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ALLOY STEEL ARTICLES AND THE METHOD OF MAKING

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ABSTRACT OF THE DISCLOSURE

A wear and corrosion resistant engine poppet-type valve and method of making same comprising a forgeable alloy steel core consisting essentially of about 10% to about 30% chromium, up to about 80% nickel and/or cobalt or combinations thereof, up to about 15% manganese, up to 0.6% nitrogen, up to 4% silicon, less than 0.7% carbon and the balance iron and conventional impurities, and a hardened casing integrally formed around at least the head portion of the valve core and of a thickness of about 0.010 to about 0.20 inch and containing at least 0.8% carbon.

This invention relates generally to alloy steel articles, and more particularly to forged alloy steel articles exhibiting a high resistance to wear and corrosive attack at elevated temperatures and to the method of producing these articles.

In the past a relatively high percentage of carbon was necessary in poppet-type exhaust valves in order that the valves would possess the necessary resistance to impact and friction wear at elevated temperatures. However, even the hot forgeable steel alloys were inadequate in carbon content and were unacceptable without further modification in most engines. Although alloy steels suitable for casting, contain high quantities of carbon, they are also high in silicon content and, as such, are susceptible to corrosive attack.

In the past, it was necessary to modify the forged and cast alloy steels so as to make their use as poppet-type exhaust valves acceptable, especially in heavy duty automotive and aircraft engines. One way was to weld or puddle a high carbon content alloy to the forged valve at the valve head and seat thereby giving the valve excellent wear properties at these critical locations. However, from an economic standpoint, this process is not entirely satisfactory since it introduces an additional critical control step into the manufacturing process which, in turn, increases the production cost per unit valve.

It is the primary object of the present invention to provide improved alloy steel articles having high strength and good forgeability characteristics and exhibiting a high resistance to wear and corrosive attack at elevated temperatures.

It is a further object of the present invention to provide an improved method of making alloy steel articles which includes the step of carburizing the articles.

It is a further object of the present invention to provide improved forged alloy steel articles of the above type suitable for use as combustion engine valves and having a case hardened outer layer of relatively high carbon content.

Further objects and advantages of the present invention will become more apparent from the following detailed description.

The present invention permits the manufacture of an alloy steel article from a forged case carburized alloy comprising between 10 percent and 30 percent chromium, between zero and about 80 percent nickel, cobalt or both, between zero and about 15 percent manganese, between zero and about 0.6 percent nitrogen, between zero and about 4 percent silicon, and the balance being substantially iron and other minor ingredients and impurities such as carbon, copper and boron, all by weight having a case hardened surface from about 0.010 to 0.20 inch thick and containing at least about 0.8 percent carbon.

Also, the present invention comprises a method of making said alloy steel articles which includes the step of case carburizing said article at a temperature between about 1550° F. and 2200° F.

Broadly described, the present invention comprises forging a relatively low carbon content iron base alloy steel valve and thereafter carburizing the valve in a high carbon atmosphere forming a case hardened outer valve layer of relatively high carbon content. The alloy selected may be any one of a number of commercially available forgeable iron base alloy steels preferably an iron base alloy having a critically low concentration of carbon and silicon, a high concentration of chromium and selected proportions of any one or a number of the constituents: nickel, manganese, nitrogen, sulfur, copper, titanium, vanadium, molybdenum, wolfram, columbium and boron.

Those alloy steels considered to be good valve steels because of their medium carbon content (up to 0.7%) cannot be cold forged at all and can be hot forged only within a narrow range of temperatures, i.e., above their recrystallization temperature, because of the rapid work hardening rate imparted to these alloys by this carbon content. The higher expense of conventional hot forging over new processes of cold forging is significant and the added expense of welding or puddling a high carbon content unforgeable alloy steel to the valve head and seat further adds to manufacturing costs.

The valves produced according to the present invention differ from those previously formed by casting in that they contain a relatively low silicon content and therefore they are much less susceptible to corrosive attack by the leaded products of combustion. Additionally, these valves differ from those previously formed by forging in that they exhibit high temperature wear-resistance properties at least comparable to those forged valves having a welded or puddled relatively high carbon content head and seat while being of one-piece construction. Additionally, by using an initially relatively low carbon content alloy, these valves can be formed by cold forging techniques, the cost of which is substantially less than any of the other forming methods.

The alloys used in effecting the principles of the present invention are critical in that the carbon and silicon content must be maintained within the range set forth below in Table I if forgeability is to be obtained and the articles are to possess a sufficient resistance to corrosive attack by the products of combustion. Additionally, these alloys contain a relatively high chromium content and may include relatively high quantities of nickel and manganese and a small quantity of nitrogen. The high chromium content in conjunction with the low silicon content yields a high resistance to corrosion at elevated temperatures and the chromium alone gives the alloy surface a hard and abrasive-resistant property. The high nickel content acts to retard grain growth during the carburizing process and produces a strong and tough valve core. Manganese acts both to increase surface hardness and core strength, and, in conjuntion with chromium, boosts the physical properties of the valve at high temperatures especially when a high silicon content alloy is used.

Table I

		Percentage by weight
Chromium		10–30
Nickel	maximum	80
Manganese	do	15
Nitrogen	do	0.6
Carbon	do	0.7
Silicon	do	3.5

Iron, balance.

An alloy particularly acceptable in forming poppet-type engine exhaust valves by hot forging and which is especially useful in heavier duty installation is set forth in Table II.

Table II

		Percentage by weight
Chromium		14–22
Nickel		1.5–15
Manganese	maximum	15
Nitrogen	do	0.6
Carbon		0.15–0.7
Silicon	maximum	0.3

Iron, balance.

It is critical that the carbon content in the alloy of Table II not exceed 0.7 percent if the alloy is to be forgeable at all and at the 0.7 percent range, the alloy is forgeable only at relatively high temperatures. Further, while the silicon content in this alloy might go as high as 3.5 percent as indicated in Table I, the preferable range of silicon content should not exceed about 0.3 percent for maximum corrosion resistance properties. However, in alloys containing relatively high percentages of silicon, the resistance thereof to corrosion can be boosted by increasing the chromium and manganese content, and even further by adding small quantities of titanium.

The alloy set forth in Table III can be formed by cold forging, for example, on a conventional bolt maker and is a more preferred alloy because of its high physical properties.

Table III

		Percentage by weight
Chromium		12–25
Nickel		6–35
Manganese	maximum	2.0
Nitrogen	do	0.25
Carbon	do	0.30
Silicon	do	0.30

Iron, balance.

In the alloy of Table III, the carbon content must be maintained below about 0.3 percent since a higher carbon content alloy is forgeable only above the recrystallization temperature. The higher nickel and lower manganese content in this alloy facilitates easier cold workability without fracture of either the alloy articles or the forging tools. This alloy is highly desirable in that valves can be formed therefrom using a cold forging bolt maker or other conventional forging machine and without the need for controlled alloy heating.

The physical properties of the alloy of Table III can further be enhanced by supplying small quantities of boron. Tests have shown that a boron content of up to 0.01 percent in the alloy of Table III adds to the hot strength of the forged articles. Additionally, quantities of copper up to 4.0 percent added to the alloy of Table III adds in the cold workability thereof without detracting from the physical properties.

The preferred cold forgeable alloy composition of the forged valve for the purposes of the present invention is indicated iin Table IV.

Table IV

		Percentage by weight
Chromium		18
Nickel		12–14
Manganese		2.0
Carbon	about	0.05
Silicon	do	0.10
Copper		3.00
Boron	about	0.01

Iron, balance.

The limited carbon content (0.7% maximum) in the alloy of Tables I–IV makes these alloys workable by hot forging techniques and in some cases, namely, the alloys of Tables III and IV, cold forging methods may be used without the danger of either the article or the forging tools cracking. However, this relatively low carbon content renders automotive exhaust valves formed therefrom unacceptable. The present invention solves this problem and makes the valves formed from the alloys of Tables I–IV highly acceptable for use as poppet-type engine exhaust valves by carburizing the forget valve in a suitable medium. This forms a case hardened outer layer or shell on the valve thereby providing a high resistance to wear and corrosion which are necessary in engine exhaust valves.

Carburizing processes are known in the art of metal working and are performed by heating the articles above the transformation temperature at which austenite begins to form in the particular alloy and in contact with a carbonaceous material. Carbon is introduced into the alloy through this process penetrating from the outer surface inwardly forming a case hardened outer shell or layer on the alloy. The depth of carbon penetration and thickness of the case hardened layer is a function of time and temperature of the particular carburizing process.

Conventionally, carburizing may be carried out by the use of solid, liquid or gaseous carbon-rich materials. Gas carburizing is a very rapid and highly accurate process and readily lends itself to mass production techniques. Water, coal and natural gas, butane and propane are all effective in carburizing alloy steels, the requirement being that the gas break down to supply carbon in such a form that it will be dissolved by the surface austenite in the alloy. The furnace heats the alloy to a temperature between about 1800° F. and 2200° F., and the carbon bombardment process is continued until the desired depth of penetration and carbon concentration is attained. Upon completion of the carburizing process, the valves are quenched or air cooled to prevent coarse grain formation and to precipitate the excess carbon immediately without harmful effect on the alloy.

In liquid carburizing and nitriding, the alloy parts are placed in a molten sodium cyanide salt bath. The bath heats the alloy to a temperature between about 1500° F. and 1750° F. The salts continually wash the surface of the sample, thereby removing any soot which may normally collect and prevent contact with active carbon and nitrogen. As the sodium cyanide is disassociated, it releases active carbon and nitrogen which reacts with a deposit-free surface and diffuses into the sample. After completion of the carburizing process, the articles are quenched or air cooled.

In solid or pack carburizing, the alloy parts are packed in a solid carburizing material and placed in suitable covered containers and heated above the lower critical temperature for the alloy. The carburizing material, which may be any charcoal, bone, leather, petroleum, coke or other carbonaceous base material mixed with a suitable accelerator such as sodium, calcium or barium carbonate, emits carbon gases with the heated alloy absorbing quantities of carbon therefrom. This process is considerably slower than the gas carburizing process, as might be expected, and is not as accurate in yielded results. However, it is safer than the gaseous process especially for alloys having a relatively high lower critical temperature and it is particularly economical for small quantity carburizing production. Again, after completion of the carburizing process, the articles are quenched or air cooled.

The preferred temperature of operation is dependent upon the method of carburization.

The depth and concentration of carbon required in the valves formed by the process will, of course, vary according to the particular engine and fuel in which these valves find use. Generally, however, a carbon concentration of at least about 0.80 percent by weight and preferably from about 1.0 percent to about 1.5 percent by weight at a depth in the range of about 0.010 inch to about 0.100 inch is adequate.

The techniques used in forming valve blanks having a constituent analysis falling within the range given in Tables I–IV can be achieved by any one of a variety of known forging processes. For example, bar stock having the above analysis can be sheared to appropriate length for forging. If needed, the stock can be annealed either before or after shearing to provide a requisite degree of ductility. The sheared blank may then be subjected to a cold extrusion operation forming the valve stem. The valve head may then be formed by a typical coin upsetting operation with the resulting article closely approaching the finished valve configuration. Conventionally, the sheared blank may be surface coated and impregnated with a lubricant to increase the cold forgeability thereof, especially in the cold forgeable steels.

The resultant valve may then be straightened and machined to a slight oversize after which a stress relieving annealing process may be performed. This is needed where high levels of residual stresses resulting from the forging process exist in the valve since these high stresses may cause warpage and dimensional distortion when the valves are carburized. Additionally, this annealing operation facilitates a structure which can be machined after the carburizing or case hardening process if any distortion or warpage occurs.

After the annealing and straightening operations, the valves are machined to within several thousandths above the final finish dimension. Thereafter, the case-hardening or carburizing process is effected and the valves may be tempered and machined to final specifications.

In order to further illustrate the present invention, the following illustrative examples are provided. It will be understood, however, that the specific alloy analysis and conditions set forth in these examples are provided for illustration only and are not intended to be limiting of the invention as set forth herein.

EXAMPLE I

A bar stock alloy having an analysis set forth in Table V was cold forged to conventional combustion engine poppet valve dimensions, being slightly oversized to permit later machining to final specifications and finish.

TABLE V

	Percentage by weight
Chromium	20.00–22.00
Nickel	10.00–12.50
Manganese	1.00–1.50
Nitrogen	0.15–0.25
Carbon	about 0.2
Silicon	about 0.3
Iron, balance.	

These valves were then carburized in a resistance heated, batch-type furnace using a carrier gas containing raw natural gas in a controlled atmosphere and at a temperature 2050° F. for 2 hours, after which the valves were cooled by water quenching. The carrier gas circulated through the furnace at a rate of 250 cubic feet per hour and had a concentration of 2.0 percent natural gas. An examination of the valve structure showed a carbon concentration of 0.95 percent at a depth of 0.20 inch and a carbon concentration of 1.95 percent at a depth of 0.13 inch, a highly acceptable range for even heavy duty aircraft engines.

EXAMPLE II

By carburizing this same steel at the same temperature and for the same length of time as above but with a 4.0 percent concentration of natural gas or 10 cubic feet of natural gas per hour, a carbon concentration of 1.10 percent at 0.20 inch and a concentration of 2.50 percent at 0.10 inch was achieved.

A more significant variant was seen to be the carburizing temperature. Thus, by heating the valves to 2100° F., an increase of 50° F., the carbon content absorbed by the valve nearly doubled. Also, as might be expected, the carbon diffusion rate was greater at the outset of the carburizing sequence than after extended processing, the diffusion rate gradually decreasing as the alloy takes on a greater carbon concentration.

EXAMPLE III

Forged poppet valves having the analysis set forth in Table V above were also pack carburized using the Houghton Pearlite T carburizing compound and heating to 2075° F. for 4 hours and then water quenching. An examination of the valves revealed a carbon concentration of 1.1 percent at 0.010 inch and 0.60 percent at 0.20 inch. Here, again, a carburizing temperature increase, this time of 75° F., to 2150° F. markedly increased the carbon absorption giving a concentration of 1.90 percent at 0.010 inch, 1.1 percent at 0.020 inch and 0.80 percent at 0.030 inch, a very satisfactory case concentration for most poppet valves. More significant increases in carbon concentration are attained at higher carburizing temperatures.

EXAMPLE IV

A test was made on forged valves having a composition according to Table VI.

TABLE VI

	Percentage by weight
Chromium	20.00–22.00
Nickel	3.25–4.50
Manganese	8.00–10.00
Nitrogen	0.38–0.50
Carbon	about 0.56
Silicon	about 0.25
Iron, balance.	

These valves were hot forged according to known techniques above the alloy recrystallization temperature. Thereafter, the valves were pack carburized using the process of Example III above and the test analysis revealed a carbon concentration of 1.3 percent at 0.010 inch, 1.2 percent at 0.020 inch and 1.0 percent at 0.30 inch when heated to 2150° F. Also, as in Example III above, an increase in the carburizing temperature significantly increases the carbon absorption.

EXAMPLE V

Tests were run on two other forgeable alloy steels, each having a composition illustrated in Tables VII and VIII below:

TABLE VII

	Percentage by weight, about
Chromium	18.0
Nickel	12.0
Manganese	1.3
Nitrogen	0.005
Carbon	0.03
Silicon	0.01
Cobalt	0.10
Boron	0.005
Iron, balance.	

TABLE VIII

Chromium	20.0
Nickel	16.0
Manganese	1.3
Nitrogen	0.005
Carbon	0.03
Silicon	0.01
Cobalt	0.005
Boron	0.10
Iron, balance.	

Poppet valves were cold forged from these alloys and were pack carburized according to the process of Example II above. When carburized at a temperature of 2075° F., the valve analysis showed a carbon concentration of about 1.6 percent at 0.010 inch, 1.1 percent at 0.020 inch, and 0.80 percent at 0.030 inch. When carburized at 2150° F., these valves showed a carbon concentration of 2.0 percent at 0.020 inch and 1.5 percent at 0.030 inch, a very significant increase.

Without carburizing these valves possessed a relatively high resistance to corrosion but severely inferior hardness and resistance to seat wear. However, when carburized, these valves retain their excellent corrosion resistance and their hardness and resistance to seat wear are increased to a level meeting even the most stringent standards for many applications.

From the foregoing, it becomes apparent that the hardness and strength as well as the resistance to corrosion attack of valves formed according to the present invention are significantly increased and are brought within the range of requirements necessary for even high output heavy duty aircraft engines.

Valve wear tests indicate that the engine poppet-type exhaust valves formed according to the present invention show an improved wear resistance which exceeds any of the previously known and used forged valves. Additionally, the corrosion rate for the valves of Example IV is from 2 to 6 times better than the best known valves. In the standard test used in testing engine valve durability, which is designed to provide the best available information of this type, test valves are provided with a small diameter hole drilled through the head at a distance spaced outwardly from the valve stem portion of the head to create a surface through which the products of combustion can flow during the ignition and expansion cycle within the cylinder. The level of orifice enlargement due to corrosion is measured and these results compared for the various valves.

In addition to the case-hardening carburizing treatment elicited above, other case-hardening techniques can be employed to further enhance the valve properties. For example, the valves may be nitrided by introducing nitrogen into the valve surface after the valve is heated above the temperature at which austenite begins to form before carburizing to increase the hot hardness thereof.

Exhaust valve steel having a composition substantially similar to that set forth in Table VII and being specifically a steel containing 0.024 percent carbon, 1.38 percent manganese, 18.48 percent chromium, 11.92 percent nickel, 0.04 percent silicon, 0.006 percent boron, 0.1 percent cobalt, remainder iron, were carburized by immersion in a molten sodium cyanide salt bath having a temperature of 1550° F. A second set of similar steels was carburized in the molten sodium cyanide salt bath at a temperature of 1650° F. This carburization treatment was found to be similar in its carburizing ability to that obtained from gas carburization at temperatures of 1800° F. and above, and formed carburized alloy steels containing comparable carbon concentrations such that the carburized materials possessed similar improved strength, wear and corrosion resistance characteristics. Moreover, the molten salt bath carburization procedure represents a preferred form of the carburizing procedure of this invention because it produces equally improved products at substantially lower temperatures than are preferred when using gas for carburizing.

While specific embodiments of the present invention have been illustrated and described in detail above, it will be appreciated that this invention is subject to modification, variation and change without departing from the novel concepts of the present invention.

What is claimed is:

1. A method of making a metal alloy article for use in high temperature surroundings which includes the steps of forging an alloy consisting essentially of between about 10 and 30 percent chromium, between zero and about 80 percent nickel, between zero and about 15 percent manganese, between zero and about 0.6 percent nitrogen, between zero and 0.7 percent carbon, between zero and about 3.5 percent silicon, and the balance substantially all iron, all by weight, and thereafter case carburizing said article at a temperature between about 1500 and 2200 degrees Fahrenheit for a period of time sufficient to obtain a case of a thickness of from about 0.010 to about 0.20 inch and containing at least 0.8 percent carbon.

2. A method of making a metal alloy article for use in high temperature surroundings which includes the steps of cold forging an alloy consisting essentially of between about 12 and 25 percent chromium, between about 6 and 35 percent nickel, between zero and about 2 percent manganese, between zero and about 0.25 percent nitrogen, between zero and about 0.3 percent silicon, between zero and about 0.3 percent carbon, and the balance substantially all iron, all by weight, and thereafter case carburizing said article at a temperature between about 1500 and 2200 degrees Fahrenheit for a period of time sufficient to obtain a case of a thickness of from about 0.010 to about 0.20 inch and containing at least 0.8 percent carbon.

3. A method of making a metal alloy article for use in high temperature surroundings which includes the steps of cold forging an alloy steel consisting essentially of between about 12 and 25 percent chromium, between about 6 and 35 percent nickel, between zero and about 2 percent manganese, between zero and about 0.25 percent nitrogen, between zero and about 0.3 percent silicon, between zero and about 0.3 percent carbon, between zero and about 4 percent copper, between zero and about 0.01 percent boron, and the balance substantially all iron, all by weight, and thereafter case carburizing said article at a temperature between about 1500 and 2200 degrees Fahrenheit for a period of time sufficient to obtain a case of a thickness of from about 0.010 to about 0.20 inch and containing at least 0.8 percent carbon.

4. A method of making an alloy steel poppet-type engine valve for use in high temperature surroundings which includes the steps of hot forging an alloy steel consisting essentially of between about 14 and 22 percent chromium, between about 1.5 and 15 percent nickel, between zero and about 15 percent manganese, between zero and about 0.6 percent nitrogen, between zero and about 0.3 percent silicon, between 0.15 and 0.7 percent carbon, and the balance substantially all iron, all by weight, and thereafter case carburizing at least the head portion of said valve at a temperature between about 1500 and 2200 degrees Fahrenheit for a period of time sufficient to obtain a case of a thickness of from about 0.010 to about 0.20 inch and containing at least 0.8 percent carbon.

5. A method of making an alloy steel poppet-type engine valve for use in high temperature surroundings which includes the steps of cold forging an alloy steel consisting essentially of about 18 percent chromium, about 12 percent nickel, about 2 percent manganese, about 0.1 percent silicon, about 0.05 percent carbon, about 0.01 percent boron, and the balance substantially all iron, all by weight, and thereafter case carburizing said valve at a temperature between about 1500 and 2200 degrees Fahrenheit for a period of time sufficient to

obtain a case of a thickness of from about 0.010 to about 0.20 inch and containing at least 0.8 percent carbon.

6. A method of making an alloy steel poppet-type engine valve for use in high temperature surroundings which includes the steps of cold forging an alloy steel consisting essentially of about 18 percent chromium, about 12 percent nickel, about 2 percent manganese, about 0.1 percent silicon, about 0.05 percent carbon, about 3.0 percent copper, about 0.01 percent boron, and the balance substantially all iron, all by weight, and thereafter case carburizing said valve at a temperature between about 1500 and 2200 degrees Fahrenheit for a period of time sufficient to obtain a case of a thickness of from about 0.010 to about 0.2 inch and containing at least 0.8 percent carbon.

7. A method of making an metal alloy article for use in high temperature surroundings which includes the steps of forging an alloy steel consisting essentially of between about 10 and 30 percent chromium, between zero and about 80 percent nickel, between zero and about 15 percent manganese, between zero and about 0.6 percent nitrogen, between zero and 0.7 percent carbon, between zero and about 3.5 percent silicon, and the balance substantially all iron, all by weight, and thereafter case carburizing said article in a molten sodium cyanide bath at a temperature between about 1500 and 1750 degrees Fahrenheit for a period of time sufficient to obtain a case of a thickness of from about 0.010 to about 0.20 inch and containing at least 0.8 percent carbon.

8. A forged, case carburized metal alloy consisting essentially of between about 10 and 30 percent chromium, between zero and about 80 percent nickel, between zero and about 15 percent manganese, between zero and about 0.6 percent nitrogen, between zero and 0.7 percent carbon, between zero and about 3.5 percent silicon and the balance substantially all iron, all by weight, and a case hardened surface between about 0.010 and 0.20 inch thick containing at least about 0.8 percent carbon.

9. A forged, case carburized metal alloy consisting essentially of between about 14 and 22 percent chromium, between about 1.5 and 15 percent nickel, between zero and about 15 percent manganese, between zero and about 0.6 percent nitrogen, between zero and about 0.3 percent silicon, between about 0.15 and 0.7 percent carbon and the balance substantially all iron, all by weight, and a case hardened surface between about 0.010 and 0.20 inch thick containing at least about 0.8 percent carbon.

10. A cold forged, case carburized poppet-type valve of a metal alloy consisting essentially of between about 12 and 25 percent chromium, between 6 and about 35 percent nickel, between zero and 2 percent manganese, between zero and 0.25 percent nitrogen, between zero and 0.3 percent silicon, between zero and 0.3 percent carbon and the balance substantially all iron, all by weight, and a case hardened surface between about 0.010 and 0.20 inch thick containing at least about 0.8 percent carbon.

11. A cold forged, case carburized poppet-type valve of a metal alloy consisting essentially of about 18 percent chromium, about 12 percent nickel, about 2 percent manganese, about 0.1 percent silicon, about .05 percent carbon, about 3.0 percent copper and the balance substantially all iron, all by weight, and a case hardened surface between about 0.010 and 0.20 inch thick containing at least about 0.8 percent carbon.

12. A cold forged, case carburized poppet-type valve of a metal alloy consisting essentially of about 18 percent chromium, about 12 percent nickel, about 2 percent manganese, about 0.1 percent silicon, about .05 percent carbon, about 0.01 percent boron and the balance substantially all iron, all by weight, and a case hardened surface between about 0.010 and 0.20 inch thick containing at least about 0.8 percent carbon.

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