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PROCESS FOR THE SEPARATION OF METALS

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10 Claims. (Cl. 75—63)

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This invention relates to the separation by chemical methods of alloyed metals and to the production of anhydrous metal chlorides. More particularly, the invention is a method for effecting such separation, and for producing such anhydrous chlorides, while maintaining the alloy in the solid state. This application is in part a continuation of our applications Ser. No. 502,040 and Ser. No. 502,042, both filed September 11, 1943, and now abandoned.

In practical use, the invention will sometimes be valued chiefly in its role as a separating method, for instance to remove one or more ingredients from an impure metal, leaving a purified metal residue. Sometimes, the preparation of an anhydrous metal chloride will be the important consideration, as for instance the manufacture of manganese chloride from a ferromanganese alloy. In many instances, such as the manufacture of pure manganese by first extracting manganese as manganese chloride from ferromanganese and thereafter precipitating manganese from the manganese chloride, both the metal-separation and the chloride-preparation aspects will be of commercial interest. Accordingly, the general objects of the invention include the separation of alloyed metals, or the preparation of anhydrous chlorides, or both, as may be desired.

In its broadest aspect, the method of the invention involves contacting at a suitably elevated temperature a solid alloy of metals having different affinities for chlorine with an anhydrous chloride of a metal having a lesser affinity for chlorine than a metal of such alloy but an equal or greater affinity for chlorine than another metal of the alloy. The reaction proceeds according to the following equation (valence being ignored):

$$MP+NCl \rightleftharpoons MN+PCl$$

where M and P are metals, P having the higher chlorine affinity, and N is a metal having a chlorine affinity less than that of P but equal to or greater than that of M. The conditions are satisfied when N is identical with M, as will be apparent from the following description.

The reaction is usually carried out for the most part at a temperature above the melting point of the chloride bath but below the melting point of the alloy. In some instances, a powdered alloy may be mixed with a solid chloride and the two heated together, and in some such cases a reaction may commence between solid ingredients; but usually a molten chloride will be present at some stage of the process.

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It is generally preferable that the alloy be in a finely comminuted state inasmuch as the reaction is substantially a surface one in which diffusion plays a significant part. During reaction, metal P must diffuse out of each particle of the comminuted alloy. A second metal N is precipitated, and usually at least partly diffuses into the alloy particles. To obtain the maximum speed of the process, the temperature should be as high, and the alloy as finely divided, as are practicable. The degree of fineness is largely dependent upon the diffusion coefficient of the metal that is to be extracted. Some metals, for instance manganese, have a high diffusion coefficient and accordingly are more rapidly available for reaction than other metals with lower diffusion coefficients. A degree of fineness sufficient to permit the alloy to pass through a 100 mesh screen (0.15 mm. openings) is generally convenient and satisfactory, but an alloy containing metal with a high coefficient of diffusion may be used in somewhat larger particle size, for instance in the form of machine turnings.

Embrittling elements may be added to the alloy to facilitate its comminution by mechanical means. Silicon is especially useful for this purpose, although other elements are known to be effective, for example magnesium or calcium may be used to embrittle copper alloys. After having served their purpose as embrittling agents, the elements may be removed if desired by reaction with other suitable metallic chlorides.

The relative chlorine affinities of the commoner metals in a molten metal chloride bath at temperatures within the range 500° to 1000° C. are indicated in the following list. In this list, the elements are arranged substantially in order of decreasing affinity:

Caesium, rubidium, potassium, barium, strontium, lithium, sodium, calcium, thorium, magnesium, vanadium, zirconium, uranium, manganese, beryllium, aluminum, zinc, cadmium, chromium, iron, thallium, lead, cobalt, copper, tin, silicon, silver, boron, mercury, antimony, nickel, bismuth, arsenic, molybdenum, tungsten, gold.

The position of the metals not included in this list has not yet been ascertained.

Some metals, such as aluminum and silicon, form fairly stable intermetallic compounds with other metals, and such compounds, which appear to have definite positions in the above order, may accordingly resist to some degree the attack by chlorides of metals which otherwise would readily replace an element of the compound; but

in practice such compounds will not often interfere seriously with the desired operation of this invention.

The alloy may be added to a chloride bath consisting merely of the molten chloride to be reacted with the alloy, but it is preferred to form a molten bath diluted with one or more chlorides of metals having a very high affinity for chlorine, for instance one or more alkali metal or alkaline earth metal chlorides. Such dilution decreases fuming and oxidation and often decreases the melting point of the bath. A particularly useful diluent is a mixture of potassium chloride and sodium chloride in a weight ratio approximating 3 parts of the potassium salt to 2 parts of the sodium salt.

Many factors, such as melting point, hygroscopicity, volatility (e. g. titanium tetrachloride and silicon chloride are very volatile at red heat), and tendency to hydrolyze when leached with water, may in a particular instance affect the choice of the metal chloride to be used for carrying out the method of the invention; but the range of possible choice is wide. Iron chloride is particularly satisfactory in commercial applications, due to the position of iron in the above-described order, to its availability at low price, and to its chemical and physical properties. Accordingly, to illustrate the best methods of carrying out the invention the use of iron chloride will be described in detail; but it will be understood that the invention is not limited to or by such specific illustration.

Iron chloride, either ferrous or ferric, can very conveniently be used with a diluent comprising, preferably, one or more of the salts, sodium chloride, potassium chloride, and calcium chloride. These salts do not take part in the reaction, owing to their high position in the chlorine affinity scale, and act as solvents only. The use of such solvents is both desirable and practical since the greater their volume the more dilute is the reacted salt in the precipitated metallic sludges and, as previously mentioned, the less is the oxidation of the reacting chlorides by air and moisture.

Iron trichloride, despite its low boiling point (317° C.), is stabilized by solution in the diluent. It loses its third atom of chlorine by reaction or by thermal dissociation, forming iron dichloride, boiling at 1023° C. Iron dichloride may be used, but the higher chloride is preferred.

A typical example of the practical uses of the invention is for preparing manganese of high purity from manganese-iron alloys, such as commercial grades of ferromanganese.

The principal use for manganese in the metallic state is in the manufacture of steel. For that use ferromanganese, which is widely available in several commercial grades and at reasonable prices, is quite satisfactory.

A purer form of metallic manganese is demanded for some other uses, for instance in the manufacture of nonferrous alloys. The demand has generally been met commercially by reducing manganese oxides with aluminum or by electrolyzing an aqueous solution of manganese sulfate. Although both of these methods yield manganese of good quality, the former requires relatively expensive iron-free manganese oxide as the raw material and the latter requires careful control of the raw material and of each step of the process to avoid impurities in the product.

In accordance with this invention, manganese of high purity is provided by an economical process which may use relatively inexpensive and readily available raw materials, for instance from iron-manganese alloys of ordinary commercial purity, such as ferromanganese.

Thus, the method of the invention comprises contacting an iron-manganese alloy with iron chloride at an elevated temperature below the melting point of the alloy, to form substantially pure manganese chloride, and thereafter recovering the manganese from the manganese chloride.

The alloy should be in a finely-divided state, at least as fine as machine turnings and preferably fine enough to pass a 60 mesh screen. The manganese content of the alloy is not critical, and may be as low as 10%, although at low percentages it may be necessary to contact the chloride bath with several successive fresh batches of alloy to eliminate most of the iron chloride. The alloy may be mixed with solid iron chloride or with a bath of molten chloride.

The chloride bath may initially consist merely of iron (preferably ferric) chloride, but it is preferred to dilute the bath with one or more chlorides of metals which have a high affinity for chlorine, for instance sodium, potassium, lithium, calcium, barium, or magnesium as described above.

The molten salt bath mixture may be maintained at a temperature considerably above the boiling point of ferric chloride (317° C.), and may appropriately be held between 650° and 1050° C. Within this range of temperatures the reaction is satisfactorily rapid.

In a typical specific instance of the practice of the first step of the invention, 210 parts by weight of ferromanganese containing 83.25% manganese, 0.1% carbon, 1% silicon, remainder iron, powdered to pass a 100 mesh screen, was heated for one-half hour at 1000° C. in a bath composed of 1000 parts of potassium chloride and 325 parts of ferric chloride. The resulting salt mixture contained as manganese chloride 92.5% of the manganese originally in the ferromanganese. The iron content of the salt mixture was only 0.22%. The salt mixture was decanted from the iron sludge and was then contacted in a graphite vessel with a small quantity of fresh ferromanganese powder; by this means the iron content of the salt mixture was reduced to 0.02%.

The salts impregnating the iron residue may be recovered by vacuum distillation, or by leaching with water, or by washing with clean, molten manganese-free salts.

As a second step of the process of this invention, the molten salt mixture containing manganese chloride resulting from the first step may be contacted with metal of the group consisting of the alkali metals, the alkaline earth metals, and magnesium. A preferred reagent for this step is magnesium. These metals, having a far greater affinity than manganese for chlorine, replace the manganese in the chloride and precipitate pure manganese in powdered form. After the reaction, most of the salt is decanted, the resulting mixture of manganese and salt is cooled and broken up, and the manganese is washed with water and then dried. Alternatively, the salts may be separated from the manganese by vacuum distillation. The reaction will readily go to completion, leaving only a very low concentration of manganese chloride.

The manganese produced by the process of this invention is pure and clean and in a uniformly sized powder well adapted for use in powder metallurgy and otherwise.

If desired, an excess of magnesium may be used in the second step to produce a magnesium-manganese alloy. For instance, the manganese-chloride salt mixture may be used as an agent for introducing manganese directly into molten magnesium-base alloys.

Other practical applications of the invention will be apparent to those skilled in the art. Accordingly, the invention is not limited to or by the foregoing illustrative example.

In our copending application Serial No. 502,041, filed September 11, 1943, now abandoned, and its continuation-in-part application Serial No. 530,752, filed April 12, 1944, now Patent 2,443,253, a specific fused chloride process involving zirconium is described and claimed. In U. S. Patents 2,396,792 and 2,396,794, issued March 19, 1946, for which application was made March 22, 1944, by William J. Kroll as sole inventor, certain processes involving nickel and fused chlorides are specifically described and claimed.

We claim:

1. The process which comprises contacting a finely comminuted solid alloy of metals having different affinities for chlorine with a molten bath essentially comprising an anhydrous chloride of a metal having a substantially lesser affinity for chlorine than a metal of said alloy and at least as great an affinity for chlorine as another metal of said alloy, maintaining said molten bath at an elevated temperature below the melting point of said alloy, continuing such contact until at least a substantial part of said first-mentioned metal of the alloy is replaced by the metal of said chloride, and separating the resulting salt from the metallic residue.

2. A process as claimed in 1, wherein said alloy is contacted with said chloride in a molten bath containing substantial proportions of at least one alkali metal chloride.

3. In a method of reacting a solid metal alloy with a molten chloride of a metal having a substantially lesser affinity for chlorine than at least one ingredient of said alloy, the improvement which comprises contacting said alloy in a finely comminuted form with a molten mixture of said chloride with at least one chloride selected from the group consisting of the alkali metal chlorides and the alkaline earth metal chlorides.

4. The improved method claimed in claim 3, wherein said mixture comprises iron chloride, sodium chloride, and potassium chloride, the weight ratio of sodium chloride to potassium chloride being about 2 parts of the former to 3 parts of the latter.

5. The process which comprises contacting a finely comminuted solid ferroalloy of a metal having a chlorine affinity greater than that of iron with iron chloride at a temperature above 500° C. but below the melting point of said ferroalloy, continuing such contact until at least a substantial part of said metal is converted to metal chloride, and separating the resulting salt from the metallic residue.

6. A process as claimed in claim 5, wherein said ferroalloy is contacted with said iron chloride in a bath containing substantial proportions of the chlorides of sodium and potassium.

7. The process which comprises contacting a finely comminuted solid ferroalloy of manganese with iron chloride at a temperature above 500° C. but below the melting point of said ferroalloy, continuing such contact until at least the major part of said manganese is converted to manganese chloride, and separating the resulting salt from the metallic residue.

8. The process which comprises contacting solid ferromanganese, comminuted to pass a 100 mesh screen (about 0.15 mm. screen openings), with a bath of iron chloride and alkali metal chloride at a temperature above 500° C. but below the melting point of the ferromanganese, continuing such contact until practically all of the manganese content of the ferromanganese is converted to manganese chloride, and separating the resulting salt mixture from the iron residue.

9. A process as claimed in claim 8, wherein said bath comprises iron chloride, sodium chloride, and potassium chloride, the weight ratio of sodium chloride to potassium chloride being in the neighborhood of 2 parts of the former to 3 parts of the latter.

10. A process as claimed in claim 5, wherein said ferroalloy is contacted with said iron chloride in a bath containing sodium chloride and potassium chloride, the weight ratio of sodium chloride to potassium chloride being in the neighborhood of 2 parts of the former to 3 parts of the latter.

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