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PREPARATION OF ALKALINE EARTH
METAL ALLOYS

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This invention relates to the preparation of alloys and, in particular, is concerned with the preparation of alloys of the alkaline earth metals.

It has long been known that alloys of alkaline earth metals can be prepared by various methods. One such method involves heating an alkaline earth metal with another metal at temperatures above their melting point and then cooling the melt to form the alloy. Likewise, by this procedure various inter-metallic compounds of the alkaline earth metals as, for example, Mg_2Ca have been prepared. By this and other known techniques for the preparation of metal alloys the alloy is obtained in massive form. These masses or agglomerates of the alloys can be powdered by crushing, grinding, and the like techniques as has been the procedure in powder-metallurgical operations. These alloys have been found suitable to a certain degree for applications in forming structural materials, such as, for example, molding the particles under high compression into particular forms. They have not been found practical for employment in various chemical reactions since they suffer the disadvantage of heterogeneous composition thereby resulting in erratic reaction rates and also greatly affecting reactivity. Further, crushing, grinding, and the like mechanical techniques for preparing the powdered alloys are costly and time consuming. As a result of my work in this field a process has now been discovered for the direct preparation of powdered alloys and, in particular, of powdered inter-metallic compounds containing an alkaline earth metal as one of the components.

It is, therefore, an object of this invention to provide a novel process for the preparation of alloys of the alkaline earth metals. A further object of this invention is the preparation of alloys of alkaline earth metals by employing an alkali metal as a solvent. Another object is the direct preparation of powdered alloys of the alkaline earth metals having definite chemical composition. A still further object of this invention is to provide novel forms of the alloys of the alkaline earth metals. Other objects will be evident from the discussion hereinafter.

The above and other objects of this invention are accomplished by a process which comprises dissolving in an alkali metal at elevated temperature an alkaline earth metal and at least one other metal soluble in alkali metal, cooling the solution to a temperature whereby solidification of an alloy of the alkaline earth metal occurs, and recovering the alloy of alkaline earth metal formed. Generally speaking, this process can be employed to form alloys of an alkaline earth metal with any other metal including a different alkaline earth metal which is soluble in the alkali metal employed as a solvent at temperatures above the melting point of the alkali metal but below the boiling point of the alkali metal. The metals to be alloyed should also be soluble in each other. The metals which we have found to be most suitable in alloying the alkaline earth metal

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are selected from the group consisting of a different alkaline earth metal, aluminum, gallium, and indium. The alkaline earth metals include beryllium, magnesium, calcium, strontium, and barium.

By the process of this invention the alloy is directly prepared in powdered form. Not only are the alloys in powdered form, but they are also of irregularly shaped crystalline structure which, when recovered from the alkali metal, are stable and free flowing. Because of the irregularly shaped crystalline structure of these alloys and the small particle sizes which are achieved, they are highly reactive in chemical reactions. They are, however, easily handled at ordinary atmospheric conditions. Thus, the process of this invention provides a method for directly producing powdered alloys of alkaline earth metals which are ideally suited for direct use in many processes without resorting to further treatment, such as crushing and grinding.

The alkali metals are employed as solvent metals in the process of this invention. These metals include lithium, sodium, potassium, rubidium, and cesium, or mixtures thereof. These metals are employed in excess quantity, that is, in quantities at least sufficient to dissolve the metals to be alloyed at the temperature at which solution is desired. Ordinarily the temperature which is employed is above the melting point of the alkali metal and temperatures as high as the boiling point of the alkali metal can be employed. Temperatures above the boiling point of the alkali metal should be avoided in most cases since these will require pressure operations. However, it is to be understood that pressures above atmospheric can be employed and temperatures above the boiling point of the alkali metal, in those instances where greater solubility is desired. The temperature to be employed during solution of the metals will depend upon the solubility of the alloying metals in the quantity of alkali metal employed as a solvent. Thus, for a given temperature of solution, sufficient alkali metal is employed to essentially completely dissolve the alloying metals.

Various alternative methods of conducting this process can be employed. For example, sufficient alkali metal can be heated to its melting point and bulk alloying metals in respective proportions to that desired in the alloy can be added to the alkali melt. When totally dissolved, the melt can be cooled to the precipitation temperature of the alloy. Another method involves adding the alkali metal and alloying metals together to a melting pot, heating the mixture to a temperature sufficient for complete solution, and then cooling to precipitate the alloy desired. Another modification would be heating a mixture of the alkali metal and alkaline earth metal to solution temperature and then dissolving the alloying metal in this solution and cooling to precipitation temperature. Still another modification is to employ a mixture of the alloying metals or, for that matter, an alloy of the metals with or without additional alloying metal for dissolving into the alkali metal. Even in this latter instance the product is obtained directly in powdered crystalline form. Other modifications will be evident to those skilled in the art.

Likewise, various methods for the recovery of the alkaline earth metal alloy from the alkali metal can be employed. For example, the suspension of the alloy in the alkali metal can be filtered to remove the alkali metal at a temperature above its melting point and adhering alkali metal can be removed from the filter cake by a suitable technique such as vaporization. Another method involves distilling the alkali metal away from the alloy, if desired, employing vacuum systems at temperatures which do not appreciably affect the alloy. A preferred

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method for separating the alkali metal from the alloy is to cool the melt to between just above the melting point of the alkali metal and about room temperature and then react the mass with an alcohol or other organic solvent which is more reactive with the alkali metal than with the alloy for a sufficient period of time to react with the alkali metal but not with the alkaline earth metal alloy. This procedure is described in more detail with regard to recovery of alkaline earth metal in U. S. 2,543,406 by Eugene F. Hill. When employing an alcohol, the reaction is enhanced when the alcohol contains a minor proportion of water; that is, up to about 15 percent by weight. The procedure is described by Hill and Soroos in U. S. 2,543,407. Generally, an excess of the alcohol over that required to consume the alkali metal is employed and the suspended alloy is then removed from the system and dried to drive off excess alcohol. The alkali metal alcoholate which is formed is of high purity and can be recovered as a by-product of this process. Still other methods of recovery of the alloy will be evident to those skilled in the art.

To demonstrate the process of this invention and the products which are thereby obtained the following examples are presented:

Example I

To a stainless steel crucible equipped with a means for agitation, external heating means, and inlet and outlet ports for a continuous blanket of inert gas, such as argon, was added 160 parts sodium, 17 parts of calcium turnings, and 23 parts of aluminum pellets. The vessel was then heated to about 850° C. while maintained under an argon atmosphere to melt the sodium and dissolve all the aluminum and calcium. The melt was then cooled with continuous agitation to 100° C. over a period of 2 hours. The suspension of the finely-divided alloy in molten sodium was then transferred to a second vessel under kerosene and cooled in this second vessel to room temperature. The kerosene was withdrawn from the solid suspension of the alloy in sodium and excess methanol containing about 2½ percent by weight of water was added to the vessel in amount sufficient to consume all of the sodium. The liquid portion was removed from the alloy and the alloy further washed successively with methanol and hexanes and dried. The yield obtained was 88 percent and the particles without further grinding or other action were less than 246 microns in size. Examination of the particles microscopically and by X-ray diffraction showed them to be multisurface, irregularly shaped (i. e., with protrusions and depressions), and crystalline. The surface to volume ratio is very high—higher than that obtained by pulverization of the bulk alloy to a similar particle size. The particles were analyzed by X-ray diffraction and were shown to be greater than 95 percent pure Al_2Ca . The pattern used in the X-ray diffraction analysis was a sample of pure Al_2Ca .

Example II

The process followed in this run was essentially the same as described in the preceding example except that 22.4 parts of calcium, 17.6 parts of magnesium, and 160 parts of sodium were employed and the cooling time was 30 minutes. Upon cooling to room temperature, the sodium was reacted first with excess isopropanol, then with methanol and the alloy washed as described in the preceding example. The product obtained was Ca_3Mg_4 of high purity in yield above 90 percent and of physical structure as described in Example I.

It is not necessary that the metals be fed essentially pure to the system and, as pointed out above, the sequence of addition of the materials can be varied. The following example demonstrates the employment of a commercially available mixture of sodium and calcium for alloying calcium with magnesium.

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Example III

To the reactor 181 parts of sludge as obtained as a by-product in the production of sodium employing a Downs cell operation (10 percent calcium, 85 percent sodium, and 5 percent calcium and sodium chlorides and oxides) was added and heated to about 800° C. To this melt was added 21.9 parts of magnesium and with mild agitation the melt was cooled to room temperature over a period of about 110 minutes. The alloy was recovered as described in Example I in finely-divided crystalline particles of less than 300 microns ranging from about 0.5 to 300 microns, and analysis shows the alloy to be the inter-metallic compound Mg_2Ca .

Example IV

An alloy of strontium and magnesium is prepared in high yield and purity according to the procedure described in Example I when employing 50 parts of strontium, 50 parts of magnesium and 150 parts of sodium.

Example V

When employing 71 parts beryllium and 27 parts calcium in excess sodium according to Example I, a powdered alloy of beryllium and calcium is formed.

Example VI

When 20 parts magnesium and 20 parts aluminum in 160 parts potassium are heated to a temperature of 700° C. and cooled employing a procedure similar to that of Example I, a powdered alloy of magnesium and aluminum is precipitated from the mixture. In employing potassium, isopropanol and high molecular weight alcohols are employed to react off the potassium in order to avoid a too vigorous reaction.

Example VII

Employing a procedure essentially as described in Example I an alloy of strontium and aluminum is prepared when 35 parts of strontium and 50 parts of aluminum are dissolved in 200 parts of lithium at about 1200° C.

Example VIII

To molten lithium (210 parts) at a temperature of 1300° C. is added 50 parts calcium and 15 parts indium. A crystalline calcium-indium alloy is precipitated in high yield and purity when separating essentially as described in Example I.

The above examples are presented merely as illustrations of the process of this invention and, as stated previously, various alloys of alkaline earth metals with another alkaline earth metal or aluminum, gallium, and indium, can be prepared by a similar process. It will be obvious that ternary alloys can be prepared by adding a third metal to the mixture of any of the above examples. Thus, for example, when dissolving calcium, aluminum, and magnesium in molten sodium according to my process, a ternary alloy of these metals is obtained. Likewise, the proportions of the alloying metals can be varied over wide limits and, in general, depend upon the composition of the alloy desired.

This process is particularly applicable to the preparation of inter-metallic compounds. In this application the relative proportions of each of the alloying metals employed should be within about 5 percent by weight of the stoichiometric amount required for the inter-metallic compound desired. For example, for preparing the inter-metallic compound Mg_2Ca , best results are achieved when between about 1.15 to 1.25 parts by weight of magnesium per part by weight of calcium are dissolved in molten sodium and the solution cooled to room temperature. In a particularly preferred embodiment, I employ the metals in substantially the stoichiometric amounts required to form the compound desired since the best crystalline structure is obtained and the range of particle size is smaller.

In the preferred method of recovery of the alloy powder from the alkali metal wherein the alcohols are employed, the alcohols which are preferred are those of low molecular weight, that is, those containing about less than 8 carbon atoms as, for example, methanol, ethanol, propanol, octanol, and the like, since these are more reactive with the alkali metal. It is to be understood, however, that other alcohols not within this range can be employed but are not preferred primarily because of availability and longer reaction time. As mentioned previously, it is desirable that the alcohol employed contain some water since this water will catalyze the reactivity of the alcohol with the alkali metal and inhibit reaction with the alkaline earth metal. Water in amounts up to about 50 percent by weight can be employed based upon the weight of the alcohol, but percentages between about 0.25 and 15 percent are preferred in order to obtain a more pure alcoholate by-product and to avoid reactivity of the alloy with the alcohols. The temperature employed during recovery using an alcohol is preferably below the boiling point of the alcohol in order to avoid pressure operation and a too vigorous reaction. Accordingly, the melt is preferably cooled to a temperature below the boiling point of the alcohol to be employed.

Now, turning to the products produced by the process of this invention, these products are, for the first time, made available to the public in a new physical form. As mentioned previously, the alloys are directly produced as powders whose particle sizes are generally less than about 500 microns. The particle size which we prefer ranges between 1 and 300 microns since these smaller sizes are more reactive. Understandably, the rate of cooling of the melt will influence the particle size of the product, that is, the longer the cooling time the larger the particle size will be and vice versa with shorter cooling periods. The particles are crystalline having many surfaces and irregularly shaped, that is, having protrusions and depressions. Thus, the surface to volume ratio is high providing greater reactive surface area. In addition to being of such fine particle size and structure, the alloys as obtained in the process of this invention are free flowing, that is, they are easily handled by ordinary techniques in which powders are employed. The powdered alloys as produced by this process are also stable to the atmosphere particularly at room temperatures and are of uniform composition. It is preferable, however, in order to avoid contamination by moisture in the atmosphere during storage, to maintain an inert or dry atmosphere in the storage vessels. Inert atmospheres can be, for example, dry air and the inert gases, argon, nitrogen, and the like. Another characteristic of the products produced by this invention is that they are not pyrophoric at room temperature. This characteristic is of particular value in that in this form they are practical for usage by minimizing the hazards involved when employing such highly reactive materials. An alloy of calcium, for example, is less reactive to the atmosphere than calcium metal itself and yet still highly reactive in chemical applications. The compositions which are preferred having the above characteristics are those of the inter-metallic compounds, in particular, Mg_2Ca and Al_2Ca . The latter alloys are more reactive forms of the calcium alloys which are particularly adapted for use in pyrotechnics. Not only are they stable to the atmosphere, but in pyrotechnic use they provide quick and uniform firing of the flares.

The present invention provides a novel process for the production of alloys of alkaline earth metals and of novel forms of these alloys. The powdered alloys, in addition to being useful in the ordinary structural uses of powdered alloys as previously known, are significant in that they are stable to the atmosphere yet more reactive in chemical applications. For example, when employing

these alloys for deoxidation of metals, it will be found that such an operation can be conducted more rapidly and efficiently. Improved pyrotechnic compositions can be prepared employing these powdered alloys because of their free flowing particulate nature and their great chemical reactivity. Likewise, because of their greater stability to the atmosphere, they are safer to handle than are, for example, such pyrotechnic materials as powdered calcium metal. Another use for these alloys is that they are admirably suited as tracers for rockets. In this application because of the brilliant flare which is achieved and because of the fact that they are in powdered form, control of the trace is easily attained. They can also be employed as additives to jet fuels and the like, particularly in the afterburners for improving the combustion characteristics of such fuels. In this use the alloys of calcium-magnesium and calcium-aluminum are ideal because of their high heats of combustion. Still other uses will be evident to those skilled in the art.

Having thus described the process of this invention and the products thereby obtained, it is not intended that it be limited except as noted in the appended claims.

I claim:

1. A process for the preparation of a powdered, stable, free flowing, irregularly shaped, crystalline alkaline earth metal alloy comprising dissolving an alkaline earth metal and at least one other metal selected from the group consisting of a different alkaline earth metal, aluminum, gallium, and indium, into molten alkali metal, cooling the melt to a temperature where the alloy formed is in solid state, and separating said powdered alloy from said alkali metal.

2. A process for the preparation of a powdered, stable, free flowing, irregularly shaped, crystalline alloy of calcium having the formula Mg_2Ca which comprises dissolving magnesium and calcium in proportions of between about 1.15 to 1.25 parts by weight of magnesium per part by weight of calcium in molten sodium, cooling the solution to room temperature, and recovering the powdered crystalline alloy thereby formed by reacting the sodium with at least the stoichiometric amount of methanol at a temperature below the boiling point of methanol.

3. A process for the preparation of powdered, irregularly shaped crystalline alloy of aluminum and calcium having the formula Al_2Ca which comprises dissolving aluminum and calcium in proportion within about 5 percent of the stoichiometric amount in molten sodium, cooling the solution to a temperature where the alloy formed is in solid state, and recovering said alloy by reacting the sodium with at least the stoichiometric amount of methanol at a temperature below the boiling point of methanol.

4. A process for the preparation of powdered, irregularly shaped, crystalline alloy of aluminum and calcium which comprises mixing about 160 parts sodium, about 17 parts of calcium turnings and about 23 parts of aluminum pellets at a temperature of about 850° C. over a period of 2 hours then cooling the melt to room temperature and adding methanol containing about 2½ percent by weight of water in amount sufficient to consume all of the sodium, removing the liquid portion from the alloy, washing the alloy successively with methanol and hexanes, and then drying the alloy.

5. A powdered alloy product consisting of stable, free flowing, irregularly shaped, discrete crystals of uniform composition comprising an alkaline earth metal and at least one other metal selected from the group consisting of a different alkaline earth metal, aluminum, gallium and indium, said crystals having a particle size between about 1 and 500 microns.

6. A powdered alloy product consisting of stable, free flowing, irregularly shaped, discrete crystals each having the composition substantially equivalent to the formula Al_2Ca and a particle size of less than 500 microns.

7. A powdered alloy product consisting of stable, free

flowing, irregularly shaped, discrete crystals each having a composition substantially equivalent to the formula Mg_2Ca and a particle size less than 300 microns.

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