Effects of Alloying Elements and Condensed Film of the Inner Wall of Vacuum Fusion Apparatus on the Carbon Monoxide and Nitrogen Extraction*

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Synopsis

The authors made some experiments with respect to the nitrogen and carbon monoxide extractions by the vacuum fusion method for the analysis of gases in steels. As for the nitrogen gas, the variation of results in the run of analysis and the influence of alloying elements were investigated to compare with the results obtained by chemical analysis. On the other hand, the lowering tendency of oxygen values in the pure iron by the addition of Al or Mn, relating with the effect of Mo-hood, was studied. Temperature measurements at the inner wall surface of the furnace tube and the analyses of the condensed metallic film on the surface and of the residual metals in the graphite crucible were also performed. (1) Ascertained that some elements like Cr, V, Mo and Al, Mn are harmful for the extraction of nitrogen and carbon monoxide, respectively. (2) Studied the cause and mechanism of the insufficient nitrogen extraction where its values are lower than those in the chemical analysis. (3) Discussed the carbon monoxide adsorption mechanism of the film of the inner wall mainly composed of Fe, Mn and Al. Then it was found that the Mo-hood was considerably effective in preventing such a phenomenon.

I. Introduction

The vacuum fusion method for the gas analysis of steels has been used in conjunction with a number of improvements introduced since 1920. Now it is regarded as a most common procedure and the data obtained through this method are considered as the basis in the other analyses.

In spite of this reliability, there are some problems to be solved, which cause errors in values. In this paper the authors concentrated on one of these problems and studied the influence of alloying elements on the extraction of gases.

As for the nitrogen, investigation was made on the relations between the extraction tendency and the blank values of the molten sample, which contained the elements of Cr, V and Mo which increase the solubility of nitrogen in liquid steels. On the carbon monoxide gas extraction it is well-known, as was pointed out by G. Thanheiser, N. Yoneda and S. Sawa that if Al or

Mn is contained in a sample, it lowers the oxygen value. Though it is said that this is caused by the carbon monoxide adsorption on the inner wall of the furnace tube, the exact quantitative relation between Al or Mn content and oxygen values have not hitherto been made clear. Therefore, in order to solve this relationship the authors studied the influence of Al or Mn addition to the pure iron and steel of various chemical compositions. Then the Mo-hood covering the quartz tube was revealed as being considerably effective for the prevention of the film condensation. In addition, after the temperature measurements at the inner surface of the furnace tube and the gas analysis were made, the analyses of the metallic film condensed on the inner surface and the residual metals in the graphite crucible were performed and at the same time the behavior of Al or Mn during the extraction of gases and the mechanism of carbon monoxide adsorption on that film were investigated.

II. Apparatus and Procedure

Both the constant volume pressure measuring type (Rigo-sha model SHO-II) and the constant pressure Orsat type (similar to that recommended by the Japan Society for the Promotion of Science for H analysis) apparatuses, shown in Figs. 1 and 2, were used.

In Table 1, the capacity and analytical conditions are compared for the two apparatus. It is noticed that the capacity of the extraction pump of the former apparatus is twice as great as that of the latter while its extraction time is less than one third of the latter.

In the analyses of the condensed film covered on the furnace tube and the residual metals in the graphite crucible, the tube and the crucible were removed from the apparatus after gas analyses, dissolved into acid solution and subjected to the chemical analysis.

* This article is in reference to the lecture delivered before the 64th Grand Lecture Meeting of The Iron & Steel Institute of Japan in October 1962. Japanese texts were received on August 15 and November 4, 1962 and separately printed in *Tetsu-to-Hagane* (Journal, Iron & Steel Institute, Japan), **50** (1964), 5, 787-793; 6, 925-933.

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Fig. 2.

Block diagram of the vacuum fusion apparatus for determining gases in metals. (Constant volume pressure measuring type)

Table 1. Comparison of the analytical conditions of the apparatus used

Apparatus	Graphite crucible		Diameter of furnace tube (mm)	Extraction capacity of Hg diff. pump (l/sec)	Sample weight (g)	Extraction temp. (°C)	Extraction time (min)
	Inner diameter (mmφ)	Depth (mm)					
Const. vol. press. measuring type	18	65	(outer) 70	max. 60	2.0	1,850	5~8
Const. press. Orsat type	11	55	(inner) 50	25~30	3.5~4.0	(Drop in at 1,550) 1,850	30

III. Experimental Results

1. Extraction of Nitrogen

By the vacuum fusion method the extraction of nitrogen in steels tends to be delayed than that of carbon monoxide as seen in some references,^{4)~6)} whereby there is discord in opinions^{7),9),18)~20)}, etc. about reliability of the nitrogen determination by this method. The authors studied this point and made experiments with the ordinary samples on the effect of the Cr, V and Mo which increase the nitrogen solubility.

(1) To observe the process of nitrogen extraction, the total extraction time of 30 min. was divided into the first half of 20 min., and the latter half of 10 min., and the composition of the gas extracted at each period was obtained. The mean values in the 10 times analyses in the latter 10 min. of the reaction for the ordinary high Cr steel (C: 0.10, Si: 0.35, Mn: 0.62, Cr: 13.10) are shown in Table 2. The ratio of the gas volumes extracted in the latter 10 min. of reaction to the total extraction amount in 30 min. is given in Table 3.

From the tables it is known that the carbon monoxide extraction was completed some 95% in the first 20 min. but for nitrogen an additional 10 min. and more were required to recover the vacuum degree to the same level as that when the sample had not yet been charged. The residue of nitrogen was increased remarkably in order of analyses and for the 4th specimen 18% of the whole nitrogen volume was extracted in the last 10 min.

(2) For the sake of revealing the variation of nitrogen values in the run of analyses, some series of standard sample No. 1 (S35C) were used and nitrogen extraction for each specimen was performed for 15 min., which is three times as long as in the ordinary one, with the

Table 2. Components of the gas extracted in the last 10 min. of a reaction period. (13 Cr-steel)

(Unit: ml/g of specimen)

Order of analysis Component	1	2	3	4
Total	0.003	0.006	0.013	0.019
N ₂	0.002	0.004	0.007	0.010
CO	0	0.001	0.004	0.005
H ₂	0.001	0.001	0.002	0.004

Note: Each data is the average of the 10 time analyses.

Table 3. Ratio of the gas extracted in the last 10 min. of a reaction period to the total extraction amount. (13Cr-steel)

(Unit: ml/g of specimen)

Order of analysis Component	1	2	3	4
Total	2.1	3.6	6.6	10.1
N ₂	3.9	8.6	12.8	18.0
CO	0.5	0.5	2.2	5.8
H ₂	3.2	7.7	10.1	20.3

Note: Each data is the average of the 10 time analyses.

const. vol. press. measuring type apparatus. From the results shown in Fig. 3, even the first specimen gave a lower value than that obtained by chemical (Kjeldahl) method and in accordance with the order of the introduction of the sample nitrogen values were decreased, and that tendency was agreed with the experiences by I. Ogahara et al.⁶⁾ with respect to 18-8 stainless steel.

(3) The blank values with the const. vol. press. measuring type apparatus were measured on the standard carbon steel No. 1, and ordinary samples of

medium Cr, V, Mo and high Cr alloy steels whose chemical compositions are shown in Table 4.

The compositions of blank gases collected for 15 min., as long as the extraction time, after several continuous analyses of these specimens, were plotted in Fig. 4. In the diagram the 1 mm height of oil manometer was equal to 0.0058 Nm³ of gases. Following in the order of specimen charge the blank values were increased and were especially remarkable for steels containing Cr, V and Mo. Hydrogen and carbon monoxide gases so scarcely increased that they hardly influenced the determination of each value of the components, but on the contrary, nitrogen rose

so remarkably up with the progress of sample charging that most part of blank gases was taken up by nitrogen. But distinct differences in the increase of nitrogen were observed by kind of steel. Namely, in order of 18Cr steel, 13Cr steel, medium Cr-V-Mo alloy and plain carbon steel increase of nitrogen gas was large and it was gradually collected even after the sample extraction time which was three times as long as in the ordinary analysis, because of the incomplete dissociation and release from the molten bath with the interferences of Cr, V and Mo. Consequently, nitrogen values for each steel were determined low.

(4) Comparison of nitrogen values of the standard samples determined by the vacuum fusion method and chemical (Kjeldahl) method is described in Table 5. It was recognized that the former gave lower values in both the const. press. Orsat type and the const. vol. press. measuring type apparatus. This is considered due to the fact that the nitrogen in the specimen was incompletely extracted as shown in Tables 2 and 3 and remained partly in the metals in the graphite crucible.

Thus it would not be proper to regard the nitrogen values of many kinds of steels obtained by the vacuum fusion method accurate, so far as the present apparatus and analytical conditions are used.

2. Extraction of Carbon Monoxide

On the carbon monoxide extraction by the vacuum

Fig. 3. Influence of a run of analyses on the nitrogen value determination. (C-steel)

Fig. 4. Variations of blank gas composition according to a run of analyses

Table 4. Chemical composition of the ordinary samples used for brank test

	Spec.	Type of steel	C	Si	Mn	P	S	Ni	Cr	Mo	W	V	Cu	Co
No. 1	S35C	Plain C-steel	0.30 ~0.40	0.15 ~0.35	0.60 ~0.85	0.030 max.	0.030 max.	0.25 max.	0.20 max.				0.30 max.	
No. 2	SKH3 SKH9	Medium Cr-, V- and Mo-steel	0.70 ~0.85 0.75 ~0.90	0.35 max. 0.35 max.	0.60 max. 0.60 max.	" " "	" " "		3.50 ~4.50 3.50 ~4.50		17.00 ~19.00 6.00 ~7.00	0.80 ~1.20 1.80 ~2.30		4.50 ~5.50
No. 3	SuS27	High Cr-steel	0.08 max.	1.00 max.	2.00 max.	0.040 max.	0.030 max.	8.00 ~11.00	18.00 ~20.00					
No. 4	SuS21 SKD11	High Cr-steel	0.12 max. 1.40 ~1.60	0.75 max. 0.40 max.	1.00 max. 0.50 max.	0.040 max. 0.030 max.	0.030 max. 0.030 max.		12.00 ~14.00 11.00 ~13.00					
								0.50 max.		0.80 ~1.20		0.20 ~0.50	0.25 max.	

Table 5. Comparison of nitrogen values determined by the chemical (Kjeldahl) and the vacuum fusion methods ($n^*=6\sim20$)

Method			Sample	No. 2 permalloy-50	No. 3 S35C	No. 4 SuS27	No. 5 En15
Chemical (Kjeldahl)				30 ppm	80 ppm	337 ppm	105 ppm
Vacuum fusion	Const. vol. press. measuring	Mo-hood used		17.7 „	58.0 „	328.3 „	30.7 „
		„ not used		19.3 „	54.0 „	274.6 „	33.4 „
	Const. press. Orsat	Mo-hood used		—	45.2 „	—	11.8 „
		„ not used		—	37.1 „	—	27.4 „

* n : the number of tests repeated.

fusion method the interference by Al and Mn has been well-known but the quantitative relations have not yet been clarified in the literatures. Accordingly the authors studied this problem, and at the same time the problems on the carbon monoxide gas adsorption by the metallic film deposited on the inner surface of the furnace tube and lowering of the oxygen determination values were investigated in detail, because there are many obscure points concerning them.

i. Temperature Measurements at the Inner Wall of the Furnace Tube and the Mo-Hood

It is said that carbon monoxide adsorbing temperature is in the range of $300^{\circ}\sim500^{\circ}\text{C}^{1),2),13)}$. The temperatures at the inner wall area, on which most of the condensed film was deposited, and at the Mo-hood covered at the top of the quartz tube were measured with the const. press. Orsat type apparatus. As shown in Fig. 5, Pt-Pt·Rh couple, corrected for the influence of high frequency induction heater, was sealed in the vacuum apparatus through the branch tube end so as to touch the inner wall by the tip.

On the Mo-hood, the Tempilstik (a sort of crayon) of 899° and 927°C were painted on the surface and the temperature when it melted was regarded as to have reached the specified degree. In Tables 6 and 7, the relations between the crucible temperature which were measured by the optical pyrometer, and temperature of the inner surface of the furnace tube or the Mo-hood are presented. It is apparent from Table 6, that when the crucible reached analytical condition of $1,850^{\circ}\text{C}$, the temperature of the inner surface of the furnace tube where the condensed film was thickest,

was $300^{\circ}\sim500^{\circ}\text{C}$, that is carbon monoxide adsorption temperature. In other words, the temperatures were $450^{\circ}\sim550^{\circ}\text{C}$ with Mo-hood, 520°C without it and 330°

A: from the top of graphite crucible 18 mm up
B: " 8 mm up
C: " 20~30 mm up
Fig. 5. Temperature measured positions at the furnace tube and the Mo-hood

Table 6. Temperature of the crucible and the inner wall of the furnace tube

$\begin{matrix} K \\ T(^{\circ}\text{C}) \end{matrix}$ $M \text{ (mm)}$		Temp. of the inner wall of the furnace tube ($^{\circ}\text{C}$)						
		Mo-hood		Quartz hood				
		20 up	30 up	20 up	20 up	30 up	30 up	35 up
2,330		646	515	559	540	458	423	405
1,850		555	434	470	430	365	335	325

K: kind of hood, M: measured position at the inner wall, T: temp. of the crucible.

Table 7. Temperatures of the crucible and the Mo-hood

Temp. of the Mo-hood (m.p. of Tempilstik) ($^{\circ}\text{C}$)		New Mo-hood		Old Mo-hood*	
		899	927	899	927
Temp. of the crucible** ($^{\circ}\text{C}$)	Distance from the top of the crucible. (Tempilstik painted position)	1,540	1,720	1,425	1,560
	$\begin{cases} 18 \text{ mm up} \\ 8 \text{ mm up} \end{cases}$				
		1,395	1,640	1,285	1,380

* After 5~6 times use. ** When the Tempilstik on the Mo-hood is melted.

~470°C with quartz hood, at the position of inner surface of the tube 20~30 mm up from the rim of the crucible. From Table 7, it is said that if the temperature of the crucible is maintained at 1,850°C, the temperature of the Mo-hood would exceed 900°C, which is far higher than the carbon monoxide adsorption temperature.

ii. Influences of Al and Mn on the Pure Iron and Common Steels

The capsule shaped pure iron specimens enclosing Al or Mn were analysed to examine the effect of such an element. When these were introduced into the graphite crucible at 1,850°C, Al or Mn was molten and mixed simultaneously with the iron whereby similar reactions were expected as to the steel samples of various contents. On the several kinds of steels with the different Al or Mn contents, the effect of the Mo-hood and the conditions of the metallic film formation were studied. Chemical compositions and mean oxygen values of the pure iron and the standard steels in the authors' laboratory are shown in Table 8.

Experimental results of oxygen determination were obtained with the pure iron samples respectively in the case of Al or Mn addition up to 1.5% and at the same time the advantage of the Mo-hood attached to the quartz tube was investigated. The number of specimens continuously analysed for each content were 11~15 by the const. vol. press. measuring type apparatus, and 4 by the const. press. Orsat type one. Thus the average oxygen values were illustrated in Figs. 6 and 7, relating with each rate of Al or Mn addition. In spite of the different apparatus adopted, Al or Mn contained samples showed the reverse tendency of a decrease in the oxygen values with the increase of such an element. Only 40% of the oxygen standard value with 1% of Mn addition and 35% of it with 1.5% of Al were obtained. The curve of 1,700°C in Fig. 6 gave a little higher value because of the higher carbon monoxide evolving speed by the faster reaction. The Mo-hood, as seen in these diagrams, considerably prevented the interference of Al or Mn on the carbon monoxide

extraction. The decrease of evaporated metal deposits was visually observed in the case of Mo-hood being used. This is considered most of the metallic vapors expelled from the graphite crucible condensed on the Mo-hood and only a little on the inner wall of the furnace tube, which resulted in the improvement of carbon monoxide extraction.

Thus, the carbon monoxide adsorption on the condensed metallic film of the furnace tube was certainly recognized as reported hitherto. The effect of Mo-

Fig. 6. Influence of Mn addition on the oxygen value determination

Fig. 7. Influence of Al addition on the oxygen value determination

Table 8. Chemical composition of the specimens

No.	Spec.	C (%)	Si (%)	Mn (%)	P (%)	S (%)	Ni (%)	Cr (%)	Cu (%)	Al (%)	Fe (%)	O (ppm) (Mo-hood used)
1	Pure Fe	0.01	0.08	0.03	0.007	0.011	0.02	tr.	0.01	0.016		* 110.2 ($\sigma=4.34$) ° 107.3 ($\sigma=7.45$)
2	50% Ni permalloy	0.006	0.05	0.21	0.003	0.004	50.04	tr.	tr.	0.010		* 196.9 ($\sigma=6.58$)
3	S35C	0.39	0.29	0.70	0.008	0.009	0.08	0.09	0.17	0.029		* 50.9 ($\sigma=1.93$) ° 47.4 ($\sigma=5.02$)
4	SuS27	0.06	0.79	1.24	0.014	0.017	9.63	19.24	0.06	0.039		* 60.7 ($\sigma=5.26$)
5	En15	0.44	0.30	1.44	0.016	0.019			0.17	0.030		* 21.7 ($\sigma=1.40$) ° 15.0 ($\sigma=2.82$)
6	Pure Fe	0.01	0.01	tr.	0.002	0.010	0.04	0.01		0.018		° 713.7 ($\sigma=5.05$)
	Elect. Mn	0.010	tr.	99.92	0.002	0.028					0.018	
	Al									>99.9		

* Const. vol. press. measuring type. ° Const. press. Orsat type.

Table 9. Influence of Al on the oxygen value determined. (Effect of Mo-hood)

Apparatus	Const. press. Orsat type						Const. vol. press. measuring type							
Sample No. & Spec.	No. 1 pure Fe						No. 1 pure Fe							
Al added (%)	0		0.5		1.0		0		0.5		1.0		1.5	
Mo-hood	use	no	use	no	use	no	use	no	use	no	use	no	use	no
O ppm ($\bar{x}$)	107.3	102.0	110.1	66.1	89.5	61.8	112.5	108.8	93.4	70.6	92.3	72.6	92.8	38.5
Std. dev. (σ)	7.5	6.5	3.5	14.6	10.3	5.8	4.6	4.2	4.5	8.1	3.8	8.7	5.9	6.3

Table 10. Influence of Mn on the oxygen value determined. (Effect of Mo-hood)

Apparatus	Const. press. Orsat type																Const. vol. press. measuring type									
Sample No. & spec.	No. 1 pure Fe								No. 3 S35C		No. 5 En15		No. 6 pure Fe				No. 1 pure Fe		No. 2 permalloy		No. 3 S35C		No. 4 SuS27		No. 5 En15	
Mn (%)	0		(0.2)*		(0.5)*		(1.0)*		0.70		1.44		0		(0.05)*		0		0.21		0.70		1.24		1.44	
Mo-hood	use	no	use	no	use	no	use	no	use	no	use	no	use	no	use	no	use	no	use	no	use	no	use	no	use	no
O (ppm) ($\bar{x}$)	107.3	102.0	88.8	81.5	80.1	55.0	82.3	45.5	49.3	29.6	15.0	6.2	713.7	718.0	711.2	694.7	112.5	108.8	193.0	186.0	50.9	30.2	60.7	29.5	21.7	8.7
Std. dev. (σ)	7.5	6.5	11.1	10.8	13.5	13.8	2.1	3.2	1.8	0.7	2.8	3.5	5.1	6.7	3.5	7.9	4.6	4.2	6.6	8.5	1.9	3.2	5.3	6.2	1.1	3.4

* The case of Mn addition.

Fig. 8. Effect of Al content on oxygen extraction rate. (Comparison in the case of Mo-hood being used and being not used)

Fig. 9. Effect of Mn content on oxygen extraction rate. (Comparison in the case of Mo-hood being used and being not used)

hood, still, was not enough to revive 100% of the oxygen content of the pure iron in the case of Al or Mn addition. The analytical values either with or without Mo-hood were compared with several specimens with addition of Al or Mn, which are shown in Tables 9 and 10.

To obtain the influence of Al or Mn quantitatively, the rate of the values without Mo-hood against those with it was computed.

$$\text{Oxygen extraction rate} = O_{no}/O_{use} \times 100$$

Where, O_{no} : oxygen value determined without the Mo-hood
 O_{use} " " " with " "

Relations between these data and the contents of Al or Mn are illustrated in Figs. 8 and 9. The reason of

employing O_{use} as the basis is that, as previously mentioned, the accurate oxygen value was not obtained even with the use of Mo-hood and so the O_{use} values were used as a temporary basis of the calculation.

By Figs. 8 and 9, it is known that the effects of Al or Mn on the oxygen determination are quantitative and similar in both apparatus. As shown in Fig. 9 the influences of Mn on the capsule shaped pure iron and alloy steels were nearly equal unrelated to the kind of samples.

3. Relations among the Analytical Results of the Condensed Metallic Film and the Residual Metals in the Crucible and the Oxygen Values Determined

It was already described that there was a close relation between the oxygen values and the condensed metallic film deposited on the inner wall of the furnace tube. To study the details of this problem the composition of main components—Fe, Mn and Al—was obtained by dissolving the film into acid solution after the gas analysis. In this experiment other metals were found negligible. At the same time on the residual metals in the graphite crucible, the quantities of remaining Mn and Al were determined. The analyses corresponding to each oxygen values in Tables 9 and 10 were performed and the results are shown in Tables 11 and 12.

From the evaporated quantity of the metals obtained by the results for residues in the crucible, it was realized that the higher the content or addition of Mn or Al, the larger its evaporated quantity.

The evaporation unit of Mn, which is equivalent to the evaporation quantity for a gram of the sample, is shown in Fig. 10 relating with Mn content. Of the Mn vaporization it was found that the evaporation unit was generally in proportion to the Mn content (or addition) regardless of the kinds of samples or the employment of the Mo-hood. The slightly lower lines with the use of Mo-hood were regarded due to its prevention of violent evaporation of Mn. The Al evaporation was, as a whole, less than that of Mn,

Table 11. Analyses of condensed film on the inner wall of the furnace tube and residual metals in the graphite crucible. (Const. press. Orsat type)

Sample	Mn or Al content (%)	Mo-hood	Oxygen value determined (ppm)	(A) Total weight of specimens	(B) Metals condensed on the inner wall of the furnace tube			Condensation unit (B)/(A)			*Residual metals in the graphite crucible			**Evaporated metals from the crucible	
					Fe (mg)	Mn (mg)	Al (mg)	Fe (mg/gr)	Mn (mg/gr)	Al (mg/gr)	C (%)	Mn (%)	Al (%)	Mn (mg)	Al (mg)
No. 3 (S35C)	Mn 0.70	use	49.3	12.76	—	29.06	0.311		1.97		7.78			47.21	
		no	29.6	14.54	992.21	47.26	0.659	60.21	2.87		8.72	0.22	—	73.79	
No. 5 (En15)	Mn 1.44	use	15.0	16.20	25.10	70.95	0.1192	1.55	4.38		7.38	0.33	⁽⁰⁾ 0.019	170.13	
		no	6.2	15.07	277.10	72.16	0.211	18.39	4.79		7.80	0.36	⁽⁰⁾ 0.018	163.75	
No. 1 (Pure iron)	Mn (added) 0.20	use	88.8	15.28	43.21	15.76	0.321	2.84	1.00		6.48	0.07	0.010	22.81	
		no	81.5	14.66	379.22	14.59	0.304	25.87	1.04		8.27	0.07	0.010	21.52	
No. 1 (Pure iron)	Mn (added) 0.50	use	80.1	15.39	31.62	21.09	0.189	2.06	1.37		8.27	0.13	⁽⁰⁾ 0.007	56.10	
		no	55.0	14.89	472.61	28.97	0.442	31.74	1.95		8.27	0.15	⁽⁰⁾ 0.010	53.17	
No. 1 (Pure iron)	Mn (added) 1.00	use	82.3	15.09	39.06	69.17	0.266	2.59	4.58		7.61	0.23	0.011	112.72	
		no	45.5	15.95	537.70	74.55	0.216	33.71	4.67		7.20	0.23	0.012	122.75	
No. 1 (Pure iron)	Al (added) 0.50	use	108.5	14.76	44.6	8.26	0.224	2.65		0.0133	8.26		0.435		0.81
		no	66.1	14.63	274.6	11.50	0.448	16.53		0.0270	7.54		0.361		16.00
No. 1 (Pure iron)	Al (added) 1.00	use	89.5	14.78	20.46	4.81	0.448	1.38		0.0303	7.64		⁽⁰⁾ 0.648		1.75
		no	61.8	14.43	485.46	3.20	1.805	33.64		0.1251	7.73		⁽⁰⁾ 0.814		7.07

* Figures in the brackets show insol. Al%. ** The value is corrected by carbon content of residual metals.

Table 12. Analyses of condensed film on the inner wall of the furnace tube and residual metals in the graphite crucible. (Const. vol. press. measuring type)

Sample	Mn or Al content (%)	Mo-hood	Oxygen value determined (ppm)	(A) Total weight of specimens	(B) Metals condensed on the inner wall of the furnace tube			Condensation unit (B)/(A)			*Residual metals in the graphite crucible			**Evaporated metals from the crucible	
					Fe (mg)	Mn (mg)	Al (mg)	Fe (mg/gr)	Mn (mg/gr)	Al (mg/gr)	C (%)	Mn (%)	Al (%)	Mn (mg)	Al (mg)
No. 1 (Pure iron)	Mn 0.03 Al 0.016	use	112.5	29.95	165.0	2.32	0.144	5.11	0.08	0.0045	9.05	0.01	⁽⁰⁾ 0.007	16.70	2.99
		no	108.8	35.35	416.6	8.08	0.576	11.16	0.22	0.0154	9.00	0.01	⁽⁰⁾ 0.008	16.23	3.00
No. 2 (Permalloy)	Mn 0.21	use	193.0	26.42	55.6	4.16	0.185	2.11	0.16		6.58	0.05	⁽⁰⁾ 0.010	40.45	
		no	186.0	29.15	325.4	13.80	0.205	11.16	0.47		4.90	0.06	⁽⁰⁾ 0.007	42.10	
No. 3 (S35C)	Mn 0.70	use	50.9	28.32		15.79	0.608		0.56		9.78	0.26		118.93	
		no	30.2	25.92		55.82	1.024		2.15		7.40	0.24		125.36	
No. 4 (SuS27)	Mn 1.24	use	60.7	28.11		15.02	0.654		0.53		7.78	0.38	^(0.0006) 0.030	224.59	
		no	29.5	21.46		86.07	0.339		4.01		7.61	0.34	^(0.0008) 0.033	182.95	
No. 5 (En15)	Mn 1.44	use	21.7	30.70	54.1	16.37	0.339	1.76	0.53		6.52	0.44	⁽⁰⁾ 0.024	289.26	
		no	8.7	26.90	305.6	140.20	0.654	11.36	5.21		6.68	0.39	⁽⁰⁾ 0.021	270.95	
No. 1 (Pure iron)	Al (added) 0.50	use	93.4	27.38			0.426			0.0156	7.12	0	⁽⁰⁾ 0.186		86.93
		no	70.6	24.46			1.760			0.0720	9.41	0	⁽⁰⁾ 0.265		37.24
No. 1 (Pure iron)	Al (added) 1.00	use	92.3	28.73			1.440			0.0501	10.85	0	⁽⁰⁾ 0.618		75.07
		no	72.6	29.11			3.680			0.1264	7.88	0	⁽⁰⁾ 0.743		53.75
No. 1 (Pure iron)	Al (added) 1.50	use	92.8	28.05			1.392			0.0496	9.11	0	⁽⁰⁾ 0.940		141.70
		no	38.5	27.99			9.720			0.3472	7.45	0	⁽⁰⁾ 1.008		127.55

* Figures in the brackets show insol. Al%. ** The value is corrected by carbon content of residual metals.

especially little in the const. press. Orsat type apparatus but with the const. vol. press. measuring type one the evaporation unit grew in proportion with the increase of Al content. But clear relation between Al evaporation amount and its content as well as method of its addition, its evaporation speed, etc. was not obtained.

Secondary, the authors investigated the analytical data of the condensed film, which was regarded as directly relating to oxygen determination. In the following considerations the condensed film on the Mo-hood was excluded since the temperature on its surface, when the analysis had been performed, had been over

Fig. 10. Relation between Mn content and evaporated Mn weight

900°C which was regarded as far higher than the carbon monoxide gas adsorption temperature.^{1),2)} In accordance with the increase of the content of Al or Mn in the samples each quantity in the condensed film was increased. The Al condensation was less than that of Mn or Fe and particularly Fe condensation was large in both apparatus in the case of Mo-hood being not used. It was recognized that the Mo-hood was very effective for the reduction of the condensation of these metals on the inner surface of the furnace tube.

Now to get the relations with the oxygen values, the condensation rate, which was calculated dividing the condensation unit in the case of Mo-hood being not used (refer to the column of the condensation unit (B)/(A) in Tables 11 and 12) by that with Mo-hood, was compared with the oxygen extraction rate.

$$\text{Condensation rate} = \frac{\text{Condensation unit}_{(\text{no})}}{\text{Condensation unit}_{(\text{use})}}$$

Where, Condensation unit_(no): condensed quantity for a gram of sample in the case of Mo-hood being not used

Condensation unit_(use): condensed quantity for a gram of sample in the case of Mo-hood being used

They were plotted in Figs. 11 and 12 relating with the oxygen extraction rate. In general a large oxygen extraction rate, regardless of the employment of Mo-hood, corresponds to a small metal condensation, consequently to approximate unity in the condensation rate. On the contrary, the reduction of oxygen extraction rate means the increase of metal condensation in the absence of Mo-hood, that is, higher condensation rate. At the same time there was some difference between the two apparatus. In the const. press. Orsat type apparatus the variation of Al or Mn condensation rate was small and unrelated to the oxygen extraction rate but that of Fe was very remarkable. Compared with each condensation unit in both apparatus in Tables 11 and 12, it is nearly equal for the specimens of the same content. So it is considered that in the const. press. Orsat type apparatus even when the Mo-hood was used Al or Mn was gathered on the surface of the furnace tube due to the conditions of the shape of Mo-hood, dis-

Fig. 11. Relation between Fe, Mn, Al condensation rates and oxygen extraction rate. (Const. press. Orsat type)

Fig. 12. Relation between Fe, Mn, Al condensation rates and oxygen extraction rate. (Const. vol. press. measuring type)

tance from the crucible, and extraction time. On the other hand, the relation of the oxygen extraction rate and the Al, Mn and Fe condensation rates for the const. vol. press. measuring type apparatus is shown in Fig. 12, from which it can be said that the prevention of deposition of metal vapors was remarkable and carbon monoxide gas was extracted sufficiently with the use of Mo-hood.

IV. Discussion

1. On the Extraction of Nitrogen

(1) It was made clear that the nitrogen extraction was inadequate even for a carbon steel (refer to Fig. 3) and that it was far more difficult for steels containing some elements which increase the nitrogen solubility^{7),10)~12)}, e.g. Cr, V, Mo, Mn, etc, under the present analytical conditions.

On this point, the reaction temperature, 1,850°C, is distinctly a satisfactory condition for dissociating the nitrides in steels completely by the heat and the carbon as indicated in the calculations by Z. M. Turovtseva, et al⁷⁾.

Thus it is considered that the nitrogen in molten steel does not exist as the nitrides which dissociate at low temperature but as the solute of the increased solubility which is caused by the activity coefficient lowered by Cr, V and Mo^{10)~12)} contained.

For example, quoting the research made by S. Maekawa, et al. on the influence of some elements on the nitrogen solubility in molten iron, it can be said that the increase of the following elements from 0 to 5% corresponds to the increase of nitrogen solubility from 400 to 1,500 ppm for V, 400 to 750 ppm for Cr, 400 to 500 ppm for Mn and 400 to 480 ppm for Mo respectively.

Consequently it is considered that the delay of nitrogen extraction results in the release of the gas, controlled only by the diffusion from the surface of the melt in the crucible to the vacuum vessel. There are of course several complex problems such as the violent boiling of carbon monoxide gas by the reaction of carbon and oxides, the solubility reduction of nitrogen by the dissolution of carbon from the graphite crucible accompanying the increase of viscosity, and the formation of a thin layer of viscous carbide at the upper part of molten metals, and therefore it may not be easy to make a decisive conclusion here.

(2) On the nitrogen adsorption by the condensed film of the inner surface of the furnace tube, no difference was seen either with the use of Mo-hood or without it as shown in Table 5. This is in accordance with other reports published^{7),9),13),19)}.

(3) To obtain the accurate nitrogen content by the vacuum fusion method, the followings are considered. (a) The employment of a suitable flux or bath metal to promote the activity of nitrogen in the molten steel, which brings about an acceleration of gas exhaustion and the prevention of the increase of viscosity. (b) The improvement of the mercury diffusion pump to accelerate the diffusion of gases from the molten metal surface that is regarded as the rate determining step of the nitrogen extraction.

2. On the Extraction of Carbon Monoxide and the Effect of Mo-Hood

(1) It was ascertained that such elements as Al and Mn lowered the oxygen values in the experiments with pure iron to which these elements were added. It was made clear that the oxygen values were reduced with the increase of these interfering elements, and the quantitative relations between Al or Mn and the

analytical values of oxygen, which has been indistinct hitherto, was caught to some degree. While a slight decrease in oxygen values was observed even in such a lower content of Mn as 0.03% and 0.05% for No. 1 and No. 7 samples of pure iron in Table 10.

(2) To interrupt the above-mentioned effect of Al or Mn, the Mo-hood covered on the quartz tube indicated a considerable merit. Because of its imperfection, however, there remain some questions in obtaining the accurate oxygen content of steels containing such harmful elements by an ordinary analytical technique.

The temperature of the interior wall of the furnace tube rises up to the maximum carbon monoxide adsorption range^{1),2)} of Fe, Mn and Al condensed film, 300°~500°C, independently of the employment of Mo-hood. As for the Mo-hood it is over 900°C during analyses, therefore little adsorption by the deposited metals occurs. Accordingly, with the use of Mo-hood the formation of the condensed film on the furnace tube is decreased, which results in the extreme reduction of the adsorption reaction area, whereby the analytical results of oxygen is improved.

3. The Analytical Results of the Components of the Condensed Film and the Residual Metals in the Graphite Crucible

From the data obtained the following can be summarized:

(1) Between the improvement of oxygen value and the reduction of Fe, Mn, and Al—the components of the condensed film—some quantitative relations are conceived.

Thus when a sample contains Mn or Al, the condensed film composed of Fe, Mn and Al adsorbs the carbon monoxide gas extracted by reaction, whereby the oxygen value in analysis is lowered.

(2) Through the analysis of the residual metals in the graphite crucible which was performed in order to investigate the condensation mechanism of the metallic film on the inner surface of the furnace tube, it was known that large quantities of Al or Mn were vaporized and flown out. The quantity was proportional to its content in the case of Mn. In some preliminary experiments, the condensation units and the evaporation units of Mn after the analyses of the first, second, and *n*th specimen respectively were found nearly constant and they were almost controlled by only the Mn content of the specimen. This is thought due to the molten metal bath being at a stationary state (a state on a half way to the equilibrium) at the end of the gas extraction of each specimen. Namely, evaporated quantity may be controlled by the vapor pressure, evaporation rate at the analytical temperature of 1,850°C and the content of each metal.

For references the evaporation rates and the vapor pressures of several metals are shown in Table 13.

From this table it is understood that vapor pressures of Mn and Al are extremely high and their vaporizations are very active at analytical temperature. The evaporation rate at 1,850°C in the table is calculated by Z. M. Turovtseva's equation⁷⁾ insert-

Table 13. Vapor pressures and evaporation rates of various metals^(6)~9)

Element	Phase	$P=1.0\text{ mmHg}$		$1,850^{\circ}\text{C}$	
		Temp. ($^{\circ}\text{C}$)	Evaporation rate ($\text{mg}/\text{cm}^2\cdot\text{sec}$)	P (mmHg)	Evaporation rate ($\text{mg}/\text{cm}^2\cdot\text{sec}$)
Al	l	○ 1,270	○ approx. 7.5		
				△ 14.20	× 101.9
		□ 1,537		□ 16.18	× 116.1
Fe	l	○ approx. 1,770	○ approx. 9.5		
		△ approx. 1,810		△ 0.77	× 7.3
		□ 1,910		□ 0.55	× 5.2
Mn	l	○ 1,240	○ approx. 15.0		
		△ 1,250		△ 238.7	× 2,241.9
				□ 140.6	× 1,320.4
Pt	l	○ 2,580	○ approx. 10.8	○ 5.0×10^{-4}	× 0.0088
		△ 2,580		△ 3.5×10^{-4}	× 0.0062
		□ 2,689		□ 4.6×10^{-4}	× 0.0081

△ J. F. Elliot & M. Gleiser¹³⁾, ○ S. Dushman¹⁶⁾, × Z. M. Turovtseva & L. L. Kunin⁷⁾,
□ Kinzoku Binran (Metals Hand-Book of Japan)¹⁷⁾ (1960).

ing the values of vapor pressure.

(3) As explained above the formation mechanism of the metallic condensed film has been studied and the eliminating method of carbon monoxide adsorption by this film is considered as follows: reducing of the maximum adsorption areas as much as possible, increasing of the extraction pump speed and, in addition, lowering of the partial pressure of Mn or Al in molten sample.

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