ON THE ACTION OF CHLORIDE FLUXES ON OXIDES CONTAINED IN ALUMINIUM.

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Introduction. The usual trouble experienced with aluminium ingot is the contamination or the formation of oxides. Hanson and Slater⁽¹⁾ attributed the chief cause of the formation of pin-holes in aluminium cast to the action of steam, and it is well known that in corroded parts of aluminium ware oxides are always detected in their centers. This being so, the injurious effect of oxides contained in aluminium is generally even more serious than that of other metals contained as impurities. The oxides in aluminium can not be removed by reducing agents such as carbon or hydrogen which are usually effective in other heavy metals. In the case of aluminium, however, it can only be cleaned or deoxidised by means of fluxes, but the fundamental chemical reactions underlying this action have never been fully elucidated so far.

I found that all the chloride fluxes have a decided cleaning power although in varying degrees, and that this deoxidising action is due chiefly to the chlorine gas liberated from these fluxes in contact with aluminium. Based on this knowledge, I made a systematic study of the action of chlorine gas and also of nitrogen gas on aluminium melt and was able to throw some light on the mechanism of cleaning.

Chloride Fluxing. As chloride fluxes the following chlorides were employed in my experiments: sodium chloride, potassium chloride, ammonium chloride, lithium chloride, calcium chloride, magnesium chloride, barium chloride, nickel chloride, manganese chloride, zinc chloride, aluminium chloride, ferric chloride, cupric chloride, stannous chloride, silicon tetrachloride, titanium tetrachloride, and carbon tetrachloride.

The aluminium ingot, 250 grams for each experiment, was melted at 700°C. in a graphite crucible, and each of the above fluxes in varying quantities packed in thin aluminium plate, was thrown into the melt kept at about 700°C. and pushed down to the bottom of the crucible by means of an iron utensil so that the deoxidising action was as complete as possible. Liquid

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chlorides were injected to the bottom part of this melt through an iron tube and well agitated.

The molten aluminium acted upon by the fluxes was then cast. The specimen casts so obtained were then subjected to analysis and to metallographic examination.

It is certain, however, that all these chloride fluxes have more or less deoxidising power depending on the kind and quantity used. Moreover, the general effect appears about the same regardless of the kind of metals of the chlorides. The conceivable reactions which may occur between these chlorides and aluminium are discussed below.

Firstly, if the number of chloride molecules which decompose without entering into reaction with aluminium, either by heat, or by catalytic action of aluminium, or by some other causes, is taken as x, then

$$x\mathrm{M}_a\mathrm{Cl}_b = ax\mathrm{M} + bx\mathrm{Cl} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1).$$

where M denotes metal.

Secondly, if the number of chloride molecules which decompose and give off chlorine that combines with aluminium is taken as y, then

$$y\mathrm{M}_a\mathrm{Cl}_b + c\mathrm{Al} = c\mathrm{AlCl}_3 + ay\mathrm{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

where $by = 3c$, hence $c = by/3$.

Lastly, if the number of chloride molecules which remain as such or go out of the sphere of reaction by sublimation or volatilisation, is taken as z, then

$$z\mathrm{M}_a\mathrm{Cl}_b = z\mathrm{M}_a\mathrm{Cl}_b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3).$$

Although it is conceivable that a certain portion of the chloride forms double salts with aluminium or aluminate, such complex cases are not included in the formula (3) for the sake of simplicity. This omission, however, does not interfere much with the main discussion, for, as has been confirmed by experiments, no chloride remains in the cooled cast of aluminium.

From the above three equations we obtain

$$(x+y+z)\mathrm{M}_a\mathrm{Cl}_b + (by/3)\mathrm{Al} = (by/3)\mathrm{AlCl}_3 + (ax+by)\mathrm{M} + bx\mathrm{Cl} + z\mathrm{M}_a\mathrm{Cl}_b \quad . \quad (4).$$

If there is no chloride that has not undergone decomposition, or in the case $z = 0$,

$$(x+y)\mathrm{M}_a\mathrm{Cl}_b+(by/3)\mathrm{Al} = (by/3)\mathrm{AlCl}_3+(ax+by)\mathrm{M}+bx\mathrm{Cl} \;\ldots\ldots\ldots\ldots\; (5).$$

Therefore, if we determine, after the treatment with a chloride, the amounts of M and Cl remaining in the aluminium and that of evolved chlorine, we can conjecture the type of the reactions which actually took place during fluxing.

For this purpose, the amount of chlorine liberated from the chloride thrown into aluminium was first determined, but it was soon discovered that the results obtained were not entirely reliable on account of several factors which made the determination very troublesome. Under the circumstances, the amount of metal remaining in the aluminium specimen was determined on one hand, and on the other hand the amount of chlorine liberated by the decomposition of the chloride alone in a heated tube at 800°C. was estimated. From the combined results of these determinations, the degree of decomposition of the chloride may be more accurately estimated.

A fixed amount of each of the above-mentioned chlorides was thrown into the molten aluminium in a graphite crucibles, and the chlorine gas evolved was absorbed by normal solution of silver nitrate, the amount of chlorine absorbed being determined by titrating the excess of silver nitrate with normal sodium chloride solution.

It must be mentioned that in order to obtain reliable figures in this experiment it is necessary to repeat the experiment at least 6 times—sometimes as often as 9 times—as it is exceedingly difficult to carry out the experiments under the same conditions exactly.

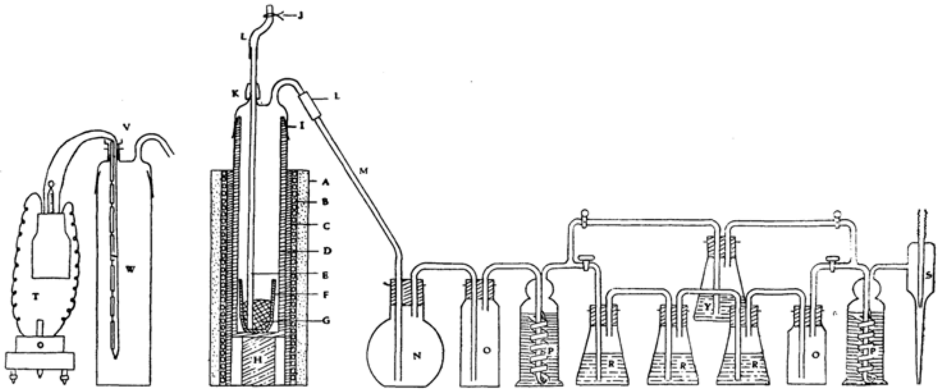


Fig. 1.

The arrangement of the apparatus for the experiment is shown in Fig. 1. A tall refractory cylinder with a closed bottom (D) is placed inside an electric furnace (ABC) supported on a block (H) and the open end of the cylinder is covered tightly with a glass cap (I) provided with a hole and a branch pipe. The aluminium specimen (G) is melted in a graphite crucible (F) placed on the bottom of the refractory cylinder, and an iron pipe (E) passing through a hard rubber tubing (K), is inserted into the molten aluminium. A thick rubber tube (L) is attached to the top of the iron pipe and is provided with a regulating cock (J). The branch pipe of the glass cap is connected with a cooling tube protruding into a dust-catcher (N), which is followed by an empty bottle (O), a gas drying bottle (P) filled with concentrated sulphuric acid, bottles (R, R, R) containing normal silver nitrate solution, another empty bottle (O), and a washing bottle of sulphuric acid (P) connected with a filter pump (S). An extra bottle (Y) containing a known quantity of normal silver nitrate solution serves for determining the end point of the reaction by sucking a part of the gas through it toward the end of reaction. If no turbidity occurs in this bottle the reaction may be considered as finished. In the case when the degree of decomposition of a chloride alone is to be examined by putting it in a hot place heated at 800°C., a cylinder (W) instead of (D) is used in which a thermo-couple is placed, the other parts being the same as the above-mentioned arrangement.

A fixed amount of a chloride was thrown into the aluminium melt through the iron pipe (E) and the suction pump (S) was set to work, adjusting at the same time the cock (J) so that the absorption of the chlorine would be complete.

A great deal of attention is required for control of suction according to the nature of the chloride—whether it is volatile or fusible. Even volatile chlorides seldom reach as far as bottle (O) or (P) on strong suction, but are generally deposited in the cooling tube (M) and are mostly caught in the bottle (N). Three bottles of silver nitrate solution were found to be sufficient on actual experiment. No accident whatever occurred even in the case of liquid chloride. The results of experiments are given in Table 1.

From these results it will be noticed that the various chlorides differ in their decomposition rates. The following chlorides were found to give off a comparatively large quantity of chlorine: NH_4Cl, $LiCl$, $MgCl_2$, $ZnCl_2$, $MnCl_2$, $AlCl_3$, $FeCl_3$, $CuCl_2$, $SiCl_4$, and $TiCl_4$. It is interesting to note that the decomposition of $LiCl$ and $FeCl_3$ is very much accelerated in the presence of aluminium. The following chlorides, on the other hand, suffer decomposition to a much less extent: $NaCl$, KCl, $CaCl_2$, $BaCl_2$, $NiCl_2$, $SnCl_2$, and CCl_4, of which $NaCl$ alone is enhanced in its decomposition rate when it is in contact with molten aluminium.

Table 1.

Chloride		NaCl	KCl	NH_4Cl	LiCl	$CaCl_2$	$MgCl_2$	$ZnCl_2$	$BaCl_2$	$NiCl_2$	$MnCl_2$	$AlCl_3$	$FeCl_3$	$CuCl_2$	$SnCl_2$	$SiCl_4$	$TiCl_4$	CCl_4
Quantity of sample taken (g.)		5	5	5	5	5	5	5	5	5	5	5	5	5	5	10 (6.56 c.c.)	10 (5.69 c.c.)	10 (6.13 c.c.)
Quantity of Cl } in the Quantity of M } sample (g.)		3.033 1.967	2.388 2.621	3.316 1.684	4.181 0.819	3.150 1.850	3.725 1.275	2.686 2.314	1.455 3.545	2.737 2.263	2.878 2.122	3.985 1.015	3.279 1.721	2.629 2.371	1.825 3.175	9.45 0.54	7.498 2.51	9.21 0.79
Analysis	Quantity of Cl evolved (g.) Number of experiments	0.7551 9	0.2282 7	1.0250 6	2.8351 6	0.0825 6	1.5553 6	1.178 6	0.0505 6	0.3703 6	1.0402 6	2.0204 6	1.0950 6	1.0404 6	0.4152 6	4.5704 6	3.5803 7	0.1203 6
	Quantity of M (g.) Number of experiments	0.4547 3	0.5392 3	nil. 2	0.4863 5	trace 3	0.5559 3	0.1240 4	nil. 3	0.4028 3	0.1033 3		0.5092 3	0.8962 4	0.8382 3	0.2360 3	0.1333 3	trace 2
Evolution rate of Cl (%)		15.1	5.8	20.5	56.7	1.7	31.1	23.6	1.0	7.4	20.8	40.4	21.9	20.8	8.3	45.7	35.8	1.2
Decomposition rate of Cl (%)		24.5	12.1	30.9	67.8	6 0	41.8	43.5	3.1	13.7	36.1	50.6	33.4	39.5	22.8	48.7	47.8	1.3
Decomposition rate of M (%)		28.2	20.4		59.3		43.6	53.5		17.8	49.4		46.5	37.8	26.4	43.7	53.0	
When the sample was thrown into an empty cylinder heated at 800°C.																		
Quantity of Cl evolved (g.) Number of experiments		0.3506 3	0.3225 5	1.0023 3	2.1052 5	0.8658 4	1.9401 3	1.4053 3	trace 3	0.5962 3	1.2448 3	2.9558 5	0.3153 5	1.6002 5	0.5303 3	8.3490 3	5.5244 3	0.0363 4
Evolution rate of Cl (%)		7.0	6.5	20.0	42.1	17.3	38.1	28.8	trace	19.9	24.9	59.1	6.3	21.2	10.6	83.5	55.2	0.4
Decomposition rate of Cl (%)		11.2	13.5	30.2	50.4	27.5	52.1	52.3		21.7	43.3	74.2	9.6	60.8	29.6	88.3	73.7	0.4

Decomposition seems to be accelerated by aluminium.
Considerable evolution of chlorine is noticeable. Such a chloride may be used as flux.
Remarkable evolution of chlorine is noted.
Very little evolution of chlorine. Such a chloride is unsuitable for flux.

Quantity of M (metal) = % of metal remaining in aluminium after reaction ÷ 100 × Original quantity of aluminium. (It is assumed that the slag contained the same percentage of metal.)
Evolution rate of Cl (chlorine) (%) = Quantity of chlorine evolved ÷ Total weight of sample × 100.
Decomposition rate of Cl (%) = Quantity of chlorine evolved ÷ Total chlorine content in sample × 100.
Decomposition of M (%) = Quantity of metal estimated ÷ Total metal content in sample × 100.

Table 2. Analysis of the Original and Cleaned Aluminium Specimens.
(250 grams aluminium kept at 750C°. for 5–10 minutes
after the flux is added.)

(A) Cleaning with Zinc Chloride.

Mark of sample	$ZnCl_2$ added (%)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Zn mean (%)	Zn lost* (%)
0	Original Al ingot	1.010 1.672 1.918 2.589 2.213 3.356	0.73	0.36	0.127	
Z8	8	0.435 0.461 0.714 0.724 0.767	0.76	0.21	3.71	0.53
Z7	5	0.582 0.459 0.468 0.403 0.802	0.75	0.26	2.20	0.16
Z6	3	0.863 0.978 0.854 1.002 1.008	0.75	0.18	1.34	0.13
Z5	2	1.063 0.975 1.065 1.927 0.726	0.77	0.21	0.92	0.10
Z4	1	0.828 0.769 0.584 0.813 0.848	0.71	0.25	0.51	0.07
Z3	0.7	0.844 0.939 0.904 0.794 0.703	0.72	0.24	0.4005	0.005
Z2	0.5	0.728 0.659 0.808 0.798 0.798	0.71	0.26	0.294	0.023
Z1	0.3	0.988 0.898 0.924 1.078 0.918	0.69	0.23	0.178	0.050

*Zn in aluminium ingot + Zn in $ZnCl_2$ added —Zn in cleaned aluminium.

(B) Cleaning with Titanium Chloride.

Mark of sample	$TiCl_4$ added (g.)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Ti mean (%)
T4	10	1.231 1.751 0.945 0.932	0.89	0.37	0.45
T3	5	1.722 2.430 0.752	0.80	0.34	0.26
T2	3	1.636 1.218 0.513 1.556	0.78	0.30	0.14
T1	1	2.165 1.020 2.051 1.644	0.73	0.36	0.06

Taking the rate of chlorine evolution into consideration the following chlorides may be recommended as suitable fluxes for the evolution of chlorine: LiCl, $AlCl_3$, $FeCl_3$, $SiCl_4$, and $TiCl_4$.

Now returning to the subject of the cleaning or deoxidising action of the chloride, it can be supposed that this is attributable to the action of either the chloride, i. e. M_aCl_b itself, or the products of decomposition, i.e. M or Cl, or $AlCl_3$ newly formed.

For example in the case of zinc chloride used as a flux, it is not likely that $ZnCl_2$ itself or $AlCl_3$ formed will reduce Al_2O_3. Besides, in the cleaned aluminium, chlorine is not detected. It is also not expected that the metallic zinc would have a deoxidising action on aluminium. Chlorine, on the other hand, is entirely non-reactive with the oxygen in aluminium, and yet the fact that cleaning has been effected is evident from the analytical results recorded in Table 2 (A). Similarly, titanium tetrachloride has also a cleaning power as shown in Table 2 (B).

Here again, the cleaning action can not be ascribed to any chemical reaction in connection with $TiCl_4$ and aluminium. It is interesting to note that the cleaning action is not necessarily proportional to the amount of the flux added, and that in the case of zinc chloride, about 0.7% of the flux gives the maximum efficiency or the condition approaches the case of equation (5) in which no chloride remains undecomposed. This percentage of flux for the maximum efficiency, however, varies with the nature of chlorides, the quality of the aluminium, and the amount of the melt.

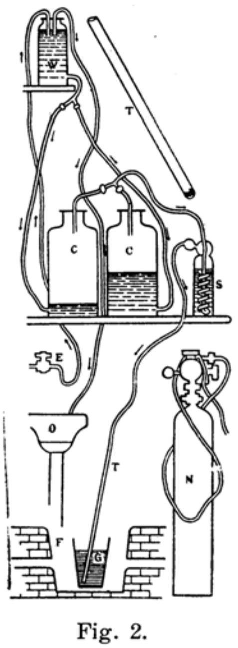


Fig. 2.

Based on the results of the above experiments, that all the chlorides show more or less a similar cleaning effect, the present author was led to think that the chlorine gas set free from the chloride may perhaps be responsible, directly or indirectly, for this deoxidising action. He, therefore, conducted experiments by using chlorine gas alone in an apparatus as shown in Fig. 2.

Chlorine gas, prepared from hydrochloric acid and potassium permanganate, is stored in bottles (C, C). By means of a water flow from a reservoir (W), whose water level is kept constant by an overflow device, the chlorine gas, after being dried over sulphuric acid (S), is bubbled, at a constant rate through an iron pipe (T) having many small holes at one end, into the molten aluminium in a graphite crucible (G). N in the figure is a nitrogen bomb, and in case nitrogen gas is used instead of chlorine gas for comparison, this bomb is directly connected to the drying bottle (S).

The results of experiments, in which chlorine gas was passed into 250 grams of aluminium melt at 750°C. for varying durations are shown in Table 3.

Table 3. Analysis of Aluminium Treated with Chlorine Gas.
(250 g. Al treated at 750°C., settled for 5-10 min. after the gas passed.)

Mark of sample	Duration of passing of chlorine	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Mark of sample	Duration of passing of chlorine	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)
0	See Table 2 (A)				C5	1 min.	0.987 0.718 0.807 0.908 0.870	0.74	0.11
C1	10 sec.	1.235 1.261 1.088 1.062 0.918	0.65	0.11	C6	1.5 min.	0.707 0.897 0.953 0.938 0.784	0.80	0.11
C2	15 sec.	1.005 1.023 1.215 1.061 0.889	0.68	0.17	C7	2 min.	0.717 0.879 0.824 0.791 0.850	0.96	0.23
C3	20 sec.	1.173 0.708 1.016 0.898 1.036	0.73	0.25	C8	2.5 min.	0.736 0.795 0.838 0.848 0.760	0.89	0.19
C4	40 sec.	0.774 0.671 0.634 0.987 0.870	0.79	0.11					

As obvious from these results, the chlorine gas alone is decidedly effective for the cleaning action, and the Al_2O_3 content approaches the level of what may be called the "limit of dissolved oxygen" with the prolongation of the treatment. By this treatment, aluminium is attacked by chlorine and some portion is lost as aluminium chloride.

Table 4. Ignition Temperatures of Various Metals in Chlorine Gas. (Sample taken, 5 grams.)

Metal	Ignition temp. °C.	Extinction temp. °C.	Duration of burning. (min. per 5 g.)
Aluminium	130	270	10
Iron	215	315	8
Silicon	440	510	22
Copper	370	380	0.5
Zinc	535 (390*)	560	30

* White fume was observed, but no active ignition occurred at this temperature.

Table 4 shows the ignition temperatures of aluminium and other metals generally contained in aluminium as impurities in the atmosphere of chlorine, as determined by the author. The same table also shows the extinction temperatures and the duration of burning when 5 grams of each of the specimens were employed for the experiment. As all the metals, contained as impurities, have a higher ignition and extinction

Table 5. Analysis of Aluminium Treated with N_2 Gas. (250 g. Al treated at 750°C., and settled at the same temperature for 5–10 min. after the passing of the gas.)

Mark of sample	Duration of passing of nitrogen	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Mark of sample	Duration of passing of nitrogen	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)
0	See the Table 1.				N5	1.5 min.	0.823 0.624 0.775 0.598 0.971	0.50	0.14
N1	10 sec.	1.423 1.388 1.298 0.663 1.617	0.53	0.15	N6	2 min.	0.818 0.633 0.597 0.729 0.659	0.70	0.13
N2	20 sec.	0.938 0.808 0.908 1.834 1.157	0.53	0.14	N7	3 min.	0.838 0.904 0.623 0.728 0.673	0.65	0.13
N3	40 sec.	0.812 0.595 0.588 0.938	0.51	0.15	N8	4 min.	0.938 0.668 0.790 1.099 0.826	0.65	0.12
N4	1 min.	0.838 0.903 0.958 0.724 0.625	0.44	0.14	N9	5 min.	0.893 0.838 0.725 0.753 0.828	0.67	0.12

temperatures than pure aluminium, they are not materially reduced in quantity by the treatment with a chloride.

During this treatment, the formed chlorides, the oxides, and other occluded impurities accumulate on the top of the melt and go into the slag, which amount increases with the duration of the treatment. By analysis, the cleaned aluminium was found to contain almost no detectable chlorine. As has already been confirmed, chlorine gas has no deoxidising action. Hence, the only possible explanation regarding the cleaning effect by chlorine must be sought mainly in its action of mechanical removal of the oxide at the time of its ascension through the molten aluminium. It is also conceivable that the undecomposed chloride or the newly formed aluminium chloride aids the removal of the impurities at the time of their sublimation or volatilisation.

If the above reasoning be correct, any kind of gas, which has no tendency to remain in aluminium as chlorine, should act in the same way. In order to test this point, I tried in a similar way with nitrogen gas for comparison, which has been found almost non-reactive with aluminium. The results of experiments with nitrogen gas are given in Table 5, which shows clearly that the above reasoning is justified.

The cleaning effect of chlorine and nitrogen is shown diagrammatically in Fig. 3; this indicates clearly that similar, if not the same, results are obtained with these gases.

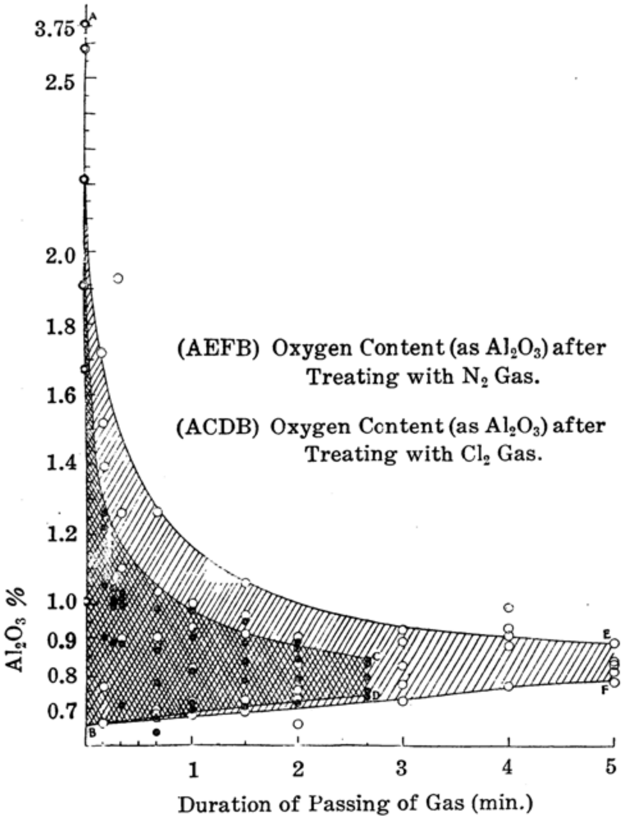
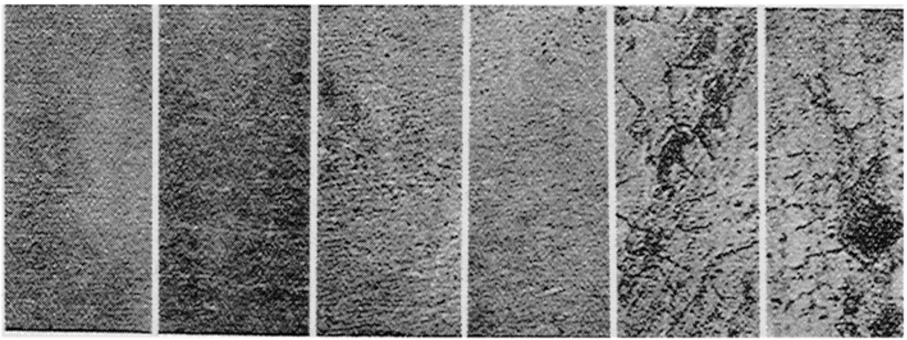
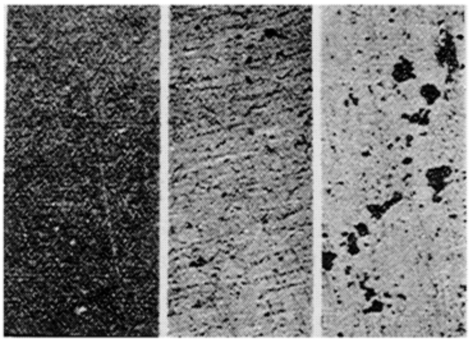


Fig. 3.

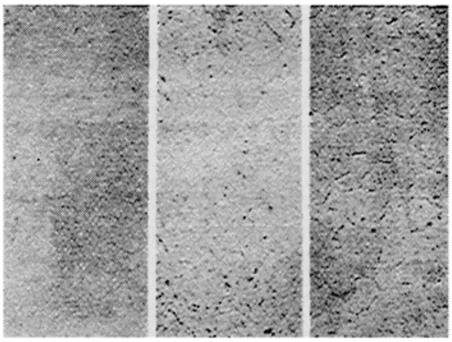
Original Aluminium Ingot



(Z 1) (Z 8)



(C 2)



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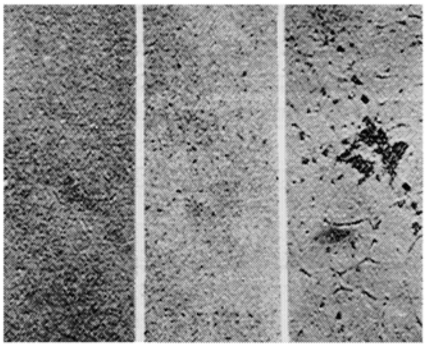
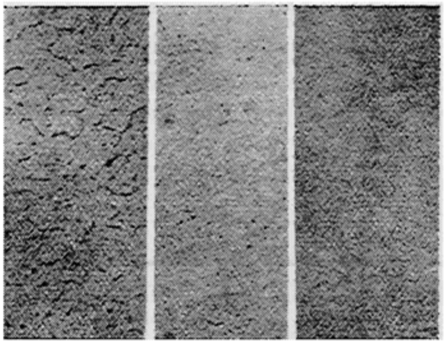
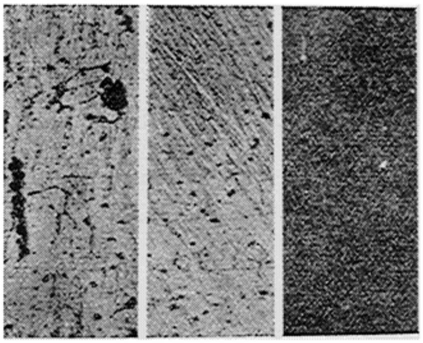
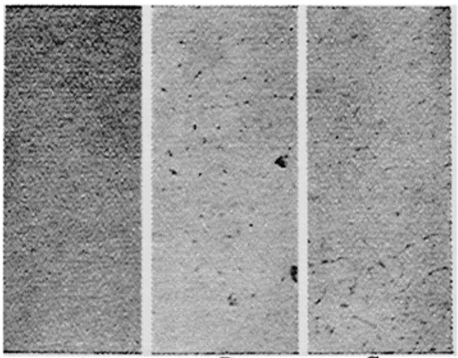


(N 1)



(N 9)





A : Macrograph ×7, B : Polished surface ×120, C : Surface etched with NaOH solution.

Fig. 4.

From the above experimental results, the author ventures to propose that any gas that is not likely to be occluded in aluminium or any compound which will liberate such a gas in molten aluminium would act as a cleaning agent. Its cleaning efficiency, however, depends on such properties as viscosity between the gas and the metal, specific gravity of the metal, etc. For a chloride flux, it is, therefore, advisable to select a compound which decomposes easily according to the equation (1) and the liberated metal, when alloyed with aluminium, does not harm the properties of the resulting aluminium.

Microscopical Examination of the Specimens. All the specimens obtained in the present investigation were microscopically examined. In Fig. 4 photographs of some representative specimens are shown.

Conclusion. When aluminium ingot is treated with chloride fluxes, the content of oxygen in the aluminium is decreased. The cleaning action of these chloride fluxes is mainly due to the chlorine gas liberated from the chlorides, which, when escaping from the aluminium melt, conveys and removes the oxide and other impurities contained in the aluminium melt. Any other gas, such as nitrogen, which is not likely to be combined or occluded by aluminium, has also the same cleaning power if used alone or in combination with other gases. When fluxes other than chlorides have to be employed for cleaning purpose, one should select such compounds which do not remain unchanged in the aluminium or as their decomposition products. Or if they remain, they should give no harmful effect to the aluminium. Compounds that give off a comparatively large quantity of harmless gas in aluminium are suitable for cleaning fluxes, and $LiCl$, $AlCl_3$, $TiCl_4$, and $SiCl_4$ are recommended for this reason.

The author might take this opportunity to say that cleaning by chlorine gas is actually carried out in several aluminium works in this country, and is giving satisfactory results.

(July 20th, 1934)