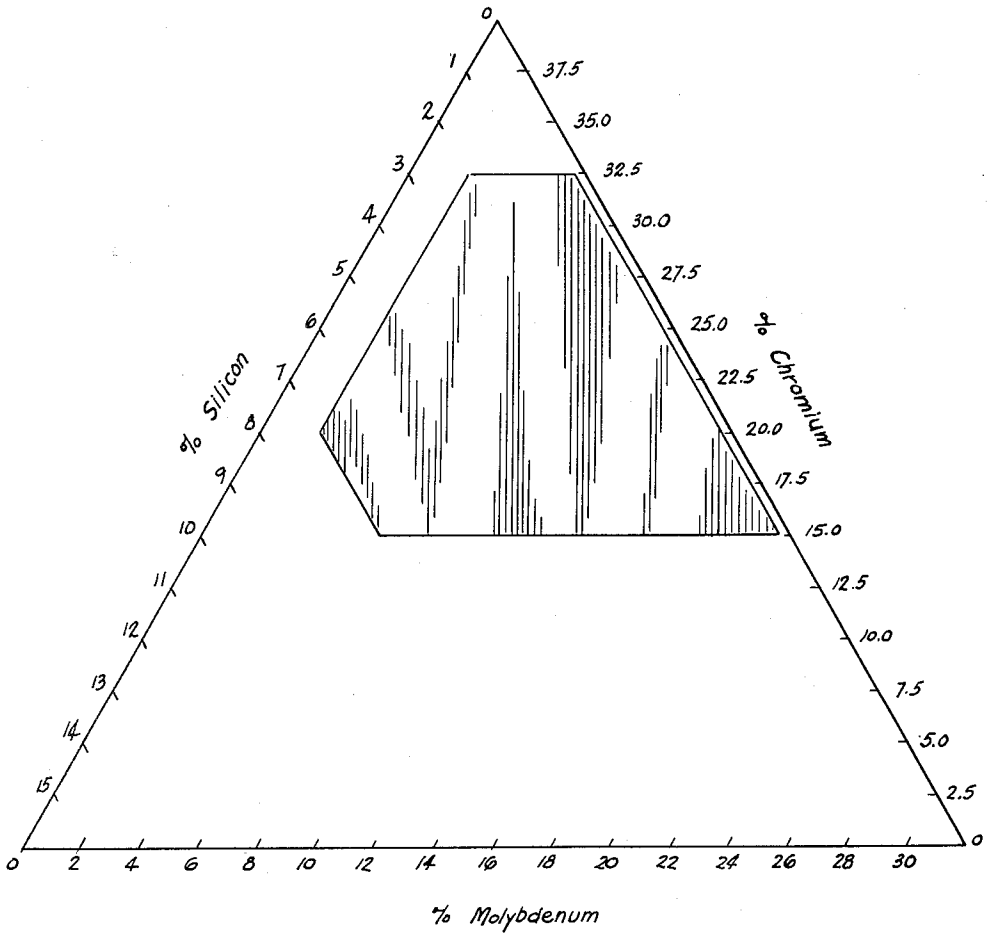
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HARDENABLE CORROSION RESISTANT STAINLESS STEEL

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HARDENABLE CORROSION RESISTANT STAINLESS STEEL

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This invention relates to stainless steels, and more particularly to a hardenable corrosion resistant stainless steel which is adapted to handle corrosives where an erosion or abrasion condition also exists.

Hitherto the popular stainless steel alloy known as the "20" type alloy has been used in considerable amount to handle such corrosives. However, due to its inherent softness (the Brinell hardness number being in the low range of 130–140), accelerated attack has been produced under conditions of high velocity of the corrodent combined with abrasion such as is caused by corrosive slurries.

The object of this invention is to so improve the "20" type alloy composition as to produce a hard steel resistant to velocity and abrasion in the presence of sulfuric and other mineral acids and corrosive salts.

Previously, I have produced a modest amount of hardness in the "20" type alloy through the use of columbium and a slight increase in silicon, with or without nitrogen, as explained in my Patent No. 2,750,282, granted June 12, 1956, and which produced some improvement in the resistance of the type "20" alloy to wear, galling and abrasion.

Now I have discovered that a much greater hardness (preferably 241 or more BHN) and accompanying further improvement in desirable resistance to this wear, galling, and abrasion may be produced in a different manner without use of columbium and nitrogen. These elements may be further added if desired, but are not necessary.

I control the hardness in my new alloy by varying the silicon, chromium and molybdenum over definite ranges, and in definite relative proportions, as described in the following specification, and as shown in the ternary diagram of the accompanying drawing, to produce a degree of hardness most suited to the specific application.

The shaded area within this plot shows combinations (common intersection points) of silicon, chromium and molybdenum, which produce a desired hardness of 241 BHN. All data given is for solution annealed material, heated to a temperature of 2050° F. to 2100° F. and held there for one hour per inch thickness of material, and then water quenched.

Hardness levels up to 400 BHN and over can be obtained by increasing the silicon, chromium or molybdenum content above the minimum levels established by the common three-component intersection point within the shaded area in the ternary diagram. The increase in these three elements to give hardness levels above 241 BHN can be done either singularly, or collectively in varying proportions, and the choice of what element or elements are increased will be predicated on obtaining maximum corrosion resistance for the desired hardness level. This effect is shown in Tables 2 through 9 inclusive.

For corrosion resistance to reducing mineral acids, the more desirable of the new alloys are those highest in molybdenum and lowest in silicon and chromium. On the other hand, the most resistant to oxidizing mineral acids are those highest in chromium and lowest in silicon and molybdenum.

A broad composition is listed in the following table,

but the minimum silicon, chromium, and molybdenum values must also be so interrelated as to intersect within the ternary plot shown in the drawing, and even a higher value must fit within the plot and within the following broad range.

Table 1

	Percent
Carbon	.07 max.
Chromium	15–32.5
Nickel	25–35
Silicon	.2–7
Manganese	.2–4
Copper	1–5
Molybdenum	2–20

In the above composition range, carbon, manganese and copper exert little if any influence on the degree of hardness produced in the alloy range taken from the drawing. Sulfur and phosphorous in small amounts, and traces of other elements are sometimes present, as naturally occurring contamination and do not in these quantities influence the herein described effects.

I shall give some specific examples of my invention, but before doing so I shall give tables of values showing alloys which were made and tested with a view to isolating the effect of changes in particular elements. Thus I have found that an increase in silicon alone in a stainless steel alloy of the "20" type does not increase hardness, as will be seen in the following table.

Table 2

	#4043	#FA-6
Carbon	.070	.050
Chromium	20.25	19.15
Nickel	29.40	30.80
Silicon	1.37	3.03
Copper	4.10	3.60
Molybdenum	3.66	3.59
BHN	140	143

In the above table the values of the elements other than silicon have been kept substantially constant. The increase of silicon from 1.37 to 3.03%, or more than double in amount, resulted in no significant increase in hardness, the change shown from 140 to 143 BHN being negligible.

Therefore increasing silicon alone in a typical "20" type analysis results in no increase in hardness. To illustrate the validity of this conclusion and also to illustrate the use of the ternary plot, reference may be made to alloy 4043 as an example. If the chromium and molybdenum contents (since they are the most important elements with regard to corrosion resistance) of this alloy are selected to obtain an intersection point on the plot, it is found that the required silicon content to give a 241 BHN is 6.20 percent. The actual silicon content (1.37) is much below this, and the hardness is well below the desired 241 BHN.

I performed a test to show the effect of increasing molybdenum alone, with the results shown in the following table:

Table 3

	#4043	#FA-13
Carbon	.070	.061
Chromium	20.25	20.20
Nickel	29.40	29.46
Silicon	1.37	.76
Copper	4.10	4.08
Molybdenum	3.66	6.26
BHN	140	172

In the foregoing it will be seen that the elements other

than silicon and molybdenum were substantially constant. (The change in silicon was unintended, and previous experiment showed that a silicon change in such low inadequate amounts did not appreciably affect hardness.) The molybdenum value here was nearly doubled, up to 6.26% and there was an increase in hardness from 140 to 172 BHN, which is appreciable but not nearly in the hardness range of over 241 BHN here being sought.

Some additional experiments showed that an increase in silicon does not appreciably increase hardness when dealing with alloys having a higher molybdenum content, say 6%. This is shown in the following table:

Table 4

	#FA-13	#FA-14	#FA-15	#FA-4
Carbon	.061	.064	.041	.052
Chromium	20.20	20.65	20.10	20.60
Nickel	29.46	29.30	30.80	29.30
Silicon	.76	2.15	3.12	4.91
Copper	4.08	4.00	3.52	3.56
Molybdenum	6.26	6.02	6.00	6.29
BHN	172	217	223	241

The chromium, nickel and copper values are substantially alike. All have substantially the same amount of molybdenum, this being relatively high, and approximately 6%. The silicon values were increased all the way from 0.76 to 4.91%. This table shows that increasing the silicon in a modified "20" type alloy at a 6% molybdenum and a 20% chromium level does not produce a hardness of 241 BHN until the silicon content is such that it agrees with the silicon content established by plotting the chromium and molybdenum content on the ternary plot. For alloy FA–4 (and the other three examples also) a plot of chromium and molybdenum gives a required silicon of about 4.70 percent silicon for a hardness of 241. If we consider the accuracy tolerance of chemical analyses and hardness measurements this agrees very well with the hardness (241) and silicon content (4.91) of this heat #FA–4.

I next considered the effect of increasing molybdenum much further, while maintaining a constant value of silicon of about 3%, and the results were as follows:

Table 5

	#FA-16	#FA-15	#FA-18	#FA-17
Carbon	.070	.041	.045	.031
Chromium	19.00	20.10	19.83	20.10
Nickel	27.90	30.80	29.90	29.40
Silicon	3.08	3.12	3.04	3.01
Copper	3.60	3.52	4.00	3.52
Molybdenum	2.09	6.00	10.50	15.28
BHN	143	223	285	336

It will be seen from the foregoing table that the chromium, nickel and copper values were substantially constant and that silicon was kept at substantially 3% in all examples. The molybdenum was increased all the way from 2.09 to 15.28%, with a gratifying and substantial increase in hardness from 143 to 336 BHN. Examples FA–18 and FA–17 bring the hardness above the desired minimum of 241 BHN, the molybdenum values being in excess for a value of 241. However molybdenum is an expensive element to use, and to increase hardness solely by the addition of molybdenum may prove prohibitively expensive for some purposes.

Table 5 shows that increasing the molybdenum at a 20% chromium level and 3% silicon level does not produce the hardness of 241 BHN until the molybdenum content is between 6.00 and 10.50 percent. From the ternary plot it can be determined that for 20% chromium and 3% silicon, the required molybdenum is 10 percent. This agrees with the results shown in the examples, when tolerance in chemical analysis and in hardness measurement are considered.

Even a very low chromium alloy can be hardened if the silicon and molybdenum are increased to come within the shaded area, as shown in the following table:

Table 6

	#FA-26	#FA-27
Carbon	.054%	.054%
Chromium	16.55	16.40
Nickel	28.80	28.40
Silicon	2.01	4.04
Manganese	.94	.81
Copper	3.40	3.40
Molybdenum	15.60	11.40
BHN	293	262

Example FA–27 shows that even very low chromium can be compensated by high molybdenum, and example FA–26 shows that low chromium and low silicon both can be compensated by high molybdenum, all within the shaded area of the ternary diagram.

Differently expressed, Table 6 shows examples of very low chromium alloys hardened by the correct balance of silicon and molybdenum. Plotting the silicon and molybdenum content of each of the above two examples gives a required chromium of about 15.5 percent for 241 BHN. Both of these heats are about 1% higher than the required minimum chromium content and consequently have somewhat higher hardness than 241 BHN.

I further experimented with the effect of increasing the chromium content, while maintaining silicon at approximately the 3% level. The results are shown in the following table:

Table 7

	#FA-7	#FA-8	#FA-1	#FA-12
Carbon	.056	.060	.053	.046
Chromium	21.85	24.00	26.95	29.80
Nickel	28.20	29.10	28.70	28.20
Silicon	3.12	2.95	2.76	2.83
Copper	3.36	3.64	3.28	3.68
Molybdenum	6.20	6.35	6.30	5.77
BHN	196	241	286	321

This table shows that an increase in chromium from 21.85% to 29.80% produced an increase in hardness of from 196 to 321 BHN, while maintaining silicon and molybdenum at the desirable levels of about 3% and 6% respectively, thereby avoiding the cost of increasing molybdenum to a much higher value than 6%. Examples FA–8, FA–1, and FA–12 reach or exceed the 241 BHN hardness, and these examples come within the shaded area of the ternary diagram.

Differently expressed, Table 7 shows that increasing the chromium at a 3% silicon and 6% molybdenum level does not produce the minimum hardness of 241 BHN until the chromium content it at least 24 percent. If the silicon and molybdenum content of alloy FA–8 are plotted on the ternary diagram it is found that the required chromium for a hardness of 241 BHN is 24.50. This agrees very well with the chromium content of this heat of 24.0 percent.

I also explored the possibility that an increase in chromium might produce the desired hardness with an increase in silicon, and without an increase in molybdenum, but the following examples show that increasing silicon alone is not effective for this purpose.

Table 8

	#FA-10	#FA-11
Carbon	.060	.068
Chromium	24.00	25.80
Nickel	28.20	28.50
Silicon	4.12	4.16
Copper	3.60	3.52
Molybdenum	3.59	3.57
BHN	228	228

Examination of the foregoing table shows that with

alloys using approximately 25% instead of 20% chromium, and with molybdenum held at about the 3% instead of the 6% level, an increase of silicon from say 3% to over 4% produced a hardness of only 228 BHN, which is inadaquate for the present purpose.

Differently expressed, this Table 8 shows that a combination of high chromium and high silicon is ineffectual in producing high hardness at a low molybdenum level. Plotting the chromium and silicon for alloy FA–10 shows that a substantially higher percent of molybdenum would be needed to give a hardness of 241 BHN.

By combining high chromium and high silicon with approximately 6% molybdenum I find that extraordinarily high hardness values are obtainable. This is illustrated in the following examples:

Table 9

	#FA-3	#FA-5
Carbon	.071	.068
Chromium	30.95	30.45
Nickel	30.60	29.95
Silicon	4.94	4.90
Copper	3.56	3.80
Molybdenum	6.42	6.52
BHN	418	444

The foregoing table shows that an increase of chromium to about 30% and an increase of silicon to near 5%, when used in an alloy having about 6% molybdenum, produced BHN values higher than 400, which is higher than needed for the present purpose. Indeed I prefer somewhat lower BHN values in order to maintain a desirable amount of ductility.

Differently expressed, Table 9 shows that high hardness values are produced with high chromium when silicon is about 5 percent, and molybdenum is about 6.5 percent. If the points of 5 percent silicon and 6.5 percent molybdenum are plotted on the ternary diagram it is found that about 19.5 percent chromium will give a hardness of about 241 BHN. In these two examples the chromium content is about 11 percent greater than the required minimum and consequently a hardness level of over 400 BHN is obtained.

It may be recalled that in my Patent 2,750,282 I taught the use of a small amount of columbium and nitrogen to harden a type "20" stainless steel alloy. I have also experimented with the addition of columbium and/or nitrogen in the following alloys, and the results are given in the following table:

Table 10

	#FA-8	#FA-19	#FA-21	#FA-22
Carbon	.060	.048	.060	.068
Chromium	24.00	24.40	24.80	24.85
Nickel	29.10	28.70	28.55	28.55
Silicon	2.95	2.93	3.00	3.18
Copper	3.64	3.44	3.40	3.52
Molybdenum	6.35	6.25	6.35	6.15
Columbium	----	.88	----	.87
Nitrogen	----	----	.13	.135
BHN	241	248	248	302

Example FA–8 shows an alloy without the addition of either columbium or nitrogen. Example FA–19 shows that the addition of columbium alone gave no appreciable increase in hardness. Example FA–21 shows that the addition of nitrogen alone produced no appreciable increase in hardness. Example FA–22 however shows that the addition of both columbium and nitrogen did produce a substantial increase in hardness of about 60 points BHN, with all of these compositions being substantially alike in other respects.

For a measure of corrosion resistance reference may be made to the following table, showing two of my alloys, and for comparison two commercially available but relatively softer alloys.

Table 11

	For Reducing Acids—#FA-23	For oxidizing Acids—#FA-29	Cast "20" Type Alloy—#4043	Cr-Ni-Mo Alloy—#3H
Carbon	.27%	.040%	.070%	.12%
Chromium	22.51	29.72	20.25	17.32
Nickel	31.00	30.54	29.40	51.16
Silicon	.95	1.01	1.37	1.02
Manganese	.62	.86	.87	----
Copper	3.86	3.80	4.10	----
Molybdenum	16.56	5.61	3.66	19.28
BHN	302	363	140	200
10% HCl Boiling i.p.m.[1]	.2140	.2792	.2495	.2200
65% H_2SO Boiling	.0166	.2130	.1825	.0210
65% HNO_3 Boiling	.0146	.0036	.0029	.1650
Wet Chlorine @100° F	.0250	.1068	.0945	.0463

[1] I.p.m. means the corrosion rate in inches penetration per month.

This table shows that in reducing hot boiling 65% sulfuric acid an alloy as balanced in Example #FA–23 may be seen to be far superior to the "20" type cast alloy and to be even slightly better than the Cr-Ni-Mo alloy type. Although worse in its resistance to boiling 65% nitric acid it is still superior to that of the commonly used Cr-Ni-Mo alloy. Its outstanding resistance in comparison to the "20" and Cr-Ni-Mo alloys is shown in warm wet chlorine gas. Alloy #FA–29 shows how resistance to strongly oxidizing boiling 65% nitric acid may be produced, but at some sacrifice in other corrosive media.

It will be understood that the hardness value of 241 Brinell represents the lowest value of an improved hardness range compared, for example, with the PH–20 alloy in my previous Patent No. 2,750,282 which has a practical upper limit of hardness two steps lower on the Brinell hardness test scale, that is, a value of 228 BHN.

In the present alloy the intersection of any three lines in the marked area of the ternary diagram represents an alloy which has a hardness of about 241 BHN. The upper limit of hardness is controlled by the composition values in the broad composition range given at the beginning of this specification. The intersection of any two lines does not limit the third element to the exact amount shown on the ternary diagram, but the third element value must be at or above the percentage as determined from the intersection on the ternary diagram.

In the foregoing tables it will be understood that the percentages are by weight, and that the balance of the composition is iron, with small amounts of impurities or other elements incidental to manufacture, i.e., traces of sulphur, phosphorous, etc. Manganese may vary from about 0.2 to 4% but more usually from 0.5 to 1.0 percent.

It is believed that the composition and characteristics of my improved precipitation hardenable stainless steel alloy, as well as the advantages thereof, will be apparent from the foregoing description. It will also be apparent that while I have shown specific examples of my alloy, changes may be made without departing from the scope of the invention, as sought to be defined in the following claims.

I claim:

1. A highly hardenable corrosion-resistant stainless steel alloy, said alloy comprising nickel in a range of from 25% to 35%, manganese in a range from 0.2% to 4%, copper in a range of from 1% to 5%, chromium in a range of from 15% to 30%, silicon in a range of from 0.2% to 7% and molybdenum in a range of from 2% to 20%, but with chromium, silicon, and molybdenum in amounts at or greater than the amounts which have a common intersection within and which if greater also come within the shaded area of the ternary diagram on the accompanying drawing; and with a carbon content not exceeding 0.07%, the remainder being essentially iron.

2. A highly hardenable corrosion-resistant stainless steel alloy, said alloy comprising nickel in a range of

from 25% to 35%, manganese in a range of from 0.2% to 4%, copper in a range of from 1% to 5%, chromium in a range of from 15% to 30%, silicon in a range of from 0.2% to 7% and molybdenum in a range of from 2% to 20%, but with chromium, silicon, and molybdenum in amounts so mutually interrelated as to approximately intersect in a common point within the shaded area of the ternary diagram on the accompanying drawing; and with a carbon content not exceeding 0.07%, the remainder being essentially iron.

3. A highly hardenable acid resistant stainless steel alloy, resistant to erosion and abrasion as by acid and other corrosive slurries, said alloy comprising approximately 20.60% chromium, 29.30% nickel, 4.91% silicon, 3.56% copper, 6.29% molybdenum, .052% carbon, with the remainder essentially iron.

4. A highly hardenable acid resistant stainless steel alloy, resistant to erosion and abrasion as by acid and other corrosive slurries, said alloy comprising approximately 22.51% chromium, 31.00% nickel, .95% silicon, 3.86% copper, 16.56% molybdenum, .027% carbon, with the remainder essentially iron.

5. A highly hardenable acid resistant stainless steel alloy, resistant to erosion and abrasion as by acid and other corrosive slurries, sand alloy comprising approximately 20.10% chromium, 29.40% nickel, 3.01% silicon, 3.52% copper, 15.28% molybdenum, .031% carbon, with the remainder essentially iron.

6. A highly hardenable acid resistant stainless steel alloy, resistant to erosion and abrasion as by acid and other corrosive slurries, said alloy comprising approximately 29.72% chromium, 30.54% nickel, 1.01% silicon, 3.80% copper, 5.61% molybdenum, .040% carbon, with the remainder essentially iron.

7. A highly hardenable acid resistant stainless steel alloy, resistant to erosion and abrasion as by acid and other corrosive slurries, said alloy comprising approximately 30.45% chromium, 29.95% nickel, 4.90% silicon, 3.80% copper, 6.52% molybdenum, .068% carbon, with the remainder essentially iron.

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