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MANUFACTURE OF ALUMINUM TITANIUM ALLOYS

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This invention relates to aluminum alloys containing titanium. It is particularly concerned with a novel method of producing Al-Ti master alloys. It is also concerned with other products useful for alloying titanium with aluminum.

Titanium is extensively used in aluminum alloys as a grain refining agent. For this purpose, it is added in amounts up to about 0.25% to aluminum alloys such as those containing zinc, copper, and zinc plus magnesium. A process widely used by producers of aluminum alloys for obtaining the desired titanium content is the addition to a molten aluminum alloy of a master alloy of aluminum with 2½%–6% titanium. Because of their low titanium content the use of such master alloys has been unduly expensive. On the other hand no satisfactory master alloys having a higher titanium content were available until recently. A copending application for patent, Serial No. 623,735, filed by Stephen F. Urban, and commonly assigned, describes the production of novel aluminum-titanium master alloys having a titanium content of from 6%–20% which are very satisfactory as addition agents for aluminum alloys.

It is an object of the present invention to provide a novel process for economically producing Al-Ti master alloys of the last-mentioned type.

Another object of the present invention is to provide a method of producing master alloys of aluminum and titanium containing from 6%–20% titanium which involves the use of readily available materials.

Another object of the invention is to provide a non-metallic product useful for adding titanium to aluminum alloys.

A further object of the invention is to provide a process for making non-metallic products of the type above mentioned.

It has been discovered that, as hereinafter described in more detail, when the reaction product of TiO_2 with certain metal salts is mixed with molten aluminum or a molten aluminum alloy there is a reaction which results in liberation of titanium and the formation of an aluminum-titanium alloy.

The following examples illustrate the production of aluminum-titanium master alloys of several compositions by the process mentioned above.

EXAMPLE 1

A mixture of 382 parts sodium bifluoride ($NaHF_2$), 200 parts potassium chloride (KCl), and 228 parts of finely divided titanium dioxide (TiO_2) was heated in a graphite crucible. When the temperature of the fluid mixture reached 1600° F. 1360 parts of aluminum in ingot form was added and melted. After thorough stirring the spent salt mixture was separated and the metal was cast. Analysis of the alloy showed a titanium content of 6.12%.

EXAMPLE 2

A mixture of 500 parts $NaHF_2$, 275 parts KCl, and 295 parts TiO_2 was heated in a graphite crucible. Ingots

of aluminum (1170 parts) were added to the crucible when the temperature of the molten contents was about 1440° F. After the aluminum melted the temperature was increased and the mixture was stirred. At 1700° F. the spent salt was separated and the alloy was cast. It was found by analysis to contain 11.37% titanium.

EXAMPLE 3

141 parts of potassium bifluoride (KHF_2), 259 parts of KCl and 33.5 parts of TiO_2 were mixed and heated in a graphite crucible. When the mix was molten it was poured into another crucible containing 200 parts of aluminum which had been melted and heated to 1470° F. The metal and salt mix were stirred and then were permitted to solidify in the crucible. After cooling, the alloy ingot was removed and analyzed, the analysis showing 6.95% Ti.

Microscopic examination of polished sections of the Al-Ti master alloys produced in Examples 1 to 3 revealed that these alloys have a structure in which the particles of the intermetallic compound Al_3Ti are nodular or rounded in shape, thus being similar in structure to the master alloys described and claimed in the copending application referred to above. Similarity to such master alloys was also found in the ease with which master alloys produced by the present novel process dissolve in aluminum and aluminum alloys and the high titanium recoveries obtained. This is indicated by the following table.

Table I

Additive		Alloyed Aluminum	
Master Alloy Sample	Ti Content, percent	Dissolved Ti, percent	Recovery Ti, percent
A	6.12	0.20	83
B	11.37	0.20	76
C	9.39	0.24	100

Samples A and B in Table I, above, are the Al-Ti master alloys of Examples 1 and 2, respectively. In addition to the tests set forth in Table I master alloys containing titanium have been used as additives to large commercial batches of aluminum alloys with consistent titanium recoveries of over 90%.

Either sodium or potassium bifluoride can be used to react with titania in the production of Al-Ti master alloys according to the present invention. Other alkali metal bifluorides are also usable but are not at present practical because of their high costs. Mixtures of alkali metal bifluorides may also be employed. The KCl employed in Examples 1 to 3 serves as a flux. While the use of a flux is not essential it is generally advisable since it decreases the viscosity of the titania-salt reaction product and thereby facilitates thorough mixing of the reaction product with the metal and separation of spent salt from the metal. Potassium chloride is preferred as a flux but other alkali metal halides such as NaCl, NaF and KF or mixtures of alkali metal halides can be satisfactorily used. In addition to their function as fluxes these halides may be used for adjusting the titanium contents of the reaction products to convenient desired percentages. Although substantially pure TiO_2 may be used a highly pure material is not required. Very satisfactory results have been obtained with the readily available and cheaper TiO_2 ore, rutile. For rapid and complete reaction between the titania and the molten bifluoride the former should be finely divided, a fineness such as to pass through a 325 mesh screen being desirable as the reaction then takes place substantially immediately after the bifluoride becomes molten.

As shown in Examples 1 to 3 the novel reaction products of alkali metal bifluoride and titanium dioxide may be employed while still molten for the production of Al-Ti master alloys. If desired, however, such reaction products may be cooled and used later, after remelting. The composition of the reaction product, exclusive of the flux if such is used, is determined by the ratio of alkali metal bifluoride to TiO_2. A molal ratio of 4:1 (bifluoride:TiO_2) will result in a fused reaction product the composition of which may, it is believed, be expressed by the formula $4MF \cdot TiF_4$, where "M" is the alkali metal of the bifluoride used. When the molal ratios of bifluoride to TiO_2 are less than 4:1 more complex reaction products are obtained which contain titanium, oxygen, fluorine and the alkali metal or metals of the bifluoride used. The exact nature of these products is not known. Nevertheless, it has been determined that the reaction products obtained with molal ratios of alkali metal bifluoride to TiO_2 of from approximately 4:1 to 2:1 are quite satisfactory for use in alloying titanium with aluminum. Thus in Examples 1 to 3, such ratios are respectively, approximately 2:1, 2:1 and 4:1. Although with molal ratios of alkali metal bifluoride to titania of less than about 2:1 reaction products are obtained, these products are not found efficient in producing Al-Ti alloys.

It will be understood that the titanium content of aluminum-titanium alloys formed by addition of alkali metal bifluoride-titania reaction products to molten aluminum or aluminum alloys will be largely determined by the titanium content of the reaction product used and the amount of such reaction product added to the metal. Thus the present novel process permits the production of master alloys of aluminum and titanium economically and efficiently. It also makes possible the alloying of small amounts of titanium with alloys of aluminum containing small amounts of other metals such, for example, as copper, zinc, and zinc plus magnesium.

The spent salts recovered or removed from the metal baths in carrying out the present novel process are of variable composition. In all cases, however, they contain sodium aluminum fluoride and when the molal ratio of alkali metal bifluoride to titania in the mix for the reaction product is less than 4:1 they also contain some titanium, probably as oxide, and alumina. These spent salts may be used as fluxes for melting aluminum and other metals and as insecticides.

Where in the foregoing description parts and percentages are mentioned it is intended that these shall refer to parts by weight and weight percentages.

I claim:

1. A process for alloying titanium with a molten metal selected from the group consisting of aluminum and aluminum base alloys which comprises mixing with the molten metal a product obtained by the reaction, in the molten state and with an alkali metal halide flux, of an alkali metal bifluoride and titania in molal ratios of from approximately 4:1 to approximately 2:1.

2. A process as set forth in claim 1 in which said alkali metal bifluoride is sodium bifluoride.

3. A product useful for introducing titanium into aluminum and aluminum base alloys which comprises the product obtained by reacting, in the molten state and with an alkali metal halide flux, an alkali metal bifluoride and titania in molal ratios of from approximately 4:1 to approximately 2:1.

4. A product as set forth in claim 3 in which said alkali metal bifluoride is sodium bifluoride.

5. A product as set forth in claim 3 in which said alkali metal bifluoride is potassium bifluoride.

6. A product as set forth in claim 3 in which said flux is potassium chloride.

7. A product as set forth in claim 3 in which said titania is used in the form of rutile.

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