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Transmutation of technetium: results of the EFTTRA-T1 experiment

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Abstract

The transmutation of the fission product ^{99}Tc was studied by neutron irradiation in the High Flux Reactor at Petten. Six metallic rods of pure Tc, distributed over three capsules, were irradiated during eight reactor cycles to a total neutron fluence of about 2×10^{26} m^{-2}. Metallographic examinations showed that no changes in the microstructure were visible after the irradiation. Electron probe microanalysis (EPMA) of the radial distribution of Ru, the product of the transmutation process, showed an increase from about 6% in the centre to 12–18% near the rim of the pellets. This effect is due to resonance-shielding of epithermal neutrons in the rim region. Mass spectrometric analysis of the pellet-average Ru concentration showed that the extent of transmutation is about 6–7%. © 1998 Elsevier Science B.V.

1. Introduction

Technetium is a non-natural element that is present in significant amounts in spent fuel from nuclear reactors: fission of ^{235}U and ^{239}Pu by thermal neutrons produces the technetium isotope ^{99}Tc in a yield of 6.2%, fission by fast neutrons gives a yield of 5.9%. With a very long half life (2.12×10^5 years) ^{99}Tc decays via β^--emission (0.29 MeV) to the stable ruthenium isotope ^{99}Ru.

Upon reprocessing of spent fuel, technetium remains in the high level waste (HLW), which is vitrified, temporarily stored and eventually disposed of by geological burial. The long-term radiological effects of geological disposal of HLW have been analysed for several types of host rocks [1], and the studies show that ^{99}Tc is, due to its long half-life and high mobility in acqueous environments, one of the risk-dominating isotopes. In order to further reduce the radiological impact of geological disposal of HLW, partitioning and transmutation have (re)gained much attention in recent years. By partitioning (separating) the long-lived radiotoxic nuclides from the HLW and transmuting them to short-lived or stable ones, the radiotoxicity of the waste as well as the risks of its disposal can be reduced significantly.

^{99}Tc can be transmuted to the stable ruthenium isotope ^{100}Ru by a single neutron capture:

$$^{99}\mathrm{Tc} + n \rightarrow {}^{100}\mathrm{Ru} + \beta^-.$$

The neutron-capture cross-section of ^{99}Tc in the thermal energy range, 19 barn, is relatively high and several strong resonance absorptions are present in the epithermal energy range, as shown in Fig. 1 [2]. Irradiation in a high-flux thermal reactor or in a moderated sub-assembly of a fast reactor seems therefore the most promising approach for transmutation. Within the EFTTRA cooperation [3] both options are being investigated by irradiations in the High Flux Reactor (HFR) in the Netherlands and in the Phénix reactor in France.

The irradiation in the HFR, which was aimed at achieving a transmutation rate of about 5%, was performed in 1994. For this experiment, which is called EFTTRA-T1, six rods of technetium metal were irradiated for eight reactor cycles to a total neutron fluence of about 2×10^{26} m^{-2}. The present paper describes the results of the joint post-irradiation examinations of these rods performed at

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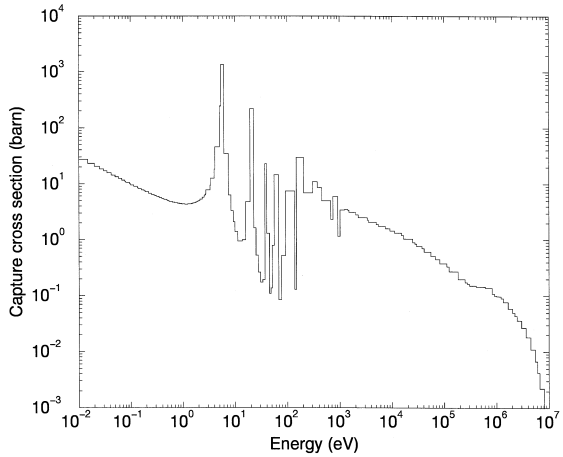

Fig. 1. The $^{99}Tc(n,\gamma)^{100}Tc$ microscopic cross-section as a function of neutron energy from the JEF2.2 nuclear data file.

the laboratories of CEA, ECN and ITU. Preliminary results have been described in Ref. [4].

2. Experimental

2.1. Samples

The irradiation capsules for the experiment were fabricated at the Institute for Transuranium Elements (ITU) in Karlsruhe. Three targets were prepared, each containing two technetium rods enclosed in a 15.15 Ti stainless steel capsule. The rods of technetium metal, 4.8 mm diameter and 25 mm length, had a density higher than 99.9% of the theoretical density. Analysis by glow-discharge mass spectrometry showed that the ruthenium concentration in the metal was less than 1 ppm. Details of the fabrication method are described in Ref. [4].

Table 1
Diameter and length of the technetium samples

Sample	Diameter (mm)		Length (mm)	
	Pre-test	Post-test	Pre-test	Post-test
A	4.80 ± 0.01	4.83 ± 0.01	25.05	25.09
B	4.81 ± 0.02	4.84 ± 0.01	25.05	25.12
C	4.81 ± 0.01	4.82 ± 0.04	25.00	25.18
D	4.81 ± 0.02	4.83 ± 0.03		
E	4.81 ± 0.02	4.81 ± 0.01		
F	4.80 ± 0.01	4.81 ± 0.01		

2.2. Irradiation conditions

The targets were positioned in peripheral holes of an aluminium sample holder designed for one leg of a TRIO in-pile irradiation facility for the HFR [5]. The sample holder consisted of a ring-shaped aluminum block with peripheral holes in which the targets were positioned. The sample holder was surrounded by three stainless steel containments with gas gaps between them which were flushed with inert gas (He or Ne) for temperature control. The temperature of the sample holder was measured by thermocouples positioned close to the samples and varied around 700 K. The central temperature in the samples was calculated to be about 1100 K.

The samples were irradiated in the central in-core position C5 of the HFR during eight reactor cycles (192.95 full power days). The neutron fluence was monitored by means of gamma-scan wires and fluence detector sets (detector foils). The results of the post-test analysis of the detector foils show that the mean total neutron fluence was about 2×10^{26} m^{-2} with a thermal component ($E < 0.7$ eV) of 3.2×10^{25} m^{-2}, a fast component ($E > 0.1$ MeV) of 8.8×10^{25} m^{-2} and an intermediate component of 7.5×10^{25} m^{-2}.

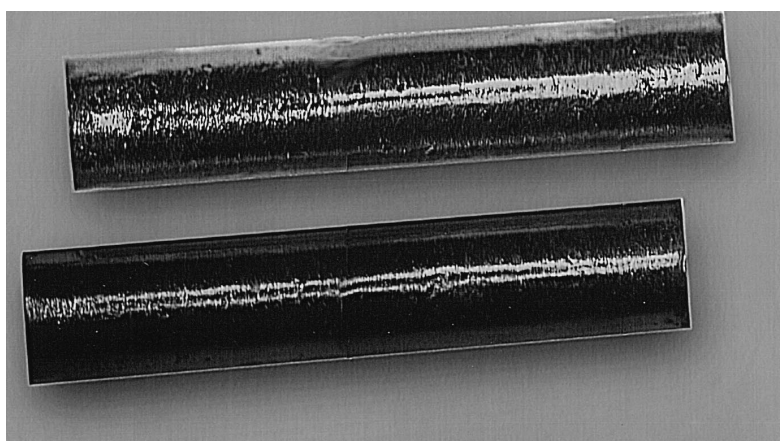

Fig. 2. The technetium rods A and B after irradiation.

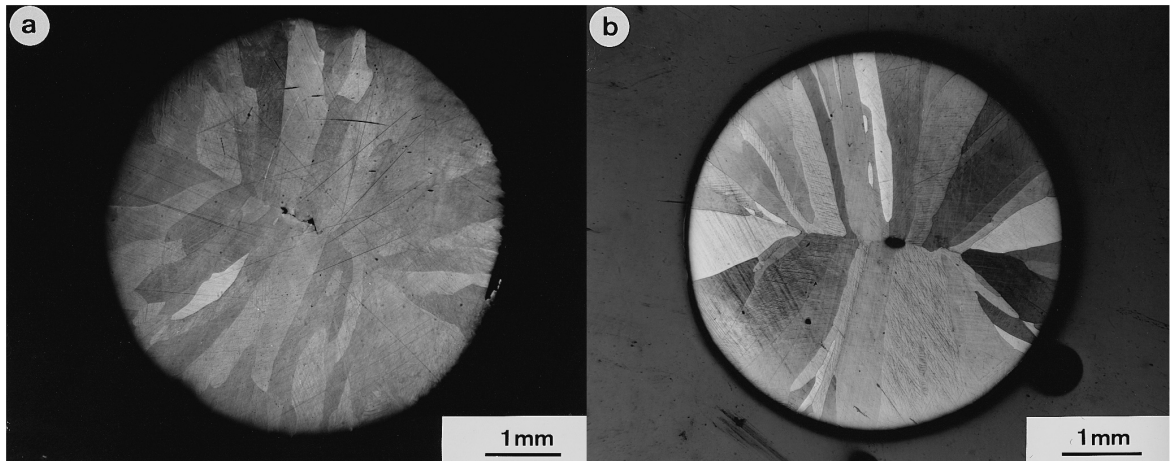

Fig. 3. The microscopic cross-section of the technetium rods: (a) the as fabricated; (b) following irradiation (section F1).

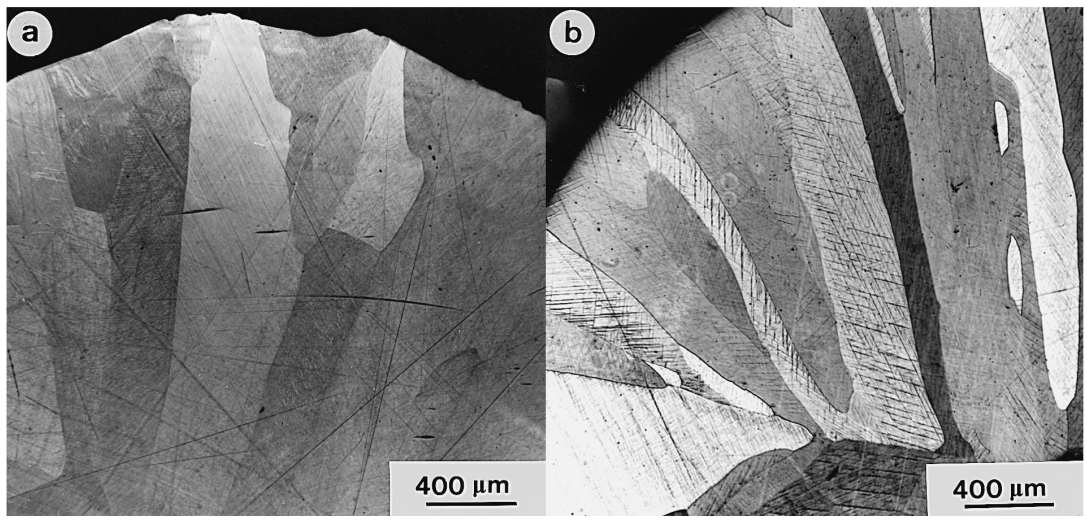

Fig. 4. Higher magnification micrographs: (a) structural details of the as fabricated material; (b) the irradiated material (section F1). Note the absence of significant structural changes, such as grain orientation, grain growth, and changes in the number and orientation of planar defects.

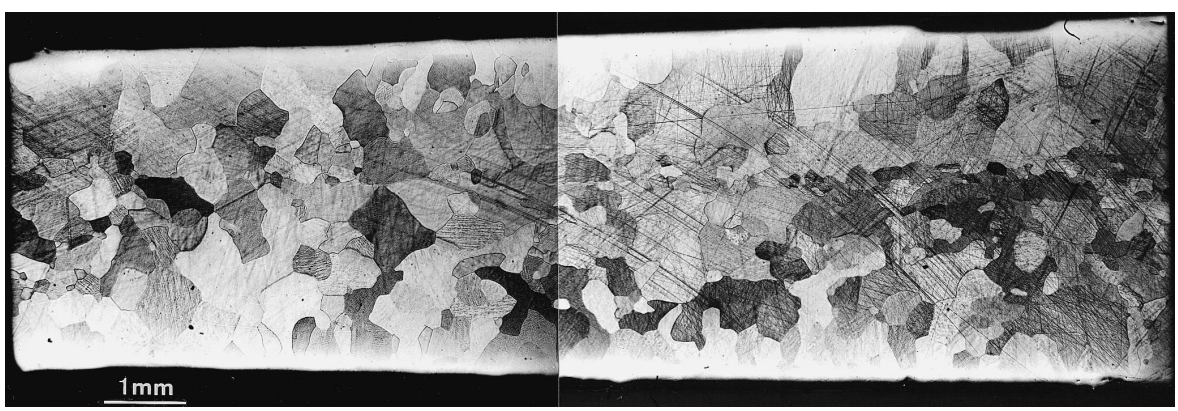

Fig. 5. Longitudinal section F3 of the irradiated technetium rod at low magnification.

2.3. Post-irradiation examinations

After irradiation, the three capsules were opened in the hot-cell laboratory in Petten. The six rods were designated A to F.

Rods A and B were visually inspected (Fig. 2) and re-encapsulated at ECN for further irradiation (EFTTRA-T2) in the HFR. At the end of 1997, the EFTTRA-T2 irradiation, aiming at a transmutation rate of $\simeq 20\%$, has been terminated and results of the post-irradiation examinations are expected in 1998.

Rod C was transported to CEA-Cadarache. Firstly, measurement of the dimensions was performed. Secondly, two transverse cross-sections were cut at 5 mm from the bottom (section C1) and the top (section C2). The samples were embedded in araldite resin, ground with SiC paper and polished with diamond paste. These two sections were examined by electron probe microanalysis (EPMA) using a CAMECA SX50 microprobe operating at 20 kV and 50 nA, using a sample composed of 5.25 wt% Ru and 94.72 wt% Tc as a standard.

Rod D was analysed at ECN. Transverse cross-sections were cut at 5 mm from the bottom (D1) and the top (D2). At the same sections, thin slices of about 100 mg were cut for chemical analysis. A longitudinal section D3 was prepared from the remaining part. The sections were embedded in hysol, ground with SiC paper and polished with diamond paste. The sections were examined by optical microscopy for which they were etched by means of an equimolar solution of HNO_3 and H_2O_2 containing a few drops of HF. EPMA was done on a CAMECA MS46R microprobe operating at 20 kV and 40 nA, using ruthenium metal as a standard. For the chemical analysis by isotope dilution mass spectrometry (IDMS), the discs were dissolved in 7 M HNO_3 to which a standard solution was added. Ruthenium was distilled from the solution as ruthenium tetroxide and collected in a NaOH solution, in which it was precipitated as ruthenium hydroxide. The hydroxide was then dissolved in concentrated hydrochloric acid. The ruthenium concentration in this solution was measured by mass-spectrometry.

Rods E and F were transported to ITU where four transverse cross-section specimens were cut at 5 mm from

Table 2
The level of transmutation for technetium derived by EPMA

Sample	Ruthenium concentration (at.%)		Integral
	Pellet center	Pellet edge	
C1	5.0	11.7	6.1
	5.3	11.6	6.1
C2	4.9	11.3	5.8
	5.5	–	5.8
D1	5.6	14.6	7.1
	5.8	12.4	6.3
D2	6.0	16.0	7.4
	5.9	13.2	6.8
E1	6.5	12.9	6.8
	–	13.0	–
E2	6.2	11.4	6.4
	6.2	17.6	7.4
F1	7.0	14.6	7.1
F2	5.3	18.1	7.2
	6.5	14.7	7.1

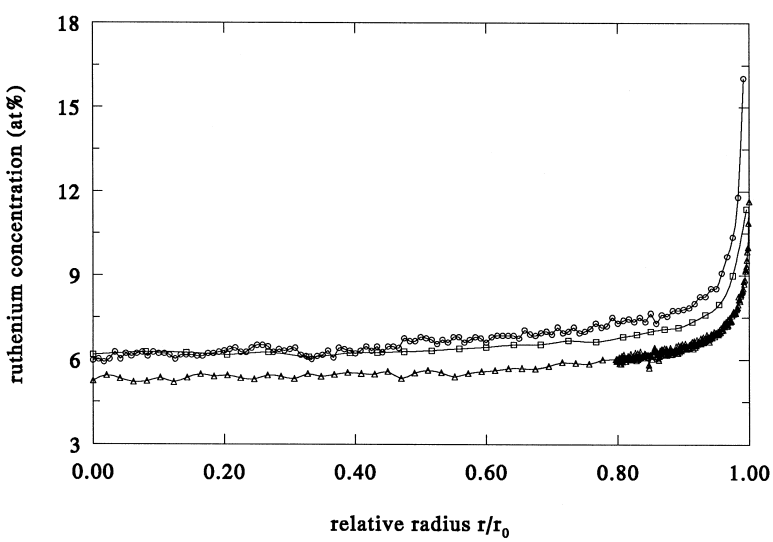

Fig. 6. Representative EPMA radial concentration profiles for ruthenium in the technetium samples. ○, section D1; □, section E2; △, section C1.

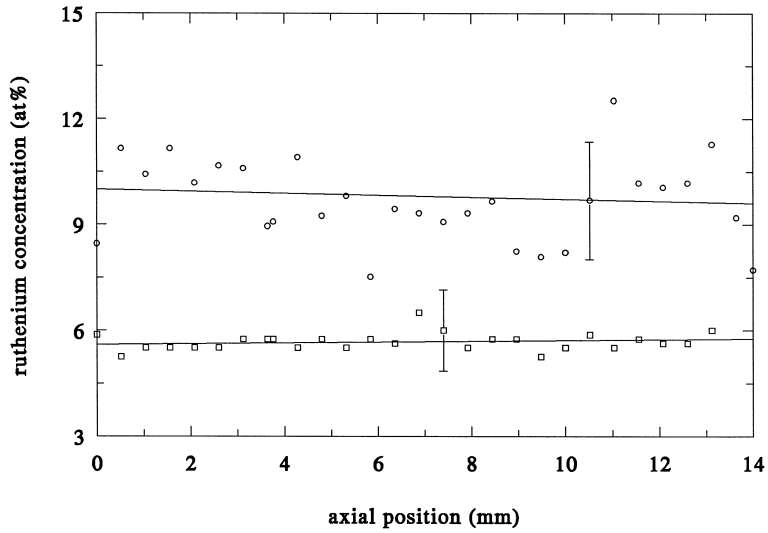

Fig. 7. The axial distribution of ruthenium in technetium as derived from EPMA line scans (section F3); □, centre-line; ○, pellet rim ($r/r_0 = 0.99$); the lines are least-squares fits of the data.

the bottom (E1 and F1) and the top (E2 and F2) of each bar. The remaining cylinders were axially sectioned and four more specimens were prepared (E3, E4, F3 and F4). Samples E4 and F4 were intended for chemical analysis and the remaining six were all characterised by optical microscopy and EPMA. All microscopy specimens were embedded in araldite resin, mechanically ground using 400 to 1200 grit paper, polished with 1 μm to 0.25 μm diamond suspension to metallographic quality and chemically etched as described above. EPMA was carried out on a CAMECA MS46 microprobe operating at 20 kV and 100 nA, using ruthenium and technetium metals as standards.

3. Results

The results of the measurements of the length and diameter of the rods are summarized in Table 1. When post-test diameters are compared with the pre-test data, it can be seen that with one exception (sample E) which remained unchanged, all other samples show a slight in-

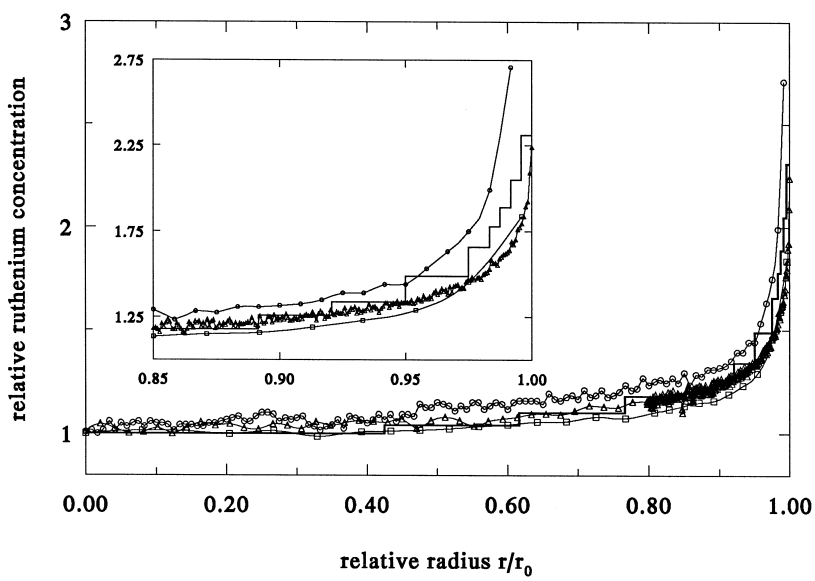

Fig. 8. Comparison of the calculated and experimental radial distributions of ruthenium in the technetium samples; step-wise thick line, MCNP results for a model in which the rod is represented by 10 concentric zones; ○, section D1; □, section E2; △, section C1.

crease in diameter. A small increase in sample length was also observed.

The metallographic examinations of all the irradiated samples revealed no significant changes in the microstructure as compared to that of the unirradiated material, showing preferentially oriented crystal growth along the {001} crystallographic directions, forming columnar grains (Figs. 3–5). Crystal growth most probably started at the periphery of the Tc cylinder and ended at the center. Such structures are usually formed during cooling along a temperature gradient, as occurred in the water-cooled mould that was used during the fabrication process [6].

The Ru concentration profiles as obtained at the different laboratories by EPMA of cross-section samples are in good agreement, as shown in Fig. 6. The profiles showed a sharp increase of the Ru concentration in the outer 150 μm of the rods, though the peak values in the rim region can vary significantly, even within one cross-section. The integral Ru concentration, as obtained by a volume integration of radial profiles varied from 5.8 to 7.4 at.% (Table 2). The longitudinal sections showed little variation in the axial direction, though the scatter along the pellet centerline is much less than that along the pellet edge (Fig. 7).

IDMS analysis of sections D1 and D2 yielded (6.1 ± 0.1) at.% and (6.4 ± 0.2) at.% for the pellet average Ru concentration, respectively.

4. Discussion

Technetium as well as its transmutation product ruthenium have a hexagonal structure and they form a continuous solid solution [7]. Although the molar volume of the solid solution decreases with increasing Ru content, anisotropic swelling due to neutron irradiation can be expected for this type of crystal. The present results, however, show negligible changes in the dimensions of the pellets for a level of transmutation of about 6–7%, indicating negligible volume changes ($\leq 1\%$).

The integral Ru concentration obtained by EPMA and IDMS are in reasonable agreement, but the results of IDMS are considered more relevant for comparison with calculated transmutation levels since they represent the average value of the cylindrical volume. In contrast, the Ru concentrations obtained by integration of 'one-dimensional' EPMA profile cannot be representative for a cylindrical volume because variation exists in the Ru concentration near the pellet edge. Possible explanations for this variation might be the roughness of the pellet surface because in this location the Tc concentration changes dramatically over small distances, or the differences in the neutron flux in the facility due to the influence of the other samples in the sample holder and other experiments in the HFR core.

The measured Ru concentrations can be compared to the results of post-test calculations by Monte Carlo techniques using the KENO-Va and MCNP codes in combination with nuclear data libraries based on the JEF2.2 evaluated file. MCNP calculations have been used to obtain the Ru concentration as a function of the radius, three-dimensional KENO calculations to obtain the sample-averaged transmutation level. Details of the calculations have been described in Ref. [8].

The normalized radial Ru concentrations obtained by EPMA are in good agreement with the results of the MCNP calculations in which the rod is represented by 10 concentric zones to model the resonance shielding of the epithermal neutrons in the resolved energy range [8]. The calculations show that at the edge of the rods the contributions of thermal and epithermal neutrons to the transmutation rate are about equal. However, the contribution of epithermal neutrons rapidly decreases from the edge to the sample inwards and in the center of the pellet thermal neutrons predominate the transmutation rate. As shown in Fig. 8, the decrease of the Ru concentration in the rim of the rods is equally pronounced in the experimental and calculated curves indicating that the effect observed in the irradiated rods is caused by resonance shielding only and that other processes are not of importance.

The mean sample-averaged transmutation level obtained by KENO for the three targets is $(5.90 \pm 0.05)\%$. This value is $\simeq 10\%$ lower than that found experimentally, whereas the mean calculated-to-experimental ratio for the reaction rates in ^{54}Fe and ^{59}Co detector foils obtained by KENO is (1.01 ± 0.02) [8]. The origin of this discrepancy might therefore be found in the thermal-capture cross-section of ^{99}Tc. This quantity is subjected to significant uncertainties as has been suggested by Harada et al. [9] who found that the thermal-capture cross-section of ^{99}Tc is (22.9 ± 1.3) barn, which is 10 to 15% higher than the value in the JEF2.2 evaluated nuclear data file (19 barn) used in the calculations.

5. Summary and conclusions

The results from the post-irradiation examinations presented here, can be summarized as follows.

- No significant change of the dimensions of the pellet has occurred during irradiation, indicating that at the a level of transmutation of about 6% swelling is at least partially compensated by a decrease of the molar volume.
- Optical microscopy indicated no changes in the microstructure of the technetium samples.
- EPMA and IDMS both showed that the pellet-average burnup was about 6.5% for a neutron fluence of $\simeq 2 \times 10^{26}$ m^{-2}, which is in fair agreement with the results of Monte Carlo calculations.

It can be concluded that the EFTTRA-T1 experiment does not reveal any technical limitations to the use of metallic technetium as a target for transmutation. However, since the extent of transmutation in this experiment

was only 6–7%, the reported excellent behaviour under irradiation of Tc has to be confirmed for higher values of the level of transmutation, which will be obtained in the EFTTRA-T2 experiment.

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