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THERMAL 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 certain 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 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 is sometimes 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 tarnish or film that is normally found on aluminum and aluminum base alloys, and 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.

My invention is predicated on the discovery that an artificially produced oxide coating on aluminum and aluminum base alloys effectively inhibits high temperature blistering. The coating is applied prior to the heating of articles made from the aluminous metal, and may be removed after the thermal treatment by any suitable means, if desired. The useful properties of the metal are in no way diminished by reason of the oxide coating, whether the coating is subsequently removed or not. The oxide coating can be produced by any of the well known methods of applying such coatings, and is substantially composed of aluminum oxide. It may also contain other components which essentially alter its specific characteristics, but these variations in properties are generally immaterial insofar as my invention is concerned.

The oxide coating may be formed by various methods, as previously stated. In one method commonly known as anodic oxidation, the aluminum alloy article is made an anode in an electrolytic cell containing an electrolyte such as a solution of sulphuric acid, chromic acid, organic acids such as oxalic acid, acid salts, etc. When electrical energy is impressed upon the cell from an external source, an oxide coating is formed on the anode. An electrolyte frequently employed in this process is an aqueous solution containing from 15 to 35 per cent sulphuric acid. In another method the article is immersed in an alkaline solution of sodium carbonate, for example, which usually contains other substances. A frequently used solution of this type contains about 2.5 per cent of sodium carbonate and 0.5

per cent of potassium dichromate, dissolved in water.

As an example of the effectiveness of the protection afforded by an oxide coating, and one manner in which such a coating can be applied, a test of an alloy composed of 4.2 per cent copper, 0.5 per cent manganese, 1.5 per cent magnesium and the balance aluminum, will be described. Specimens from sheets of this alloy were given an oxide coating by immersing them in an aqueous solution containing about 15 per cent of sulphuric acid, and applying electrical energy at a potential of 16 volts to produce a direct current flow of 12 amperes per square foot. This treatment was continued for 5 minutes with the temperature at about 73° F., and the specimens were then removed from the bath and washed. These specimens were then heated at 925° F. for 16 hours in an air atmosphere which was saturated at 20° C. with water vapor. Similar specimens which had not been coated were also heated in the same atmosphere at the same temperature for 16 hours. At the end of the treatment the uncoated specimens possessed a dark gray color and were liberally covered with blisters, while the coated specimens were completely free from blisters and discoloration. The oxide film was whitened by exposure to the heat, but the underlying metal was not colored in any way.

The protection afforded by a coating produced by immersion in an alkaline solution is illustrated by the following test. Specimens from sheets of the alloy mentioned in the preceding paragraph were immersed in a solution containing 2 per cent of sodium fluoride, 2 per cent of potassium dichromate, and 0.5 per cent of sodium carbonate. The temperature of the solution was 207° F., and the specimens were held therein for 30 minutes to form a protective coating. Groups of these coated specimens were heated at 920° F. in an air atmosphere saturated with water vapor for lengths of time varying from 1 to 8 hours. Uncoated specimens were included with each group for the sake of comparison, and after heating they were blistered and discolored similarly to those described in the previous example. The coated specimens, however, were entirely free from blisters and permanent discoloration of the metal, as in the previous case.

Aluminum base alloys are generally more susceptible to high temperature blistering than aluminum, and of the aluminum base alloys those containing between 0.1 and 12 per cent magnesium show a greater tendency to blister. Other elements such as copper, silicon and zinc may be present in the alloys in amounts of from 0.1 to 14 per cent, and they appear to render the alloys even more susceptible to high temperature blistering, especially when magnesium is also present. The presence of nickel in amounts up to 5 per cent, and the presence of such elements as manganese, chromium, titanium, molybdenum, tungsten and the like, in amounts less than 2 per cent, may also increase the susceptibility of aluminum base alloys containing magnesium to high temperature blistering. The magnesium may be present as the major alloy component aside from aluminum, or it may be a minor constituent as in the examples given hereinabove.

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

The artificially produced oxide coatings employed in accordance with my invention also afford protection to aluminous metals during extended periods of exposure to elevated temperatures.

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. In the art of thermally treating aluminous metals, the method of protecting said aluminous metal against high temperature blistering, comprising applying an artificial oxide coating to said metal before subjecting it to thermal treatment within the temperature range where high temperature blistering normally occurs.

2. The method of thermally treating aluminous metal, comprising applying an artificial oxide coating to said metal to prevent high temperature blistering, and thereafter heating said metal in an air atmosphere at a temperature above 800° F. but below the temperature of incipient fusion.

3. The method of thermally treating an aluminum base alloy containing magnesium without high temperature blistering, comprising applying an artificial oxide coating to said alloy, and thereafter heating the alloy to a temperature within the range in which high temperature blistering normally occurs.

4. The method of protecting an aluminum base alloy containing magnesium against high temperature blistering during thermal treatment at a temperature above 800° F. but below the temperature of incipient fusion, which comprises applying an artificial oxide coating before subjecting said alloy to said thermal treatment.

5. In the art of thermally treating aluminum base alloys containing from 0.1 to 12 per cent magnesium, the method of protecting such an alloy against high temperature blistering during thermal treatment at temperatures between 800° F. and 1100° F., comprising applying an artificial oxide coating to said alloy prior to said thermal treatment.

6. The method of thermally treating aluminum base alloys containing from 0.1 to 12 per cent magnesium at temperatures above 800° F. in an atmosphere conducive to high temperature blistering, comprising applying an artificial oxide coating to said alloys, and thereafter heating said alloys in the said atmosphere without high temperature blistering.

7. The method of protecting aluminum base alloys from high temperature blistering during thermal treatment under conditions conducive to such blistering, comprising anodically applying an artificial oxide coating to said alloys prior to said thermal treatment.

8. The method of thermally treating aluminum base alloys containing from 0.1 to 12 per cent

magnesium in an air atmosphere without high temperature blistering, comprising anodically oxidizing said alloys, and thereafter heating them in an air atmosphere to a temperature between 800° F. and 100° F.

9. The method of protecting aluminum base alloys from high temperature blistering during thermal treatment under conditions conducive to such blistering, comprising applying an artificial oxide coating to said alloys by immersion in an alkaline solution prior to said thermal treatment.

10. The method of protecting aluminum base alloys containing from 0.1 to 12 per cent magnesium against high temperature blistering during thermal treatment at temperatures above 800° F., comprising applying an artificial oxide coating to said alloys by electrolytically oxidizing them in an aqueous solution containing from 15 to 35 per cent of sulphuric acid prior to said treatment.

11. The method of protecting aluminum base alloys containing from 0.1 to 12 per cent magnesium against high temperature blistering during thermal treatment at temperatures above 800° F., comprising applying an artificial oxide coating to said alloys by immersing them in an aqueous solution containing sodium carbonate and potassium dichromate prior to said thermal treatment.

12. In the art of thermally treating aluminum base alloys which contain from 0.1 to 12 per cent magnesium and 0.1 to 14 per cent of at least one of the elements copper, silicon, and zinc, the method of preventing high temperature blistering of said alloys during thermal treatment at temperatures between 800° and 1100° F., comprising applying an artificial oxide coating to said alloys before subjecting them to said treatment.

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CERTIFICATE OF CORRECTION.

Patent No. 2,092,034. September 7, 1937.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 5, claim 8, for "100° F." read 1100° F.; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of November, A. D. 1937.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)

magnesium in an air atmosphere without high temperature blistering, comprising anodically oxidizing said alloys, and thereafter heating them in an air atmosphere to a temperature between 800° F. and 100° F.

9. The method of protecting aluminum base alloys from high temperature blistering during thermal treatment under conditions conducive to such blistering, comprising applying an artificial oxide coating to said alloys by immersion in an alkaline solution prior to said thermal treatment.

10. The method of protecting aluminum base alloys containing from 0.1 to 12 per cent magnesium against high temperature blistering during thermal treatment at temperatures above 800° F., comprising applying an artificial oxide coating to said alloys by electrolytically oxidizing them in an aqueous solution containing from 15 to 35 per cent of sulphuric acid prior to said treatment.

11. The method of protecting aluminum base alloys containing from 0.1 to 12 per cent magnesium against high temperature blistering during thermal treatment at temperatures above 800° F., comprising applying an artificial oxide coating to said alloys by immersing them in an aqueous solution containing sodium carbonate and potassium dichromate prior to said thermal treatment.

12. In the art of thermally treating aluminum base alloys which contain from 0.1 to 12 per cent magnesium and 0.1 to 14 per cent of at least one of the elements copper, silicon, and zinc, the method of preventing high temperature blistering of said alloys during thermal treatment at temperatures between 800° and 1100° F., comprising applying an artificial oxide coating to said alloys before subjecting them to said treatment.

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