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VALVE MATERIAL

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The present invention relates broadly to metal alloys, and in its specific phases to alloys for poppet valves which are exposed to extremely corrosive products of combustion under conditions of use.

Poppet valves used in internal combustion engines, such as automobile engines, have had to be made better and better to meet engine and fuel developments. For instance, about 1908 to 1910 the maximum temperatures which valves had to withstand was about 1000° F. By 1915–1916 developments had raised valve temperatures to approximately 1200° F. and tungsten steels came into use so that the valves would stand up under these higher temperatures. Since that time engine speeds have been increased, fuels have been improved, octane ratings raised, and compression ratios increased, so that valves in such automobile engines are now subjected in operation to temperatures in the neighborhood of 1600° F. Along with the effects of such heat on the valves and the alloy from which they are made, are the added lead and corrosive influences involved so that these valves must now possess qualities of high strength, high hardness, and high resistance to corrosion oxidation and scaling not at these high temperatures, but also at room temperatures. Also there has been practically no change in valve size and yet such valves need practically twice as much strength as originally even at the higher temperatures involved. To meet this, and the fact that some people use poor gasoline which is still more injurious than usual on the valves, the valve manufacturers have been forced to constantly improve the valve steels in order to make their valves stand up. It was a recognition of these problems, and difficulties involved, which led to the conception and development of the present invention.

Many types of steels have been proposed and later discarded for valve use as temperatures and corrosion effects of the hot products of combustion gradually increased. Austenitic and also martensitic steels enter into this picture and the development of the valve material of the present invention, which will handle 1600° F. readily, will now be described in detail.

The most widely used austenitic steels are of the chrome-nickel types which usually cannot be hardened by heat treatment. Such steels, however, can be hardened to some extent by coldworking or by workhardening at relatively low forging temperatures. This type of hardness is, in general, lost as a result of elevated temperatures encountered by exhaust valves in service in an automobile engine.

The martensitic steels (particularly the 9 percent chromium, 3 percent silicon type) are the most readily forgeable exhaust valve materials in service, however, these steels lose hardness if the operating temperature exceeds about 900° F. At 1500° to 1600° F., all these steels are relatively lacking in strength and hardness. The higher hot hardness of the chromium-nickel austenitic steels makes them less readily forgeable than the martensitic steels.

The mechanical and chemical properties of an exhaust

valve material, in respect to preventing failure, are intimately associated and unfortunately cannot be satisfactorily separated. Thus, a material may have outstanding resistance to high temperature chemical attack (burning) by any of the constituents of the combustible charge which is burned to produce power, but despite this chemical inertness, the material may fail much more rapidly than a much less inert material. In such cases, the failure of the inert material may be due to lack of the following: hot strength, creep resistance (resistance to stretching), and hot hardness. This lack of necessary hot mechanical properties may result in the valve deforming so that it does not completely contact the seat, and may also result in it riding the cam or cam operated push rod so that continual blow-by results. In any event, whenever incomplete seating of the valve occurs, due to lack of mechanical properties or other causes, the result is a sharp increase in valve temperature which may even result in melting a portion of the valve head. A less inert material with superior mechanical properties may remain in such mechanical condition as to operate at a far lower temperature (under normal operating conditions), and as a result be effectively much more inert to the unburned charge, and to the combustion products.

Accordingly among primary objectives of this invention is the showing of ways and means to provide an alloy steel suitable for the manufacture of exhaust valves, or the like, which more closely approaches and possesses the desirable characteristics of an ideal exhaust valve material.

The foregoing objective, and other important objects and desirable features inherent in and encompassed by my new valve alloy development, together with many of the purposes and uses thereof, will become readily apparent from the following description which will set forth factors behind the critical alloy range which tests have shown to meet the extreme requirements of present day internal combustion engine valves.

A further outstanding object of this invention is to provide a valve material which is cast to form valves without forging. The cast structure has proved itself capable of withstanding stresses at high temperatures by a large body of evidence from creep and stress structure testing and from long periods of operation. A cast structure is free from porosity and does not have the directional properties of a forged piece. Grains in the cast material of my invention are very coarse by comparison with wrought material standards. Coarse grain size, however, is beneficial here since most failures are intergranular, and by having less grain boundary, the coarse grained steels of the present invention are less prone to intergranular failure. This is even of more importance to the valve material since this material is operating at high temperatures at which the grain boundaries become weaker. The characteristic failure of metals at low temperature is by fracture through the crystals themselves, whereas failure at high temperatures occurs at crystal boundaries. Coarse grain austenite, such as is found in my cast alloy, has been proven by tests to be more stable than the finer grain structures and further this stability contributes to higher limiting creep stress values.

In preferred composition, my improved material includes components in approximately the following amounts:

	Percent
Carbon	1.05
Silicon	0.80
Manganese	6.00
Chromium	21.00
Molybdenum	0.50
Aluminum	1.00
Nitrogen	0.30

The remainder being substantially iron.

Preferably, for desired hardness at the high temperatures encountered in actual use of the valve, the carbon content should range from 0.90–1.20%. Due to the high carbon content permanent carbides appear in the microstructure which confers upon the metal notable wear resistance. The resulting alloy, however, does not respond to heat treatment and this, in turn, requires that the machining, such as grinding, must be done on the hardened structure to produce the finished valve.

Wrought alloys normally contain less than 0.50% silicon, whereas in my alloy the silicon content is in the range of 0.60–1.00%. If in the present composition the silicon runs higher than 1%, serious brittleness may take place. If we keep the silicon too low (lower than 0.60%) we will lose too much of the effect silicon has on the scaling resistance and also impair the weldability of the alloy. The latter is important since it is a generally accepted procedure to weld a hard material to the valve face and, or, martensitic steel stem to the neck of the cast alloy head. As for the effect of the silicon on the scaling resistance, this consideration is based on the fact that the scale preventing film is made up of oxide of this element which possesses a marked scale resisting ability at high temperatures and is two to three times as strong in comparison with chromium. The higher silicon content is also important in promoting castability of the alloy but, in conjunction with the high chromium, tends to make castings of the austentic grades partially ferritic and, hence, magnetic (sigma promoter). Such partially ferritic alloys have corrosion resistance essentially equivalent to the fully austenitic alloys. Further, a small amount of ferrite associated with austenite is often advantageous under high temperature service. Its plasticity can permit more rapid adjustment to suddenly applied or occasional overloads by yielding to provide a more uniform stress distribution.

The chromium content is preferred to be 20.00–22.00%. In respect to scaling resistance, chromium appears to be the most important element.

Chromium-iron-carbon alloys, however, are lacking in hot strength and hot hardness and the addition of an austenizing element is necessary where these properties are of pronounced importance, as they are with exhaust valves. Nickel is the most widely used austenizing element at present. However, in respect to scaling resistance the effects of nickel are somewhat indefinite. Further, in my alloy, nickel was found to be undesirable since it produces a metal with poor stretching resistance. Nickel in the steels of the stainless grade often has also an adverse effect upon the corrosion resistance of valve products while operating in the presence of hot lead compounds. By supplanting with manganese a substantial quantity of the nickel ordinarily required for providing a steel of austenitic quality, an austenitic steel is obtained and the adverse effect of nickel upon corrosion resistance to the combustion products of leaded fuels is importantly dispelled. In my alloy, manganese and nitrogen are used instead of nickel to provide improved austenitic qualities suitable for exhaust valve use. Manganese contributes markedly to strength and hardness. The effectiveness of manganese in my alloy depends largely upon the high carbon content, for higher carbon steels are more affected by manganese than are the lower carbon steels. Another function of manganese is to decrease the minimum or critical cooling rate. The manganese with the high carbon content of my alloy has also a tendency to lower ductility and thus improve this desired quality of my valve steel.

The addition of 1.00% aluminum and 0.50% molybdenum give my alloy the characteristic of a high yield point value at the elevated temperatures encountered by exhaust valves, and higher yield ratio at room temperature. This is of great importance since a high yield ratio at room temperature assures a higher hot strength and great toughness at the operating temperatures of the valve

and a minimum of elongation with almost no change over the entire temperature range. It is the small amount of these elements as well as the ratio by which they are selected which produces results so advantageous for my valve material.

Nitrogen was found to confer significant hot strength, toughness and ductility as well as to retain the austenitic structure under the combined action of thermal and mechanical forces. This element was used in my alloy in combination with manganese to further improve the alloy for valve use. Chromium and manganese increase the solubility of nitrogen in iron which, in return, makes it possible to raise the nitrogen content in comparison with the maximum available in wrought valve material having a high nickel content.

It is my intention to increase the strength and the hardness because high hardness without brittleness actually increases the amount of elastic deformation which can be tolerated. In determining the best suited elastic modulus of the material and the highest possible hardness, I have chosen a composition which has a low atomic weight sum and a high melting temperature. In this respect, the cast material shows a great difference when compared with the commercially available valve materials (wrought materials). The work hardenability of my cast material results in an increase of the elastic modulus while most steels have virtually no change made in their elastic modulus by heat treatment of any kind.

Since currently used valve steels lose their hardness at elevated temperatures, stem hardness requirements cannot be held and the valve must be made from two different materials. In the case of my cast material, the stem can be cyanide hardened and, therefore, if desired, the valve can be cast in one piece and comply with all requirements.

The hardness of my cast material is not diminished due to elevated temperatures and operation but, in contradiction, it is increased due to work hardening. For instance a new valve which goes in the engine (in the "as cast" condition) with a Rockwell "C" hardness of 30 attains a Rockwell "C" hardnesss of 41–45 after a short time of operation, which thus improves its ability to efficiently function under current valve operation conditions.

The particular amounts of the elements present in the composition of my improved valve alloy assure excellent heat resistance, high heat shock resistance, low ductility, high creep resistance, high hot strength, high wear resistance against battering or upsetting at the valve seat and scuffing at the guides. The high creep resistance is highly desirable in respect to stretching and dishing behavior. My alloy, having a relatively coarse grain structure, has a higher creep strength than the commercially available valve steels with fine grains, which are used due to ease of forming by conventional forging procedures. We must not forget, however, that the grains in my alloy are somewhat refined by the addition of the small amount of nitrogen.

The carbon content of my alloy has been raised to such a maximum that permanent carbides develop which confer upon the metal notable wear resistance. The ductility of my alloy is also intentionally held low (which distinguishes this material very much from any other valve material) since the application of this material to valve service will not permit very much plastic deformation. Whenever this low ductility was tried with another composition, the alloy obtain turned out to be too brittle and in application the valve broke after a short time of operation.

The range of component percentages meeting the requirements of my improved valve material for high temperature use under the corrosive conditions to which valves are exposed in present day internal combustion engines, is rather narrow and critical. The preferred

composition for my improved valve material, as described above, is as follows:

	Percent
Carbon	0.90–1.20
Silicon	0.60–1.00
Manganese	5.00–7.00
Chromium	20.00–22.00
Molybdenum	0.40–0.60
Aluminum	0.75–1.25
Nitrogen	0.20–0.40

The remainder being substantially iron.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the materials employed, provided the elements stated by any of the following claims or the equivalent of such stated elements be employed.

I therefore particularly point out and distinctly claim as my invention:

1. An alloy steel having substantially the following composition:

	Percent
Carbon	0.90–1.20
Silicon	0.60–1.00
Manganese	5.00–7.00
Chromium	20.00–22.00
Molybdenum	0.40–0.60
Aluminum	0.75–1.25
Nitrogen	0.20–0.40

The remainder being substantially iron.

2. A valve for internal combustion engines made from an alloy steel having substantially the following composition:

	Percent
Carbon	0.90–1.20
Silicon	0.60–1.00
Manganese	5.00–7.00
Chromium	20.00–22.00
Molybdenum	0.40–0.60
Aluminum	0.75–1.25
Nitrogen	0.20–0.40

The remainder being substantially iron.

3. An alloy steel having substantially the following composition:

	Percent
Carbon	1.05
Silicon	0.80
Manganese	6.00
Chromium	21.00
Molybdenum	0.50
Aluminum	1.00
Nitrogen	0.30

The remainder being substantially iron.

4. A valve for internal combustion engines made from an alloy steel having substantially the following composition:

	Percent
Carbon	1.05
Silicon	0.80
Manganese	6.00
Chromium	21.00
Molybdenum	0.50
Aluminum	1.00
Nitrogen	0.30

The remainder being substantially iron.

5. An alloy steel having a relatively coarse grain austenitic structure with some permanent carbides and a small amount of ferrite associated therewith, said alloy having high corrosion resistance, hot strength, hot hardness, creep resistance, wear resistance, and high yield point values with work hardenability even at temperatures in the neighborhood of 1600° F., such alloy having substantially the following composition:

	Percent
Carbon	0.90–1.20
Silicon	0.60–1.00
Manganese	5.00–7.00
Chromium	20.00–22.00
Molybdenum	0.40–0.60
Aluminum	0.75–1.25
Nitrogen	0.20–0.40

The remainder being substantially iron.

6. A valve for internal combustion engines, made from an alloy steel having high corrosion resistance, hot strength, hot hardness, creep resistance, wear resistance, high yield point values with work hardenability even at temperatures in the neighborhood of 1600° F., and a relatively coarse austenitic structure with some permanent carbides and a small amount of ferrite associated therewith, said alloy steel having substantially the following composition:

	Percent
Carbon	0.90–1.20
Silicon	0.60–1.00
Manganese	5.00–7.00
Chromium	20.00–22.00
Molybdenum	0.40–0.60
Aluminum	0.75–1.25
Nitrogen	0.20–0.40

The remainder being substantially iron.

References Cited in the file of this patent

UNITED STATES PATENTS

2,127,245	Breeler	Aug. 16, 1938
2,698,785	Jennings	Jan. 4, 1955

FOREIGN PATENTS

309,841	Great Britain	Apr. 15, 1929

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,868,637 January 13, 1959

Leland W. Kirkpatrick

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 36, after "oxidation and scaling not" insert -- only --.

Signed and sealed this 9th day of June 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents