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Determination of Alloyed Elements in Special Steels by X-Ray Fluorescent Spectroscopy. II Influence of Diverse Elements*

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Synopsis

A semiquantitative method of estimating the influences of various elements in the samples was examined. This method was based on the application of the equation, $I_{ae} = K_{ae} W_a / \Sigma_b W_b (\mu_b / \rho_b)$, which was used by E.N. Davis and which could also be derived from Beattie-Brissey's or from other's approximate equation.

I. Introduction

As described in the previous report, the calibration curve methods are often used, in analysing special steels by X-ray fluorescent spectroscopy. And in the case of non-destructive analysis, the influence of diverse elements is generally found. In order to estimate qualitatively the influence of diverse elements, two methods were carried out: (1) to consider the mass absorption coefficient of the accompanying elements in the spectral line of the element to be analysed; (2) to consider the position of absorption edge of each element. In some cases, the mutual enhancement effect was present. These tendencies could be obtained quantitatively by using absorption parameter from Brissey's⁽¹⁾ equation. However, in the multiple system this method is difficult to apply because it requires many standard samples and procedures. Therefore, the approximate equation which can also be derived from Beattie-Brissey's equation was used. This equation shows the relation between the X-ray intensity and the content of the element to be analysed. It may be possible to obtain the influence of the diverse elements semiquantitatively in some concentration range by using this equation. From this standpoint, the experiments on Cr-Fe and Ni-Fe system, were carried out.

II. Experimental results and discussion

Instruments, standard samples and measuring methods were the same as those in the previous report⁽²⁾.

* The 1065th report of the Research Institute for Iron, Steel and Other Metals.

(1) R.M. Brissey et al., *Anal. Chem.*, **26** (1954), 980 ; C. Sautier, *Rev. Mét.*, **54** (1957), 1.

(2) K. Hirokawa, *J. Japan Inst. Metals*, **24** (1960), 692; *Sci. Rep. RITU*, **A14** (1962), 277.

1. Principle and a few studies

In fluorescent X-ray spectroscopy, the approximate equation for the relationship between the X-ray intensity and the content of the element to be analysed is shown by E.N. Davis^{(3)~(5)} as equation (1).

$$I_{ae} = \frac{K_{ae} W_a}{\sum W_b (\mu_b/\rho_b)}, \quad (1)$$

where I_{ae} is X-ray intensity of the element to be analysed, W_a the composition of the component a, W_b that of the component b, (μ_b/ρ_b) mass absorption coefficient of b, and K_{ae} a constant containing excitation probability and others. The same equation was derived by the transformation of Beattie-Brissey's equation which shows the relation of the X-ray fluorescent intensity and the content of the element to be analysed under a definite condition. When K_{ae} is obtained to be nearly constant for an alloy in some concentration range, a suitable correction can be made or a suitable standard sample can be selected to obtain the necessary precision. Under this consideration, the possibility of applying this equation to Ni-Fe and Cr-Fe system was examined. Absorption coefficients of iron, manganese, nickel and chromium for nickel K_α line ($\lambda=1.659\text{\AA}$) and chromium K_α line ($\lambda=2.291\text{\AA}$), and X-ray intensity obtained experimentally were introduced into Eq. (1). The K_{ae} was obtained as shown in Table 1. In this case the excitation source was 20 kV and 15 mA, and K_{ae} value increased with the increase of

Table 1. Parameter K_{ae} of Ni in Fe-Ni alloy and Cr in Fe-Cr alloy.

Ni (%)	K_{Ni-Fe}	Cr (%)	K_{Cr-Fe}
10.97	5.93×10^5	3.44	1.63×10^5
19.71	$5.43 \times "$	9.54	$1.43 \times "$
38.46	$5.23 \times "$	18.38	$1.24 \times "$
49.78	$4.68 \times "$	28.90	$1.11 \times "$
59.74	$4.45 \times "$	40.50	$1.02 \times "$
69.70	$4.02 \times "$	48.52	$0.92 \times "$
79.76	$3.54 \times "$	59.96	$0.88 \times "$
89.41	$3.01 \times "$		

excitation potential. From the results in this table, it is said that K_{ae} value has a little deviation in a wide range of concentration but has little deviation in the range of any 10 per cent. Then it is considered that the equation can be used for Ni-Fe system or for Cr-Fe system. When K_{ae} value is nearly constant, the influence of the diverse elements can be estimated semiquantitatively by mathematical elimination of K_{ae} or by using K_{ae} obtained from the major system of alloys. Examples of application of this consideration are given as follows.

2. The influence of diverse elements on the determination of nickel and chromium in nickel-chromium steel

(3) E.N. Davis and R.A. Nordstrand, Anal. Chem., **26** (1954), 973.

(4) W.J. Campbell et al., Anal. Chem., **28** (1956), 960.

(5) H.A. Liebhafsky et al., Anal. Chem., **30** (1958), 580.

From Eq. (1), K_{ae} value for nickel-iron alloys of about 20 per cent of nickel, $K_{Ni-Fe}=5.5 \times 10^5$, was obtained. From this value the X-ray intensity for nickel was calculated, and the deviation of the X-ray intensity in the presence of chromium was also calculated. For chromium of 18 per cent in chromium-iron alloy, $K_{Cr-Fe}=1.24 \times 10^5$ was used, and the influences of nickel, molybdenum and titanium on the X-ray intensity of chromium were obtained. These results are shown in Table 2. From these results, the presence of 20 per cent nickel and 2 per cent of molybdenum tends to give low value of 1~2 per cent to 18

Table 2. Calculation of error using parameter.

Element to be analysed (%)	Coexisting element (%)	K_{ae}	X-ray intensity c. p. s.	Error (%)
Ni : 20	Fe : bal.	5.5×10^5	334	—
Ni : 20	Cr : 20 Fe : bal.	5.5×10^5	346	+0.7
Cr : 18	Fe : bal.	1.24×10^5	202	—
Cr : 18	Ni : 8 Fe : bal.	1.24×10^5	197	-0.2
Cr : 18	Ni : 20 Fe : bal.	1.24×10^5	191	-0.1
Cr : 18	Ni : 8 Mo : 2 Fe : bal.	1.24×10^5	186	-2.0

per cent of chromium. Therefore, when chromium of about 18 per cent is analysed with X-ray within the relative error of about 0.5 per cent by using the calibration curve of chromium-iron system, samples which has variations in nickel within 10 per cent, in molybdenum within 1 per cent and in titanium within 0.3 per cent should be selected. These results are also recognized from the data in Table 6 in the previous report⁽²⁾. When it is ascertained from the known samples that the value

Table 3. Composition of standard samples used to the determination of Cr in 25-20 stainless steel.

Sample	Ni(%)	Cr(%)	Other elements (%)
A	16.98	18.91	Mn : 0.48
B	21.15	24.16	Mn : 0.38, Si : 0.79
C	20.08	24.78	Mn : 1.4, Si : 1.84

of K_{ae} is nearly constant, and the major component of alloy is variable in the concentration range of 10 per cent, the influence of the diverse elements in the samples which have major component similar to that of the known sample can be obtained by the mathematical elimination of K_{ae} value or by using this value. In other words, the measuring error can be predicted when the calibration curve is made by standard samples which have major component similar to that of

samples to be analysed, and the error of the sample can be controlled by selecting a suitable standard sample. When the fixed time method is employed for measuring, the accuracy and the measuring time can properly be selected. The results of the application of this method to 25 per cent chromium-20 per cent nickel steel are given in the following. In this case chromium in these steels was tested. The composition of the sample which has the composition similar to that of the standard samples can be determined within the relative error of about 0.05 per cent. The calibration curve made with these standard samples is shown in Fig. 1. The measuring conditions were as follows: zinc

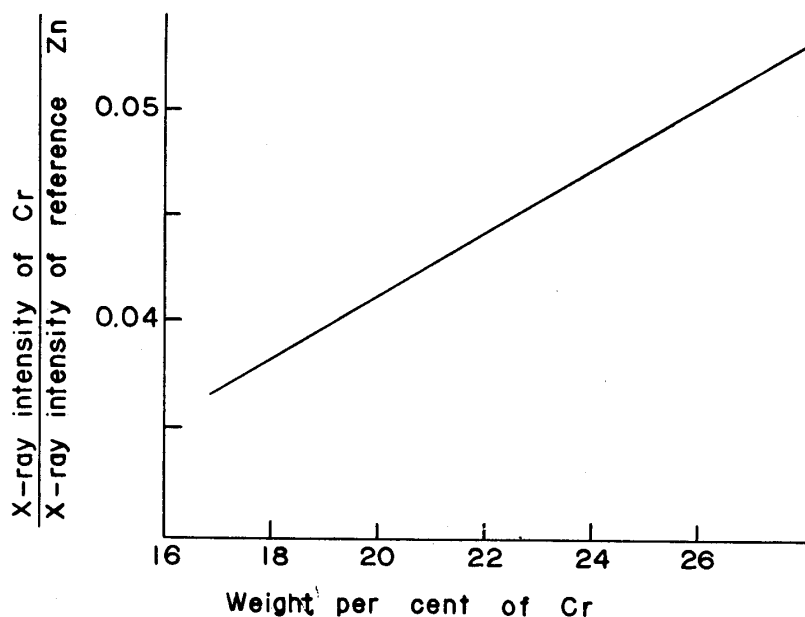


Fig. 1. Calibration curve for Cr in 25Cr-20Ni stainless steel.

metal window plate as compensative standard, chromium K_{α} line, and excitation source of 20 kV and 15 mA. The analytical results are shown in Table 4.

Table 4. Determination of Cr in 25-20 stainless steel.

Sample	Chemical analysis (%)	X-ray analysis (%)
a	24.76	24.72
		24.63
b	24.29	24.25
		24.28

These investigations were also applied to some nonferrous metals.

3. Studies on some nonferrous alloys

The application of Eq. (1) to copper alloy and to some nonferrous alloys will be described.

The application was first carried out with copper in brass samples containing 76

per cent copper, 2 per cent aluminium and residual zinc. $K_{\text{Cu-Zn}}$ value of this sample 3.5×10^5 was obtained from Eq. (1). Using this value, the accuracy of the analysis of practical samples containing about 0.5 per cent iron or nickel was calibrated. From this result, it was predicted that these actual samples would be determined within the accuracy of ± 1 per cent. When this $K_{\text{Cu-Zn}}$ value was eliminated mathematically, the accuracy was obtained within ± 0.7 per cent. This prediction was tested by comparing with the electrolytical results and X-ray analysis results, and the results are shown in Table 5. From this results it was recognized that the error was within the predictive limit. The measuring condi-

Table 5. Determination of Cu in Cu-Zu alloy.

Sample	X-ray analysis (%)	Chemical analysis (%)	Difference (%)	Other elements
C	75.67	76.79	-0.42	Al, P
D	76.25	75.97	+0.28	Al, Si, As
F	75.45	75.99	-0.50	Al, P, Fe
L	75.65	75.69	-0.04	Al, Ni, Sb
M	77.01	76.40	+0.61	Al, Fe, Bi
N	75.76	75.92	-0.16	Al, Ni, As
O	75.81	75.87	-0.06	Al, Ni, P
S	76.03	76.12	-0.09	Al, Ni, P
U	75.97	75.85	+0.12	Al, As

tions were as follows: copper K_{α} line, excitation source of 20 kV and 10 mA, and the background was taken at $2\theta=47^\circ$.

Copper in aluminium-copper alloys was next examined. For major component of 5~10 per cent copper and residual aluminium, the $K_{\text{Cu-Al}}$ value 2.2×10^5 was obtained from some standards. Now, X-ray intensity of copper in aluminium-copper alloy of 5 per cent copper was obtained 235 cps from Eq. (1). When this alloy contains 1 per cent of iron, the X-ray intensity of copper was calculated as 223 cps, and copper content was obtained to be 4.7 per cent. The presence of 1 per cent of magnesium gave the X-ray intensity of 236 cps and its influence is negligibly small. The presence of 1 per cent of manganese similarly gave about 0.3 per cent low value to 5 per cent of copper in X-ray analysis. These facts were also recognized from the actual samples with the calibration curve of copper-aluminium system. Again this equation was applied to iron in zinc, $K_{\text{Fe-Zn}}$ of about 9.0×10^6 was obtained for 0.05~0.5 per cent iron in zinc at the excitation source of 45 kV and 15 mA. Thus, when the X-ray intensity of the detectable limit was equal to that at the background, the detectable limit of iron in zinc was obtained to be 0.005~0.01 per cent by the calculation. This value agreed with the previous experimental value of about 0.01 per cent⁽⁶⁾.

As described above, to determine semiquantitatively the influence of diverse

(6) K. Hirokawa, Sci. Rep. RITU, A13 (1961), 263.

elements, the application of Eq. (1) was attempted with nickel and chromium in nickel-chromium steel, and iron, copper in some nonferrous alloys. From these results it was seen that the application of this equation was considerably effective. With other alloys except the previous samples, the effect of diverse elements may be obtained semiquantitatively from this method without trial and error method.

Summary

When nickel and chromium in stainless steel and alloyed elements in some alloys were analysed by nondestructive method, the influences of diverse elements should be examined. In many cases, the influences of diverse elements were ascertained from composition of major components of alloys and their mass absorption coefficients.

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