ELSEVIER

Journal of Nuclear Materials 280 (2000) 360–364

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Optical properties of γ-irradiated synthetic sapphire and yttria-stabilized zirconia spectroscopic windows

Leon Fuks [a,*], Claude Degueldre [b,1]

[a] Institute of Nuclear Chemistry and Technology, 16 Dorodna St., 03195 Warsaw, Poland
[b] Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Received 11 January 1999; accepted 23 March 2000

Abstract

Synthetic sapphire and yttria-stabilized zirconia single-crystals were irradiated by increasing doses of γ-radiation to study the changes of their optical properties. The optical transparency of α-Al_2O_3 was nearly constant up to the γ-radiation dose of 150 kGy for the spectral range of 400–1000 nm, while yellowish-brown coloration of $(Zr_{0.89}Y_{0.11})O_{1.94}$ appeared for irradiation above 1 kGy. However, after a short-term heating in the temperature of 210°C stable discoloration of zirconia can be achieved. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Extremely difficult measurement conditions for examination of the corrosion progress occurring in nuclear installations in the course of their operation (circulation of high-temperature/high-pressure water) result in numerous analytical methods which are currently under consideration. At present, the most frequently used, appear to be the electrochemical methods, e.g. corrosion potential measurements (ECP), high-temperature conductivity and pH measurements, impedance and electrochemical noise spectroscopy, amperometric determination of O_2, H_2, NH_3, N_2H_4, and other chemical species. Other techniques, such as ion chromatography, γ-spectrometry, ^{10}B determination by means of neutron absorption and optical methods are still rarely applied [1,2].

It has already been shown that continuous, non-invasive monitoring of the formation of corrosion layers in the reactor operating mode can be effectively performed using optical spectroscopy. A novel technique for monitoring the oxide layer growth online, reflectance spectroscopy (RS) seems to be most attractive. Its development, verification and application was recently reported [3–8]. As the number of factors influencing RS spectra are relatively large, their interpretation may be in some cases more complex than that obtained by transmission. However, when properly recorded for a long series of successive measurements, diffuse reflection spectroscopy (DRS) provides directly, a great number of relevant data about the corrosion process.

One of the crucial points for reliable optical measurements is the long-term stability of window materials in the presence of nuclear reactor water. It should be transparent and has to act as a pressure/temperature barrier for a relatively long time. Considering the measurement conditions (BWR operating conditions, thermo-mechanical stresses, optical transparency and commercial availability), α-aluminum oxide in the form of synthetic sapphire (SS) and cubic yttria-stabilized zirconium oxide single-crystals (c-YSZ) have been chosen as the most promising window materials on the basis of both initial literature scanning and preliminary experimental tests [7,8].

Present investigations have been undertaken to study the influence of γ-radiation doses on the UV–Vis–NIR light transmission through both above-mentioned optical materials. The problem is of importance, because numerous corrosion products can be released into the circulating nuclear reactor water and some of them can

* Corresponding author. Fax: + 48-22 811 1532.
E-mail addresses: lfuks@orange.ichtj.waw.pl (L. Fuks), degueldre@psi.ch (C. Degueldre).
[1] Fax: +41-56 310 22 05.

0022-3115/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(00)00048-9

be activated. It is known that radiation emitted by water, circulating in the primary circuit of nuclear installations (about 450 Sv yr^{-1} [9]) comes not only from the ^{16}N radionuclides produced by the ^{16}O (n, p) ^{16}N reaction, but also from the ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{58}Co and especially from ^{60}Co radionuclides.

2. Experimental

2.1. Materials

Synthetic sapphire: Hexagonal single-crystal of α-Al_2O_3 was supplied by Saphirwerk Industrieprodukte (Brügg, Switzerland) as commercial product synthesized for the watch-glass industry. Crystals of the sapphire were grown by the Verneuil method [10]. It has already been found that the total content of the impurities is less than 0.01 mass% [8,10].

Yttria-stabilized zirconia oxide: Cubic single-crystal material (produced by means of the skull method) with about 90.5 mol% of ZrO_2 was provided by MaTecK (Jülich, Germany). The manufacturer of c-YSZ testifies, that the material contains about 2 mol% of impurities [11].

Optical specimens were formed as carefully polished disks with the diameter of 15 mm and thickness of 5 mm. The producer of c-YSZ disks declares, that the surface roughness of, the disks are 1 (average) and 3 nm (maximum) [11]. Data describing the surface of the SS specimen are not available.

2.2. Irradiation procedure

The investigated specimens were irradiated with γ-rays at room temperature in the channel of the ^{60}Co-source (Gamma-cell 220, AECL, Canada). The source has been calibrated with water, showing emitted dose rate of 3.45 kGy h^{-1}.

The minimum irradition dose was 0.1 kGy. Next, the dose was increased in consecutive experiments up to 150 kGy. After each irradiation, both investigated materials were examined accurately whether they did not exhibit the radioluminescence generated in the experiment. It has been found that neither SS nor YSZ demonstrate such a side effect of irradiation, which may disturb any optical measurement performed in the nuclear installations.

2.3. Optical measurements and calculations

The optic fiber probe of the Guided Wave Model 260 Spectrum Analyser was used to supply the samples with light and to collect the transmitted light. The incident and reflected light beams had a diameter of about 2 mm and the angle of the beam cone was about 6.5°. Non-γ-irradiated sapphire samples have been taken as the reference material. It has been already shown that the region of wavelengths below 1000 nm should only be examined because of strong light absorption in water [4, 5].

UV–Vis–NIR optical data were recorded and processed with the PC software (GW1 ver. 1.1) supplied by Guided Wave. The Savitzky–Golay smoothing method [12] has been applied. It performs a local polynomial regression to determine the smoothed value for each data point. The method is superior to adjacent averaging procedures because it tends to preserve features of the data such as peak height and width, which are usually washed out by these methods.

3. Results

It has been observed, that the color of SS specimens did not change significantly after γ-irradiation up to $D_\gamma = 150$ kGy. On the contrary, the color of c-YSZ samples changed rapidly from totally transparent to transparent yellowish-brown for doses exceeding 1 kGy (two to three times higher than the total dose of radiation emitted by nuclear installation primary circuit water). Selected optical transmission spectra obtained for the SS and c-YSZ specimens irradiated with different doses are presented in Figs. 1–3, respectively.

As one can see in Figs. 1 and 2 , spectra obtained for the SS samples differ slightly from the spectrum of non-irradiated material. A broad plateau of the transparency in the range of 500–1000 nm seems to be stable and transmission coefficients are nearly 100% independent of the radiation dose. On the contrary, a significant decrease in the transparency upon the action of γ-radiation can be observed in the region below 400 nm. The obtained data seem to be in good agreement with those presented by Orlinski et al. [13].

Fig. 4, in turn, presents selected residual spectra, i.e., the difference between the spectra of irradiated and non-irradiated samples, calculated for the sapphire window which was γ-irradiated with selected doses up to 150 kGy. As one can see, the spectra can be deconvoluted showing two separate absorption bands in the region of 300 (4.2 eV) and 400 nm (3.1 eV), respectively. The results obtained in the present paper seem to be consistent with the data published earlier [13–15]. Unfortunately, the spectra recorded here do not permit a precise deconvolution in the UV region of 200–250 nm (6.1–4.9 eV). The origin of the γ-ray induced coloring of α-Al_2O_3 is still not clear but it has been suggested, that γ-irradiation causes the generation of hole centers with an absorption band close to 400 nm (about 3.1 eV) and electron centers in the UV region [14,15]. So, the observed slight decrease of transmission upon irradiation, in the case of sapphire windows, can be related to formation of optical centers as a result of appearing lattice defects.

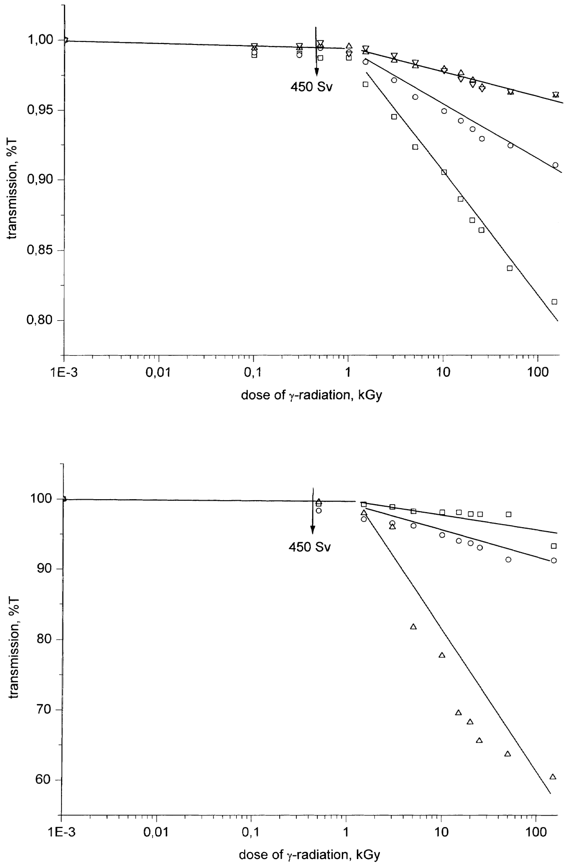

Fig. 1. Changes of optical transmission with increasing γ-radiation dose for SS (lower plot) and for YSZ (upper plot). Points denoted as □ concern the spectral wavelength of 900 nm, ○ −700 nm, △ −500 nm and ▽ −300 nm.

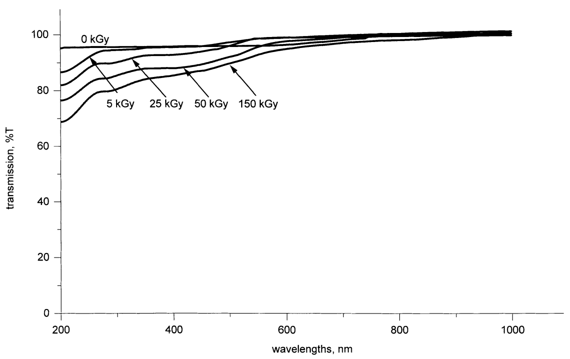

Fig. 2. Transmission spectra of the SS irradiated with various doses of γ-radiation.

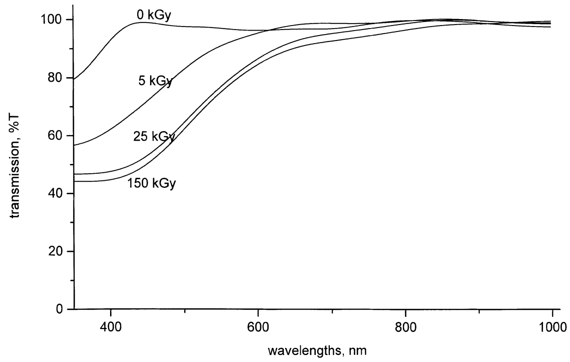

Fig. 3. Transmission spectra of YSZ irradiated with various doses of γ-radiation.

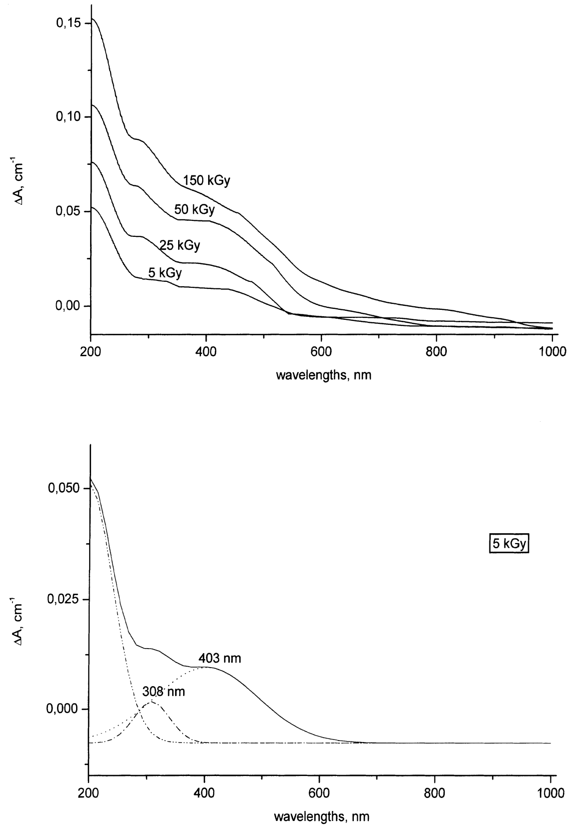

Fig. 4. Residual optical absorption spectra for SS irradiated with selected doses of γ-radiation (upper plot); deconvolution of peaks for spectrum attributed to 5 kGy dose (lower plot).

The dose dependence of the light transmission through YSZ windows is presented in Figs. 1 and 3. It can be seen that lower wavelength values, which describe the plateau of the transparency increase from 400 to 750 nm. The plateau length shortens rapidly for low γ-radiation doses (3–10 kGy), later keeping constant values up to the dose of $D_\gamma = 150$ kGy. Similarly as for SS, transmission coefficients forming the plateau weakly depend on the radiation dose.

As one can see in Fig. 5, residual spectra calculated for γ-irradiated c-YSZ in the region of 350–1000 nm show one broad absorption peak with a maximum around 395–405 nm (i.e., for transitions with an energy of about 3.1 eV). It corresponds to the value of 3.2 eV (395 nm) reported by Dietrich et al. [16] and assigned by them as responsible for the yellowish-brown coloration of polycrystalline yttria-stabilized tetragonal zirconia (t-YZP). The spectral peak of 3.2 eV has been described by the authors as related to the transition occurring in an unknown extrinsic defect, associated with tracer impurity ions existing in the zirconia polycrystal [17].

Due to the requirements of optical measurement conditions (temperature of about 300°C), samples of both the investigated materials have been heated after several consecutive irradiation procedures. Temperature increase has been started from 150°C and it has been found that several minutes of heating above 210°C cause permanent discoloration of zirconia windows. Optical transmission spectra recorded for both materials after the heating process were similar to those for the non-irradiated samples. So, it can be suggested that *inline* monitoring of the corrosion process occurring in nuclear installations operating under the BWR conditions by means of the optical DRS method, can be performed applying both the SS and YSZ windows. In order to minimize side effects generated by γ-radiation occurring in the installation reference, the spectra should be carefully recorded prior to the start of the measurements.

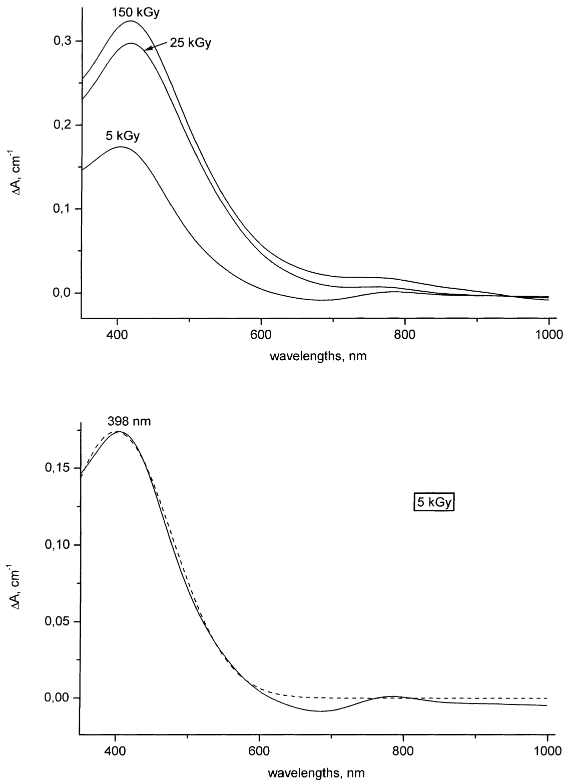

Fig. 5. Residual optical absorption spectra for YSZ irradiated with selected doses of γ-radiation (upper plot); deconvolution of peaks for spectrum attributed to 5 kGy dose (lower plot).

4. Conclusions

From the work performed, the following conclusions can be drawn:

- For low-temperature measurements (i.e., below 200°C), SS can satisfy the requirements of the radiation stability of optical properties in the whole 350–1000 nm spectral region.
- For low-temperature measurements in the region of wavelengths $\lambda > 600$ nm, optical transparency of YSZ is independent of the doses of γ-radiation up to 150 kGy. So, zirconia can be recommended as the potential optical window material for low-temperature measurements only in the limited spectral region. However, it should be mentioned that heating above 210°C causes discoloration of the material by extension of the spectral region of measurements to wavelengths >450 nm.
- Both investigated materials can be recommended as the long-term stable window materials for optical measurements in the presence of circulating high-temperature (i.e., above 200°C)/high-pressure nuclear reactor water containing γ-emitting radionuclides.
- Considering the BWR measurements of nuclear installations (temperature about 290°C), main mechanical properties and resistance towards the chemicals in connection with optical properties favor the sapphire windows material [8].

Acknowledgements

The authors are grateful to Mr Michael Steinemann from the Paul Scherrer Institute for irradiation assistance of the examined materials. This research was supported by the International Atomic Energy Agency (Research Contract No POL8426). Thanks are due to the State Committee for Scientific Research (KBN; Poland) for financial assistance in the scientific cooperation between INCT (Warsaw) and PSI (Villigen), as well as to the Swiss Federal Nuclear Safety Inspectorate (HSK) for partial financial support.

References

[1] H.P Alder, W. Francioni, C. Degueldre, Online Measurement of Particles in Reactor Water of BWRs, in: Proceed-

ings of the Sixth International Conference on Water Chemistry of Nuclear. Reactor Systems, Bournemouth, BNES, 1992, p. 133.
[2] C. Degueldre, J.C. Dran, E. Schenker, J. Nucl. Mater. 188 (1992) 255.
[3] H.P. Alder, C. Degueldre, E. Schenker, Non-invasive monitoring of corrosion in the light water reactor by optical methods, in: Proceedings of the Seventh International Conference on Water Chemistry of Nuclear Reactor Systems, Bournemouth, BNES, 1996, p. 272.
[4] C. Degueldre, S. O'Prey, W. Francioni, Corros. Sci. 38 (1996) 1763.
[5] C. Degueldre, L. Fuks, E. Schenker, Meas. Sci. Technol. 9 (1998) 809.
[6] C. Degueldre, L. Fuks, E. Schenker, Appl. Surf. Sci. 134 (1998) 254.
[7] L. Fuks, C. Degueldre, Materials for in situ monitoring of light water reactor (LWR) water chemistry by optical methods, Institute of Nuclear Chemistry and Technology (Warsaw) Annual Report 1997, INCT, 1998, p. 99.
[8] L. Fuks, Materials for in situ monitoring of light water reactor (LWR) water chemistry by optical methods, MAEA Research Coordination Meeting, High Temperature On-line Monitoring of Water Chemistry and Corrosion (WACOL), Helsinki, 1999, unpublished data.
[9] Private communication from a local NPP staff.
[10] W. Weber, Saphirwerk Industrieprodukte AG, private communication (Saphirwerk Industrieprodukte AG internet home page: http://www.saphirwerk.ch/).
[11] MaTecK, GmbH, internet home page: http://www.mateck.de/.
[12] A. Savitzky, M.J.E. Golay, Anal. Chem. 36 (1964) 1627.
[13] D.V. Orlinski, I.V.A. Tovsky, T.A. Bazilevskaya, V.T. Gritsyna, V.I.I. Kov, I.A. Ivanin, V.D.K. Chuk, A.V.K. Nikov, D.V. Pavlov, Y.A. Tarabrin, S.I. Turchin, V.S. Vojtsenya, I.L. Yudin, J. Nucl. Mater. 212–215 (1994) 1059.
[14] R.A. Hunt, R.H. Schuler, Phys. Rev. 89 (1953) 664.
[15] P.W. Lewy, Phys. Rev. 123 (1961) 1226.
[16] A. Dietrich, R.B. Heimann, G. Willmann, J. Mater. Sci. 7 (1996) 559.
[17] J.H. Crawford Jr., J. Nucl. Mater. 108 (1982) 644.