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METHOD FOR DEGASSING ALUMINUM ARTICLES BY MEANS OF A VAPOROUS FLUORIDE

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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.

This application is a continuation-in-part of my co-pending applications, Serial Nos. 723,989 and 723,990, filed March 26, 1958.

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 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, 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 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 a substantially gas-free and void-free aluminum article can be produced by a method in which the aluminum article containing gas and voids is initially exposed to a vaporous fluoride to develop a film thereon which substantially destroys or prevents the accumulation of monatomic hydrogen at the metal surface, heated at a temperature above 750° F. for a length of time sufficient to diffuse occluded gas into the atmosphere surrounding the article, and thereafter worked to plastically deform the metal sufficiently to heal voids in the metal article.

To bring about the extraction of gas from the aluminum article, the heating step must be conducted under conditions which prevent the development of high monatomic hydrogen partial pressures at the surface of the article. It has been found that this can be accomplished by initially exposing the article to a vaporous fluoride that reacts with the aluminum to form a protective film on the metal surface which reduces greatly, if not altogether eliminates, the existence of monatomic hydrogen at the metal surface, as well as tending to inhibit oxidation. The nature of the mechanism is not fully understood; however, its primary action seems to be promoting the combination of monatomic hydrogen into molecular hydrogen. In this manner, the degassing or prolonged heating step may be carried out in an undried atmosphere, thus removing one of the great economic handicaps to the use of long-time heating procedures to extract gas from aluminum articles.

The term "vaporous fluoride," as used herein, refers to any vaporous fluoride that will react with aluminum and its alloying constituents to provide a fluoride film. Examples of such fluorides are boron trifluoride, silicon tetrafluoride, carbon tetrafluoride, difluoromethane and hexafluoroethane. The vaporous fluorides may be used singly and in combination. Although hydrogen fluoride may be used for this purpose, it is less desirable because of hygiene problems and because of the often severe corrosion of the article which it may effect. In some instances, the surface of the aluminum will become more reactive to the fluoride at higher temperatures, so the treatment is conveniently effected in a heat-treating furnace.

The vaporous fluorides may be provided by any one of the following methods. Solid inorganic carrier compounds may be deposited in a conventional air atmosphere furnace which will decompose upon heating to yield the vaporous fluoride in a reactive state. As an alternative, vaporous fluoride from a suitable source may be injected into the furnace atmosphere. An atmosphere composed entirely of the vaporous fluoride may be employed but this is not generally practical since highly satisfactory results are obtained with a relatively dilute atmosphere of the fluoride, even to the point where the fluoride constitutes only a few percent of the atmosphere. In still another method, the surface of the aluminum article may be coated with a carrier compound which will decompose upon heating to yield the vaporous fluoride; however, an organic carrier compound is preferred for this application to minimize the staining and corrosion which might ensue by use of metallic salts.

The term "carrier," as used herein, refers to those compounds, both organic and inorganic, which contain the vaporous fluoride in chemically combined or sorbed form and which will yield the vaporous fluoride in a reactive form when heated.

The surface of the article should develop the fluoride film below the temperatures at which the onset of high-temperature oxidation becomes pronounced in order to obtain the greatest benefit therefrom. Generally, this temperature will depend upon the length of exposure in an untreated air atmosphere, the humidity of the fur-

nace atmosphere and the composition of the metal. Generally, the high temperaure oxidation effect becomes pronounced at temperatures above 750 to 800° F. For aluminum-base alloys containing magnesium, it is often desirable to develop the film at even lower temperatures to secure maximum benefit and to eliminate staining, as is disclosed fully in my copending applications Serial Nos. 684,641 and 684,642, filed September 18, 1957, now abandoned.

Although any vaporous fluoride which will react with aluminum and its alloying constituents may be used in the practice of this invention, boron trifluoride is preferred because of its moderate action upon the aluminum which develops only a relatively thin fluoride film and because it does not constitute either an industrial or hygiene hazard and is feasible costwise. However, other reactive fluorides may be employed albeit with more problems regarding control of fume and attack. When using boron trifluoride, it is generally desirable that the surface of the article be at a temperature above 400° F. to develop the fluoride film.

Among the carrier compounds which decompose or yield boron trifluoride are ammonium fluoroborate, calcium fluoroborate and the various organic ammonium fluoroborates such as di-n-butyl ammonium tetrafluoroborate, n-octadecyl-N,N,N trimethyl ammonium tetrafluoroborate and di-n-amyl ammonium tetrafluoroborate. Also various organic compounds in which the boron trifluoride is merely absorbed may also be used.

Among the many other carrier compounds which may also be employed are sodium fluosilicate, ammonium fluosilicate, potassium fluosilicate, ammonium fluoride and zinc fluoride.

The amount of vaporous fluoride required in the atmosphere is not large. For example, as little as 0.075 gram of boron trifluoride per cubic foot of furnace atmosphere has been effective, although an amount in excess of 0.27 gram per cubic foot is preferred and generally employed. When coating the article itself, an alcoholic solution containing at least 0.2 percent and preferably about 0.8 percent of boron trifluoride has been found to yield sufficient fluoride vapor to develop the desired film. My copending applications Serial Nos. 684,641 and 684,642, now abandoned, disclose more fully the details of the film-forming step.

Generally, exposure to the vaporous fluoride for one minute to one hour is sufficient to establish the desired film, the length of time being dependent upon the concentration of the vaporous fluoride, its reactivity and/or the reactivity of the aluminum surface at the temperature of the treatment. Where a carrier compound is applied to the surface of the article, sufficient time should be allowed for decomposition to occur and establish the desired atmosphere, as well as to permit substantially complete decomposition and vaporization of the carrier compound.

After the exposure to the vaporous fluoride, the article may be degassed in a conventional air atmosphere furnace. No drying of the air need be undertaken as moisture can now be tolerated in the gas extraction step, thus permitting employment of conventional undried industrial 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.

The term "atmosphere," as used herein, includes air, gases inert to aluminum, or combinations thereof.

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 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 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 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 hours/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 hours/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 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. 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 under which the compact was prepared.

Subsequent to the heating step, the article must be subjected to a working for effecting plastic deformation of the metal to heal voids left by the diffused hydrogen. The various working methods 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. 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.

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

Example 1.—A lot of forgings of an alloy composed of aluminum, 4.3 percent zinc, 3.3 percent magnesium, 0.60 percent copper, 0.2 percent manganese, 0.18 percent chromium and 0.06 percent titanium was divided into two groups. The forging weighed approximately 600 pounds and varied in thickness from about ½ inch to 3½ inches. The first group containing 37 forgings was pretreated by exposure for about 15 minutes at a temperature of about 500° F. in an undried air atmosphere containing boron trifluoride generated by the decomposition of ammonium fluoroborate deposited within the furnace (1.31 grams of boron trifluoride per cubic foot of furnace volume). After pretreatment, the forgings were heated at a temperature of 940° F. for 72 hours in an undried air atmosphere. The second group of 38 forgings was neither pretreated nor degassed.

Both groups were then subjected to a second blocking step and a finishing forging step, after which they were solution heat-treated at 830° F., quenched in water and subsequently precipitation hardened at 240° F. After heat treatment the forgings were ultrasonically inspected, the reject standard being an indication equal to or larger than that obtained from a No. 5 Series "B" Alcoa Ultrasonic Standard Reference Block of the appropriate metal distance. The ultrasonic report on the first or treated group was as follows:

32 pieces—clear (free from ultrasonic indications)
1 piece—1 (#3); 3 (#3+)
2 pieces—1 (#3); 4 (#3+); 2 (multiple #3)
1 piece—1 (#5)
1 piece—1 (#5); 2 (#5+)

or a total of 16 ultrasonic indications and a rejection of only two forgings. All of the forgings in the second group revealed ultrasonic indications and the group contained a total of 403 indications ranging from #3 to mutiple #8+; from this group 22 forgings or 58 percent were rejected.

The difference in the two groups indicated by the ultrasonic evaluation is most significant. That thirty-two of the forgings were completely free from indications is clearly convincing of the efficacy of the present invention in facilitating degassing of aluminum-magnesium alloy articles.

Example 2.—A lot of forgings of an alloy composed of aluminum, 4.4 percent copper, 0.8 percent silicon, 0.8 percent manganese and 0.4 percent magnesium was divided into two groups of 87 pieces each. The forging weighed about 115 pounds and varied in thickness between about ¾ inch and 3 inches. The first group was pretreated by exposure for fifteen minutes at a temperature of about 500° F. in an undried air atmosphere containing boron trifluoride generated by the decomposition of ammonium fluoroborate (1.41 grams of boron trifluoride per cubic foot of furnace volume), and was then heated at a temperature of 940° F. for about 72 hours in an undried air atmosphere. Both the degassed forgings and the untreated group were subjected to a blocking step and a finishing forging step after which they were solution heat-treated at 940° F., quenched in water, and then precipitation hardened at 340° F. Ultrasonic inspection indicated that the first group was substantially free from indications and all pieces passed inspection standards; the second group was found to contain numerous indications and 65 pieces were rejected for a recovery rate of only 25 percent.

Example 3.—A lot of forgings of the alloy described in Example 2 and which weighed about 135 pounds each and varied in thickness between about ½ inch and ¾ inch were divided into two groups. The first group was pretreated by exposure for about fifteen minutes at a temperature of about 500° F. in an undried air atmosphere containing boron trifluoride generated by the decomposition of ammonium fluoroborate (1.41 grams of boron trifluoride per cubic foot of furnace volume). The pretreated specimens were then heated at a temperature of 940° F. for about 72 hours in an undried air atmosphere. Both the degassed forgings and the untreated group were subjected to a second blocking step and a finishing forging step, after which they were solution heat-treated at 940° F., quenched in water and precipitation hardened at 340° F. Upon inspection, the first group was found to be substantially free from ultrasonic indications and all pieces passed inspection standards while the second or untreated group contained numerous indications and only 50 percent of the forgings met acceptance standards.

Having thus described the invention, I claim:

1. A method for the production of substantially gas-free and void-free wrought aluminum articles comprising: exposing an aluminum article containing gas and voids to a vaporous fluoride to develop a film thereon that substantially prevents the accumulation of monatomic hydro-

gen at the surface thereof; heating said article at a temperature above 750° F. for a length of time sufficient to diffuse occluded gas into the atmosphere around said article; and thereafter working the metal of said article sufficiently to heal voids in 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 is a conventional undried industrial atmosphere.

4. A method for the production of substantially gas-free and void-free aluminum articles comprising: exposing an aluminum article containing gas and voids to a vaporous fluoride to develop a film thereon that substantially prevents the accumulation of monatomic hydrogen at the surface thereof; heating said article at a temperature above 850° F. for a time at least equal to 16 hours per inch of thickness to diffuse occluded gas into the atmosphere around said article; and thereafter working the metal of said article to heal voids in said article.

5. A method for the production of substantially gas-free and void-free wrought articles of an aluminum base alloy containing 0.1 to 15 percent magnesium comprising: exposing an aluminum-magnesium alloy article containing gas and voids to a vaporous fluoride to develop a fluoride film thereon; heating said article at a temperature above 750° F. for a length of time sufficient to diffuse occluded gas into the atmosphere around said article; and thereafter working the metal of said article sufficiently to heal voids in said article.

6. The method in accordance with claim 5 wherein said vaporous fluoride is boron trifluoride.

7. The method in accordance with claim 1 wherein said working is effected by forging of the metal article.

8. A method for the production of substantially gas-free and void-free wrought aluminum articles comprising: exposing an aluminum article containing gas and voids to a vaporous fluoride to develop a fluoride film thereon; heating said article at a temperature above 750° F. for a length of time sufficient to diffuse occluded gas into the atmosphere around said article, said atmosphere containing from 1.5 to 30 grains of water per cubic foot; and thereafter working the metal of said article sufficiently to heal voids in said article.

9. The method in accordance with claim 8 wherein said atmosphere is air.

10. A method for the production of substantially gas-free and void-free aluminum articles comprising: exposing an aluminum article containing gas and voids to boron trifluoride vapors to develop a film thereon; heating said article at a temperature above 750° F. in an air atmosphere containing 1.5 to 30 grains of water per cubic foot for a length of time sufficient to diffuse occluded gas into the said atmosphere; and thereafter working the metal of said article sufficiently to heal voids in said article.

No references cited.