Semi-Quantitative Analysis of Electron Probe Micro-Analyzer for Zr-2.5Nb Pressure Tube Material

Y. S. Choo*, Y. J. Kim, B. O. Yoo, S. J. Baik, Y. G. Jin, K.S. Heo, H. M. Kim, and S. B. Ahn
Irradiated Materials Examination Facility, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, Republic of Korea
*Corresponding author: yschoo@kaeri.re.kr

1. Introduction

The electron probe micro-analyzer (EPMA) is widely applied to analyze the chemical compositions of unknown materials, especially for irradiated nuclear fuels [1].

To know materials of unknown specimens for PTs, qualitative analyses, line analyses, mappings, and quantitative analyses are carried out without the standard specimen with the EPMA machine through calculating the K-raw(%).

When quantitative analyses is done without the standard specimen, semi-quantitative analyses are alternatively performed by adapting the mathematical method of probability and statistics designed and supplied by the JEOL.

In this paper, the adapted probability and statistics supplied by the JEOL is not only investigated, but also unknown specimens for PTs Zr-2.5Nb materials are analyzed.

2. Experimental & Results

2.1 Specimen

Four (4) specimens as shown in Fig. 1 are used to investigate the adapted probability and statistics for the semi-quantitative analysis.

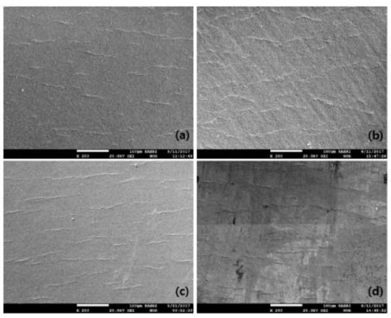

Fig. 1. The specimens of unknown for PTs material, (a) H82, (b) H122, (c) D82, and (d) D122.

2.2 Electron probe micro-analyzer (EPMA)[2]

EPMA was carried out using a state of the art shielded JEOL JXA-8230 model specially shielded and modified to permit the analysis of irradiated nuclear fuels shown in Fig. 2. This equipment has 4 WDXs (Wave Dispersive Spectrometers) to analyze elements from Boron to Uranium, and an additional function of SEM (Scanning Electron Microscope).

Fig. 2. The appearance of the EPMA at hot lab. in IMEF.

2.3 K-raw(%)

The K-raw(%) is calculated by using following equation (1).

$$\mathrm{K-raw}(\%) = \frac{X\text{−}ray\ Intensity_{UNK_{net}}}{X\text{−}ray\ Intensity_{STD_{net}}} \times 100 \quad (1)$$

,where
X-ray Intensity : counts per beam current in cps/uA,
net : net count in cps,
UNK : unknown specimen,
STD : standard specimen.

But, the standard specimen is not used so the X-ray intensity of standard specimen is also not known. Then the semi-quantitative analysis is done by the machine, i.e., EPMA.

2.4 Semi-qualitative analysis

From the result of qualitative analysis, the semi-qualitative analyses were performed to know the contents (wt.%) of an unknown specimen under the following conditions, and the test results are shown in Table 1.

- HT (kV) & beam current (A) : 20.0/1.0E-08
- CH-3(Zr, PETH/Cal_STD)
- CH-3(Nb, PETH/Cal_STD)

2.5 Coefficients Semi-qualitative analysis for crystals

The coefficients of CH-3(PETH) crystal for Zr (z=40) and Nb (z=41) elements are suggested by the JEOL, and those are calculated by an equation (2) and summarized in Table 2.

$$\ln(\mathrm{I}) = a + b\ \times Z + c\ \times Z^2 + d \times Z^3 \quad (2)$$

, where I = cps/100pA, Z= ln(z), z = atomic number

Table 1. The test results from the The EPMA of H122 (unknown) specimen by semi-quantitative analysis for Zr and Nb elements

Element	Zr			Nb		
Frequency	1st	2nd	3rd	1st	2nd	3rd
Peak(mm)	194.586	194.559	194.564	183.458	183.509	183.508
Net(cps)	10895.1	10675.5	10767.9	175.6	199.4	183.5
Bg-	56.8	65.6	63.2	26.6	30.2	31
Bg+	37.2	41.8	30.8	46.6	44.4	47.6
S.D.(%)	0.3	0.31	0.31	2.84	2.63	2.79
D.L.(ppm)	294	314	294	406	409	420
K-raw(%)	104.612	102.299	103.133	2.637	2.987	2.751
Curr.(A) :	2E-08	2E-08	2E-08	1.04E-08	1.04E-08	1.04E-08
Intensity (cps/uA)	5.45E+05	5.33E+05	5.37E+05	1.69E+04	1.92E+04	1.76E+04
Remarks	0104QNT			0105QNT		

Table 2. The coefficients of crystals CH-3(PETH) & CH-3(PETH) for Zr and Nb elements estimated/suggested by the JEOL and calculated results

Elememt	Zr	Nb	Remarks
Channel	CH-3	CH-3	
Crystal Name/ Orbital	PETH/La	PETH/La	
z	40	41	Atomic No.
a	-1.97409	-1.97409	
b	-53.0312	-53.0312	
c	27.82146	27.82146	
d	-3.52669	-3.52669	
ln(Z)	3.688879	3.713572	
ln(I)	3.958137	4.155133	
cps/100pA	52.35967	63.76046	
CA(cps/uA)	523596.7	637604.6	Calculated
ME(cps/uA)	497069.8	605278.0	Measured
Difference	26528.6	32326.6	= CA-ME

2.6 Probability and statistics

If the population is known to normal as shown in Fig. 3, the sampling distribution of $\bar{X}$ will follow a normal distribution exactly, no matter how small the size of the samples [3]. So the confidence interval for μ is calculated by an equation (3).

$$\bar{x} - z\alpha/_2 \frac{\sigma}{\sqrt{n}} < \mu < \bar{x} + z\alpha/_2 \frac{\sigma}{\sqrt{n}} \qquad (3)$$

, where

$$Z = \frac{\bar{X} - \mu}{\sigma/\sqrt{n}}, \qquad P\left(-z\alpha/_2 < Z < z\alpha/_2\right) = 1 - \alpha$$

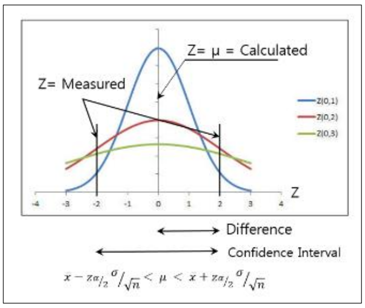

Fig. 3. The meaning of confidence Interval in normal distribution.

2.7 Calculation by adapting the probability and statistics

According to clause 2.6, confidence interval and probability of it were calculated by equation (4) and the whole results are shown in Table 3.

$$\mathrm{CI(Confidence\ Interval)} = \left(z_{value} - \frac{\sigma_{UNK}}{100}\right),$$
$$\mathrm{PCI(Prob.\ of\ it)} = \mathrm{P(Z < CI)} - P(Z > -CI), \quad (4)$$
$$\mathrm{K-raw(\%)} = K - raw(\%) - 1 \times PCI$$

2.8 Summary and discussion

The K-raw(%) values are almost same as shown in Table 1 and Table 3. As explained in clause 2.3, the K-raw(%) in Table 1 is calculated by program developed by JEOL considering the confidence interval with difference between calculated and measured X-ray intensity(cps/uA) for each elements such as Zr and Nb.

In case of testing the quantitative analysis for unknown specimen without standard specimens, therefore, it must be considered that the analysis results are carried out by the semi-quantitative analysis with probability 95.45%(2σ), and 97.33%(3σ).

Table 3. Final results for the elements of Zr and Nb

Element	Zr			Nb		
Frequency	1st	2nd	3rd	1st	2nd	3rd
Intensity_unk (cps/uA)	5.45E+05	5.33E+05	5.37E+05	1.69E+04	1.92E+04	1.76E+04
Intensity_Measured (cps/uA)	497073.8	497073.8	497073.8	605278.0	605278.0	605278.0
K-raw(%)-1	1.0965	1.0722	1.0810	0.0279	0.0317	0.0292
Confidence Interval	1.9970	1.9969	1.9969	1.9716	1.9737	1.9721
Probability of Confidence Interval	0.9541	0.9541	0.9541	0.9513	0.9515	0.9514
Probability of Difference	0.9493	0.9493	0.9493	0.9493	0.9493	0.9493
Z-value	2	2	2	2	2	2
K-raw(%)	104.62%	102.30%	103.14%	2.65%	3.01%	2.77%

3. Conclusions

Throughout the results of the semi-quantitative analyses between measured from the machine and calculated from calculations, the following items were investigated and concluded.

(1) The results, i.e. population, produced by the machine are seemed to have the normal distribution, $N(\mu, \sigma^2)$.

(2) Without standard specimen, the equation (2) is applied theoretically to obtain the calculated X-ray intensity for CAL_STD spectrometer.

(3) The theoretical calculated value includes the errors, i.e., the approximate 2.5 ~ 5.0% uncertainty basically.

REFERENCES

[1] S. Bremier et al., "Electron probe microanalysis of a METHPHIX UPuZr metallic alloy fuel irradiated to 7.0 at.% burn-up", Journal of Nuclear Materials 480 p.109 (2016).

[2] Y.S Choo et al., "The Development of Dismantling Machine for Capsule and HANARO fuel bundle Irradiated at HANARO", KAERI/TR-1078/98, KAERI (1998).

[3] R.Walpole et al., "Probability and Statistics for Engineers and Scientists", third edition, ISBN 0-02424170-9 (1985).