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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 treated 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.

Recent investigations have indicated that one of the prime factors in the failure to degas aluminum articles heated in an air atmosphere furnace has been the existence of relatively high monatomic hydrogen partial pressures at the surface of the aluminum article, which may be the result of oxidation of the aluminum by small amounts of moisture in the furnace atmosphere at the temperature of treatment. The aluminum-water vapor reaction becomes pronounced at temperatures above 650° F., and especially above about 750° F.

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 the aluminum body containing gas and voids is coated with at least one metal selected from the group consisting of cobalt, molybdenum, palladium, rhodium and iridium, and is heated in a gaseous atmosphere at a temperature above 750° F. but below that at 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.

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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 cobalt, moylbdenum, palladium, rhodium or iridium or a combination of these metals, to form 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 reabsorbing 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 one or more of the metals named above, the surface of the article should be treated to remove any oxide film. This may be conveniently accomplished by dipping or otherwise applying a 1% aqueous solution of hydrofluoric acid to the article. Other suitable solutions can be used, of course. The metallic 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 multilayer coating of one or more metals may be employed or the layer may consist of an alloy of two or more of the metals as might be applied in spraying.

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 nondeleterious 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 required 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 articles 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 the 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

The above time values can be converted to inches and in terms of the full thickness of the metal body by multiplying them by a factor of 1.613.

For most aluminum articles, 850 to 1000° F. (450 to 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 was degassed at 940° F. in only 1 minute. Because of the difficultly 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 articles, 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 one or more of the group of metals referred to above may be in the form of a casting, compressed powder product or 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 some of the metals of the present invention and heated to extract occluded gas.

EXAMPLE 1

To determine the effect of a cobalt coating upon the degassing of aluminum some 0.091" thick panels of the metal of 99% minimum purity were tested. The panels were given a copper strike followed by electroplating with cobalt thus producing a coating of 0.1 to 0.2 mil in thickness. These panels as well as bare ones were heated in a normal air atmosphere at 940° F. for 15 minutes. The cobalt coating was electrolytically stripped from the panels in a sulfuric acid bath after they had cooled to room temperature. Both groups of panels were then subjected to a blister anneal test in which they were heated to 1100° F. under a vacuum of 1 micron mercury pressure. Upon cooling to room temperature the panels were examined for surface blisters to determine whether any gas might have been released within the metal during the heating period. It was observed that there were no blisters on the panels that had been coated with cobalt whereas those which had not been so treated (the bare panels) were severely blistered thus indicating that the gas content of the coated material had been reduced to a level where substantially none remained.

EXAMPLE 2

The effect of a palladium coating upon the degassing of aluminum was determined in the same manner as described in the preceding example. Panels of the same purity of metal and of the same thickness as stated above were first given a copper strike and then electroplated with palladium to provide a coating 0.1 to 0.2 mil in thickness. After heating these and bare panels at 940° F. for 15 minutes in a normal air atmosphere the palladium coating was electrolytically stripped and both groups subjected to the blister annealing test described above. The panels which had been coated with palladium were free from blisters while those that had received no coating were severely blistered thus indicating the removal of substantially all of the gas from the palladium-coated material.

EXAMPLE 3

The effect of a molybdenum coating upon the degassing of aluminum was determined by spraying panels of the same kind as referred to in the two preceding examples with metallic molybdenum in a conventional manner. The coating so produced had a thickness of about 5 mils. The coated panels along with bare ones were heated at 940° F. for 15 minutes in a normal air atmosphere, cooled to room temperature, and the molybdenum coating electrolytically stripped from the panels upon cooling to room temperature. Both groups of panels were subjected to the blister anneal test mentioned above. The

panels which had been coated with molybdenum revealed no blisters whereas the bare panels were badly blistered. This was considered to show that gas had been removed from the coated panels to the point where substantially none remained.

Having thus described our 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 cobalt, molybdenum, paladium, rhodium and iridium and thereafter 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.

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 selected is cobalt.

5. The method in accordance with claim 1 wherein the metal selected is molybdenum.

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 cobalt, molybdenum, palladium, rhodium and iridium; 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 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 cobalt, molybdenum, palladium, rhodium and iridium; 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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CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 30, for "treated" read -- traced --.

Signed and sealed this 12th day of December 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC