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Elemental characterisation of aluminium used in reactors by optical emission spectroscopic methods

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Abstract. Using AC spark, AC arc and DC arc excitations in optical emission spectroscopic systems, the Al metal used in reactors can be characterised for its minor or trace element composition. The best precision of ± 6% is obtained with an AC spark in which the rod sample is taken as a self electrode and elements Cu, Fe, Mn, Si and Ti are determined in the concentration range 0·01-1%. The oxide powder sample with DC arc excitation provides best minimum detection limits of 10 ppm in general and 21 trace elements are determined by it. The AC arc method also uses oxide powder standards prepared synthetically and determines B and Mg in addition to the elements determined in AC spark excitation with a precision of ± 9%.

Keywords. Aluminium; optical emission spectroscopy; excitation sources; precision; elemental characterisation.

1. Introduction

Aluminium metal is used in reactors as cladding or calandria material. In the metal so used the high thermal neutron absorbing impurity B should be absent for neutron economy though its presence in the metel is desirable for certain other metallurgical properties. Also the presence of elements Cu, Mn and Ti in minor amounts improves the metal and it gives better castings, can withstand higher temperatures and is better suited for machining. Table 1 gives the maximum permissible limits of 14 impurity and/or alloying elements in Al metal used as a cladding material in thermal reactors. The concentration of these elements varies from 10-4000 ppm. This range can be adequately covered in OES by using AC spark, AC arc and DC arc excitations. For a few elements in relatively high concentrations, like Fe, Si, Cu, Mn and Ti an AC spark method (Chandola and Karnik 1971) having a precision of ± 6% is opted for. For the elements present at a low concentration of 10 ppm or so a sensitive method using DC arc excitation (Chandola and Machado 1975) is used. Since the AC spark method uses commercially available rod standards, an alternate method using AC arc excitation (Chandola *et al* 1977) is developed in which the synthetically prepared oxide powder standards are used for comparison. Significant features of these methods are described in this paper.

Table 1. Maximum permissible weights of elements in Al used as cladding material in reactors.

Element	Weight %	Useful excitation
Co	0·001	DC arc
B & Cd	0·002	DC arc
Cr, Ni & Zn	0·005	DC arc
Cu, Mn, Mg & Ti	0·01	AC spark/AC arc
Ga & V	0·025	DC arc
Si	0·2	AC spark/AC arc
Fe	0·4	AC spark/AC arc

Table 2. Analytical data for AC spark method.

Element	Analysis line Å	Estimation range %	Standard deviation %
Copper	3247·5	0·006–0·15	7·3
Iron	2600·2	0·1 –0·76	6·7
Manganese	2595·8	0·007–0·15	3·1
Silicon	2516·1	0·1 –0·59	5·3
Titanium	3349·4	0·011–0·06	7·3
Aluminium	3054·7	Internal standard	

2. Experimental procedure

2·1. *AC spark method*

In AC spark method, a $\frac{1}{4}$ inch diameter rod sample is used as lower self electrode against a similar graphite counter electrode. A Bausch and Lomb AC spark unit, with a capacitance in its circuit, provides a 15 kV discharge through a 4 mm analytical gap between the electrodes. The resulting radiation is dispersed by a large quartz prism in a Hilger spectrograph and the spectrum is recorded in Ilford N. 30 plates, with an exposure time of 90 sec, in the wavelength region 2450-3500 Å. It is found by racking plate method that the intensity of analyte elements falls after 90 sec, probably due to formation of oxide on the discharge surface; therefore the discharge surface of the sample is filed to expose fresh metal after each exposure. The standards are supplied by Johnson Matthey and Co. under series AA and their composition is given in ASTM Report (Michaelis 1956). The selected lines for analysis, the Al internal standard line, the determination range and the precision data are given in table 2.

2.2. *DC arc method*

For the DC arc method, the metal is converted to oxide by dissolution in HCl, precipitation with NH_4OH, drying the precipitate and supernatant solution

Table 3. Analytical data for DC arc method

Element	Analytical line Å	Estimation range ppm	Standard deviation † %
Antimony	2598·1	10-1000	7
Bismuth**	3067·7	5-500	–
Boron	2497·7	10-200	–
Cobalt	2424·9	10-1000	18
Cadmium	3261·1	20-500	5
Copper*	3274·0	5-200	22
Chromium	2835·6	5-1000	7
Gallium	2944·2	8-50	15
Indium**	3256·0	10-500	–
Iron	2599·4	13-1000	7
Lead	2833·1	5-100	14
Magnesium	2779·8	10-200	21
Manganese	2605·7	5-100	7
Molybdenum**	3170·3	10-500	–
Nickel	3050·8	10-200	7
Silicon	2435·2	70-1000	–
Silver*	3280·7	5-500	7
Tin**	2840·0	10-500	–
Titanium	3199·9	10-1000	12
Vanadium	3183·4	10-200	15
Zinc	3282·3	100-1000	–
Aluminium	2669·2	Internal standard	

*Measured in 10% transmission step
†From 11 deteminations for 50 ppm standard
**Only visual estimate is done

together and ignition. The alumina so obtained is mixed with pure graphite powder spectroscopic buffer in the weight ratio 1:1. Standards are prepared on pure alumina (Johnson Matthey and Company) by dry-mixing the Spex-Mix powder containing 49 elements and subsequent dilutions. The standards are also mixed with buffer similar to samples. A charge of 20 mg of sample-graphite mixture is placed in the cavity of $\frac{1}{4}$ inch diameter graphite electrode. A $\frac{1}{8}$ inch diameter graphite rod pointed at one end serves as a counter electrode and the analytical gap is kept at 4 mm. A DC arc at a current of 10 A is passed in the analytical gap making the sample electrode an anode. The resulting radiation is dispersed and photographed similar to AC spark method. A neutral filter giving 100% and 10% transmission steps is placed in front of the slit for the determination of Ag and Cu which fall in the high background region of the spectrum. The 21 elements analysed by this method and other analytical data are given in table 3.

2·3. *AC arc method*

The AC arc method also takes oxide powder as sample, 10 mg of which is stuck to a pair of flat topped $\frac{1}{4}$ inch diameter graphite electrodes with the help of a sticking cement–like Stickfast or radio TV service cement. Standards containing B, Cu, Fe, Mg, Mn, Si and Ti are prepared by dry-mixing the appropriate amounts of compounds of these elements to alumina. The sample is excited by an AC arc source (JACO Custom Varisource) and the resulting radiation is dispersed by a 15,000 lines per inch grating and photographed on Kodak SA–1 plates giving an exposure time of 60 sec. A neutral filter giving 100% and 18% transmission is placed in front of the slit to cover the required concentration range. The analytical data are given in table 4.

3. Results and discussion

The working curves relating log concentration with log intensity ratio are found to be linear in the concentration ranges given in tables 2, 3 and 4. The precision in terms of percent standard deviation is also given in these tables and is averaged as ± 6% for AC spark, ± 12% for DC arc and ± 9% for AC arc.

Accuracy was tested for Cu, Fe, Mn and Si by DC arc method by analysing some AA series standards after their conversion to oxide. The accuracy was found to be good and it was shown that for these elements there is no loss during conversion of metal to oxide by the procedure adopted. A separate set of experiments showed that there is no loss of element B during the conversion thus making the method useful for reactor technology application.

4. Conclusions

Three simple procedures described in this paper enable the complete elemental characterisation of the reactor cladding Al. These procedures are routinely in

Table 4. Analytical data for AC arc method.

Element	Wavelength Å	Concentration range %	Standard deviation %
Boron	2497·7	0·025-0·1	4
Boron*	,,	0·1 -1	–
Copper*	3247·5	0·025-0·25	17
Iron*	2599·6	0·05 -1	7
Magnesium	2779·8	0·025-0·1	12
Magnesium*	,,	0·25 -1	–
Manganese	2605.7	0·025-1	6
Manganese*	,,	0·1 -1	–
Silicon*	2514·3	0·1 -1	7
Titanium	3234·5	0·025-0·25	8
Titanium*	,,	0·1 -1	–
Aluminium	2652.5	Internal standard	

*Measured in 18 % transmittance step.

use at the Spectroscopy Laboratories of BARC, Bombay and have solved many problems which arise during the construction and operation of reactors at this Centre.

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