

1

3,533,758

FERROUS ALLOY HEAT STORAGE APPARATUS
Edward James Lowe, Stourton, near Stourbridge, and
Sidney Benjamin Hartley, Halesowen, Birmingham,
England, assignors to Electric Reduction Company of
Canada Ltd., Toronto, Ontario, Canada, a Canadian
company

No Drawing. Filed Apr. 25, 1967, Ser. No. 633,397

Claims priority, application Great Britain, May 9, 1966,
20,491/66; Dec. 19, 1966, 56,606/66

Int. Cl. C22c 37/00; F24h 7/00

U.S. Cl. 29—180

5 Claims

ABSTRACT OF THE DISCLOSURE

The inhibition of high temperature oxidation in storage heaters containing a thermal reservoir by constructing said reservoir of a ferrous alloy consisting essentially of between about 4.5% and 10% P, between about 1% and 5.5% Si, between about 1.5% and 3% C and the balance Fe.

The present invention relates to ferrous alloys, and in particular ferrous alloys containing a proportion of free iron and having an enhanced resistance to oxidation at elevated temperatures, and to certain articles of manufacture constructed therefrom.

Normal cast iron contains small proportions of carbon, phosphorus, silicon, manganese and traces of other elements. A part of the iron is present in a chemically combined form as carbide, silicide or phosphide and the bulk of the alloy consists of chemically free metallic iron, which may be alloyed with other metals. Metallurgists have hitherto taken great care to avoid the presence more than small quantities of phosphorus in cast iron or steels, since ferrous alloys containing more than about 0.2–0.5% by weight of phosphorus are known to be undesirably brittle and the brittleness is believed to increase with increasing phosphorus content.

For certain special purposes ferrous alloys have been recommended containing 0.5 to 1% by weight of phosphorus, but it has never been envisaged that an alloy of chemically free iron containing more than 1% by weight of phosphorus could usefully be employed in the construction of articles of manufacture.

Existing alloys of chemically free iron suffer from the disadvantage that they tend to undergo oxidation, especially when used at high temperatures, e.g. in furnace components, fire bars, storage heaters and similar applications. Such oxidation results in corrosion, scaling and, at sufficiently high temperatures may even result in pyrophoric combustion, at least locally. We have discovered that there exist alloys containing chemically free iron and from 2 to 15% by weight and preferably 5 to 10% by weight of phosphorus which exhibit a surprising persistence to high temperature oxidation, a property which renders them of value in the construction of articles adapted for use at high temperatures.

Our invention therefore provides articles of manufacture adapted for use in environments favouring high temperature oxidation of cast iron and constructed, at least in part, of an iron/phosphorus alloy comprising a major proportion of iron part of which is present as the chemically free metal, and from 2 to 15% by weight of phosphorus.

A particularly preferred embodiment of our invention provides a storage heater comprising a thermal reservoir constructed at least in part of an iron/phosphorus alloy as aforesaid, means for supplying heat thereto, and means for withdrawing useful heat from the reservoir.

Further embodiments of our invention provide industrial or domestic boiler components, ingot moulds (par-

2

ticularly ingot moulds for use with non-ferrous metals, such as aluminium and zinc), regenerative heat exchangers, slag ladles (for non-basic slags), fire bars and hearths tunnel kiln conveyors, hot plates, components of ovens, kilns and furnaces and plant and apparatus for handling certain corrosive chemicals, all constructed at least in part of an iron/phosphorus alloy as aforesaid. We have also discovered that iron/phosphorus alloys as aforesaid are of value in the construction of mills and grinding equipment. For example a rotary mill may be constructed containing cast balls, rods or other articles formed from an iron/phosphorus alloy as aforesaid.

According to a further embodiment our invention provides alloys which are of value in constructing articles according to our invention comprising a major proportion of iron, part of which is present as the chemically free metal, from 4.5–10% by weight of phosphorus and a minor proportion of other elements commonly present in cast iron and in ferrophosphorus.

Preferably alloys according to our invention, or for use in the construction of articles according to our invention, contain more than 5% and most preferably more than 6% by weight of phosphorus, especially for applications in which resistance to high temperature scaling over long periods is an important factor. For such applications alloys containing 6–9% of phosphorus are preferred. However, if greater strength or ease of casting is required, the phosphorus content may be reduced, giving alloys having for example 2.5–5% by weight of phosphorus. Desirably the alloys contain elements other than iron and phosphorus in a total proportion of less than 10% by weight, e.g. 2 to 7% by weight. Other elements which may be present include carbon, silicon, vanadium, chromium, manganese, cobalt and nickel. The silicon content is normally from 1 to 5.5% by weight and preferably no greater than will be provided by incorporating ferrophosphorus into a conventional grey iron casting e.g. 2 to 3%. The total proportion of silicon and phosphorus is less than 15% by weight, since at higher proportions the composition ceases to be an alloy of free iron and consists of a mixture of iron phosphides and/or iron silicides. The carbon content is preferably less than 5% by weight and most preferably less than 3%. Typically the amount of carbon is 1.5 to 2.5% by weight. Other compatible metals are commonly present in a proportion of 0 to 5% by weight.

The alloys according to our invention may conveniently be prepared by adding ferrophosphorus to a molten iron or other ferrous alloy containing a major proportion of iron, or by melting iron and ferrophosphorus together. Alternatively elemental phosphorus may be added direct to a molten iron or ferrous alloy. The iron may conveniently be a melt suitable for the preparation of conventional cast iron, e.g. grey cast iron.

The term "ferrophosphorus" as used herein refers to the iron/phosphorus composition obtained as a by-product of the electric reduction process for making phosphorus and comprising a mixture of iron phosphides. Usually ferrophosphorus contains a major proportion of iron, from 20–30% of phosphorus and other elements (such as silicon, vanadium, chromium, manganese, cobalt and nickel) in a total proportion of less than 15%.

The novel alloys of our invention are of particular value in the construction of storage heaters. Our U.S. Pat. No. 3,381,113 proposed the use of ferrophosphorus for constructing storage heaters, it having been discovered that ferrophosphorus has an unusually high heat capacity. However, ferrophosphorus has the disadvantage that, owing to its brittleness and low crushing strength, it is difficult to construct sufficiently strong self supporting castings for ordinary use in storage heater cores. Hitherto it has proved necessary to sinter granular ferrophosphorus with

a ceramic binder such as fireclay to provide a material sufficiently strong for such uses. This has the disadvantage that the resulting composite has a markedly reduced heat capacity, so that the heater reservoirs must be unduly bulky to provide adequate heat storage: this has been an important drawback especially for domestic room heaters. Ceramic materials and composites also have a low thermal conductivity, which inhibits storage and recovery of heat.

It has also been proposed to employ ordinary cast iron for constructing storage heaters. Cast iron however suffers from two serious disadvantages. Firstly, it has an undesirably low heat capacity. Secondly, cast iron undergoes oxidative corrosion and scaling at the normal operating temperatures of storage heaters. This corrosion limits the useful temperature range over which it is possible to use cast iron.

Surprisingly, we have discovered that novel alloys of this invention have a markedly greater heat capacity over their useful range than either normal cast iron or than

coke-heated cupola. The following alloy compositions were prepared:

	Example				
	5	6	7	8	9
Percent phosphorus.....	4.4	5.6	7.0	8.3	9.7
Percent carbon.....	2.48	2.45	2.02	1.70	1.43
Percent silicon.....	1.53	1.45	1.08	1.19	1.24
Percent chromium.....	0.05	0.10	0.11	0.13	0.16
Percent manganese.....	0.21	0.37	0.33	0.37	0.30

The balance consisted, in each case, substantially of iron, with less than 0.2% of other elements.

The samples were all readily cast into blocks which exhibited good resistance to high temperature oxidation, and were particularly suitable for use in constructing storage heater cores.

EXAMPLE 10

The alloy of Example 8 was compared against the three most commonly used heat storage materials.

	Alloy No. 8	Cast iron	Firebrick	Magnesite
Heat capacity/unit volume (b.t.u./ft. ³ , ° F.).....	64.9	62.9	32.9	45.5
Useful temperature range (° F.).....	122-1,382	122-1,112	212-1,292	212-1,292
Heat capacity/unit volume over the useful temperature range (b.t.u./ft. ³).....	81,900	62,300	35,500	49,100

ceramic materials hitherto proposed. Thus, it has been possible to use alloys according to the present invention to construct efficient domestic storage heaters which are slenderer and less bulky than those hitherto available. Additionally, it has been found that the alloys of our invention possess greatly improved resistance to high temperature corrosion. This is surprising since they contain chemically free iron and would therefore have been expected to corrode readily.

The novel alloys of this invention are substantially stronger than ferrophosphorus and may readily be cast to form self supporting cores for storage heaters. They have significantly greater thermal conductivity than fireclay or the ceramic compositions containing granular ferrophosphorus employed hitherto. Alloys according to our invention may be used for constructing thermal reservoirs in any of the ways described and illustrated in U.S. Pat. No. 3,381,113.

The invention also provides composites of an alloy according to the invention sintered with a ceramic material.

Alloy compositions according to the invention are illustrated by the following examples:

EXAMPLES 1 TO 4

Cast iron scrap and ferrophosphorus containing 24.8% phosphorus were melted in 10 lb. batches in a carbon crucible heater by induction. The following alloy compositions were prepared:

	Example			
	1	2	3	4
Percent phosphorus.....	12.0	5.6	4.2	2.0
Percent carbon.....	1.2	2.3	3.1	3.25
Percent silicon.....	1.9	2.6	2.2	2.2

The balance in each case consisted substantially of iron with less than 0.5% of other elements.

The alloy samples were all readily cast into blocks having a greater crushing strength than ferrophosphorus. The blocks were found to be relatively resistant to high temperature corrosion compared with a conventional grey iron casting.

EXAMPLES 5 TO 9

Ferrophosphorus and cast iron scrap were melted in a

It will be seen from these figures that substantially more heat can be stored in a given volume of the alloy of our invention than in any of the other materials commonly used for building thermal reservoirs.

We claim:

1. In storage heaters containing a thermal reservoir, means for supplying heat to said reservoir, and means for recovering heat from said reservoir in useful form, the improvement which consists in constructing said reservoir of a ferrous alloy consisting essentially of between about 4.5% and 10% by weight of phosphorus, between about 1% and 5.5% of silicon, the total of silicon and phosphorus being a maximum of 15%, between about 1.5% and 3% carbon, and the balance iron.

2. An improved storage heater according to claim 1 wherein said ferrous alloy is an alloy of cast iron with ferrophosphorus.

3. An improved storage heater according to claim 2 wherein the proportion of phosphorus is from 6 to 9% by weight.

4. An improved storage heater according to claim 2 wherein the proportion of silicon is from 2 to 3% by weight.

5. An improved storage heater according to claim 2 wherein the proportion of carbon is from 1.5 to 2.5% by weight.

References Cited

UNITED STATES PATENTS

1,527,165	2/1925	Bennett	75-123
1,690,352	11/1928	Williams	75-123
2,289,365	7/1942	Jerabek	75-123
3,109,733	11/1963	Tisdale et al.	75-123
3,193,383	7/1965	Butler	75-123
3,381,113	4/1968	Jacques et al.	75-132 X

FOREIGN PATENTS

464,095	4/1937	Great Britain.
1,034,929	7/1966	Great Britain.

CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

75-123; 148-35; 219-378