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ALUMINUM DEGASSING SYSTEM

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This invention relates to the degassing of aluminum and aluminum base alloys. More particularly, the invention concerns a novel method for the fluxing and degassing of aluminum with mixtures of chlorine gas and carbon monoxide gas, or with mixtures of chlorine gas, carbon monoxide gas, and a diluent gas.

This is a continuation-in-part application relative to co-pending application Serial No. 747,368, filed July 9, 1958, now abandoned.

It has been common practice in the aluminum and aluminum alloys industry to pass chlorine through molten metal in order to remove dissolved gases, chiefly hydrogen, and further to free the metal from porosity and oxide inclusions, and other solid impurities. This process, also known as fluxing or degassing, generally employing chlorine gas in full strength or 100% concentration, is expensive in that it consumes large quantities of chlorine and also results in loss of aluminum as volatile aluminum chloride. It also causes unsatisfactory working conditions by reason of the corrosive and toxic gaseous effluents. In the prior art, proposals have been made at various times to save chlorine by carrying out the degassing with combinations of chlorine and a diluent, such as dry air or nitrogen (N_2), or by conducting the treatment in an atmosphere of dry air. It has also been proposed to utilize nitrogen gas for degasification of aluminum. In U.S. Patent 2,380,863, the use of either carbon dioxide or carbon monoxide is suggested for treatment of molten magnesium-base alloys prior to casting. However, in connection with aluminum, it has been generally thought that the use of carbon dioxide or carbon monoxide would be deleterious in that these gases in contact with molten aluminum would be reduced to free carbon, which in turn would react with the aluminum to form undesirable aluminum carbide, Al_4C_3. Hence in U.S. Patent 2,369,-213, the use of a treating mixture of chlorine and boron trichloride is proposed in order to bring about decarburization of the molten metal bath and the avoidance or destruction of undesirable metal carbides. Hence it was both surprising and unexpected to discover, in accordance with the present invention, that a marked improvement was brought about in the fluxing and degassing of aluminum and aluminum alloys by the use of a fluxing gas containing both chlorine and carbon monoxide.

The use of a fluxing mixture of chlorine gas and carbon monoxide gas, in accordance with this invention, accomplishes degasification of aluminum or aluminum base alloys to a far greater extent than is attainable by the use of either of these gases separately. Thus, as measured by the rise in the density of the metal in a standard vacuum gas test, the degasification of the aluminum or aluminum base alloy is completed in half the time required for degasification using 100% chlorine gas. Even those alloys known to be most recalcitrant to degasification yield to the new treatment in greatly shortened periods of time.

The carbon monoxide enhances the effect of the chlorine gas by its presence and hence is not acting merely as a diluent for the chlorine gas. In contrast thereto, a mixture of chlorine and a true diluent gas, such as nitrogen, shows fluxing characteristics approximately the same as those exhibited by 100% chlorine, even where the amount of nitrogen present is as high as 95%.

In accordance with this invention, molten aluminum or aluminum base alloys are treated by bubbling through the molten metal either (*a*) a gaseous mixture of chlorine and carbon monoxide, or (*b*) a gaseous mixture of chlorine, carbon monoxide, and a diluent gas. The use of a diluent gas is a matter of choice or convenience and does not materially influence the results.

In accordance with another aspect of this invention, molten aluminum or aluminum base alloys are treated by means of chlorine gas, or of chlorine gas in admixture with a diluent gas, in the presence of a material capable of liberating carbon monoxide under the conditions of treatment. Thus, there may be used in combination with the chlorine gas, solid fluxes which are capable of releasing carbon monoxide in contact with the hot molten aluminum bath. Preferably, however, the carbon monoxide in this aspect of the invention is supplied by a material which is capable of generating or liberating it under the fluxing conditions. Thus, if carbon dioxide and chlorine, or a mixture of carbon dioxide, chlorine and a diluent gas or gases, is supplied to the molten aluminum through a carbon (graphite) tube at the high temperature in question, the carbon dioxide is at least partially reduced to carbon monoxide, under contact with the hot carbon of the tube.

When using pure carbon dioxide gas in combination with chlorine, or with chlorine and a diluent gas, a slight excess percentage by volume is supplied in order to provide the desired concentration of carbon monoxide to be obtained by carbon reduction in the graphite tube.

It might be supposed that under these conditions there would be a tendency toward formation of toxic carbonyl chloride or phosgene gas, but at the elevated temperatures which prevail, this product is either not formed, or if temporarily formed, is immediately decomposed, since tests at the tube exit have failed to indicate its presence in the effluent gases.

When it is desired to utilize a readily available source of carbon dioxide (and some monoxide), it has also been found, in accordance with another embodiment of the invention, that the chlorine may be supplied to the molten aluminum admixed with a suitable volume of an exothermic gas such as produced by General Electric Company's "Exogas" generator. Said gas is used to furnish a protective atmosphere for heat treating in the steel and aluminum industries, and is made by burning natural gas or hydrocarbons such as methane, propane, butane, liquefied petroleum gas, and the like with air in presence of a nickel catalyst. "Exogas" has the approximate composition 11.8% CO_2, 1.8% CO, 0.2% O_2, traces of hydrogen and methane, balance nitrogen, and a dewpoint of approximately +65° F., thus providing a source of both carbon dioxide (and carbon monoxide) and nitrogen. In accordance with this invention, it has been found that favorable fluxing results are obtainable with a mixture of approximately 10% chlorine and 90% of "Exogas" by volume, introduced through a hot graphite tube.

In accordance with one aspect of this invention, molten aluminum or aluminum base alloys are treated by passing through the molten material a gaseous mixture consisting essentially of chlorine and carbon monoxide. The ratio of the two gases is subject to a wide degree of variation, and good results can be obtained with mixtures containing as little as 5% of chlorine and 95% of carbon monoxide, by volume. Conversely, there can be used a mixture containing, for example, 95% chlorine and 5% of carbon monoxide. Preferably, however, the ratio of chlorine to carbon monoxide will range from about 2:1 to about 1:4, i.e. from a mixture containing about 67% chlorine and about 33% carbon monoxide, to a mixture containing about 20% chlorine and about 80% carbon monoxide. The treatment temperature of the metal is between its melting and vaporization points, and ordinarily lies in the

range of about 1300° F. to about 1500° F. but this temperature is not critical. The treating mixture may be supplied to the molten metal through a carbon (graphite) or an iron fluxing tube. However, where a carbon fluxing tube is used, the appropriate mixture may be produced in situ by passing chlorine and carbon dioxide through the tube, the carbon dioxide being at least partially reduced to carbon monoxide in contact with the carbon of the tube. Alternatively, such a mixture of chlorine and carbon dioxide may itself also contain some carbon monoxide, the content of the latter being augmented by the carbon monoxide resulting from reduction of the carbon dioxide present.

In accordance with a second aspect of the invention, molten aluminum or aluminum base alloys are treated by passing through the molten metal a gaseous mixture of chlorine, carbon monoxide, and a diluent gas. The diluent gas may be, for example, nitrogen or air. As indicated previously, the use of a diluent gas is a matter of convenience or economy and does not materially affect the results. Within the mixture of chlorine, carbon monoxide, and diluent gas, the ratio of chlorine to carbon monoxide is again subject to wide variation, as is the proportion of chlorine gas in the mixture. The proportion of chlorine may range from about 5% to about 90% by volume. Advantageously, however, the concentration of chlorine in the mixture of chlorine, carbon monoxide and diluent gas, is maintained at between about 5% and about 15% by volume, and preferably at about 10% by volume. While a ratio of 10:1 of chlorine to carbon monoxide, i.e. about 0.5% carbon monoxide by volume will produce good results, the ratio of chlorine to carbon monoxide in the mixture preferably lies between about 2:1 and about 1:4. The proportion of volume of carbon monoxide will preferably, however, be about equal to that of chlorine. Thus, a preferred embodiment of the invention is a treating mixture consisting, by volume, essentially of 10% chlorine, 10% carbon monoxide, and 80% diluent gas, such as nitrogen or air. Here also the treating mixture may be supplied to the molten metal through a carbon (graphite) or iron tube. The treatment temperature also lies between the melting and vaporization temperatures of the metal, and generally between about 1300° F. and 1500° F., but this temperature is not critical. As mentioned previously, where a graphite tube is employed, there can be supplied a mixture of chlorine and carbon dioxide and a diluent gas, the carbon dioxide being reduced to carbon monoxide by the carbon of the tube. For this purpose, the mixture of chlorine and "Exogas" previously described is especially suitable.

The novel method of the present invention is applicable to pure aluminum and also to aluminum alloys. Among the commercially important aluminum alloys which have hitherto presented formidable obstacles to effective degassing when using pure chlorine, but which exhibit a faster degassing rate and higher final density when treated with the chlorine-carbon monoxide mixture of the present invention, may be mentioned No. 7075, an alloy containing about 2.1–2.9% magnesium, 1.2–2.0% copper, 5.1–6.1% zinc, 0.18–0.40% chromium, up to 0.50% silicon, 0.70% iron, 0.30% manganese, and 0.20% titanium, balance substantially aluminum; No. 2014, an alloy containing about 3.9–5.0% copper, 0.20–0.80% magnesium, 0.40–1.20% manganese, 0.50–1.20% silicon, up to 1.0% iron, 0.10% chromium, 0.25% zinc and 0.15% titanium, balance substantially aluminum; and No. 6063, an alloy containing about 0.20–0.60% silicon, 0.45–0.90% magnesium, up to 0.35% iron, 0.10% copper, 0.10% manganese, 0.10% chromium, 0.10% zinc, 0.10% titanium, balance substantially all aluminum. The process will generally be applicable prior to casting, but is not limited thereto since it may be used wherever aluminum is remelted.

No definite explanation is presently available for the unusual and unexpected improvement introduced by the combined chlorine and carbon monoxide treating procedure. While applicant does not wish to be bound by any particular theory, it is suggested that in the aluminum alloy to be degassed, hydrogen gas is adsorbed on colloidal particles of dispersed aluminum oxide. The action of the chlorine is believed to convert the aluminum content of the oxide particles to aluminum chloride, and the oxygen liberated thereby oxidizes the carbon monoxide to form carbon dioxide. The release of the hydrogen is noted by the increased density of the metal.

The rate of gas flow feed may be adjusted to any desired value, depending upon the type of treating apparatus employed, the melting temperature of the metal being fluxed, size of the feeding tube, and the like.

The fluxing process of this invention may be carried out in any suitable and conventional apparatus customarily used for this purpose, such as, for example, a melting furnace of the reverberatory or open hearth type fitted with one or more graphite or steel tubes for introducing the gaseous treating mixture. The chlorine, carbon monoxide, and other gases may be metered in from their respective supply cylinders in any desired mixture using a mixing valve, flow meters, and the like.

The progress of the treatment may be measured by a standard vacuum gas test, in accordance with which a sample of molten metal is placed in a chamber under a given degree of vacuum, e.g. 50 mm. mercury, and allowed to solidify, expanding gas bubbles. The sample is then weighed and its density (grams per cc.) measured in order to ascertain how closely it approaches the theoretical density of the alloy or pure metal. The density may be plotted against the fluxing time, the slope of the resulting curve furnishing an indication of speed of the degassing of the metal.

The process of the present invention results not only in greatly accelerated degassing time and in higher final density of the treated metal, but in more complete degassing, a diminished tendency of the metal to regas, and in a reduction of the toxicity problem in view of the greatly reduced concentrations of chlorine used in processing. Thus, in treating No. 7075 alloy, fluxing was found to be complete after only 15 to 20 minutes when using a mixture of 10% chlorine and 90% of "Exogas" (introduced through a graphite tube), as compared with 25 to 40 minutes fluxing time when using 100% chlorine gas, a saving in time of approximately 100%.

The following examples and tables serve to illustrate the favorable results obtainable with the present invention, but they are not to be regarded as limiting.

EXAMPLE 1

A laboratory, gas-fired open hearth furnace was charged with 400 pounds of No. 7075 alloy, and temperature of the bath was maintained at between 1300° and 1350° F. Fluxing gas was fed into the molten metal through a graphite tube 2" O.D., ½" I.D., and 6 feet long, entering the melt at approximately a 45° angle, to a depth of approximately 12 inches. The treating gas was passed in at a rate of 5 cubic feet per hour, and duplicate samples taken for density tests at 10 minute intervals until visual observation indicated that degasification was complete or until no further substantial increase in density of the metal was noted. Comparative results (obtained using 100% chlorine, and 10% chlorine–90% "Exogas") are as follows.

(*a*) 100% chlorine:

Indicated density, g./cc.—	Time (mins.)
2.2	[1] 0
2.35	10
2.50	20
2.65	30
2.70	40

[1] Start.

Hence 40 minutes were required to achieve an indicated

density of 2.70, which means a good true density close to the theoretical density of 2.80 of this alloy.

(*b*) 10% chlorine–90% "Exogas" (compressed "Exogas" at 10 p.s.i.g. back pressure):

Indicated density, g./cc.—	Time (mins.)
2.2	[1] 0
2.46	10
2.71	20

[1] Start.

Hence a good density was achieved in only 20 minutes.

EXAMPLE 2

Tests were carried out as in Example 1, but using an iron tube, 2" O.D. 1¾" I.D., and 6 feet long. With 100% chlorine, the results were approximately the same. Using a mixture of 80% nitrogen, 10% carbon monoxide, and 10% chlorine, supplied at a rate of 5 cubic feet per hour, from separate cylinders, the following results were obtained:

Indicated density, g./cc.—	Time (mins.)
2.2	0
2.64	10
2.70	13

Thus, with the optimum Cl_2–CO–N_2 mixture, a good density was achieved in only 13 minutes, as compared with 40 minutes using pure chlorine alone.

Substantially similar results were achieved using mixtures consisting essentially of chlorine and carbon monoxide, and containing 67% chlorine and 33% carbon monoxide, 50% chlorine and 50% carbon monoxide, and 20% chlorine and 80% carbon monoxide, respectively, all by volume.

EXAMPLE 3

Two 400 pound lots of No. 2014 alloy were treated, respectively, with 100% chlorine and with a mixture of 10% chlorine and 90% air at a flow rate of 5 cubic feet per hour through a graphite tube.

(*a*) 100% chlorine:

Indicated density, g./cc.—	Time (mins.)
2.2	0
2.31	10
2.42	20
2.53	30
2.64	40
2.70	50

(*b*) 10% Cl_2 and 90% air:

Indicated density, g./cc.—	Time (mins.)
2.2	0
2.45	10
2.65	20
2.70	30

With this difficultly degassable alloy, a good density was achieved in 30 minutes using a gaseous mixture and technique according to the invention, as compared with 50 minutes using pure chlorine.

EXAMPLE 4

Using a 400 pound batch of No. 6063 alloy, and a graphite tube as in Example 1, the following comparative results were obtained.

(*a*) 100% chlorine:

Indicated density, g./cc.—	Time (mins.)
2.2	0
2.26	10
2.32	20
2.37	30
2.42	40
2.45	50

(*b*) 10% Cl_2 and 90% air:

Indicated density, g./cc.—	Time (mins.)
2.2	0
2.3	10
2.4	20
2.5	30
2.6	40

Even on prolonged fluxing, this alloy could not be brought to good density, but with the technique according to the invention, a high density of 2.6 was attained in a reasonable time.

The average ratio of density to flux time, i.e. the slope of the curve wherein density is plotted against time, is a measure of the efficiency of the process. The following tables show the comparative effects of using iron and graphite tubes for treatment with various gas compositions:

Table 1

IRON TUBE [1]

Test No.	Metal treated	Gas feed composition	Average ratio of density: flux time
1	7075	10% chlorine, 90% ambient air	1.38
2	7075	10% chlorine, 10% carbon monoxide, 80% nitrogen.	4.4
3	7075	10% chlorine, 90% carbon dioxide	1.4
4	7075	10% chlorine, 20% carbon monoxide, 70% nitrogen.	2.0

[1] 2" O.D., 1¾" I.D., 6 ft. long, temperature 1350° F., 400 pound batch. Rate of gas feed 5 c.f.h.

It will readily be apparent from Table 1 that in the fluxing of No. 7075 alloy, the preferred composition of the present invention, namely 10% Cl_2, 10% CO, and 80% N_2 greatly exceeded in efficiency any of the other compositions.

Table 2

GRAPHITE TUBE [1]

Test No.	Metal treated	Gas feed composition	Average ratio of density: flux time
1	7075	100% chlorine	1.48
2	7075	5% chlorine, 95% nitrogen	1.40
3	7075	80% chlorine, 20% nitrogen	1.33
4	7075	60% chlorine, 40% nitrogen	1.38
5	7075	10% chlorine, 90% nitrogen	1.63
6	7075	100% nitrogen	0.75
7	7075	10% chlorine, 5% carbon monoxide, 85% nitrogen.	2.50
8	7075	10% chlorine, 90% Exogas—10% Co_2	2.55
9	7075	10% chlorine, 90% ambient air	2.55
10	2014	do	2.45
11	2014	100% chlorine	1.10
12	6063	do	0.55
13	6063	10% chlorine, 90% ambient air	1.00

[1] 2" O.D., ½" I.D., 6 ft. long, 400 pound batch, temperature 1350° F., rate of gas feed 5 c.f.h.

What is claimed is:

1. Process for degassing aluminum and aluminum base alloys which comprises passing through the molten metal a gaseous mixture consisting essentially of chlorine and carbon monoxide, the proportion of chlorine being between about 5% and about 90% by volume, the proportion of carbon monoxide being at least about 0.5% by volume.

2. Process for degassing aluminum and aluminum base alloys which comprises passing through the molten metal in contact with carbon a gaseous mixture consisting essentially of chlorine and carbon dioxide, the carbon dioxide being at least partially reduced to carbon monoxide by contact with the carbon.

3. Process for degassing aluminum and aluminum base alloys which comprises passing through the molten metal a gaseous mixture consisting essentially of chlorine, carbon monoxide, and a diluent gas, the proportion of chlo-

rine being between about 5% and about 90% by volume, the volume ratio of chlorine to carbon monoxide ranging from about 2:1 to about 1:4, the balance of the mixture being diluent gas.

4. Process for degassing aluminum and aluminum base alloys which comprises passing through the molten metal in contact with carbon a gaseous mixture consisting essentially of chlorine, carbon dioxide, and a diluent gas, the carbon dioxide being at least partially reduced to carbon monoxide by contact with the carbon.

5. Process for degassing aluminum and aluminum base alloys which comprises passing through the molten metal a gaseous mixture consisting essentially of approximately 10% chlorine, 10% carbon monoxide, and 80% nitrogen, by volume.

6. Process of degassing aluminum and aluminum base alloys which comprises passing through the molten metal in contact with carbon a gaseous mixture consisting essentially of approximately 10% chlorine, 10% carbon dioxide, and 80% nitrogen, by volume, the carbon dioxide being at least partially reduced to carbon monoxide by contact with the carbon.

7. Process of degassing aluminum and aluminum base alloys which comprises passing through the molten metal in contact with carbon a gaseous mixture consisting essentially of approximately 10% by volume of chlorine and 90% by volume of a mixture of about 10–12% carbon dioxide, 1.8–2.0% carbon monoxide, balance nitrogen, by volume, the carbon dioxide being at least

partially reduced to carbon monoxide by contact with the carbon.

8. A composition for degassing of molten aluminum and aluminum base alloys consisting essentially of approximately 10% chlorine, 10% carbon monoxide, and 80% nitrogen, by volume.

9. In a process for degassing aluminum and aluminum base alloys by passing through the molten metal a gaseous mixture containing chlorine as the principal active ingredient, the improvement which comprises concurrently introducing carbon monoxide into the molten metal.

10. A composition for degassing of molten aluminum and aluminum base alloys consisting essentially of chlorine, carbon monoxide, and a diluent gas, the proportion of chlorine being between about 5% and about 90% by volume, the proportion of carbon monoxide being at least about 0.5% by volume, and the volume ratio of chlorine to carbon monoxide ranging from about 2:1 to about 1:4, the balance of the mixture being diluent gas.

References Cited in the file of this patent

UNITED STATES PATENTS

2,060,133	Summey	Nov. 10, 1936
2,160,812	Alden et al.	June 6, 1939
2,184,885	Muskat et al.	Dec. 26, 1939
2,840,463	Stroup et al.	June 24, 1958

OTHER REFERENCES

The Journal of the Institute of Metals, vol. XLIX, 1932, No. 2, pages 301–315.