

ON THE MOVEMENTS OF ABSORBED GASES IN ALUMINIUM

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ABSORPTION of gases by aluminium is well known¹⁻³ and many workers⁴⁻⁶ have investigated into the problem of porosity in castings.

This paper deals chiefly with the effect of absorbed gases on the fluidity of molten aluminium and elucidates the relationship between fluidity and viscosity. It is shown that gases absorbed in molten aluminium profoundly affect both the fluidity and viscosity of the metal and that the melting rather than the casting atmosphere chiefly influenced its fluidity. The results obtained also indicate the significance of temperature control in the melting of aluminium.

Experimental procedure

A metal-mould having a straight flowing path and circular section (Fig. 1) was used for the measurement of the fluidity of the molten metal. This mould was in two parts, the contact surfaces of which were super-precision finished. The mould could be maintained at the temperature of testing by preheating it in a furnace.

The molten metal was poured from a No. 2 graphite crucible having a hole at the bottom, which could be closed with a graphite rod (Fig. 2). Molten metal maintained at a constant temperature was allowed to flow through the hole and the metal cast in the metal-mould. Using this method, the personal factor of error was eliminated.

Viscosity was measured in an apparatus shown diagrammatically in Fig. 3. "A" is a tubular Ni-Cr wound electric furnace in which a quartz tube "B" is inserted and a graphite Tammann tube "C" is held inside this tube. This tube "C" has a hole 1.5 mm dia. at the bottom stoppered with a 4 mm dia. quartz tube which also acted as a thermocouple sheath. The specimen under test was melted in this Tammann tube "C", and allowed to flow down to the receptacle "E" placed on the pan of a rough balance. The time needed for the flow of a pre-determined weight was

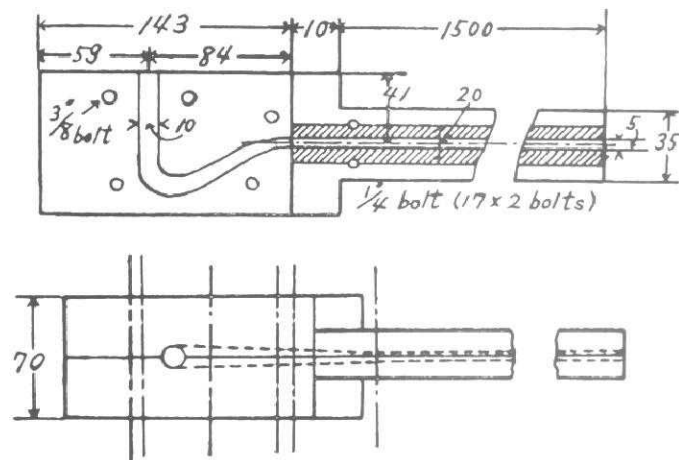


Fig. 1.
The metal mould for measuring fluidity.

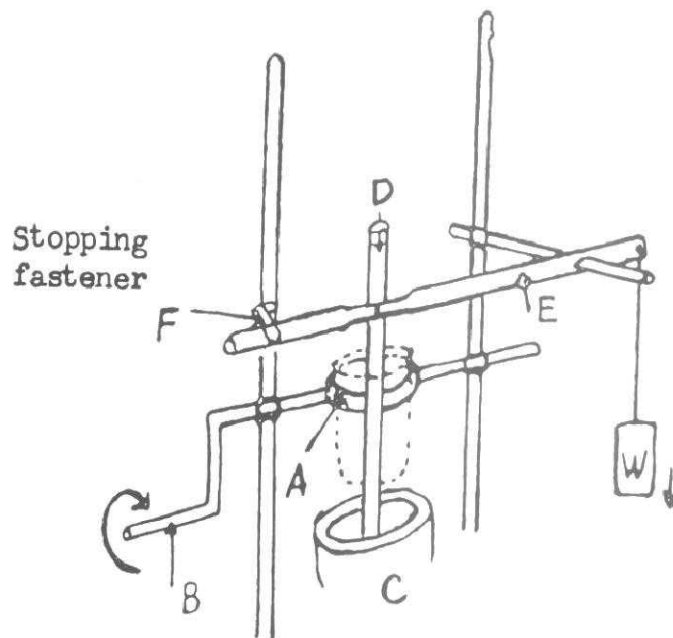


Fig. 2.
Pouring apparatus for casting.

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measured by a stop watch. Viscosity was calculated using Poiseuille's formula for viscosity :

$$\eta = \pi r^4 p t / 8 v l = t (\pi r^4 p / 8 v l)$$

Where r = radius of capillary tube,

p = statistical pressure for liquid.

l = length of capillary tube, and v = volume of liquid flowing in "t" seconds.

This general formula had to be calibrated for application in this study.

The apparatus used for the measurement of gas absorption is shown in Fig. 4 and is a modified Sieverts' apparatus⁷. "A" is a quartz tube, "B", a small crucible to keep the specimen inserted in "A", "C" is a thermocouple, "D" is a compact stopper, "E" is a Ni-Cr wound heating furnace, and "F" is the cooling system for the tube "A". "I" and "J" are absorbent KOH and CaCl₂ respectively. The gas supply from "M" and "G" is connected to the vacuum pump. Changes in gas volume are shown in the notched tube "H".

The aluminium was 99.998% purity, with 0.001% each of Si and Fe as impurities.

Observations and results

(a) *Effect of casting temperature and treatments of molten metal on fluidity of aluminium:* Fig. 5 shows the changes in the fluidity of aluminium melted in air and cast at different temperatures. Fluidity first increased with an increase of casting temperature up to about 900°C, above which there was a steady decrease. This decrease in the fluidity at higher temperatures in the aluminium melted in air is not due to any adverse effects of the Al₂O₃ (alumina) content of the molten metal. In fact the quantity of Al₂O₃ decreased with an increase in the casting temperature as shown in Table I. It may, however, be caused by the absorption of gases.

TABLE I
The contents of alumina.

Temperature	Al ₂ O ₃ %
900°C	0.0231
1050°C	0.0225

Hydrogen is known to be absorbed by molten aluminium⁸ which is released on solidification, resulting in pin-hole porosity. Various degassing treatments⁹⁻¹² have been suggested by earlier workers. A study was carried out of the various treatments detailed in Table II under experimental conditions given in Table III. The results obtained are shown in Fig. 6, which depicts the remarkable changes occurring in the flow properties of the metal by the various treatments. The casting temperature was kept fixed at 750°C while the maximum melting temperature was changed. The

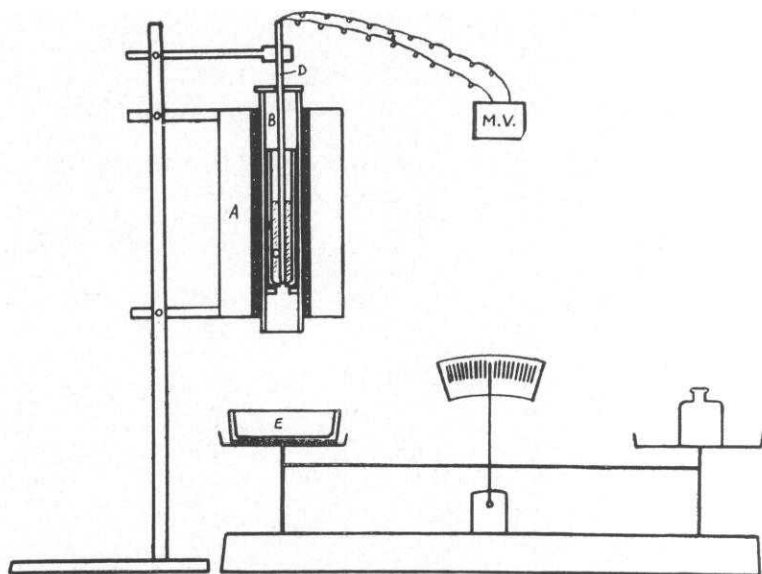


Fig. 3.
Apparatus for viscosity.

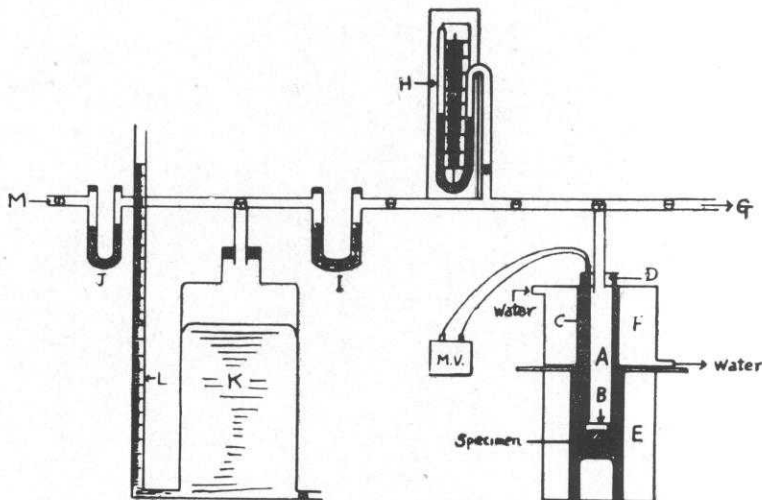


Fig. 4.
Apparatus for gas absorption.

change in the fluidity of the metal with change in the maximum melting temperature even when the casting temperature was kept fixed, is highlighted by this experiment, and shows the importance of controlling the maximum melting temperature rather than the casting temperature.

In the untreated metal, the fluidity fell steeply above 850°C but the rate of fall decreased with degassing until flux treatment prevented gas absorption, when fluidity continued to increase with an increase in melting temperature.

TABLE II
The conditions of degassing.

Name of treatment	Method of treatment
Not treated	Cast by no treated.
Slag off	Slag removed at max. melting temp. and removing by 50°C cooling till cast.
Agitation	After slag removed agitated by graphite bar and slag removed again and cast.
Remelt	After slag is removed, cooled till 665°C and kept 30 min. and heated to 750°C to cast rapidly.
Flux	Covered with NaCl (45%), KCl (55%).

TABLE III
The conditions of experiments.

Heating velocity (H.V.)	...	10°C/min.
Keeping time at max. melting temp. (K.T.)	...	0 min.
Cooling velocity to casting temp. (C.V.)	...	3°C/min.
Pouring temp. (P.T.)	...	800°C
Casting temp. (C.T.)	...	750°C
Mould temp. (M.T.)	...	50°C
Waiting temp. (W.T.)	...	300°C
Max. melting temp. (M.M.T.)	...	800°C
Max. melting temp. (M.M.T.)	...	850°C
Max. melting temp. (M.M.T.)	...	900°C
Max. melting temp. (M.M.T.)	...	950°C
Max. melting temp. (M.M.T.)	...	1000°C
Max. melting temp. (M.M.T.)	...	1050°C

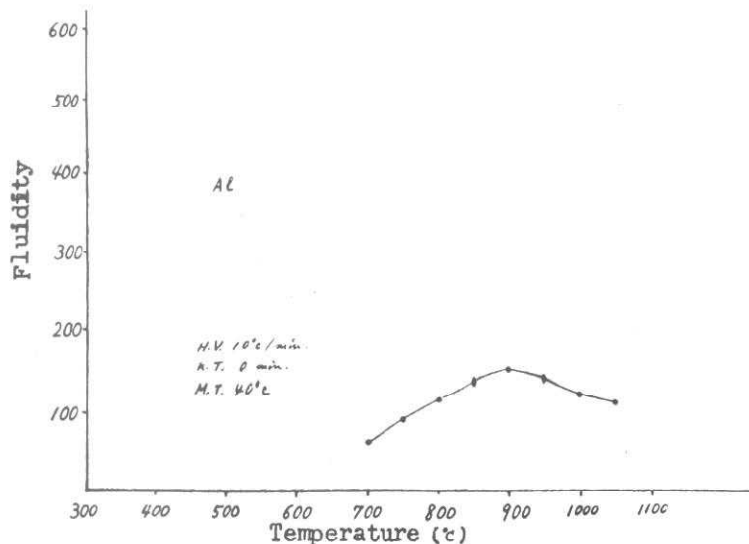


Fig. 5.
Graph showing the fluidity of aluminium.

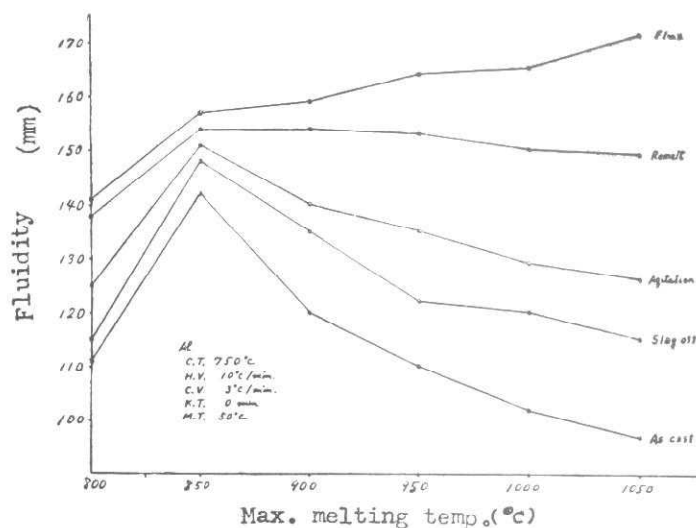


Fig. 6.
The fluidity of treated casting.

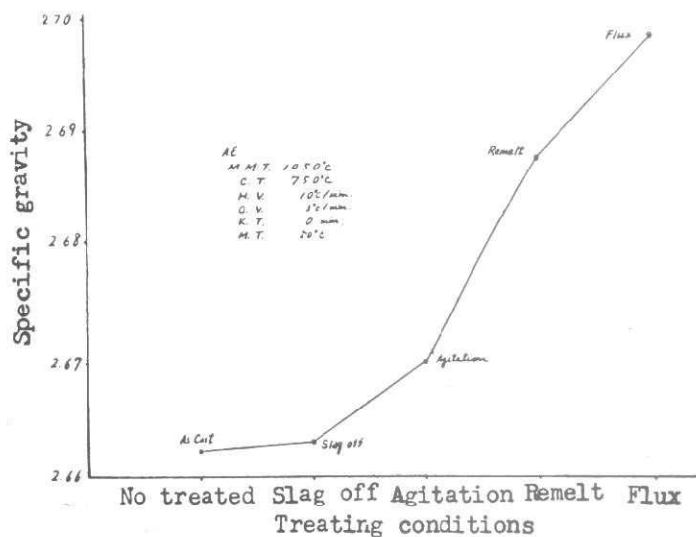


Fig. 7.
The measurement of specific gravity.

These results show that gases absorbed in the molten metal considerably affect its fluidity which is also dependent on the quantity of gases absorbed (the quantity being higher at higher melting temperature). They also indicate that the melting of aluminium at more than 200°C above its melting point would be a dangerous practice.

Figs. 7 and 8 show the specific gravity and gas contents of the untreated and differently degassed melts (calculated from specific gravity by recognising the existence of voids) respectively. The values of Fig. 8

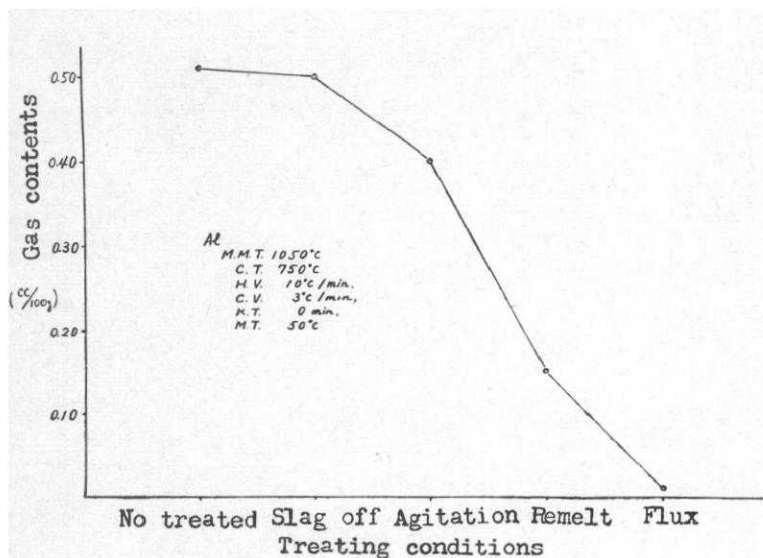


Fig. 8.

The calculation of gas content.

show very good agreement with those actually obtained by gas absorption measurements⁸. The microstructure of these melts is as in Fig. 9 which shows clearly the presence of voids and gives a qualitative support to the results obtained by specific gravity measurements.

(b) *Relation between fluidity and viscosity of molten aluminium*: No relationship between fluidity and viscosity of molten aluminium has previously been recognised¹³. The effect has been studied in air and neutral atmosphere (Fig. 10). It is seen that in the case of neutral atmosphere the viscosity fell with rise in temperature while in the air atmosphere, the viscosity fell initially but increased above a certain temperature (about 900°C in the present experiment).

It was seen in Fig. 6 that the fluidity of aluminium, melted under a suitable flux, increased with an increase in the maximum heating temperature. Fig. 11 shows the fluidity and viscosity of the metal heated to different temperatures. It is seen that the fluidity and viscosity are inversely related inasmuch as when one increases the other decreases.

This relationship however did not hold in the case of molten metal containing absorbed gases. In general, while the decrease in viscosity was caused merely by an increase in temperature, small amounts of absorbed gases, also, were found to have this effect. This can be explained if we consider that the structure of molten metal would change by the inclusion of gas atoms, and that this promotes hole formation and results in a decrease in viscosity. On the other hand, at high temperatures this inclusion of a large number of gas atoms would disturb the free movements of the metal atoms and thus increase the viscosity of the molten metal.

The author advocates the name "Disturbance Theory" for this explanation, which belongs to the realm of liquid structure in Physics.

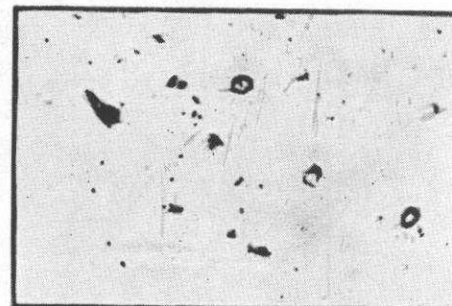
Treatment.
Flux (NaCl, KCl)



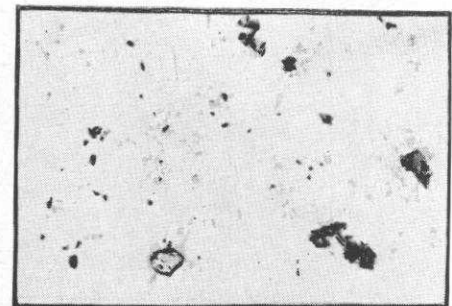
Treatment.
Remelted.



Treatment.
Agitation.



Treatment.
Slag off.



Treatment.
No treated.

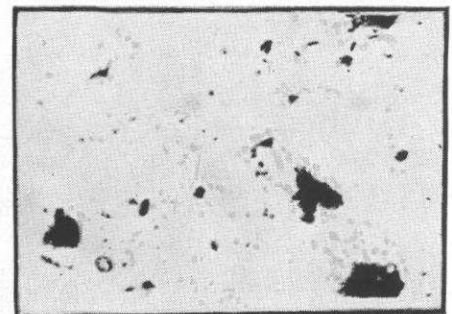


Fig. 9.

The microscopic structure.

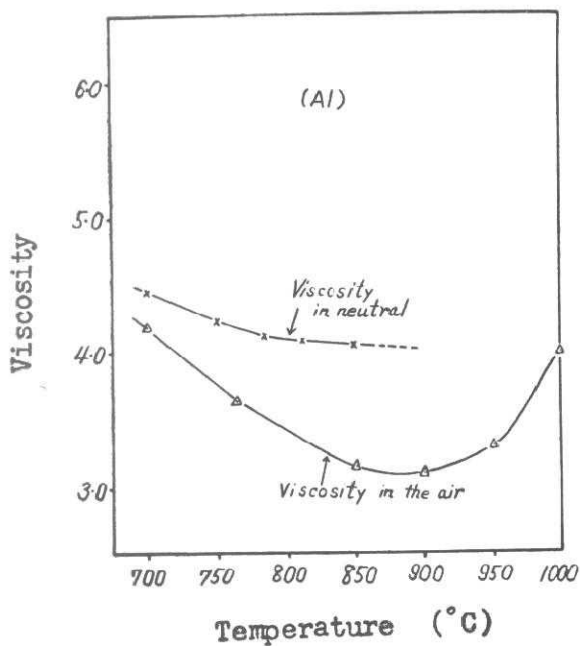


Fig. 10.
The results of viscosity.

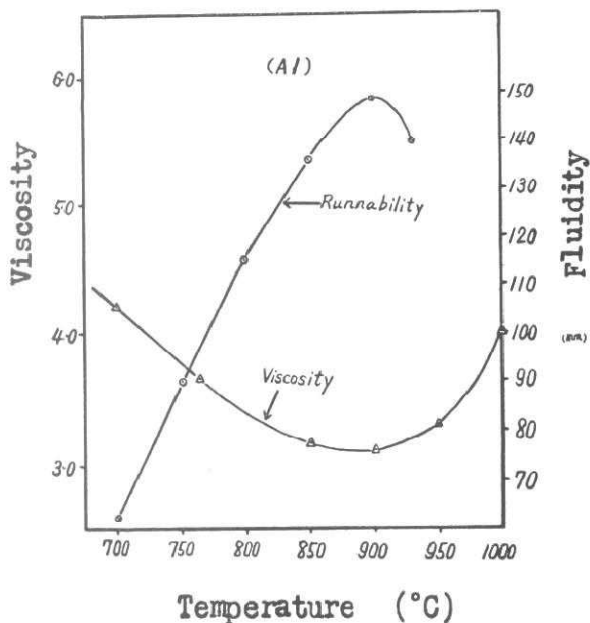


Fig. 11.
The comparison of viscosity and fluidity.

(c) *Changes in gas absorption in molten aluminium:* Since the fluidity and viscosity of molten aluminium are affected by absorbed gases, a measurement of the quantity of gas absorbed in melting was carried out

in a modified Sieverts' apparatus, under different conditions. Fig. 12 shows a comparison between a blank test and absorption of hydrogen. Curve I is blank and curve II is for hydrogen. The difference between I and II gives the amount of gas absorbed.

It was observed that the time for which metal was heated at a certain temperature also controlled the amount of gas absorbed and that equilibrium was reached at all temperatures after a heating period of 3 hours (Fig. 13). The quantities of hydrogen absorbed at different temperatures (as determined on the basis of Fig. 12 after 3 hours' heating) are shown

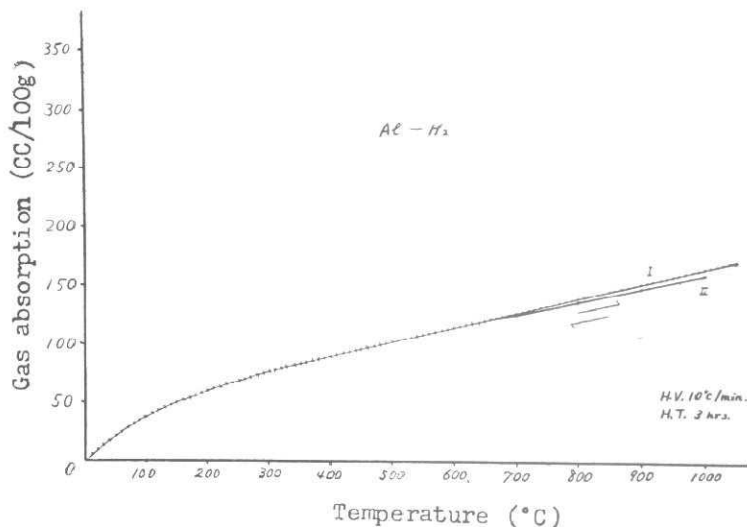


Fig. 12.
The result of pre-experiment.

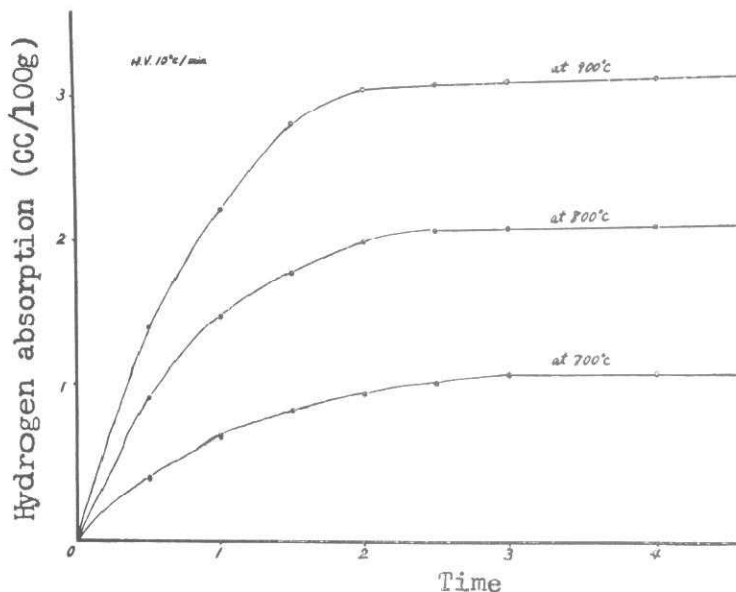


Fig. 13.
The effects of keeping time for absorption.

in Fig. 14. The amount of gas absorbed by aluminium has been studied by several earlier workers^{1-3, 14} and the present values show a good agreement with the earlier values, thus indicating the accuracy of the method.

Absorption of various other gases, such as air, oxygen, hydrogen and nitrogen was also studied (Fig. 15). In the case of air and oxygen, a very large proportion of the gases absorbed appears to be involved in a chemical reaction forming aluminium oxide, because only a very small fraction of these gases could be recovered. In measuring gas absorption in air, the absorbed gases recoverable would perhaps be other than oxygen. The absorption of hydrogen was reversible, while nitrogen had very little solubility and that, too, at very high temperatures possibly due to the formation of aluminium-nitride which was unstable. Fig. 15 also shows the variation of viscosity when metal is melted in neutral atmosphere and in air.

It may be pointed out that the amounts of hydrogen and air estimatable at the minimum viscosity of the metal, viz. at 900°C were hydrogen: 1.8 cc/100 g, and air 0.1 cc/100 g.

(d) *Effect of melting and casting atmospheres on the fluidity of molten aluminium:* As has been shown above, absorption of gas by molten aluminium profoundly affects the fluidity and viscosity of the metal. It was considered that gas absorption occurred in both melting and casting atmospheres. A study of the effects of various atmospheres used for melting and casting was undertaken to determine the chief source of gas absorption. For this purpose the various atmospheres shown in Table IV were used and the results are shown in Fig. 16. It will be seen that when melting and casting respectively were in hydrogen-air, hydrogen-nitrogen, air-air, and air-nitrogen, the fluidity decreased at higher temperatures, whereas it showed continuous rise when the melting was done in an atmosphere of nitrogen followed by casting either in air or in nitrogen.

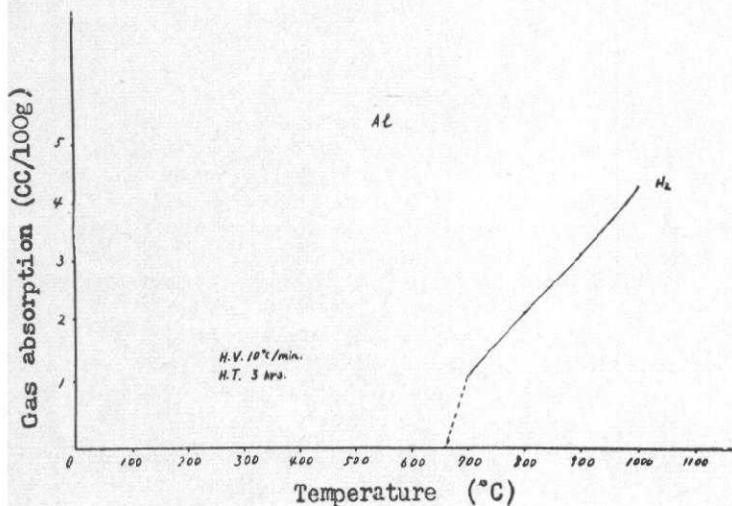


Fig. 14.
The result of absorption of hydrogen.

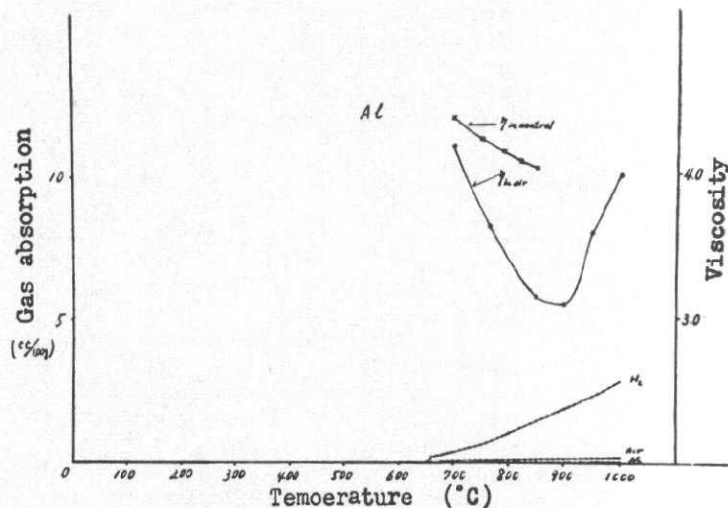


Fig. 15.
The comparison of viscosity and gas absorption.

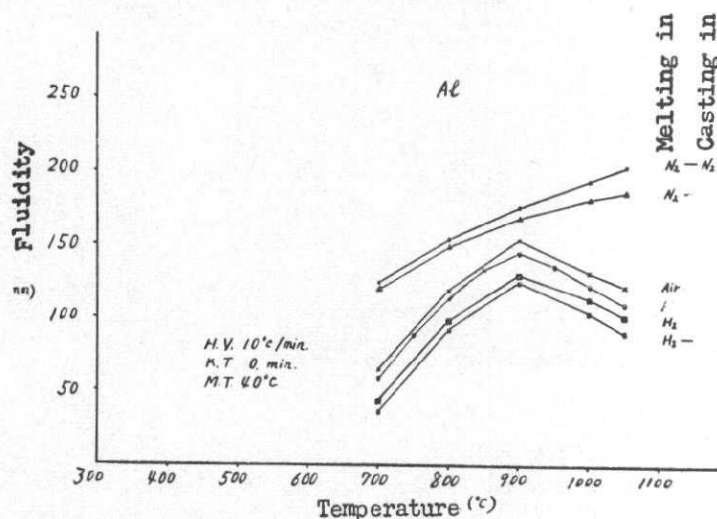


Fig. 16.
The results of experiments.

TABLE IV
The conditions of atmosphere.

Specimen	Atmosphere of melting	Atmosphere of casting
Aluminium	Air	Air
"	Hydrogen	"
"	Nitrogen	"
"	Air	Nitrogen
"	Hydrogen	"
"	Nitrogen	"

These results clearly demonstrate that the melting atmosphere has a dominant effect on the absorption of gas in the molten metal and that melting in nitrogen

or any other neutral atmosphere results in gas-free melts and thus greatly helps in increasing the fluidity of the metal with rising temperature. This may be explained as being the result of the prevention of oxidation by the neutral atmosphere.

Conclusions

- (i) The fluidity of molten aluminium changes with a change in the maximum melting temperature, irrespective of the temperature of casting.
- (ii) Gases absorbed in molten aluminium considerably affect its fluidity, which is also dependent on the quantity of gases absorbed, being reduced with the increase in gas absorption (at higher temperatures).
- (iii) Fluidity of molten aluminium increases with an increase in temperature when gas absorption is prevented by the effective use of fluxes for degassing.
- (iv) Viscosity of molten aluminium is inversely related to its fluidity. This relationship does not hold when the molten metal contains absorbed gases.

- (v) Air and oxygen, when absorbed by molten aluminium, react with the metal and affect its fluidity and viscosity due to the formation of oxide. Absorption of hydrogen is reversible and nitrogen is practically not absorbed by the molten aluminium.
- (vi) The melting atmosphere has a profound effect on the fluidity of molten aluminium. Melting in nitrogen or neutral atmospheres has been shown to give the increased fluidity to the molten metal.

References

- 1 Rontgen and Braun, *Metallwirts.*, 11 (1932), 459.
- 2 Rontgen and Moller, *Metallwirts.* 13 (1934), 81.
- 3 Bircumshaw, *Trans. Faraday Soc.*, 31 (1935), 1439.
- 4 Hanson and Slater, *J. Inst. Metals*, 46 (1931), 187.
- 5 W. Claus, *Z. Metallk.*, 21 (1929), 268.
- 6 Mizutani, *Aluminium*, 1 (1941), 41.
- 7 Sieverts, *Z. Metallk.*, 21 (1929), 37.
- 8 T. Iwamura, *N.K. G.*, (1943), 508.
- 9 Archbutt, *J. Inst. Metals*, 33 (1925), 227.
- 10 Ihokido and Ishida, *N. K. G.*, 3 (1939), 91.
- 11 Tullis, *J. Inst. Metals*, 40 (1928), 55.
- 12 Sugano and Ichikawa, *Aluminium*, 2 (1942), 154.
- 13 G. Sachs, *Praktische Metallk.*, 1 (1933).
- 14 C.E. Ransley and H. Neufeld, *J. Inst. Metals*, 74 (1948), 599.

DISCUSSIONS

Mr. R. W. Flint, Greaves Foundry Service Ltd., Bombay: The experimental data appear to be inconclusive and as the temperature increases, Al_2O_3 should increase and as temperature increases, H_2 increases. Decrease in fluidity could be caused by increase in Al_2O_3 .

Mr. N. G. Banerjee, NML: I congratulate Dr. Hori for his interesting paper. I agree with Mr. Flint in what he has remarked about the absorption of oxygen. As a matter of fact, solubility of oxygen increases with rise of temperature, so the oxygen value given by the author is misleading. According to him nitrogen has also got some solubility in molten aluminium. It is also interesting to note that hydrogen affects the fluidity of the molten aluminium to a great extent. It is true that the hydrogen content is different in upper and bottom portions of the ingot, due to different cooling rates.

Dr. Y. N. Trehan, NML: About the hydrogen pick-up and effect of oxygen, the author says that oxygen absorption takes place but it is in the form of oxide. At higher temperatures, this oxide decomposes and,

possibly, the oxygen is liberated. The amount of absorption of gas as such is very low; that is his observation.

Dr. B. R. Nijhawan, Director, NML: If aluminium oxide could decompose in the absence of any reducing agent, the explanation was plausible. Aluminium oxide decomposes at high temperatures and is reformed at low temperatures, but I don't think the same analogy can be applied to alumina, silica or Fe_2O_3 . I doubt if these oxides would at all decompose by themselves.

Dr. Y. N. Trehan, NML: I would not say that oxides do not really decompose. From experiments on copper oxides, it is known that on being heated in air at about $650^\circ C$ cupric oxide starts decomposition, whereas the actual decomposing temperature (i.e. where complete dissociation takes place) is $1100^\circ C$. So the decomposition does start at $650^\circ C$ even in the atmosphere. I don't know if a similar phenomenon is not happening in Al_2O_3 .

Mr. R. W. Flint, Greaves Foundry Service Ltd., Bombay: Actually Al_2O_3 is decomposed by passing

fluorine gas through it. The problems of removal of Al_2O_3 arise from a practical point of view. In the making of die-castings, they virtually take an electric arc furnace, load it with the metal, superheat it because die-casting is the worst form of foundrymen's risk, leave it to cool for hours on end, again superheat and then start to bring it to the required temperature when they find trouble in die-casting. Hence there is always a good chance of Al_2O_3 being present in the die-cast metal and lot of people used to run into trouble through inclusions which apparently were a touch of corundum formed by aluminium oxide and some thing else combining in the crucible. A really difficult case was brought to us by an aircraft company who were trying to remove hot-spots in their aluminium alloys. They had about 18 tons of ingot contaminated with the oxide which they could not get rid of. We tried to flush the metal with fluorine to remove the Al_2O_3 and found that it was not so easy.

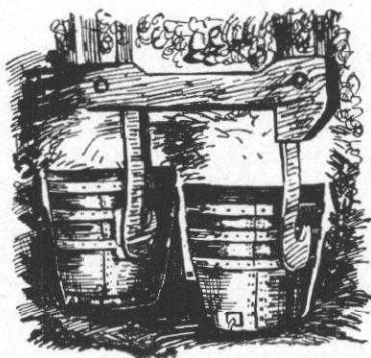
Dr. B. R. Nijhawan, Director, NML: Mr. Flint has raised some pertinent points which need closer scrutiny by the author for a suitable reply.

Dr. Kazuo Hori (Author): I would like to thank all who have participated in the discussions on this paper. It is true that the oxide film is formed on the surface of molten aluminium in air and increases with temperature, but in the experiments detailed in the paper, bottom casting was adopted thereby eliminating the

oxide. Actually the content of Al_2O_3 decreased in higher temperature as can be seen in the paper. It was considered that the separation and flotation of alumina in molten aluminium would be easier in higher temperatures, as the specific gravity of Al_2O_3 is less than that of aluminium and the viscosity of the molten metal decreases in higher temperatures.

As regards the decomposition of Al_2O_3 at higher temperature, I am not in a position to answer as the experiment was not carried out but the solubility of oxygen in molten aluminium to a small extent was evident from the experiment carried out.

It was clearly established from the experimental results that the cause of decrease of fluidity in higher temperature was not dependent upon the mixture of Al_2O_3 but it was considered that the absorbed gas affected the decrease of fluidity. Even in reducing atmosphere of hydrogen over the molten bath, the fluidity decreased in higher temperatures as mentioned in the paper. It was considered difficult to explain these phenomena based on the mixture of Al_2O_3 . After all, with rising temperatures, the viscosity of molten metal decreases; the oxide increases and the absorption of other gases will increase. But the oxide separates and floats off to the surface of the molten metal as viscosity decreases and the molten metal will be clean. The decrease of fluidity was considered based on the effect of absorbed gases.



- Air

- N_2

Air - Air

- N_2

- Air