July 31, 1945. C. H. LORIG 2,380,854

VALVE ELEMENT

Filed March 22, 1941 2 Sheets-Sheet 1

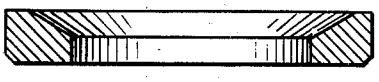


FIG. 3

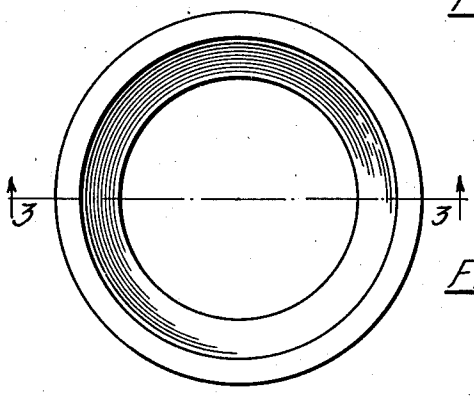


FIG. 2

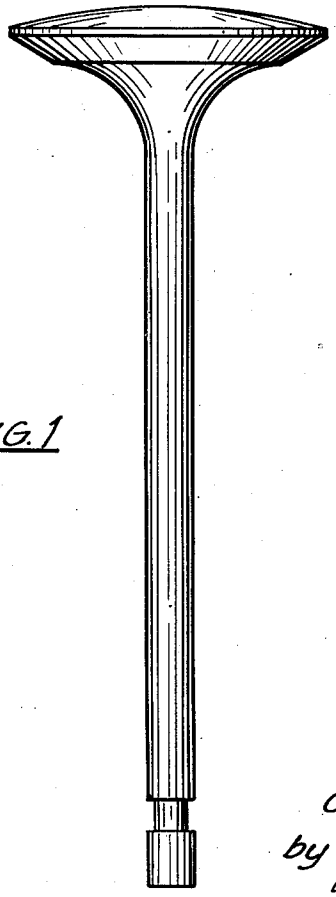


FIG. 1

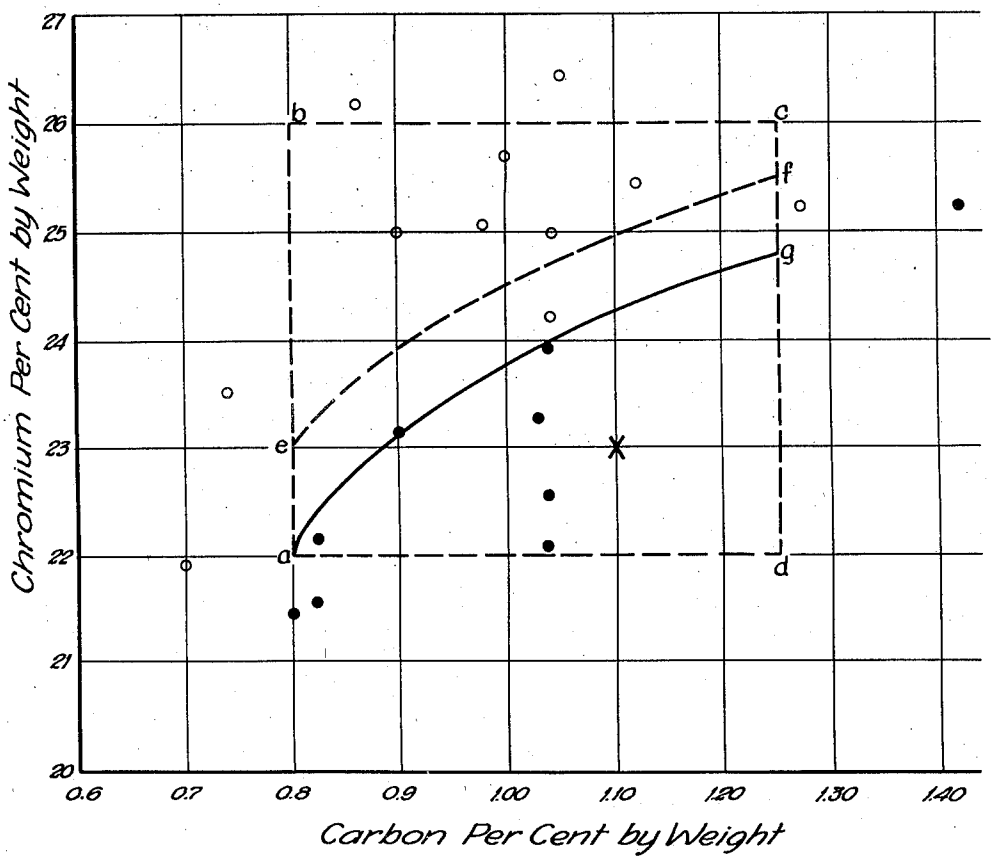
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VALVE ELEMENT

Filed March 22, 1941 2 Sheets-Sheet 2

Fig. 4.



● - Austenite

○ - Austenite plus Ferrite

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UNITED STATES PATENT OFFICE

2,380,854

VALVE ELEMENT

Clarence H. Lorig, Columbus, Ohio, assignor to Battelle Memorial Institute, Columbus, Ohio, a corporation of Ohio

Application March 22, 1941, Serial No. 384,720

7 Claims. (Cl. 123—188)

My invention relates to internal combustion engines and particularly to valve elements for use therein having improved corrosion resistance to the products of combustion of gasolines containing anti-knock compounds such as tetraethyl lead, improved hardness and strength at temperatures of the order encountered by exhaust valves in actual service, and improved strength and hardness retaining characteristics after exposure to such temperatures.

Valve elements of the general type referred to herein are shown in the accompanying drawing, but since the invention resides in the composition of the elements rather than in their form or shape, the showing must be understood as merely illustrative of the commoner forms of such elements.

Fig. 1 is an elevation view of a poppet valve for an internal combustion engine;

Fig. 2 is a plan view of a seat or seat insert for such a valve; and

Fig. 3 is a section of Fig. 2 in the plane 3—3.

Fig. 4 is a diagram illustrating how the character of the microstructure of the alloy used in my valve elements varies with the carbon and chromium contents when the manganese is about 10% and the alloy has been quenched in water from 2000° F.

The valves embodying my invention are formed of steel containing the following, essential, alloying elements within the ranges set forth below:

	Per cent by weight
Carbon	0.80– 2.70
Chromium	22.00–26.00
Manganese	8.50–20.00

For various reasons, which I shall point out, the limits within which each of the above elements may be employed are quite critical. At least 22% of chromium is necessary to provide adequate resistance to scaling and burning because, as the chromium content is decreased below this prescribed minimum there is a marked decrease in this resistance, particularly in the range, 22%–20%. I have also determined the maximum amount of chromium which may be used in the production of my improved valve elements and find that it is related to the carbon content in such a manner that as the chromium is increased from about 22 to 26% the carbon must also be increased from a minimum of not less than 0.80% to at least 1.25%. It has been found that if the chromium is increased without a corresponding increase in the carbon content the alloys will be partly ferritic and that such alloys, especially if there is a considerable percentage of the ferritic structure in them, do not have the necessary hot hardness and hot strength and, furthermore, that the high chromium ferrite structure tends to change at valve operating temperatures into what has been referred to in the literature as the brittle constituent, the sigma constituent, or the intermetallic compound FeCr. Therefore, I find it necessary to limit the maximum chromium content in my valve elements to about 26% because certain manufacturing difficulties are encountered when the carbon content is increased so as to keep the desirable balance between it and chromium in quantities above 26%. In a preferred range of chromium I may use about 22 to 23.5% which provides good scaling and burning resistance and if I use with this chromium content a carbon content of about 1 to 1.1%, I have an alloy which can be produced in the wholly austenitic condition. For the higher chromium contents, I find it desirable to use higher carbon contents, up to 1.25% or more, in order to make the alloy wholly austenitic. In addition, the increased carbon content has certain other advantages, for example, improved hardness and improved wear resistance. While a carbon content of about 1.25% seems to be the preferred upper practical limit for my alloys when they are used for the production of valve elements by hot working processes such as forging, upsetting, extruding, and the like, it is feasible to use higher carbon contents up to 2.70% when the valve elements are manufactured by processes in which hot working properties are not a controlling factor.

Manganese is an important and an essential constituent of my alloy. Among other things, manganese contributes to the stability of the austenitic structure and makes it possible for this structure to be retained at valve operating temperatures which would not be the case were the manganese present in concentrations substantially below the ranges specified in the claims. From extensive researches it has been found that manganese in the range of about 8.5 to 20% should be employed to obtain satisfactory results. For some purposes, a manganese content in the range of about 9 to 12% is satisfactory and good results have been obtained with 10% of manganese. Increasing the manganese content above about 8.5% tends to improve the stability of the alloy and it also adds, contrary to certain patent and technical literature, other desirable characteristics such as improved resistance to scaling and corrosion in the products of combustion of gasoline containing such anti-knock compounds as tetraethyl lead, and to some extent improves the hot hardness and hot strength. Manganese also functions to a degree in promoting the formation of austenite in the steel but it is more important in contributing to the stability of the austenitic structure. Manganese is a cheaper alloying element than nickel which has been used in some of the steels of the prior art and therefore effects some saving in the production of valve elements. It also appears to be superior to nickel in improving resistance to corrosion in the products of combustion of leaded gasolines as well as those containing relatively high sulphur.

As indicated above, the carbon content of alloys of this type is important and must be relatively high in order to obtain an austenitic or substantially austenitic structure, as will more clearly appear hereinafter. The machinability

of my alloys can be improved by adjusting the chromium/carbon ratio to provide some ferrite in the structure. In general, the machinability is improved as the quantity of ferrite is increased up to 10 to 20% of this structure. On the other hand, the hot strength and the creep resistance tend to decrease as the amount of ferrite in the structure increases so that it is necessary to limit the quantity of ferrite. The quantity of ferrite in the structure can be determined by microscopic examination and also by magnetic permeability tests.

The preferred silicon content for this alloy steel is relatively low, usually of the order of .20 to .50%. If the silicon content is materially increased, it is necessary to make a corresponding adjustment of the chromium content because silicon, like chromium, is a ferrite promoter. It is preferable to keep the sulphur and phosphorus contents of the alloy at low values.

Steels of the type of my invention when melted under usual conditions and using commercial materials in the charge will generally contain of the order of .04 to .06% of nitrogen but such nitrogen contents are not considered detrimental in valve elements. Other alloying elements may be present in small amounts provided they do not harmfully affect the desirable properties outlined above.

In Tables I, II, III and IV are presented scaling and corrosion data showing how additions of chromium improve the scaling and corrosion resisting properties of steel base alloys as well as alloys containing the other essential elements disclosed in my application.

The scaling and corrosion data presented herein were obtained from tests designed especially to reproduce, as nearly as possible, the kinds of attack resulting from the products of combustion of gasolines containing tetra ethyl lead. The scaling tests were designed to simulate the types of atmosphere existing in the combustion chamber of an internal combustion engine after ignition of the gaseous charge. The specimens were alternately heated (maximum temperature 1800° F.) and cooled (minimum temperature about 600° F.) in an atmosphere of the products of combustion of a fuel containing tetraethyl lead. Scaling tests were run under both oxidising (excess air) and reducing (excess fuel) conditions since both conditions exist at various times in the operation of an internal combustion engine.

Table I.—Effect of chromium on the resistance of a mild steel base to corrosive attack by molten lead compounds

Heat No.	Chemical composition				Loss in mg./minute/cm.[2]		
	C	Mn	Cr	Si	$PbOPBbr_3$ 1,550° F.	PbO 1,800° F.	$3PbO.2PbSO_4$ 1,800° F.
1845	0.02	Low	2.12	0.008	46.0	128.0	141.0
1848	(1)	do	11.2	Low	21.0	24.0	1.0
1851	(1)	do	19.5	do	22.0	4.0	0.6
1852	(1)	do	22.6	do	21.0	4.0	0.4
1853	(1)	do	25.5	do	4.0	4.0	Nil
1854	0.05	do	28.4	0.07	2.0	3.0	Nil

[1] Carbon .02 to .05%.

Table II.—Effect of chromium on resistance to scaling in products of combustion of fuel containing tetraethyl lead [1]

Heat No.	Chemical composition				Weight loss in Mg./Specimen	
	C	Cr	Mn	Si	Oxidizing 1,800° F. max.	Reducing 1,800° F. max.
1851	(2)	19.5	Low	Low	282	710
1852	(2)	22.6	do	do	30	30
1853	(2)	25.5	do	do	60	87
1854	0.05	28.4	do	.07	60	72

[1] Tests run about 200 hours.
[2] Carbon 0.02 to 0.05%.

Table III.—Effect of chromium on corrosion attack in molten lead compounds using steels of about 1% carbon and 10% manganese

Heat No.	Chemical composition				Loss in mg./minute/cm.[2]		
	C	Cr	Mn	Si	$PbOPbBr_3$ 1,550° F.	PbO 1,800° F.	$3PbO.2PbSO_4$ 1,800° F.
6165	1.02	19.68	9.96	0.35	1.08	46.2	0.2
6172	1.02	22.18	10.05	0.46	1.6	7.5	0.3
6177	1.07	23.64	9.95	0.43	1.5	----------	0.3
3650	1.12	25.4	9.9	0.45	1.2	1.8	0.2

Table IV.—Effect of chromium on resistance to scaling in products of combustion of fuel containing tetraethyl lead using steels of about 1% carbon and 10% manganese

Heat No.	Chemical composition				Loss in mg./specimen	
	C	Cr	Mn	Si	Oxidizing max. 1,800° F.	Reducing max. 1,800° F.
6165	1.02	19.68	9.96	0.35	1,835	1,115
6172	1.02	22.18	10.05	0.46	100	382
6177	1.07	23.64	9.95	0.43	120	112
3650	1.12	25.4	9.9	0.45	115	115

Table V.—Effect of chromium on structure and hot hardness of steels of about 1% carbon and 10% manganese

Heat No.	Chemical composition				Micro-structure	Brinell hot hardness, test temperature		
	C	Cr	Mn	Si		1,110° F.	1,290° F.	1,470° F.
6165	1.02	19.68	9.96	0.35	Wholly austenitic	146	117	82
6172	1.02	22.18	10.05	0.46	do	150	110	74
6177	1.07	23.64	9.95	0.43	do	138	117	79
O-4885	1.06	24.9	10.1	0.26	Small amt. ferrite	148	116	72
W-11054	1.00	26.71	9.98	0.26	Austenite matrix with some ferrite	120	86	62

Corrosion tests in molten lead compounds were designed to test specifically the resistance of a particular alloy to the attack of each of the lead compounds, lead oxybromide, lead oxide and lead oxysulphate which are recognized, by those versed in the art, as probably being the most corrosive of the products resulting from the burning of gasolines containing tetraethyl lead.

It is apparent from the data contained in the foregoing tables that chromium largely determines the scaling and corrosion resistance of the alloys to the attack of these products. It is likewise apparent both in the straight iron-chromium series (Tables I and II) as well as the carbon, chromium, iron, manganese series (Tables III and IV) that a minimum chromium content of about 22% is essential for obtaining adequate scaling and corrosion resistance.

As was indicated previously the maximum chromium content of my alloy was placed at 26% because with the carbon range found most desirable for the purposes herein considered, higher chromium contents resulted in a reduction of strength and hardness at both room and elevated temperature. The data given in Tables V and VI show these relations at elevated temperatures.

This reduction in mechanical properties is related to the appearance of the high temperature ferritic (delta) phase found in the austenitic matrix of alloys of the type disclosed in my application when the chromium/carbon ratio is not balanced to provide a wholly austenitic structure. In the higher ranges of chromium (24–26%) the more desirable carbon content, on the basis of other requirements, is not sufficiently great to provide a wholly austenitic structure thus resulting in the presence of the ferritic (delta) phase.

Despite the lower mechanical properties of alloys represented by the higher chromium ranges of composition of my disclosure, such alloys do have a field of application, namely, where service requirements are not too severe or wherein the more favorable conditions of machinability are a special consideration.

Table VI.—Effect of chromium on structure and strength at 1600° F. of steel of about 1% carbon and 10% manganese

Heat No.	Chemical composition				Microstructure
	C	Cr	Mn	Si	
6165	1.02	19.68	9.96	0.35	Wholly austenitic.
6172	1.02	22.18	10.05	0.46	Do.
6177	1.06	23.64	9.95	0.43	Do.
W-11054	1.02	25.77	9.94	0.29	Austenitic matrix with some ferrite.

Heat No.	Yield strength at 0.2% def. p. s. i.	Tensile strength, p. s. i.	Elongation in 2 in. percent	Reduction of area percent
6165	13,000	20,900	93.5	80.7
6172	12,600	20,300	120.0	90.0
6177	10,600	18,400	88.5	87.4
W-11054	8,200	14,100	72.0	71.4

In Table VII are given data indicating the effect of manganese on the structural stability of the austenite found in alloys of the type disclosed in my application. One method of determining the structural stability of austenitic alloys is to note whether or not the magnetic saturation of such alloys increases during prolonged heating at elevated temperatures. This was the method used in obtaining the data presented in Table VII. It is apparent that when the manganese content of the alloys indicated in Table VII is below about 10%, the austenite of such alloys is not entirely stable on heating at 1300° F. for 100 hours but undergoes an austenite to ferrite transformation. In the case of Heat P278 containing 5.85% manganese this transformation is complete after about 100 hours of heating while in the case of Heat P283 (8.72% Mn) the alloy might be characterized by being called essentially austenitic, i. e., the rate of austenite decomposition is far more sluggish and presumably would not transform during the normal period of life of an exhaust valve to such an extent that satisfactory performance would not be obtained. Above about 9% manganese and up to the maximum manganese content claimed herein (20%) the austenitic structure of such alloys is stable and appears to remain essentially so throughout long periods of heating.

From the data shown in Table VIII it appears that manganese has some beneficial effects on the corrosion resistance of my alloy to molten lead compounds and it is certainly indicated that it does not impair this property. It is probable that other investigators, having run scaling tests in an air or oxygen atmosphere, have erred in concluding that because the scaling resistance of high chromium-manganese alloys is not so good under these conditions such alloys would likewise be inferior in an atmosphere of the products of combustion of gasolines containing tetraethyl lead.

The data presented in Table IX serve to show the relation of carbon to chromium, at three different chromium levels and indicate the ratio of chromium to carbon required in order to produce wholly austenitic alloys as quenched from 2000° F. or alloys containing an austenitic matrix within which are grains of the high temperature ferritic (delta) phase. Somewhat similar data are presented graphically in Fig. 4 of the drawings under the same conditions of heat treatment.

Table VII.—Effect of manganese on stability of austenite in aging tests at 1300° F. for 100 hours

Heat No.	Chemical composition				Magnetic saturation: gausses	
	C	Cr	Mn	Si	Before test	After test
P278	1.02	22.22	5.85	0.33	25	12,600
4588	1.04	22.52	10.03	0.47	100	100
P282	1.04	22.06	10.79	0.42	25	100
6376	1.04	22.0	14.0	0.55	0	0
P283	0.98	23.40	8.72	0.33	125	2,560
6374	1.04	23.9	9.5	0.52	100	226
P284	1.03	23.29	10.89	0.38	125	125
4280	1.02	25.71	2.09	0.31	2,810	12,700
P287	0.97	25.28	7.14	0.36	3,080	7,480
5676	1.03	25.10	8.97	0.47	1,955	3,770
5677	1.04	25.03	10.79	0.47	1,655	226
3651	1.12	25.1	19.6	0.53	1,100	0

Table VIII.—Effect of manganese on resistance of about 1% carbon and 25% chromium steels to corrosive attack by molten lead compounds

Heat No.	Chemical composition				Loss in mg. minute/cm.[2]		
	C	Cr	Mn	Si	PbOPbBr[3] 1550° F.	PbO 1800° F.	3PbO.2PbSO[4] 1800° F.
3743 [1]	1.0	25	0.5	Low	2.2	3.0	0.3
4281 [1]	1.0	25	2.0	do	1.5	3.2	0.3
4183 [1]	1.0	25	5.0	do	1.9	3.0	0.4
4184 [1]	1.0	25	7.5	do	1.4	2.7	0.4
3650	1.12	25.4	9.9	0.45	1.2	1.8	0.2
3651	1.12	25.1	19.6	0.53	0.2	1.7	0.2

[1] Calculated charge analysis.

In Fig. 4 of the drawings which illustrates how the microstructure of the alloy varies with the carbon and chromium contents when the manganese is about 10% and the alloys have been been quenched in water from 2000° F., the field *a b c d* is confined to the preferred carbon range for use in the production of valve elements by hot working processes, but it is to be understood, as stated above, that higher carbon, up to 2.7%, may be used where the elements are manufactured by processes in which hot workability is not a controlling factor. Line *a g* indicates approximately the boundary between wholly austenitic alloys (below) and alloys which contain increasing amounts of ferrite (above) as the distance above the line *a g* increases. The line *e f* is drawn to indicate the approximate limit of the amount of ferrite which may be present in such alloys for satisfactory use in valve elements but for some applications, where scaling and corrosion resistance are the principal requirements, alloys above line *e f* may be used with satisfactory results. Increasing the manganese above 10% tends to shift slightly the position of line *a g* to higher chromium values but, as pointed out above, manganese serves a more important function in stabilizing the austenite so that it does not decompose or transform on reheating in the temperature range in which exhaust valves are known to operate. The point X at 23% chromium and 1.10% carbon indicates a preferred composition within the field of wholly austenitic alloys so as to provide a safe melting range as is required in steel melting practice.

In Table IX alloys considered as wholly austenitic have a magnetic saturation of the order of 0–100 gausses while alloys having some of the ferritic (delta) phase have magnetic saturatons in excess of 100 gausses with those alloys having the greatest amount of ferrite (delta) having the highest magnetic saturation. In Fig. 4 the alloys designated by solid circles are wholly austenitic while those designated by open circles have an austenitic matrix in which grains of ferrite (delta) are present. The amount of ferrite (delta) in a particular alloy is not indicated, although for a clearer understanding of the diagram it may be stated that for a given carbon content the amount of ferrite will increase with an increase in chromium. In like manner it may be said that the amount of ferrite (delta) for a fixed chromium content increases with a decreasing carbon content.

Table IX.—Effect of carbon and chromium on magnetic saturation of steels containing about 10% manganese as quenched in water from 2000° F.

Heat No.	Chemical composition				Magnetic saturation: gausses as water quenched from 2000° F.
	C	Cr	Mn	Si	
P111	0.70	21.96	11.75	0.35	1,230
5091	0.82	22.18	10.23	0.47	75
4588	1.04	22.52	10.03	0.47	100
5096	0.74	23.52	9.73	0.23	3,260
4088	0.90	23.17	9.83	0.27	25
6177	1.06	23.64	9.95	0.43	0
3146	0.53	25.61	9.83	0.59	8,490
11054	1.00	25.71	9.93	0.26	3,160
V. B. B	1.42	25.26	10.4	Low	0

Thus, from the data presented in Table IX and in Fig. 4, it is apparent that consideration must be given to the chromium-carbon relation in selecting a particular composition having the properties desired. For example, I have found that the wholly austentitic alloys have higher tensile strength at both room and elevated temperatures and, in general, this is also true of hardness and other mechanical properties. On the other hand, alloys having an austenitic matrix in which grains of the high temperature ferritic (delta) phase exist have better machinability although poorer mechancal properties.

Thus if a wholly austenitic alloy is desired having a chromium content of 22% the carbon range could vary over the entire range claimed, namely, 0.8 to 2.7%. However at higher chromium levels the permissible carbon range would be narrower, e. g., at 23% chromium wholly austenitic alloys are limited to carbon in the range of about 0.90% and up while at 24% chromium the wholly austenitic alloys are limited to carbon in the range of from about 1.05% and up.

Improved machinability can be obtained in alloys of my invention by readjustment of the carbon and chromium relation so that the resulting alloy contains some of the ferritic (delta) phase. This, however, results in some decrease in mechanical properties. For example, if a more readily machinable alloy is desired containing about 23% chromium this could be accomplished by lowering the carbon content to within the range of 0.8–0.9%. In like manner a similar adjustment can be made at lower or higher chro-

mium contents. The same result can also be obtained by holding the carbon constant and increasing the chromium content. Such alloys of improved machinability fall mostly in the range between lines *a g* and *e f* in Fig. 4.

While the data used for Table IX and in Fig. 4 are largely based on alloys having about 10% manganese, some displacement in the lines outlining the respective fields of austenite or austenite plus ferrite (delta) may be expected from variations in manganese. However, my investigations indicate that, within the ranges of composition claimed, manganese has only minor influence on the amount of austenite formed and that this is largely a function of carbon and chromium. Thus for all practical melting purposes the phase relationships as indicated in Fig. 4 hold.

A summary of road test data is given in Table X in which exhaust valves made from alloys of my invention were run in comparison with exhaust valves made from steels used extensively today. These comparisons were made simultaneously, i. e., half of the required number of exhaust valves used in a particular engine was made from my alloys while the remaining number used was made from one of the commercial valve steels.

Table X.—Illustrative road-life test data for exhaust valves of steel of my invention and of commercial steels

Type steel	Type composition					Average miles to failure	Status of test
	C	Cr	Mn	Si	Ni		
Experimental	1.0	25.0	10.0	0.5	------	[1] 67,479	In progress.
Commercial	0.45	8.5	------	3.25	------	[2] 18,677	
Experimental	1.0	25.0	10.0	0.5	------	[1] 44,673	Do.
Commercial	0.75	21.0	------	2.0	1.5	[2] 35,530	
Experimental	1.0	25.0	10.0	0.5	------	[1] 29,867	Do.
Commercial	0.75	21.0	------	2.0	1.5	[1] 24,132	
Experimental	1.0	25.0	10.0	0.5	------	[1] 56,649	Test discontinued.
Commercial	0.45	23.75	{Mo 3.0}	1.0	4.75	[2] 37,231	

[1] One or more valves included in this average have not failed.
[2] All original valves included in this average have failed and have had to be replaced one or more times.

One of the novel features of my alloy and valve elements made therefrom is found in the combination with chromium in substantial quantities of comparatively high carbon and high manganese. Many of those who have heretofore investigated chromium-manganese steels have concluded that it is essential to keep the carbon low in order to impart desirable corrosion resistance properties to the alloy. In my alloy I have found that high carbon contents which are necessary to produce austenitic structures can be used without detracting from their scaling and corrosion resistance at valve operating temperatures. Moreover, the high carbon content produces more hard particles in the steel which beneficially affect its wear resistance and hardness.

Some investigators have concluded that additions of manganese in substantial quantities to high chromium containing steels decrease scale resistance and produce a steel having a large grain size and coarse crystallization. Others have concluded that such additions produce a steel which becomes undesirably brittle upon prolonged heating at temperatures of the order of 1200° to 1500° F.

Insofar as steel alloys containing chromium, manganese and carbon within my limits are concerned, it has been quite definitely established that they are neither coarsely crystalline as cast nor do they become so as a result of hot working. Furthermore, extensive road and dynamometer tests of my valves have indicated that they are not susceptible to embrittlement resulting from prolonged exposure to valve operating temperature.

By the term, "valve element" as used in this specification and in the appended claims, I mean to include valves and parts thereof, valve seats, valve seat inserts, and other parts of internal combustion engines, which, in normal use, are subject to contact with the fuel employed or to the products of combustion thereof. It is also to be understood that the percentages mentioned are percentages by weight.

What I claim is:

1. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being at least predominantly austenitic as cooled from temperatures in the range of about 2000° to 2300° F. and after reheating at temperatures up to 1600° F., by having high resistance to scaling and corrosion in the products of combustion of gasolines containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures and high retained strength and hardness after long exposure at such temperatures; said steel comprising a plurality of elements of which the following in the ranges stated are the only elements necessary to attain said characteristics, chromium in the range of 22.0 to 26.0%, manganese in the range of 8.5 to 20%, carbon in the range of .80 to 2.7%, with the balance substantially iron.

2. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being at least predominantly austenitic as cooled from temperatures in the range of about 2000° to 2300° F. and after reheating at temperatures up to 1600° F., by having high resistance to scaling and corrosion in the products of combustion of gasoline containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures and high retained strength and hardness after long exposure at such temperatures; said steel comprising a plurality of elements of which the following in the ranges stated are the only elements necessary to attain said characteristics, chromium in the range of 22–26%, manganese in the range of 10–15%, carbon in the range of .80 to 2.70%, and the balance substantially iron.

3. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being substantially austenitic as

cooled from temperatures in the range of about 2000° to 2300° F. and after reheating at temperatures up to 1600° F., by having high resistance to scaling and corrosion in the products of combustion of gasolines containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures and high retained strength and hardness after long exposure at such temperatures; said steel comprising a plurality of elements of which the following in the ranges stated are the only elements necessary to attain said characteristics, chromium and carbon in the ranges indicated by the area *a e f d* in Fig. 4, manganese in the range of 8.5–20%, and the balance substantially iron.

4. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being substantially austenitic as cooled from temperatures in the range of 2000° to 2300° F. and after reheating at temperatures up to 1600° F., by having high resistance to scaling and corrosion in the products of combustion of gasolines containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures and high retained strength and hardness after long exposure at such temperatures; said steel comprising a plurality of elements of which the following in the ranges stated are the only elements necessary to attain said characteristics, chromium and carbon in the ranges indicated by the area *a e f d*, in Fig. 4, manganese in the range of 10–15%, and the balance substantially iron.

5. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being wholly austenitic as cooled from temperatures in the range of about 2000° to 2300° F., and after reheating up to temperatures of 1600° F., by having high resistance to scaling and corrosion in the products of combustion of gasolines containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures and high retained strength and hardness after long exposure at such temperatures; said steel comprising a plurality of elements of which the following in the ranges stated are the only elements necessary to attain said characteristics, chromium and carbon in the ranges indicated by the area *a g d* in Fig. 4, manganese in the range of 10–20%, with the balance substantially iron.

6. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being wholly austenitic as cooled from temperatures in the range of about 2000° to 2300° F., and after reheating up to temperatures of 1600° F., by having high resistance to scaling and corrosion in the products of combustion of gasolines containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures and high retained strength and hardness after long exposure at such temperatures; said steel comprising a plurality of elements of which the following in the ranges stated are the only elements necessary to attain said characteristics, chromium and carbon in the ranges indicated by the area *a g d* in Fig. 4, manganese in the range of 10–15%, with the balance substantially iron.

7. An internal combustion engine valve element formed, at least in part, from an alloy steel characterized by being wholly austenitic as cooled from temperatures in the range of about 2000° to 2300° F., and after reheating up to temperatures of 1600° F. by having high resistance to scaling and corrosion in the products of combustion of gasolines containing tetraethyl lead, by having high strength and high hardness at valve operating temperatures, and high retained strength and hardness after long exposure at such temperatures; said steel having the approximate composition of 22.5–23.5% chromium, 9.5–10.5% manganese, 1.05–1.15% carbon, with the balance substantially iron.

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