DETERMINATION OF IMPURITY ELEMENTS IN ALUMINIUM

Hou Xiaolin(侯小琳) and Zhang Yongbao (张永保)

(*China Institute of Atomic Energy, Beijing 102413, China*)

ABSTRACT

Twenty five impurity elements in aluminium applied as reactor material are determined. Titanium and nickel are determined with epithermal neutron activation analysis (NAA), magnesium and silicon by inductance coupling plasma emission spectra (ICP), other elements by thermal NAA. The fission coefficient of uranium is given by an experiment, the interferences of uranium to Ce, Nd, Mo, Zr, La, Sm are subtracted. The detection limits of these methods to all of impurity elements in aluminium are calculated.

Keywords Aluminium, Impurity element, Neutron activation analysis, Miniature neutron source reactor, Reactor materials

1 INTRODUCTION

Aluminium and its alloy are widely applied in nuclear industry. This is mainly due to its low neutron absorption cross section (σ=0.23 b) and the rapid decay of the neutron-induced ^{28}Al ($T_{1/2}$=2.3 min). But the presence of some high capture cross section nuclides such as B, REs and others may limit its use for nuclear industry. So the controlling of impurity elements is very important for application of aluminium in the industry.

The method of neutron activation analysis (NAA) has been widely used for multi-element determination simultaneously in aluminium[1−4]. In this paper, 23 elements in aluminium are determined with instrumental NAA with miniature neutron source reactor (MNSR).

2 EXPERIMENTAL

2.1 Preparation of samples and standards

The pieces of aluminium samples were soaked with 1 mol/l HNO_3 about 30 min, washed with deionized water, then by acetone and then by deionized water again, each 10 min. They were dried at room temperature.

The standard reference materials (SRM) used here in this paper are coal fly ash (NBS-1633a) and Chinese SRM soil (GBW-07405). The suitable standard solutions dropped on the analytical filter paper with diameter 10 mm was dried at room temperature. Weighted cleared sample (200 mg for short or 500 mg for long time irradiation) and above mentioned SRM were sealed in a 5 cm×5 cm polyethylene film cleaned beforehand with HNO_3:H_2O=1:1 solution and deionized water.

Manuscript received date: 1994–03–25

2.2 Irradiation and γ-spectrum measurement

A rabbit capsule carring the prepared sample or standard was sent into irradiating sit by the pneumatic transfer system. The neutron source is a miniature reactor in China institute of atomic energy. The experimental conditions are listed in Table 1.

Table 1

The conditions of NAA of impurity elements in aluminium

Neutron flux /n·cm^{-2}·s^{-1}	Irradiation time /h	Cooling time	Counting time /s	Elements determined
5×10^{11}	3	5–10 h	600	Cu, Ga, Au, Mn, W, Zn
5×10^{11}	25	4–5 d	1200	As, La, Mo, Sb, Sm, U
5×10^{11}	25	11–13 d	3600	Ba, Ce, Co, Cr, Fe, Nd, Ni, Sc, Th, W, Zn, Hf

The irradiated samples are placed on the shift of HpGe detector. The multichannel analysis system consists of HpGe detector, PCA-II-8000 multi-channel analyzer and IBM-386 computer is used to aquire γ-spectrum, the resolution of the system is 1.96 keV for the 1332 keV peak of ^{60}Co, relative detecting efficiency is 25 %, peak-to-Compton ratio is 48:1. The NAA software CIAE/SPAN is used for identification of the radionuclides, the relative method is used to calculated element content.

3 RESULTS AND DISCUSSION

The analytical results are listed in Table 2. LT-27 is Al-Si-Fe alloy. LT-21 is Al-Mg-Si alloy. L-2 is industrial purity aluminium. The analytical results show that besides Al, Fe and other alloy elements, the contents of impurity elements are less than 200 μg/g, for high neutron absorption cross section elements such as Hf, RE and others the contents are less than 2 μg/g. It is generally showed that all of aluminium samples have lower impurity.

3.1 Determination of magnesium and silicon

There are two nuclear reactions may be used to determine Mg in NAA, ^{26}Mg(n,γ)^{27}Mg and ^{24}Mg(n,p)^{24}Na. In the presence of large aluminium the determination of magnesium is difficult, because of interfering reaction ^{27}Al(n,p)^{27}Mg and ^{27}Al(n,α)^{24}Na. There are 3 nuclear reactions may be used to determine silicon, ^{30}Si(n,γ)^{31}Si, ^{29}Si(n,p)^{29}Al and ^{28}Si(n,p)^{28}Al, the last one can not be used obviously. Since the cross section of ^{30}Si(n,γ)^{31}Si (σ=0.11 b) and isotope abundance of ^{30}Si (θ=3.1 %) are lower, the analytical sensitivity of Si is lower. Moreover, ^{24}Na produced by ^{27}Al(n,α)^{24}Na reaction raises the detection limit of Si. The experimental results show that the detection limit of Si in aluminium is no less than 0.74 % with this reaction. Although ^{29}Si(n,p)^{29}Al can be used for determination of Si in aluminium[5], however, the interference of ^{28}Al is too large. So epithermal NAA was tried to determine the content of Si in 3 aluminium samples, but it was failed in analysis of LT-27 and L-2 due to lower contents of Si in sample (less than 0.5 %). So the inductance coupling plasma emission spectrum method is used to determine the contents of Mg and Si in aluminium and its alloy. The results are listed in Table 2.

3.2 Determination of nickel and titanium

Two reactions $^{64}Ni(n,\gamma)^{65}Ni$ and $^{58}Ni(n,p)^{58}Co$ may be used to determine nickel with NAA. The analytical sensitivity of Ni with first reaction is lower, because the abundance of ^{64}Ni and the activation cross section of this reaction is lower, moreover, ^{24}Na produced by $^{28}Al(n,\alpha)^{24}Na$ raises the background counts of ^{65}Ni. In use of $^{58}Ni(n,p)^{58}Co$, ^{59}Fe, ^{46}Sc, ^{65}Zn and others cause the much background to ^{58}Co γ-ray peak. Because the resonance integral cross section of this reaction is larger, epithermal NAA is chosen with Cd as shielding material.

Table 2

Analytical results of impurity elements in aluminium $\mu g/g$

Element	Aluminium sample			NBS-1633a		GBW-07405	
	LT-27	LT-21	L-2	This work	Certified value	This work	Certified value
As	0.65	0.63	0.397	145	145±15	411	412
Au	0.00446	0.000439	0.000510	–	–	259	260
Ba	13.2	<3.5	7.5	1480	1500	290	296
Ce	0.761	1.05	1.17	172	180	90.5	90
Co	1.28	0.546	0.466	47.0	46	12.4	12.3
Cr	130	4.87	5.59	193	196±6	123	118
Cu	186	33.9	38.2	116	118±3	158	144
Fe	4440	1400	1806	93900	94000	88200	88190
Ga	67.5	114	63.4	59.4	58	38.2	31.7
Hf	0.120	0.0579	0.360	7.68	7.6	8.14	8.1
La	0.0511	0.472	0.293	80.5	–	35.6	35.7
Mn	26.4	28.8	33.7	188	190	1290	1360
Mo	0.0735	0.679	1.05	31.5	29	4.58	4.6
Nd	0.589	0.343	0.450	72.5	–	23.1	23.8
Ni	102	9.99	50.3	128	127±4	39.5	40
Sb	0.172	0.0108	0.0117	6.82	7	35.3	35.4
Sc	0.0752	0.0644	0.0892	38.7	40	17.3	17.2
Sm	0.413	0.0361	0.0058	18.0	–	3.92	4.0
Th	0.0766	0.134	0.123	25.8	24.7	23.6	22.7
Ti	406	56.4	106	8030	8000	6270	6290
U	0.499	0.479	0.982	10.8	10.2±0.1	6.84	6.5
W	1.66	0.370	0.502	5.70	–	34.0	33.5
Zn	147	24.3	29.7	218	220±10	213	210
Mg	89	5700	68	4530	4550±100	3690	3680
Si	1120	5200	180	22.83%	22.8±0.8%	24.63%	24.5%

The determination of titanium in aluminium is difficult applying nuclear reaction $^{50}Ti(n,\gamma)^{51}Ti$, because the interference of ^{28}Al is very large. Xiaolin Li[6] studied the determination of titanium in Al_2O_3 and found that the analytical sensitivity of Ti with epithermal NAA is higher than by using fast neutron reaction $^{47}Ti(n,p)^{47}Sc$. In this work, the determination of titanium in aluminium is carried out by epithermal NAA with Cd as shielding material. In the experimental condition the interference from Ca by $^{46}Ca(n,\gamma)^{47}Ca(\beta)^{47}Sc$ reaction can be neglected.

3.3 The subtraction of uranium interference to determination of La, Ce, Nd, Zr, Mo, Sm

In NAA of La, Ce, Nd, Zr, Mo, Sm, the interference from uranium fission nuclides must be subtracted, because the irradiation of uranium can produce fission nuclides such as ^{140}La, ^{141}Ce, ^{147}Nd, ^{95}Zr, ^{153}Sm, ^{99}Mo and others, they cause the superimposition of nuclides produced by (n,γ) reaction of La, Ce, Nd, Zr, Mo and Sm. For subtracting this interference, the uranium fission coefficients f_U(g/gU) must be determined beforehand. Because the cross sections of fission or (n,γ) reactions are function of neutron energy, the fission coefficients must be determined by experiment. All of the fission nuclides mentioned above are from second to fifth daughter nuclides, their mother nuclides mostly have very short half-life, so when the irradiation or decay time are long enough, the presence of mother nuclides can be eliminated automatically. The fission coefficients of uranium to Ce, Nd, Mo, Zr and Sm do not vary with decay time. But it can be seen from the decay chain of ^{140}La: $^{140}\text{Xe} \xrightarrow{16\,\text{s}} {}^{140}\text{Cs} \xrightarrow{63.7\,\text{s}} {}^{140}\text{Ba} \xrightarrow{12.6\,\text{d}} {}^{140}\text{La} \xrightarrow{40.3\,\text{h}} {}^{140}\text{Ce}$, ^{140}La is gradually accumulated from ^{140}Ba, and the fission coefficient of uranium to La is gradually increased (see Table 3).

Table 3

Uranium interference coefficients g/gU

Element	La	Ce	Nd	Mo	Zr	Sm
Cooling 5 d	0.0118	0.161	0.137	0.450	4.43	0.105
Cooling 12 d	0.356	0.162	0.136	0.452	4.40	0.104

In instrumental NAA of Sm and U, besides uranium fission interference, the spectral interference of 103.7 keV from ^{239}Pu produced by $^{238}\text{U(n,}\gamma)^{239}\text{U}(\beta)^{239}\text{Np}(\beta)^{239}\text{Pu}$ is very serious to determination of Sm, this interference can be subtracted by determining counting ratio of 103/277 keV of ^{239}Pu and ^{239}Np, the sum interference coefficient of uranium to Sm is listed in Table 3.

Table 4

Detection limits of impurity elements in aluminium μg

Element	Detection limit	Element	Detection limit	Element	Detection limit
As	0.000348	Ga	0.025	Sc	0.00110
Au	0.0000542	Hf	0.0114	Sm	0.00083
Ba	0.42	La	0.0032	Th	0.0046
Ce	0.0187	Mn	0.089	Ti	0.89
Co	0.0049	Mo	0.0031	U	0.0035
Cr	0.0102	Nd	0.079	W	0.0468
Cu	2.2	Ni	1.28	Zn	0.82
Fe	11.2	Sb	0.0012		

3.4 Analytical quality assurance

For certifying accuracy of analytical results, the standard coal fly ash (NBS-1633a) and soil (GBW-07405) are determined simultaneously, the determined values (Table 2) are agreed with recommended ones.

3.5 Analytical sensitivity

The detection limits of impurity elements in aluminium are calculated according to Currie formula[7], the results are listed in Table 4.

4 CONCLUSION

In this paper, the content of 23 impurity elements in aluminium and its alloy samples is determined with thermal and epithermal NAA. Besides aluminium, this method can also be applied to determine impurity elements in other materials such as beryllium, silicon, magnesium, manganese, titanium and other metals and their compounds.

REFERENCES

1 Pitrus R K. J Radioanal Nucl Chem, 1988; 120(1):133
2 Mizohata A, Mamuro T, Tsujimoto T. J Radioanal Nucl Chem, 1978; 42(1):143
3 Beurton G, Beyssier B, Angella Y. J Radioanal Nucl Chem, 1977; 38(1–2):257
4 Brishay T Z. J Radioanal Nucl Chem, 1973; 13(1):87
5 Sorek H, Griffin H C. J Radioanal Nucl Chem, 1983; 79(1):135
6 Li Xiaolin. Nuclear Techniques (in Chinese), 1991; 14(8):454
7 Currie A. Anal Chem, 1968; 40(3):586