
Chromium	8.50	10	8.50
Vanadium	1.50	1.50	1.75
Carbon	0.65	0.80	0.75
Silicon	0.75	0.75	0.30
Manganese	0.50	0.50	0.30
Cobalt	4	0	3.50
Iron	The remainder		

Dies made of the above high chromium, low tungsten, molybdenum steels are tougher and more resistant to checking than the tungsten steels heretofore used. The steels are extremely durable when used for "sprue cutters" against which a stream of hot metal flows and by which it is divided as it enters a casting die.

If the steel is to be used for high speed hot-hard cutting tools a composition such as the following may be used:

	Effective composition	Preferred composition
	Percent	*Percent*
Molybdenum	8 –15	8 –12 or 13
Tungsten	0 – 5	0.25–2
Chromium	8 –17	8 –12 or 15
Vanadium	0 – 5	0.50– 3
Carbon	0.50– 1.75	0.60– 1.15
Silicon	0 – 1.50	0 – 1
Manganese	0 – 1.50	0 – 1
Cobalt	0 –15	3 –12.50
Iron	The remainder	

More specifically, for metal forming tool steels of this composition containing 8–10% chromium and 8.50 to 10% molybdenum are extremely durable. The following examples illustrate representative steels—

	Percent	Percent	Percent
Molybdenum	8.50–9	8.50–9	9.50–10
Tungsten	0.50–2	0 –0.50	0.50– 2
Chromium	8 –8.50	8.50–9	9 –10
Vanadium	1.40–1.75	1.25–2	1 – 2
Carbon	0.75–1.25	0.75–1	0.75– 1
Silicon	0 –1.10	0 –1	0 – 1
Manganese	0 –1.10	0 –1	0 – 1
Cobalt	3.50–4	3 –4	3 – 4
Iron	The remainder	The remainder	The remainder

	Percent	Percent	Percent	Percent
Molybdenum.	8.50	11	10.50	10.50
Tungsten	1	0.25	1.50	0.50
Chromium	8.50	11	11	10.50
Vanadium	1.50	1.50	1.50	2
Carbon	0.90	0.95	1	1
Silicon	0.50	0.50	0.50	0.50
Manganese	0.50	0.50	0.50	0.50
Cobalt	3.50	4	5	13
Iron	The remainder	The remainder	The remainder	The remainder

In these steels the vanadium can be increased to 3 or even 5% to advantage for certain types of metal working tools requiring sharp and durable cutting edges. The cobalt may also be raised as to 7 or 12% to provide greater toughness and improved cutting qualities as in other similar steels. The steel of the last example above having about 10.50% molybdenum, 10.50% chromium and 13% cobalt can be hardened by quenching from a temperature below 1900° F.

The principle of increasing the chromium with high molybdenum may be effectively applied to very high cobalt steels. Such a steel may contain—

	Per cent
Molybdenum	8 – 9
Chromium	8 – 9
Vanadium	0 – 1.50
Carbon	0.10– 0.30
Cobalt	34 –37
Iron	The remainder

Where good forgeability is required the maximum carbon should not be used with the maximum limits in chromium and molybdenum shown for my alloy. The maximum limits of molybdenum, chromium and cobalt have not been ascertained by experiment but the experiments made indicate that up to about 13% molybdenum, about 15% chromium and about 15% cobalt are permissible in forgeable steels.

Higher carbon is necessary with high molybdenum, low tungsten and high chromium for the reason that the steel is progressively softer after heat treatment as the chromium is increased. The increase of chromium from 8.50 to 10.50% will require an increase in the carbon content of about 0.25% to obtain the same relative hardness, for example in a steel for cutting tools.

The cobalt toughens the steels above described. Cobalt up to about 4% in a steel containing about 8.50 chromium, about 8% molybdenum and about 1% tungsten toughens the steel to improve its shock resistance together with some improvement in the quality of its cutting edge. About 7 or 7.50 to about 12% or perhaps 15% cobalt substantially improves the cutting quality and generally in proportion to the amount added.

Because of the low hardening range (1800 to 2050° F. or in some cases 2150° F.) of these steels containing 8% and more of both chromium and molybdenum with up to 2% tungsten and 0.1 to 12% of cobalt or more it is possible to hold and soak these steels at or near this range of temperatures for a long period of time to cause the solution of the carbides without the risk of burning and severe scaling as would be the case when long heating and soaking at temperatures of 2150 to 2500° F. are used as for other types of high speed tool and die steels.

The steels herein particularly described are readily forgeable and may be hardened for example by heating to their hardening temperatures and quenching in oil or air as is usual practice and they may be tempered by reheating to about 600 to 1100° F. or a secondary hardness may be developed by further heating as above explained.

The various known high melting point metals may be added to the above described alloy without sacrificing the advantageous features of the invention except as, in some cases, they increase the cost of the steel, when desired to give to the steel the qualities which these high melting metals are known to give. Vanadium already mentioned has the effect of raising the drawing temperature, toughening the steel and improving its cutting qualities. Uranium up to 3% has an effect substantially similar to the effect of vanadium. Tantalum up to 10% increases the initial hardness of the steel when quenched and raises the tempering temperature. The tantalum forms stable carbides and therefore adds to the hardness. Such formation of carbides may make desirable an increase in the total carbon content. Columbium up to 10% toughens the steel. Titanium or zirconium up to 3% increases the hardness obtained upon quenching and increases the hardening and drawing temperatures while it also tends to make the steel brittle. Nickel up to 5% reduces the hardening temperature and reduces the initial hardness but it does not affect the drawing temperature. It tends to make the alloy tougher but increases the hot shortness. The preferred steels made to embody the principles of the invention do not contain more than about 5% of the above high melting point metals.

The steels described have the decided advantage that they can be produced at much less cost than high tungsten steel having more or less similar properties and yet when containing the preferred proportions of the alloying metals they are for many purposes as good as or decidedly superior to more expensive steels heretofore produced.

It seems from examination of tools after use that the high chromium and high molybdenum high speed steel herein described has a particularly low galling property under the chip as shown by the smooth condition of the edge of the tool after cutting. This may account in part for the greater cutting efficiency of the high chromium, high molybdenum, low tungsten steel as compared with 18—4—1 high speed steel.

The low chromium molybdenum tungsten steels (containing 4% chromium) must be hardened or heat treated in special atmospheres furnaces to overcome the marked tendency to decarburize and demolybdenize or they must be protected by a coating of borax or the like with all of the inconvenience and expense that this involves. In marked contrast to this the high chromium steels of the present invention can be heated in furnaces without atmosphere control for hardening and hot working and can be worked at high temperatures without perceptible deterioration of surfaces or sharp edges.

This feature of preventing decarburization and demolybdenization, is especially valuable in greatly simplifying manufacturing processes since the low chromium-molybdenum steels have also a marked tendency to lose a considerable proportion of their carbon and molybdenum at the surface when being rolled and forged. The decarburization and/or demolybdenization frequently extends to a depth of $\frac{1}{32}$'' and more, depending on the time at heat. Chromium, when used in substantially equal proportions with molybdenum, in steels of the type under consideration, particularly when these two elements are in excess of 8% each, has the extremely valuable effect of inhibiting decarburization and demolybdenization. It almost, if not quite, entirely prevents this. Naturally, the absence of decarburization and demolybdenization at the surface of tools made from it greatly increases the surface hardness and therefore, the effective cutting qualities of these tools as compared with tools of molybdenum steels containing 8.50% of molybdenum or more with only 3–5% of chromium.

The higher chromium, 8% and over, especially in combination with the molybdenum of 8% and more, greatly increases the scale resistance of such steels. This condition, unlike the case of the low chromium molybdenum steels, permits the high chromium (8% or more) molybdenum steels to be hardened in the ordinary standard type of heat treating furnace used for high tungsten high speed steels and other non-molybdenum tool and die steels.

It should be emphasized that a valuable effect of the high chromium (8% or more) and particularly 9% or more, with 8% and more of molybdenum, is found in the lowering of the effective hardening temperature necessary to obtain full hardness of the steel. For example, a steel containing .79% carbon, 8.92% molybdenum, 0.35% tungsten, 0.98% vanadium and 3.31% chromium requires a temperature of 2150–2250° F. for full hardening whereas steels of the present invention can be fully hardened when quenched from temperatures below 2100° F. Experiments have established that many of the steels compounded in accordance with the invention and within the range 8–11% molybdenum, 0 to 2% tungsten, 8–11% chromium, 0–3% vanadium, 0–15% cobalt, and 0.2–1.50% carbon have hardening temperatures between 1800 and 2000° F. For example, steels containing 10.50 to 11% molybdenum, less than 1% tungsten, 10.50 to 11% chromium, up to 15% cobalt and the necessary carbon within the range of 0.75 to 1.25% have a hardening temperature for full hardening at about 1800 to 1900° F. This represents a considerable advantage over 2350° F. required for full hardening of the standard 18—4—1 high speed steel, and over 2500° F. required for full hardening of the standard 18—4—1 steel with 12% cobalt. The value of this lower hardening temperature in hardening tools, especially tools having fine edges, will prove to be very great in the manufacture of such tools because of the elimination of the hazard of breakage and burning or wasting of the fine edges.

The expression "complete hardening" is used herein to define the ordinary hardening that is satisfactory in use in dies, cutting tools and the like and is obtained by quenching from what are commonly referred to as "hardening temperatures," but the use of this language is not intended to mean that the same steel may not be hardened to a slightly greater hardness by special heat treatment, nor that other heat treatments may not be found which will produce a slightly greater degree of hardness.

The term "tool" as used in the claims is used in its broad significance to include dies as well as other tools.

The term "hot working" is used to include both rolling and forging.

The expression "the remainder substantially all iron" as used in the claims is intended to include, in addition to iron, minor impurities and small proportions of alloying elements not sufficient to change the general character of the steel or destroy the advantages of the combination of molybdenum, tungsten and chromium in the proportions defined.

It is contemplated that variations from the illustrative compositions will be made in accordance with well understood metallurgical principles without departing from the spirit of the invention or sacrificing the advantages thereof. The proportions stated are not intended as defining limits beyond which none of the benefits of the invention can be obtained. The high chromium content gives high resistance to corrosion and stain. The composition is such that the steel can be effectively nitrided to provide great surface hardness for certain uses as for example for drawing dies. Furthermore, suitable additions of titanium, above suggested, or of aluminum may be included when the steel is to be nitrided.

This application is a continuation in part of applicant's co-pending application Serial No. 51,224 filed November 23, 1935, now Patent No. 2,099,509 granted November 16, 1937.

I claim:

1. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures comprising as its principal alloying ingredients approximately 8.50% molybdenum, 8.50% chromium, 1% tungsten, 4% cobalt, 0.75 to 1.50% vanadium and 0.30 to 0.65% carbon, with the remainder substantially all iron.

2. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures and by being capable of complete hardening when quenched from a hardening temperature below 2050° F., comprising as its principal alloying ingredients approximately 8 to 10% molybdenum, 8.50 to 9% chromium, an effective amount up to 2% tungsten, an effective amount up to 5% cobalt, an effective amount up to 3% vanadium and 0.20 to 1.50% carbon, with the remainder substantially all iron.

3. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures and by being capable of complete hardening when quenched from a hardening temperature below 2100° F. comprising as its principal alloying ingredients approximately 8 to 10% molybdenum, 8.50 to 9% chromium, an effective amount up to 2% tungsten and 0.20 to 1.50% carbon, the major portion of the remainder being iron.

4. A forgeable steel comprising as its principal alloying ingredients approximately 8 to 10% molybdenum, chromium sufficient in amount to practically prevent decarburization and demolybdenization of the steel at its hot working and hardening temperatures, said chromium being more than 8% and not substantially more than 10%, an effective amount up to 2% tungsten, an effective amount up to 4% vanadium and 0.20 to 1.50% carbon, the major portion of the remainder being iron.

5. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures and by being capable of complete hardening when quenched from a hardening temperature below 2050° F., comprising as its principal alloying ingredients approximately 8 to 10% molydenum, 8.50 to 10% chromium, an effective amount up to 1% tungsten, an effective amount up to 3% vanadium and 0.20 to 0.80% carbon, the major portion of the remainder being iron.

6. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures, comprising as its principal alloying ingredients approximately 8 to 13% molybdenum, 8 to 10% chromium, an effective

amount up to 2% tungsten, an effective amount up to 15% cobalt, an effective amount up to 3% vanadium and 0.20 to 1.50% carbon, with the remainder substantially all iron.

7. A forgeable steel comprising as its principal alloying ingredients approximately 8 to 13% molybdenum, chromium sufficient in amount to practically prevent decarburization and demolybdenization of the steel at its hot working and hardening temperatures, said chromium being more than 8% and not substantially more than 10%, an effective amount up to 2% tungsten, an effective amount up to 3% vanadium and 0.20 to 1.50% carbon, the major portion of the remainder being iron.

8. A forgeable steel comprising as its principal alloying ingredients approximately 8 to 13% molybdenum, chromium sufficient in amount to practically prevent decarburization and demolybdenization of the steel at its hot working and hardening temperatures, said chromium being more than 8% and not substantially more than 10%, an effective amount up to 2% tungsten and 0.20 to 1.50% carbon, the major portion of the remainder being iron.

9. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures and by being capable of complete hardening when quenched from a hardening temperature below 2050° F. comprising as its principal alloying ingredients approximately 8 to 13% molybdenum, 9 to 12% chromium, an effective amount up to 2% tungsten, and 0.75 to 1.15% carbon, the major portion of the remainder being iron.

10. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working temperature and by being capable of complete hardening when quenched from a hardening temperature below 2100° F. comprising as its principal alloying ingredients approximately 8 to 13% molybdenum, more than 8% but not more than 15% chromium, an effective amount up to 5% tungsten, an effective amount up to 15% cobalt, 0.20 to 1.50% carbon and an effective amount up to 5% of metal selected from the group consisting of vanadium, tantalum and columbium, the remainder being substantially all iron.

11. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures, comprising as its principal alloying ingredients approximately 8 to 13% molybdenum, 8 to 17% chromium, an effective amount up to 5% tungsten, an effective amount up to 4% vanadium and 0.20 to 1.50% carbon, the major portion of the remainder being iron.

12. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures and by being capable of complete hardening when quenched from a hardening temperature below 1900° F. comprising as its principal alloying ingredients approximately 9.50 to 11% molybdenum, 9.50 to 11% chromium, an effective amount up to 0.50% tungsten, 11 to 15% cobalt, 1.50 to 2.50% vanadium, and 0.80 to 1.15% carbon, with the remainder substantially all iron.

13. A forgeable steel characterized by being substantially stable against decarburization and demolybdenization at its hot working and hardening temperatures, comprising as its principal alloying ingredients approximately 9 to 11% molybdenum, 9 to 11% chromium, an effective amount up to 0.75% tungsten, 0.50 to 2% vanadium and 0.30 to 1.15% carbon, the major portion of the remainder being iron.

14. A forgeable steel comprising as its principal alloying ingredients approximately 8 to 9.25% molybdenum, chromium sufficient in amount to practically prevent decarburization and demolybdenization of the steel at its hot working and hardening temperatures, said chromium being more than 8% and not substantially more than 10%, 2% tungsten, 0.90 to 1.50% vanadium and 0.60 to 0.90% carbon, the major portion of the remainder being iron.

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