

UNITED STATES PATENT OFFICE

1,998,467

METHOD OF TREATING ALUMINUM-BASE ALLOYS

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No Drawing. Application June 30, 1934,
Serial No. 733,248

11 Claims. (Cl. 75—58)

This invention relates to the treatment of aluminum-base alloys for the purpose of removing certain impurities therefrom.

It is well recognized in the alloy art that very small amounts of certain elements have a very pronounced effect upon the properties of an alloy, seemingly quite out of proportion to the quantity present. The presence of these substances, whether intentionally added or not, frequently determines whether an alloy can be employed for some particular type of service. These elements may, for example, reinforce a specific property of an alloy or they may inhibit the formation of some undesirable internal structure. Small quantities of some elements are always present as impurities in commercial alloys and they not infrequently have a deleterious effect upon the properties of the final product. Various means of overcoming the harmful influence of such impurities have been proposed, such as adding some other element to neutralize the effect of the impurity, removing the impurity by a refining treatment, or utilizing only material of high purity to minimize the influence of the impurities.

Some metals and alloys, such as steel, which is an iron alloy, may be treated to remove impurities during the preparation of the alloy. Aluminum and its alloys, however, are not amenable to the refining treatments generally employed with such metals. A common method which has been employed to control the impurity content of aluminum alloys is the use of materials of exceptionally high purity. This practice is obviously expensive since materials of high purity are more difficult to obtain and therefore command a premium price. This condition has militated against the wide adoption of alloys requiring the use of such metal. Electrolytic methods of refining aluminum of commercial purity have been devised, but these methods are not generally adaptable to removing impurities from aluminum-base alloys. Where relatively large amounts of certain undesired elements may be associated with aluminum, it is sometimes possible to separate a substantial portion of these elements from the base metal in the molten condition by the addition of still other elements that will combine with the undesired ingredients to form a solid which sinks to the bottom of the metal bath. While this method is useful in removing certain undesired elements from aluminum when present in substantial amounts, it has not been applicable to cases where only about 0.1 per cent of an unwanted element is present.

Alkali and alkaline earth metals often occur in

aluminum and aluminum-base alloys, particularly the latter when secondary metal has been used in making the alloy. For many purposes the presence of these elements is not objectionable, but in other instances they have been found to have a deleterious effect. In fact, in certain alloys, the metal must be virtually free from magnesium in order to render thermal treatment effective. The magnesium content must be kept below about 0.01 per cent to obtain the maximum benefit from the treatment. This limitation on the purity of the metal used in making the alloy has practically precluded the utilization of secondary metal which is cheaper than the virgin high purity aluminum. My invention is concerned with making larger sources of metal available for purposes requiring an especially low content of alkali and alkaline earth metals in the base alloy.

An object of my invention is to remove substantially all of the alkali or alkaline earth metals from aluminum and its alloys by simple treatment in the foundry. A particular object is to treat molten aluminum and aluminum-base alloys contaminated with small amounts of magnesium with a substance that removes virtually all of the magnesium. Another object is to effect the removal of the undesired elements without appreciably disturbing the proportions of the desired alloy ingredients. A further object is to employ a means of removing alkali and alkaline earth impurities from aluminum-base alloys that is readily adapted to use under prevailing foundry conditions.

My invention is based on the discovery that gaseous fluorinated hydrocarbon organic compounds effectively remove the alkali and alkaline earth metals when introduced in molten aluminum and aluminum-base alloys containing said metals. These compounds react with the alkali and alkaline earth impurities and yield an insoluble, powdery, non-metallic appearing substance that rises to the surface of the molten metal bath and may then be easily skimmed off. The gas may be introduced into the metal by any suitable means such as passing the gas through a refractory tube whose open end is held beneath the surface of the molten charge. The treatment, in general, need not last more than a few minutes to accomplish the desired results. Other alloying constituents present in the alloy such as copper, silicon, nickel, manganese, and the like, are not appreciably affected by the treatment as far as I have observed, and hence the fluorinated hydrocarbon compounds may properly be regarded

as having a selective action on certain impurities in aluminum and aluminum-base alloys.

I have found that the aliphatic hydrocarbon compounds containing fluorine are effective in removing impurities of the nature disclosed hereinabove. Other halogen derivatives of the aliphatic series have been used in treating aluminum and its alloys, but they do not produce the result obtained from using fluorine-containing compounds. Furthermore the behavior of compounds other than those in the aliphatic series is uncertain, but tests which I have conducted indicate that the so-called open chain carbon compounds act in the desired manner. The term "aliphatic series" as here employed refers to both the saturated and unsaturated open chain hydrocarbon compounds. The position of the fluorine atoms in the hydrocarbon molecule is immaterial as far as removal of the impurities from aluminum and its alloys is concerned. Again, the number of fluorine atoms present in the molecule does not alter the behavior of the compound for the purposes of my invention, although all of the compounds are not equally efficient in removing impurities. The compound should in any event be gaseous at the temperature of the molten metal and under ordinary atmospheric pressure in order to be easily handled and to produce the most effective action. Substances which are in liquid or solid form at room temperature and pressure may be rendered gaseous by heating, and employed in this condition. I prefer, however, to use compounds that are gaseous at ordinary temperatures and pressure. Compounds having the following empirical formulas are illustrative of the foregoing class: CH_2F_2 , CHF_3 , CH_3F , CF_4 , C_2F_6 .

While gaseous aliphatic compounds which contain only fluorine as a representative of the halogen group of elements are effective in removing alkali and alkaline earth impurities from aluminum, I have also found that compounds containing fluorine and another member of the halogen family will produce the same result. The fluorine, in any case, is regarded as being the essential constituent of the compound with respect to effecting the purpose of my invention. Compounds having the following empirical formulas— CFCl_3 , CF_2Cl_2 , CF_3Cl , CH_2ClF , CHCl_2F , CHClF_2 , $\text{C}_2\text{Cl}_2\text{F}_4$, C_2ClF_5 are representative of the foregoing heterohalogen group of substances. The term "heterohalogen" as here employed refers to those aliphatic compounds containing fluorine and one or more other halogen elements.

The compound, dichlorodifluoromethane, CF_2Cl_2 , has proved to be particularly advantageous in removing the magnesium impurity from aluminum-copper alloys. For example, an alloy composed of about 4.5 per cent copper, 0.8 per cent manganese, 0.8 per cent silicon and 0.026 per cent magnesium, in addition to other impurities commonly found in aluminum, balance aluminum, was melted under normal conditions and brought to a temperature of about 750°C . The gaseous CF_2Cl_2 was then bubbled through the melt at a moderate rate for a period of about 5 minutes. A chemical analysis of the alloy after treatment showed that the proportions of copper, manganese and silicon were practically unchanged, but the magnesium content had been reduced to 0.005 per cent. In another test made on the same alloy with an initial content of 0.02 per cent magnesium, only 0.003 per cent of this element was found in the alloy after treatment. In each case a powdery, non-metallic-appearing dross came to the surface of the melt during passage of gas

through the metal. The dross was easily skimmed off before pouring the metal into the mold.

Dichlorodifluoromethane is a commercial product that is readily available in liquid form in steel cylinders, as are many of the more common compressed gases. The gas may be taken directly from the storage tank and introduced into the molten metal bath without any intermediate treatment. It is not poisonous and has no toxic effect on the workmen. Under ordinary foundry conditions there is sufficient ventilation to remove any dangerous gases that might be formed from the reaction of the fluorinated aliphatic compound with the metal.

If the magnesium or other alkali or alkaline earth metal content of the aluminum or aluminum-base alloy exceeds about 0.1 percent, a considerable length of time is required to reduce this to less than 0.01 per cent; hence for practical purposes I prefer to employ my treatment where the alkali and alkaline earth metal impurity is less than 0.1 per cent. As a matter of experience, I have seldom found virgin metal, or carefully selected secondary metal, wherein the amount of impurities of this nature exceeds 0.1 per cent. While the use of fluorinated aliphatic compounds is not designed to separate large amounts of the impurities from aluminum and its alloys, these compounds are very effective in removing small amounts which it has heretofore been very difficult to disengage from the base metal. For the purposes of my invention, aluminum and aluminum-base alloys containing less than 0.01 per cent of the type of impurities herein described are regarded as being substantially free from said impurities.

The time required to bring about the reduction in the impurity content of the metal depends upon the quantity of impurity present, the amount of metal being treated, the rate of introduction of the gas and the extent to which it is desired to reduce the impurity content. A treatment of from 1 to about 15 minutes' duration is generally sufficient to reduce the amount of impurity to less than 0.01 per cent.

In turn, the amount of gaseous fluorinated compound required for a particular case depends, obviously, upon the impurity content, the quantity of metal being treated, and also to some extent upon the compound used, since all fluorine-containing aliphatic substances are not equally efficient, although they exhibit the same property of attacking the impurities. The amount of gas needed to treat a particular charge of molten metal may be easily determined by experiment. For the treatment of aluminum base alloys containing from 0.02 to 0.03 per cent magnesium, as in the examples given above, I have found that about 0.3 ounces of dichlorodifluoromethane per pound of charge is sufficient to reduce the magnesium content to less than 0.005 per cent.

The rate of reaction of the fluorinated compound with the metal has been observed to vary with the temperature of the metal, the reaction proceeding at a more rapid rate at the higher temperatures. At high temperatures the dross produced may be blackened by the presence of carbon resulting from the decomposition of the organic compound. It is unnecessary, however, to superheat the charge in order to get a satisfactory removal of the impurities. The usual range of temperature employed in melting aluminum and its alloys lies between about 660 and 825°C ., and the reaction within this range is

sufficiently rapid to meet production requirements.

The molten metal may be separated from the dross resulting from the reaction with the impurities by any convenient means. For example, the floating non-metallic residue may be skimmed from the surface of the molten metal bath. A separation may also be effected by tapping off the molten metal through an opening in the container below the surface of the metal charge as in the case of bottom-pouring melting or holding pots. The object, in any case, is to prevent mixing of the dross with the metal passing into the mold.

The term aluminum as employed herein and in the appended claims refers to both the non-alloyed metal containing impurities and aluminum-base alloys containing more than 50 per cent aluminum. The elements herein designated as alkali and alkaline earth impurities include lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium and barium.

I claim:

1. A method of reducing the alkali and alkaline earth impurity content of aluminum, comprising melting the aluminum, introducing a gaseous fluorinated aliphatic hydrocarbon compound into said molten charge, and separating the metal from the accumulated dross.

2. A method of removing substantially all of the alkali and alkaline earth impurities from aluminum, comprising melting the aluminum, introducing a gaseous fluorinated aliphatic compound into the molten charge and continuing the passage of gas until less than 0.01 per cent of said impurities remain in the metal, and separating the metal from the accumulated dross.

3. A method of removing substantially all of the alkali and alkaline earth impurities from aluminum wherein the total amount of said impurities does not exceed about 0.1 per cent, comprising melting the aluminum, introducing a gaseous fluorinated aliphatic compound into the molten charge having a temperature of less than 825° C., continuing the passage of gas until less than about 0.01 per cent of said impurities remain, and separating the metal from the accumulated dross.

4. A method of reducing the alkali and alkaline earth impurity content of aluminum, wherein the total amount of said impurities does not initially exceed about 0.1 per cent, to less than 0.01 per cent, comprising melting the aluminum, maintaining the metal at a temperature between the melting point and 825° C., passing a gaseous fluorinated aliphatic compound through said metal for a period of from about 1 to 15 minutes and separating the metal from the accumulated dross.

5. A method of removing substantially all of the alkali and alkaline earth metal impurities from aluminum wherein the total amount of said impurities does not exceed about 0.1 per cent, comprising melting the aluminum, maintaining the molten bath at a temperature not substan-

tially greater than 825° C., and passing a gaseous hetero-halogen aliphatic compound through said metal bath for a period of 1 to 15 minutes, and finally separating the purified metal from the dross.

6. A method of removing substantially all of the magnesium impurity from aluminum wherein less than about 0.1 per cent of said impurity is present, comprising melting the aluminum, maintaining the bath at a temperature of about 660 to 825° C., introducing a gaseous fluorinated aliphatic compound into said metal bath and finally separating the magnesium-free metal from the accumulated dross.

7. A method of removing substantially all of the magnesium impurity from aluminum wherein less than about 0.1 per cent of said impurity is present, comprising melting the aluminum, maintaining the bath at a temperature of about 660 to 825° C., passing a gaseous hetero-halogen aliphatic compound through said molten metal bath, and separating the metal from the accumulated dross.

8. A method of removing substantially all of the magnesium impurity from aluminum wherein less than about 0.1 per cent of said impurity is present, comprising melting the aluminum, maintaining the bath at a temperature of about 660 to 825° C., passing a gaseous hetero-halogen aliphatic compound through said molten metal bath for a period of from about 1 to 15 minutes, and separating the metal from the dross accumulated on the surface of the molten bath.

9. A method of removing substantially all of the magnesium impurity from aluminum wherein said impurity content does not exceed about 0.1 per cent, comprising melting the aluminum, maintaining the bath at a temperature between about 660 and 825° C., passing gaseous dichlorodifluoromethane through said molten metal for a period of about 1 to 15 minutes and separating the metal from the dross accumulated on the surface of the molten bath.

10. A method of removing substantially all of the magnesium impurity from aluminum wherein said impurity content does not exceed about 0.1 per cent, comprising melting the aluminum, maintaining the bath at a temperature between about 660 and 825° C., passing gaseous dichlorotetrafluoroethane through said molten metal for a period of about 1 to 15 minutes and separating the metal from the dross accumulated on the surface of the molten bath.

11. A method of removing substantially all of the magnesium impurity from aluminum wherein said impurity content does not exceed about 0.1 per cent, comprising melting the aluminum, maintaining the bath at a temperature between about 660 and 825° C., passing gaseous monofluorotrichloromethane through said molten metal for a period of about 1 to 15 minutes and separating the metal from the dross accumulated on the surface of the molten bath.

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