X–Ray Fluorescence Analysis of Iron, Nickel, and Copper in Titanium– and Zirconium–Based Alloys by Aqueous Solution Method*

Hidehiro Gotô and Akira Saitô

The Research Institute for Iron, Steel and Other Metals

(Received April 30, 1968)

Synospsis

A simple, rapid, and accurate method is described for the determination of iron, nickel, and copper in samples containing some refractory metals. Samples are dissolved in a mixture of nitric and hydrofluoric acid and saturated boric acid solution is added to the mxiture to mask the excess of hydrofluoric acid. Iron, nickel, and copper are determined directly in the final sample solution by X-ray fluorescence analysis. The effect of the concentration of hydrofluoric acid on the X-ray intensity of the element in interest was negligible below 2 normal. The interelement effects of iron, nickel, and copper, however, were considerably large, so a correction had to be considered for the diverse element. This proposed method brought the result so rapidly that it took only about 10 minutes for the analysis of one sample through. The relative errors of analytical results were below 3 per cent. This method, moreover, may have a broad applicability in the analysis of refractory metals in alloy steels and other alloys.

I. Introduction

The solution method in X-ray fluorescence analysis is effective for the samples which can be varied into solution, because of its simplicity, rapidity, and high accuracy. In practising, however, some problems have been left in this field, that is, the X-ray fluorescence intensities are affected by the concentrations of acids which are used to dissolve samples. Moreover, it is often difficult for the ordinary acids to dissolve the samples containing some refractory elements.

As for the absorption-enhancement effects and the variation of background intensity owing to the variation of acids and acid concentrations, various discussions have been done on the nitric, hydrochloric, sulfuric, and perchloric acids in the analysis of chromium, manganese, iron, nickel, and yttrium.[1]-[5] On the other hand, molybdenum, niobium, tantalum, and tungsten in steel samples were determined after the separation from the matrices.[6]

* The **1372nd** report of the Research Institute for Iron, Steel and Other Metals.
(1)   W.W. Houk and L.Silverman, Anal. Chem., **31** (1959), 1069.
(2)   R.W. Jones and R.W. Ashlay, ibid., **31** (1959), 1629.
(3)   B.J. Mitchell and H.J. O'hear, ibid., **34** (1962), 1620.
(4)   T. Shimanuki, K. Hirokawa and H. Goto, Sci. Rep. RITU, A **15** (1963), 124.
(5)   E. Asada and M. Matusda, Japan Analyst, **15** (1966), 1104.
(6)   M.L. Tomhins, G.A. Borum and W.A. Fahlbusch, Anal. Chem., **34** (1962), 1260.

In the present investigation, a simple preparation method was carried out for the X-ray fluorescence solution analysis of the samples containing large amounts of titanium and zirconium by using hydrofluoric acid.   In the results, 10 to 20 per cent of iron, nickel, and copper in titanium- and zirconium-alloys could be analyzed in a short time and with high accuracy.

II. Reagents and instrument

1. Reagents

Standard solutions of titanium, zirconium, iron, nickel, and copper: Metals of over 99 per cent purity were dissolved in nitric and hydrofluoric acid and made up to 5.00 mg/ml solutions.

Acid mixture for sample dissolution: 20 ml of nitric acid (60%), 20 ml of hydrofluoric acid (46%), and 60 ml of distilled water were mixed, which was preserved in polyethylene container.

Saturated boric acid solution: Boric acid was dissolved in warm water, and after cooling, the supernatant solution was used.

2. Instrument

The instrument was newly prepared in our laboratory.   It has an X-ray tube of Philips production and a scanner (Johanson type) of ARL production,

Table 1.   Operating condition of the X-ray spectrometer.

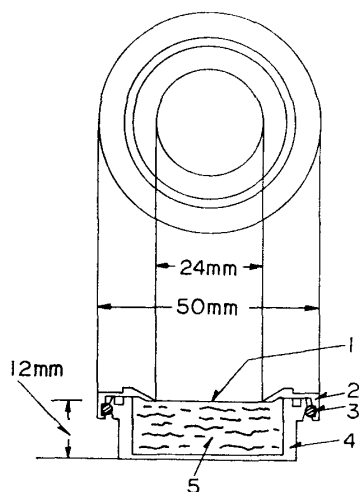|	
X-ray tube	W-target
X-ray tube voltage and current	FeKα 40KV-20mA
	NiKα CuKα } 30KV-10mA
Analyzing crystal	11″-Quartz
Detector	Kr-Multitron counter
Method of counting	Fixed time method
Counting time	30 sec

Fig. 1.   Sample cell for solution.
1. X-ray irradiation surface (6μ Myler film)
2. Aluminium
3. O-ring
4. Polystylene
5. Sample solution

and other parts were constructed by Shimadzu Seisaku-sho. The operating condition of the instrument is shown in Table 1.

A sample cell for solution was used as shown in Fig. 1.

III. Experimental conditions

In the solution method, the absorption effects of acids containing sulfur or chlorine on the X-ray fluorescence intensity are so large that the acid concentration of the sample solution should be strictly controlled in the accurate analysis. [2,3] For the elimination of absorption effect of acid concentration, on the other hand, an internal standard method was proposed[3]. These methods, however, are not only time-expensive but also little applicable to the samples containing titanium and zirconium.

In the present investigation, therefore, a mixture of nitric acid and hydrofluoric acid was used for the sample dissolution. This mixture can easily dissolve the refractory elements and has little absorption effect. Boric acid was used for preventing glasses from the corrosion by the hydrofluoric acid.

In the sense of elimination of the daily variation of the instrument operation, intensity ratios of the sample solutions to the standard sample solution were used instead of X-ray intensity.

1. Effect of the concentration of hydrofluoric acid

There have not been mentioned about the hydrofluoric acid in solution method. Therefore, the effect of the hydrofluoric acid concentration on the X-ray intensity was studied. As shown in Fig. 2, the intensities of Fe Kα and Ni Kα lines showed little variation up to 2 normal of hydrofluoric acid.
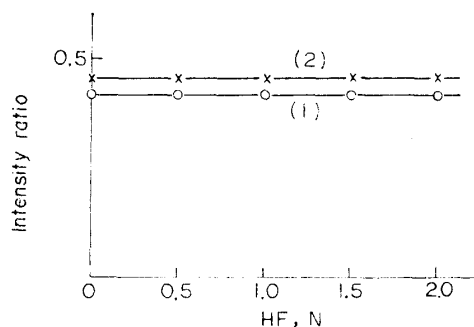

Fig. 2. Effect of concentration of hydrofluoric acid on the X-ray intensity of FeKα and NiKα.
(1) 1.00 mgFe/ml   (2) 1.00 mgNi/ml

2. Absorption effect of accompanying elements

The samples to which this method was applied contained titanium and zirconium as major component, and about 10 to 20 per cent of iron, nickel, and copper. Therefore, the interelement effects of them were discussed. The effects
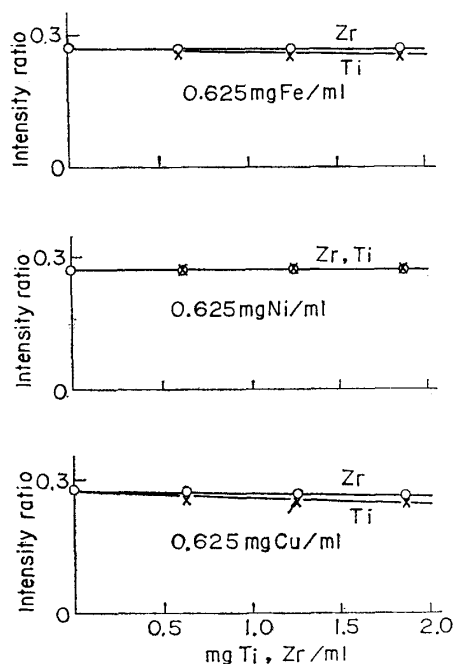
Fig. 3.   Fig. 4.

Fig. 3. Effect of concentration of titanium and zirconium on the X-ray intensity of FeKα, NiKα, and CuKα.

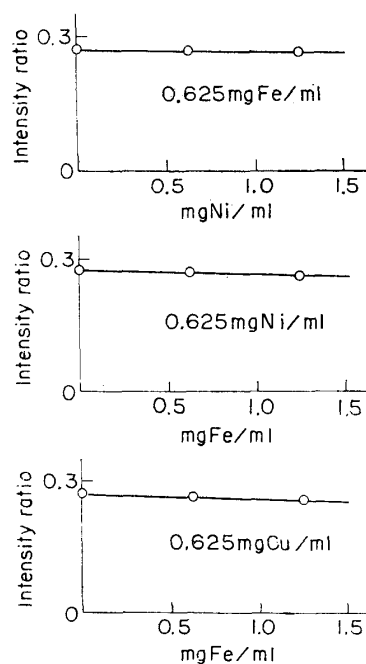Fig. 4. Effect of concentrion of nickel on the X-ray intensity of FeKα and of iron on that of NiKα and CuKα.

of concentration of titanium and zirconium on the intensities of Fe Kα, Ni Kα, and Cu Kα are shown in Fig. 3. In the present case, because of low concentrations of titanium and zirconium and because of dilution effect of a large amount of water, the effects of accompanying elements can be considered to be varied rectilinearly. Therefore, it was clarified that the intensities of Fe Kα decreased in the ratios of 1.9 and 1.6 per cent, and that of Cu Kα 2.2 and 1.1 per cent, in the presence of 1 mg/ml of titanium and zirconium respectively. On the other hand, however, the effect was recognized on the intensity of Ni Kα line. In Fig. 4, mutual absorption effects of iron, nickel, and copper are shown. In this case, each of X-ray intensities decreased in the presence of the others. The intensity of Fe Kα showed 1.2 per cent decrease in the presence of 1 mg/ml of nickel, and those of Ni Kα and Cu Kα showed 3.1 and 3.9 per cent decrease, respectively, in the presence of 1 mg/ml of iron. Therefore, a definite quantity of samples, the calibration curves in the presence of titanium and zirconium, and the correction for the absorption effect of accompanying elements were necessary for the analysis of iron, nickel, and copper by this method. Although dilution of the sample solution suppresses the absorption effect, it decreases the concentration of elements in interest, and therefore, lowers the analytical accuracy.

3. Calibration curve

20 ml of saturated boric acid solution, 10 ml of acid mixture (finally 1N-HF and $0.5N$-HNO_3), and $0 \sim 25$ ml of standard solution of iron were taken in flask of 50 ml and diluted to volume with water. Each aliquot of these solutions was transferred to the sample cup, and the intensities of Fe $K\alpha$ were measured. In Fig. 5 the calibration curves for iron are shown. In this figure, the ordinate shows the intensity ratio of each solution to the solution of 2.5 mgFe/ml, and the abscissa shows the concentration of iron in mgFe/ml. The calibration curve in the presence of titanium and zirconium was calculated under the condition of the total concentration of metal being 2.5 mg/ml.

The calibration curves for nickel and copper were prepared in the same way as for iron.
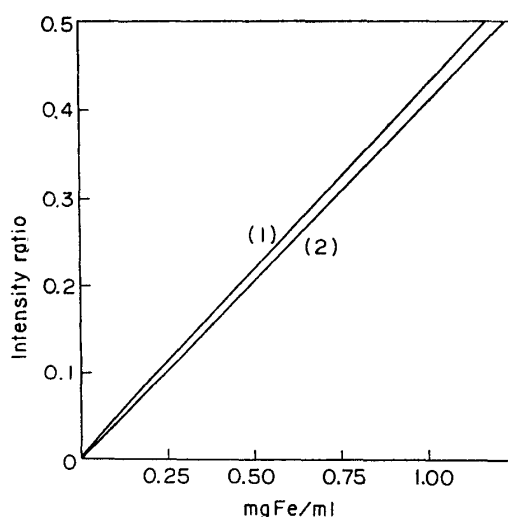

Fig. 5. Calibration curves for iron.
(1) Iron alone   (2) In the presence of titanium and zirconium

4. Analytical procedure

0.125 g of sample was dissolved in 10 ml of acid mixture in polyethylene beaker, with warming if necessary. After the dissolution, 20 ml of saturated boric acid solution was added. The solution was transferred to a volumetric flask of 50 ml and diluted to volume with water. An aliquot of this solution was transferred to the solution cell, and X-ray intensity of each element was measured under the conditions shown in Table 1. Analytical values were obtained with the calibration curves.

IV. Results and discussion

1. Analytical results of mixed solution samples

This proposed method was applied to the synthetic solution samples that consisted of some combination of elements. The results are shown in Table 2, which

Table 2. Analytical results of mixed solution samples.

No.	Element taken (mg/ml)					Element found (mg/ml)			Relative error (%)		
	Ti	Zr	Fe	Ni	Cu	Fe	Ni	Cu	Fe	Ni	Cu
1	1.000	—	0.500	1.000	—	0.501	0.969	—	0.2	− 3.1	—
2	1.000	—	—	0.500	1.000	—	0.490	1.002	—	− 2.1	0.2
3	1.000	—	1.000	—	0.500	0.980	—	0.512	− 2.0	—	2.4
4	—	1.500	0.500	0.500	—	0.508	0.492	—	1.6	− 1.6	—
5	—	1.500	—	0.500	0.500	—	0.509	0.511	—	1.8	2.2
6	—	1.500	0.500	—	0.500	0.499	—	0.502	− 0.2	—	0.4

show that each value had a relative error of below 3 per cent.

2. Analytical results of actual samples and discussion

As the satisfactory results were obtained with the above-mentioned synthetic solution samples, this method was applied to the actual samples. They were pressed plates of three layers which consisted of the center layer of titanium or zirconium, and the outer layer of iron, nickel, and/cr copper. Before analysis, these samples were cut into small pieces and used. The comparison of the analytical results by this method with another showed good agreement, as shown in Table 3.

Table 3. Analytical results of actual samples.

Sample	Fe (%)		Ni (%)		Cu (%)	
	Proposed method	Other * method	Proposed method	Other * method	Proposed method	Other * method
Ti-Ni-Cu	—	—	18.3	18.5	11.2	11.2
			18.5		11.2	
Zr-Ni-Cu	—	—	10.9	11.2	10.1	10.0
			10.9		10.2	
Zr-Fe-Cu	11.8	11.7	—	—	8.3	8.2
	12.0				8.2	
Ti-Ni-Fe	14.5	14.8	20.2	20.5	—	—
	14.7		20.3			
Zr-Ni-Fe	7.0	7.1	15.0	15.1	—	—
	7.2		15.3			

* EDTA titration method after separation of each element

Although this method was applied to the analysis of iron, nickel, and copper in the samples of which the major component was titanium or zirconium, it has more broad applicability, that is, this method was applicable to the analysis of niobium-zirconium, niobium-molybdenum, and zircalloy. In the determination of niobium and molybdenum, however, a white precipitation was caused by the addition of boric acid, because of the instability of the fluoride complex. An addition of small quantity of hydrogen peroxide prevented the white precipitation. Moreover, this method should make it possible to determine tantalum, tungsten, niobium, and molybdenum in high-temperature alloys without the separation of these elements.

The only one defect is that this method cannot be applied to the determination of the elements which produce insoluble fluorides, such as alkaline earths and rare earths.

The time for analysis of one sample is as short as 10 minutes, so this method is very effective as a rapid analytical method for the samples containing some refractory metals.