FIG. 1
TAPPET CONTACT FACE

CARBON UP TO 1.5%
MANGANESE 3% TO 12%
SILICON UP TO 4.5%
CHROMIUM 12% TO 25%
NICKEL 2% TO 7%
IRON REMAINDER

NITRIDED CASE 0.004" THICK.
HARDNESS ABOUT ROCKWELL C69.

VALVE FACE
(STELLITE)

FIG. 2

CARBON UP TO 1.5%
MANGANESE 3% TO 12%
SILICON UP TO 4.5%
CHROMIUM 12% TO 25%
NICKEL 2% TO 7%
IRON REMAINDER

NITRIDED CASE 0.004" THICK.
HARDNESS ABOUT ROCKWELL C69.

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BY
His ATTORNEY
My invention relates generally to internal combustion engine valves and like articles displaying a high degree of surface hardness.

Among the objects of my invention is the provision of internal combustion engine valves and like articles fabricated from comparatively inexpensive alloys involving minimum use of rare, scarce and strategically important metals consistent with required good results that can be readily nitrided to display a high degree of hardness to adequate depth, which articles display enhanced wear-resisting qualities under high temperature operation in the presence of corrosive atmospheres even when subjected to repeated stressing, possessing a high degree of surface hardness to adequate depth effectively resisting both wear and corrosion, without detrimental scouring, spalling or galling under high temperature operation in the presence of corrosive atmospheres.

Other objects and advantages will be obvious in part and in part more fully pointed out hereinafter during the course of the following description, taken in the light of the accompanying drawings.

My invention accordingly resides in the combination of elements, composition of materials and in the relation of each of the same with one or more of the others, the scope of the application of all of which is more fully set forth in the claims at the end of this specification.

In the drawing, Figures 1 and 2 respectively disclose, in vertical section, a hollow-stem aircraft valve, and a solid-stem, heavy-duty valve as typically employed in truck engines and other heavy automotive or stationary equipment, while Figures 3, 4 and 5 disclose micro-hardness determination, at 250X magnification, at and adjacent the surface of articles according to my invention.

As conducing to a better understanding of my invention it may be noted that in many instances the high resistance to wear so advantageously displayed by many steels and alloy metals at room temperatures becomes appreciably diminished when subjected to the higher ranges of temperature. Particularly this unsatisfactory situation is encountered when, at elevated temperatures, the metals are subjected to corrosive atmospheres. For when the metal parts are subjected to movement relative to each other under such conditions, important and highly detrimental wear and abrasion are almost invariably encountered. Repeated stressing under such conditions frequently results in rapid wear, corrosion and early failure. Such unsought phenomena assume particular importance in internal combustion engines, this including not only the conventional gasoline engine but as well both the full diesel and the semi-diesel engines. For these engines have in common that the valves thereof, particularly the exhaust valves, are subjected to high temperature operation.

While it is true that the valve stem operates at a temperature considerably lower than the head, this by consequence of the internal cooling means provided for the valves, it is here that the combination of mechanical wear at substantial temperatures is directly felt. And although it is common practice to employ valve inserts, formed illustratively of Stellite (cobalt, chromium and tungsten alloys) to resist wear under the high temperatures at the face of the valve, where it contacts against the valve seat, the high cost of these alloy metals, the undesirable use of strategic materials in important quantities and the cost of machining precludes this series of alloys for the production engineer. Moreover, despite the characteristic hardness and corrosion resisting qualities of this series of alloys, other inherent qualities render them out entirely suited for the formation of the stem of the valve.

In the prior art the 14-16-2 alloy has proved quite satisfactory for valve construction. This alloy, comprising 14% chromium, 14% nickel, and 2% tungsten, and the balance substantially all iron, was long used in the standard aircraft exhaust valves. This metal, however, has largely given way, since World War II, to the present standard aircraft exhaust valve made from an alloy known in the trade as TPM, the familiar designation for the low carbon alloy comprising 73% nickel, 16% chromium, 3% titanium and remaining iron. The inherent detriment exists in TPM, however, that not only is nickel employed in lavish proportions at great expense, but the very use of such important percentages of this highly strategic material in itself is most undesirable.

An important object of my invention, therefore, is to avoid in substantial measure the many disadvantages heretofore confronting the art, and in so doing provide an alloy valve involving the use of non-strategic metals of low cost and comparatively widespread availability which may be successfully hardened at the wearing surface in ready, simple and predictable manner so as to display requisite hardness and resistance to both wear and corrosion when exposed to comparatively high temperatures in the presence of corrosive atmospheres and this even when subjected to repeated stressing.

And now having reference more particularly to the practice of my invention I have found that surprisingly, chromium-bearing stainless steels of low nickel content and high manganese content can be successfully nitried in ready and simple manner to provide a surface casing of adequate depth and displaying highly advantageous resistance to both wear and corrosion under high temperature operation in the presence of importantly unfavorable atmospheric conditions. By the use of such alloy, treated in the foregoing manner, I achieve important savings in nickel, presently an extremely important and strategic metal in short supply, without sacrifice in the desired good qualities. As well, all use of both titanium and tungsten is effectively avoided. Moreover, I find that to a certain extent the desirable results I achieve can be even further improved to moderate extent by including sulfur and nitrogen in the alloy.

By illustration, a typical but non-limitative analysis of alloy article responding to my invention includes up to about 0.60% carbon, about 9.00% manganese, phosphorus up to about 0.03% maximum, sulfur up to about 0.07%, silicon up to about 0.15%, chromium about 21.00%, nickel about 4.00%, and the balance substantially all iron. Certain advantages are had when even broader ranges of the ingredients are employed, such as carbon up to 1.5%, manganese 3% to 12%, silicon up to 0.45%, chromium 12% to 25%, nickel 2% to 7%, and remaining substantially all iron. Where desired sulfur up to about 0.20% and/or nitrogen up to about 0.6% may be included.

I have found that such alloy steels are successfully nitried in ready and simple manner following known techniques, for example as shown in the U. S. Patent
It will be seen that the three test heats are substantially alike in manganese, chromium and nickel contents but that in the 21-4 Mn (N-S) grade the carbon content is high, with moderate sulfur and high nitrogen. In the modified 21-4 Mn (N-S) grade the carbon content is appreciably less, together with high sulfur and high nitrogen content. In the straight 21-4 Mn grade the carbon content is high while sulfur and nitrogen contents are negligible.

In Table II I set forth the results attending upon nitriding and determined by appropriate microscopic and physical tests. I carried out these microscopic hardness determinations, both along the nitrided case and the original materials, with an Eberach micro-hardness testing machine.

### TABLE II

<table>
<thead>
<tr>
<th>Grade</th>
<th>Heat</th>
<th>Size</th>
<th>Heat Treated Condition</th>
<th>Hardness Rockwell C</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-4 Mn (N-S)</td>
<td>041001</td>
<td>5/6&quot; x 4&quot; long.</td>
<td>Hot Rolled</td>
<td>35</td>
</tr>
<tr>
<td>Mod. 21-4 Mn</td>
<td>061013</td>
<td>Do</td>
<td>Do</td>
<td>29</td>
</tr>
<tr>
<td>21-4 Mn</td>
<td>18506</td>
<td>5/6&quot; x 3/8&quot; long.</td>
<td>200F-1 Hr. Wq.</td>
<td>23</td>
</tr>
</tbody>
</table>

### TABLE III

<table>
<thead>
<tr>
<th>Grade</th>
<th>Heat</th>
<th>Avg. Depth of Case, inches</th>
<th>Average Case Hardness</th>
<th>VIN</th>
<th>Ht</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-4 Mn (N-S)</td>
<td>041001</td>
<td>0.005</td>
<td>1070</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>Mod. 21-4 Mn (N-S)</td>
<td>081015</td>
<td>0.006</td>
<td>904</td>
<td>68.5</td>
<td></td>
</tr>
<tr>
<td>21-4 Mn</td>
<td>18506</td>
<td>0.006</td>
<td>914</td>
<td>68.5</td>
<td></td>
</tr>
</tbody>
</table>

From Table III it will be seen that the articles of my invention possess a case hardening extending to a depth of about 0.004 inch, with hardness of 1014 Vickers, equivalent to about Rockwell C 69. This responds extremely well to the requirements of the industry that the hardened case of nitrided aircraft valve stems display a minimum thickness of at least 0.003 inch with a hardness at 5 kilograms load of at least 750 Vickers, equivalent to at least 62.5 Rockwell C. Moreover, it will be seen that in addition to the nitrided articles of the straight grade of 21-4 chromium-manganese steels, of low silicon and nitrogen contents, the nitrided articles of the 21-4 manganese steel including both sulfur and nitrogen in moderate to substantial amounts possess excellent wear resisting properties. Both the low carbon and high carbon alloys respond equally to nitriding.

In all instances it will be seen that the case depth is adequate and that a high degree of surface hardening is obtained. This is rather forcibly shown in the several photographs depicted in Figures 3, 4 and 5. In these figures the effective gradation of hardening to the interior of the metal to the surface is strikingly emphasized both as to depth of penetration and the average hardness had. And it will be noted that the average depth of nitrided case amounts to 0.003 inch, 0.006 inch and 0.004 inch respectively. The corresponding average case hardnesses are Rockwell C 70.0, 68.5, and 66.5.

In my valves and the like substantial savings in nickel are made possible, with satisfactory hardness and resistance to both corrosion and wear even under high temperature, corrosive atmospheric conditions. In aircraft engines, these valves, operating in the guides at temperatures of about 900° F. display long life with only moderate wear. And this is true, despite the highly-corrosive condensate which forms at the valve head and seat, and then clings to the valve stem.

The case-hardening, while perhaps not penetrating quite to the same depth as in the carbon steels, extends to a depth adequate to insure satisfactory operating under even these extreme temperature and atmospheric conditions. The average depth of case-hardening I achieve, about 0.004 inch, is substantially in excess of the minimum requirements of the industry, and effectively fulfills all requirements encountered in practice.

In my opinion there is no tendency of the metal to spall off the surface. This is in sharp and surprising contrast with the conventional chromium-nickel steels. For here when attempt is made to nitride them, the surface layers tend to expand, putting the metal under compression. As a result there is a strong tendency for the surface layers to burst and spall off. Perhaps this tendency is resisted in my valve steels by the formation of manganese nitrides at the surface of the metal. These nitrides are more stable than the chromium-nitrides formed in conventional steels and may tend to resist the bursting and spalling. While I suggest this as a possible explanation, I am by no means certain this explanation is correct, and I do not desire to be bound thereby. It is certain, however, that the nitriding produces manganese nitrides. And I conclude that little, if any, chromium is tied up in the form of nitrides, leaving this element free to impart to the metal, even after case-hardening, its characteristic corrosion-resisting qualities.

A further advantage of my invention is that it now becomes entirely practical to form heavy duty valves, such as those employed in truck and bus engines, in a single piece. This is a distinct advantage over the prior two-piece construction in which it is necessary to weld the head, formed of one alloy, onto the stem, formed of another alloy, in order to achieve the combination of the required wear-resistance of the stem with the corrosion-resistance of the head. My 21-4 manganese nitrided valves effectively resist the corrosive atmospheres encountered at the prevailing valve head temperatures of approximately 1600° F., as well as the stem wear at 700°--1000° F., this displaying long, useful life.

All the foregoing, as well as many other highly practical advantages, attend upon the practice of my invention.

It is at once apparent that following initial disclosure of my invention, many embodiments will readily suggest themselves to those skilled in the art, accordingly I intend the foregoing disclosure to be considered as illustrative, and not as a limitation.
I claim as my invention:

1. Internal combustion engine valve free of tungsten and titanium in composition and essentially consisting of carbon from about 0.30% to about 0.65%, manganese about 8% to about 10%, sulfur up to about 0.2%, silicon up to about 0.45%, chromium about 20% to 22%, nickel from about 2.5% to about 4.5%, nitrogen up to about 0.4%, and the balance iron having a surface case of at least 0.003 inches thick essentially including nitrogen and with hardness at least about Rockwell C-69.

2. Internal combustion engine valve essentially consisting of about 0.30% to 0.65% carbon, about 9% manganese, about 3% to 4% nickel, about 21% chromium, up to 0.2% sulfur, up to 0.4% nitrogen, and the balance iron having an exterior case approximately 0.004 inch thick consisting largely of manganese nitrides and with hardness of approximately Rockwell C-69.

3. An internal combustion engine valve having a head portion and a stem portion in which the stem portion at least essentially consisting of approximately 0.30% to 0.65% carbon, chromium about 20% to 22%, nickel about 3.0 to 4.5%, manganese about 8% to 10%, nitrogen up to approximately .4%, sulfur up to approximately .10%, silicon up to approximately 0.45%, and the balance iron having a surface case of at least 0.003 inches thick essentially including nitrogen and with hardness at least about Rockwell C-69.

4. A hollow stem internal combustion engine valve essentially consisting of about 21.0% chromium, from about 2.5% to about 4.5% nickel, from about 8.0% to about 10.0% manganese, carbon ranging from 0.30% to about .65%, sulfur up to about 0.10%, silicon up to about 0.45%, nitrogen ranging up to about 0.4%, and the balance iron, having a surface case of at least 0.003 inches thick essentially including nitrogen and with hardness at least to about Rockwell C-69.

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