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HEAT TREATMENT OF ALUMINOUS METALS

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This invention relates to the thermal treatment of aluminum and aluminum base alloys. It is more particularly concerned with protecting such materials against a type of attack which may occur at elevated temperatures under some atmospheric conditions.

Some kind of thermal treatment is generally used during the fabrication of articles from aluminum and aluminum base alloys, such as preheating the metal before hot working it, or applying a solution heat treatment to certain alloys to increase their strength and hardness. These treatments are frequently carried out in furnaces having air atmospheres because such furnaces are convenient and economical to operate. It has been observed occasionally that when aluminum and aluminum base alloys have been exposed to sufficiently elevated temperatures for a considerable length of time in an air atmosphere, the metal may be subject to a certain type of attack which differs from the surface oxidation that normally occurs with aluminum. The attack is characterized by such an objectionable blistering and permanent discoloration of the metal surface that the articles must usually be discarded, since it is generally not economical to reclaim them.

The blisters which appear under the above described conditions are readily distinguishable in shape and mode of occurrence from those blisters that are sometimes found on sheets of annealed metal. The latter type of blister results from the release of sorbed gas in the metal during the annealing operation, and for this reason it is commonly referred to as a gas blister. The blisters which characterize the high temperature attack may even occur on metal that is substantially free from gas. The discoloration referred to hereinabove varies between a dull gray and a black, and it is further characterized by a fused appearance, although there is no microscopic evidence of any incipient fusion. This discoloration is easily distinguishable from the dull oxide film that is normally found on aluminum and aluminum base alloys. Furthermore, it is of so permanent a nature that it is impractical to remove it by the ordinary commercial etching solutions. Because this type of attack differs from normal oxidation, and for the sake of convenience in referring to it, I shall designate it hereinbelow as high temperature blistering.

An investigation of the instances where high temperature blistering has occurred disclosed the fact that there is a greater susceptibility to blistering where the air atmosphere contains certain

constituents such as water vapor, ammonia, or sulphur compounds. It has also been found that the presence of certain elements in the alloys, notably magnesium in combination with copper, nickel, silicon and/or zinc, tends to increase the susceptibility to this attack. In practically all cases, the blistering occurred at temperatures above about 800° F., which is above the range usually employed for annealing the cold worked metal.

Although aluminum and aluminum base alloys do not always suffer from high temperature blistering, even at temperatures above 800° F., such blistering does sometimes occur, and because of its objectionable character, it becomes important to minimize or eliminate even an occasional occurrence. A principal object of my invention is to provide a method of inhibiting this high temperature blistering without impairing any of the useful properties of the alloys subject thereto. A further object is to provide a method of protecting aluminum and aluminum base alloys which does not require the installation of new equipment and is adapted to use in the ordinary type of air furnace.

I have discovered that the foregoing objects may be realized by introducing into a furnace employed for thermal treatment certain fluorine compounds which are capable of producing a vaporous product, and allowing them to volatilize or decompose under the influence of heat as the case may be. The presence of these fluorine-containing products in the air at elevated temperatures inhibits the high temperature blistering of solid aluminum and aluminum base alloys, without adversely affecting the useful properties of the metal or interfering with any subsequent finishing operations. Only a relatively small amount of the fluorine-bearing substances, from a determinable trace up to about 0.1 pound per cubic foot of heating chamber volume, is needed to accomplish this result. The protection afforded by these substances extends over the entire temperature range in which the attack occurs, and it is particularly effective in the range of maximum susceptibility between 800° F. and the temperature of incipient fusion.

Aluminum base alloys are more susceptible to high temperature blistering than aluminum, and of the aluminum base alloys, those containing between about 0.1 and 12 per cent magnesium apparently have a greater tendency to blister. Other elements such as copper, silicon and zinc may also be present in the alloy in amounts of from 0.1 to 14 per cent, and these elements, espe-

cially in combination with magnesium, appear to render the alloys even more susceptible to high temperature blistering. Aluminum base alloys containing up to 5 per cent nickel, as well as such elements as manganese, chromium, titanium, molybdenum, tungsten and the like in amounts of less than 2 per cent, may also be subject to this blistering. The magnesium may be present as the major component of the alloy aside from aluminum, or as a minor constituent, as in the example given hereinbelow.

The high temperature blistering of aluminum alloys becomes important only where temperatures above about 800° F. are encountered. The deleterious attack does not occur at the usual annealing temperatures of 650 to 700° F., but may occur at temperatures in excess of 800° F. such as are included in the temperature ranges normally employed for preheating ingots, billets, slabs, etc., before hot working them, or for solution heat treatment of aluminum base alloys. The temperatures used in such thermal treatments seldom, if ever, exceed 1100° F., and therefore higher temperatures may be disregarded. However, my method of protecting the alloys herein described is effective even at temperatures above 1100° F.

A protective atmosphere containing the vaporous fluorine-bearing compounds makes it unnecessary to employ the extreme precautions heretofore required to minimize high temperature blistering. These substances in the furnace atmosphere are also particularly effective in inhibiting the action of certain constituents often found in the air, namely, water vapor, ammonia, and sulphur compounds. Since it is both expensive and time-consuming to remove these substances from the air used in the furnaces, it is highly advantageous to overcome their deleterious effects without resorting to atmosphere-purifying methods. Inasmuch as the air ordinarily contains moisture, and industrial atmospheres also contain other harmful substances, such as sulphur compounds, the term atmosphere or air as herein employed includes the presence of these constituents.

The fluorine constituent may be added to the furnace atmosphere either by heating solid fluorine-containing salts in the furnace or by introducing vaporous fluorides such as hydrogen fluoride, boron fluoride, or fluorinated aliphatic hydrocarbons in gaseous form. In the former case, the solid material may be deposited on the floor of the furnace or in some container and allowed to vaporize or decompose under the influence of the heat. In the latter case, the gas may be fed directly to the heating chamber from a suitable source of supply. I have found that the former method is most convenient and generally most economical. The compounds may be used in existing furnaces without any changes in design or operation, and no particular skill is required in handling the salts.

I have found that the heating of certain fluorine-containing compounds produces vaporous substances which protect the above described alloys, whereas other fluorine compounds do not yield protective substances when similarly heated. The exact composition of the vaporous fluorine-bearing substances which are effective in the practice of my invention is undetermined, but probably some hydrogen fluoride is present. The precise steps by which the vaporous substance is produced from a solid are unimportant, whether by volatilization and subsequent decomposition

or by decomposition caused by reaction with substances such as water vapor, carbon dioxide, or sulphuric acid. The important feature is that some vaporous fluorine-bearing substance be produced.

Not all of the fluorine-containing salts are suitable for my purpose; calcium fluoride, sodium fluoride, potassium fluoride and cryolite, for example, do not afford any protection to the aluminum against the high temperature blistering. On the other hand, compounds which yield a vaporous product at the temperatures employed in the thermal treatment of aluminum alloys, usually below 1000° F., are suitable. Among such compounds there are included sodium fluosilicate, sodium fluoborate, potassium fluosilicate, potassium fluoborate, aluminum fluoride, zinc fluoride, ammonium fluoborate, ammonium fluoride. The gas, hydrogen fluoride, also inhibits this kind of blistering. Gaseous fluorinated or fluorine-substituted aliphatic hydrocarbons of the type represented by such compounds as difluoromethane, carbon tetrafluoride, hexafluoro-ethane, difluorodichloro-methane, dichloro-tetrafluoro-ethane, and trifluoro-monochloro-methane, are also useful in the furnace atmosphere as inhibitors of high temperature blistering and discoloration. Under some conditions it may be desirable to simultaneously employ two or more of these, or equivalent, fluorine-containing substances. My invention comprehends the use of any of these substances, separately or in combination.

The amount of fluorine-containing substance required to provide the desired protection is not large, and as a matter of practice I generally use for the initial treatment less than 0.1 pound per cubic foot of heating chamber volume. I have found that when a protective atmosphere of this type is used in a furnace, enough of the fluoride substance, or a reaction product thereof, is often taken up in the walls of the furnace to protect at least one subsequent heat of metal. It therefore appears that even a trace of the fluorine-containing substance, such as 0.0001 pound per cubic foot of heating chamber volume, is adequate for my purposes. Amounts larger than 0.1 pound per cubic foot may be employed if desired, but for economic reasons it is not ordinarily desirable to employ these higher concentrations, and it is seldom necessary to do so, even when severe conditions are encountered. Generally speaking less protection is needed as the moisture, ammonia, and sulphur contents of the furnace atmosphere decrease, and also as the furnace temperature decreases, for example, to 800° F., as compared with 950° or 1000° F.

When starting a furnace operating with a protective atmosphere such as is described hereinabove, I prefer to put in the heating chamber about 0.0001 to 0.1 pound of the fluorine-containing salt or other compound per cubic foot of heating chamber volume, and one such charge per heat of metal is generally sufficient to give the required protection during the entire length of the run. As a matter of precaution in treating subsequent heats of metal, I prefer to put some of the salt in the heating chamber at the beginning of each heat.

The effectiveness of vaporous fluorine-bearing compounds in inhibiting the high temperature blistering and discoloration of aluminum alloys under severe conditions is illustrated in the following tests. An alloy composed of aluminum, 4.2 per cent copper, 0.5 per cent manganese and 1.5 per cent magnesium in the form of sheet

0.064 inch in thickness was heated for 20 hours at 920° F. in an atmosphere saturated with water vapor. The 20-hour period is much longer than is ordinarily employed in commercial practice, but it was employed in order to obtain a severe attack and to determine the effectiveness of the inhibitor under such conditions. Other samples of sheet from the same alloy were divided into three groups and heat treated at the same temperature for the same length of time, 20 hours, in water vapor-saturated atmospheres containing a fluorine-bearing constituent derived from heating three different salts, namely, sodium fluoborate, sodium fluosilicate and zinc fluoride. About 0.005 pound of salt per cubic foot of furnace volume was placed on the floor of the furnace at the beginning of the heat and allowed to decompose or volatilize. No other additions of the salt were made during the 20-hour period. The specimens that had been heated in the non-fluoride-containing atmosphere were badly blistered and discolored, whereas those that had been exposed to the fluoride-bearing atmosphere were entirely free from blisters and the dark color. The fluoride products obtained from heating the different fluoride salts were equally effective in inhibiting the attack, there being no significant difference in the appearance of the specimens in the three groups tested.

An even more severe test was made on the protective effect of a fluorine-containing substance by heating sheets of the foregoing alloy in a steam atmosphere which, of course, is 100 per cent water vapor. One group of samples was heated for 20 hours at 920° F., and the second group was heated for the same length of time and at the same temperature in a steam atmosphere containing fluorine substances derived from the heating of 0.005 pound of aluminum fluoride per cubic foot of heating chamber volume. Again, the specimens which were heated in the fluorine-bearing atmosphere were free from blisters and discoloration, while the other specimens were severely blistered and were nearly black in color. Similar results were obtained when heating for shorter periods.

Articles made from aluminum and aluminum base alloys and heated in atmospheres containing vaporous fluorides, as described hereinabove, may be worked and formed or given any finishing treatment to which such articles are normally subjected, without requiring any special preparations or extra operations by reason of having been exposed to the aforesaid atmospheres. The term aluminum as herein employed refers to the metal of commercial purity containing the usual impurities, and the term aluminum base alloys refers to those alloys containing more than 50 per cent aluminum. Both aluminum and aluminum base alloys are comprehended within the term aluminous metal or material.

Having thus described my invention and certain embodiments thereof, I claim:

1. The method of inhibiting the high temperature blistering of aluminous metal during thermal treatment, comprising heating a fluorine-containing compound capable of yielding a vaporous fluorine-containing product under the influence of heat at temperatures below 1000° F., and supplying said vaporous product to the atmosphere where said thermal treatment is conducted.

2. In the art of thermally treating aluminous metals, the method of inhibiting the high temperature blistering of said aluminous metal when

heated in an air atmosphere, comprising introducing into the furnace atmosphere where the metal is heated, between 0.0001 and 0.1 pound of a vaporizable fluorine-containing compound per cubic foot of heating chamber volume, and heating said metal in said atmosphere.

3. In the art of thermally treating aluminous metals, the method of inhibiting high temperature blistering of said aluminous metal during heating in an air atmosphere above about 800° F. but below the point of incipient fusion, comprising employing a vaporous fluorine-containing compound in the atmosphere surrounding the heated metal, said fluorine-containing substance being derived from heating a fluorine-containing compound capable of yielding a vaporous product at temperatures below 1000° F.

4. In the art of thermally treating aluminum base alloys containing from 0.1 to 12 per cent magnesium, the method of inhibiting the high temperature blistering of said alloys when they are heated in a gaseous atmosphere, which comprises providing in said atmosphere a vaporous fluorine-containing substance derived from heating a fluorine-containing compound capable of yielding a vaporous product at temperatures below 1000° F.

5. The method of inhibiting the high temperature blistering of aluminum base alloys which contain from 0.1 to 12 per cent magnesium when they are subjected to thermal treatment in an air atmosphere, comprising employing in the said atmosphere a vaporous fluorine-containing substance derived from the heating of at least one compound selected from the group composed of sodium fluosilicate, sodium fluoborate, potassium fluosilicate, potassium fluoborate, zinc fluoride, aluminum fluoride, ammonium fluoride, ammonium fluoborate, hydrogen fluoride, boron fluoride and difluoro-dichloro-methane.

6. The method of inhibiting the high temperature blistering of aluminum base alloys which contain from 0.1 to 12 per cent magnesium during thermal treatment in an air atmosphere at temperatures above about 800° F. but below the point of incipient fusion, comprising employing a vaporous fluorine-containing substance in the atmosphere surrounding the metal during said treatment, said fluorine-containing substance being derived from heating a fluorine-containing compound capable of yielding a vaporous product below 1000° F. under the influence of heat.

7. The method of inhibiting high temperature blistering of aluminum base alloys which contain 0.1 to 12 per cent magnesium when they are subjected to thermal treatment in a furnace atmosphere at temperatures between 800° F. and the temperature of incipient fusion, comprising introducing into the furnace atmosphere between 0.0001 and 0.1 pound of a vaporizable fluorine-containing compound per cubic foot of heating chamber volume.

8. In the art of thermally treating aluminum base alloys, the method of inhibiting the high temperature blistering of said alloys when they are heated in an air atmosphere, comprising thermally treating the alloy in an air atmosphere containing a vaporous fluorine-bearing substance derived from heating solid sodium fluosilicate.

9. In the art of thermally treating aluminum base alloys, the method of inhibiting the high temperature blistering of said alloys when they are heated in an air atmosphere, comprising thermally treating the alloy in an air atmosphere containing a vaporous fluorine-bearing substance

derived from heating solid sodium fluoborate.

10. In the art of thermally treating aluminum base alloys, the method of inhibiting the high temperature blistering of said alloys when they are heated in an air atmosphere, comprising thermally treating the alloy in an air atmosphere containing a vaporous fluorine-bearing substance derived from heating solid aluminum fluoride.
- 10 11. In the art of thermally treating aluminum base alloys, the method of inhibiting the high temperature blistering of an aluminum base alloy which contains about 4.4 per cent copper, 0.5 per cent manganese and 1.5 per cent magnesium
- 15 when said alloy is heated in a furnace atmosphere to temperatures above about 800° F., com-

prising conducting the thermal treatment in a furnace atmosphere containing a vaporous fluorine-bearing substance in an amount between 0.0001 and 0.1 pound per cubic foot of heating chamber volume.

12. The method of inhibiting the high temperature blistering of aluminous metals when subjected to thermal treatment at temperatures above about 800° F., comprising supplying to the furnace atmosphere where said treatment is conducted a vaporous fluorine-bearing substance in an amount corresponding to at least about 0.0001 pound per cubic foot of atmosphere, and conducting the treatment in said atmosphere.

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