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METHOD OF THERMAL TREATMENT

Philip T. Stroup, New Kensington, Pa., assignor
to Aluminum Company of America, Pittsburgh,
Pa., a corporation of Pennsylvania

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This invention relates to the art of thermal treatment of objects made of magnesium or its alloys, by which latter term is meant those magnesium alloys containing about 70 per cent by weight or more of magnesium, the balance being other elements which have been added to the magnesium to add to, enhance, modify, or change its basic properties. Magnesium and its alloys are peculiarly susceptible to deterioration during thermal treatment. While the rate and extent of the deterioration may be affected by the temperature of treatment, the time at temperature, the humidity of the atmosphere, and other factors and may, therefore, be severe in some cases and merely incipient in others, the tendency to deteriorate is apparently always present. Thus, particularly when quantities of articles of magnesium or of its alloys are being manufactured, the greatest care possible under any given set of manufacturing conditions may not suffice to prevent deterioration developing under the inevitable fluctuation of these factors, and often a thermal treatment, the normal result of which is satisfactory, will produce inferior products. The commercial problem thus presented is further complicated by the insidious nature of the deterioration. The effect is not always evidenced by surface discoloration, or other obvious change in surface properties, but will in some instances consist of a decrease in physical properties, such as strength or elongation, or in some chemical property, such as resistance to corrosion. Therefore, the operator may have no immediate indication that the thermal treatment is producing an inferior product.

Thermal treatments are necessary steps in the production of many products made of magnesium or of its alloys. Whether the desired product be produced by casting, by deformation under applied force, or by other methods, thermal treatments play an important, and often necessary role. A cast or worked product is sometimes submitted to treatment at a determined elevated temperature for the purpose of increasing strength, ductility, stability, corrosion resistance, or other property. A cast billet, slab, or ingot is often heated or preheated prior to being deformed by familiar operations such as rolling, forging, extrusion, and the like. Such working operations are often interrupted so that the partially deformed or worked product can be annealed, i. e., heated to develop in the metal the ductility necessary to further deformation. These are but instances of that large class of operations which involve the application of heat to

metal objects for the purpose of developing desirable properties or of curing defects. The possibility, if not the fact, of deterioration arises when these thermal treatments are applied to magnesium and its alloys.

The primary object of this invention, whatever its other objects and incidental advantages, is to minimize or prevent deterioration of magnesium and its alloys during thermal treatment thereof by improvements which are adaptable to large scale production.

The present invention includes, as its broadest aspect, the thermal treatment of magnesium and its alloys as above defined, in an atmosphere into which a fluorine-containing substance has been introduced in the form of a vapor. The resultant atmosphere exerts an effect during the thermal treatment which reduces the tendency of magnesium and its alloys to deteriorate and thus minimizes to a marked extent the possibility that the thermal treatment will seriously impair the metal subjected to it. In its narrower and preferred form, the invention consists in increasing or activating the beneficial effect of this fluorine-containing atmosphere by incorporating into the magnesium or an alloy thereof an amount of either or both of the elements calcium or beryllium. The mechanism or reaction by which the beneficial effect of the fluorine-containing atmosphere is increased by the presence, in the metal undergoing heat treatment, of either or both of these elements is not known, but the effect produced is substantial and definite to the end that the tendency of the magnesium to deterioration is suppressed, and the risk that thermal treatment will cause unsatisfactory results is very greatly minimized if not eliminated.

Whether the broad or the narrower aspect of the invention be practiced, a fluorine-containing substance in vapor form is introduced into the atmosphere which surrounds the magnesium, or alloy thereof, during thermal treatment. The usual atmosphere in commercial operations is air sometimes containing small amounts of sulphur dioxide or combustion products and further contaminated, of course, by industrial gases, moisture, and the like. But the atmosphere may be some inert gas or even a partial vacuum in which residual gas is present. Where considerations of cost do not interfere, it is advantageous to use an atmosphere of carbon dioxide, preferably dry, and this is a preferred step in the practice of this invention. Whatever the atmosphere (by which is meant the medium surrounding the metal object being treated), it should contain, in

accordance with the principles of this invention, fluorine-containing substance in vapor form. Under some conditions of thermal treatment where the tendency to deterioration of the magnesium or alloy thereof is not marked, as little as 0.5 grain of fluorine-containing vapor per cubic foot of atmosphere may be effective. Under many conditions of treatment, amounts of fluorine-containing vapor as high as 100 grains per cubic foot of atmosphere may be advisable. Simple test will determine a proper amount. The source of the fluorine-containing vapor may be conventional. Gas, such as hydrogen fluoride, boron fluoride, or other gaseous fluorides, including the organic fluorides, may be separately generated and introduced into the atmosphere. A convenient method consists in heating solid fluoride salts or salts containing fluorine, such as sodium or potassium fluoborate, to produce the required vapor. Where the temperatures employed during thermal treatment are sufficiently high, the fluorine salt may be introduced into the furnace or other thermal treatment chamber and the temperature therein relied upon to generate from the salt the fluorine-containing substance vapor. These methods are only indicative, and other methods of introducing the fluorine-containing substance in vapor form into the atmosphere surrounding the magnesium during thermal treatment will be apparent to those skilled in the art.

To prepare for the practice of the narrower and preferred aspect of the invention, it is necessary to add to the magnesium, or alloy thereof, which is later to undergo thermal treatment an amount of either one or both of the elements beryllium and calcium. Such additions are conveniently made to the metal at any time prior to the thermal treatments here described. It is the presence of these elements in material amount in the magnesium or alloy thereof which increases the effectiveness of the fluorine-containing atmosphere to prevent deterioration during thermal treatment. Therefore, so long as the element, or elements, is effectively present, the exact amount of the element is not important to the precepts of this invention. However, the functions and properties of the final magnesium or magnesium alloy product must be considered and, therefore, it is desirable generally to limit the amount of beryllium or calcium, or the total of these elements, to that which is effective for the purpose here under discussion. Further amounts may, of course, be added for other purposes.

Calcium.—When used in the absence of beryllium, calcium in amounts as low as 0.01 per cent by weight of the total metal is effective to increase the power and effect of the fluorine-containing substance in the thermal treatment atmosphere. Very good results have been obtained by the use of 0.05 per cent of this element. Generally the amount of calcium present in commercial magnesium alloys is limited to 1.0 per cent or less, often to about 0.2 per cent.

Beryllium is effective for the purposes of this invention when present in amounts as low as 0.0005 per cent by weight. For other reasons than those connected with this invention, it may be advisable to limit its use to about 0.0015 per cent by weight of the alloy because of the detrimental effect of larger amounts in increasing the size of the grain of magnesium or alloys thereof. However, where size of grain is of

no importance or is controlled by other constituents of the alloy or by the method of casting used, beryllium may be used in larger amounts, such as 2 per cent, although usually it is difficult to hold more than about 0.2 per cent by weight uniformly in the alloy. Beryllium in amounts of 0.0001 to 0.01 per cent is preferred.

As before stated, the tendency of magnesium and its alloys to deterioration during thermal treatment may be suppressed or limited according to the principles of this invention by the use of a fluorine-containing substance in vapor form in the atmosphere surrounding the metal during the thermal treatment, and indeed in some cases when the tendency to deterioration under the conditions of the thermal treatment is not marked or is merely sporadic, the presence of fluorine-containing substance in the atmosphere may be sufficient. However, in most instances it is preferred to practice the invention in its narrower aspect and to increase the effectiveness of the fluorine-containing atmosphere by including calcium or beryllium or both in the magnesium. Such practice minimizes the possibilities that variations in the atmosphere will not suddenly cause deterioration. For example, in one instance where articles made of a magnesium alloy (of the magnesium-aluminum-zinc type) were undergoing thermal treatment in the month of April, the operator was using only that aspect of the invention which consists of including a fluorine-containing substance in vapor form in the furnace atmosphere, and results were satisfactory, no deterioration being encountered. This practice was continued into the following month of May, and early in that month relatively warm humid weather was encountered and deterioration immediately took place in the articles under treatment. This deterioration was later prevented by the addition of 0.005 per cent beryllium to the magnesium alloy. If such beryllium content had been present at all times, the trouble experienced by suddenly shifting weather would have been minimized. Under very severe conditions of thermal treatment it is often advisable to use carbon dioxide as an atmosphere. The presence of vaporous fluorine-containing substance in a carbon dioxide atmosphere may be completely effective to prevent deterioration.

It will be understood that the word "alloys" as used in the appended claims refers to alloys containing about 70 per cent or more of magnesium, and that the words "thermal treatment" do not imply the heating of the object made of magnesium or an alloy thereof to temperatures which would cause substantial melting of the metal.

I claim:

1. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which comprises providing a fluorine-containing substance in vapor form in the atmosphere surrounding the metal.

2. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which comprises surrounding the metal with an atmosphere of carbon dioxide in which is included in vapor form a fluorine-containing substance.

3. In the art of thermally treating magnesium

and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment beryllium in amounts from about 0.0005 to about 0.2 per cent by weight of the total metal, and surrounding the metal during the treatment with an atmosphere containing fluorine-containing substance in vapor form.

4. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment beryllium in amounts from about 0.0001 to about 0.01 per cent by weight of the total metal, and surrounding the metal during the treatment with an atmosphere containing fluorine-containing substance in vapor form.

5. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment calcium in amounts from about 0.01 to about 1.0 per cent by weight of the total metal, and surrounding the metal during the treatment with an atmosphere containing fluorine-containing substance in vapor form.

6. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment calcium in amounts from about 0.01 to about 0.2 per cent by weight of the total metal, and surrounding the metal during the treatment with an atmosphere containing fluorine-containing substance in vapor form.

7. In the art of thermally treating magnesium and alloys containing at least 70 per cent by

weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment beryllium in amounts from about 0.0001 to about 0.01 per cent by weight of the total metal, and surrounding the metal with an atmosphere of carbon dioxide in which is included in vapor form a fluorine-containing substance.

8. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment beryllium in amounts not less than about 0.0005 per cent or more than about 2 per cent by weight, calcium in amount not less than about 0.01 per cent or more than about 1.0 per cent by weight, and surrounding the metal during the treatment with an atmosphere containing fluorine-containing substance in vapor form.

9. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment beryllium in amounts from about 0.0005 to about 2 per cent by weight of the total metal, and surrounding the metal during the treatment with an atmosphere containing fluorine-containing substance in vapor form.

10. In the art of thermally treating magnesium and alloys containing at least 70 per cent by weight of magnesium, the method of minimizing deterioration of the metal during treatment which includes providing in the metal prior to the treatment calcium in amounts from about 0.01 to about 0.2 per cent by weight of the total metal, and surrounding the metal with an atmosphere of carbon dioxide in which is included in vapor form a fluorine-containing substance.

PHILIP T. STROUP.