Analysis of Nickel-Base and Cobalt-Base Heat-Resistant Alloys by Single Column Anion Exchange Chromatography and Inductively Coupled Plasma-Atomic Emission Spectrometry

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Single-column anion exchange chromatography has been combined with inductively coupled plasma-atomic emission spectrometry (ICP-AES). A complex Ni-base or Co-base heat-resistant alloy was dissolved in a mixed acid containing hydrofluoric acid. A strongly basic anion exchange resin was used to separate the alloying elements. Hydrofluoric acid was removed by fuming or was masked after elution in order to use a glass sample introduction system for the ICP-AES. Thirteen alloying elements were determined in Ni-base and eleven in Co-base heat-resistant alloys. Good results were obtained by both the calibration curve method and the internal standard method. Synthetic standard solutions were used for the calibration. Magnesium was used as an internal standard element.

Keywords   Nickel-base alloys, cobalt-base heat-resistant alloys, anion exchange chromatography, ICP-AES, calibration curve method, internal standard method

Complex heat-resistant alloys contain more than ten alloying elements, including a lot of refractory metals. The ICP-AES is suitable for the analysis of the heat-resistant alloys because of its ability of simultaneous determination and its high sensitivity for the refractory metals. The present authors[1] developed an analytical method using hydrofluoric acid-resistant sample introduction systems for the determination of major and minor alloying elements in Ni-base and Co-base heat-resistant alloys which had been dissolved in a mixed acid of hydrofluoric acid and nitric acid. Construction and use of the hydrofluoric acid-resistant sample introduction system are, however, not so simple.

Several analytical methods using an ordinary glass sample introduction system in the ICP-AES has been developed for the analysis of Ni-base alloys.[2-6] These alloys did not contain W and the dissolution methods were rather simple. Only one method used hydrofluoric acid, and boric acid was added to mask excessive hydrofluoric acid.[3] These analytical methods[2-6] did not use separation procedures. Mutual spectral interferences of the alloying elements are sometimes severe in the ICP-AES when the separation procedure is not used. Without an expensive computer, much time is needed for the correction of the spectral interferences and calculation errors may be large.

Chemical separation is necessary to solve the problem of spectral interferences; ion exchange separation was chosen in this study. Wilkins[7] used an anion

exchange resin (Dowex 1×8) to separate alloying elements in a composite Ti-base high temperature alloy. The alloying elements were determined by titration and gravimetry after the elution. Montgomery[8] determined Mo in high-Ni alloys by potentiometric titration after the elution using an anion exchange resin (Bio-Rad AG1-X8). The present authors developed a single-column anion exchange chromatography which was fit for the ICP-AES. Major and minor alloying elements in complex Ni-base and Co-base heat-resistant alloys were separated with the anion exchange resin and were determined by the ICP-AES.

Experimental

Anion exchange resin column

A strongly basic anion exchange resin MCI Gel CA08P (Mitsubishi Chemical Industries, Japan; cross linkage 8%, exchange capacity>1.3 meq cm^{-3}, chloride form) was used. Particle size was 75-150 μm. A polyethylene burette (10 mm i.d.×30 cm length) was used for column tubing. Twenty cm^3 of the resin was contained in the column tubing. Sample solution and eluents were passed through the resin column from the polyethylene separatory funnel (300 cm^3) which had been connected to the upper end of the column tubing with silicone rubber. The eluent over the surface of the resin was kept 5 cm in depth to minimize disturbance

of the elution. The anion exchange resin column was previously conditioned with 100 cm³ of 2.2 mol dm⁻³ hydrofluoric acid. The flow rate of the eluent was adjusted to about 1.2 – 1.4 cm³ min⁻¹.

Apparatus

A Shimadzu Model ICPV–1000 polychromator (Shimadzu, Japan) was used. Instruments used were the same as those shown elsewhere.[9] Table 1 summarizes the operating conditions of the ICP–AES. Optical path between the polychromator and ICP was purged with Ar. Carrier gas was moistened with water to minimize the clogging of the nebulizer. Sample and synthetic standard solutions were introduced into the ICP by a Shimadzu Model AS–1 auto sampler. Triton X–100 solution (0.1 w v⁻¹%) was used to wash the inside of the PTFE sample-uptake tubing (1.0 mm i.d.×80 cm length) to improve the wetting property of the PTFE. Each solution was analyzed twice, and the average value was used for the calculation.

Reagents

Hydrofluoric acid (50%) was of semiconductor grade (Daikin Industries, Japan). Hydrochloric acid (35%), nitric acid (60%), perchloric acid (60%), hydrogen peroxide (31%), citric acid and boric acid were of analytical reagent grade.

All stock standard solutions (1 – 20 mg cm⁻³) of metals except for V were prepared by dissolving high-purity metals (Johnson Matthey Chemicals, U.K., or Spex Industries, U.S.A.) in acids. A stock standard solution of V was prepared from vanadium pentoxide (Spex Industries). Dilute standard solutions were prepared by serial dilution of the stock standard solutions with dilute acids before use. An internal standard solution of Mg (0.1 mg cm⁻³) was prepared by dissolving high-purity metal (Kanto Chemical Co.,

Japan) in dilute nitric acid. Triton X–100 (Eastman Kodak, U.S.A.) was of scintillation grade.

Procedure

Dissolution of alloy.   Weigh 0.5 g of chips or turnings of a heat-resistant alloy into a 300-cm³ PTFE beaker. Cover the beaker with a PTFE lid. Add 20 cm³ of concentrated hydrochloric acid and heat the solution on a hot-plate. Add 2 cm³ of concentrated hydrofluoric acid. Add 31% hydrogen peroxide little by little untile the sample dissolves. After the dissolution, evaporate the solution to dryness. Repeat the drying with hydrochloric acid and hydrofluoric acid and then three times with hydrofluoric acid and water. Dissolve the residue in about 70 cm³ of 2.2 mol dm⁻³ hydrofluoric acid on heating. After cooling, transfer the solution to a separatory funnel with about 30 cm³ of 2.2 mol dm⁻³ hydrofluoric acid.

Elution and treatment of effluent and eluates.

(a)   Use PTFE beakers to collect effluent and eluates. Pass the sample solution through the anion exchange resin column. Elute Al, Co, Cr, Cu, Fe, Mn, Ni and V with 150 cm³ of 2.2 mol dm⁻³ hydrofluoric acid. Add 5 cm³ of concentrated perchloric acid to the effluent and evaporate the solution to fumes of perchloric acid to remove the greater part of fluoride ions. Cool the solution, wash the inside of the beaker and evaporate the solution to fumes again.

(b)   Elute Ti, W and Zr with 100 cm³ of a mixed 2.5 mol dm⁻³ hydrofluoric acid–7 mol dm⁻³ hydrochloric acid eluent. Discard the first 10 cm³ aliquot of eluate. Evaporate the eluate to about 1 cm³. Add 1 cm³ of concentrated hydrofluoric acid, 1.5 – 2 cm³ of 20 w v⁻¹% citric acid and 20 cm³ of 4 w v⁻¹% boric acid.

(c)   Elute Nb with 140 cm³ of a mixed 0.05 mol dm⁻³ hydrofluoric acid–6 mol dm⁻³ hydrochloric acid eluent. Discard the first 10 cm³ aliquot of eluate. Evaporate the eluate to a small volume. Add 1 cm³ of concentrated hydrofluoric acid and 20 cm³ of 4 w v⁻¹% boric acid.

(d)   Elute Mo with 130 cm³ of a mixed 1 mol dm⁻³ hydrofluoric acid–1 mol dm⁻³ hydrochloric acid–1 mol dm⁻³ nitric acid eluent. Evaporate the eluate to a small volume and add 5 cm³ of concentrated hydrochloric acid.

(e)   Elute Ta with 300 cm³ of a mixed 0.3 mol dm⁻³ perchloric acid–1.5 mol dm⁻³ hydrofluoric acid–0.35% hydrogen peroxide eluent. Discard the first 90 cm³ aliquot of eluate. Evaporate the eluate to fumes of perchloric acid. Add 1 cm³ of hydrofluoric acid and 20 cm³ of 4 w v⁻¹% boric acid.

After the above-mentioned treatment of the effluent and eluates, transfer the solutions into 100-cm³ polypropylene volumetric flasks. Add 10 cm³ of 0.1 mg Mg cm⁻³ internal standard solution and dilute the solutions to the mark with water.[1] Use these solutions for the ICP–AES.

Synthetic standard solutions for calibration.   Combine appropriate volumes of the stock or dilute standard

Table 1   Operating conditions

Frequency	27.12 MHz	
Output power	1.2 kW	
Reflected power	5 W	
Flow rate of Ar		
Outer gas	14 dm³ min⁻¹	
Intermediate gas	1.5 dm³ min⁻¹	
Carrier gas	1.0 dm³ min⁻¹	
Purge gas	3 dm³ min⁻¹	
Observation height above coil	13 mm	
Pre-spraying time	40 s	
Integration time	15 s	
Cleaning time	40 s	
Wavelength used/nm		
Al I 396.15	Mg II 279.55[a]	Ta II 248.87
Co II 228.62	Mn II 257.61	Ti II 337.28
Cr II 267.72	Mo II 202.03	V II 311.07
Cu I 327.40	Nb II 319.50	W II 207.91
Fe II 259.94	Ni II 231.60	Zr II 343.82

a. Internal standard element.

solutions and adjust the kinds and concentrations of acids to prepare calibration solutions for the above-mentioned sample solutions. Add $10 cm^3$ of the internal standard solution and dilute the solutions to $100 cm^3$.

Results and Discussion

Sample dissolution

Hydrofluoric acid is necessary for the dissolution of complex heat-resistant alloys which contain a lot of refractory metals including W. A mixed acid of hydrofluoric acid and hydrochloric acid was used to dissolve heat-resistant alloys. Hydrogen peroxide was added to improve oxidation power. Repeated drying was necessary to decompose carbides of Cr, Nb and V and to evaporate hydrochloric acid. The residue was finally dissolved in dilute hydrofluoric acid solution for anion exchange chromatography.

When the sample decomposition by the above-mentioned dissolution reagents becomes difficult, it is advisable to use nitric acid as a component of the reagents. In this case, repeated drying of the sample solution is necessary mainly to remove nitrate ions;[8] otherwise, a lower recovery for V in the effluent will occur. When nitrate ions were present, the greater part of V was eluted in the Ti group, and elution volumes for the other elements in the effluent were increased.

Spectral interferences.
Spectral interferences were studied by using the dilute standard solutions of pure elements. Table 2 shows interferents whose spectral interference coefficients exceed 10^{-3} for analytes. As shown in Table 2, most of the severe spectral interferences arise from refractory metals. Elements which show severe interferences were separated into an element or element group. Single-column anion exchange chromatography was chosen for simplicity. The correction of spectral interferences was minimized under the limited elution steps.

Table 2 Interferents whose spectral interference coefficients for analytes exceed 10^{-3}

Analyte	Interferent
Al	Nb, Mo, Ta, Zr
Co	Ti
Cr	Mg[a]
Cu	Nb, Ta, Zr
Mg[a]	Zr
Mo	Ta
Nb	Ta
Ni	Co, Mg[a], Ta
Ta	Mg[a], Mn, Nb, V, W
Ti	Zr
V	Ta, Ti, Zr
W	Al, Mg[a], Mo, Ta, Ti, V

a. Internal standard element.

Anion exchange and treatment of effluent and eluates

An MCI Gel CA08P anion exchange resin was used because it was easily obtained and not so expensive. The published methods[7,8] were modified to develop an anion exchange chromatography which was fit for the ICP-AES.

Exchange capacity of the anion exchange resin and composition and concentration of eluents were studied by using the dissolved Ni-base alloy, IN-738 LC, to which minor elements (Cu, Fe, Mn and V) were doped. Twenty cm^3 of the resin was sufficient for 0.5 g of the alloy sample. Composition and concentration of the acids in eluents were optimized for each element or element group as follows.

(a) Concentrations of hydrofluoric acid were changed from 1.2 to $3 mol dm^{-3}$ to elute Al, Co, Cr, Cu, Fe, Mn, Ni and V. At low molarity of hydrofluoric acid, a large volume of eluent was needed and some parts of the other elements (Mo, Ti, W and Zr), which should be retained on the column, were also eluted. On the other hand, at high molarity of hydrofluoric acid, the eluent volume was small. However, a part of Mo and Zr was eluted. The concentrations of $2.2-2.6 mol dm^{-3}$ were optimum for keeping the other alloying elements completely retained on the column. The $2.2 mol dm^{-3}$ of hydrofluoric acid was chosen under consideration of the dissolution of the residue. Fuming of the effluent with perchloric acid was used to drive off the greater part of the fluoride ions. Aluminum showed a peak at about $50 cm^3$ of the effluent. Vanadium was weakly adsorbed on the column and was desorbed with a large volume of the eluent. These elements were completely eluted with $150 cm^3$ of $2.2 mol dm^{-3}$ of hydrofluoric acid.

(b) Optimum concentrations of hydrofluoric acid ($1-3.5 mol dm^{-3}$) and hydrochloric acid ($4-9 mol dm^{-3}$) in the eluent for the elution of Ti, W and Zr were studied by keeping the concentration of another acid constant. A mixed $2.5 mol dm^{-3}$ hydrofluoric acid-$7 mol dm^{-3}$ hydrochloric acid eluent was most effective to elute these elements and to retain Nb, Mo and Ta on the column. If Hf were present in the alloy, Hf would be eluted in the eluate of Ti group. Excessive hydrofluoric acid in the eluate was evaporated. However, a small amount of hydrofluoric acid was necessary to keep Ti, W and Zr in the solution. Citric acid was also added; otherwise a precipitate of W was formed when boric acid was added to mask hydrofluoric acid.

(c) Concentrations of hydrofluoric acid ($0.01-0.3 mol dm^{-3}$) and hydrochloric acid ($5-10 mol dm^{-3}$) were changed for the most effective elution of Nb and retention of Mo and Ta on the column. A mixed $0.05 mol dm^{-3}$ hydrofluoric acid-$6 mol dm^{-3}$ hydrochloric acid eluent was chosen. After evaporating the eluate to a small volume, hydrofluoric acid was added to keep Nb in the solution and excessive hydrofluoric acid was masked with boric acid.

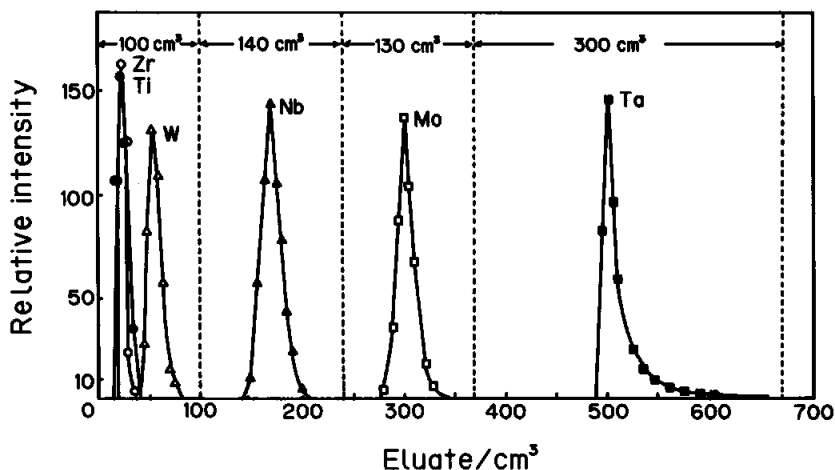(d) Wilkins[7] used a mixed 14% ammonium chlo-

Fig. 1 Elution curves for Mo, Nb, Ta, Ti, W and Zr.

ride–4% hydrofluoric acid eluent for the elution of Mo. This eluent was not used in this study because of the highly dissolved salts in the eluate. So other eluents were investigated. A mixture of hydrofluoric acid (0.5 – 4 mol dm⁻³)–hydrochloric acid (0.25 – 4 mol dm⁻³)–nitric acid (0.5 – 4 mol dm⁻³) was effective. A mixture of 1 mol dm⁻³ hydrofluoric acid–1 mol dm⁻³ hydrochloric acid–1 mol dm⁻³ nitric acid eluent was optimum. The greater part of hydrofluoric acid in the eluate was driven off by evaporating the solution to a small volume. The solution was converted to hydrochloric acid solution for the ICP–AES.

(e) Wilkins[7] and Montgomery[8] used a mixed 14% ammonium chloride–4% ammonium fluoride eluent for the elution of Ta. When this eluent was used, the highly dissolved salts needed the dilution of the eluate for measurement to minimize the clogging of nebulizer and/or the deposition of salts in the orifice of injection tubing of the ICP torch. The authors attempted to use other eluents which could be concentrated to a small volume. A mixed perchloric acid (0.1 – 3 mol dm⁻³)–hydrofluoric acid (0.2 – 3 mol dm⁻³)–hydrogen peroxide (0.17 – 1.4%) eluent was effective to elute Ta. A mixed 0.3 mol dm⁻³ perchloric acid–1.5 mol dm⁻³ hydrofluoric acid–0.35% hydrogen peroxide was chosen. The eluate was evaporated to near fumes of perchloric acid and a small amount of hydrofluoric acid was added. Excessive hydrofluoric acid was masked with boric acid. Recovery of Ta was above 97%.

Volumes of the eluents used for the elutions were much less than those used by Wilkins[7] and Montgomery.[8] Figure 1 shows the elution curves of the elements retained on the anion exchange column. Emission intensity at each 5 cm³ fraction was measured. Volumes of the eluents were determined from these curves. Figure 2 shows the elution sequence of the anion exchange chromatography developed for the ICP–AES of the complex heat-resistant alloys. Repeated use of the anion exchange resin was tried. All the elements except Mo and V were quantitatively recovered.
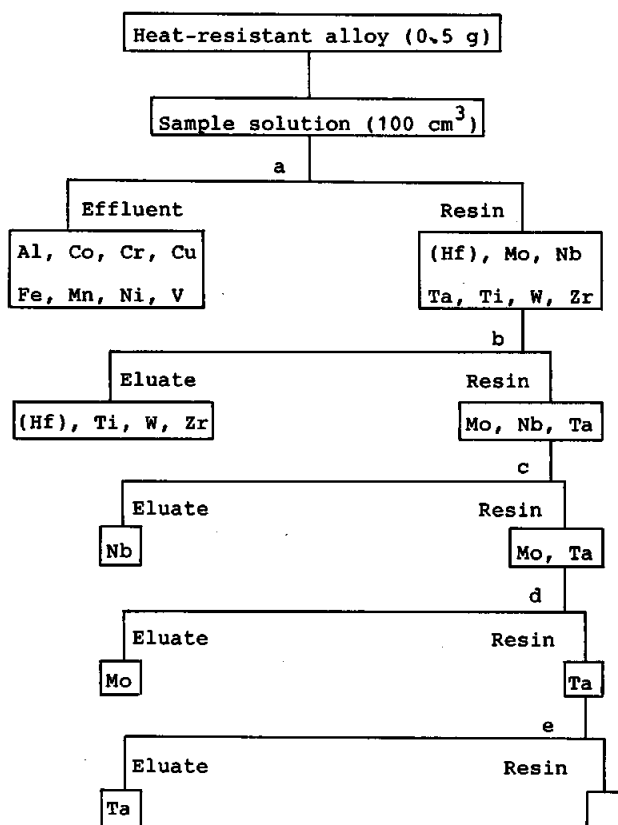

Fig. 2 Elution sequence of anion exchange chromatography for ICP-AES of heat-resistant alloy. a, 2.2 mol dm⁻³ HF 150 cm³; b, 2.5 mol dm⁻³ HF–7 mol dm⁻³ HCl 100 cm³; c, 0.05 mol dm⁻³ HF–6 mol dm⁻³ HCl 140 cm³; d, 1 mol dm⁻³ HF–1 mol dm⁻³ HCl–1 mol dm⁻³ HNO₃ 130 cm³; e, 0.3 mol dm⁻³ HClO₄–1.5 mol dm⁻³ HF–0.35% H₂O₂ 300 cm³.

Operating conditions for ICP-AES

The above-mentioned sample solutions were used to choose the operating conditions of the ICP–AES. Univariate study was carried out. Compromised operating conditions thus determined are summarized in Table 1.

Table 3   Analytical results of Ni-base heat-resistant alloy (IN-738 LC) ($\bar{x}\pm\sigma$, %)

| | ICP–AES (n=9) | | Reference value |
	Calibration curve method	Internal standard method	
Al	3.6±0.1	3.6±0.1	3.40[a], 3.49[b]
Co	8.18±0.07	8.15±0.06	8.27[a], 8.40[b]
Cr	15.5±0.1	15.35±0.09	15.77[a], 15.84[b]
Cu	0.0300±0.0002	0.0293±0.0003	0.031[c]
Fe	0.169±0.006	0.167±0.006	0.21[a], 0.16[b], 0.18[c]
Mn	0.0028±0.0005	0.0027±0.0005	0.0026[c]
Mo	1.77±0.04	1.754±0.005	1.77[a], 1.73[b], 1.71[c]
Nb	0.750±0.008	0.806±0.002	0.78[a], 0.72[b]
Ta	1.67±0.01	1.640±0.003	1.67[a], 1.70[b]
Ti	3.41±0.05	3.54±0.02	3.38[a], 3.51[b]
V	0.00120±0.00005	0.0010±0.0002	0.0014[c]
W	2.60±0.03	2.72±0.01	2.55[a], 2.70[b]
Zr	0.093±0.001	0.0980±0.0007	0.10[a], 0.10[b]

a. Company value.
b. X-ray fluorescence value.
c. Flame atomic absorption value.

Table 4   Analytical results of Co-base heat-resistant alloy (NBS SRM 168) ($\bar{x}\pm\sigma$, %)

| | ICP–AES (n=7) | | Certified value |
	Calibration curve method	Internal standard method	
Cr	20.3±0.2	20.0±0.3	20.33
Cu	0.0480±0.0005	0.048±0.001	0.035
Fe	3.36±0.03	3.38±0.05	3.43
Mn	1.48±0.01	1.52±0.02	1.50
Mo	3.9±0.4	3.91±0.01	3.95
Nb	2.92±0.06	3.0±0.2	2.95
Ni	20.4±0.2	20.3±0.4	20.25
Ta	0.953±0.008	0.932±0.003	0.95
Ti	0.063±0.002	0.0631±0.0003	0.06
V	0.022±0.002	0.024±0.002	0.03
W	3.99±0.07	3.98±0.01	3.95

Analysis of heat-resistant alloys

A Ni-base (IN-738 LC) and a Co-base (NBS SRM 168) heat-resistant alloys were analyzed for alloying elements. An internal standard element which was not contained in the heat-resistant alloys was added to the solution to improve the precision of the determination.[1] Analytical results obtained by the calibration curve method and by the internal standard method are summarized in Tables 3 and 4. Cobalt-base heat-resistant alloy, NBS SRM 168, was decomposed with a mixed acid of hydrofluoric acid, hydrochloric acid and nitric acid because the dissolution reagents mentioned in *Dissolution of alloy* were less effective. The sample solution was dried five times to expel nitrate ions. The average value ($\bar{x}$) and standard deviation (σ) were obtained from 9 and 7 independently dissolved samples for IN-738 LC and NBS SRM 168, respectively. The analytical values obtained by the anion exchange chromatography and ICP–AES are in good accord with reference values or certified values. The internal standard method did not necessarily improve the precision compared with the calibration curve method. This may be due to the compromised operating conditions used in the ICP–AES.

This anion exchange chromatography and ICP–AES will be useful for developing analytical methods of refractory metals and alloys.

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