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CORROSION-RESISTING FERROUS ALLOY

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This invention relates to corrosion-resisting ferrous alloys; and it relates more particularly to ferrous alloys or alloy steels characterized by a relatively high content of nickel and chromium, together with a further content of supplementing or fortifying constituents comprising copper, molybdenum and, usually, silicon in carefully adjusted but somewhat variable percentages that are comparatively small, molybdenum being always present in substantially greater proportion than silicon. The new alloys are characterized by a high degree of resistance to corrosion and, in addition, by the fact that sound castings can be produced therefrom and that they may also be forged and rolled hot with far less loss than has been unavoidable with alloy steels of generally comparable type heretofore known.

Corrosion-resistant austenitic alloy steels of high nickel-chromium content, fortified or reinforced with small amounts of silicon, copper and molybdenum, have been heretofore known and used for certain purposes. But their range of practical utility has been greatly restricted because they possessed certain inherent troublesome characteristics rendering them unsuitable for certain purposes or their fabrication into required products very expensive. For example, it has been very difficult to produce from such alloys satisfactorily sound castings, such as valve and pump parts, that must be tight against hydrostatic pressure. Furthermore, in hot forging and rolling ingots of such prior alloy steels into bars, rods and sheets, for instance, the yields obtainable in practice seldom exceeded 50 per cent and were commonly lower, due to excessive but unavoidable waste, thus greatly increasing the cost of the forged or rolled products and naturally limiting their use to special situations where such high cost would not be prohibitive.

It has now been found that the foregoing objections and disadvantages characterizing such prior alloy steels can be largely overcome by properly adjusting and controlling the relative proportions and total amounts of the before-mentioned reinforcing or fortifying constituents, that is, silicon, copper and molybdenum, in the manner hereinafter set forth; and that when this is done, the mechanical and physical characteristics of the resultant alloy steels are greatly improved. Furthermore, their corrosion resistance is not only fully as good as that characterizing prior alloy steels of this general type but, in the best embodiment of the invention, is substantially enhanced.

The percentages of nickel and chromium char-

acterizing ferrous alloys of the present invention, although capable of fairly wide variation, are relatively large in all cases, and are never less than 15 per cent for each of these components which, together, constitute not less than 30 per cent of the entire alloy and as much as 60 per cent as a practical upper limit, although usually not more than about 45 per cent. As a general rule, subject to some possible exceptions as hereinafter noted, the percentage of nickel is never less than that of chromium and, most desirably, is substantially greater. Iron, the largest single component, always constitutes at least about 45 per cent of the alloy and usually more than 50 per cent.

Although the marked effect of copper in high nickel-chromium steels as a fortifying agent to increase corrosion resistance has long been recognized, its employment for this purpose, even in very small proportions, e. g., as low as 0.10 per cent, has been attended heretofore with serious difficulties and objections, especially because of its adverse effect upon the hot-working properties of such alloy steels through a tendency to produce hot shortness.

According to the present invention, the fortifying or reinforcing elements are so proportioned that the highly desirable effect of copper in increasing corrosion resistance can be utilized fully while at the same time eliminating or sufficiently reducing its tendency to produce hot shortness. It has been found that, in order to accomplish this, it is vital to have the percentage of molybdenum always substantially greater than that of silicon, and most desirably at least two or more times as great. In fact, the percentage of silicon may, within the broad scope of the invention, be reduced to a mere trace or as low as is practically feasible. But, since in the action of molybdenum and silicon to increase corrosion resistance, each supplements the other, the presence of at least 0.25 to 0.50 per cent silicon is of distinct advantage, and as much as 2 per cent is permissible in practice. It is generally very much better, however, to keep the silicon well below 2 per cent, and indeed not to let it greatly exceed 1 per cent. For best results, the molybdenum content of the new alloy steels should be in the neighborhood of 3 to 3.5 per cent, ranging normally in practice from 2.0 to 4.0 per cent. However, smaller percentages of molybdenum are permissible within the broad scope of the invention down to as low as 0.25 to 0.50 per cent, subject always to the condition that the silicon percentage must be still lower; but the properties of

the alloy steel are markedly less advantageous when the molybdenum content is so low, especially in respect to corrosion resistance, and consequently a substantially higher content is to be recommended. Also, the upper limit of 4 per cent in the above indicated range for molybdenum may be somewhat exceeded although this is apt to render the alloy steel less easily forged and rolled. It is also very important that the total or combined percentage of molybdenum and silicon content shall not substantially exceed 5 per cent, an upper limit of 4.5 per cent being ordinarily distinctly preferable to observe. A higher aggregate percentage of these constituents is found to have a pronounced unfavorable effect upon the hot working properties of the alloy.

Alloy steels of the present invention are also characterized essentially by a very small content of carbon, 0.20 per cent being the extreme upper limit permissible and restriction to a much lower maximum being decidedly better practice. Indeed, it is only in exceptional cases that it is advisable to permit the carbon content to exceed 0.10 per cent. Ordinarily it is found that about 0.06 to 0.08 per cent carbon is extremely satisfactory in most cases, and a range of 0.04 to 0.07 per cent may be regarded as optimum. Too high a carbon content must be avoided because it increases vulnerability of the alloy to intercrystalline corrosion, especially upon exposure to contact with sulphuric acid, and the forging and rolling properties are in some cases also adversely affected. These undesirable effects are so completely suppressed or minimized when the carbon percentage is kept below 0.10 as to render the new alloy steels of this specific description distinctly superior to those containing between 0.10 and 0.20 per cent carbon, even though these latter are materially better than previously available alloys of this general type.

It will be understood that the new ferrous alloys may contain manganese in variable small percentages, e. g. 0.40 to 0.75 per cent, as an incidental component not significant for purposes of the present invention; also minute quantities of the common impurities such as phosphorus and sulphur which, together, do not amount to more than 0.04 per cent or thereabouts in the type of iron suitable to use in manufacturing alloy steels of the type here in question.

By maintaining the ratio of molybdenum to silicon such that the molybdenum always substantially predominates, with their combined percentages not substantially exceeding 4.5 per cent, and by observing the other precautions herein set forth, it becomes possible to employ, for example, from 1 to 3 per cent of copper, or even more, in an alloy steel containing, say, 20 per cent chromium and from 22 to 28 per cent nickel, which is of particularly great industrial value not only because of its high degree of corrosion resistance to sulphuric acid and other drastic corroding agents over a wide range of practical conditions, but also because sound, tight castings can be made from it and, furthermore, it can be easily forged and rolled with remarkably high yields of desired products. As a rule, such an alloy steel contains at least 50 per cent iron. While ordinarily a nickel content of at least 20 per cent and a chromium content of at least 18 are to be recommended as most desirable, lower percentages of these components may be employed in some cases, average practical working ranges being 17 to 25 per cent for nickel and 15 to 24 per cent for chromium in most instances,

with nickel predominating ordinarily although not invariably.

Heretofore, in order to produce an alloy steel of this general type giving a forging yield of even 50 per cent, it was necessary to keep the copper content down to about 0.3 per cent as a maximum. The ability to use a much higher copper content in such alloy steels and thus to enhance materially their corrosion resistance, while obtaining not only as good but far higher forging and rolling yields, is of the greatest importance industrially.

In order to illustrate further the underlying principles of the invention, and without intending thereby to limit its scope, the compositions or analyses of a number of the new alloy steels that are typical and representative are given in the following table showing percentages of the essential components other than iron.

Example No.	Ni	Cr	Si	Cu	Mo	C
1.....	20.0	19.0	0.5	1.0	3.5	0.07 (0.05-0.08)
2.....	22.0	21.0	0.5	0.5	3.5	0.07
3.....	20.0	18.0	1.0	1.0	3.5	0.07
4.....	21.0	18.0	1.0	1.0	3.0	0.07
5.....	22.0	21.0	1.0	0.5	3.5	0.07
6.....	20.0	17.0	1.5	1.0	3.5	0.07
7.....	20.0	17.0	1.5	0.5	3.5	0.07
8.....	23.0	22.0	1.0	1.0	2.0	0.07
9.....	20.0	18.0	0.5	1.0	4.0	0.07
10.....	21.0	20.3	0.5	0.9	3.4	0.07
11.....	21.0	20.8	0.5	1.0	3.5	0.12
12.....	20.8	18.5	1.0	0.9	3.2	0.08
13.....	21.5	17.8	1.5	1.0	3.1	0.07
14.....	21.5	17.5	1.4	0.9	3.0	0.08
15.....	21.1	17.4	1.6	0.9	3.2	0.06
16.....	21.6	18.1	1.0	1.0	2.9	0.06
17.....	21.5	18.1	1.3	2.8	3.4	0.07

Alloy steels of the character represented by the foregoing analyses are all characterized by the fact that the reinforcing elements relied upon to give increased corrosion resistance as compared to ordinary high chromium-nickel steels are carried in a uniform, stable, solid solution even at ordinary temperatures. When subjected to drastic tests with the usual corroding reagents under conditions ranging from reducing through neutral to strongly oxidizing, and at widely varying temperatures, the new alloy steels show extremely high corrosion resistance, notably so toward sulphuric acid. Their mechanical properties are also excellent. Whereas standard bend test specimens of prior alloy steels of generally comparable type fail at less than 90° when bent cold, similar test specimens of the new alloy steels show no cracking or other failure when bent 90° nor, in many cases, even when bent 180°. This is evidently due to the superior micro structure of the new alloy steels which is found upon examination to be homogeneous in character, there being little or no precipitation of ferrite on the crystallographic planes or intracrystalline faces. Also there is practically no formation of insoluble carbides at the grain boundaries; and accordingly these new alloy steels are especially free from attack through intergranular corrosion. Thin sections of castings produced from the new alloys are much less or not at all subject to the severe coring or "double wall effect," commonly characterizing castings from comparable prior alloy steels, which coring is not only conducive to porosity (leaky castings) but lowers corrosion resistance as well as the elastic limit of the metal.

Alloy steels having analyses approximately as given in the table given hereinabove are regarded as particularly advantageous embodiments of the invention because combining very high cor-

rosion resistance with exceptionally good casting and hot working characteristics. For example, in actual mill operation with an alloy steel having substantially the analysis given in Example No. 10, the yield from poured ingot to finished rolled bar was 73 per cent in a typical instance. This contrasts with a maximum obtainable yield of only about 50 per cent when rolling prior alloy steels of most nearly comparable type. Similar marked increases in forging and rolling yields are characteristic of the new alloy steels generally.

Where it is desired that the alloy steel contain more copper than in the examples given in the above table of typical analyses, the nickel content should also be substantially increased above the normal average in order to maintain the good hot working characteristics characterizing alloys of the present invention. Thus, typical alloys containing such higher percentages of copper may desirably have the following percentage ranges for the essential components other than iron:

Nickel	28.0 - 30.0
Chromium	19.0 - 21.0
Molybdenum	2.7 - 3.2
Silicon	0.75 - 1.1
Copper	4.50 - 5.0
Carbon (max.)	0.07

A high copper alloy steel within the scope of the invention, but lower in chromium than usual, may have the following percentage composition for essential components other than iron:

Nickel	30.0
Chromium	10.0
Molybdenum	4.0
Silicon	0.5
Copper	5.0
Carbon (max.)	0.07

The new alloy steels may be manufactured by ordinary methods well known to those skilled in the art of making high nickel-chromium alloy steels, no special expedients or precautions being required. So also, production of castings, ingots, bars, sheets, etc., from these steels, and the heat treatment thereof, may be carried out in the usual way. It is accordingly unnecessary to describe these methods here.

What is claimed is:

1. A corrosion-resistant alloy whose principal constituent is iron, said alloy containing not less than 15 per cent chromium, not less than 17 per cent nickel which is always in larger percentage than the chromium, carbon not exceeding 0.20 per cent, copper from about 0.10 to about 5.00 per cent, molybdenum from about 0.25 to about 4 per cent, and silicon from a trace to about 2.00 per cent, but always less than the percentage of molybdenum, the molybdenum and silicon together not substantially exceeding 5 per cent,

and at least 95 per cent of the balance being iron, a standard test specimen of said alloy as cast being capable of withstanding a 90° cold bend without failure.

2. An alloy as defined in claim 1, further characterized by the fact that its carbon content is within the range 0.04 to 0.07 per cent.

3. An alloy comprising chromium, at least 15 per cent, together with nickel in larger proportion and never less than 17 per cent; carbon, not exceeding 0.20 per cent; copper, 0.10 to 5.0 per cent; molybdenum, 0.25 to 4.0 percent; and silicon, a trace to 2.0 per cent, but always less than the percentage of molybdenum, and the molybdenum and silicon together not substantially exceeding 5 per cent, at least 95 per cent of the balance being iron, which is never less than 45 per cent of the alloy, said alloy being corrosion-resistant and possessing good casting properties, a standard test specimen of said alloy as cast being capable of withstanding a 90° cold bend without failure.

4. An alloy comprising the following elements in proportions falling within ranges of percentages substantially as follows:

	Percent
Nickel	over 23 to 28
Chromium	19 to 21
Copper	1 to but not including 3
Carbon up to	0.2
Molybdenum and silicon together not substantially exceeding	4.5

the molybdenum always exceeding silicon, and substantially all the balance to make 100 per cent being iron; said alloy being corrosion-resistant and possessing relatively good hot working and casting properties; a standard test specimen of said alloy as cast being capable of withstanding a 90° cold bend without failure.

5. An alloy comprising the following elements in proportions falling within ranges of percentages substantially as follows:

	Percent
Nickel	over 23 to 28
Chromium	20
Copper	1 to but not including 3
Carbon up to	0.2
Molybdenum and silicon together not substantially exceeding	4.5

the molybdenum always exceeding silicon, and substantially all the balance to make 100 per cent being iron; said alloy being corrosion-resistant and possessing relatively good hot working and casting properties; a standard test specimen of said alloy as cast being capable of withstanding a 90° cold bend without failure.

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