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DEGASSING ALUMINUM ARTICLES

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This invention relates to a method for the extraction of gas and the elimination of voids and flakes in wrought aluminum and aluminum base alloy articles.

The term "aluminum" will be used herein to encompass aluminum and aluminum base alloys which contain at least 50 percent by weight of aluminum.

Finished and semi-finished aluminum articles occasionally contain occluded gas, principally hydrogen, which may give rise to objectionable discontinuities in the metal structure. Some of the hydrogen is usually considered to be in solution in the solid metal, i.e. it is in the monatomic state, although pockets or voids filled with molecular hydrogen have also been observed. In the fabrication of wrought articles from the ingot, some thermal treatments are generally employed to aid in working the metal or to develop the desired strength, and it is considered that such heating also produces diffusion of the monatomic hydrogen to any voids or discontinuities within the metal whereat association into molecular form takes place. The problem of so-called "flakes" within the internal metal structure has been traced to these hydrogen-filled voids.

Because of the gas pressures developed by the molecular gas, subsequent working of the metal does not effect a healing of the void or discontinuity, and heating of the article at elevated temperatures may increase such pressures to the point where the metal suffers local plastic deformation.

The problem of occluded gas has become increasingly important with the growing requirements for high strength aluminum articles. Any gas-filled void may not only constitute an area of weakness in the final article, but may give rise to flakes, blisters, slivers and other defects which result in rejection. These problems have prompted investigations to find a method for the elimination of occluded gas and voids associated therewith.

It has heretofore been proposed that hydrogen gas contained in aluminum articles may be driven out of the metal by heating under a vacuum at temperatures on the order of 500–1000° F. Commercial utilization of this procedure has not proven feasible and attempts to remove gas in an undried air atmosphere have been unsuccessful. Also, it has been suspected that the degassed articles are prone to again absorb gas.

It has now been discovered that an aluminum article having a low gas content, or substantially none, can be produced by a method in which an aluminum body containing gas and voids is coated with at least one metal selected from the group consisting of nickel and chromium and heated in a gaseous atmosphere at a temperature above 750° F., but below that which any substantial amount of fusion occurs, for a length of time sufficient to diffuse occluded gas into the atmosphere surrounding the article. The metal article may be thereafter worked to plastically deform the metal article. The metal coating is also highly beneficial in preventing oxidation and blistering of the aluminum during subsequent heating operations.

To bring about the extraction of gas from the aluminum article, the heating step must be conducted under conditions which facilitate gas removal. It has been found that this can be accomplished by initially coating the article with nickel or chromium or both metals to form

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a film on the metal surface which reduces greatly, if it does not altogether eliminate, the existence of monatomic hydrogen at the metal surface, as well as tending to inhibit oxidation of the aluminum. The nature of the mechanism by which the gas is driven out of the aluminum article is not fully understood; however, it seems to involve an irreversible conversion of monatomic hydrogen into molecular hydrogen. By employing the metal film on the article, the degassing or prolonged heating step may be carried out in a normal atmosphere without danger of re-absorbing gas, thus removing one of the great economic handicaps to the use of long-time heating procedures to extract gas from aluminum articles.

Prior to coating the surface of an aluminum article with nickel or chromium, or both, the surface of the article should be treated to remove any oxide film. This may be conveniently accomplished by dipping or otherwise applying at 1% aqueous solution or hydrofluoric acid to the article. Other suitable solutions can be used, of course. The nickel and chromium coatings may be deposited on the surface in any convenient manner. Electro-plating and electro-less plating techniques have been highly successful, as have been metallic spray coatings. The thickness of the coating is not critical, and apparently it need not be continuous, but it should be relatively thin; such as normally produced by plating or spraying procedures. For example, coatings of less than 0.1 mil have been satisfactory. Furthermore, a coating initially applied to plate has been found to protect it through the ensuing reduction steps to sheet.

The electrolytic coatings may be applied directly or they may be applied over a base coating or "strike" of another metal, such as copper, in accordance with conventional practice. The copper strike has no effect on the treatment of the present invention. If desired, a duplex coating of nickel and chromium may be employed wherein an initial layer of one metal is deposited and the second one applied to the first coating. It is also possible to mingle the two metals, nickel and chromium, as in applying a sprayed coating.

The coating and degassing steps may be conducted at any step of the working operation. Coatings applied to plate slabs have been found to provide protection throughout the rolling sequence and its various preheating operations. For this reason, it is often desirable to leave the protective metal coating on the aluminum article until after the final heat treatment.

The coating may be removed by any convenient method. Generally, it is most convenient to strip the metal electrolytically in a sulfuric acid electrolyte.

After the metal coating has been applied, the article may be degassed in a conventional air atmosphere furnace. No drying of the air need be undertaken as moisture can be tolerated in the gas extraction step, thus permitting employment of conventional industrial furnace atmospheres which generally contain 1.5 to 30 grains of water per cubic foot. Gases which are inert or non-deleterious to aluminum may be employed in place of air such as nitrogen, argon, helium and fuel gas, or such gases may be used in admixture with air.

The term "atmosphere," as used herein, includes air, gases inert to aluminum, or combinations thereof, and moisture associated with air and other gases.

The duration of the heating step will be dependent upon the thickness of the article being treated (the shortest diffusing path), the desired final gas content of the metal and the temperature employed. The rate of diffusion increases almost exponentially with increase in temperature. Since commercial degassing of large quantities of aluminum articles requires space-consuming heating equipment, it is desirable that the heating step

be of as short duration as possible. Therefore, a temperature at least above 750° F., and generally above 900° F., should be used. The temperature is preferably below the temperature of incipient fusion, but temperatures above the melting point of one or more of the phases have been successfully employed where the amount is very small and eutectic melting has not been a concern. However, the article should not be heated at temperatures which adversely affect the properties of the metal. When the gas-containing metal is heated in this manner, the major portion of the gas is driven off within a reasonably short time, a proportionately longer time being required to remove the last few percent of gas. For purposes of this application, an article will be considered substantially degassed or gas-free if the gas has been substantially diffused out of the internal discontinuities to permit subsequent healing, although some may remain in solution in the metal. Generally, this will require removal of at least 75 percent or more of the occluded gas, although it may often be desirable to extract as much as 90 percent, or more.

Theoretically, the length of time for degassing increases as the square of the half-thickness of the metal body. Therefore, in some cases, it may be desirable only to seek extraction of the gas from relatively thin cross-sections of the articles where the strength characteristics are of primary concern rather than to degas the entire article which might require a much longer time.

Indicative of the variables governing the diffusion step, Tables I and II are a guide to the time theoretically necessary at several temperatures for removing various percentages of gas, as based on Fick's law and the diffusion constant for hydrogen in aluminum. These tables give a time factor per centimeter half-thickness (or radius) which may be converted to the ideal length of time necessary to degas a given thickness of metal by multiplying the factor by the square of the half-thickness of the metal body in centimeters.

$$T = t \times \left(\frac{d}{2}\right)^2$$

where:

T=time necessary for degassing article (in hours)

t=time factor for unit thickness (from table)

d=thickness (or diameter) of article (in centimeters)

TABLE I

[Time factor for sheet, plate, or rectangular cross-section, hrs./unit centimeter half-thickness]

Percent Removal	Temp., ° C.			
	450	500	550	600
25.....	3.5	.82	.25	.07
75.....	18	4	1	.34
90.....	30	6.8	1.7	.52
95.....	38	8.6	2.4	.7
99.....	60	13	3.8	1.1

TABLE II

[Time factor for rod or bar, hrs./unit centimeter radius]

Percent Removal	Temp., ° C.			
	450	500	550	600
25.....	1.6	.34	.095	.03
75.....	7.5	1.7	.47	.14
90.....	13	2.5	.75	.24
95.....	16	3.7	.95	.34
99.....	26	5.6	1.5	.47

For most aluminum articles, 850-1000° F. (450-540° C.) is a temperature range conveniently employed. In practicing the invention at a temperature of 940° F. (505° C.), since commercial conditions are far from

ideal, a rule of thumb figure has been to maintain aluminum forgings at temperature at least 16 and preferably 24 hours or more per inch of thickness for adequate gas removal. However, occasionally articles having a thickness of over several inches require shorter times but often require more than 24 hours per inch of thickness. In the treatment of rolled articles at the same temperature, at least about 4 hours and preferably six hours are used for a half-inch thickness. However, thinner sheet products degas very quickly, .091 inch thick sheet has been degassed at 940° F. in only 1 minute. Because of the difficulty in removing gas from some articles, it is conceivable that the rate may vary with the mode of fabrication or grain orientation or with the surface condition. For this reason and (also for obtaining a more definite determination of the time necessary to degas a particular article, the testing of samples is desirable for the establishment of conditions for the heating step. Similarly, the time necessary for degassing compressed aluminum powder products will vary with the conditions under which the compact was prepared.

Subsequent to the heating step, the article is subjected to a working operation for effecting plastic deformation of the metal and to heal voids left by the diffused hydrogen. The various working methods may be employed singly or in combination to effect the welding of the voids. The term "forging" includes both hammer-forging and press-forging methods. The amount of working or percentage of reduction necessary will be dependent upon the nature of the article and the original content of voids. In some cases, especially in larger articles such as die forgings, a relatively small reduction may be sufficient to heal or weld the discontinuities in the structure. Generally, in die forgings a reduction of from ½ to 50 percent by a blocking or finishing operation has been found to be satisfactory, although even greater reductions may occasionally be necessary; hand forgings may necessitate reductions of 2 to 50 percent. Although extrusion operations will generally heal discontinuities, it is frequently desirable to first forge the metal billets to a reduction in thickness of 2 to 50 percent. Similarly, a preliminary forging is sometimes desirable before a rolling operation.

The degassed and healed aluminum articles may then be subjected to further heat treatments. Because the voids or discontinuities within the metal structure no longer exist, the problem of gassing (or regassing) is minimized unless new discontinuities are subsequently created within the metal structure.

The problem of gaseous occlusions is most pronounced in the case of aluminum base alloys containing magnesium and/or zinc. However, other aluminum base alloys as well as aluminum itself may often require degassing dependent upon the conditions to which the aluminum article or its parent ingot have been exposed, or the gas content in the ingot as cast. It is to be understood that the article to be coated with nickel, chromium, or both metals, may be in the form of a casting, compressed powder product, or a wrought article. Conditions necessary to effect degassing will, of course, be influenced by the structure of the article.

Illustrating the efficacy of the present invention are the following examples in which aluminum articles were coated with nickel or chromium and heated to extract occluded gas.

Example I

A lot of commercial purity aluminum (99.00 percent minimum) plate panels, 6" x 9", of two different thicknesses, 0.95 and 0.35 inch, was divided into two groups. The first group was chemically plated with nickel to a thickness of 0.1 mil whereas the second group was left bare. Both were then heated at 940° F. in a conventional air atmosphere furnace, the 0.95 inch material for 24 hours and the 0.35 inch material for 3 hours. The

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nickel coating was then electrolytically stripped in a sulfuric acid bath. The two plate sizes were then rolled to a thickness of 0.35 and 0.25 inch, respectively, annealed at 1100° F. for 1 hour in a conventional heat-treating furnace and inspected for blisters. The coated group was found to be blister-free whereas 80 percent of the untreated group was rejected as having 1 or more blisters per panel surface.

Example 2

A lot of brazing sheet panels 14½" x 20" and 0.040 inch thick comprised of a core of aluminum-7.5% silicon alloy and cladding sheets nominally composed of aluminum and 1.2 percent manganese was divided into two groups. The first group was electrolytically plated with nickel, 0.1 to 0.2 mil thick, over a copper strike, whereas the second was not so treated. Both groups were subjected to a degassing operation by heating at 1000° F. for 1 minute. The metal coating was electrolytically stripped in a sulfuric acid bath. The two groups were then pressure-formed into evaporator sheet at 1100° F., after which they were inspected by X-ray to determine the presence of "rivulets" or dark spots, which are considered to be gas-filled voids. The treated group was found to be free from any such indications whereas the untreated was all rejected because of such indications.

Example 3

A lot of commercial purity aluminum (99.00 percent minimum) sheet, 0.091 inch thick, was divided into two groups, the first being electrolytically plated with chromium (directly), 0.1 to 0.2 mil thick. Both groups were subjected to degassing by heating at 940° F. for 15 minutes, after which the coated group was electrolytically stripped in a sulfuric acid electrolyte. The material was then subjected to a blister anneal test, in which occluded gas is determined by heating the specimen under vacuum at 1100° F. and observing the formation of blisters. The treated specimens were free from blister formation whereas the untreated were highly blistered.

Having thus described the invention, we claim:

1. The method of substantially reducing the gas content of aluminum articles comprising: coating the surface of an aluminum article containing gas with at least one metal selected from the group consisting of nickel and chromium; and thereafter heating said coated article in a gaseous atmosphere at a temperature above 750° F.,

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but below the temperature at which any substantial amount of fusion occurs, for a length of time sufficient to diffuse occluded gas into the atmosphere around said article.

2. The method in accordance with claim 1 wherein said atmosphere is air.

3. The method in accordance with claim 1 wherein said atmosphere contains from 1.5 to 30 grains of water per cubic foot.

4. The method in accordance with claim 1 wherein the metal coating is nickel.

5. The method in accordance with claim 1 wherein the metal coating is chromium.

6. The method of substantially reducing the gas content of aluminum articles comprising: coating the surface of an aluminum article containing gas with at least one metal selected from the group consisting of nickel and chromium; heating said coated article in a gaseous atmosphere at a temperature above 750° F., but below the temperature at which any substantial amount of fusion occurs, for a length of time sufficient to diffuse occluded gas into the atmosphere around said article and thereafter stripping said coating from said article.

7. The method of substantially reducing the gas content and voids in aluminum articles comprising: coating an aluminum article containing gas and voids with at least one metal selected from the group consisting of nickel and chromium, heating said article in a gaseous atmosphere at a temperature above 750° F., but below the temperature at which any substantial amount of fusion occurs, for a length of time sufficient to diffuse occluded gas into the atmosphere around said article; and thereafter working said article to heal any voids therein.

8. The method in accordance with claim 7 wherein said atmosphere is an air containing 1.5 to 30 grains of moisture per cubic foot.

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