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DETERMINATION OF IMPURITIES IN ZIRCONIUM OXIDE BY NEUTRON ACTIVATION ANALYSIS*

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ABSTRACT

The instrumental method of neutron activation analysis was applied to the determination of impurities in zirconium oxide samples produced at IPEN-CNEN/SP.

The samples and the standards of the elements to be determined were irradiated in the IEA-R1 research reactor under a thermal neutron flux from 10^{11} to 10^{12} $n.cm^{-2}.s^{-1}$ for a period that varied from 3 min to 8 h and after adequate cooling time they were counted in a Ge(Li) detector coupled to a multichannel analyzer. The impurities of Al, Dy, Eu, Fe, Hf, Mn, Sc, Ta, Tb, Th and V were determined quantitatively in zirconium oxide samples. The relative standard deviations of the results for several impurities were, in general, lower than 15%.

In order to investigate the accuracy obtainable with the method a standard reference material Zircaloy 2 - SRM-360a from NIST was analysed. The quantitative determination limit was also evaluated for impurities present in zirconium oxide samples.

(*) Paper presented on the 41st Annual Meeting of the Brazilian Society for the Advancement of Science. Fortaleza-Ceara, July 9-15, 1989.

DETERMINAÇÃO DE IMPUREZAS EM ÓXIDO DE ZIRCÔNIO PELO MÉTODO DE ANÁLISE POR ATIVAÇÃO COM NEUTRONS

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RESUMO

O método instrumental de análise por ativação com neutrons foi aplicado na determinação de impurezas em amostras de óxido de zircônio produzido no IPEN-CNEN/SP.

Este método consistiu na irradiação de amostras e padrões no reator de pesquisa IEA-R1 sob um fluxo de neutrons térmicos de 10^{11} a 10^{12} $n.cm^{-2}.s^{-1}$ por um período de 3 min a 8 h e a seguir, decorridos adequados tempos de resfriamento, foram realizadas as suas contagens no detetor de Ge(Li) ligado a um multianalisador de raios gama de 4096 canais. Nas amostras de óxido de zircônio foram determinados, quantitativamente, os elementos Al, Dy, Eu, Fe, Hf, Mn, Sc, Ta, Tb, Th e V e estes resultados apresentaram, em geral, desvios padrões relativos menores que 15%.

Para examinar a exatidão do método, foi analisado material de referência Zircaloy 2 - SRM-360a proveniente do NIST. Determinaram-se também os valores dos limites de determinação quantitativamente para impurezas presentes em óxido de zircônio.

(*) Trabalho apresentado na 41ª Reunião Anual da Sociedade Brasileira para o Progresso da Ciência - Fortaleza-Ceará, 9 a 15 de Julho de 1989.

INTRODUCTION

Zirconium is widely used as structural material in nuclear reactors because of its small neutron absorption cross section (0.19 barns) as well as to its mechanical properties, resistance to corrosion and high melting point (1852°C). This element is also largely used in the chemical industries and in the manufacture of ceramic and refractory materials.

Consequently the purity control of the zirconium oxide production is very important in nuclear technology. However zirconium occurs together with hafnium and the presence of this element is undesirable because of its high neutron absorption cross section (105 barns).

Several analytical methods are applied in the characterization of impurities in zirconium oxides but the conventional methods are, in many cases, not sufficiently sensitive for analysis of nuclear grade zirconium oxide.

The instrumental method of neutron activation analysis (INAA) offers some advantages over other methods for trace analysis and it has been used by various researchers[4,6,8,9]. The method is simple, highly sensitive for multielemental analysis and it does not require the chemical separation of hafnium from zirconium, which is very difficult due to their similar chemical properties. Recently, Serbinovich et al[11] have presented a review of the methods of determining zirconium and hafnium in the presence of one another in a wide variety of materials.

In the present study the INAA method was applied to the determinations of hafnium and other impurities in Zircaloy-2 (SRM-360a) from the National Institute of Standards and Technology (NIST) and in zirconium oxide samples produced at the Department of Metallurgy of the IPEN-CNEN/SP[2].

EXPERIMENTAL

Preparation of synthetic standard of the elements. These standards were prepared by pipetting known volumes of the solutions of elements into a small piece of Whatman nº 42 filter paper and drying under an infrared lamp. Elemental standard solutions were obtained by dissolving a known amount of oxide, salt or metal of the elements to be analysed with adequate reagents and then diluted with distilled water. All the reagents used were p.a grade.

Procedure for analysis. Zirconium oxide samples were provided in the form of a fine powder or of small grains and in this case the grains were crushed in an agate mortar for homogeneization. Zircaloy 2 in the form of chips was previously washed using dilute solutions of nitric acid and distilled water to remove eventual contamination in their surfaces.

Aliquots of 10 to 50 mg of sample were weighed in small plastic bags or in polyethylene capsules and irradiated under thermal neutron flux of 10^{11} to 10^{12} $n.cm^{-2}.s^{-1}$ in the IEA-R1 research reactor for three different periods of 3 min, 30 min and 8 h depending on the radioisotope to be measured. The synthetic standards were also placed into the bags or capsules and irradiated together with the samples ensuring the same irradiation geometry. The presence of elements to be analysed in these bags or capsules was previously examined and was found to be negligible.

After an adequate decay period the irradiated sample and standards were counted with a Ge(Li) detector coupled to a Hewlett Packard (HP) 4096 channel analyzer connected to an HP 2100A minicomputer. The resolution (FWHM) of the system was 2.4 keV for the 1332 keV of ^{60}Co gamma rays. A computer program FALA[5], in Basic language, was used to locate peak position and energies and to calculate net areas. Table 1 shows the experimental conditions adopted in this work as well as the half-lives and gamma ray energies of each radioisotope selected for use.

RESULTS AND DISCUSSION

Reproducibility of results for hafnium determination in zirconium oxide samples is shown in Table 2. The precision expressed by relative standard deviation varied from 2.5 to 14% depending on the concentration of hafnium in the sample. In this work the radioisotopes ^{180m}Hf ($T_{1/2}$ = 5.5 h) and ^{181}Hf ($T_{1/2}$ = 44.6 d) were utilized for hafnium analysis. ^{181}Hf allowed analysis of lower concentration of this element than ^{180m}Hf. However when ^{180m}Hf could be detected the irradiation and decay time were shortter and the analysis was carried out within 12 h.

Table 3 shows the results obtained for Zircaloy 2 together with the certified values for standard reference material SRM 360a Zircaloy 2 and also the specification limits[10] for these elements in Zircaloy 2. The result for Hf analysis is not certified by NIST. Consequently our result was compared with the value published in ref(1).By comparing the results it can be concluded that there is a good agreement between the results. The relative errors obtained were lower than 10%. A major discrepancy occured in the case of Cu (relative error of 17,5%) due to bad counting statistics for the 1345 keV peak of ^{64}Cu.

Table 4 shows the results obtained for zirconium oxide samples produced at IPEN-CNEN/SP as well as the results of quantitative determination limit of elements evaluated according to Currie[3]. These limits were obtained using as sample, zirconium oxide containing 11 ppm of Hf. In Table 4, it can be seen that the results present a good precision, with relative standard deviations lower than 15%. The less precise results were obtained for Tb and V that present concentrations lower than 1.6 ppm.

In conclusion, the method presented here is rather simple and it can be applied for routine analysis of high purity zirconium compounds.

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TABLE 1 - Experimental Conditions and Nuclear Data Used in this Work

Irradiation Period (Neutron Flux)	Decay Period	Radioisotope Measured	Half-Life	Gamma Ray Peak (KeV)
3 min (3.7×10^{11} $n.cm^{-2}.s^{-1}$)	3 min	^{28}Al	2.31 min	1779
		^{52}V	3.76 min	1434
	30 min	^{165}Dy	2.36 h	546 ; 362
		^{56}Mn	2.58 h	846 ; 1811
30 min (1.7×10^{12} $n.cm^{-2}.s^{-1}$)	3 - 15 h	^{152m}Eu	9.35 h	841
		^{180m}Hf	5.5 h	215 ; 332
8 h (10^{12} $n.cm^{-2}.s^{-1}$)	~ 7 d	^{58}Co (Ni)	71.3 d	810
		^{51}Cr	27.8 d	320
		^{64}Cu	12.8 h	1345
		^{59}Fe	45.1 d	1098
		^{181}Hf	44.6 d	482
		^{46}Sc	83.9 d	889
		^{182}Ta	115.1 d	1221 ; 1231
		^{160}Tb	73.0 d	879
		^{233}Pa (Th)	27.0 d	312

TABLE 2 - Results of Hafnium Determination in Zirconium Oxide Samples. (Values in ppm.)

Determination Nº	Sample		
	ZrO_2-A	ZrO_2-B	ZrO_2-C
1	6.37	55.6	1567.8
2	5.68	63.6	1538.9
3	7.75	69.4	1615.5
4	5.80	64.0	
Mean	6.4 ± 0.9	63 ± 6	1574 ± 39
Rel.Std.Dev(%)	14	9.5	2.5

ZrO_2-A and ZrO_2-B samples were analysed by measurement of ^{181}Hf and ZrO_2-C by ^{180m}Hf .

TABLE 3 - Concentration of Trace Elements in Zircaloy-2

Element	Zircaloy-2		
	This Work	Certified Value for SRM 360a[7]	Specification Limit[8]
Cr (%)	0.099 ± 0.004	0.106	0.15
Cu (ppm)	151 ± 27	140	50
Fe (%)	0.14 ± 0.01	0.144	0.2
Hf (ppm)	87 ± 7	(94 ± 0.5)[*]	200
Ni (ppm)	538 ± 28	554	800

(*) - Result from Ref(9).

TABLE 4 - Results of Analysis of Zirconium Oxide Samples with Different Purity Grade Produced at the IPEN-CNEN/SP and Results of Determination Limit

Element	Zirconium Oxide Samples			Determination Limit
	A	B	C	
Al (ppm)	4.6 ± 0.6	60 ± 6	364 ± 15	NDD
Dy (ppm)	149 ± 9	59 ± 9	ND	4.9
Eu (ppm)	ND	0.04	ND	2.3
Fe (%)	ND	0.20 ± 0.01	ND	0.02
Hf (%)	4.1 ± 0.3	1.5 ± 0.2	8.7 ± 1.0	0.0011[a] / 0.0296[b]
Mn (ppm)	1.3 ± 0.2	1.2 ± 0.2	49.0 ± 0.7	0.9
Sc (ppm)	ND	1.0 ± 0.1	ND	0.2
Ta (ppm)	6.6 ± 0.6	ND	ND	13
Tb (ppm)	ND	140 ± 30	ND	1.7
Th (ppm)	348 ± 30	93 ± 10	36.4 ± 0.6	12
V (ppm)	1.6 ± 0.5	1.5 ± 0.3	4.8 ± 0.5	0.3

ND - Not detected NDD - Not determined

a - Result obtained by measurement of ^{181}Hf

b - Result obtained by measurement of ^{180m}Hf

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