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PRODUCTION OF VOID-FREE ALUMINUM AND ALUMINUM BASE ALLOY ARTICLES

Matthew Scott Hunter, New Kensington, and Edmund C. Franz, Penn Hills Township, Allegheny County, Pa., assignors to Aluminum Company of America, Pittsburgh, Pa., a corporation of Pennsylvania

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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 75 percent aluminum.

Finished and semi-finished aluminum articles occasionally contain occluded gas, principally hydrogen, which may give rise to objectionable discontinuities in the metal structure. A large proportion 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 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 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 untreated 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 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 substantially gas-free and void-free wrought aluminum articles can be produced by a method in which an aluminum article containing gas and voids is heated in an atmosphere containing less than 2.0 grains of water per cubic foot at a temperature above about 750° F. for a sufficient length of time to diffuse occluded gas into the atmosphere and thereafter effecting sufficient plastic deformation of the metal to heal or weld

voids. In referring to the atmosphere surrounding the aluminum articles it is to be understood this does not include a vacuum or a partial vacuum.

The heating step must be conducted in a non-deleterious atmosphere of low enough moisture content to prevent the development of high monatomic hydrogen partial pressures at the surface of the article. This may be accomplished in air which has been dried to a low moisture content or in any other substantially moisture-free atmospheres inert or non-deleterious to aluminum, such as nitrogen, argon, helium or fuel gas (if free from corrosive sulfur compounds). The moisture content should be below about 2.0 grains per cubic foot of furnace atmosphere and is preferably below about 0.8 grain per cubic foot for more consistent results. If air is used, the drying may be accomplished by any convenient means such as the conventional refrigerant-dehumidifiers and desiccants. Electric heated furnaces are particularly desirable although radiant tube and other types of heating equipment wherein the products of combustion and/or moisture are not discharged into the furnace atmosphere are also satisfactory.

The terms "atmosphere" or "non-deleterious atmosphere," as used herein, include air, gases inert to aluminum, or combinations thereof. As is well known, aluminum develops an oxide film in contact with oxygen and a nitride film if exposed to nitrogen at elevated temperature, but for the present application such oxide or nitride films have no deleterious effect upon the properties of the article.

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 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 healing, although it may be 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 1 and 2 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 1

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 2

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 to 1000° F. (450 to 540° C.) is a temperature range conveniently employed. In practice, 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. 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 powder metallurgy products will vary with the conditions by which the compact was prepared.

Subsequent to the heating step, the article must be subjected to a working to heal voids left by the diffused hydrogen. Forging, extrusion and drawing operations may be employed singly and 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.

The degassed and healed aluminum articles may then be subjected to further heat treatments. Because the voids or dicontinuities 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.

Illustrating the efficacy of the present invention are the following examples in which aluminum articles were treated to extract occluded gas and subsequently worked to yield substantially gas-free and void-free articles.

EXAMPLE 1

A lot of thirty-eight blocked forgings and fourteen preform forgings of an alloy nominally composed of aluminum, 5.6 percent zinc, 2.5 percent magnesium, 1.6 percent copper and 0.3 percent chromium, and varying in thickness from 4½ inches to 9½ inches was ultrasonically inspected. Each of the blocked forgings gave numerous ultrasonic indications in excess of that obtained from a No. 3 series "B" Alcoa Ultrasonic Standard Reference Block of equivalent metal distance and failed to pass Class "B" Ultrasonic Inspection Standards. The preform forgings also contained numerous ultrasonic indications.

The forgings were heated at 887° F. for 77¼ hours in an air atmosphere having an average dew point of −30° F. (0.13 grain per cubic foot). After the heating step, the blocked forgings were given a finish forging step effecting a reduction in cross-section varying from 6 to 25 percent.

Subsequently, the finished forgings were solution heat treated at 870° F., quenched in water and precipitation hardened at 250° F. The ultrasonic inspection report on the treated articles was as follows:

25 pieces—clear (free from ultrasonic indications)
9 pieces—1 (#3)
1 piece—2 (#3) but more than 1 inch apart
2 pieces—1 (#5)
1 piece—1 (#5+)

EXAMPLE 2

Five blocked forgings of an alloy nominally composed of aluminum, 4.4 percent copper, 0.8 percent silicon, 0.8 percent manganese and 0.4 percent magnesium were ultrasonically inspected and each was found to contain ultrasonic indications including at least one indication exceeding that obtained from a No. 5 Series "B" Block.

The forgings were maintained at a temperature of 940° F. for 72 hours in an air atmosphere having an average dew point of −23° F. (0.19 grain per cubic foot) after which they were subjected to a finish forging step with a reduction varying from about 16 to 25 percent. The finished forgings were solution heat treated at 940° F., quenched in water and subsequently precipitation hardened at 340° F. Upon ultrasonic inspection, all the forgings were found to be free from ultrasonic indications.

EXAMPLE 3

Four extrusion ingots, 12 inches in diameter, of an alloy nominally composed of aluminum, 4.4 percent copper, 0.8 percent silicon, 0.8 percent manganese and 0.4 percent magnesium were cast utilizing a fluxing technique to lower the gas content. One, however, was only lightly fluxed to obtain a relatively high gas content (0.38 ml./100 g. STP) as compared to the other three (0.17 ml./100 g. STP). One of the low gas ingots and the high gas ingot were

heated at 1000° F. for 144 hours in an air atmosphere having a dew point of —26° F. (0.16 grain per cubic foot). Another low gas ingot was heated at 1000° F. for 6 hours in a furnace having a dew point of +20° F. (1.3 grains per cubic foot). The fourth low-gas ingot received only the standard treatment of preheating for 24 hours at 1000° F. in a conventional undried atmosphere having a dew point in excess of 80° F. (>11 grains per cubic foot). The ingots were extruded into bars having a 3 inch square cross-section, heat treated at 930° F., quenched, stretched and precipitation hardened at 320° F. Upon ultrasonic inspection, the bars produced from the degassed ingots were found to be completely free from indications whereas the low-gas ingot which had been treated according to standard practice was found to contain numerous indications equal to a No. 3 Standard Reference Block.

EXAMPLE 4

Three forgings of an alloy composed of aluminum, 4.4 percent copper, 0.9 percent silicon, 0.8 percent manganese, 0.4 percent magnesium and having a thickness of two inches, were found to contain numerous ultrasonic indications and each had at least one indication exceeding that from a No. 5 Reference Block. Six sections of plate 1⅛ inches in thickness and nominally composed of an alloy of aluminum, 1.6 percent copper, 2.5 percent magnesium, 5.6 percent zinc and 0.3 percent chromium, also contained numerous ultrasonic indications equal to or greater than a No. 5 Reference Block.

All but one of the forgings and one of the plate sections were heated at 940° F. for 48 hours in an air atmosphere having a dew point of about —26° F. (0.16 grain per cubic foot). All pieces were press-forged with a reduction of about 50 percent and were subsequently solution heat-treated at 940° F., quenched in water and precipitation hardened at 340° F. Upon ultrasonic inspection, the treated pieces were found to be free from ultrasonic indications whereas the untreated specimen from the first group contained six indications larger than that from a No. 5 Block and the untreated plate section contained 7 indications larger than a No. 5.

Having thus described the invention, we claim:

1. The method for the production of substantially gas-free and void-free aluminum articles comprising: heating an article having a natural surface condition and containing gas and voids to a temperature above 750° F. but below the temperature of incipient fusion of the metal in an atmosphere containing less than 2.0 grains of moisture per cubic foot and composed of at least one gaseous substance selected from the group consisting of air and gases inert toward aluminum, and, in addition, any gas derived from the article being treated, said atmosphere being at a pressure not less than atmospheric pressure, said atmosphere surrounding and in contact with a substantial portion of the surface of said article, said heating being continued for a length of time sufficient to diffuse a major portion of the occluded gas to the surface of said article and thence into the surrounding atmosphere, removing said article from the treating atmosphere and immediately thereafter hot working the article sufficiently to heal any degassed voids.

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 less than 0.8 grain of moisture per cubic foot.

4. The method for the production of substantially gas-free and void-free aluminum articles comprising: heating an article having a natural surface condition and containing gas and voids to a temperature above 850° F. but below the temperature of incipient fusion of the metal in an atmosphere containing less than 2.0 grains of moisture per cubic foot and composed of at least one gaseous substance selected from the group consisting of air and gases inert toward aluminum and, in addition, any gas derived from the article being treated, said atmosphere being at a pressure not less than atmospheric pressure, said atmosphere surrounding and in contact with a substantial portion of the surface of said article, said heating being continued for a length of time at least equal to 16 hours per inch of metal thickness to diffuse occluded gas to the surface of said article and thence into the surrounding atmosphere, removing said article from the treating atmosphere and immediately thereafter hot working the article sufficiently to heal any degassed voids.

5. The method for the production of substantially gas-free and void-free aluminum articles comprising: heating an article having a natural surface condition and containing gas and voids to a temperature above 850° F. but below the temperature of incipient fusion of the metal in an atmosphere containing less than 0.8 grain of moisture per cubic foot and composed of at least one gaseous substance selected from the group consisting of air and gases inert toward aluminum, and, in addition, any gas derived from the article being treated, said atmosphere being at a pressure not less than atmospheric pressure, said atmosphere surrounding and in contact with a substantial portion of the surface of said article, said heating being continued for a length of time at least equal to 16 hours per inch of metal thickness to diffuse occluded gas to the surface of said article and thence into the surrounding atmosphere, and immediately thereafter hot working the article sufficiently to heal any degassed voids.

References Cited in the file of this patent

UNITED STATES PATENTS

2,262,696	Nock et al.	Nov. 11, 1941
2,506,364	Jarvie et al.	May 2, 1950
2,841,512	Cooper	July 1, 1958
2,885,313	Milliken	May 5, 1959
2,885,316	Milliken	May 5, 1959
2,995,478	Keller	Aug. 8, 1961
2,995,479	Cochran	Aug. 8, 1961

OTHER REFERENCES

Vacuum Metallurgy, edited by Rointan F. Bunshah (compilation of lectures given June 10–14, 1957). Copyright 1958 by Reinhold Publishing Corp. Library of Congress Call No. 58–13584, pp. 282–286; p. 285 relied upon.

Engineering Metals and Their Alloys, by Carl H. Samans. Copyright 1949 by Macmillan Co., pp. 219–222; p. 221 relied upon.

"Metals Handbook," 1948 edition by ASM, p. 769.

"Gases in Metals," by ASM, p. 41, Library call Number TA 460 A44g.