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Determination of Hydrogen in Aluminium by the Argon-Carrier Hot Extraction Method*

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Synopsis

The argon carrier hot extraction method for the determination of hydrogen in metals previously reported was applied to the case of aluminium with satisfactory results. Sufficient sensitivity was attained by using an oil manometer as the detector. The sample was scraped with an ordinary lathe under a dry condition and heated to 600°C in a stream of purified argon to extract hydrogen. The hydrogen extracted was filtered through a palladium tube at 550°C and determined manometrically. Through this palladium tube, even 10~20 μ l of hydrogen could be filtered quantitatively. The extraction time was about 1 hr and the shape of the extraction curve resembles that obtained by hot extraction in vacuo. Surface gas was determined by re-turning the degassed sample followed by extraction. It was found that the amount of surface gas was dependent not only upon the smoothness but also upon the freshness of the surface of sample. Coefficients of variation of the internal gas (the mean value of which was 0.36 Nml/100 g) and the surface gas (the mean value of which was 3.2×10^{-4} Nml/cm²) of 99.9% aluminium were 7.8% and 11%, respectively.

I. Introduction

Aluminium metal and its alloys contain hydrogen which is responsible for bulging and pin-holes at the time of finishing. There are several methods for the determination of hydrogen in aluminium metal,⁽¹⁻⁶⁾ the representative of which is the vacuum hot extraction method of Ramsley.⁽⁴⁾ However, this vacuum process requires skill and the method is not rapidly accomplished.

So, the argon-carrier hot extraction method⁽⁷⁾ reported earlier was tried for the determination of hydrogen in aluminium metal. In this method, the sample is heated in argon atmosphere, the argon-hydrogen mixture thereby formed is filtered through a palladium tube, and hydrogen is collected and measured.

* The 1334th report of the Research Institute for Iron, steel and Other Metals.

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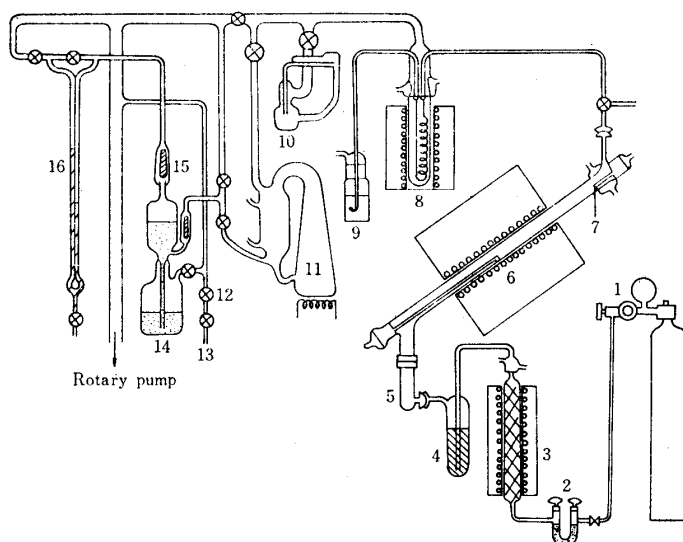
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II. Apparatus

The apparatus used is a gas analyzer for metals which was developed in our laboratory, the schematic diagram of which is given in Fig. 1. Argon is led through the reducing valve (1) into the phosphorus pentoxide column (2), where it is dehydrated, and passes through the sponge titanium column (3) heated to about 600°C to be deoxygenated. The sample is placed on a spoon (7) attached to the stopper of the extraction tube (6) tilted by 35° to a horizontal plane. The air which has entered the tube when the stopper is taken out is driven out with a stream of argon, and the sample is dropped into the extraction tube by turning the



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|---|--|
| 1. Reducing valve. | 2. P ₂ O ₅ column. |
| 3. Sponge titanium. | 4. P ₂ O ₅ column. |
| 5. Sample holder. | 6. Extraction tube. |
| 7. Spoon. | 8. Palladium tube. |
| 9. H ₂ SO ₄ seal. | 10. Rotary McLeod gauge. |
| 11. Mercury diffusion pump. | 12. Leak controller. |
| 13. Leak. | 14. Automatic Toepler pump |
| 15. Stopper valve. | 16. Oil manometer. |

Fig. 1. Schematic diagram of the apparatus.

spoon. The extraction tube (6) is heated at the highest temperature allowable before the sample melts and the temperature is held constant by an automatic temperature controller. Hydrogen extracted from the sample by diffusion is transported by argon stream and is filtered through the palladium tube (8) heated at 550°C, whose temperature is also kept constant by an automatic temperature controller. Argon is expelled through the sulfuric acid sealing. The low pressure side of the palladium tube is maintained at 10⁻⁴ to 10⁻⁵ mm Hg by the mercury diffusion pump (11) and the filtered hydrogen is collected in the gas reservoir of the oil manometer (16) by the mercury diffusion pump and the automatic Toepler pump (14), and the volume is calculated from reading the pressure. The automatic Toepler

pump is worked by intermittent movement of the vacuum pump whose micro-switch is worked by a cam revolving once in 30 sec.

III. Experimental procedures and results

1. Calibration curve

The calibration curve was obtained by calculation from the cross-section of the manometer, the volume of gas reservoir of the manometer, and the specific gravity of the sealing liquid. The values of the cross-sectional area and the volume of gas reservoir are given in Table 1 and the calibration curve in Fig. 2. The manometer oil used was a machine oil of low viscosity which was left alone in vacuum to remove volatile components and dissolved air. Its specific gravity was 0.838 g/ml at 20°C. The calibration curves are given for both cases using an oil manometer and mercury manometer. The calibration curve was examined by introducing a known volume of hydrogen into the apparatus and the values obtained are plotted in Fig. 2, which shows that the plots agree approximately with the calculated

Table 1. Cross section areas of the manometers and volumes of the gas holders.

	Cross section area (cm ²)	Volume of gas holder (ml)
Oil manometer	0.03063	0.905
Mercury manometer	0.00950	0.721

curve. Hydrogen was introduced by using the gas mixing apparatus for a gas chromatography. The reason why the point at 0.02 ml has deviated from the calculated value may be due to the fact that this volume of gas is close to the minimum limit permissible. In the determination of hydrogen in aluminium, the use of 10 g of the sample will give pressure difference of 100~200 mm in oil column height.

2. Analytical procedure

Argon (high-grade quality for spectral analysis) is passed at the flow rate of 40 ml/min, and the sponge titanium column, the sample extraction tube, and the palladium tube are respectively heated to about 600°, i.e. the highest temperature permissible before the sample melts when analyzing alloy samples of low melting point, and to 550°C. The sample is made into a rod about 10 mm in diameter and about 35 mm in length by a lathe without using cutting oil, and the surface is finished to be as smooth as possible. The sample is placed on spoon, air that entered the tube when stopper was removed is expelled with a stream of argon introduced for 10~15 min, and the sample is dropped into the extraction tube by turning the spoon. The reading of the oil manometer is taken every 5 min and the

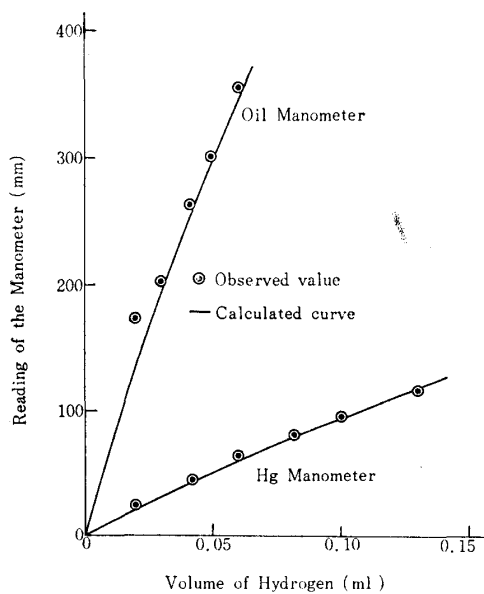


Fig. 2.

Fig. 2. Working curve.

Fig. 3. Extraction curve of pure aluminium.

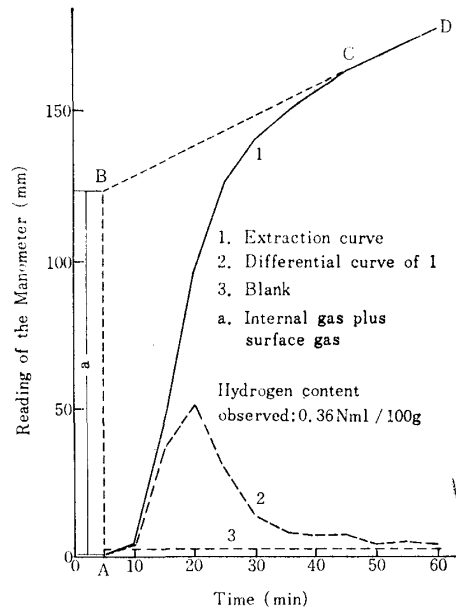


Fig. 3.

extraction curve is plotted. Preliminary extraction is completed in about 45 min, but final extraction is continued for further 15 min and then the values are read as the blank. When the extraction is completed, the sample is dropped into the sample reservoir and the next analysis is carried on.

To obtain the surface gas volume, the sample used is cooled to room temperature with argon stream in the reservoir, taken out, and the surface is finished with a lathe. This is again submitted to the same extraction procedure.

In the extraction curve so obtained, as shown in Fig. 3, the part (D-C) which increases at a constant rate is considered as the blank value, and this line is extrapolated towards the left to subtract the blank value by drawing. The initial 5 min of extraction (A) does not reach the blank value (curves 2 and 3 in Fig. 3), and the *a* value in Fig. 3 is taken as the sum of internal and surface gases. The values of internal gas plus surface gas are calculated from the *a* value by using the calibration curve. Similarly, the value of surface gas is calculated, and the value of internal gas is calculated from the difference of the two values.

3. Examples of analysis

Examples of extraction curves of pure aluminium, 63S alloy, and aluminium-4 per cent magnesium alloy are given in Figs. 3 and 4. In all these cases, the extraction was completed within approximately 45 min and fairly constant blank values followed thereafter. The extraction curves are about the same as that obtained by the vacuum hot extraction method. Curve 2 in Fig. 3 is the differential curve of the extraction curve and shows that the greatest extraction per unit time it

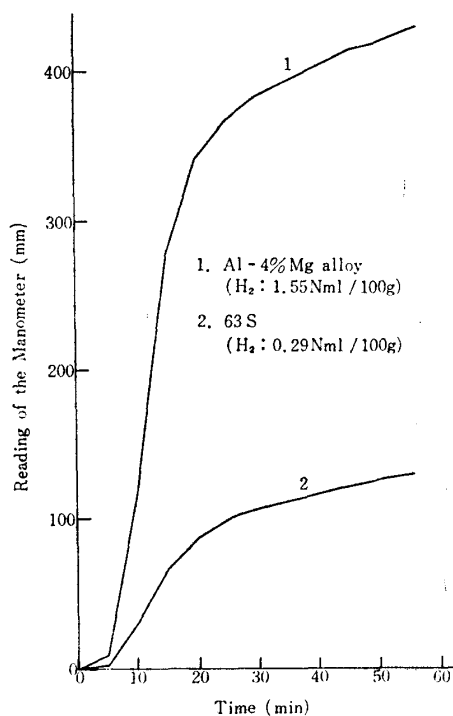


Fig. 4. Extraction curves of alloy.

found at 20 min after addition of the sample. This is 20 min later than the extraction curve theoretically calculated from the diffusion constant of hydrogen in aluminium by Ransley and others.⁽⁴⁾ This may be explained from the rate of temperature rise of the sample itself and the time required for the extracted hydrogen to be transported by an argon stream. The extraction curve is slightly different from the blank value even after 1 hr (curves 2 and 3 in Fig. 3). This is considered to be due to the tailing of extraction, as well as the presence of hydrogen formed by the reaction of the sample on a trace of moisture contained in the carrier gas.

Fig. 4 shows the extraction curve of an alloy containing magnesium (curve 1 in Fig. 4). The shape of this extraction curve is normal. In this case, brown semiluent magnesium was seen to adhere to the internal wall of the extraction tube near the sample. This vaporized substance differs in the following two points from that by the vacuum fusion method, and the analytical values obtained are considered to be close to the true value:

(1) Since the substance was formed in the argon stream, its getter action towards hydrogen is considered to be fairly small.

(2) The substance forms only in the part close to the sample, where the temperature is the highest. Consequently, even if it adsorbs hydrogen, hydrogen is likely to be re-extracted.

The reproducibility of this analysis was examined by using a special aluminium metal (purity 99.9%) and the result so obtained is given in Table 2. In order to avoid segregation, the aluminium metal was made into a rod by cold rolling, the

Table 2. Reproducibility.

No.	Sample weight (g)	Surface area (cm ²)	Total hydrogen (Nml)	Surface gas (Nml)	Result (Nml/100g)	Deviation
1	4.3922	8.75	0.0200	0.0028	0.392	+0.033
2	4.8967	10.16	0.0219	0.0032	0.382	+0.023
3	4.7598	9.90	0.0217	0.0032	0.389	+0.030
4	4.3943	9.39	0.0187	0.0030	0.358	-0.001
5	4.6384	9.79	0.0181	0.0031	0.324	-0.035
6	4.3817	9.34	0.0172	0.0030	0.324	-0.035
7	4.5758	9.69	0.0199	0.0031	0.367	+0.008
8	4.6085	9.71	0.0208	0.0031	0.384	+0.025
9	4.6135	9.78	0.0187	0.0031	0.338	-0.021
10	4.4538	9.30	0.0177	0.0030	0.330	-0.029

Mean value: 0.36 Nml/100 g, Standard deviation: 0.028 Nml/100 g, Coefficient of variation: 7.8%.

Table 3. Examples of the analysis.

Sample	Results (Nml/100g)						Mean (Nml/100g)
Pure Al 1	0.41	0.39	0.39				0.40
" 2	0.22	0.20	0.17				0.20
" 3	0.18	0.22	0.18	0.14			0.18
" 4	0.22	0.28	0.25	0.22			0.24
" 5	0.25	0.22	0.21				0.23
" 6	0.16	0.13	0.13	0.13			0.14
63 S	0.29	0.28					0.29
2 S	0.15	0.15	0.13	0.16	0.15		0.15

surface was cut by a lathe without the use of a cutting oil, and finished into a rod about 8 mm in diameter and about 35 mm in length. This sample showed average value of 0.36 N ml/100 g, standard deviation of 0.028 N ml/100 g, and coefficient of variation of 7.8 per cent.

Analytical results of samples are given in Table 3. The samples were cast into the Ransley type and finished by a lathe. The analysis required 70 min and samples can be prepared while extraction (of other samples) is going on.

IV. Discussion

1. Palladium tube

Palladium tube is the heart of this apparatus and examinations were therefore made of various properties of the palladium tube. The relationship between the heating of the palladium tube and the rate of hydrogen recovery was approximately the same as in the preceding case.⁽⁷⁾ The relationship between the flow rate of argon and the hydrogen recovery rate is shown in Fig. 5. This relationship varies slightly with the difference in the palladium tube and other conditions. In the present apparatus, an increase in the flow rate (of argon) resulted in a rapid decrease of the recovery rate of hydrogen at the point of 50 ml/min. This is con-

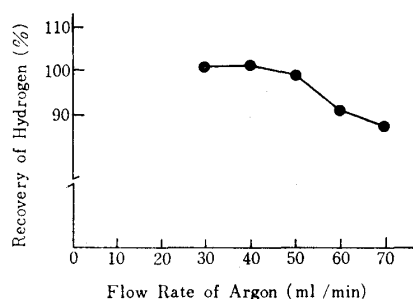


Fig. 5. Relation between recovery of hydrogen and flow rate of argon.

sidered to be due to the cooling of the palladium tube by argon stream as well as the decrease in the time of the presence of argon in the palladium tube when its flow rate increases.

When the heating temperature of the palladium tube and the argon flow rate are appropriate, it is necessary to have the partial pressure of hydrogen outside the palladium tube sufficiently low in order to filter hydrogen quantitatively. The external pressure of hydrogen outside the palladium tube can be measured with the rotary McLeod tube (10 in Fig. 1), being about 3×10^{-5} mm Hg. If the hydrogen pressures inside and outside the palladium tube are in equilibrium, the amount of hydrogen expelled with argon without being filtered will be approximately 1×10^{-4} ml, at the argon flow rate of 40 ml/min and at 1 hr after analysis. This amount is negligible. The good agreement between calculated and experimental values in the calibration curve (Fig. 2) indicates correct working of the palladium tube.

The blank values are related to the heating temperature of the palladium tube and the argon flow rate, and this relationship is shown in Figs. 6 and 7. The relationship between the blank value and the argon flow rate is approximately linear, and this is due to impurities in argon. The relationship between the blank

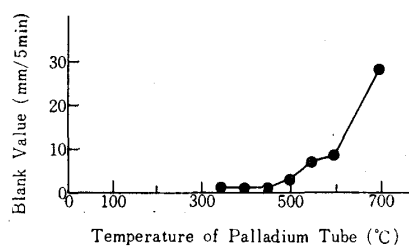


Fig. 6

Fig. 6. Relation between blank value and temperature of Pd tube.

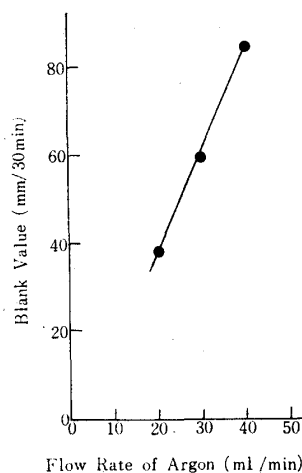


Fig. 7

Fig. 7. Relation between blank value and flow rate of argon.

value and the heating temperature of the palladium tube suggests that these impurities decompose in the palladium tube. This was endorsed by the fact that collection of the gas giving the blank values and the analysis of the gas giving the blank values by the mass spectrometer showed that the gas was almost pure hydrogen.

2. Surface gas

In the determination of hydrogen in aluminium, the surface gas estimation is of the most difficult problem, and so, the values hitherto reported are fairly inconsistent with one another (cf. Table 4). In the present series of experiments,

Table 4. Surface gas reported in literatures.

Author	Surface gas (Nml/100g)	Literature
Griffith et al.	0.0014 ~ 0.0027	(3)
Ransley et al.	0.0001 ~ 0.00035	(4)
Deoras et al.	0.00018	(6)
Brandt et al.	0.00035	(8)
Shigematsu	0.00005 ~ 0.00009*	(9)
Danilkin et al.	Mean: 0.00049 σ : 0.00018**	(10)

* The value was calculated from the data given in the literature by the authors.

** Standard deviations were calculated from the data in the literature by the authors.

examinations were made to reduce the surface gas to a negligible state. Variation in the amount of surface gas with various methods of surface treatment is shown in Table 5. Extraction curves for surface gas at different extraction temperatures are given in Fig. 8. From these experimental results, the surface gas was found to have the following properties:

(1) Surface gas is greatly dependent on the coarseness of the surface, as seen from samples of Nos. 2, 3, 4, and 5.

(2) From samples of Nos. 2, 6, 7, and 8 in Table 5, it is seen that surface gas is dependent not only on the coarseness of the surface but also on the freshness of the surface. Sample No. 2 was polished with an emery paper after degassing by heating and the surface gas value was extremely large. Samples of Nos. 6 and 7 were degassed by heating after polishing the surface with an emery paper. Although the coarseness of their surfaces was the same as that of sample No. 2 and

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(8) S. Shigematsu, *J. Japan Inst. Metals*, **24** (1960), A-177.

(10) V.A. Danilkin, K.M. Konstantinov and B.I. Bulatova, *Zavod. Lab.*, **27** (1961), 259.

Table 5. Relation between surface gas and surface treatment.

No.	Sample	Surface treatment	Surface gas (Nml/cm ²)
1	99.9% Al	Not treated.*	Ca. 0.016
2	"	Degassed, then polished with emery paper. The surface coarser than that of No. 3. The atm. temp. 25°C, humid. 70%.	0.018
3	99.5% Al	Degassed, then filed. The surface coarser than that of No. 4. The atm. temp. 25°C, humid. 70%	0.0033
4	"	Degassed, then dry turned with a table turning lathe. The surface coarser than that of No. 5. The atm. temp. 25°C, humid. 70%.	0.0015
5	99.9% Al	Degassed, then dry turned with an ordinary turning lathe. The surface very smooth, the atm. temp. 25°C, humid. 70%.	0.00033
6	"	Polished with emery paper, then degassed. After degassing, the sample was exposed to air for 5 hrs.	0.0016
7	"	Polished with emery paper, then degassed. After degassing, the sample was exposed to air for 25 hrs.	0.0016
8	"	Degassed, then polished with emery paper. After polishing, the sample was exposed to air for 27 hrs and then re-polished with emery paper.	0.012
9	"	Degassed, then polished with emery paper. After polishing, the sample was exposed to air for 20 days.**	Ca. 0.019
10	99.5% Al	Degassed, then filed in an air conditioned room, where the temp. 21.5°C, humid. 51%.	0.0045
11	99.9% Al	Degassed, then dry turned with a table turning lathe in argon stream.	0.0079

* The sample had not been degassed, therefore, the surface gas includes a small amount of internal gas. The extraction curve made no plateau.

** The extraction curve made no plateau.

the oxide film on their surfaces is also considered to be the same as that of sample No. 2, or more, the surface gas was smaller than that of sample No. 2 by one digit, and no increase in surface gas by absorption of moisture by the oxide film can be seen even when these samples of Nos. 6 and 7 are left in air. If these samples are polished with an emery paper, the amount of surface gas increases immediately (sample No. 8). Ransley and others⁽⁴⁾ stated that, the surface gas was hydrogen formed as a result of reaction between aluminium and the water adsorbed to the oxide film. However, the foregoing experiments show that the volume of surface gas increases when the sample surface is fresh rather than when there is an oxide film.

(3) Comparison of samples of Nos. 1, 2, and 9 in Table 5 with one another shows that the substance which creates surface gas is formed with polishing and does not increase if the sample is left in air. If the sample is left in air for a very long time, the extraction curve of the surface gas does not reach a definite value and shows tailing.

(4) From the comparison of samples of Nos. 3 and 10, and of Nos. 4 and 11 in Table 5 with one another, the value of surface gas is considered to undergo practically no change even if the moisture in the atmosphere varies during polishing.

(5) Fig. 8 indicates that there is entirely no possibility for separatory extraction of internal and surface gases by changing the method of heating.

Considering the properties of the surface gas as revealed from these data, it would seem best to finish the surface as smooth as possible by cutting the surface of the sample with a lathe, followed by extraction of the total gas, to cool the sample in argon stream, to finish again the surface as before, and to extract the gas

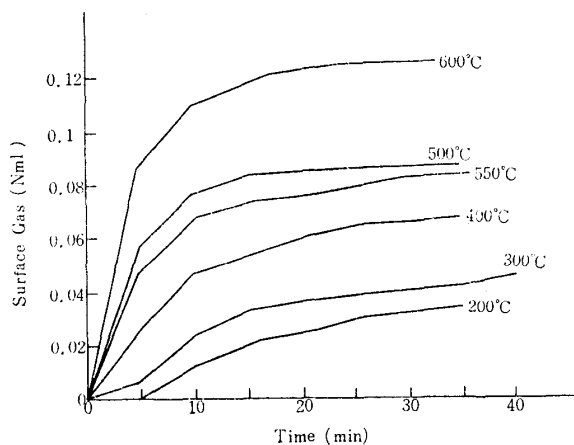


Fig. 8. Extraction curves of surface gas at different extraction temperatures.
 Sample: 99.9% Al, Surface area: Ca 8 cm².
 Surface: polished with emery paper.

Table 6. Reproducibility of surface gas.

No.	Surface area (cm ²)	Total surface hydrogen (cm oil)	Surface gas (Nml/cm ²)	Deviation (Nml/cm ²)
1	8.64	2.24	0.00035	+0.00003
2	9.81	2.45	0.00033	+0.00001
3	9.32	2.10	0.00031	-0.00001
4	8.39	2.05	0.00032	0.00000
5	9.13	2.30	0.00033	+0.00001
6	9.39	2.32	0.00032	0.00000
7	9.46	2.20	0.00031	-0.00001
8	9.27	2.67	0.00039	+0.00007
9	9.08	1.77	0.00026	-0.00006

Mean value: 0.00032 Nml/cm², Standard deviation: 0.000035 Nml/cm², Coefficient of variation: 11%

again. This would give the volume of surface gas. In finishing the surface with a lathe, no cutting oil should be used and the sample should not be left in air for a long period before analysis.

The reproducibility of the surface gas when the above conditions are followed is shown in Table 6. The sample was special aluminium metal of 99.9 per cent purity. The amount of surface gas shows different values when the composition of the sample is varied; but when samples, of the same composition are used, it is not necessary to measure the surface gas each time, if the coefficient of variation of 11 per cent is permissible. The value of 3.2×10^{-4} Nml/cm² in Table 6 agrees approximately with the values of Ransley, and Danilkin obtained by the vacuum heating method (Table 4).

Summary

The argon carrier-hot extraction method was applied to the determination of hydrogen in aluminium and satisfactory analytical values were obtained. It was found that the procedure was simplified and the time of analysis was shortened. Analytical precision when using special aluminium metal (0.36 N ml/100 g of hydrogen) was 7.8 per cent in the coefficient of variation.

The amount's of surface gas was dependent not only on the coarseness of the surface but also on its freshness. It was found that the lowest value of surface gas was obtained when the surface was finished with a lathe without using cutting oil. When this surface treatment was done, the value of 3.2×10^{-4} Nml/cm² was obtained with special aluminium metals, although the value would change with the composition of the sample. The reproducibility of the measurement of surface gas was of 11 per cent in the coefficient of variation. By the present method, various samples were analyzed. Average time of analysis was 70 min.