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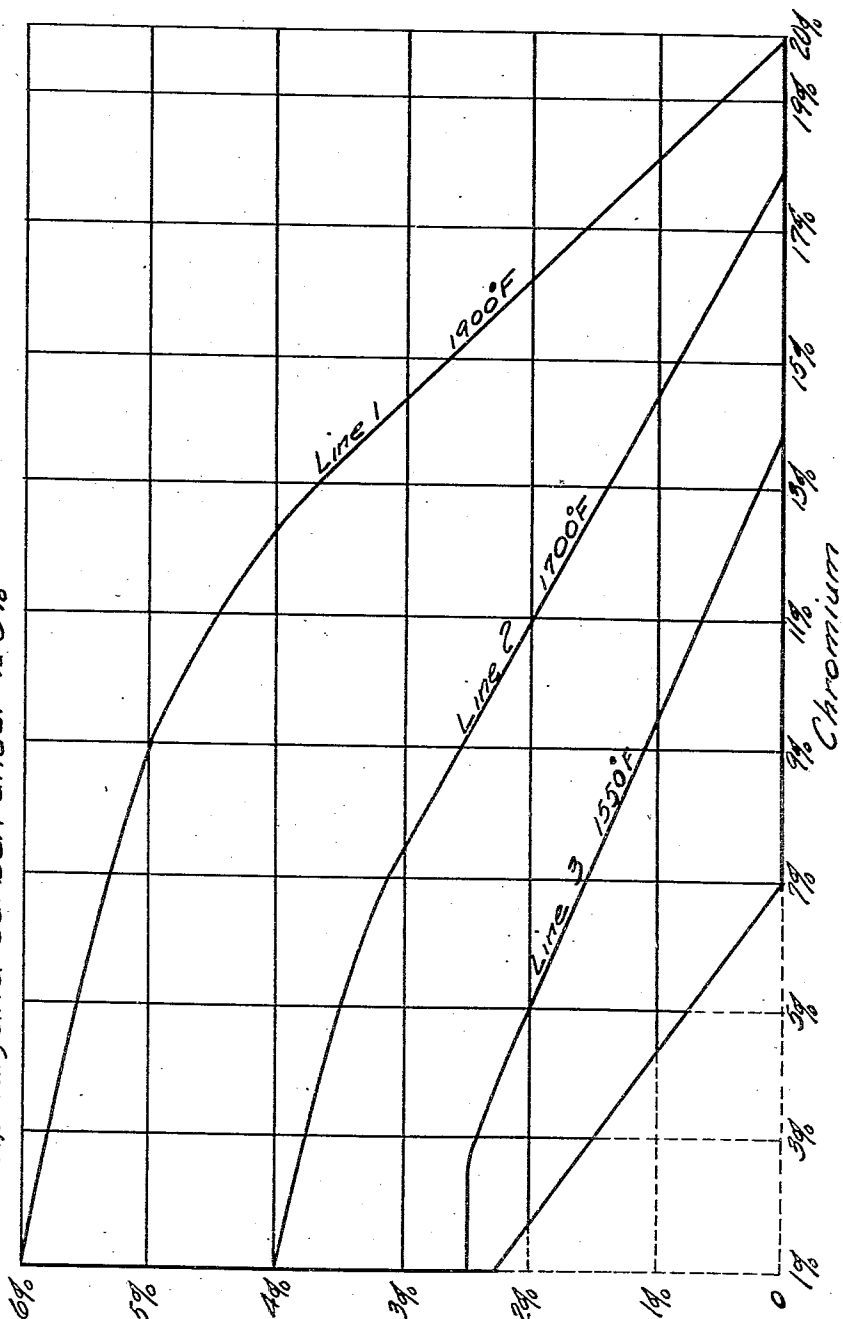
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HEAT, RUST, AND ACID RESISTING FERROUS ALLOY

Filed June 19, 1925

Scaling temperatures for alloy of chromium with aluminum, or aluminum and silicon, balance iron, with usual manganese, phosphorus, and sulphur, and carbon under .20 %



Aluminum or Silicon

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HEAT, RUST, AND ACID RESISTING FERROUS ALLOY

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My invention relates to a ferrous alloy containing chromium, aluminum and iron with or without carbon. Manganese can be used, also high melting point elements, and silicon can be used to replace in part the necessary aluminum content in about the same volume as the portion of aluminum replaced.

My alloy will contain the usual phosphorus and sulphur generally found in high grade alloy irons. The phosphorus and sulphur content should be kept low.

The essential elements are aluminum, chromium, and iron. Aluminum can be replaced in part with silicon. The chromium content should be over 1% and under 20%, aluminum under 6%, silicon under 4%, manganese under 2%, carbon under 1.25% and preferably under 75%. Nickel under 5% may be used, but the alloy is preferably nickel free, as nickel detracts from the heat resisting surface properties.

High melting point elements such as tungsten, molybdenum, uranium, zirconium, tantalum, columbium, boron, vanadium, copper and cobalt, should be under 5% each, particularly boron, which induces great brittleness, unless the quantity used is very small. Boron seems to have the effect of maintaining a small crystal size in the forged bar and in a small casting, about .001 to .002% of boron seems to be sufficient.

Chromium and iron alloyed together become increasingly scale resistant to high temperatures as the chromium content is increased.

This valuable property is greatly enhanced in the lower ranges of chromium by additions of aluminum. 3% of chromium in iron with nearly 6% of aluminum is as non-corrosive to heat oxidation at high temperatures, as 18 to 20% of chromium with practically no aluminum.

In the accompanying drawing the single figure is a chart depicting in graphic form the scale breakdown point of my alloy at various temperatures. Line 1 represents in a rough way the minimum chromium and aluminum that can be used if the alloy is to withstand a temperature of 1900 degrees F.; line 2 the minimum alloy content for those

alloys that have to withstand 1700 degrees F., and line 3 the minimum alloy content that should be used if a temperature of 1550 degrees F. is to be employed. The representation of the chart does not afford an absolutely accurate representation for obviously no hard and fast line can be drawn as the conditions under which the alloy works, type of heat, and composition of heated gases to which it is subjected all play an important part. Nevertheless the chart affords a very excellent guide for ordinary heat applications and for short time runs at heat. The following tabulation gives the analysis of a number of embodiments of my invention and the temperature at which they can generally run without progressive scaling at elevated temperatures.

C	Cr	Al	Si	Mn	Fe	Temperature at which the alloy appears to scale materially
.03	1%	2.10	.50	.41	Balance...	1550° F.
.20	2.05	2.50	.10	.35	Balance...	1550° F.
.65	1.60	3.50	.41	.31	Balance...	1550° F.
.74	2.04	3.30	.75	.22	Balance...	1550° F.
.04	5.00	1.80	.21	.40	Balance...	1550° F.
.18	7.60	1.25	.20	.10	Balance...	1550° F.
.52	9.14	.05	.54	.46	Balance...	1550° F.
.10	12.10	.20	.32	.38	Balance...	1550° F.
.27	11.03	.65	.25	.34	Balance...	1550° F.
.06	13.00	.35	.07	.15	Balance...	1550° F.
.03	14.50	.59	.46	.38	Balance...	1650° F.
.04	1.05	3.90	.25	.32	Balance...	1700° F.
.09	3.10	3.60	.28	.15	Balance...	1700° F.
.35	3.25	3.40	.30	.60	Balance...	1700° F.
.15	5.10	3.00	.20	.31	Balance...	1700° F.
.18	7.50	3.05	.18	.07	Balance...	1700° F.
.45	8.51	2.85	.30	.48	Balance...	1700° F.
.48	9.05	3.00	.40	.42	Balance...	1700° F.
.32	10.51	2.00	.36	.24	Balance...	1700° F.
.75	11.10	2.50	.68	.40	Balance...	1700° F.
.06	11.32	1.90	.25	.15	Balance...	1700° F.
.05	13.80	.30	.30	.20	Balance...	1650° F.
.04	15.06	.80	.15	.06	Balance...	1700° F.
.08	17.00	.25	.18	.26	Balance...	1700° F.
.72	17.30	.82	.31	.45	Balance...	1700° F.
.09	14.50	.75	.68	.42	Balance...	1700° F.
.15	1.05	6.04	.25	.41	Balance...	1900° F.
.04	2.05	5.60	.62	.25	Balance...	1900° F.
.08	4.18	5.20	.56	.15	Balance...	1900° F.
.12	5.40	4.80	1.00	.53	Balance...	1900° F.
.30	6.89	5.60	.38	.21	Balance...	1900° F.
.42	8.20	4.90	.51	.45	Balance...	1900° F.
.56	8.35	5.00	.60	.42	Balance...	1900° F.
.06	8.60	4.60	.56	.15	Balance...	1900° F.
.03	10.05	4.20	.42	.18	Balance...	1900° F.
.18	12.10	3.80	.54	.26	Balance...	1900° F.
.07	15.30	2.20	.75	.31	Balance...	1900° F.
.03	17.62	.71	.86	.06	Balance...	1900° F.
.09	15.20	1.75	1.10	1.25	Balance...	1900° F.
.11	19.16	.41	.20	.16	Balance...	1900° F.
.62	19.80	.65	.40	.27	Balance...	1900° F.
1.25	16.50	.40	.25	.30	Balance...	1750° F.

All the foregoing examples can be forged.

	C	Cr	Al	Si	Mn	W	Ta and Cb	Zr	Va	Ni	Mo	Fe	Scaling temper- ature
5	.06	2.10	1.75	.62	.24	1.90	---	---	---	---	---	Balance	1650° F.
	.10	1.80	2.30	1.00	.45	2.30	---	.45	---	---	---	Balance	1700° F.
	.35	2.75	3.05	.30	.38	---	2.42	---	---	---	---	Balance	1700° F.
	.07	5.10	4.10	.25	.60	1.20	1.60	---	---	---	---	Balance	1800° F.
	.40	7.00	3.80	1.10	.25	---	1.00	---	---	3.00	---	Balance	1700° F.
	.03	9.40	4.00	.45	.52	4.80	---	---	---	---	---	Balance	1900° F.
10	.07	9.22	3.80	1.00	.45	---	4.20	---	---	---	---	Balance	1900° F.
	.10	8.76	3.98	1.05	.25	---	---	---	---	---	3.00	Balance	1800° F.
	.45	8.50	3.25	.36	.52	---	2.80	---	---	---	---	Balance	1800° F.
	.48	8.64	2.05	1.50	.24	---	2.10	---	---	---	---	Balance	1750° F.
	.42	8.32	3.40	.40	.52	2.50	---	---	---	---	---	Balance	1800° F.
	.50	8.90	1.80	1.60	.48	2.10	---	---	---	---	---	Balance	1800° F.
	.65	8.80	3.20	.36	.30	1.87	---	---	---	---	---	Balance	1800° F.
	.61	8.68	3.10	.75	.45	---	2.41	---	---	---	---	Balance	1800° F.
	.45	7.06	2.50	.88	.62	---	---	3.00	.25	---	---	Balance	1800° F.
15	.07	13.10	1.25	.51	.40	---	---	2.10	---	---	---	Balance	1800° F.
	.08	15.00	.75	.60	.25	1.80	---	---	---	---	---	Balance	1850° F.
	.10	15.20	.89	.40	---	---	---	1.75	---	---	---	Balance	1850° F.
	.08	14.80	.90	.28	---	---	2.24	---	---	---	---	Balance	1850° F.

All the foregoing examples can be forged.

It will be observed on comparison with the chart that in the fifth sample of the second list containing 3% of nickel, the scaling point is reduced by at least 150° F. by the nickel present.

The acid and rust resisting properties of the alloy are dependent upon the content of aluminum and chromium plus the amount of other elements also included. Generally speaking it is the iron that rusts, therefore, the less the quantity of iron present by volume the less the alloy will corrode in the atmosphere.

My alloy owes its non-corrosive property to its film forming characteristic and the great speed in which another film is formed in the event of the protecting film being broken.

It is well known that aluminum has this property, hence it is generally considered to be non-corrosive to some atmospheres. This property is present in my alloy, though somewhat different in extent and kind.

The film that forms on my alloy is generally cathodic to the underlying metal and would cause corrosion in the presence of an electrolyte such as a damp atmosphere if it were not for the non-porous nature of the film. Should the conditions to which the alloy is subjected be excessively corrosive, then the film becomes thicker and the alloy has the appearance of surface discoloration or even superficial rust. For resistance to hot oxidation the film is generally sufficiently protective if the alloy content of aluminum and chromium is at least 8% by volume of the total and more than 40% by volume is not necessary for the purposes of this invention. For atmospheric corrosion resistance I prefer to use not less than 12% by volume of the total alloying content. The alloy is increasingly resistant to all forms of corrosion as the alloying content is increased. Owing to the chromium content of my alloy it is not very resistant to sulphuric, hydrochloric or hydrofluoric acids, but the high volume content

alloys are very resistant to air diluted fumes or very dilute acids. Passivity is generally readily produced under these conditions.

Pickling the surface with nitric acid causes the alloy to take on an oxide like film that is very resistant to atmospheric corrosion. Where circumstance will permit I prefer a nitric acid pickle surface finish. The surface of my alloy can be polished but care should be taken not to scorch the surface, as by dry polishing, since such surface seems to be very easily corroded.

Electrolytic pickling gives good results against atmospheric corrosion. I prefer to have the alloy the positive terminal of an outside E. M. F. direct current, and if the pickling medium is chromic acid there is a very excellent oxide appearing film formed upon the surface of one alloy, which in this instance is very heat resisting, beside being resistant to atmospheric corrosion.

The outside E. M. F. can be direct current of any ordinary voltage; 6 to 300 volts seems to work very well.

My alloy will not harden when quenched from high temperatures unless the carbon is carried to the higher side of my limit. Where hardening is required the carbon should be over .20% and the aluminum under 5% if the chromium is on the low end of my range, and under 2% aluminum if the chromium is at the high end of my range.

Where hardening can be produced the alloy should be heated to 1800 to 1950° F. and quenched in oil. Annealing for all analysis is preferably at 1550 to 1650° F. and slow cooling is necessary only if maximum softness is required.

If high carbon is employed the carbides will cause corrosion, as they are cathodic and the film that forms seems to be easily broken down by these cathodic areas, therefore, the carbides should be rendered as harmless to the surface as possible by dissolving them as far as convenient by a heat treatment process. The carbides seem to fairly readily dissolve in the alloy if heated to about 1900° F. and can be maintained in the dissolved state by fairly speedy cooling as by quenching in oil. Subsequent reheating to remove strains and undesirable hardness, if any is present, will cause the surface to more readily discolor than if the alloy was not reheated after the carbide dissolving treatment. No advantage with respect to corrosion is obtained by heat treatment when the alloy is heat treated and afterwards subjected to hot oxidation. There are, of course, some physical advantages. Carbon seriously detracts from the scale resistant properties of the alloy. Therefore, unless high physical properties are required carbon should be as low as practical.

The high melting point elements, such as tungsten, molybdenum, tantalum, colum-

bium, vanadium, and zirconium, have a marked effect upon the alloy as far as the physical properties are concerned, tending to raise the proportional limit in the soft condition and also to increase the strength of the alloy where raised to high temperatures. There does not seem to be any particular reason for using more than 5% each and generally 1% to 3% is sufficient. High melting point elements such as tungsten, tantalum, columbium and zirconium increase the resistance of the alloy to hot oxidation at high temperatures, also add to the corrosion resistant surface film at atmospheric temperatures, and the resistance to corrosion arising from steam, salt water and the like. These added properties are not present if the aluminum or aluminum and silicon content is very low, that is under .25%.

Nickel somewhat improves the acid corrosion resistant property of my alloy and often adds to the toughness, it detracts from the scale resisting property of the alloy at high temperature, and adds to rolling and machine troubles, therefore, for general applications I prefer to keep the nickel low or leave it out.

In melting my alloy I prefer to use an electric furnace, either induction type or the indirect arc, although the direct arc type can be used. Also crucible melting can be employed.

The high aluminum content is not readily obtained as aluminum will readily reduce the slag and contained oxides, therefore, special attention has to be paid to the addition of this element, and the bath must be well degasified either by addition of aluminum to the molten metal or by some other degasifier.

The bath should be kept as cool as possible, preferably just above freezing point, before adding the aluminum. If the slag is rich in alumina the aluminum loss is lower. Shutting off the arcs and letting the slag cool is very excellent way of preventing aluminum loss. The induction furnace is well suited to making the alloy because the slag is always fairly cool, as the current does not flow through the slag as readily as through the metal. The basic furnace is well suited, as with an acid slag the silica is apt to be reduced, raising the silicon content to undesirable quantities. A very excellent way for making the addition of aluminum is to melt down in one furnace, add all the desired elements, except aluminum, then either just before pouring add molten or solid aluminum to the bath, or teem the melt into a ladle and add the molten or solid aluminum at that time.

My alloy rolls very well and casts very solid. With about the middle range of aluminum it gives no trouble at all in rolling and pierces readily into tubes. If the aluminum

is carried to the upper limit more care has to be exercised during hot working.

The alloy to be pierced contains preferably not higher than 18% of chromium as a certain amount of brittleness is present with the high chromium content.

My alloy cold rolls very well and a high finish is readily produced for cold rolling or working. The carbon is preferably kept on the low side.

My alloy offers great resistance to abrasive wear, which adapts it for many working parts that rotate or reciprocate.

My alloy is particularly well suited for automobile engine valves because the protecting surface film is tightly adhering and of smooth surface texture, does not readily pick up bits or pit, the protecting film arising from the high aluminum alloyed with the chromium and iron is not of a sticky nature that is present with chromium and silicon that is aluminum free.

With the carbon substantially over .20% the tappet ends of the valves, which are preferably made all in one piece, that is to say, formed from a single piece of metal, can be hardened so as not to be battered up by the cam or tappet blows, the stems run well in the guides and appear to take on wear resisting characteristics from rubbing in the guides, and the valve head and valve seat do not scale when subjected to the very high heats encountered in use, as in aeroplane exhaust valves, for example.

My alloy gives excellent service used as containers subject to elevated temperatures, or for apparatus required to resist acids and liquid or atmospheric corrosion, such as saline solutions, sea water, river water, or various chloride solutions. For these purposes and where great malleability is desired, as particularly for cooking utensils, I prefer to use an alloy that has an alloying content of more than 12% by volume of the total, and having a ratio by volume of aluminum content to the chromium content of about 1 to 5. The lower the volumetric ratio, i. e. 2:5, and so forth, of aluminum to chromium, with a given amount of chromium, the greater in general is the resistance to corrosion by any medium to which the alloy is at all resistant.

The chart of the accompanying drawing can be used as a guide to choose alloys that are resistant to corrosion other than that due to hot oxidation. Generally speaking, the higher the temperature the alloy will withstand before beginning to scale progressively, the greater will be the resistance of a similar analysis in withstanding ordinary corrosion.

As shown in the examples set forth above, I have in two cases incorporated as many as three of the high melting point elements and in other cases two of these elements, and as stated these may, if desired, be used in quantities up to 5% each. Also, as stated above,

the manganese content may range up to 2% and the carbon content may go as high as 1.25%, and these taken with two of the high melting point elements in their maximum quantity, together with the phosphorus and sulphur, make a total of approximately 14%. Thus when in the ensuing claims I use the phrase "the balance being principally iron" I intend that the sum of the iron, chromium, aluminum and silicon shall be not less than about 86% of the whole.

I claim:

1. A stable surface alloy steel which is resistant to hot oxidation and is readily workable containing about 9% chromium, about 3% aluminum, and silicon within the usual ranges encountered in steel making practice but not more than about 1%, the remainder being principally iron.

2. A stable surface alloy steel which is resistant to oxidation under heat containing about 6% to 10% chromium, 1½% to 4.5% aluminum, and silicon within the usual ranges encountered in steel making practice, the remainder being principally iron.

3. A ferrous alloy comprising chromium between about 1% and 20%, aluminum between about .4% and 4.5% and silicon under 2% and not in excess of the aluminum, the balance being principally iron, and the sum of the silicon and aluminum ranging between about .5% and 5.5% and the sum of the chromium, silicon and aluminum amounting to at least 3.5%.

4. An alloy as specified in claim 3 in which the chromium is between 4% and 20% and the sum of the silicon and aluminum does not exceed 5%.

5. An alloy as specified in claim 3 in which the chromium is between 4% and 17% and the sum of the aluminum and silicon is between about .75% and 5%.

6. An alloy as specified in claim 3 in which the chromium is between 5% and 16% and the sum of aluminum and silicon is between about .75% and 5%.

7. A ferrous alloy comprising chromium between about 1% and 10%, aluminum between about 1% and 4.5%, and silicon under 2% but not in excess of the aluminum, the balance being principally iron.

8. A stable surface alloy steel which is resistant to oxidation under heat containing about 6% to 14% chromium, 1% to 4.5% aluminum and silicon within the usual ranges encountered in steel making practice, but under 1%, the balance being principally iron.

9. An alloy steel valve characterized by its resistance to hot oxidation within the following analysis: chromium 6% to 16%, aluminum 1% to 4.5% and silicon within the usual ranges encountered in steel making practice, but under 1%, the balance being principally iron.

10. A valve for internal combustion engines

characterized by its resistance to hot oxidation, of substantially the following analysis: chromium between about 1% and 20%, aluminum between about .4% and 4.5%, and silicon under 2% and not in excess of the aluminum, the balance being principally iron, and the sum of the silicon and aluminum ranging between about .5 and 5.5% and the sum of the chromium, silicon and aluminum amounting to at least 3.5%.

11. An alloy steel valve element for internal combustion engines characterized by its resistance to hot oxidation and by its forgeability and ability to be hardened, of an analysis within the following ranges: chromium between 4% and 18%, aluminum between about .4% and 4.5% and silicon under 2% and not in excess of the aluminum, the balance being principally iron, and in which the sum of the silicon and aluminum is between about 1% and 4% for chromium in the middle range, but is not less than 1.5% for the lower end of the chromium range, or over 2.5% for the upper end of the chromium range.

12. An alloy steel valve for internal combustion engines characterized by its resistance to hot oxidation, of substantially the following analysis: chromium between about 1% and 10%, aluminum between about 1% and 4.5%, and silicon under 2%, but not in excess of the aluminum, the balance being principally iron.

13. An alloy steel valve for internal combustion engines, characterized by its resistance to hot oxidation, of the alloy specified in claim 7.

14. An alloy steel valve characterized by its resistance to hot oxidation of substantially the following analysis: chromium about 9%, aluminum about 3%, and silicon within the usual ranges encountered in steel making practice but under 2%, the balance being principally iron.

In testimony whereof, I have signed my name hereto.

PERCY A. E. ARMSTRONG.

CERTIFICATE OF CORRECTION.

Patent No. 1,850,953.

Granted March 22, 1932, to

PERCY A. E. ARMSTRONG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 18, for "75%" read .75%; page 4, after line 89, insert the following as claim 12:

12. An alloy steel valve element for internal combustion engines characterized by its resistance to hot oxidation and by its forgeability and ability to be hardened, of the following analysis: chromium between 6% and 14%, aluminum between about 1% and 4.5% and silicon under 2% and not in excess of the aluminum, the balance being principally iron, the sum of the silicon and aluminum being between .75% and 5%.

line 90, for claim number "12" read 13; same page, strike out lines 98 to 101, comprising present claim 13; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of May, A. D. 1932.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.