Journal of the Korean Nuclear Society
Volume 24, Number 2, June 1992

Determination of Trace Impurities in High Purity Aluminum by Instrumental Neutron Activation Analysis

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(Received January 13, 1992)

고순도알루미늄의 비파괴 중성자방사화분석

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(1992. 1. 13접수)

Abstract

Nondestructive neutron activation analysis of copper in high purity Aluminum samples which can be used as a parameter of impurity is investigated and determined. Other 23 trace impurity elements in the samples are also determined. In the analysis of copper, the new irradiation method using thermal column was applied to reduce the interfering activity of ^{24}Na produced by $^{27}Al(n,\alpha)^{24}Na$ reaction induced by fast neutron. As a result, the interference can be reduced to 100 times more than other activation methods. Also the influence by activity of ^{24}Na is found in the range of 2-3 %. It has been observed that the copper contents in so-called "six nine" class standard aluminum samples are about 0.54 ± 0.08 ppm. By the comparison with other values reported, our results are reasonable and can be available as a improved routine analysis.

요 약

고순도알루미늄중 불순물의 Parameter 로 이용될수 있는 구리의 비파괴 방사화분석법의 고찰 및 23 종의 극미량불순성분원소의 함량을 분석하였다. 즉 구리의 분석은 원자로의 속중성자에 의한 $^{27}Al(n,\alpha)^{24}Na$ 반응으로 생성되는 ^{24}Na 의 방사능을 감소시키기 위하여 Thermal Column 을 이용하였고 다른 조사공을 이용할 경우보다 약 100 배 정도 방해요인을 감소시킬수 있었다. ^{24}Na 에 의한 영향은 2-3 % 범위 이하 이었다. 이 방법에 의해 표준알루미늄(6 nine class)시료로 부터 구리를 정량하였고 아울러 기타 불순원소들을 일상 방사화분석법에 의해 정량하였다.구리의 함량은 0.54 ± 0.08 ppm 이었다. 이러한 결과는 문헌값과 비교할때 타당성이 있었고 일상분석에 이용할 수 있는 좋은 방법으로 여겨진다.

1. Introduction

Aluminum is not only widely used in various industrial fields because of its excellent mechanical properties but also one of the important nuclear reactor materials because of its profitable nuclear

properties.[1] Thus it is important to determine the impurity elements concentrations for quality control and assurance. Since the concentrations of various trace elements in high purity aluminum are of ppb or ppm level, multielement trace analyses by conventional chemical analysis is very difficult and troublesome.[2] Instrumental neutron activation analysis (INAA) followed by high resolution gamma-ray spectrometry makes it possible to analyze many trace elements simultaneously and nondestructively for the various kind of samples.[3-6] However, for neutron activation analysis of trace elements in high purity materials, special attention should be paid to the interference by the radionuclides produced from the matrix elements through other reactions than (n, γ). When aluminum is irradiated with usual reactor neutrons, ^{24}Na produced through $^{27}Al(n, \alpha)^{24}Na$ reaction interferes with the determination of Na as well as other trace elements. Particularly, the determination of copper content is one of the convenient methods to predict the parameter of the impurities level rapidly.

In this work, in order to reduce the production of ^{24}Na through the interfering reaction, aluminum samples were irradiated at the thermal column in which the fraction of thermal neutron flux density is larger than other irradiation sites. The influence of the irradiation is investigated and the contents of copper and other impurity elements were observed.

2. Experimental

About 500 mg of spectrograde aluminum samples, so-called 6-nine class standard aluminum shot, were washed in dilute HNO_3/distilled water/acetone to remove any external contamination and then weighed accurately. These were wrapped in an Al foil, then packed into self-manufactured aluminum container with the standard of copper for neutron irradiation.

Neutron irradiation were carried out in a graphite thermal column(TC) and a rotary specimen rack (RSR) of the TRIGA MARK-Ⅲ, KAERI. Neutron fluxes were 2.6×10^{10} n/cm^{2}s and 8.0×10^{12} n/cm^{2}s, respectively. Table 1 shows the quality of thermal neutron flux in the irradiation facilities with cadmium ratios.

Gamma-ray spectra of the irradiated samples were measured with a high purity Ge semiconductor detector, EG&G ORTEC, shielded with 10 cm lead against natural background radiation and connected to a personal computer and 8K multichannel analyzer, EG&G ORTEC Mastro-Ⅱ, with advanced application software for NAA. The detector resolution was 1.9 keV for the 1332 keV photopeak of ^{60}Co. The concentration of copper was quantitatively determined by comparison with the induced activity of the standard which was simultaneously activated and other elements were directly determined by the activity equation and

Table 1. The distribution of neutron flux at the irradiation facilities of the TRIGA MARK-Ⅲ reactor.

Irradiation Facility	Neutron Flux, ϕ = n/cm^{2}s		Cadmium Ratio	ϕ_t/ϕ_f
	Thermal, ϕ_t	Fast, ϕ_f		
Graphite Thermal Column, TC	2.5×10^{10}	9.5×10^4	26.08	2.74×10^5
Rotary Specimen Rack, RSR	8.0×10^{12}	7.0×10^8	2.57	1.14×10^4
Pneumatic Transfer System, PTS	1.25×10^{13}	3.0×10^{10}	1.88	4.0×10^2

Table 2. Irradiation and measurement conditions of the aluminum samples.

Irradiation Site	Neutron Flux n/cm^2s	Irradiation Time	Cooling Time	Counting Time	Nuclides Analyzed
TC	2.6×10^{10}	11 hr	12 hr	1000 sec	^{64}Cu
		47 hr	24 hr	2000 sec	〃
RSR	8.0×10^{12}	47 hr	5 da	2000 sec	^{46}Sc, ^{76}As, ^{122}Sb, ^{187}W, ^{198}Au
	〃	〃	15 da	4000 sec	***

*** ^{51}Cr, ^{59}Fe, ^{75}Se, ^{86}Rb, ^{110m}Ag, ^{113}Sn, ^{131}Ba, ^{141}Ce, ^{169}Yb, ^{177}Lu, ^{181}Hf, ^{182}Ta, ^{198}Au, ^{233}Pa, ^{239}Np.

nuclear data[7] for each element. Also the detection limits of various elements are achieved by Currie's equation[8] under our counting system and the analytical conditions. Table 2 shows the analytical conditions applied for irradiation,cooling and measurement.

3. Results and Discussion

–Analysis of Copper

There are several problems to consider for the analysis of copper in the high purity aluminum by nondestructive neutron activation analysis. Even though radionuclides ^{64}Cu and ^{66}Cu are available for the analysis, the 511 and 1346 keV photopeaks from ^{64}Cu must be used because of the matrix effects. It is also desirable to use the 511 keV peak of which the relative intensity is 200 times higher than the 1346 keV peak. The analytical methods using the 511 keV peak from ^{64}Cu is, therefore, considered in this work. Thermal column, in which the ratio of thermal neutron flux and fast neutron flux ($\phi t/\phi f$) is relatively high, is selected as the irradiation site to reduce the interferences caused by the secondary pair production from $^{27}Al(n,\alpha)^{24}Na$ reaction and scattering from the interaction of γ–ray with materials. Firstly, the ratios of ^{24}Na photopeak intensity from the (n, α) reaction and the 511 keV peak intensity at the different sample counting positions are calculated to find out the counting position factors. The results are shown in Table 3 as counts/counting efficiency and peak intensity ratio. The effect becomes significant with increasing source–detector distance. Secondly, to check the effect of fast neutron at the different irradiation positions the activity ratio of ^{24}Na produced from the $^{27}Al(n,\alpha)^{24}Na$ and $^{23}Na(n,\gamma)^{24}Na$ reactions at each irradiation site is calculated by the following approximate equation.

Table 3. The effects of pair production at various source–detector distances.

Source Position (cm)	Counts/Counting efficiency			Peak Ratio	
	511	1369	2754	511/1369	511/2754
#1 (2.5)	5.0 E5	3.1 E7	2.9 E7	0.04	0.09
#2 (4.7)	8.1 E5	3.0 E7	3.0 E7	0.07	0.15
#3 (6.9)	13.8 E5	2.9 E7	2.7 E7	0.12	0.26
#4 (9.1)	20.3 E5	2.6 E7	2.5 E7	0.20	0.39

$$A_R = A_{Na,t}/A_{Al,f}$$

where $A_{Na,t}$ and $A_{Al,f}$ are the activities produced by thermal and fast neutrons, respectively. Interference factors shown in Table 4 are relatively compared with 511 keV annihilation peak and 1369 and 2754 keV photopeaks. As a result the interference can be reduced to 100 times more than one at the other irradiation sites. The influence of ^{24}Na activity is less than the range of 2.3–2.8 % when thermal column is used for irradiation. Copper content of 6-nine class Al samples is 0.54 ± 0.08 ppm under the analytical condition where the reference was also used for the comparative method. This analytical method is good enough comparing to another reported value[6] and can be used as a improved routine analysis of aluminum.

–Analysis of other trace elements

It was impossible to analyze short half–life nuclides because of the strong interfering radioactivities produced by matrix elements. Intermediate and long–half life nuclides which have the good analytical sensitivities were quantitatively analyzed under the established analytical condition in advance. Detection limits of each nuclide are calculated by Currie's definition[8] allowing 10 % uncertainty.

$$\text{Detection Limit} = K^2/2\{1+(1+4B/K^2)^{1/2}\}$$

where, K is the value of 100 divided by allowable uncertainty in % and B is the total counts of natural background, compton scattering, and electronic noise. Table 5 shows the results of quantitative analysis of 23 trace impurity elements. These results are satisfactory comparing to other results[9,10]. This analytical method, therefore, can be used as a routine analysis accompanying with the analysis of copper in aluminum.

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Table 4. Comparison of thermal with fast neutron induced nuclear reactions. Source position : #1 (2.5 cm)

Irradiation Facility	Al		Na, STD		Al/Na,STD	
	511/1369	511/2754	511/1369	511/2754	511/1369	511/2754
R S R	0.045	0.095	0.038	0.079	1.187	1.201
P T S	0.044	0.093	0.037	0.077	1.189	1.203
T C	1.609	4.180	0.039	0.081	41.469	51.925
TC/RSR	35.76	44.01	1.024	1.018	34.922	43.232
TC/PTS	36.57	44.95	1.049	1.041	34.862	43.180

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Table 5. Analytical results of impurity elements in the aluminum samples.

Element	This Work(6-nineclass)		Other Values[6] (5-nine class)
	Content, ppb (RSD)	Det. limit, ppb	
Ag	5.25±1.53 (29.2)	3.9	< 60
As	1.92±0.34 (18.1)	1.5	36.5 (18.3)
Au	0.14±0.02 (17.5)	0.005	
Ba	76.29±2.80 (3.7)	79	2000 (6)
Ca*	3.27±0.60 (18.3)	2.9	
Cr	49.76±7.02 (14)	0.1	82.5 (22.3)
Cu*	0.54±0.08 (15)	0.007	< 5 (50)
Fe*	2.15±0.26 (12.4)	0.2	6.45 (23.7)
Hf	2.17±0.33 (15.2)	0.26	13 (9)
Mo	13.43±1.52 (11.2)	5.6	
Rb	5.43±1.79 (33)	8.1	
Sb	27.12±1.64 (6)	0.8	55.8 (25.5)
Sc	28.95±1.09 (3.8)	0.03	94.8 (4)
Se*	0.10±0.005 (5.6)	0.003	< 30
Sn*	5.70±1.94 (34.2)	7.3	
Ta*	0.13±0.01 (11)	0.002	
W	71.55±7.34 (10.2)	5.0	< 15
Zn	13.29±7.71 (58)	8.3	890 (11)
La	0.71±0.19 (27.5)	0.03	190 (5)
Ce	0.06±0.02 (40)	0.02	460 (7)
Sm	11.45±8.35 (73)	0.7	55.3 (13.5)
Yb	2.44±0.19 (8.1)	0.09	14 (21)
Lu	0.04±0.02 (46)	0.02	2.1 (15)
U	1.85±0.45 (24.5)	1.0	
Th	0.53±0.09 (16.8)	0.3	109 (5)

* Concentration in ppm.