Inductively Coupled Plasma Atomic Emission Spectrometric Analysis of Cobalt-base Superalloys*

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This paper describes the procedure developed for the accurate analysis by ICP-AES of Co-base superalloys, using yttrium as an internal standard. The chemical composition of these materials makes the development of spectroscopic analytical methods difficult due to the presence of major elements that exhibit intense and complex ICP emission spectra. A quantitative sample dissolution procedure and careful selection of the analytical lines used was carried out. The elements investigated were Co, Cr, Ni, W, Fe, Ta, Nb, Al, Mo and Mn. Synthetic solutions were used for calibration, and standard samples were analysed to demonstrate the precision and accuracy of the developed method.

Keywords: Cobalt-base superalloys; inductively coupled plasma atomic emission spectrometry

Cobalt solid-solution alloys can be sub-divided in three simple groups on the basis of use: (a) alloys for use primarily at temperatures from 650 to 1150 °C; (b) fastener alloys for use to about 650 °C; and (c) wear resistant alloys.¹⁻³

The range of concentrations of elements present in Co-base superalloys are as follows: Co, 48–67; Cr, 19–32; Ni, 0.5–24; W, 0.5–16; Fe, 0.5–20; Ta, 0.1–10; Nb 0.1–2; Al, 0.1–5; Mo, 0.1–2; and Mn, 0.1–2%.

The most widely used method for analysing Co-base superalloys involves laborious gravimetric and titrimetric procedures. However, inductively coupled plasma atomic emission spectrometry (ICP-AES) is now a well established technique for the analysis of metallurgical samples. The objective of the present study was to establish a single and accurate ICP analytical method, using internal standardisation, that was suitable for the determination of the fundamental components in Co-base superalloys.^{4,5}

The major elements normally present in these materials exhibit intense and complex ICP atomic emission spectra. At high concentrations, the more intense lines of an element may emit significant radiation several nanometres either side of the selected wavelength, increasing the likelihood of interferences from spectral overlap, and selection of the correct analytical lines is therefore difficult.

In order to select the wavelengths to be used, spectral scans of solutions containing, approximately, the background equivalent concentration (BEC) of the element being considered and the maximum expected concentrations of all the other possible elements, were taken. The most prominent line of each element was investigated first, and if an interference was found, then the next most prominent line was checked, until one was found which had no significant interference.

The precision and accuracy of the developed method were checked, first with synthetic samples prepared with the appropriate proportions of the pure metals, and finally with three MBH standard samples (MBH Reference Materials, Barnet, Hertfordshire, UK).

Experimental

Instrumentation

A Jobin-Yvon, JY 38 P, ICP sequential emission spectrometer with a scanning monochromator (0.60-m JY HRS 2), mounted at 90 ° to the JY 38 P optical path was used.

Specifications

Spectrometer, JY 38 P. Focal length, 1-m, Czerny - Turner; grating, holographic 2.400 grooves per mm; spectral range, 175–700 nm; dispersion, 4 Å per mm at 200 nm; and accuracy, 0.5 Å.

Generator. Plasma Therm, 27.12 MHz, maximum power rating 1.5 kW.

Torch. Monoblock Scott - Fassel, modified with a cylindrical injector and argon sheath gas flow (Fig. 1).

Nebuliser. Jobin-Yvon, with Pt - Ir capillary and PTFE nozzle.

Instrument control and data processing. Apple IIe computer with associated EPSON RX 80 F/X printer.

Analytical operating conditions

The conditions used were as follows: power, 1.2 kW forward; outer gas flow-rate, 15 l min⁻¹; aerosol carrier gas, humidified, 0.55 l min⁻¹; argon sheath gas flow-rate, 0.1 l min⁻¹; sample delivery rate, 1.6 ml min⁻¹; and observation height, 14–16 mm. Using these gas rates and the modified torch employed, RSDs of ≤ 0.4% were obtained.

Sample Dissolution

Dissolve 0.5 g of sample in a PTFE beaker with 50 ml of aqua regia containing 2 ml of hydrofluoric acid; add 25 ml of sulphuric acid (33% V/V) and 25 ml of phosphoric acid (33% V/V) and evaporate to fumes; dilute to ca. 40 ml with hydrochloric acid (10% V/V). If undissolved matter remains,

Fig. 1. Monoblock Scott - Fassel torch, modified with cylindrical injector and argon sheath gas flow

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Fig. 2. Spectral interferences for nickel: for A-C, see text

Fig. 3. Spectral interferences for chromium

Fig. 4. Spectral interferences for iron

Fig. 5. Spectral interferences for cobalt

Fig. 6. Spectral interferences for tantalum

Fig. 7. Spectral interferences for niobium

Fig. 8. Spectral interferences for aluminium

Fig. 9. Spectral interferences for tungsten

Fig. 10. Spectral interferences for molybdenum

filter the solution, transfer the filter-paper into a platinum crucible and dry. Ignite the filter-paper, then heat at about 1000 °C for about 15 min. Allow to cool, then add 2 ml of sulphuric acid, 5 ml of hydrofluoric acid and, dropwise, about 1 ml of nitric acid to the crucible. Heat gently then, when the acids have evaporated, heat again at 1000 °C for a few minutes and fuse the residue with 0.5 g of sodium carbonate. Extract the cooled melt into the main acid solution and dilute to 500 ml with hydrochloric acid (10% V/V).^{6,7}

The assay solution was prepared by adding 50 p.p.m. of yttrium to 25 ml of the main acid sample solution and diluting to 100 ml with 10% HCl (V/V). A solution of yttrium was prepared by dissolving 1.25 g of Y_2O_3 in 100 ml of nitric acid (1 + 1) and diluting to 1000 ml with water; 5 ml of this solution contained 50 p.p.m. of yttrium. The assay solution therefore contains 0.025 g of sample plus 5 µg of yttrium per 100 ml.

Fig. 11. Spectral interferences for manganese

Table 1. Lines examined for each element

Element	λ/nm	Element	λ/nm
Co	238.892	Fe	238.204
	228.616		239.562
Ta	226.230		259.940
	240.063	Ni	221.647
	268.517		232.003
	233.193		231.604
	296.516		216.556
	228.916		217.467
Al	309.271		230.300
	396.152		227.021
Cr	205.552		225.386
	267.716		234.554
	283.546		239.452
	206.149		241.614
Mo	202.030	Nb	352.454
W	207.911		309.418
		Mn	316.340
			257.616

Table 2. Certified and ICP-AES results for MBH samples

Element	Sample	Certified value, %	Found value, % ($\bar{X} \pm t$)*	RSD,† %
Co	14937H	Remainder‡	59.84 ± 0.25	0.20
	X405B	Remainder‡	54.95 ± 0.20	0.18
	12671F	Remainder‡	63.37 ± 0.25	0.21
Cr	14937H	26.48	26.60 ± 0.10	0.17
	X405B	24.24	24.17 ± 0.10	0.18
	12671F	20.48	20.57 ± 0.10	0.20
Ni	14937H	2.43	2.45 ± 0.015	0.28
	X405 B	10.80	10.76 ± 0.060	0.22
	12671F	0.77	0.76 ± 0.005	0.20
W	14937H	2.52	2.45 ± 0.012	0.24
	X405 B	7.62	7.56 ± 0.040	0.28
	12671F	10.88	10.87 ± 0.062	0.18
Fe	14937H	0.77	0.75 ± 0.006	0.26
	X405B	1.19	1.25 ± 0.010	0.19
	12671F	1.08	1.00 ± 0.010	0.12
Ta	12671F	(0.10)	0.13 ± 0.010	0.38
Nb	12671F	2.27	2.30 ± 0.040	0.34
Al	14937H	1.17	1.22 ± 0.035	0.40
Mo	14937H	5.90	6.00 ± 0.12	0.33
Mn	14937H	0.32	0.35 ± 0.024	0.31
	12671F	0.61	0.60 ± 0.025	0.24

* $\bar{X}$, Mean value from six different assay samples.
 t , tolerance = $t_{0.5,5} \frac{S}{\sqrt{n}}$, $n = 6$.
† RSD values were obtained from 20 consecutive measurements of the same assay solution.
‡ Remainder of sample composition.

Selection of Analytical Lines

The most prominent lines of the elements being considered were checked,⁸⁻¹² until lines were found that had no interferences. The number of lines examined for each element was different as it depended on the spectral interferences that were seen. The lines that were examined are shown in Table 1. To demonstrate the absence of significant spectral interferences, scans were taken using the same operating conditions employed to measure assay samples. The solutions used for the scans were: A, near equivalent background concentration

(BEC) of each assay element; B, maximum expected concentration levels of the other elements normally present in the assay solutions and 50 p.p.m. of Y; and C, blank, containing a similar acid concentration to that of the assay solution. Figs. 2-11 show the results of spectral interference studies that were made. As a result of the complexity of the spectra because of the interfering lines, it is very difficult to differentiate these three solutions in the graphics; for this reason A, B and C are only indicated on the selected interference free lines.

Results

The wavelengths that were selected for use in the proposed method were: Co, 228.616; Cr, 206.149; Ni, 352.454; W, 207.911; Fe, 259.940; Ta, 228.916; Nb, 316.340; Al, 396.152; Mo, 202.030; and Mn, 257.610 nm. The sample preparation procedure used provided quantitative dissolution of the sample and the corresponding test solution (0.025 g of sample plus 5 µg of yttrium per 100 ml) does not disturb the saline concentration required for the nebulisation.

The operating conditions used provided a good signal to background ratio (I/I_b) and low background values at the concentration levels being considered. On account of the linear response of the ICP technique, calibrations were based on two solutions, at similar acid concentrations to the assay sample, containing 50 p.p.m. of yttrium and amounts of each element being considered equivalent to the minimum and the maximum concentrations normally present in Co-base superalloys. Measurements were taken employing yttrium ($\lambda = 371.030$ nm) as the internal standard.

The developed method was tested at each stage of the analytical technique: firstly, by means of synthetic samples prepared by mixing, in suitable proportions, the respective pure powdered metals and finally with standard reference materials from MBH. Results are presented in Table 2. This table shows that the developed ICP-AES procedure can be successfully applied to the analysis of Co-base superalloys.

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