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Determination of Manganese in Ferromanganese and Chromium in Ferrochromium by X-Ray Fluorescent Spectroscopy*

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Synopsis

In order to determine alloying elements in ferromanganese and ferrochromium, the application of calibration curve method and of calculation method by Hirokawa's equation was examined. Samples for X-ray irradiation were powder samples and solution samples. Powder samples were prepared by mixing the acid solution of samples with the graphite powder, which was evaporated to dryness. However, the solution samples were prepared by dissolving ferromanganese with nitric acid and by fusing ferrochromium with sodium peroxide. Using these samples, manganese in ferromanganese or chromium in ferrochromium was determined within the standard deviation of about 3.5 per cent.

I. Introduction

X-ray fluorescent spectroscopy was applied in the analysis of high alloy steels and other metals⁽¹⁾, but this method has been hardly applied in the determination of alloying elements in ferroalloys.

One superiority in X-ray fluorescent spectroscopy is nondestructive method, but for this purpose, homogeneous samples were required. Generally, segregation or porosity exists in ferroalloys, and it is necessary to prepare homogeneous samples by making powder or solution. In this report, the determination of major alloying elements in the ferroalloys were examined, and practical and rapid analytical methods for ferromanganese and ferrochromium were established.

II. Apparatus, samples and reagents

1. Apparatus

G.E. X-ray spectrometer type XRD-5 with Machlett AEG-50 S tungsten target, LiF analyzer, 0.010-inch solar slit and 2SPG detector were used. X-ray irradiated area was controlled by aluminium plate with a round window 15 mm in diameter. Polyethylene dishes 12 mm in diameter and 3 mm in depth were used as the powder samples and a polyethylene cell which was shown in Fig. 1 was used in the solution

* The 1087th report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in *J. Japan Inst. Metals* **26** (1962), 443.

(1) K.P. Koh and B. Caugherty, *J. Appl. Phys.*, **23** (1952), 427; K. Hirokawa, *Sci. Rep. RITU*, **A 14** (1962), 278.

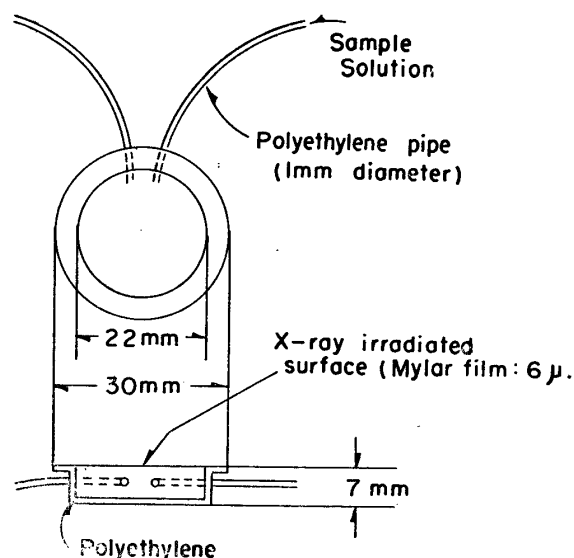


Fig. 1. Polyethylene cell used for solution sample

method.

2. Samples and reagents

Ferromanganese was ground to powder under 120 mesh. Ferrochromium was prepared by breaking with shaper to about 20 mesh. Standard samples were prepared by mixing electrolytic manganese or chromium with electrolytic iron. Graphite powder of 200 mesh which contained less than 150 ppm of ash, sulfuric acid, nitric acid, perchloric acid and sodium peroxide were used.

III. Determination method

1. Measurements

In the X-ray fluorescent spectroscopy of alloys, the interelement-effect must be taken into consideration. The absorption parameter method^{(2),(3)} and the other methods^{(4),(5)} have been used to compensate the effect. The ferromanganese and ferrochromium are considered as the binary alloy with iron. Therefore, the greater part of interelement-effect of these samples are considered caused by iron. In this paper the dilution method was used to eliminate the interelement-effect.

The X-ray intensity was measured under the following condition. The excitation source was 30 kV and 15 mA, the spectral lines used were manganese K_{α} line and chromium K_{α} line, and the selected position of background was 68.0 ($2\theta_{LiF}$) for manganese and 74.0 for chromium. The counting method used was the fixed count-

(2) H.J. Beattie et al., *Anal. Chem.*, **26** (1954), 980.

(3) K. Hirokawa, *Sci. Rep. RITU, A* **14** (1962), 288.

(4) B.J. Mitchell, *Anal. Chem.*, **30** (1958), 1894.

(5) E.L. Gunn, *ibid.*, **29** (1957), 184; F. Claisse, *Norelco Repr.*, **4** (1957), 3.

ing method. At the peaks of spectrum 1000~20000 counts were taken and 100~400 counts were taken at the backgrounds. The average counting values of 5 times were taken as analytical values.

2. Sample preparation

(i) Powder sample

The powder sample is generally prepared by pressing the powder, or mixing the sample with the material of low absorption effect such as graphite powder, cellulose powder and others⁽⁶⁾. In order to obtain a high accurate value by the powder method, it is necessary to make the powder of about 400 mesh down. However, it is almost impossible to pulverize rapidly ferromanganese and ferrochromium. Therefore, the powder sample for X-ray irradiation was prepared as follows:

In 100 ml beaker was placed 0.100 g sample to be dissolved with 10 ml of nitric acid for ferromanganese or 10 ml of hydrochloric acid for ferrochromium. To this solution 1.00 g of graphite powder was added and mixed well. The mixture was evaporated on the hot plate kept at 300~400°C. After drying, the heating was continued for 2~3 hours under this condition to remove completely excess of acids. The dried material was pulverized and mixed well in an agate mortar. Standard samples for preparation of working curves was prepared from a mixture of electrolytic manganese or chromium with proper amounts of electrolytic iron, and was treated in the same way as above.

(ii) Solution sample

When solution samples were used the X-ray intensity was affected by kind and concentration of reagents in the solution, especially decomposition reagents of the sample. This was also pointed out by Houk and others⁽⁷⁾. To test this effect, the following experiments were performed. X-ray intensity of manganese in the various acid concentration of nitric acid or sulfuric acid was measured. X-ray intensity of chromium in the various concentration of perchloric acid was tested. Again in the case of ferrochromium, a sample was fused with sodium peroxide and diluted to 250 ml with water. After dry filtration, X-ray intensity of chromium, i.e. the effect of sodium hydroxide, was also measured. These results are shown in Figs. 2 and 3. There was a little absorption effect of X-ray intensity of manganese in nitric acid solution. The effect of chlorine on X-ray intensity of chromium was great, but the effect of sodium peroxide was little. By making reference to these experiments, the solution samples were prepared by the following procedures.

In 10 ml of concentrated nitric acid 0.500 g of ferromanganese was dissolved and a few drops of hydrogen peroxide solution were added, then diluted to 50 ml with water in a volumetric flask.

In a nickel crucible 1.000 g of ferrochromium was fused with 10 g of sodium peroxide and decomposed with water. The solution together with the precipitate

(6) K. Hirokawa, *Sci. Rep. RITU*, **A 13** (1961), 263.

(7) W.W. Houk and L. Silverman, *Anal. Chem.*, **31** (1959), 1069

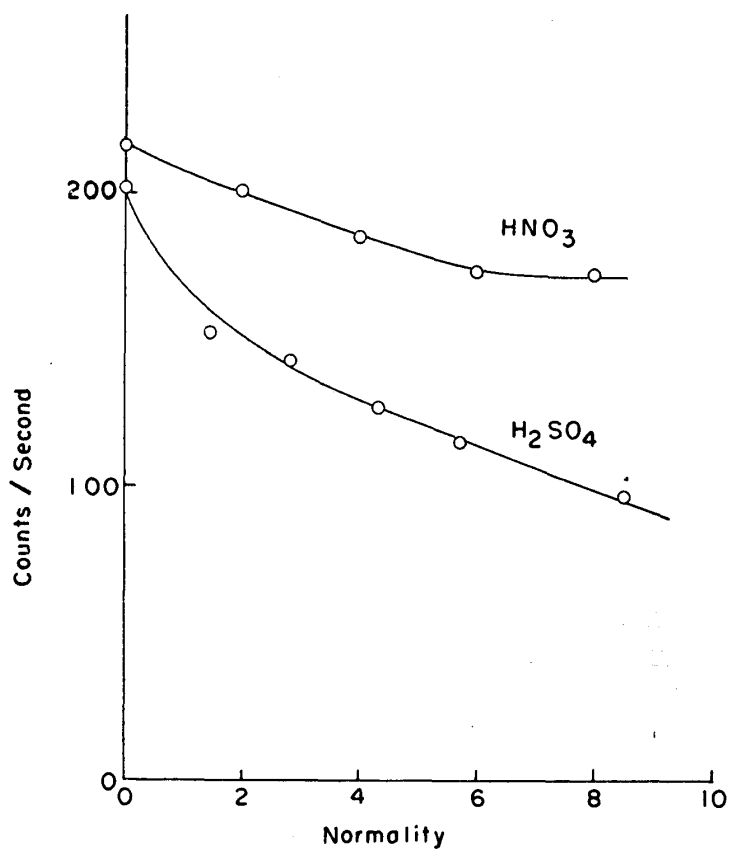


Fig. 2. Effects of acids on X-ray intensity of manganese. (Mn : 4mg/ml)

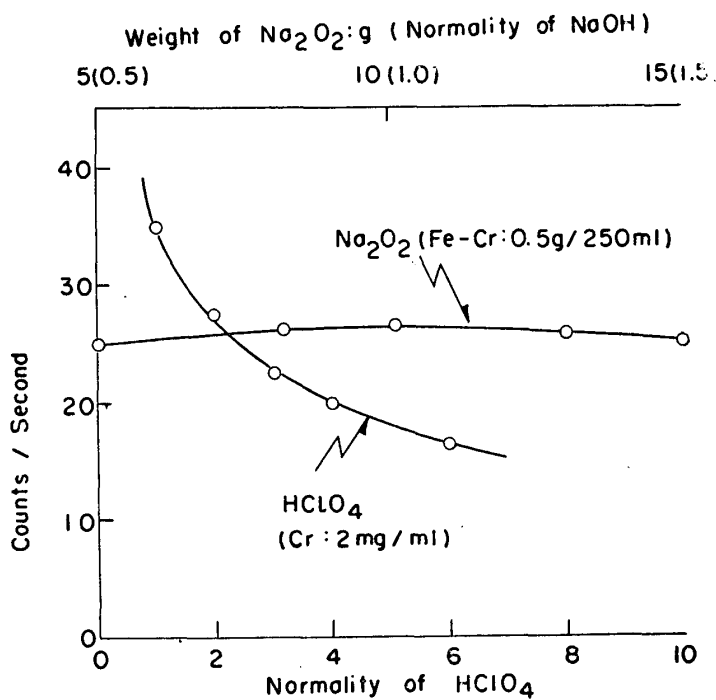


Fig. 3. Effect of acid or alkali on X-ray intensity of chromium.

of ferric hydroxide was transferred to a 250 ml volumetric flask and diluted with water to the mark. The filtrate was used as a sample for X-ray irradiation. Standard samples were prepared by the same method by mixing the electrolytic manganese or chromium with proper amounts of electrolytic iron.

3. Working curve

(i) Powder sample method

As the compensative reference sample electrolytic manganese or chromium was treated in each method. The results are shown in Fig. 4. In this study, the true concentration of manganese or chromium in X-ray irradiated samples was less than about 10 per cent. A linear calibration curve was obtained, for 0~100 per cent manganese in ferromanganese but a convex calibration curve was obtained for chromium in ferrochromium. It was assumed that chromium K_{α} line was affected more greatly by iron than manganese K_{α} line, and respectable chlorine remained in the X-ray sample of ferrochromium owing to the dissolution with hydrochloric acid, i.e., this extra chlorine considerably affected the X-ray intensity, accompanied by an increase in chromium content in the sample. It was considered that the linear calibration curve could have been obtained if the dilution ratio had been increased 2 times that in this experiment. However, this notion was not carried out in this experiment, for the following solution method was much better than the powder method in many points.

(ii) Solution sample method

The calibration curves for 60~90 per cent manganese and for 50~70 per cent

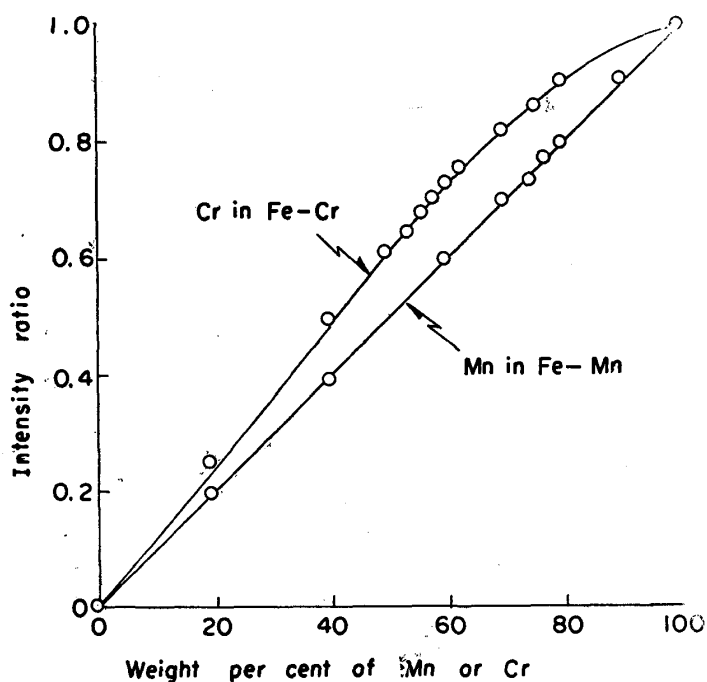


Fig. 4. Calibration curves obtained by powder sample method.

chromium are shown in Fig. 5. The concentration range was selected from the concentration range of Japanese Industrial Standard of ferroalloys. The mixed standard sample of 60 per cent chromium and 40 per cent iron for ferrochromium or of 75 per cent manganese and 25 per cent iron for ferromanganese was used as the compensative reference. The calibration curves were straight lines in this concentration range.

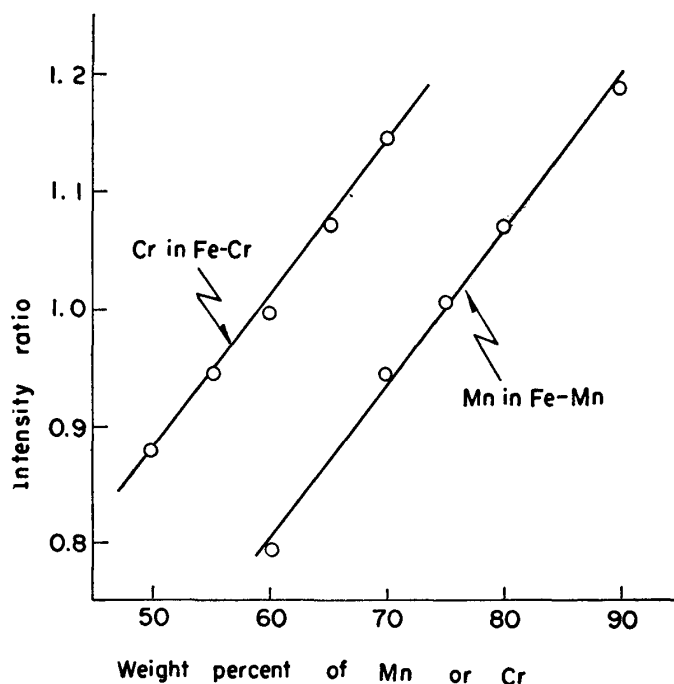


Fig. 5. Calibration curves obtained by solution sample method

4. Results

By using the calibration curves shown in III-3, manganese and chromium were determined from practical samples of ferromanganese and ferrochromium. The analytical results are shown in Table 1. The precision of these methods is shown in Table 2. From these results it was recognized that the solution samples gave better accuracy than the powder sample. Many factors were considered to be responsible a little errors in the powder method, the factor most responsible was the remains of decomposed reagents of the samples. For example, it was ascertained in experiments that the X-ray intensity of analyzed element was affected by the remaining reagents when the removal of the reagents was incomplete. Compared with this method, the solution method had little interelement-effect, for the matrix was water which contained a definite amount of nitric acid or sodium hydroxide. In the determination of ferromanganese, the iron in the sample remained in the solution, but it had little effect on the X-ray intensity owing to the dilution with water. In the determination of ferrochromium, iron was separated from the solution as hydroxide and nickel which may have been dissolved from the nickel crucible was

Table 1. Results of determination of manganese in ferromanganese and chromium in ferrochromium.

Samples		Chemical analysis (%)	X-ray analysis (%)			
			Powder method		Solution method	
			Results	Deviation	Results	Deviation
Cr in ferro-chromium	A	62.01	62.07	+0.06	62.17	+0.16
	B	63.41	62.28	-1.13	63.64	+0.23
	C	63.52	63.30	-0.22
	D	64.80	63.75	-1.05	64.72	-0.08
Mn in ferro-manganese	A	76.06	76.85	+0.71	76.43	+0.37
	B	75.28	75.33	+0.05	75.32	+0.04
	C	75.03	74.48	-0.55	75.16	+0.13
	D	74.54	75.06	+0.52	74.49	-0.05

Table 2. Precision of the analytical results.

Method of X-ray analysis	Samples	Analytical results (%)	Average (c/s)	Standard deviation (%)
Powder method	Fe-Cr A	62.01	836.6	2.67
	Fe-Mn D	74.54	2154	3.45
Solution method	Fe-Cr A	62.01	53.80	0.93
	Fe-Mn D	74.54	356.7	1.16

adsorbed with ferric hydroxide. This fact was experimentally ascertained from the charts of the X-ray spectrogram of the sample solution. Then the solution method was considered to be more efficient than other methods for rapid routine analysis.

IV. Application of the calculation method

The calculation method reported by K. Hirokawa⁽⁸⁾ was applied to these samples. In the calculation method, two standard samples containing the same components as the sample to be analysed were used. That is, the X-ray intensity of each standard sample was measured, and the contents of the element in the unknown sample was calculated from its X-ray intensity. The equation is as follows:

$$\frac{\frac{I_a}{I_b} \cdot \frac{W_b}{W_a} - 1}{W_b - W_a} = \frac{\frac{I_a}{I_x} \cdot \frac{W_x}{W_a} - 1}{W_x - W_a}$$

I: X-ray intensity of the objective element.

W: Weight fraction of the objective element.

a and b: Subscript of standard sample a and b.

x: Subscript of unknown sample.

(8) K. Hirokawa and H. Gotô, *Z. anal. Chem.*, **185** (1962), 124.

Table 3. Calculation results of solution sample method.

Sample		Chemical analysis (%)	X-ray analysis			
			Intensity (c/s)	Calibration curve method (%)	Calculation results (%)	Deviation (%)
Cr in ferro-chromium*	A	62.01	53.80	62.17	62.23	+0.06
	B	63.41	54.65	63.64	63.44	-0.20
	C	63.52	54.38	63.30	63.05	-0.25
	D	64.80	5.41	64.72	64.52	-0.20
Mn in ferro-manganese**	A	76.06	356.6	76.43	76.43	0.00
	B	75.28	360.4	75.32	75.29	-0.03
	C	75.03	359.8	75.16	75.15	-0.01
	D	74.54	356.7	74.49	74.46	-0.03

* Standard samples: Wa=0.55, Ia=48.57, Wb=0.95, Ib=55.75

** Standard samples: Wa=0.75, Ia=359.1, Wb=0.80, Ib=381.9

Table 4. Calculation results of powder sample method.

Samples		Chemical analysis (%)	X-ray analysis			
			Intensity (c/s)	Calibration curve method (%)	Calculation results (%)	Deviation (%)
Cr in ferro-chromium*	A	62.01	836.6	62.07	62.62	+0.55
	B	63.41	838.9	62.28	62.70	+0.42
	D	64.80	855.6	63.75	64.20	+0.45
Mn in ferro-manganese**	A	76.06	2216	76.85	77.10	+0.25
	B	75.28	2162	75.33	75.23	-0.10
	C	75.03	2138	74.48	74.39	-0.09
	D	74.54	2154	75.06	74.93	-0.13

* Standard samples: Wa=0.40, Ia=554.5, Wb=0.80, Ib=1040

** Standard samples: Wa=0.20, Ia=577, Wb=0.90, Ib=2587

The results calculated from the X-ray intensity of the solution samples and the powder samples are shown in Tables 3 and 4. Standard samples were selected from the standard samples used in the preparation of the calibration curves.

From these results, it was seen that this calculation method corresponds to the calibration curve method in precision. Moreover, it was not necessary to prepare many standard samples to make calibration curves. It was a very efficient method.

V. Discussion

The solution method was more accurate and quicker than the powder method for X-ray fluorescent analysis of ferroalloys, and so applications of the solution method to some other ferroalloys were conceivable. Sodium peroxide procedure can be applied to the element that forms metal peroxide ion in alkaline solution, such as ferromolybdenum, ferrotungsten and ferrovandium. The acid solution methods can be applied to all the ferroalloys which dissolve in acids. In this

method, it must be taken into consideration that there is a difficulty of keeping the dissolved reagents at a constant concentration, for the X-ray intensity is affected by the concentration of reagents. On the other hand, such characteristic X-ray with short wave length as zirconium or molybdenum, i.e., zirconium K_{α} or molybdenum K_{α} line, is hardly affected by the reagents. Therefore, the major component of these ferroalloys is easy to be determined by using the acid solution.

In the case of the powder method, it is not necessary to take into consideration the kind and the concentration of reagents, but it requires a considerably long time to remove the excess of reagents by heating. If the effects of remaining reagents can be eliminated completely, the powder method may be used for the analysis of all ferroalloys.

Summary

The rapid determination of manganese in ferromanganese and chromium in ferrochromium by X-ray fluorescent spectroscopy was investigated. In order to obtain a homogeneous sample for X-ray irradiation, samples were treated as follows. Powder sample: Graphite powder ten times the sample was mixed with the nitric acid solution of ferromanganese sample or hydrochloric acid solution of ferrochromium sample, and the mixture was evaporated and dried.

Solution samples: Ferromanganese was dissolved in nitric acid, and ferrochromium was fused with sodium peroxide. By using the powder samples manganese in ferromanganese or chromium in ferrochromium was determined within the standard deviation of about 3.5 per cent and the solution samples within about 1.5 per cent.

The calculation method by Hirokawa's equation was also applied to these ferroalloy samples with good results which were in agreement with those obtained by the calibration curve method.