PROTON ACTIVATION ANALYSIS
OF TRACE IMPURITIES IN PURIFIED COBALT

M. ISSHIKI, Y. FUKUDA,* K. IGAKI

*Department of Materials Science, Faculty of
Engineering, Tohoku University, Sendai-shi,
980 (Japan)*

Nondestructive activation analysis by proton beam bombardment has been applied to cobalt specimens. Thick target yields were measured on 18 elements for the purpose of quantitative analysis. In order to detect precisely the radionuclides with different half-lives, gamma-ray spectrometry was repeated three times after different cooling times of 1, 15 and 250 hrs from the finish of bombardment for 1 hr by 10.4 MeV proton beam. It was found that Ti, Cr, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Zr, Nb, Mo, Cd, Sn, Sb, and Te of the order of ppm or less could be detected accurately. Using the proton activation analysis developed, the purification effects of anion exchange, electrolytic extraction, and floating zone-refining have been examined. It was confirmed that the concentrations of the impurity elements contained in the starting material decreased stepwise upon the application of each purification method.

Introduction

Examination of the distribution and concentration of the impurity elements remaining in purified specimens should be required for the investigation of their real properties and for the further purification of materials. In the case of iron[1,2] aluminium,[2] chromium,[3] and nickel,[4] neutron activation analysis played an important role in examining what kinds of impurities remained after the application of respective purification methods. The suitable purification process was selected taking the analytical results into consideration. If neutron activation analysis is applied to cobalt specimens, strong radioactivity would be induced from the matrix ^{59}Co through (n, γ) reaction.

Proton activation analysis (PAA) is most suitable for the analysis of trace impurities in the cobalt specimens, because no nuclear reaction is induced from the cobalt matrix ^{59}Co by the proton bombardment at the energy range lower than 11 MeV. BENABEN et al.[5] reported on PAA of cobalt, however, the PAA proposed by them cannot be easily applied without information on the thick target yields of impurity elements. In

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*Graduate student, Tohoku University. Present address: Research and Development Division, Victor Company of Japan, Ltd. Yokohama Plant, 12,3-chome, Moriya-cho, Kanagawa-ku, Yokohama 221, Japan.

the present paper, the thick target yields for 18 elements were measured and the quantitative analysis on the specimens purified was carried out to confirm the effectiveness of the purification processes adopted.

Experimental

Thick target yields were measured on 18 reactions (see Table 1). Main impurities in commercial grade high purity cobalt were mostly covered. The materials used for the thick target yield measurement were mainly commercial high purity materials. Nominal purity of Ti, Zr, Nb, and Mo is 99.9% and that of Fe, Cu, Zn, Ge, Se, Cd, Sn, Sb, Te, and Pb is 99.99%. Concerning Ni, Cr, Ga, and As, a commercial stainless steel and a high purity GaAs wafer were used as target materials. The specimens for analysis were the cobalt purified by anion exchange, electrolytic extraction, and floating zone-refining,[6] starting from a commercial reagent grade $CoCl_2 \cdot 6H_2O$. Some of the specimens were prepared by arc-melting of the cobalt powders obtained by hydrogen reduction of the anhydrous cobalt chlorides.

The specimens for the thick target yield measurement were mounted on a turning target holder and bombarded simultaneously. The cobalt specimens were bombarded separately in a helium atmosphere. All the specimens were bombarded for 1 hr through a collimator (5 or 8 mm in diameter), a flux monitor (20 μm thick Ti foil), and a 10 μm thick Al foil for stopping recoiled atoms. The energy of the proton beam was 10.4 MeV at the surface of the specimens. The current of the incident beam for the analysis and the thick target yield measurement were 1–2 and 0.04 μA, respectively.

After the bombardment, the gamma-ray spectrum of each specimen was measured by a Ge(Li) detector. The measured peak areas of the relevant gamma-rays were corrected for the counting efficiency of the detector and the gamma-ray branching ratio. The impurity concentrations of the cobalt specimens were assessed from the comparison of the radioactivities from the impurities with the thick target yields measured after making correction for the range of the proton beam in both cobalt and the elements of which the thick target yields were measured.

Results and discussion

The thick target yields measured on 18 reactions are given in Table 1 with the half-lives and the energy of the gamma-ray peaks used for the measurement of radioactivities. In the table, the thick target yields measured are expressed as the radioactivity produced by the bombardment of 1 μA proton beam for 1 hr. In the case of Ni, ^{61}Cu can also be

Table 1
Thick target yields measured

Element	Reaction	Energy of γ-ray, keV	Half-life, h	Yield, $\mu Ci/\mu A \cdot h$
Ti	$^{48}Ti(p, n)^{48}V$	983.5	383.42	72.6
Cr	$^{52}Cr(p, n)^{52}Mn$	1434.1	134.2	31.7
Fe	$^{56}Fe(p, n)^{56}Co$	846.8	1890	13.1
Ni	$\binom{^{61}Ni(p, n)^{61}Cu}{^{60}Ni(p, \gamma)^{61}Cu}$	656.0	3.408	114
Cu	$^{63}Cu(p, n)^{63}Zn$	669.6	0.634	27 300
Zn	$^{66}Zn(p, n)^{66}Ga$	1039.4	9.45	1010
Ga	$^{69}Ga(p, n)^{69}Ge$	1106.4	39.05	939
Ge	$^{72}Ge(p, n)^{72}As$	834.0	26.01	1210
As	$^{75}As(p, n)^{75}Se$	264.6	2483	22.5
Se	$^{82}Se(p, n)^{82}Br$	776.5	35.34	154
Zr	$^{90}Zr(p, n)^{90}Nb$	1129.2	14.61	2180
Nb	$^{93}Nb(p, n)^{93m}Mo$	1477.1	6.96	6400
Mo	$^{95}Mo(p, n)^{95}Tc$	765.8	20.01	210
Cd	$^{111}Cd(p, n)^{111}In$	245.4	67.94	58.4
Sn	$^{122}Sn(p, n)^{122}Sb$	564	64.34	15.9
Sb	$^{121}Sb(p, n)^{121}Te$	573.1	402.7	1080
Te	$^{130}Te(p, n)^{130}I$	536.1	12.36	435
Pb	$^{206}Pb(p, n)^{206}Bi$	803.1	149.8	2.22

produced through the reaction $^{60}Ni(p, \gamma)$ ^{61}Cu, judging from the threshold energy of the reaction. The thick target yield of ^{61}Cu is considered to be the sum of the yields on both $^{61}Ni(p, n)$ ^{61}Cu and $^{60}Ni(p, \gamma)$ ^{61}Cu reactions.

Since the half-lives of the radioisotopes used are scattered from 0.63 to 1890 hrs, gamma-ray spectrometry should be repeated after different cooling times. The gamma-ray spectra measured on the starting material 1, 15, and 250 hrs after the bombardment are shown in Fig. 1. In the figure, ^{59}Fe, ^{60}Co, and ^{56}Mn are the products through the reactions ^{59}Co(n, p) ^{59}Fe, ^{59}Co(n, γ) $^{60, 60m}$Co, and ^{59}Co(n, α) ^{56}Mn, respectively, by neutrons from (p, n) reactions, and ^{40}K is due to the natural isotope in the circumstances. It is obvious from the figure that the repetition of gamma-ray spectromet-
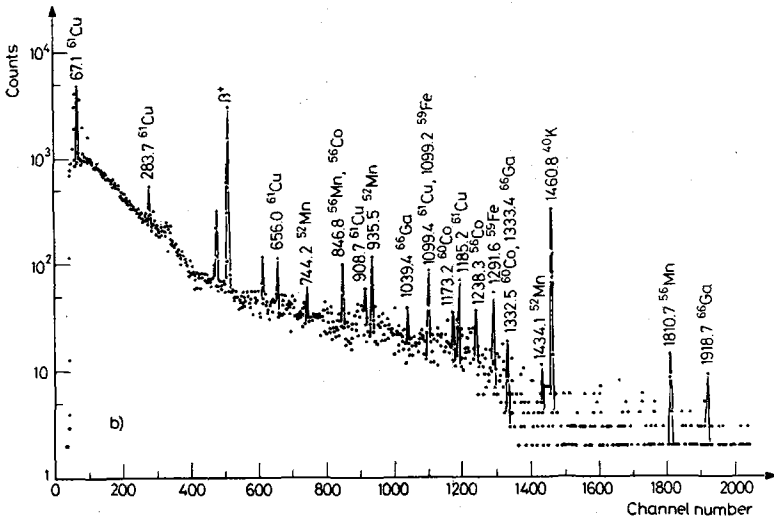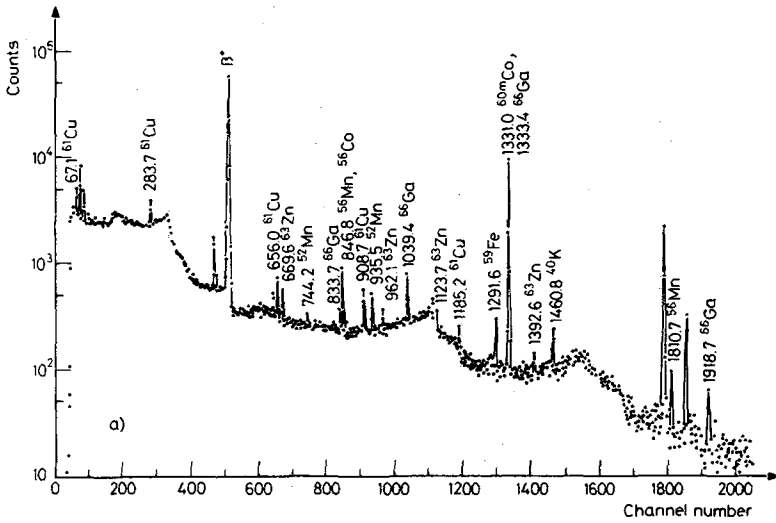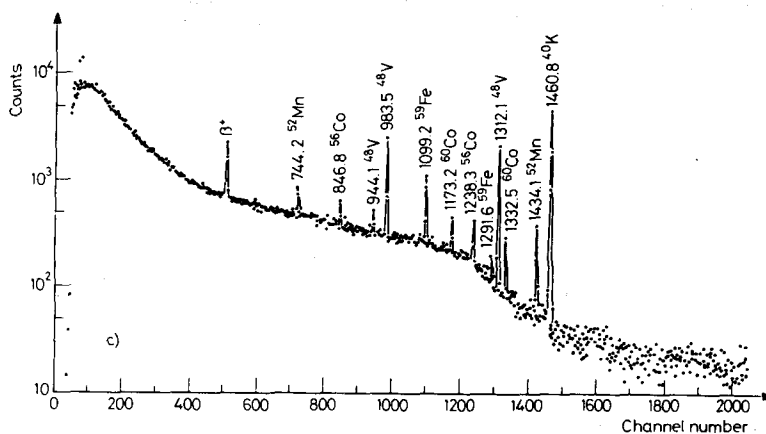
Fig. 1. Gamma ray spectra measured on the starting material 1 h(a), 15 h(b), and 250 h(c) after the bombardment. The accumulation times for (a), (b), and (c) are 2, 4, and 80 ks, respectively

ry after different cooling times should be required to detect the radionuclides with different half-lives. For example, the gamma-ray peaks from ^{48}V (944.1, 983.5, and 1312.1 keV), not observable in Fig. 1(a) and (b), were recognized clearly in Fig. 1(c) as the result of the decrease of the background level due to the decay of the radionuclides with relatively short half-lives.

In the case of activation analysis, special attention must be paid to interfering nuclear reactions which produce the same radionuclides as the marked one. Considering the energy of the proton beam used in the present work, the interference is estimated to be negligible. In order to perform the analysis non-destructively, however, another interference due to the superposition of the gamma-ray peaks emitted from the different radionuclides must be taken into account. For the examination of this type of interference, the concentrations of the impurities detected on the starting material were assessed from the relatively strong gamma-ray peaks of each radionuclide detected in Figs. 1(a), (b), and (c). It is clear from the results given in Table 2 that some interferences take place. For example, the gamma-ray peak of 846.8 keV from ^{56}Co is superimposed on that of 846.8 keV from ^{56}Mn. However, the 846.8 keV peak from ^{56}Co can be utilized for the analysis of iron after the decay of ^{56}Mn. Judging from the results given in Table 2 and the ratio of the peak to background counts, the gamma-ray peak of 983.5 keV in (c) is available for ^{48}V, 744.2 keV in (c) for ^{52}Mn, 846.8 keV in (c) for ^{56}Co, 656.0 keV in (b) for ^{61}Cu, 962.1 keV in (a) for ^{63}Zn, and 833.7 keV in (a) for ^{66}Ga. For the other radionuclides, the gamma-rays of the highest intensity were used for the calculation of the detection limits.

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Table 2

Impurity concentrations (wt ppm) in the starting material estimated
from various gamma-ray peaks measured after different
cooling times of 1 h(a), 15 h(b), and 250 h(c)

Element	Radioisotope	Half-life, h	Energy of γ-ray, keV	(a)	(b)	(c)
			944.1	—	—	14.2
Ti	[48]V	383.42	983.5	—	—	14.8
			1312.1	—	—	24.0
			744.2	24.1	22.6	21.5
Cr	[52]Mn	134.2	935.5	23.2	20.6	19.8
			1434.1	25.0	24.4	24.6
			846.8	529	21.6	21.4
Fe	[56]Co	1890				
			1238.3	53.3	22.3	23.2
			656.0	268	272	—
Ni	[61]Cu	3.408	908.7	372	295	—
			1185.2	515	282	—
			669.6	48.7	—	—
Cu	[63]Zn	0.634				
			962.1	45.3	—	—
			833.7	32.2	32.7	—
Zn	[66]Ga	9.45	1039.4	44.2	33.7	—
			1918.7	54.6	50.5	—

The detection limits and concentrations of the impurities in the cobalt specimens are summarized in Table 3. It is clearly observed that anion exchange, electrolytic extraction, and floating zone-refining are very effective to eliminate Ti, Cr, Ni, Cu, and Zn. Since the values of the detection limit were assessed from the counts of the background in the gamma-ray spectra, the values of the detection limit were affected by the times for accumulation and cooling. It should be noted that the values of the detection limit and the impurity concentration are very low except for Pb. This fact indicates that proton activation analysis is very effective for the analysis of trace impurities in cobalt specimens.

Table 3
Analytical results (wt ppm) for the specimens at each purification step.
The energy of gamma-ray used for the calculation is also listed.
Floating zone-refining was performed on the specimen extracted
electrolytically from the cobalt chloride aqueous solution purified by
anion exchange

Element	RI (γ-ray energy in keV)	Starting material	Anion-exchanged	Electrolytically extracted	Floating zone-refined
Ti	^{48}V(983.5)	15	1.7	0.2	< 0.08
Cr	^{52}Mn(744.2)	22	< 0.4	< 0.09	< 0.09
Fe	^{56}Co(846.8)	21	14	3.8	3.3
Ni	^{61}Cu(656.0)	272	< 4	< 0.2	< 0.2
Cu	^{63}Zn(962.1)	45	0.08	0.01	< 0.006
Zn	^{66}Ga(833.7)	32	< 2	< 1	< 0.3
Ga	^{69}Ge(1106.4)	< 5	< 0.9	< 0.04	< 0.01
Ge	^{72}As(834.0)	< 4	< 0.2	< 0.4	< 0.4
As	^{75}Se(264.7)	< 1	< 1	< 4	< 4
Se	^{82}Br(776.5)	< 6	< 2	< 1	< 0.7
Zr	^{90}Nb(1129.2)	< 1	< 0.2	< 0.05	< 0.03
Nb	^{93m}Mo(684.7)	< 0.01	< 0.005	< 0.003	< 0.002
Mo	^{95}Tc(765.8)	< 3	< 1	< 0.5	< 0.7
Cd	^{111}In(254.4)	< 30	< 8	< 2	< 1
Sn	^{122}Sb(564)	< 3	< 2	< 1	< 0.6
Sb	^{121}Te(573.1)	< 0.2	< 0.02	< 0.02	< 0.02
Te	^{130}I(536.1)	< 0.1	< 0.09	< 0.02	< 0.02
Pb	^{206}Bi(803.1)	< 200	< 40	< 80	< 90

Conclusion

Proton activation analysis has been applied to the analysis of trace impurities in cobalt specimens. Thick target yields of 18 reactions were measured for performing the quantitative analysis. The half-lives of the radionuclides induced by (p, n) reactions from the impurities were widely scattered, therefore, gamma-ray spectrometry was repeated after three different cooling times of 1, 15, and 250 hrs. In these experimental conditions, trace impurity elements of the order of ppm or less could be detected accurately.

It was found that anion exchange, electrolytic extraction, and floating zone-refining were effective to remove Ti, Cr, Ni, Cu, and Zn.

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