

UNITED STATES PATENT OFFICE

2,069,705

PROCESS OF MANUFACTURE OF METALLIC
GLUCINUM AND ITS ALLOYS

Robert André Gadeau, St. Jean de Maurienne,
France, assignor to "Compagnie de Produits
Chimiques et Electrometallurgiques Olais,
Froges et Camargue," Paris, France, a corpora-
tion of France

No Drawing. Application April 25, 1935, Serial
No. 18,263. In Germany April 30, 1934

6 Claims. (Cl. 75-150)

It is known to obtain alloys of glucinum and of a metal less electropositive than glucinum by causing reducible compounds of glucinum to react upon magnesium, in presence of the metal less electropositive than glucinum.

So far as I am aware, the question has never been applied in an industrial manner, and the necessary distinction between the various reducible compounds of glucinum has never been made.

It comes immediately into mind to employ glucinum oxide. But the tests I have carried out have proved that glucinum oxide is not reduced at all by magnesium in industrial conditions. It is probable that this lack of success is due to the fact that solid glucinum oxide cannot react upon metals which do not wet it; there would undoubtedly be a reaction if the glucinum oxide were dissolved in a suitable flux, but there is known at present no halogenated flux capable of dissolving glucinum oxide.

In order to produce industrially alloys of glucinum by reduction with magnesium, it has been found to be indispensable that the reducible compound and the magnesium alloy shall enter into reaction in the molten state and that the product of the operation shall be itself molten; in these conditions alone, there can be had a sufficient mobility of the ions for obtaining a complete reduction with good yields.

Consequently, since it is a question of producing industrial alloys melting at temperatures of the order of 1000° C., the use of glucinum chloride is not possible industrially, that compound distilling at 500° C.

There remain, as reducible compounds, only the fluorine compounds of glucinum.

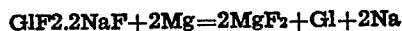
Glucinum fluoride GlF_2 could be suitable, but the tests I have made have shown that it has the great disadvantage of giving a bath still too viscous at 1000° C., which renders the reaction difficult. Moreover, it is a costly compound and difficult to prepare, to handle and to store, by reason of its hygroscopic properties.

The alkali double fluorides of glucinum are the least costly industrial compounds, because they can be obtained directly in the process of attacking beryl with alkali fluorsilicates, a process universally employed at the present time. The possibilities of reduction of these double fluorides by magnesium and its alloys do not seem to have been studied up to this date.

I have found, and this is what characterizes the present invention, that alloys of glucinum with metals, less electropositive than glucinum,

can be prepared industrially by reducing, with an alloy of magnesium and of a metal less electropositive than glucinum, alkali double fluorides of glucinum, containing less alkali fluoride, in proportion to the glucinum fluoride, than is indicated by the formula $\text{GlF}_2 \cdot 2\text{NaF}$.

It is known that magnesium reduces alkali fluorides as well as glucinum fluoride (all) in the molten state; it likewise reduces their mixtures. Nevertheless, I have verified that the reaction of magnesium upon the alkali double fluorides of glucinum is violent and total, with setting free of the alkali metal, according to the reaction:



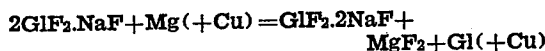
this evolution of vapours of sodium, in an almost explosive reaction, renders this reaction unsuitable for any industrial working.

I have found that, contrary to all expectation, the reducing properties of magnesium are altogether different when this magnesium is alloyed with a metal, less electropositive than glucinum, in particular with copper, aluminium, etc.

Magnesium alloyed with the metals less electropositive than glucinum has no longer any reducing action upon the molten alkali fluorides. It retains, on the contrary, its reducing action upon molten glucinum fluoride.

The tests I have made have proved that the normal double fluoride $\text{GlF}_2 \cdot 2\text{NaF}$ is not reduced at all by magnesium alloyed with metals, less electropositive than glucinum, at temperatures of the order of 900° to 1100° C. On the contrary, the alkali double fluorides richer in glucinum, such as $\text{GlF}_2 \cdot \text{NaF}$, are reduced by magnesium alloyed with metals less electropositive than glucinum, but they give up only a part of their glucinum and the reaction stops when the composition $\text{GlF}_2 \cdot 2\text{NaF}$ is attained.

The reaction is of the type:



As there is no reduction of the alkali fluoride, therefore no freeing of gaseous alkali metal, the reaction is perfectly quiet and regular; there is no production at all, as in the reductions with pure magnesium, of local overheatings which cause losses of bath by volatilization; moreover, there is saved the large quantity of magnesium which would be lost in the reduction of alkali fluoride in the case of pure magnesium.

It is necessary to take account, in practice, of the fact that magnesium boils at about 1100° C., and of the fact that the alkali double fluorides

of glucinum volatilize already to a considerable extent at this same temperature. One is thus limited to the preparation of glucinum alloys melting below 1100°C ., and preferably about 1000°C .

It is necessary, of course, to avoid the presence of metallic fluorides reducible by magnesium, such as those of iron, silicon, aluminium, etc., for those metals would contaminate the final alloy. The alkaline-earth fluorides can, without disadvantage, be present in the bath in any proportions compatible with the melting point and fluidity desired.

Good industrial results are obtained with the following mode of operation, which forms part of the present invention.

There is employed a crucible or a furnace lined internally with a suitable refractory material, adapted to resist the fluoride baths and the reducing action of magnesium, for example graphite, magnesia or glucina.

There is melted therein a bath of alkali double fluoride of glucinum containing more than one molecule of glucinum fluoride to two molecules of alkali fluoride, such as $\text{GlF}_2\cdot\text{NaF}$, for example. Into this bath there are thrown alloy ingots of magnesium and of a metal less electropositive than glucinum, having a magnesium-content corresponding to the glucinum-content which it is desired to obtain in the final alloy (24 kgs. of magnesium being replaced by 9 kgs. of glucinum). The whole is stirred, in order to facilitate the reaction, while maintaining a temperature higher than the melting point of the final alloy of glucinum and of the metal less electropositive than glucinum.

There are then poured out on the one hand the desired glucinum alloy, and on the other hand the residual bath which, when it is exhausted, contains an alkali double fluoride of glucinum such as $\text{GlF}_2\cdot 2\text{NaF}$, some magnesium fluoride, a small amount of carbides (in the case of a graphite furnace-lining) and oxides.

Magnesium fluoride and the various impurities being insoluble in water, there is readily recovered, in the pure state, an alkali double fluoride of glucinum, by simple lye-washing of the residual bath. By any known means, this double fluoride is brought back to a formula such as $\text{GlF}_2\cdot\text{NaF}$ and passes again into manufacture.

In practice, it is advantageous to exhaust the bath completely by operating in two phases, as follows:—

1st phase.—A bath of alkali double fluoride of glucinum is treated with a quantity of alloy of magnesium and of a metal, less electropositive than glucinum, in slight excess over the quantity theoretically necessary for the exhaustion of the bath.

There are obtained from this operation: an alloy of glucinum and of the metal less electropositive than glucinum, containing still some percents of magnesium, and a spent residual bath which passes to the recovery.

2nd phase.—The metal obtained in the 1st phase is remelted in a fresh bath, following the same mode of operation. The large excess of reducible glucinum favours the complete elimination of the rest of the magnesium.

There are obtained from this operation: the final glucinum alloy which contains no more than traces of magnesium, and a bath still almost new which passes back to the 1st phase.

In the case, the most frequent, of the manu-

facture of the copper-glucinum alloy, the operation takes place in the following way:

Example 1.—In a graphite crucible, there are melted 50 kgs. of $\text{GlF}_2\cdot\text{NaF}$, and the temperature is raised to about 1000°C . There are thrown into the bath 25.5 kgs. of copper-magnesium alloy containing 26.7 percent of Mg in pieces. The whole is stirred for 15 to 20 minutes with a graphite spatula while maintaining the temperature.

There are then poured out separately: about 54 kgs. of spent bath which passes to the recovery, and about 21 kgs. of copper alloy containing on an average 11 percent of glucinum and 3 percent of magnesium.

In a fresh bath of 50 kgs. of $\text{GlF}_2\cdot\text{NaF}$, this alloy is remelted and stirred for some twenty minutes with the graphite spatula, at a temperature of about 1000°C .

About 21 kgs. of copper-glucinum alloy having 12 percent of glucinum are poured out, this alloy containing no more than 0.2 to 0.3 percent of magnesium, on the average. The bath poured at the same time will serve for a fresh operation.

The yield is excellent and exceeds 90 percent of the glucinum brought into the operation, that is, of the difference of the weights of glucinum contained on the one hand in the initial double fluoride, and on the other hand in the recoverable residual bath.

The process according to the invention is not limited to the manufacture of copper-glucinum alloys; it may serve for the industrial manufacture of alloys of glucinum with all metals capable, on the one hand of alloying with magnesium, on the other hand of giving with glucinum alloys melting below 1100°C .

I prepare industrially copper-glucinum alloys containing up to 12.5 percent of glucinum, aluminium-glucinum alloys containing up to 10 percent of glucinum, zinc-glucinum alloys of the same contents, etc.

The process described above permits likewise of obtaining compact pure metallic glucinum. It has already been proposed to make the said metal by reduction processes, but none of these can give an industrial result.

It has for example been attempted to reduce glucinum-fluoride with an excess of magnesium, in such a way as to obtain a magnesium-glucinum alloy from which the magnesium is eliminated by distillation. That is an impossibility, for it has been shown since that glucinum cannot alloy with magnesium (W. Kroll and E. Jeh—Scientific communication from the Bel Air Laboratory—Luxemburg—Siemens Concern—10—No. 2—pages 29/32—1931).

It has in another case been tried to reduce with magnesium an excess of glucinum fluoride in order to obtain compact pure glucinum directly. The tests I have carried out have shown that this process cannot give an industrial result. Glucinum melting at 1280°C . in order to obtain it pure in compact form, it is necessary to obtain it molten, that is to carry out the reduction contemplated above 1280°C . which is impossible, for magnesium boils at 1100°C . and the glucinum fluorides themselves volatilize in an almost complete manner at this last temperature.

On the other hand, as pure magnesium reduces the sodium fluoride as well as the glucinum fluoride, the reaction is violent and explosive because of the evolution of sodium, which forbids carrying it out on the industrial scale.

The process of obtaining compact pure glu-

cinum according to the invention is based upon the fact that zinc alloys with the majority of ordinary metals and upon the fact that it boils at 918° C.; tests carried out by me have proved that glucinum alloys with zinc and that the alloys containing less than 10 percent of glucinum are molten or pasty at about 900° C.

According to the invention, there is prepared, below 918° C., an alloy of zinc and glucinum asaying 5 to 10 percent of glucinum and this alloy is then heated above 1280° C. in a suitable flux, in order to distill off the zinc and to agglomerate by fusion the pure glucinum remaining.

The first operation, which is the preparation of the zinc-glucinum alloy, is carried out in the manner indicated for the manufacture of the copper-glucinum alloy.

In the second operation, the zinc-glucinum alloy is heated above 1280° C., in a graphite crucible, or better in a glucina crucible (magnesia being reduced by glucinum at this temperature), in a flux containing no glucinum, intended only to prevent the oxidation of the metal. As flux, there can be employed a mixture of alkali or alkaline-earth chlorides or a mixture of alkaline earth chlorides and fluorides; it is necessary, of course, that the flux employed shall be fluid below 1300° C. and not volatilize too much at this temperature. There is employed advantageously a mixture in equal parts of barium chloride and barium fluoride.

Heating is continued so long as any zinc is given off, which burns at the exit from the crucible and forms zinc oxide which is easily recovered by any known processes. After cessation of the evolution of zinc, the molten glucinum left in the crucible is cast.

The operation is carried out for example in the following manner:

Example II.—In a graphite crucible, 50 kgs. of GIF_2NaF are melted and the temperature is raised to about 900° C.

Into this bath there are thrown 34.5 kgs. of zinc-magnesium alloy containing about 18.8 percent of magnesium.

The whole is stirred for 15 to 20 minutes with a graphite spatula, while keeping the temperature at about 900° C.

There are then poured out separately: about 54 kgs. of spent bath, which passes to the recovery, and about 30.5 kgs. of zinc-glucinum alloy containing on an average 7.5 percent of glucinum, with still some percents of magnesium.

In a graphite crucible, this alloy is heated to about 1350° C., in a flux composed of a mixture in equal parts of barium chloride and fluoride. Heating continues so long as any zinc is given off, which is converted into oxide upon contact with the air.

There are then poured off about 2 kgs. of pure molten glucinum, which floats in the bath.

The remaining magnesium, volatile at 1100° C., has been eliminated at the same time as the zinc, and there remain only traces of these metals in the pure glucinum, which assays 96 to 98 percent, according to the purity of the primary materials.

There is a yield which exceeds 80 percent of the glucinum brought into the operation.

A modification of this process allows of preparing readily any alloys whatever of glucinum, provided that the metals to be entered into the alloy are capable of alloying with zinc and that these metals are not volatile at about 1300° C.

For this, there is added to the original zinc-

magnesium alloy the desired quantity of the metal, less electropositive than glucinum, which it is desired to alloy with glucinum; the operation is carried out by reduction, according to the invention, which gives a ternary alloy of zinc, of magnesium and of metal less electropositive than glucinum. By heating, the zinc is distilled off and there remains the desired alloy of glucinum in the molten state.

Of course, in order to have suitable melting points, according to the content in metal, less electropositive than glucinum, which it is desired to alloy with the glucinum, it may become necessary to put only a part of this metal, less electropositive than glucinum, into the original zinc-magnesium alloy, so that this alloy shall remain fusible at 918° C.; the rest of the metal, less electropositive than glucinum, will simply be added in the crucible of the second melting, where the zinc is eliminated.

The operation is easier, and is carried out with even better yield than in the case of the manufacture of pure glucinum; in fact, alloys are prepared melting normally at lower temperatures than pure glucinum, the higher density of these alloys permits of agglomerating them more easily by fusion at the bottom of the crucible, and the added metal, less electropositive than glucinum, retains the glucinum and completely prevents losses by carriage-over with the zinc vapours.

The operation may be carried out, for example, in the following manner:

Example III.—There is first prepared, by any known means an alloy of zinc containing 17.1 percent of magnesium and 6.13 percent of iron.

In a graphite crucible, 50 kgs. of GIF_2NaF are melted and the temperature is raised to about 900° C.

Into the molten bath, 36.75 kgs. of the zinc-iron-magnesium alloy are thrown.

The whole is stirred for 15 to 20 minutes, with a graphite spatula, while keeping the temperature at about 900° C.

There are then poured out separately: about 54 kgs. of spent bath, which passes to the recovery, and about 32.75 kgs. of zinc-iron-glucinum alloy containing about 7 percent of glucinum and 7 percent of iron, with still 1 to 3 percent of magnesium.

In a graphite crucible, this alloy is heated to about 1300° C. in a flux, which is for example a mixture in equal parts of barium chloride and fluoride. Heating is continued so long as any zinc is given off, which is converted into oxide upon contact with the air.

There are then poured out more than 4 kgs. of alloy containing 50 percent of iron and 50 percent of glucinum, left at the bottom of the crucible in the molten state.

There remain only traces of magnesium and zinc in this alloy, and the yield has been appreciably better than in the case of the preparation of pure glucinum.

This example, given simply by way of indication, is not limitative. I prepare industrially, by this process, industrial alloys of iron and nickel containing about 50 percent of glucinum; it is easy likewise to prepare copper alloys rich in glucinum, as well as numerous other alloys.

What I claim is:

1. A process for the manufacture of alloys melting at a temperature below 1100° C. of glucinum and of a metal less electropositive than glucinum capable of alloying with magnesium and

with glucinum, consisting in reducing, by an alloy of magnesium and of the said metal less electropositive than glucinum, a double fluoride of an alkali metal and of glucinum, richer in glucinum than the double fluoride containing two molecules of alkali fluoride for one molecule of glucinum fluoride.

2. A process for the manufacture of compact pure metallic glucinum, consisting in preparing an alloy of glucinum and zinc by reducing, by an alloy of magnesium and of zinc, a double fluoride of an alkali metal and of glucinum, richer in glucinum than the double fluoride containing two molecules of alkali fluoride for one molecule of glucinum fluoride and in heating the said alloy of glucinum and zinc, in a bath, at a temperature higher than 1280° C., so as to distil off the zinc and to melt the glucinum.

3. A process for the manufacture of alloys of glucinum and of a metal less electropositive than glucinum, and less volatile than zinc, consisting in reducing, by an alloy of magnesium, of zinc and of the said metal less electropositive than glucinum and less volatile than zinc, which it is desired to alloy with glucinum, a double fluoride of an alkali metal and of glucinum, richer in glucinum than the double fluoride containing two molecules of alkali fluorides for one molecule of glucinum fluoride; in heating the alloy of glucinum, of zinc and of the said metal, in a bath, at a temperature higher than its melting point, so as to distil off the zinc and to agglomerate the residual alloy by melting.

4. A process for the manufacture of alloys melt-

ing at a temperature below 1100° C. of glucinum and of a metal less electropositive than glucinum capable of alloying with magnesium and with glucinum, which comprises reducing, by means of an alloy of magnesium and this metal less electropositive than glucinum, a double fluoride of an alkali metal and glucinum, containing one molecule of alkali fluoride for one molecule of glucinum fluoride.

5. A process for the manufacture of compact pure metallic glucinum which comprises preparing an alloy of glucinum and zinc by reducing, by means of an alloy of magnesium and zinc, a double fluoride of an alkali metal and glucinum containing one molecule of alkali fluoride for one molecule of glucinum fluoride, and heating the alloy of glucinum and zinc, in a bath, at a temperature higher than 1280° C., so as to distil off zinc and melt glucinum.

6. A process for the manufacture of alloys of glucinum and a metal less electropositive than glucinum and less volatile than zinc, which comprises reducing, by means of an alloy of magnesium, zinc and this metal, less electropositive than glucinum and less volatile than zinc, which is to be alloyed with glucinum, a double fluoride of an alkali metal and glucinum containing one molecule of alkali fluoride for one molecule of glucinum fluoride, and heating the alloy of glucinum, zinc and said metal, in a bath, at a temperature higher than its melting point, so as to distil off zinc and to agglomerate the residual alloy by melting.

ROBERT ANDRÉ GADEAU.