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PROCESS OF MAKING ALLOYS

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The present invention relates to a process of making alloys generally, and more particularly to a method of making alloys of beryllium with other metals, especially alloys of beryllium with copper, aluminum, or nickel, and combinations thereof.

An object of the present invention is the provision of a novel method of making beryllium alloys, from a beryllium compound without going through the difficult step of first producing free metal.

In general, the method of the present invention consists in reducing a beryllium salt dissolved in a fused bath of one or more other salts, by a reducing metal alloyed with one or more of the constituents of the desired final alloy.

The salt or salts of the constituents of the desired alloy contained in the fused bath are preferably only those of beryllium, the other constituents of the desired alloy being alloyed with the reducing metal. The reducing metal in combination with one or more of the constituents of the desired alloy, is preferably slowly added to the bath in the form of a coarse powder or chips. When the alloy containing the reducing metal is added to the bath a reaction takes place between the reducing metal and the beryllium salt or salts. In this reaction the beryllium of the desired alloy present as a salt in the bath replaces the reducing metal in the auxiliary alloy and thus form the desired alloy.

After the reaction, the desired alloy is present in the bath either as melted metal or in the form of dispersed pellets or flakes, depending on the temperature of the bath and the melting point of the alloy produced. In the former instance the metal is cast directly, while in the latter case the metal may be melted together by the further heating of the bath to the necessary temperature, or it may be washed free of the salts of the bath by means of water or suitable reagents, and then melted together.

There are certain precautions that must be taken in the practice of the present process. The salt or salts of the bath other than the beryllium salt are preferably water soluble and must be so chosen that they will not react with the reducing metal used, or if a reaction does take place it must be of such a character that the end products thereof will not alloy with the desired alloy or otherwise interfere with the process. As an example, suppose that the bath consists of sodium chloride, and that to this is added beryllium chloride. If there is now added a powdered alloy of copper and magnesium, for the purpose of

making a copper-beryllium alloy, it may be that the magnesium reacts to a limited degree with the sodium chloride to produce sodium. However, even if this does take place the free sodium apparently reacts at once with beryllium chloride to free beryllium so that the end products of the reaction are not objectionable, and are in fact as desired. Even if some free sodium should remain it does not alloy appreciably with the desired copper-beryllium alloy, and it either vaporizes out of the bath or remains in such small quantities that it can be leached out harmlessly. In general, most of the halides of the alkali and the alkaline earth metals and of magnesium answer very well the requirements of a suitable bath for the present process.

The use of an inert salt as part of the bath, such as a halide of an alkali or alkaline earth metal as mentioned in the preceding paragraph, provides a diluent which reduces the violence of the subsequent reaction and prevents deterioration of the other metallic salts present. Although desirable it is not absolutely necessary to have such a diluent present at the beginning of the operation, as it is possible to begin with a bath consisting only of a beryllium salt, and as the reducing metal is added, the reaction produces in place a salt of the reducing metal which acts as a diluent. In general, however, it is better to add the diluent before the beginning of the reaction, rather than to form it in place.

For the purposes of the present invention, the beryllium salt or salts forming a part of the bath are preferably the bromides, iodides, and chlorides. Chemically, the bromides and iodide are quite suitable, but they are not economical because of their high cost and low metallic content. The most generally suitable is the chloride, because it is substantially completely decomposed by a properly chosen reducing metal, and also because it is easy and economical to produce and use.

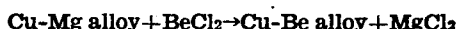
The reducing metal must be capable of displacing from its salt or salts the beryllium desired in the alloy, and capable of alloying with the remaining constituents of the desired alloy. The reducing metal must also be capable of being completely displaced from auxiliary alloy by the beryllium salts present in the bath. All these requirements are met by magnesium.

The practice of adding the reducing metal as an auxiliary alloy with the other desired constituents, except of course the beryllium which is added as a salt or salts, produces the most intimate degree of mixing between the ingredients

and is most conducive to the alloying action that takes place after the reaction in the bath. Such alloys are also usually quite brittle and may more easily be reduced to fine powders than the pure metals themselves.

The making of copper-beryllium alloy offers a good illustration of the preferred method of the present invention. As a preliminary step an auxiliary alloy of copper and magnesium is first made containing say twenty-five percent of magnesium by weight. The copper-magnesium alloy is quite brittle and may readily be reduced to powder by crushing or grinding. A fairly coarse powder passing through a fifty mesh sieve is quite satisfactory. A quantity of sodium and potassium chlorides in approximately equal parts is then fused in a suitable vessel which may be of iron or ferro-chrome, but is preferably a fused silica crucible. Other salts such as barium, calcium, or magnesium chlorides, or the like, may be used, either alone or in combination, but sodium and potassium chlorides are desirable because of their cheapness and the fact that they form a fairly low melting point eutectic.

After the bath of sodium and potassium chlorides has been fused, and while it is not much above its melting point, a quantity of a suitable beryllium salt is added, preferably beryllium chloride. The amount of the beryllium salt added is preferably about one-third, by weight, of the other salts making up the bath, although this proportion is not at all critical. The proportion of beryllium salt may readily be from 5% to 75% of the total bath. After the addition of beryllium salt to the bath is completed the previously prepared powdered alloy of copper and magnesium is added slowly, a little at a time, and stirred thoroughly. A reaction between the beryllium chloride contained in the bath, and the magnesium contained in the copper magnesium alloy takes place, which probably proceeds as follows:



Whether this transition takes place in one step as indicated or whether it is accompanied by intermediate reactions is not known, and is immaterial for the present purpose. In any event the final result is as indicated by the above reaction.

The amount of auxiliary alloy to be added is preferably such that its magnesium content is ninety to ninety-five percent of the theoretical amount required to reduce all of the beryllium chloride in the bath. This allows for some loss of beryllium chloride by vaporization during the reaction, and insures that the resulting alloy shall be free of magnesium. During the operation a draft can be maintained over the reaction vessel, and directed into a suitable condensing system, which will catch the vaporized salts so that they may be recovered and reworked.

After the reaction between the copper-magnesium and the beryllium chloride has been completed, the newly formed copper-beryllium alloy sinks to the bottom. The clear supernatant portion of the bath may be poured off and the metal remaining behind with just enough salt to protect it from oxidation is permitted to solidify. It is then crushed and leached out with water, leaving the pure alloy in the form of small grains and pellets. The appearance of this metal under the microscope, its specific gravity, its melting point, and its other physical properties all indicate that it is already a true alloy and not merely a conglomerate. Another method of recovering the newly formed alloy is to heat the bath further

after the reaction with the copper-magnesium has been completed. In this way the newly formed copper-beryllium alloy can be melted in place. The supernatant bath can then be poured off and the alloy cast directly in suitable molds.

Where the presence of the reducing metal in any substantial amount in the desired alloy is objectionable it is especially advantageous to maintain the bath at a comparatively low temperature, that is just below the melting point of the alloy to be produced and also, where possible, below the melting point of the reducing metal or the auxiliary alloy comprising the same. The reason for this is apparently that the reducing metal or its auxiliary alloy, if melted in the bath, agglomerates into drops or bodies of considerable dimension and hence exposes less reaction surface. As a result not all the reducing metal reacts with the bath and some of it is left as an undesirable ingredient in the final alloy produced. Further, if the bath is operated at a temperature above the melting point of the alloy to be produced, any reducing metal trapped in the main melted body of the alloy being produced is considerably hindered from reacting with the bath and again remains in the final alloy as an undesirable ingredient. However, if the temperature of the bath is below the melting point of either the reducing metal or its auxiliary alloy and the alloy being produced, then all the metals are present as fine powder dispersed through the bath offering a maximum of reaction surface. These conditions favor the most complete utilization of the reducing metal and its minimum retention in the final alloy.

Without being limited in any way to the specific proportions and other details given, a specific operation illustrating in detail the process of the present invention will be described. In the preparation of a beryllium-copper alloy, 300 grams of sodium chloride and 300 grams of potassium chloride were fused at a temperature of about 650° C., and 195 grams of beryllium chloride containing theoretically about 22 grams of beryllium, added thereto. Two hundred grams of powdered copper-magnesium alloy in the form of powder that would pass through a 60 mesh screen was then added. Previous analysis of this alloy showed that it contained 26.3% magnesium with the balance substantially copper. The amount of magnesium in the 200 grams of alloy was therefore 52.6 grams and would reduce an amount of beryllium which bears the same ratio to 52.6 that the atomic weight of beryllium 9.02 bears to the atomic weight of magnesium, 24.32, or about 19.5 grams which in the present case was about 88.6 of the theoretical amount of beryllium in the chloride. The amount of copper in the copper-magnesium alloy added was 147.4 grams, which with the maximum amount of beryllium that could be reduced, namely 19.5 grams, would theoretically make an alloy containing 11.7% beryllium.

After the reaction was completed the bath was heated until the contained alloy melted, and the alloy was then cast as a single piece. This piece weighed 160 grams and on analysis was found to contain 11.3% beryllium, against 11.7% theoretically possible as calculated above. The 160 gram ingot of copper-beryllium recovered therefore contained about 18.1 grams of beryllium which is about 82% of the total theoretical amount present in the chloride used, and about 95% of the total amount possible to recover with the weight of magnesium used. The analysis of the ingot

also showed that it contained only .022% of magnesium.

Alloys of aluminum with beryllium and nickel with beryllium can be made in substantially the same manner except that in the former instance a powdered alloy of aluminum and magnesium is added to the bath, while in the latter instance a powdered alloy of nickel and magnesium is used. The results obtained are of the same order already described for copper-beryllium and the resultant alloys are equally free from magnesium.

It is obvious that alloys of beryllium and metals other than those already mentioned can be formed by this process, and that it can likewise be applied to which alloys of more than two components.

It has heretofore been proposed to make alloys of beryllium from beryllium fluoride, using magnesium as a reducing metal, usually at temperatures of 1300° C. or higher. The difficulties of this practice are very great in comparison with the present invention. At the high temperature necessary the losses of both the reducing metal and the beryllium fluoride are very high. It is also difficult to find suitable refractories for holding fused fluorides at such temperatures. The overall recoveries are very low, and the alloy formed must be remelted several times to free it from the refractory bath materials. The alloy formed is also always objectionably high in magnesium content.

In comparison, the present process can be carried on at a relatively low temperature, actually below the melting point of the alloy thus formed, and in silica or similar ware that does not introduce impurities. Losses by vaporization are negligible. The alloy produced is practically free of magnesium and can be melted easily and with high recoveries. Ordinarily it can be recovered in pure form as flakes or granules by a simple leaching, since soluble salts may be used in the bath instead of the usually insoluble fluorides. The over-all recoveries are high. Also when magnesium is used as a reducing metal with a chloride of the metal desired in the final alloy, it is transformed to an anhydrous chloride from which it is easily recoverable as metal by electrolysis.

While the preferred embodiment of the method of the present invention has been illustrated in detail, we do not wish to be limited by the specific proportions or other details given, and we particularly point out and claim as our invention, the following:

1. The method of making a nickel beryllium alloy which comprises treating a fused salt bath comprising beryllium chloride and a salt not reducible by magnesium with an alloy of nickel and magnesium, said bath being maintained at a temperature below the melting point of the alloy being formed.

2. The method of making an aluminum beryllium alloy which comprises treating a fused salt bath comprising beryllium chloride and a salt not reducible by magnesium with an alloy of aluminum and magnesium, said bath being main-

tained at a temperature below the melting point of the alloy being formed.

3. The process of making a beryllium alloy which comprises the following steps: preparing an auxiliary alloy of magnesium and a metal which it is desired to alloy with beryllium, and introducing this alloy into a fused salt bath comprising beryllium chloride and a salt not reducible by magnesium, said bath being maintained at a temperature below the melting point of the alloy being formed.

4. The process of making a beryllium alloy which comprises the following steps: preparing an auxiliary alloy of magnesium and a metal which it is desired to alloy with beryllium, and introducing this alloy into a fused salt bath maintained at a temperature below the melting point of the alloy being formed, said bath comprising beryllium chloride and a halide of any of the metals of the alkaline and alkaline earth groups.

5. The process of making a beryllium alloy which comprises the following steps: preparing an auxiliary alloy of magnesium and a metal which it is desired to alloy with beryllium, and introducing this alloy into a fused salt bath comprising beryllium chloride and a chloride of any of the metals of the alkaline and alkaline earth groups while said bath is maintained at a temperature below the melting point of the alloy being formed.

6. The process of making a copper-beryllium alloy which comprises the following steps: preparing an auxiliary alloy of copper and magnesium, and introducing this alloy into a fused salt bath comprising beryllium chloride and approximately equal parts of sodium chloride and potassium chloride, said bath being maintained at a temperature below the melting point of the copper-beryllium alloy being formed.

7. The process of making a copper-beryllium alloy which comprises the following steps: preparing an auxiliary alloy of copper and magnesium, and introducing this alloy into a fused salt bath comprising beryllium chloride and approximately equal parts of sodium chloride and potassium chloride maintained at a temperature below the melting point of the copper-beryllium alloy being formed, the amount of magnesium in the auxiliary alloy added being less than the theoretical amount required to replace all of the beryllium of the beryllium chloride.

8. The process of making a copper-beryllium alloy which comprises the following steps: preparing an auxiliary alloy of copper and magnesium, introducing this alloy in powder form into a fused salt bath comprising beryllium chloride and approximately equal parts of sodium chloride and potassium chloride maintained at a temperature below the melting point of the copper-beryllium alloy being formed, the amount of magnesium in the auxiliary alloy added being somewhat less than the theoretical amount required to replace all of the beryllium of the beryllium chloride, and subsequently leaching out the copper-beryllium alloy formed.

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