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著者	HIROKAWA Kichinosuke
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	14
page range	278-287
year	1962
URL	http://hdl.handle.net/10097/27096

Determination of Alloyed Elements in Special Steels by X-Ray Fluorescent Spectroscopy. I

Nickel and Chromium in Nickel-Chromium Steel and Tungsten in Tungsten Steel*

Kichinosuke HIROKAWA

The Research Institute for Iron, Steel and Other Metals

(Received July 4, 1962)

Synopsis

In order to analyze alloyed elements in some special steels, a calibration curve method was examined, in which the metal of the window of sample holder was used as the compensative reference. This method was recognized to be simpler and more suitable than other method for rapid analysis. Further, the influence of diverse elements on the result was considered in a binary system.

I. Introduction

The non-destructive analysis of non-ferrous metals ⁽¹⁾ and binary and ternary alloys ⁽²⁾ have been carried out by X-ray fluorescent method. This X-ray fluorescent analysis was also applied in determining tungsten in tungsten steels, and nickel and chromium in nickel-chromium steels, and some informations could be added to other previous investigations. ⁽³⁾–⁽¹⁰⁾

II. Experiment

1. Instruments

G.E. XRD-5 spectrometer with Machlett AEG-50S tungsten tube, lithium fluoride analyzer, 0.010 inch solar slit and 2SPG detector was used. To control

* The 1064th report of the Research Institute for Iron, Steel and Other Metals.

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the irradiation area of the sample, window plates made of zinc, lead and aluminium with irradiation area of 3.0 mm×17.0 mm or 3.5 mm×12.0 mm were used. The schematic diagram of the holding of sample is shown in Fig. 1. The beam flux coming into the detector was controlled with the beam tunnel. There-

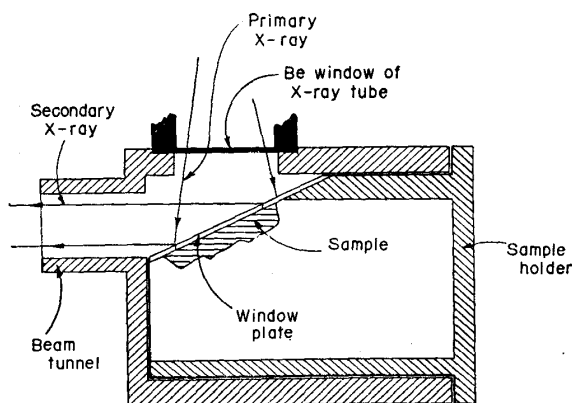


Fig. 1. Schematic diagram of sample holding

fore, a little deviation of the position of irradiation window can be allowable, if it is not out of the tunnel. However, when the metal of window plate is mild like lead, it is necessary to be cautious of the variation in the counting rate because of the bending of it.

2. Samples

The compositions of the samples used for the determination of tungsten in tungsten steel are shown in Table 1. Similarly, those of nickel-iron system and

Table 1. Chemical composition of Fe-W standard samples.

Sample	W(%)	Other elements (%)
W-0.5	0.46	Mn : 0.45
W-1.0	1.13	Mn : 0.50
W-2.5	2.49	Mn : 0.47
W-9	6.99	Mn : 0.43
W-8	10.03	Mn : 0.71
W-12	13.15	Mn : 0.88
W-16	15.10	Mn : 0.41
W-20	25.65	Mn : 0.51
W-27	28.38	Mn : 0.69
CoW-2.5	2.66	Mn : 0.60 Co:5.30

chromium-iron system are shown in Tables 2 and 3. The samples were all about 30 mm in length and 5.0~8.0 mm in diameter. Halves of these samples were cut into chips for chemical analysis and the others were used for X-ray analysis. The surfaces of the samples for X-ray analysis were finished smoothly with a shaper.

Table 2. Chemical composition of Fe-Ni standard samples.

Sample	Ni(%)	Other elements(%)
N-1	10.97	Mn : 0.25
N-2	19.71	Mn : 0.11
N-3	20.05	Mn : 0.16
N-4	38.46	Mn : 0.16
N-5	49.78	Mn : 0.14
N-6	59.74	Mn : 0.16
N-7	69.70	Mn : 0.17
N-8	79.76	Mn : 0.14
N-9	89.41	Mn : 0.16
N-10	99.9	

Table 3. Chemical composition of Fe-Cr standard samples.

Sample	Cr(%)	Other elements(%)
C-0.2	0.35	Mn : 0.20
C-2	1.20	Mn : 0.1
C-6	3.44	Mn : 0.1
C-8	7.81	Mn : 0.28
C-10	5.73	Mn : 0.1
C-16	9.54	Mn : 0.08
C-24	10.72	Mn : 0.1
C-28	29.90	"
C-30	18.38	"
C-33	33.78	"
C-38	37.42	Mn : 0.46
C-40	40.50	Mn : 0.51
C-45	44.06	Mn : 0.24
C-50	48.52	Mn : 0.36
C-55	52.90	Mn : 0.58
C-60	59.96	Mn : 0.48
C-100	99.9	

There was a little difference in the X-ray intensity whether surfaces of the samples were finished smoothly or not. The surface of sample was finished with a shaper to avoid the contamination with polishing materials⁽¹⁾.

3. Measurements

In the case of the calibration curve method, the major component of the sample⁽¹⁾, the pure metals of the element to be analysed^{(2),(3),(5),(6)}, and sample which has composition similar to that of the sample to be analysed^{(7),(8),(9)} were used as compensative reference. The major component cannot be used in the case of the special steels which contain various accompanying elements. Other methods are necessary to keep standard samples which have the suitable irradiated surfaces. In the present experiment, the method using the spectral line from the window plate as compensative reference was examined in order to simplify the procedure and to avoid keeping many standard samples. This method was carried out on consideration that the focus of primary X-ray on the window plate had a constant area and the strength of the X-ray was constant under the same condition. In

this case metals which can be used as a window plate of the sample holder should satisfy the following conditions: (1) the element in the sample should not be included in the metal of the window plate; (2) the metal of the window plate is most pure and can be obtained in plate form; (3) the spectral line of this element exists near the spectral line of the element to be analysed, but they do not overlap each other.

Lead, zinc, and copper metals which satisfy the previous conditions were tested as a window plate of the compensative reference. Pure metals of the elements to be analysed and the actual samples which have composition similar to that of the analysis samples were used as standards. Excitation sources were 20kV, 15 mA and 35 kV, 15 mA. Spectral lines used and backgrounds are shown in Table 4. The measuring was done by a fixed counting method, and 1000~200000 counts were measured at the peak of the spectral line, and 100~4000 counts were taken at the background.

Table 4. Analytical spectral lines used for analysis.

Element	Atomic number	Spectral line	Wave length (Å)	2θ angle LiF crystal	
				Spectral line	Background
W	74	L _{α1α2}	1.476	43.0	30.0
			1.487		
W	74	L _{β1}	1.282	37.12	30.0
Ni	28	K _α	1.659	48.64	46.5
Cr	24	K _α	2.291	69.34	74.0
Pb	82	L _{αα12}	1.175	34.0	30.0
			1.186		
Pb	82	L _{α1} 2nd	1.175	71.39	73.0
Zn	30	K _α	1.437	41.80	46.5

III. Results and discussion

1. Calibration curve for tungsten in tungsten steel

Under the conditions described in section II-3, the spectrograms of lead, zinc and copper window plates were tested together with samples. The charts are shown in Fig. 2, from which it will be seen that lead satisfies the required conditions. Zinc and copper have high backgrounds for tungsten and a strong intensity compared

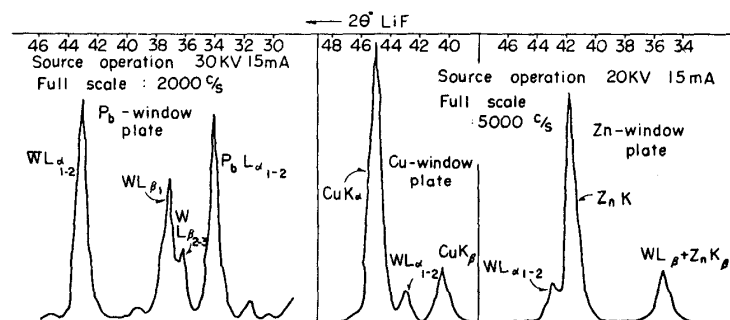


Fig. 2. Spectrograms with various window plate

with tungsten, because of their high quantum efficiency and large irradiation area. These results led to the use of the lead window plate or tungsten metal as compensative standard at the excitation source 35 KV and 15 mA. These results are shown together in Fig. 3. From this figure, it is recognized that these calibration curves have a high background of tungsten spectrum from the target. For $L_{\alpha 1}$,

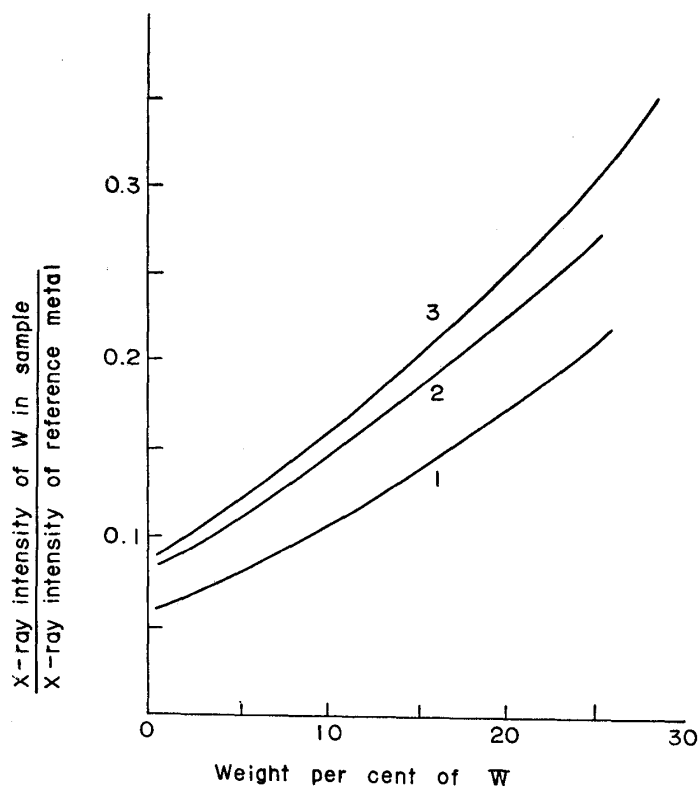


Fig. 3. Calibration curves for W

- 1: WL_{α} and Pb window plate
- 2: WL_{β} and Pb window plate
- 3: W metal as reference used

and $L_{\beta 1}$ lines of tungsten, the absorption effect of iron appeared and curves became convex.

2. Calibration curves for nickel and chromium in nickel-chromium alloys

On nickel-chromium alloys several works have been reported. In the system of Ni-Fe the calibration curve for nickel using nickel metal as compensative standard is concave, and for chromium in Cr-Fe system it is convex. These results are the same as those of Koh's and others. From the present author's and Koh's results the absorption parameters were calculated by Beattie and Brissey's method. These values are shown in Table 5. From these results it is recognized that the higher the excitation voltage, the smaller the absorption parameter becomes. Koh and others have not explained this phenomena, and the present author considers this as follows. By the Daune-Hunt's law the higher

Table 5. Absorption parameters of Ni in Fe-Ni alloys and Cr in Fe-Cr alloys.

Author	Tube source	Parameter of Ni	Parameter of Cr	Apparatus
Hirokawa	20kV, 15mA	2.314	0.572	G. E. XRD-5
"	30kV, 15mA	—	0.525	"
"	35kV, 10mA	2.318	0.509	"
P. K. Koh	20kV, 34.5mA	2.750	0.860	G. E. XRD-3
B. Caugherty ⁽⁵⁾	35kV, 34.5mA	2.153	0.708	"
"	50kV, 34.5mA	1.845	0.688	"
H. D. Durnham, J. Hower, L. C. Johnes ⁽⁶⁾	30kV, 10mA	2.279	0.541	North American Philips
B. J. Beattie, R. M. Brissey ⁽⁵⁾	48.5kV, 24.1mA 48.5kV, 49.6mA	2.420 —	— 0.271	G. E. XRD-3S "

the excitation voltage becomes, the shorter the critical wave length of short side of primary X-ray becomes. The maximum wave length λ_{\max} is given by the equation $\lambda_{\max}=1.5\lambda_c$. Therefore, elements which have short wave length will be more excited and the mutual enhancement effect increases. In addition to this, the element which does not emit the characteristic X-ray because of its high excitation potential will emit it by the higher applied voltage. From these results, the X-ray intensity of short wave length becomes stronger. In general, the mass absorption coefficient of each element is small at short wave length, and the absorption effect decreases. Therefore, it is necessary to measure X-ray intensity under the same condition as that under which the calibration curve is prepared. The calibration curves for nickel using the window plate of zinc, and for chromium using zinc and lead plate were also prepared. The irradiation area of these window plates was 3.5 mm \times 12.0 mm. The spectral lines used for zinc plate are shown in Table 4, the excitation source being 20 kV and 15 mA. For lead plate Pb $L_{\alpha 1}$ line (2nd), and 35 kV at 15 mA were used. The results for nickel and chromium are shown in Figs. 4 and 5, respectively. From these calibration curves the absorption effect of iron on nickel and the mutual enhancement effect of iron on chromium were observed.

3. Analytical results of the actual samples

By using the calibration curves of Figs. 3, 4 and 5, tungsten in tungsten steel, and nickel and chromium in nickel-chromium steels were determined. The results are shown in Table 6. From these results, it will be seen that for tungsten in tungsten steel, or nickel in nickel-chromium steel, the calibration curves which were made for several concentration ranges of Fe-W system or of Ni-Fe system could be used. For tungsten in tungsten steel, the mass absorption coefficient of $W L_{\alpha}$ line ($\lambda=1.476\sim 1.478$) and $W L_{\beta}$ line ($\lambda=1.242\sim 1.279$) is about 200~300,

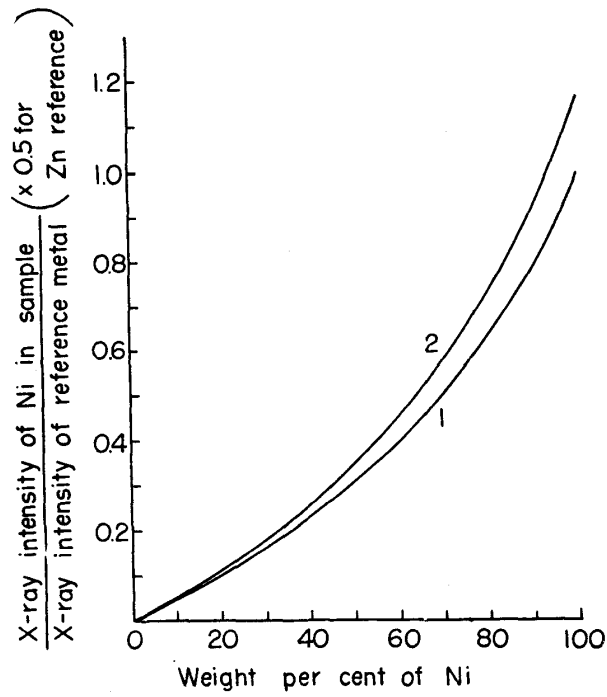


Fig. 4. Calibration curves for Ni
 1: Ni metal 2: Zn window plate as reference used

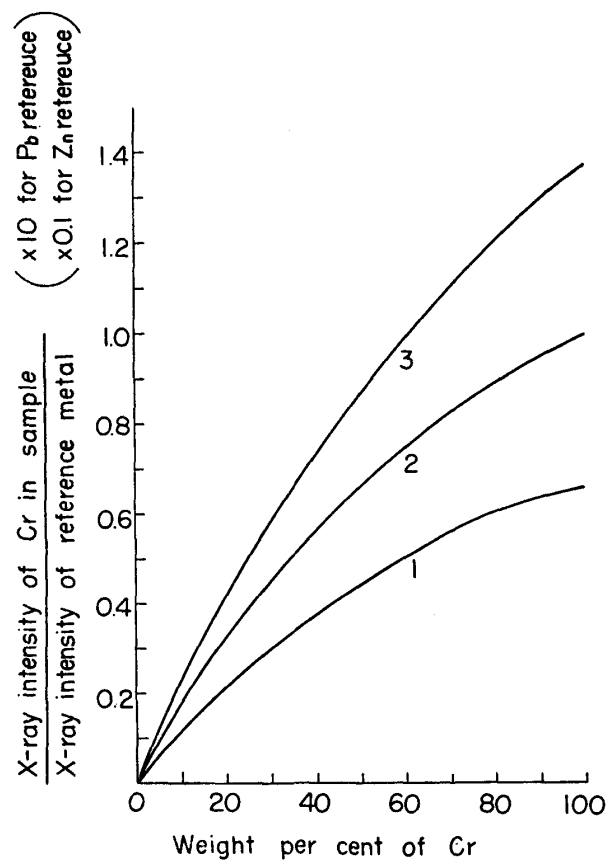


Fig. 5. Calibration curves for Cr.
 1: Pb window plate 2: Cr metal 3: Zn window plate as reference used

and that of cobalt is a little larger than that of iron, but the mass absorption coefficients of manganese, chromium and vanadium are 100~250. Therefore, the most effective element for tungsten is iron because of its large mass absorption coefficient and large content. When a sample contains in large quantity chromium, vanadium and molybdenum that have a smaller mass absorption coefficient for $W L_{\alpha_1}$ line than iron, the high measuring value is expected. This fact can be recognized from the results shown in Table 6. For nickel in nickel-chromium steel, the difference between X-ray analysis and chemical analysis is small; for example, the presence of about 20 per cent chromium has a little effect

Table 6. Determination of W in W steel, Ni and Cr in Ni-Cr steel, and Cr in Cr steel.

Sample	Element	Chemical analysis (%)	X-ray analysis (%)	Other elements (%)	
W steel	A	W	18.87	18.90	Cr : 3.76 Mn : 0.38 V : 0.97
	B	W	19.74	19.75	Cr : 4.62 V : 1.42 Co : 16.48 Mn : 0.73
	C	W	11.11	11.50	Cr : 4.40 V : 2.07 Mn : 0.31
	D	W	11.98	12.25	Cr : ca 4 V : ca 5
	E	W	3.28	3.40	Cr : 4.62 V : 2.03 Mo : 9.42 Mn : 0.49
Ni-Cr steel	A	Ni Cr	19.98 18.91	19.65 18.00	
	B	Ni Cr	19.81 19.51	19.90 18.50	Nb : 0.66
	C	Ni Cr	19.82 19.80	19.74 18.30	Ti : 0.064 Mn : 0.069
	D	Ni Cr	20.03 19.62	20.05 17.85	Mo : 1.90
	E	Ni Cr	18.81 19.15	20.00 16.55	Mo : 4.03
	F	Ni Cr	20.58 24.29	20.70 22.60	Si : 1.83 Mn : 1.43 Mo : 0.33
	G	Ni Cr	21.15 24.16	20.70 22.35	Si : 0.79 Mn : 0.38
Cr steel	A	Cr	10.72	10.75	Mn : 0.46
	B	Cr	18.23	18.60	Mn : 0.32

on the determination of nickel. This fact is similarly explained by the mass absorption coefficient of the diverse elements for nickel K_{α} line. For nickel K_{α} line, iron has the largest absorption coefficient in the matrix, followed by manganese, chromium, titanium and molybdenum in the order named. Therefore, if the calibration curve of Ni-Fe is used, the effect of presence of manganese, chromium and titanium having a smaller mass absorption coefficients than iron will be negligible. In this case, the presence of silicon and molybdenum having a small absorption coefficient gives high measuring value. These facts are also shown in Table 6.

Chromium in nickel-chromium alloy was next examined. When the calibration curve for Cr-Fe system was used, most measuring values except chromium steel were lower. The mass absorption coefficient also plays an effective part in this phenomenon. The mass absorption coefficients of iron, nickel, niobium, molybdenum and titanium at chromium K_{α} line are 115, and 145, 415, 439 and 603 respectively. When 20 per cent of chromium in nickel-chromium steel is determined, the variation of nickel in samples should be so controlled as to be below 10 per cent, molybdenum and niobium below 1 per cent and titanium below 0.5 per cent. The reason for this is that, when chromium of 20 per cent in chromium steel is determined, the presence of about 15 per cent of nickel, about 2 per cent of molybdenum or niobium, about 0.5 per cent of titanium gives a low value of 1~2 per cent to chromium compared with the standard value.

As described above, the influence of diverse elements can be examined by a trial and error method. In these experiments, it was recognized that the analysis error would be smaller if the standard samples which have composition similar to that of the sample to be analysed were used. However, it is doubtful whether the influence of the diverse elements can be estimated semiquantitatively or not when the mass absorption coefficient is used. These results will next be reported.

Summary

(1) The non-destructive analysis of tungsten in tungsten steel, and nickel and chromium in nickel-chromium steel was investigated with X-ray fluorescent spectroscopy.

(2) The calibration curve method using the metal of window plate as the compensative reference was examined. In this method it was not necessary to keep the standard samples as is the case with usual method. The results obtained by this method were as satisfactory as those obtained by the usual method.

(3) Tungsten in tungsten steel or nickel in nickel-chromium steel is influenced by iron that exists as major component in matrix. In these cases, the chemical analyses of these elements were in agreement with the results obtained by X-ray fluorescent spectroscopy using the calibration curve of Fe-W system or the calibration curve of Ni-Fe system. Chromium changes its X-ray intensity by the presence of a small amount of titanium or molybdenum. In this case the

composition of the sample should be determined by using the standard samples which have composition similar to that of the samples to be analysed or should be determined by using the suitable correction factors.

Acknowledgement

The author expresses his deep gratitude to Prof. Hidehiro Gotô for his guidance, to Prof. Shirô Ogawa and members of X-ray Service Division for technical cooperation in the use of X-ray instruments.