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MODIFICATION OF ALUMINUM, ALUMINUM ALLOYS, AND ALLOYS CONTAINING ALUMINUM

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This invention relates to the "modification" of aluminum, aluminum-base alloys, and alloys containing aluminum. In using the term "modification" I refer to the treatment of metals (including thereby alloys also) by adding thereto a substance or material which changes the internal physical structure of the metal, and by putting the impurities or alloying ingredients or both, as the case may be, in a finely divided and highly dispersed condition produces a beneficial effect upon the physical properties and often upon the chemical properties also of the metal so treated.

One object of the invention is to provide a new method of modifying aluminum, aluminum base alloys, and alloys containing aluminum, as for instance iron and steel containing aluminum, which will increase the homogeneity of the metal, improve the physical properties, and have the useful effects hereinafter described. Among the further objects of the invention is to provide a method of modification which will require less care and control in practicing it in a foundry than the previously known methods.

Hitherto the modification of aluminum, aluminum base alloys, and alloys containing aluminum, all of which are hereinafter referred to collectively as aluminum alloys, has been accomplished by adding to the melted alloy a metal or compound of a metal, such as fluorides of the alkali metals, oxides and hydroxides of the alkali metals, alkali metals in the metallic state, bismuth, and some other substances. Especially when the aluminum alloy contains silicon has a modifying effect been attained.

In the case where fluorides have been used it has been found that only those which by reaction with the aluminum produce an alkali metal are generally successful. There is another class of fluorides which, even when they contain an alkali metal, do not appear to react in the same way to give a satisfactory modification, and when they do not contain alkali metal have only a little or no satisfactory effect. Among those fluorides are the alkaline earth fluorides, such as calcium and barium, the light metal fluorides, such as aluminum and magnesium, the heavy metal fluorides, such as manganese and zinc, and the double fluorides, including the double fluorides which contain an alkali metal as well as some other metal. For convenience in describing and setting forth my invention I hereafter refer to this group of fluorides which do not produce a satisfactory modifying effect, or which produce no substantial modifying effect, as stable fluorides.

The invention is based on my discovery that if the molten aluminum alloy is treated with a mixture of one or more of the stable fluorides and an alkali metal carbonate, a modification will be obtained. Therefore, mixtures are used which decompose simultaneously by reactions and whose decomposition products, which may be supposed to be in statu nascendi, act upon the molten metal. In this case the mixture which is placed on the molten metal is composed of fluorides which in themselves can not be decomposed immediately on contact with the molten metal on the one hand, and alkali metal carbonate on the other hand. Such fluorides are, for example, the double fluorides of the alkali metals, such as sodium-aluminum fluoride and sodium-silico fluoride, also alkaline earth fluorides, such as calcium fluoride, barium fluoride, and finally aluminum fluoride, magnesium fluoride and also fluorides of the heavy metals, such as manganese fluoride and the like. While these stable fluorides, when used alone, show no refining effect, it has been shown in a surprising manner that in mixtures with alkali metal carbonates they are decomposed at normal treating temperature and, on the other hand, decompose the alkali carbonates and thus exert an increased effect on the dispersion of all alloy constituents, as compared to the former processes. It is not known in detail whereon the increased combination effect of mixtures of fluorides and carbonates decomposed by reaction with each other is based. It is only supposed that the formation of alkali fluorides with simultaneous development of carbonic acid is a measure of the effect produced according to the invention.

The alkali carbonates used with fluorides in the mixture according to the invention can also be used singly or mixed together. Of these alkali carbonates, lithium carbonate is to be preferred because it tends to exert a great influence on the dispersion of the alloy constituents, such as iron, copper, manganese and the like. Aluminum alloys containing copper particularly, and in this case especially the rolling and casting alloys which are to be improved by means of heat treatment in the form of annealing, quenching and aging, are considerably improved, as the lithium is introduced in a simple and inexpensive manner; it is also to be used with magnesium which is very effective in treatment, and particularly in combination with magnesium shows very high heat treating effects.

The salt mixtures which have been used heretofore, particularly in alloys for granulation, for removing non-metallic impurities from the melt

and for dissolving the aluminum oxides, such as alkali chloride and calcium chloride, do not react in the sense of the present invention, but only effect a mechanical purification and are, therefore, to be considered only as fluxing mediums or covering salts.

In alloys containing aluminum which melt at higher temperatures, such as aluminum bronzes, steel containing aluminum, or precious metal alloys containing aluminum, the reaction mixture is used satisfactorily without further addition. In the treatment of aluminum melts and aluminum alloys with high aluminum contents, on the other hand, it has proved advantageous to add to the reaction mixture substances which reduce the melting temperature of the mixture. In this case alkali chlorides, for example a mixture of 60 parts potassium chloride and 40 parts sodium chloride, of which mixture about 30 to 100 parts are added to the fluoride-carbonate mixture, are to be considered in the front ranks. Also borates and other known fluxing mediums may be used to advantage.

The use of the reaction mixture is especially advantageous for increasing and dispersion of aluminum-silicon alloys, and therein, apart from the silicon content, the other alloy constituents, such as iron and copper, are also reduced to a finely divided state. It has been shown hitherto that the iron content in binary as well as in aluminum-silicon alloys containing other elements must be kept very low, that is, not over 0.6 per cent if possible, as otherwise there will be a deleterious effect on the elongation. The process according to my invention has a great advantage in that it does not make the production of high percentage alloys either wholly or partially dependent on assumptions, such as mass content, applicability of certain metals and the like, such as has been the case in former modifying processes. While, for example, the production of satisfactory aluminum-silicon alloys containing iron is based on the assumption that the iron content should not exceed 0.6 per cent if possible, and in such case considerable portions of the raw aluminum produced can not be used for this purpose, the process according to the invention permits the use of double the amount of iron, and thereby makes use of considerable amounts of original materials which have hitherto been considered unusable in the production of high percentage alloys.

The aluminum alloys with 12 to 13 per cent silicon and about 0.8 per cent copper and, if necessary, 0.2 to 0.5 per cent manganese, which are preferred particularly for lightly constructed aircraft motors on account of their high oscillating capacity, are considerably improved by the treatment with the reaction mixture. The increased tendency to porosity which is noticeable in these alloys containing copper is restrained, so that they become suitable in the fabrication of cylinder blocks, cylinder heads and the like in a larger measure, for which purposes they should be given preference, as compared with other alloys, on account of their great hardness, good workability and high elastic limit. The copper content in this case may also considerably exceed the former usual limit of 0.8 per cent and thereby considerably increase the greatly desired oscillating capacity as well as the resistance to distortion.

The process is also very suitable in the treatment of alloys having high silicon contents, which, with contents of 20 to 30 per cent silicon, are used principally in the production of pistons and similar construction parts.

The application of the process is to be explained in more detail in the light of the following examples.

An aluminum alloy containing about 13 per cent silicon and 1.14 per cent iron was mixed with a mixture of 5 parts calcium fluoride and 6.5 per cent sodium carbonate which was pulverized after fusing. The proportion of this mixture amounts to about 1½ per cent of the weight of the treated alloy. After solidification the alloy showed a fine distribution of all components of the alloy and in the mechanical test showed a tensile strength of over 20 kg. and an elongation of 5 to 6 per cent. The amounts of the mixture generally amounted to about 0.5 to 3 per cent. The microscope showed that the crystals containing iron were much smaller in size as well as in number than in previously treated and normally modified alloy.

The process may also be used in direct combination with the electrolytic reduction of the virgin aluminum or alloys containing aluminum. In this case the procedure is such that an equal portion of alkali carbonate is added to the fluoride used, for example to electrolytes containing cryolite, so that the reaction mixture is produced by the use of the fluid electrolyte, and the so treated alloys show the same favorable properties as when the treatment is accomplished in a special process, independent of the electrolysis, For example, one can, by remelting, return a portion of the slag which has already been produced, if necessary by the addition of certain fluorides, such as calcium fluoride, in the electrolytic reduction corresponding to subsequent working, to the remelted metal, in certain amounts, and, at the same time, add the necessary amounts of alkali carbonate. In this connection, slag is understood to mean the electrolyte mass.

In some cases it has been found desirable to replace the calcium fluoride entirely or partially with barium fluoride.

The following examples are given as other such reaction mixtures:

Example 1

	Gram
Mixture: 50 gr. potassium	
50 gr. sodium chloride	8
Calcium fluoride	5
Sodium carbonate	6.5

Example 2

	Gram
Mixture: Sodium-aluminum fluoride 42 gr.	
Sodium carbonate 32 gr	18.5
(50 sodium—50 gr. potassium chloride)	8

Example 3

	Per cent
Sodium chloride	20.5
Potassium chloride	20.5
Calcium fluoride	25.6
Sodium carbonate	33.4

While heretofore the amount of alkali added had to be calculated very carefully, and the amounts used were not permitted to exceed about 0.1 per cent, as otherwise there was apt to be considerable formation of pores, one can, particularly in the production of aluminum alloys containing silicon according to the new modifying process, carry out a combination of the modifying processes by means of the reaction mixture

on one hand and the treatment with sodium on the other hand, by using increased amounts of sodium. For example, if the reaction mixture is fused and the sodium is introduced into the alloy through the salt which has become fluid, it is possible to obtain dispersion of the alloy constituents by increasing the amount of sodium added, without producing the formation of pores observed hitherto. In this manner the structure of the aluminum alloys containing 5 to 15 per cent silicon may be modified to a much greater degree than has hitherto been possible. This also produces a considerable improvement in the elongation. For example, a cast alloy containing 13 per cent silicon which has been modified with an addition of 0.1 per cent sodium shows an elongation of approximately 7 per cent, while after modification with 0.3 per cent sodium, in the presence of reaction mixture according to the invention as the covering salt, it shows an elongation of about 10 per cent.

Moreover, it is possible to produce a eutectic structure in aluminum alloys with silicon contents of over 15 per cent in a surprising manner, although on the basis of the melting point diagram which has been set up one must assume that primary disintegration of the silicon must already be present with such silicon contents; thus, by means of an addition of 0.3 per cent alkali metal in the presence of a covering salt one could permit even alloys with a 17 per cent silicon to solidify in purely eutectic structure. The eutectic structure is of considerable importance for many applications, as such alloys possess great advantages on account of their fine-grained structure.

It has also proved very advantageous to use fluorides which show an acid constituent. For example, one can use bifluorides which still contain acid radicals, also silico-fluorides of every type. Possibly an alkaline reaction of the alkali metal is restrained by the introduction of an acid radical and the blister formation thereby prevented. Products produced according to the invention can also be subjected to subsequent mechanical or thermal treatment and thereby used for all purposes in which the physical properties are subjected to high stresses.

I claim—

1. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides which in themselves are not decomposed by the melt and alkali carbonates in substantially molecular proportions.

2. The process of improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of double fluorides and alkali carbonates in substantially molecular proportions.

3. The process of improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises treating a molten bath of such alloys with a reaction mixture of fluorides and alkali carbonates, and subsequently introducing metallic sodium in amounts up to 0.6 per cent into the molten bath through the molten salts.

4. The method of improving aluminum-silicon alloys containing more than 15 per cent silicon and incidentally small percentages of iron or copper, which comprises adding to a molten bath of the metal to be treated mixtures of one or more fluorides and alkali carbonates in substantially molecular proportions.

5. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides comprising a silico-fluoride or bifluoride which in themselves are not decomposed by the melt, and alkali carbonates.

6. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides which in themselves are not decomposed by the melt, and lithium carbonate.

7. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides which in themselves are not decomposed by the melt, and calcium carbonate.

8. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides which in themselves are not decomposed by the melt and alkali carbonates in substantially molecular proportions, and a fluxing medium, as for example, alkali chlorides or their mixtures, or borates for lowering the melting temperature of the reacting mixture.

9. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides which in themselves are not decomposed by the melt and alkali carbonates in substantially molecular proportions, from 30 to 40 per cent of such mixture being composed of a mixture comprising from 50 to 60 parts of potassium chloride and from 40 to 50 parts sodium chloride.

10. Process for improving aluminum alloys to produce a highly dispersed structure of the alloy constituents, which comprises adding to a molten bath of the original material to be treated mixtures of fluorides which in themselves are not decomposed by the melt and alkali carbonates, subjecting the alloys so formed to a heat treatment consisting in annealing at temperatures above 400 degrees, quenching, and aging at ordinary or elevated temperatures.

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