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STABLE PHOSPHIDE ALLOYS OF AT LEAST
QUATERNARY CONSTITUENCY

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This invention relates to high phosphorus iron alloys distinguished by the quality of inherent resistance to both physical and chemical deteriorating influences encountered in the use of articles made therefrom; and particularly alloys of at least quaternary structure, which, by virtue of individual immunizing of their metallic constituents; the method of combining said constituents one with another; and the improvement of grain structure and protection of grain boundaries resulting from the assembly, have the aforesaid quality bestowed upon them in an increasingly important degree.

This application constitutes an improvement upon the subject-matter of my U. S. Letters Patent No. 2,117,191, issued May 10, 1938, for Acid resisting alloys, in which I have claimed an alloy resistant to chemical deterioration and consisting of a foundation metal, typified by iron, with a high proportion of phosphorus that converts at least a substantial portion of the foundation metal into its phosphide, and a disembrittling or strengthening element, comprising a metal capable of combining with phosphorus to form its own phosphide also in solution in the alloy, and physically conditioning the alloy in the sense of lending to it physical properties appropriate to the uses for which it is intended, in addition to its capacity to resist chemical attack. In the said Letters Patent only ternary alloys were considered, and copper and chromium were given as elements typical of the many metals having the capacity to physically condition high phosphide alloys.

The present application deals with alloys that are quaternary or more complex than quaternary. It has been found that while the ternary alloys are very resistant to attacks of corrosive influences, they are nevertheless, on long exposure to concentrated strong acids, subject to intergranular corrosion which deteriorates them with respect to the special purposes for which they are made. Hence, under the present invention, I add to the iron, phosphided to the desired degree, a plurality of corrective metals, themselves noble or forming noble phosphides, which in their immune condition, dissolve in the crystals of the iron and one another and prevent, substantially or entirely, not only deterioration of the iron, but the inter-granular corrosion to which ternary alloys are susceptible; the improvement resulting from this addition being due to the formation of finer grained alloys resulting in better intra-metal solution, better grain envelopment and more even distribution of the constituents of the

chemical compound; also to the fact that a chemical compound of quaternary or more complex constituency produces a more complex and therefore more stable oxide space lattice; and to the fact that an alloy of inter-metallic compounds and solid solutions gives the most stable form of alloy and one having a lower affinity for oxygen than would follow from the rule of mere mixtures as distinguished from chemical compositions.

The invention proceeds upon the principle of forming alloys of quaternary or more complex constituency, in which two of the constituent elements are iron and phosphorus and the additional two or more constituent elements are selected from the group of elements, nickel, copper, chromium, molybdenum, tungsten, manganese, titanium, tin, antimony, cobalt, lead, vanadium, zirconium and boron; these additional elements being themselves noble or combined with phosphorus to form noble phosphides and having the capacity of alloying with the foundation metal, iron and the phosphorus to form the complete phosphides; and the selection of these additional elements being governed by the suitability with respect to the physical or chemical properties bestowed by their phosphides upon the resultant alloys, considering the uses to which the alloys are to be put.

Numerous experiments prove that the improved chemical resistance bestowed upon metal products by the present invention is largely contributed by those proportions of the added metals that remain compounded with phosphorus in the alloy. Hence, if instead of a ternary alloy, consisting merely of iron, phosphorus and a metal which physically conditions iron phosphide, the foundation metal is made to also contain, in solution therewith, a third metal, a portion or all of which remains compounded with phosphorus when in solution and thus renders the alloy quaternary in constituency, or a fourth or even fifth additional metal, portions or all of which are compounded with phosphorus when in solution in the foundation metal, thus making alloys more complex than quaternary, not only do these additional third, fourth or fifth metals leave the phosphided foundation metal properly conditioned physically, but the compounded or phosphided portions thereof are largely responsible for giving to the alloy exceptional resistance to severe chemical attack, as well as physical integrity. They also leave the alloy with an initial chemical resistance proportional to the portions of the added metals that become compounded with phosphorus. They also provide

- alloys in which, under prolonged severe chemical attack, the metallic portions of the exposed surface slowly yield to reaction until there is left a surface made up so largely of the compounded or phosphided constituents of the alloy as to cause a tapering off of the rate of solution of even those alloys which are lower in percentages of the compounds or phosphides, until the continued rate of yield to chemical attack upon the newly exposed surface of the compounded ingredient in an alloy having a lower percentage of composition ingredients, drops off to approximately that of quaternary or more complex alloys having higher percentages of phosphide compounds. As a result of this, where exact sizes on machined surfaces are not a factor, alloys of lower percentages of composition ingredients (phosphided metals) can be made to build up excellent resistance to the most severe corrosive influences. The importance of these points will be appreciated when it is recognized that in a coarse-grain ternary phosphide alloy, inter-granular corrosion would to a large extent lower chemical resistance by loosening and removing compounded surface constituents and establishing progressive corrosion of the metallic constituents, whereas in the present invention initial corrosion merely exposes a new compounded surface substantially immune to corrosion.
- The objects of the invention may be realized in articles or materials produced by casting, rolling, extruding, drawing or forging of the quaternary or more complex phosphide alloys having high resistance to a wide range of corrosive influences.

The quaternary or more complex alloys of this invention may be made with any phosphorus content between 1.70% phosphorus, which forms a saturated solid solution of iron phosphide in iron (10.91% Fe_3P in iron), and a content of about 25% phosphorus which, in the instance of iron, would form the compound Fe_2P . Similarly, 7.09% of copper phosphide (Cu_3P) in which the phosphorus is 1.00%, will dissolve in and form a saturated solid solution with copper. And so with other metals.

Alloys containing from 5% to 50% of the quaternary or more complex phosphide compounds are capable of being processed by rolling or other metal working methods, while those alloys compounded with more than 50% of metal phosphides are best shaped by casting and finishing by machining or grinding.

An alloy of the higher phosphorus type, which I identify as "D-36001-A" and which has very good mechanical and machining properties and a Rockwell hardness of 26 on the C scale, analyzed, including the desirable but not indispensable manganese and the carbon and silicon essentials or impurities, is—

	Per cent
Carbon	.08
Manganese	.13
Silicon	.06
Phosphorus	6.38
Nickel	24.27
Copper	24.25
Iron	44.76

This alloy has a solution rate in all concentrations of sulphuric acid and hydrochloric acid, at all temperatures of .003 inch penetration per year.

Another alloy of an allied group of metals which I distinguish by the arbitrary mark "B-1" and

which has good machining properties and a Rockwell hardness of 36 on the C scale, is—

	Per cent
Carbon	.29
Manganese	.14
Sulphur	.03
Silicon	.12
Phosphorus	23.88
Nickel	6.79
Copper	5.85
Iron	62.78

The solution rate of this alloy is .0045 inch per year in sulphuric and hydrochloric acids. The carbon, manganese, sulphur and silicon existing in fractions of 1% are believed not to materially lend to or affect properties bestowed by the invention.

Another alloy of this group having only fair machining properties I identify as "D-36003-C." It has a Rockwell hardness of 45 on the C scale. It is

	Per cent
Carbon	.14
Manganese	.48
Silicon	.15
Phosphorus	10.01
Nickel	36.54
Copper	11.72
Iron	40.96

This alloy has a solution rate of .002 inch per year in all concentrations of sulphuric and hydrochloric acids, at all temperatures. The carbon, manganese and silicon are non-essentials.

Alloys embodying the essentials of the foregoing formulas together with additional elements but which are not capable of machining and must be shaped by grinding, are illustrated by the three following typical examples, designated, respectively, as "M-2", "5-F-1" and "F-36018", to-wit:

M-2

	Per cent
Carbon	.15
Manganese	.12
Phosphorus	14.61
Nickel	35.49
Copper	9.34
Tungsten	2.18
Iron	38.03

Rockwell hardness of this sample is 48 on the C scale and the solution rate in sulphuric and hydrochloric acids is .001 inch per year. The carbon and manganese are non-essentials.

5-F-1

	Per cent
Carbon	.32
Manganese	.16
Phosphorus	9.34
Nickel	33.11
Copper	8.32
Molybdenum	1.42
Iron	47.30

Solution rate of this alloy is .0018 inch per year in sulphuric and hydrochloric acids and a Rockwell hardness of 52 on the C scale. The carbon and manganese are non-essentials.

F-36018

Per cent

Carbon	31
Manganese	2.08
Silicon	.26
Phosphorus	15.53
Chromium	17.63
Nickel	7.43
Iron	56.71

Solution rate of this alloy is .0032 inch penetration per year in nitric acid and its Rockwell hardness is 62 on the C scale. In this formula the carbon is merely an incident of essential elements. The manganese is in a proportion that causes it to contribute refinement of grain.

Examples of alloys in the lower phosphorus group which have excellent machining and mechanical properties and are capable of being rolled or forged are those which are designated "F-5" and "F-11", as follows:

F-5

Per cent

Carbon	.09
Manganese	.27
Silicon	.12
Phosphorus	2.96
Nickel	23.15
Copper	20.07
Iron	53.34

Solution rate of this alloy in sulphuric and hydrochloric acids is .0038 inch per year and its Rockwell hardness is 20 on the C scale.

F-11

Per cent

Carbon	.08
Manganese	.19
Silicon	.14
Phosphorus	2.43
Nickel	8.31
Chromium	18.26
Iron	70.54

Solution rate of this alloy is .006 inch penetration per year in nitric acid and its Rockwell hardness is 18 on the C scale.

The alloys herein described may be prepared by melting together the constituents of the alloy, in which case a homogeneous alloy will result. Or they may be prepared by the process of my Letters Patent No. 2,007,978, issued July 16, 1935, in which case the foundation metal in the non-fused state is subjected to the reaction of high phosphorus alloys in the fused state and under conditions which will cause the high phosphorus fused alloys to enter into solution with the foundation metal and convert the latter into an alloy of all of the ingredients to a depth depending upon duration of submergence, heat of the bath and other conditions which promote the reaction.

What is claimed is:

1. A physically and chemically resistant iron phosphorus alloy comprising iron in a proportion of from about 35% to about 71%; phosphorus from about 1.70% to about 25%; nickel from about 6% to about 37% and in addition to said nickel, from about 5% to about 25% of one or more other nonferruginous corrective metals having the capacity of combining with phosphorus to form their own phosphides and the

capacity of alloying with the nickel and with iron phosphide, said other nonferruginous metals being taken from the list copper, chromium, molybdenum, tungsten, manganese, titanium, tin, antimony, cobalt, lead, vanadium, zirconium and boron; a substantial proportion of each metal of the alloy being in solution therein in the form of its own phosphide.

2. The alloy described in claim 1 when the proportion of phosphorus combined with each metal of the alloy produces the eutectic phosphide of said metal and the solution of the said phosphide in the metal itself is a saturated solution.

3. A high phosphorus iron alloy as described in claim 1 in which the proportions of the phosphides of the corrective metals exceed those which the iron phosphide will contain in solid solution and such phosphides largely permeate the grain-boundaries of the iron phosphide.

4. A high phosphorus alloy as described in claim 1 in which the nonferruginous corrective metals other than nickel comprised in the alloy are copper and one of the metals molybdenum or tungsten.

5. An alloy as described in claim 1 in which the nonferruginous corrective metals other than nickel comprise copper and molybdenum of which the molybdenum is in a proportion of about 1.42% of the alloy.

6. An alloy as described in claim 1 in which the nonferruginous corrective metal other than nickel comprises chromium.

7. An alloy as described in claim 1 in which the nonferruginous corrective metal other than nickel comprises chromium from about 17% to about 19%.

8. An alloy as described in claim 1 in which the nonferruginous corrective metal other than nickel comprises chromium in a proportion of about 17% and manganese in a proportion of about 2%.

9. An alloy as described in claim 1 in which the iron is about 70.54%; the phosphorus is about 2.43%; the nickel is about 8.31% and the nonferruginous corrective metal other than nickel comprises chromium about 18.26%.

10. An alloy as described in claim 1, in which the non-ferruginous corrective metals comprise nickel in a proportion of from about 6% to about 37%; and copper in a proportion of from about 5% to about 25%.

11. An alloy as described in claim 1, in which the iron is from about 44% to 54%; the phosphorus is from about 3% to about 7%; and the nonferruginous corrective metals comprise nickel in a proportion of from about 24 to about 25% and copper in a proportion of from about 20% to about 25%.

12. A low carbon, high phosphorus alloy having substantial resistance to both physical and chemical influences, said alloy being of at least quaternary constituency and comprising essentially, iron about 44.76%; phosphorus about 6.38%; nickel about 24.27% and copper about 24.25%; each of said metals existing largely in the form of its phosphide and the nickel and copper phosphides being partly in solid solution with the iron phosphide and partly in the grain boundaries thereof.

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