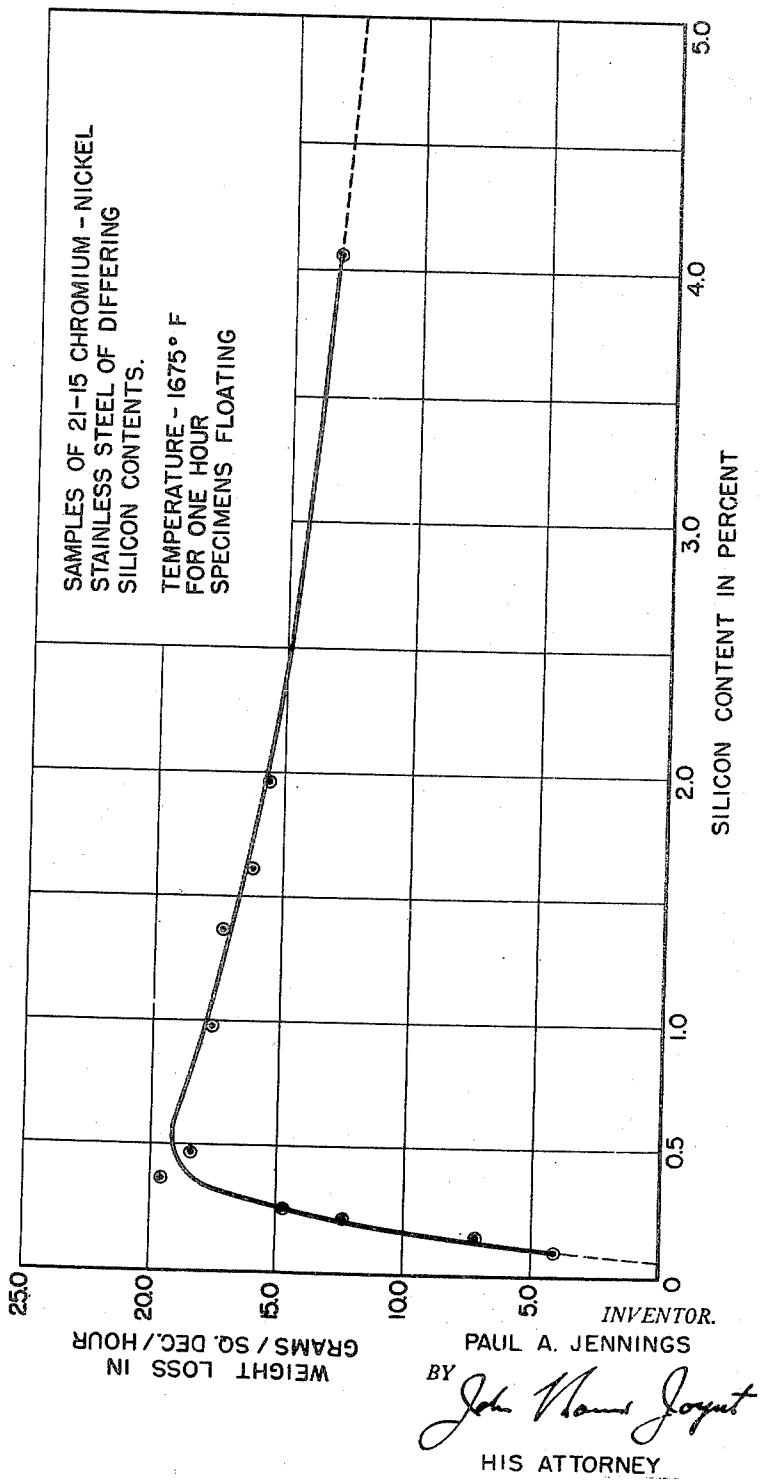
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INTERNAL-COMBUSTION ENGINE VALVE

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INFLUENCE OF SILICON CONTENT OF CHROMIUM-NICKEL STAINLESS STEEL ON CORROSION RESISTANCE IN MOLTEN LEAD OXIDE



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INTERNAL-COMBUSTION ENGINE VALVE

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This invention relates to high temperature stainless steel articles, and is especially pertinent to stainless steel valves and valve parts which operate while hot and in corrosive atmospheres.

An object of my invention is the provision of strong, tough and durable austenitic chromium-nickel stainless steel internal combustion engine parts for elevated temperature use, which possess great strength at high temperatures and which offer substantial resistance to corrosion in the heated condition in atmospheres such as those containing the combustion products of so-called anti-knock gasoline of the tetra-ethyl lead variety.

A further object of my invention is that of providing high temperature austenitic chromium-nickel stainless steel valves and valve parts which in view of the excellent properties of the particular steel employed achieve highly satisfactory functions in such fields as passenger car, truck, aircraft, Diesel and marine vessel exhaust valve use.

Other objects of the invention in part will be obvious and in part pointed out more fully hereinafter.

The invention accordingly consists in the combination of elements, composition of materials and features of products, and in the relation of each of the same to one or more of the others as described herein, the scope of the application of which is indicated in the following claims.

The single figure of the accompanying drawing graphically illustrates certain features of my invention.

As conducive to a clearer understanding of certain features of my invention, it may be noted at this point that many heat resistant valves and valve parts known in the prior art for exposure to the hot gases of internal combustion engines, and the like, often corrode at a rapid rate where leaded fuels as of the anti-knock varieties and their combustion products are encountered. Others suffer a loss of hardness when operated at high temperatures and, in addition, are inclined to stretch. In passenger cars, for example, the average temperature frequently reaches as high as 700° F. or more on the fuel intake side of the engines and as high as 1100° F. to 1450° F. or more on the exhaust side. Usually, these temperatures are considerably higher in truck or aeroplane engines especially at the region where the exhaust valves operate.

Among the classes of valves which heretofore have been used in internal combustion engines, or the like, are those of the straight chromium

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martensitic or ferritic grades. In some of these, there is a high-silicon content and, as a result, they enjoy adequate scaling resistance. Unfortunately, however, they have rather poor resistance to corrosion by lead compounds and are decidedly inferior in the properties of hot hardness and stretch resistance under operating conditions.

Apart from straight-chromium stainless steel valves, there are valves in the prior art made of certain grades of austenitic chromium-nickel stainless steel. The amounts of silicon in the conventional chromium-nickel stainless steel valve ranges from about 0.50% to 4.0% or more. As a general class, it may be noted that the austenitic steel valves have a more favorable lattice structure for resisting stress-rupture and creep at elevated temperatures than do the ferritic or martensitic products. It is also true that the relatively high alloy content of the chromium-nickel austenitic steels favors resistance to scaling from heat at elevated temperatures.

A further advantage of the austenitic chromium-nickel valves is their freedom from phase transformation and in this respect freedom from volume changes and any resulting tendencies such as warping, sticking or cracking during the heating and cooling cycles brought about by the heat from the engine and its operation. Despite the many advantages of the heretofore known austenitic chromium-nickel stainless steel valves, however, much is left to be desired of their resistance to corrosive attack by the combustion gases of leaded fuels.

An outstanding object of my invention, accordingly, is the provision of high temperature heat and corrosion resistant austenitic chromium-nickel stainless steel internal combustion engine valves, valve parts and other engine components which possess great hardness at the high operating temperatures encountered, resist stretching at these temperatures and yet withstand oxidation and scaling, and effectively and reliably resist attack by leaded fuels, and their combustion products.

Referring now more particularly to the practice of my invention, my stainless steel manufactures, such as poppet valves, valve components, illustratively casings, head, stems, springs, cladding, linings, or surfacing, are importantly austenitic and contain chromium and nickel and have a critically low silicon content. In preferred composition, my products include about 0.08% to 1.50% carbon, from 12% to 30% chromium, 2%

to 35% nickel, from very small amounts up to about 0.20% silicon, and the remainder substantially all iron. The carbon content preferably amounts to some 0.40% to 1.50% to achieve desired hot-hardness. By keeping the silicon content below about 0.20% and preferably below 0.15%, and even better at amounts ranging from about 0.10% down to substantially zero, I find sharp improvement in resistance of the steel products to corrosion and attack by products of combustion from the burning of leaded fuel. Surprisingly enough, I find this is not adversely affected by the high carbon content.

My stainless steel valves, and engine components, and valve parts have a sulphur content which may be some quantity below about 0.04%, or even as much as 0.50% or more. The larger quantities of sulphur, and especially those between about 0.15% to 0.50%, contribute to the effect of the low silicon content in promoting resistance to attack by the combustion products of leaded gasolines and the like. The larger quantities of sulphur, say those beyond 0.04%, usually improve the machining properties of the steel. Amounts of sulphur much beyond 0.50% often introduce hot working difficulties with certain of the steels which I employ; also, the rate of improvement of resistance to lead-oxide corrosion usually decreases for the larger amounts. The phosphorus content of my steel valves and parts preferably is below 0.04%. Likewise, the nitrogen content usually is below 0.30%, this at times partially replacing the carbon and nickel. Manganese, where present at all, seldom exceeds 1%, this element normally appearing in some small amount as an incident to production of the alloy steel. There are occasions too where my stainless steel valves include in the alloy composition thereof, as for special purposes, one or more such elements as molybdenum, titanium, columbium, tungsten, vanadium, cobalt, copper, tantalum, aluminum, zirconium, or the like, ranging from quite small to substantial amounts not inconsistent with properties desired.

The particular amounts of such elements as chromium and nickel present in the austenitic stainless steel valve products which I provide contribute to heat resistance and oxidation resistance at the high temperatures of product use. The amount of carbon employed not only serves to promote the austenitic structure, as does nickel, but also contributes to the hardness at the high temperatures encountered in use. Also, the restriction of silicon to the critically small amounts indicated, importantly contributes to corrosion resistance of the products when subjected to the combustion products of the leaded fuels, as where the steel takes the form of an exhaust valve or part exposed to aircraft, truck or passenger car engine exhaust gases.

By virtue of the austenitic quality of the steel, my valve products are not susceptible to phase transformation during heating and cooling cycles and, accordingly, are free of volume changes and difficulties often following upon change of phase. The valves are hard, strong and tough at the high temperatures encountered. They resist scaling, warping and cracking at full temperature and upon being cooled and reheated.

In Table I below, and in the accompanying drawing, the approximate effect of different amounts of silicon on corrosion-resistance of 21% chromium-15% nickel stainless steel valves in molten lead oxide, is graphically illustrated. The corrosion attack of each steel by molten lead oxide is represented by weight loss in grams per square decimeter per hour, the tests being taken with the molten lead oxide at a temperature of 1675° F.

TABLE I

Influence of silicon content of chromium-nickel stainless steel on resistance to molten lead oxide

Sample	Silicon Content, Per cent	Weight Loss, 1675° F.
A	0.08	4.30
B	0.14	7.18
C	0.20	12.37
D	0.24	13.94
E	0.35	19.98
F	0.45	18.55
G	0.97	18.04
H	1.36	17.51
I	1.59	16.48
J	1.96	15.87
K	4.06	13.31

In this table, and in the graph, it is clear that by lowering the silicon content of the steel from about 0.20% (Sample C), a sharp improvement is had in the resistance to lead-oxide corrosion. This is a highly valuable property, as represented, for example, by the samples having 0.14% silicon and 0.08% silicon (Samples B and A).

Hardness values at 1400° F are given in Table II below for two samples of my valve steel as compared with a conventional valve steel. Additionally, there are given comparative corrosion losses in molten lead oxide at 1675° F. for one hour. Hardness values are in Brinell, using a cold ball penetrator. Lead oxide corrosion is represented by weight loss in grams per square decimeter per hour.

TABLE II

Comparative corrosion-resistance to molten lead oxide and hot-hardness values for several valve steels

Sample	C	Mn	Si	Cr	Ni	Weight Loss, 1675° F.	Hot-Hardness at 1400° F.
XB	.713	.64	1.85	20.83	2.26	16.43	68
B	.075	.46	.14	20.89	15.00	7.18	108
L	.609	.56	.11	20.97	14.77	7.93	137

The first example given illustrates the excessive weight loss in molten lead oxide encountered by the commonly known type XB martensitic valve steel. As contrasted with this showing, excellent resistance to corrosion by molten lead oxide is enjoyed by the next two samples, these being in accordance with my invention. It also is noted that these steels possess great hardness at the high temperatures encountered in internal combustion engines, this hardness at high temperatures significantly increasing with carbon content. Both hot-hardness values, however, substantially exceed that had in the conventional martensitic steel (type XB).

Excellent results likewise are had in a steel containing about 21% chromium, 12% nickel, .20% silicon or less, with remainder substantially all iron. Thus, for example, a steel containing 21.6% chromium, 12.35% nickel, .15% silicon, .08% carbon and remainder iron is found to have a weight loss of only 8.0 gms./sq. dec./hour at 1675° F., combined with substantial hardness at high temperatures.

Similarly, excellent results are had in a 20–35 chromium-nickel stainless steel containing .20% silicon or less. Thus a sample having about 20.0%

chromium, about 35.0% nickel, about .08% carbon, .19% silicon has a weight loss of 9.18 gms./sq. dec./hour at 1675° F., while a sample analyzing 19.97% chromium, 35.12% nickel, .07% carbon, with .09% silicon and remainder iron has a loss of 3.98 gms./sq. dec./hour at 1675° F., substantial hardness at high temperature being enjoyed by both.

Thus it will be seen that in this invention there are provided a wide variety of low silicon austenitic chromium-nickel stainless steel articles and products, in which the various objects noted hereinbefore together with many thoroughly practical advantages are successfully achieved. It will be also seen that the products are well suited for resisting corrosion by the combustion products of fuels such as those containing tetraethyl lead.

While certain of the articles which I provide take the form of valves for internal combustion engines, it will be understood that the invention at times includes other products of the low-silicon steel, among which are high temperature gas turbine nozzles, turbine parts adjacent to the nozzle, and any of a variety of supercharger components.

As many possible embodiments may be made of my invention, and as many changes may be made in the embodiments hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative and not as a limitation.

I claim:

1. Chromium-nickel stainless steel having substantial hardness at high temperatures and low stretch in combination with substantial resistance to corrosion at high temperatures in the presence of leaded fuel combustion products, and containing about 0.08% to 1.50% carbon, about 12% to 30% chromium, 2% to 35% nickel, all in such proportions as to assure a substantially fully austenitic structure, silicon not exceeding about 0.20%, 0.15% to 0.50% sulphur, phosphorus not exceeding 0.04%, and the remainder substantially all iron.

2. Austenitic chromium-nickel stainless steel internal combustion engine valves having great hardness at high temperatures and low stretch in combination with substantial resistance to corrosion in the presence of leaded fuels or their combustion products at operating temperatures, and containing about 0.08% to 1.50% carbon, 12% to 30% chromium, 2% to 35% nickel, silicon not exceeding about 0.20%, sulphur about 0.15% to 0.50%, phosphorus not exceeding 0.04%, and the remainder substantially all iron.

3. Austenitic chromium-nickel stainless steel having great hardness at high temperatures and low stretch in combination with substantial resistance to the combustion products of leaded fuels, and containing about 0.4% to 1.5% carbon, about 21% chromium, about 15% nickel, silicon not exceeding 0.20%, and the remainder substantially all iron.

4. An austenitic chromium-nickel stainless steel internal combustion engine exhaust valve and containing about 0.08% to 1.50% carbon, about 20% chromium, about 35% nickel, silicon about 0.10% or less, and the remainder substantially all iron.

5. Chromium-nickel stainless steel having substantial hardness at high temperatures and low stretch in combination with substantial resistance to corrosion in the presence of leaded fuel combustion products, and containing about 0.40% to 1.50% carbon, 12% to 30% chromium, 2% to 35% nickel, all in such proportions as to assure a substantially fully austenitic structure, with the silicon content not exceeding about 0.20%, and the remainder substantially all iron.

6. Chromium-nickel stainless steel having great hardness at high temperatures and low stretch in combination with substantial resistance to the combustion products of leaded fuels at high temperatures, and containing about 12% to 30% chromium, 2% to 35% nickel, 0.40% to 1.50% carbon, all in such proportions as to assure a substantially fully austenitic structure, silicon not exceeding 0.10%, and the remainder substantially all iron.

7. An austenitic chromium-nickel stainless steel internal combustion engine exhaust valve containing about 0.40% to 1.50% carbon, about 21% chromium, about 15% nickel, silicon not exceeding 0.20%, and the remainder substantially all iron.

8. An austenitic chromium-nickel stainless steel internal combustion engine exhaust valve containing about 0.40% to 1.50% carbon, about 21% chromium, about 12% nickel, silicon not exceeding about 0.20%, and the remainder substantially all iron.

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