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METHOD OF USING A CARBURIZED AUSTENITIC STAINLESS STEEL

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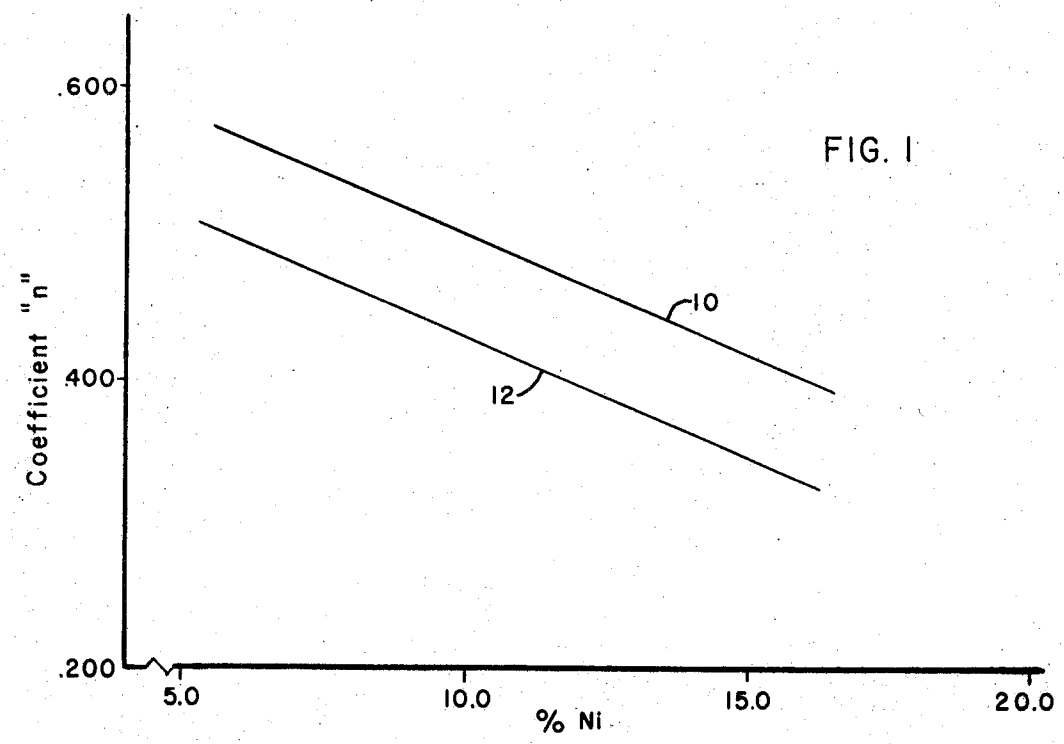


FIG. 1

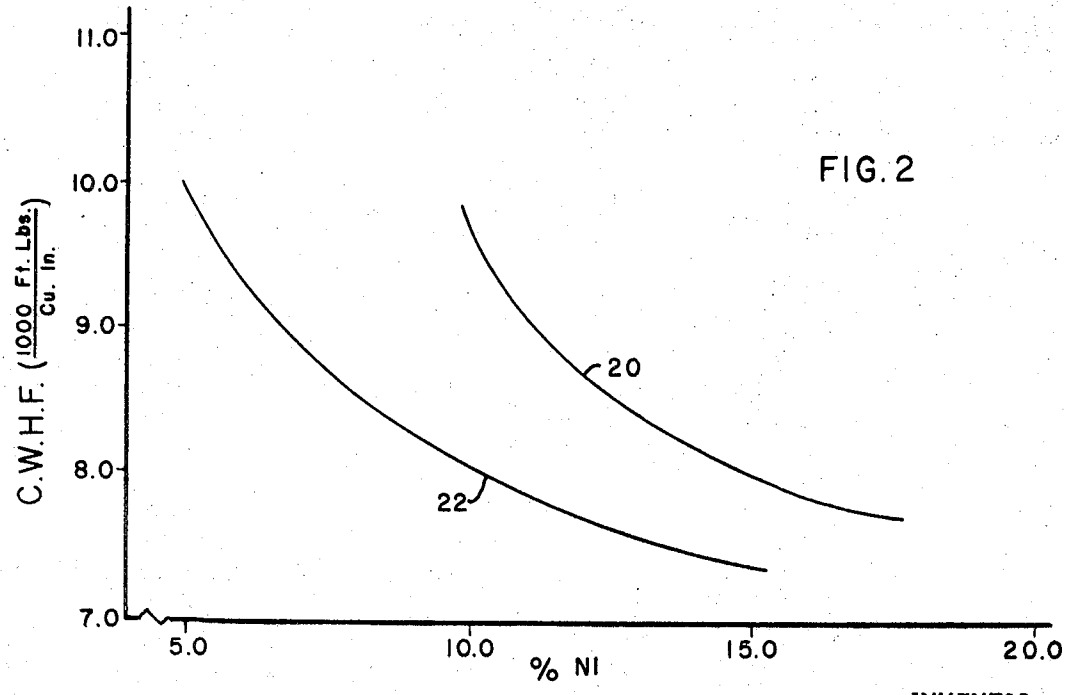


FIG. 2

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METHOD OF USING A CARBURIZED AUSTENITIC STAINLESS STEEL

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Continuation of application Ser. No. 407,298, Oct. 29, 1964. This application Feb. 9, 1968, Ser. No. 704,944

Int. Cl. C22c *35/00*

U.S. Cl. 148—139 5 Claims

ABSTRACT OF THE DISCLOSURE

An austenitic steel is described which is suitable for use as valves and valve components for use in an internal combustion engine after the article has been carburized. The steel possesses a composition which includes up to 0.10% carbon, up to 0.20% silicon, up to 0.70% manganese, 0.06% maximum nitrogen, 13% to 22% chromium, 9% to 20% nickel and up to 33% copper, the sum of the nickel plus copper being within the range between 10% and 21% with the balance essentially iron. The steel is characterized by a low rate of work hardening and excellent ductility. Data was presented to demonstrate the cold workability by means of the slope of the true stress-true strain curve and the cold work hardening factor. Equations are presented for balancing the alloying components to obtain the desired cold work hardening rate.

This application is a continuation of application 407,298 filed Oct. 29, 1964, now abandoned.

This invention relates to austenitic stainless steels, and in particular to austenitic stainless steel which are suitable for use as valves and valve components in an internal combustion engine.

The utilization of wrought austenitic type corrosion resisting steels for both intake and exhaust valves in an internal combustion engine has been known for at least two decades. These austenitic type steels usually employ about 21% chromium, high amounts of manganese, a nickel content which may vary up to 12%, and a carbon plus nitrogen content which generally varies from about .4% up to about 1.5%. These austenitic type steels have been employed because of their stability throughout the operational temperature range of an internal combustion engine. As a result of their structural stability, one of the primary criteria for the selection of austenitic materials for exhaust valves resided in the material's ability to maintain a high hardness at elevated operational temperatures. Characteristically, this hardness which is a criterion of wear and abrasion resistance has been specified as about 140 BHN. In order to meet this requirement, as well as possess an austenitic stability such that the steel would not transform to a different microstructural phase during operation, it became necessary to stabilize the prior art steels by including high amounts of carbon and/or nitrogen. While these high amounts of carbon and nitrogen also provided the required hot hardness, it further became necessary to increase the chromium content in order to obtain the high degree of corrosion resistance necessary where such materials are used as exhaust valves.

This problem of corrosion resistance has become even more acute during the past two decades, since design engineers have increased the compression ratio of the internal combustion engine in order to obtain higher powered performance from said engines. This has resulted in a cooperation with the petroleum industry in developing fuels which have certain additives in order to obtain a high octane rating and thus insure high powered performance in the operation of these power plants. Thus, when these gasolines are utilized, such additives as tetraethyl lead and ethyl bromide are employed, and the combustion products resulting from the use of such "doped" gasolines have proved to be highly corrosive in exhaust systems. Consequently, it has become necessary for steel manufacturers to provide an added measure of corrosion resistance to these high carbon steels, with the result that most exhaust valve materials contain a chromium content of about 21%.

Because of the highly alloyed nature of these steels, the valve manufacturers were required to hot-form the valves, either by forging, upsetting or extruding, following which the hot-formed valves were thereafter cooled to room temperature and finish-machined or ground to final tolerances. Attempts have been made in the past to cold-form these materials with a consequent savings in cost. However, the presently available materials which are suitable for valves or valve components have an exceedingly high rate of work hardening, with the result that they are totally unsuited for cold forming to the close tolerances which are necessary and desirable for use in today's internal combustion engine. In addition, presently used valve materials may also contain certain machinability improving additives such as sulfur, phosphorus and selenium with the result that the hot working temperature range is markedly narrowed to avoid hot shortness. In order to alleviate the shortcomings of the presently existing materials which are suitable for use as valves and valve components, the steel of the present invention is balanced in order to obtain a low rate of work hardening and yet contain sufficient corrosion resistance and hot hardness so that the steel may be used as an exhaust valve in a high performance internal combustion engine.

An object of the present invention is to provide a stable austenitic stainless steel having a high degree of corrosion resistance and a low rate of work hardening.

Another object of this invention is to provide a stable austenitic stainless steel which is suitable for use as valves and valve components.

A further object of this invention is to provide a stable austenitic stainless steel which is suitable for carburizing and/or carbonitriding when the steel is cold-formed into valves and valve components.

An additional object of the present invention is to provide a corrosion resisting stable austenitic stainless steel which may be cold-formed to close tolerances into valves and valve components which may be thereafter carburized and/or carbonitrided and employed in an internal combustion engine.

A more specific object of the present invention is to provide a low carbon, low nitrogen, low prosphorus

stable austenitic stainless steel having a controlled composition wherein chromium, nickel and copper are balanced to provide a stable, austenitic structure having a low rate of work hardening.

Other objects of the present invention will become apparent when taken in conjunction with the following description and the drawings in which:

FIG. 1 is a plot of the slope of the true stress-true strain curve versus the nickel content, and

FIG. 2 is a plot of the cold work hardening factor versus the nickel content.

In its broader aspects, the steel of the present invention contemplates a carbon content of up to .10% maximum, and a nitrogen content of .06% maximum with the sum of the carbon and nitrogen not more than 0.15%. Manganese may be present up to 0.7%, and silicon up to 0.2%. Preferably, the chromium content is maintained within the range between about 13% and 22%, and the nickel content is present within the range between about 9% and about 20%. The steel of the present invention may optionally contain up to 3.5% copper, and in this respect, where copper is present the sum of the nickel and copper must be maintained within the range between about 10% and about 21%. In the steel of the present invention, the phosphorus may not exceed about 0.04%. The balance of the steel consists essentially of iron with not more than about 0.03% sulfur, and other common steel-making elements which would normally be found as impurities in the commercial manufacture of these steels.

Within the broad range of alloying components given hereinbefore, various preferred ranges are also employed, the alloying components performing various functions, as hereinafter explained. While up to .10% carbon can be employed in the steel of the present invention, it is desirable to maintain the carbon content as low as possible commensurate with economic furnace practice and about 0.075% is a realistic preferred maximum. It has been found that when the carbon exceeds about 0.10%, the rate of cold work hardening appears to begin to be adversely affected. Where the carbon content is maintained at not more than 0.075%, the steel of the present invention has an excellent cold work hardening rate.

Nitrogen, another strong austenite forming element, which is usually found to be present in most of the currently employed austenitic valve steels in a minimum amount of about 0.10%, is also limited in the steel of the present invention to not more than about 0.06% maximum. This limit of 0.06% maximum is placed upon the nitrogen content present as an unintentional addition of nitrogen resulting from pick-up during melting, either from the atmosphere, the particular furnace practice, or the raw materials. In any event, nitrogen is not intentionally added to the steel of the present invention. While it is preferred to maintain the nitrogen content at less than 0.04%, it should be pointed out that the sum of the carbon plus nitrogen should be limited to about 0.15% maximum in the broad range, whereas optimum results are obtained where the sum of the carbon plus nitrogen is limited to not more than 0.12%.

The steel of the present invention also contemplates the presence of manganese therein resulting from normal steel melting operations. The manganese is used predominantly as a deoxidizer, and while some effect may be observed on the austenitic stability of these steels, this effect is relatively minimal.

The silicon content of .20% maximum results from a deoxidation product and accordingly is desired to be kept at a very low value. No untoward expense is incurred through utilizing a .20% maximum silicon content in the commercial melting of these steels, and preferably the silicon content is maintained as low as possible, since it is recognized that lower silicon contents promote a greater degree of corrosion resistance within the steels of the present invention.

The steel of the present invention contains chromium within the range between 13% and 22%. If the chromium content is less than about 13%, the steel, while possessing an adequate degree of cold workability, will nonetheless have an impaired corrosion resistance when used in an atmosphere containing combustion products of "doped" fuels. While the chromium content can be increased up to about 22% maximum for an added corrosion resistance, further increases, that is, beyond about 22%, result in an instability in the austenitic structure, do not show any improvement in the mechanical properties, and may adversely affect the work hardening rate possessed by the steel of the present invention. Improved results appear to be obtained where the lower limit of the broad range of the chromium is about 15% and optimum results are obtained where the chromium is present within the range between about 16% and about 19%. This outstanding combination of properties includes corrosion resistance, low rate of work hardening, and austenitic stability.

The nickel is preferably present within the broad range of about 9% to about 20%. Nickel is a strong austenite forming element, and at least 9% is necessary in order to obtain a stable austenitic structure. Nickel contents in excess of about 20% do not appear to give a significantly greater stability to the austenitic microstructure of this steel, and clearly do not further reduce the rate of work hardening. Excellent mechanical properties, corrosion resistance and a low work hardening rate are possessed by the steel of the present invention where the nickel content is maintained within the range between about 12% and about 16%.

The steel of the present invention optionally contains copper. The broad range for copper is up to 3.5%, and in this respect the copper may be substituted for a part of the nickel content. Copper is highly beneficial in reducing the rate of cold work hardening and does not adversely affect the mechanical properties or the corrosion resistance of the steel. Where the copper is present in the steel of the present invention, it is preferred to maintain the sum of the nickel and copper contents between the broad range of about 10% and about 21%. The lower limit of 10% for the sum of the nickel and copper is necessary in order to obtain the low rate of work hardening, whereas increasing the sum of the nickel and copper beyond about 21% does not further decrease the rate of work hardening. Moreover, no other beneficial effects have been noted with higher contents of the sum of nickel and copper, and optimum results appear to be obtained where the sum of the nickel and copper is maintained within the range between about 12% and 18%.

It is highly significant to point out that in the steel of the present invention, phosphorus is preferably limited to an amount not exceeding about 0.04%. This results from the fact that phosphorus is a potent solution strengthener, and has a marked effect on the rate of cold work hardening. Phosphorus contents in excess of 0.04% appear to seriously adversely affect the rate of cold work hardening, and in addition these higher phosphorus contents apparently contribute to the cold shortness when these materials are cold formed or cold pressed or cold extruded on high speed production equipment. Moreover, phosphorus contents in excess of 0.04% tend to make the steel of the present invention hot-short. Thus it is desirable to maintain the phosphorus content in the steel of the present invention as low as possible, and preferably, it should not exceed 0.04% maximum. The balance of the steel consists essentially of iron and the normal steel mill melting impurities. In this respect, it is preferred to maintain the sulfur content at less than .03% and to maintain the other impurities within commercial limits.

Reference is directed to Table I which sets forth the broad range and the preferred range in tabular form, and clearly shows the limits within which the alloying components may be varied.

TABLE I.—CHEMICAL COMPOSITION

Element	General range, percent by weight	Optimum range, percent by weight
C	0.10 maximum	0.075 maximum.
Si	0.20 maximum	Low.
Mn	0.70 maximum	0.50 maximum.
P	0.04 maximum	0.04 maximum.
N	0.06 maximum	0.04 maximum.
Cr	13–22	16–19.
Ni	9–20	12–16.
Cu	0–3.5	0–3.5.
Ni+Cu	10–21	12–18.
Fe	Balance	Balance.

The steel of the present invention may be made in any of the well-known steel mill manners, the details of which are well known to those skilled in the art and need not be set forth in detail. It is sufficient to state that the steel can be melted in a carbon electrode electric arc furnace, and may be conventionally cast into ingots which may thereafter be hot rolled into bar stock. The bar stock, as is well known, may be annealed, pickled and thereafter, if of the proper dimensions, may be fed directly into cold forming machines which directly form the steel into valves and valve components. In this respect, since the steel of the present invention has an excellent cold workability and a very low rate of work hardening, the steel may be formed to the finish dimensions and thereafter subjected to a case hardening treatment which, at the same time, will effect heat treatment of the steel. It is preferred to case harden the steel of the present invention by carburizing, nitriding or carbonitriding when used as a valve or valve component in order to provide the steel with sufficient hot hardness. It has been determined that, when the steel of the present invention was formed into an exhaust valve and tested for corrosion resistance in an engine wherein "doped" gasoline containing additives for obtaining a high octane rating was employed, the steel lacked sufficient hot hardness with the result that the valve seat face was deformed during operation. This test was run in a commercial engine, and while indicating that the steel possessed an outstanding degree of corrosion resistance which surpassed even that of the presently employed commercial austenitic valve steels, still the lack of hot hardness was a problem to be overcome. The problem was sufficiently alleviated by carburizing the steel of the present invention. The carburized steel showed no derogatory effects as relates to the corrosion resistance. In particular, the steel of the present invention in its uncarburized condition possesses a hot hardness, when measured at 1400° F. in the annealed condition, which lies within the range between about 60 and about 90 BHN. As stated hereinbefore, it is preferred to have the steel from which an exhaust valve for an internal combustion engine is manufactured, possess a hardness in the neighborhood of about 140 BHN. When the steel of the present invention was carburized to obtain a nominal carbon content of about 0.7%, the hot hardness measured at 1400° F. and using a cold ball indenter exceeded about 140 BHN.

As stated hereinbefore, the steel of the present invention has an outstandingly cold work hardening rate, thus permitting the steel to be used on high speed presses of cold forming into the various valves and valve components. In this respect, the steel was tested to evaluate the cold work hardening rate and the effect of some elements on the rate of cold work hardening. To evaluate the cold work hardening rates, bar stock material was machined to a standard tensile test specimen. This was pulled in a tensile testing machine and the true stress and true strain values were obtained. From a recording of the true stress versus true strain and the plotting of these values, the thus-obtained curve of the tensile test was employed in order to determine the slope thereof. The slope of the true stress-true strain curve can be expressed as a coefficient n which is a measure of the cold work hardening rate and the plotting of the coefficient n for the various nickel contents gives an indication of the effect of nickel

on the rate of work hardening, that is, lower n values exhibit a lower rate of work hardening than a correspondingly high value.

In order to evaluate the cold work hardening rate employing this criterion, a series of heats were made and tested, the chemical compositions of which are set forth hereinafter in Table II.

TABLE II

Heat No.	Chemical composition (percent by wt.) C	Mn	P	Si	Cr	Ni	Cu	Fe
JA-12	.072	0.52	.012	.094	16.35	10.05	----	Bal.
RV-1442	.068	0.013	.010	.010	16.30	11.70	----	Bal.
JA-13	.072	.24	.012	.10	15.85	11.79	----	Bal.
H2-42	.069	.68	.013	.056	16.23	14.10	----	Bal.
W-96443	.042	1.37	.014	.38	18.38	11.78	----	Bal.
H-28316	.045	.78	.03	.47	15.99	18.07	----	Bal.
JA-43	.070	5.89	.013	.10	15.85	4.99	1.84	Bal.
JA-41	.068	.43	.018	.10	15.69	9.09	3.02	Bal.
RV-1443	.067	.006	.008	.014	16.05	12.01	3.25	Bal.
JA-16	.075	.50	.014	.10	15.46	12.36	2.97	Bal.
HZ-46	.070	.68	.014	.066	16.01	14.10	2.80	Bal.
JL-92A	.064	.36	.010	.13	16.01	12.09	3.08	Bal.
JL-92B	.064	.36	.16	.13	16.01	12.09	3.08	Bal.

In Table II reference is directed to the fact that some of the steels are devoid of copper, whereas other steels contain various amounts of copper, as set forth therein. When these steels were tested employing the true stress-true strain tensile test, the value of the slope of each of the curves thus obtained was calculated, and the results are set forth hereinafter in Table III.

TABLE III.—SLOPE OF TRUE STRESS-TRUE STRAIN CURVE

Heat No.	Percent Ni	Percent Cu	Annealed
JA-12	10.05	----	.516
JA-13	11.79	----	.452
HZ-42	14.10	----	.446
JA-43	4.99	1.84	.530
JA-41	9.09	3.02	.443
JA-16	12.36	2.97	.412
HZ-46	14.10	2.80	.376

Comparing the test results in Table III, it may be observed that sustantially lower nickel contents can be employed to obtain the same low work hardening coefficient where copper is added to the composition. In this respect, reference is directed to the curves of FIG. 1 which demonstrate the effect of nickel on the work hardening coefficient n both for copper-bearing and copper-free steels. In FIG. 1 curve **10** is a plot of the true stress-true strain slopes for the copper-free steels, and curve **12** is a plot of the copper-bearing steels. Comparing curves **10** and **12**, it clearly appears that the addition of about 3% copper to a 9% nickel-bearing steel results in a work hardening factor which is of approximately the same level as that of a 13% nickel-containing steel. Accordingly, at the low end of the nickel range 1% copper can replace more than 1% nickel and the same rate of cold work hardening may be obtained. Thus, the addition of copper results in a savings of the nickel content, thereby resulting in obvious economies to the steel of the present invention. Substantially similar results were obtained in an independent evaluation of the cold work hardening rate, as will be set forth more fully hereinafter.

While the plot of the slope of the true stress-true strain curve verses the nickel content resulted in a fairly straight line relationship, an independent method was utilized for evaluating the rate of cold work hardening in order to corroborate the previous conclusions. This method consists of employing a sample which is compressed in a tensile testing machine between die blocks to effect a reduction in the height of 62½%. A load reduction curve was obtained from this test, and the area under the whole compression curve represents the total amount of work required to deform the specimen. The total amount of work, however, comprises at least two distinct portions, that is, a yield strength factor, which is the work required to elastically compress the sample and is related to the

compressive yield strength of the material, and a "cold work hardening factor," which in this test is related to the work required to plastically deform the sample. The cold work hardening factors is calculated by employing a planimeter and measuring the total area under the load-reduction curve and substracting therefrom the areas of the compressive yield strength portion of the curve. This factor is then divided by the volume of the specimen, and through dimensional constants, the units of foot-pounds per cubic inch are obtained. Upon this basis the comparison is made with respect to compositional differences.

Reference is directed to Table IV which summarizes the work hardening factor as determined by the above-described test as relates to the chemical composition of the steels involved:

TABLE IV.—COLD WORK HARDENING FACTOR 1,000 FT. LBS./CU. IN.

(A) Copper-free heats		
Heat No.	Percent Ni	Annealed
JA-12	10.05	9.81
JA-13	11.79	8.70
HZ-42	14.10	8.41
H-28316	18.07	7.70
(B) Copper-containing heats		
JA-43	4.99	10.10
JA-41	9.09	7.98
JA-16	12.36	7.85
HZ-46	14.10	7.59

From the test results recorded in Table IV, it is clear that both nickel and copper are effective for significantly decreasing the cold work hardening rate of the steel of the present invention. These data clearly illustrate that increasing the nickel content within the range set forth hereinbefore is effective for decreasing the cold work hardening factor. Moreover, the inclusion of copper is effective for further lowering the cold work hardening factor. It is of interest to note that where copper is employed in the steel of the present invention, it is more effective where the nickel content is maintained near the lower end of its permissible range than where the nickel is present in amounts near the upper end of its range. Stated in other terms, the substitution of copper for a portion of the nickel is more effective where the nickel content is maintained near the lower end of its range, the substitution there being that 1% copper will replace more than 1% nickel.

This phenomenon is more clearly illustrated by reference to the accompanying FIG. 2 which illustrates a plot of the cold work hardening factor versus the nickel content. Curve **20** illustrates the test results on a copper-free steel whereas curve **22** illustrates the test results on a copper bearing steel. The convergence of the curves **20** and **22** near the upper stated limit of the nickel content clearly illustrates that the effect of copper diminishes with increasing nickel content. Conversely, the trend is clearly apparent that with decreasing nickel contents the divergence of the curves **20** and **22** clearly illustrates the potent effect of copper on the cold work hardening factor. Moreover, the displacement of curve **22** downwardly and to the left of curve **20** clearly demonstrates the beneficial effect of optionally including copper in the steel of the present invention.

As stated hereinbefore, it is desired to limit the steel of the present invention to a phosphorus content not in excess of 0.04%. Where the phosphorus content is increased above the stated maximum as set forth hereinbefore in Table I, the cold work hardening rate of the steel of the present invention is adversely affected. In substantiation of this fact, Heat No. JL 92A and Heat No. JL 92B having the composition set forth in Table II were made and tested. The cold work hardening factor, as determined by the method of the load-reduction curve as described previously, indicated that where about .16% phosphorus was present, the effect of about 3% copper was completely nullified. Stated in other terms, the beneficial effect on the cold work hardening rate obtained by adding 3% copper to a nominal 16% chromium-12% nickel steel is completely eliminated where the phosphorus content is about 0.16%. Accordingly, in the steel of the present invention, it is desired to control the chemical composition so that the phosphorus content does not exceed about 0.04% in order for the steel to have an outstanding degree of cold workability.

The data which has been set forth hereinbefore in Tables III and IV, and in FIGS. 1 and 2 are corroborative of one another. While the values differ, the trends contained therein clearly substantiate one another and this same trend has also been noted where the steels are employed in a production run.

With the good agreement of the data, a mathematical relation has been derived which closely predicts the cold word hardening factor based strictly on the chemistry of the steel so long as it maintains a composition within the limits set forth in Table I. Based on the observed test data derived from the calculation of the cold work hardening factor, it has been determined that the following equation predicts the cold work hardening factor with a good degree of accuracy.

$$13.80-.733(\%\ \mathrm{Ni})+0.182(\%\ \mathrm{Ni}^2)+.0688(\%\ \mathrm{Cr})-.113(\%\ \mathrm{Mn})-.427(\%\ \mathrm{Cu})+2.17(\%\ \mathrm{C}+\mathrm{N})=6.9-9.9$$

When employing the equation set forth hereinbefore and calculating the cold work hardening factor based strictly on the chemistry of the steel as limited to the ranges set forth in Table I, it has been found that there is 85% agreement between the observed cold work hardening factor and the calculated cold work hardening factor. Thus, the equation set forth hereinbefore predicts with very good accuracy the cold work hardening factor based strictly on the chemical composition as can be demonstrated by plotting the observed vs. calculated cold work hardening factors. It has been found that where the cold work hardening factor is maintained within the range between about 6.9 and about 9.9, the steel of the present invention will possess an optimum combination of corrosion resistance and cold work hardening rate so that the steel is suitable for use in the cold forming of valves and valve components which may be later carburized and used in an internal combustion engine. It should be pointed out however, that the steel of the present invention, when possessing a balanced composition according to the terms of the ranges set forth in Table I, and as more particularly set forth within the equation set forth hereinbefore, will exhibit these optimum combinations of properties as stated previously.

In addition to the aspect of cold work hardening rate, the steel of the present invention must also possess adequate creep rupture strength. Two of the heats having the composition set forth hereinbefore in Table II were tested under a variety of stresses in both the uncarburized and carburized condition. The heats selected to demonstrate the creep rupture properties are identified as RV 1442 and RV 1443. Samples from these heats were carburized at 2000° F. for one hour and thereafter diffused at 2050° F. for a time period of three hours. Heat RV 1442 had an average carbon content of 1.20%, whereas heat RV 1443 had a carburized carbon content of about 1.07%. These steels were subjected to a standard stress rupture test at a temperature of 1350° F. under various states of stress. The time to produce 1% total plastic deformation was employed as the criterion, and from a plot of the log of the stress vs. the log of the time, the stress for 1% plastic strain in 100 hours was obtained. These test results are set forth hereinafter in Table V.

TABLE V.—STRESS TO PRODUCE 1% TOTAL STRAIN IN 100 HOURS AT 1350° F.

Heat No.	Condition	Stress, p.s.i.
RV 1442	Uncarburized	5,000
RV 1442	Carburized	11,250
RV 1443	Uncarburized	9,000
RV 1443	Carburized	12,500

From the test results recorded in Table V, it is noted that the carburization of heat RV 1442 was effective for producing an outstanding increase in the stress required to produce 1% total strain in a time period of 100 hours. While the levels set forth therein may seem to be somewhat on the low side in comparison with the austenitic age hardenable steels in the forged and aged condition, nonetheless these test results indicate that the steel of the present invention, when carburized, will possess outstanding properties in relation to the uncarburized steel, such that the steel of the present invention is suitable for use as valves and valve components. The test results set forth in Table V also show that even at a lower carburized carbon content, the steel of the present invention exhibits better high temperature creep rupture properties where copper is present than where copper is absent, as demonstrated in heats RV 1443 and RV 1442, respectively. These properties are more than adequate to make the steel especially suitable for use as an exhaust valve in an internal combustion engine. These steels, when actually employed in the carburized condition in a commercial engine and tested under controlled conditions employing "doped" fuels, demonstrated an outstanding life in comparison with presently used austenitic age hardening stainless steels, and in the carburized condition, no adverse effect had been noted on the corrosion resistance exhibited by the steel of the present invention. Moreover, the carburized material had sufficient hot hardness and abrasion resistance to prevent deformation and wear during said test.

The steel of the present invention may be manufactured without employing any special equipment or skills. Because of the low rate of cold work hardening, the steel is readily adaptable to the cold production of valves formed on high speed machinery wherein the valve is cold formed to very close tolerances with a minimum of finishing operations. The valves may be thereafter carburized employing standard procedures without any untoward warpage or distortion during said treatment.

I claim:

1. In a method of operating an internal combustion engine having valves, in highly corrosive gasoline products, the improvement comprising use of a corrosion resistant carburized valve, having a carburized area with a carbon content of at least about 0.7%, of an alloy consisting essentially of by weight:

	Percent
Carbon	Up to .1
Silicon	Up to .2
Manganese	Up to .7
Chromium	13–22
Nickel	9–20
Copper	Up to 3.5

Balance essentially iron with incidental impurities; the sum of the nickel plus copper being within the range between 10 and 21%; the alloy being characterized by exhibiting a cold work hardening factor within the range between about 9.9 and 6.9 as the alloy possesses a balanced composition according to the relationship:

$$CWHF=13.80-.733(\%\ Ni)+.0182(\%\ Ni^2)+.0688(\%\ Cr)-.133(\%\ Mn)-.427(\%\ Cu)+2.17(\%\ C+\%\ N)$$

2. In a method of operating an internal combustion engine having valves, in highly corrosive gasoline products, the improvement comprising use of a corrosion resistant carburized valve, having a carburized area with a carbon content of at least about 0.7%, of an alloy consisting essentially of by weight:

	Percent
Carbon	Up to .1
Manganese	Up to .7
Silicon	Up to .2
Chromium	13–22
Nickel	9–20
Copper	Up to 3.5
Nitrogen	Up to .06
Phosphorus	<.04

Balance essentially iron with incidental impurities; the alloy being characterized by exhibiting a cold work hardening factor within the range between about 9.9 and 6.9 as the alloy possesses a balanced composition according to the relationship:

$$CWHF=13.80-.733(\%\ Ni)+.0182(\%\ Ni^2)+.0688(\%\ Cr)-.113(\%\ Mn)-.427(\%\ Cu)+2.17(\%\ C+\%\ N)$$

3. In the method of operating an internal combustion engine having valves, in highly corrosive gasoline products, the improvement comprising use of a corrosion resistant carburized valve, having a carburized area with a carbon content of at least about 0.7%, of an alloy consisting essentially of by weight:

	Percent
Carbon	Up to .1
Manganese	Up to .7
Silicon	Up to .2
Chromium	16–19
Nickel	12–16
Copper	Up to 3.5
Nitrogen	Up to .06
Phosphorus	<.04

Balance essentially iron with incidental impurities; the alloy being characterized by exhibiting a cold work hardening factor within the range between about 9.9 and 6.9 as the alloy possesses a balanced composition according to the relationship:

$$CWHF=13.80-.733(\%\ Ni)+.0182(\%\ Ni^2)+.0688(\%\ Cr)-.133(\%\ Mn)-.427(\%\ Cu)+2.17(\%\ C+\%\ N)$$

4. In the method of operating an internal combustion engine having valves, in highly corrosive gasoline products, the improvement comprising use of a corrosion resistant carburized valve, having a carburized area with a carbon content of at least about 0.7%, of an alloy consisting essentially of by weight:

	Percent
Carbon	Up to .1
Manganese	Up to .7
Silicon	Up to .2
Chromium	13–22
Nickel	12–16
Copper	Up to 3.5
Nitrogen	Up to .06
Phosphorus	<.04

Balance essentially iron with incidental impurities; the sum of the nickel plus copper being present within the range between 12 and 18%; the alloys being characterized by exhibiting a cold work hardening factor within the range between about 9.9 and 6.9 as the alloy possesses a balanced composition according to the relationship:

$$CWHF=13.80-.733(\%\ Ni)+.0182(\%\ Ni^2)+.0688(\%\ Cr)-.133(\%\ Mn)-.427(\%\ Cu)+2.17(\%\ C+\%\ N)$$

5. In the method of operating an internal combustion engine having valves, in highly corrosive gasoline prod-

ucts, the improvement comprising use of a corrosion resistant carburized valve, having a carburized area with a carbon content of at least about 0.7%, of an alloy consisting essentially of by weight:

	Percent
Carbon	Up to .075
Silicon	Up to .2
Manganese	Up to .5
Chromium	16–19
Nickel	12–16
Copper	Up to 3.5

Balance essentially iron with incidental impurities; the sum of the nickel plus copper being within the range between 12 and 18%; the alloy being characterized by exhibiting a cold work hardening factor within the range

between about 9.9 and 6.9 as the alloy possesses a balanced composition according to the relationship:

$$CWHF=13.80-.733(\%\ Ni)+.0182(\%\ Ni^2)+.0688(\%\ Cr)-.113(\%\ Mn)-.427(\%\ Cu)+2.17(\%\ C+\%\ N)$$

References Cited

UNITED STATES PATENTS

2,496,248	1/1950	Jennings	75—128
2,687,955	8/1954	Bloom	75—125
3,303,023	2/1967	Dulis	75—125

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75—128