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The colour of medical-grade zirconia (Y-TZP)

A. DIETRICH*, R. B. HEIMANN*, G. WILLMANN‡
Institute of Mineralogy, Freiberg University of Mining and Technology, DO9599 Freiberg, Germany
‡*Medical Product Division, CERASIV Innovatives Keramik-Engineering GmbH, D73207 Plochingen, Germany*

Optical spectroscopy, ESR spectroscopy, and standard and wavelength- and-temperature-resolved thermoluminenscence spectroscopy of as-sintered and γ-irradiated medical-grade yttrium-stabilized tetragonal zirconia polycrystal (Y-TZP) material showed that the pronounced colour change, after irradiation, from off-white to a purplish-grey shade can be related to two electronic transitions at local defects in the crystal lattice. The first transition could be associated with an electron–hole state characterized by an oxygen ion trapped in the vicinity of a yttrium ion ($Y'_{Zr}O^*$) and can be correlated with an optical absorption band at 2.6 eV (480 nm). The second transition is presumably an extrinsic defect correlated with an optical absorption band at 3.2 eV (395 nm). From the experimental results it can be concluded that those local electronic defects responsible for the colour change on γ-irradiation do not influence safety-related mechanical or chemical properties of the ceramic femoral ball heads of hip endoprostheses produced from Y-TZP.

1. Introduction

Today about 0.1% of the population in Europe and North America are in need of a total hip replacement (THP). The goal was, and still is, to improve the performance and longevity of systems used for THPs. The articulating components of hip endoprostheses are a femoral head (spherical ball) and an acetabular cup. Table I shows the state-of-the-art materials of several clinically used combinations. The objective is to find and use those combinations of material with extremely low wear since worn particles, in particular polyethylene, cause osteolysis and aseptic loosening of the titanium alloy stem or the acetabular cup. Hence a potentially risky revision operation is required [1].

Among others, alumina femoral heads were developed because their extreme hardness and excellent corrosion resistance are important prerequisites for load bearing and articulating implants (Tables II and III). Moreover, alumina ceramics proved to be a good material for femoral ball heads in contact with an acetabular cup made from ultra high-molecular weight polyethylene (PE-UHMW), and an excellent material for the combination of alumina head and alumina cup (Tables II and III). When ceramic heads articulate against PE-UHMW the wear rate is reduced by a factor of four to ten compared to the pair metal/PE-UHMW (Table 4). More than 2 million alumina ceramic heads have been successfully used to date [3]. Most of them have a diameter of 28 mm and still articulate against PE-UHMW even though it has been found recently that advanced "hard/hard" alumina combinations have a lower linear wear rate of below 5 μm/year (Table I) [4].

In 1974 the German Federal Government started to fund an R&D programme to develop ceramic components for improved hip endoprostheses. In 1986 stabilized zirconia ceramics were introduced to the orthopaedic communities in France and the USA [5] since they are very attractive materials in terms of higher bending strengths and fracture toughnesses compared to alumina (Tables II and III) [6, 7]. Of the several types of zirconia available today, up to now Y-TZP (yttria-stabilized tetragonal zirconia polycrystals) has proved the best material for medical application, i.e. for femoral ball heads articulating against a PE-UHMW acetabular cup (Table IV). During the last few years, zirconia material has been very much improved for industrial applications, in particular Y-TZP material. Mg-PSZ (magnesia-partially stabilized zirconia) has been used occasionally in Australia and the USA. CERASIV GmbH developed a novel Y-TZP under the licensed name ZIOLOX® (Table II). But even though it is a proven fact that the wear rates of ceramics, i.e. alumina and zirconia, articulating

TABLE I Material combinations for acetabular cups and femoral ball heads presently in clinical use

Combination	Acetabular cup	Femoral ball head
Soft/hard	PE-UHMW	Cobalt–chrome alloy
	PE-UHMW	Alumina ceramics
	PE-UHMW	Zirconia ceramics
	PE-UHMW	Coated metal
	CFRP	Alumina ceramics
Hard/hard	Cobalt–chrome alloy	Cobalt–chrome alloy
	Alumina ceramics	Alumina ceramics

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TABLE II Selected properties of medical-grade alumina and zirconia

Property	Alumina (BIOLOX®)	Zirconia Y-TZP(ZIOLOX®)	Zirconia Mg-PSZ
Material	$Al_2O_3 + MgO$	$ZrO_2 + Y_2O_3$	$ZrO_2 + MgO$
Type of material	Polycrystalline corundum	Polycrystalline tetragonal	Partially stabilized
Standards	ISO 6474	Draft ISO/DIS 13356	None
Modulus (GPa)	380	210	210
Hardness ($HV_{0.1}$)	2000	1250	1250
Bending strength (MPa)	>500	>950	>500
Toughness ($MPa\sqrt{m}$)	4	8	10
Thermal conductivity (W/mk)	25	2	2
Wetting angle	<50	>50	>50
Grain size (μm)	<3	<0.5	≈ 30
Application	Femoral heads Acetabular cups Components for shoulder and knee	Femoral heads	Femoral heads

TABLE III Important properties for ceramic femoral ball heads [2]

Basic Property	Prerequisite for
Extreme hardness No plastic deformation Very low elastic deformation No creep	Wear resistance over many years
Fine-grained microstructure Dense (not porous)	Excellent surface finish for low wear rate
No creep	Load-bearing ability
High bending strength	High fracture strength
High compression strength Good fatigue properties	Safe product
Extremely good corrosion resistance	Bioinert
Electrical insulation	No galvanic reactions, no fretting corrosion

TABLE IV Wear data measured from radiography of retrieved endoprostheses [8, 9]

Combination	Linear wear (μm/a)
Metal/PE-UHMW	up to 200
BIOLOX®/PE-UHMW	<25
BIOLOX®/CFRP	<4
BIOLOX®/BIOLOX®	<5
ZIOLOX®/PE-UHMW	??
Y-TZP/Y-TZP	Disastrous

against PE-UHMW are lower than those of metal heads, it is still controversial whether alumina or zirconia are preferable for femoral ball heads.

Both alumina and zirconia ceramics are manufactured using standard methods of ceramic powder processing. The basic steps are as follows [10]. For the production of high-tech alumina or zirconia only synthetic raw materials are used. To achieve the properties listed in Tables II and III the raw materials must be purified and finely grained (grain size < 1 μm). Components with simple geometry (cylinders) are being cold-pressed and green-machined to obtain shapes very close to those of the end product (near net-shape technology). Then the components are sintered in air. Often the parts will be hot isostatically pressed to enhance the density and thus the mechanical properties. To achieve the tolerances required for application in hip implant systems the sintered components have to be machined using diamond tools, and subsequently polished.

Some of the mechanical and functional properties of medical-grades alumina (BIOLOX®) and zirconia (ZIOLOX®) are listed in Table II. For alumina there are standards available, e.g. ISO 6474, ASTM F 603; for zirconia there is only a draft, ISO/DIS 13356.

2. Colour development in bioinert ceramics

A total hip joint replacement is a complex and highly involved procedure that requires an extremely high degree of experience, skill and responsibility of the performing surgeons. This responsibility is not just limited to the actual mechanics of the operation procedure but includes that for the implants the surgeons use. Since surgeons generally lack equipment as well as experience to decide whether the implants they are provided with conform to accepted specifications (EN 14630) and are thus safe to use, they have to rely totally on the materials information obtained from the manufacturer. Therefore the manufacturer bears the burden of an almost unprecedented degree of Total Quality Management (TQM), surpassing any normal warranty regulations.

Apart from checking for visible flaws, chipping or cracking of the implant and, in particular, the ceramic femoral ball head, the only criterion of "visual quality control" the surgeons have at their disposal is colour identification. If a surgeon detects that the colour of a ceramic implant deviates in a somewhat unusual manner from the norm, he or she may feel insecure and thus may reject the part. This, of course, has severe consequences for the market share the producer of the implant commands. For this reason, the development of colour in the ceramic femoral ball heads during the sintering process, and its possible change during gamma-ray sterilization have to be investigated, clarified and made accessible to and understood by the medical community. In the following text some major causes of colour development and changes are pointed out. In particular, it is indicated which of these processes may potentially be deleterious to the mechanical integrity and thus the long-term *in vivo* performance of the ceramic materials.

2.1. Additives to alumina and zirconia

To produce very dense alumina ceramics with high bending strength and reasonable fracture toughness excessive grain growth during high temperature sintering must be avoided since large grains in a matrix of very fine-grained crystals lead to stress concentration and thus to an increased risk of crack initiation during cyclic loading. Additions of small amounts of magnesia (MgO), typically 0.2%, prevent grain growth by "poisoning" of the grain boundaries by a very thin layer of magnesia–alumina spinel phase. Femoral ball heads produced from very pure medical-grade alumina (Table II) and doped with magnesia are off-white in the as-fired state. Their colour may be classified as ivory [10].

Information on the dependence of the colour of fully (cubic) or partially stabilized (tetragonal) zirconia on the type and the concentration of photochromic impurities can be gleaned from the synthetic gemstone industry (Table V). Fully stabilized (cubic) zirconia grown by the so-called "skull" melting technique [11] has optical properties, i.e. refractive index and optical dispersion, approaching those of diamond. Additions of various photochromic rare earth elements (REE) or transition metal (TM) oxides at concentration levels typically below 0.1% lead to a wide array of coloured synthetic zirconia gemstones (Table V). This is already the level of impurities in medical-grade zirconia (Table II). While the phase-stabilizing yttrium oxide atoms replace zirconium atoms in the crystal lattice and thus create vacancies in the oxygen atom sublattice owing to the charge deficit between trivalent yttrium and fourvalent zirconium, the REE or TM oxide impurities may accumulate at grain boundaries of the polycrystalline tetragonal zirconia and form glassy or other crystalline phases. In particular, alumina impurities can form yttrium aluminium garnet (YAG) phases that, due to its rather high solubility, decrease the mechanical strength of the Y-TZP in the very corrosive environment of the human body over long periods of time. Therefore the amount of such additives has to be minimized. But even if great care has been taken to purify the starting medical-grade zirconia (ZIOLOX®), after sintering the ceramic is off-white, displaying a slightly greyish hue.

TABLE V Photochromic rare earth element (REE) and transition metal (TM) oxides producing colour in Y-stabilized zirconia

Element	Concentration (mol %)	Colour
Iron		Yellow-brown
Nickel	1	Reddish brown
	10	Dark green
Cobalt	1	Purple
Cerium	1	Orange red
Praseodymium	1	Golden yellow
Neodymium	1	Purple
Erbium	1	Pink
Europium	1	Light pink

2.2. Sintering atmosphere

To densify the green-machined zirconia femoral ball heads and thus to obtain the mechanical and chemical properties required, sintering is performed. Solid-state sintering is a very complex process that involves diffusion of matter across grain boundaries without the involvement of a liquid phase. Important process parameters are the integral temperature–time characteristics, the sintering atmosphere, i.e. air, inert gases such as argon or nitrogen, or vacuum, and the gas pressure. Most sintering processes are performed in air at ambient pressure but for maximum density ceramics more complex treatments such as uniaxial hot pressing (HP) or hot isostatic pressing (HIP) are applied. In the latter process, oxygen contamination plays a large role when the sintering is performed at reduced pressure or in the presence of nitrogen or argon.

In general, when the sintering process is optimized attention is focused on the correlation between the temperature–time transformation (TTT) characteristics and the structural material properties, i.e. density, microstructure and mechanical strength. While in most applications the objective is to maximize the mechanical strength, the colour of the ceramic product will not be part of the specification unless there is a known correlation with an important mechanical, optical, electrical or magnetic property. For the material under discussion, Y-TZP, such correlations are tentative at best. Although it is well known that a range of properties including the colour of the ceramic are indeed influenced by the sintering atmosphere, in particular by the oxygen partial pressure, no clear-cut information exists on the synergistic interaction of sintering atmosphere, temperature, time, gas pressure, powder grain size, impurity levels, etc. Hence there is a need to study these interactions in detail.

2.3. Radiation-induced colouration

Gamma-ray irradiation is a standard procedure to sterilize the ceramic and metallic parts of hip endoprostheses. The acetabular cups of hip endoprostheses and tibia plateaus of knee endoprostheses frequently made from polyethylene undergo changes in density, crystallinity and mechanical properties when gamma-sterilized more than once [12] and are thus prone to degradation [13]. On the other hand, the metallic implant parts will not noticeably change their appearance and properties on gamma-ray sterilization. This means that neither their mechanical properties will be influenced nor any substantial degradation takes place. Hence the metallic implants look the same before and after gamma-ray sterilization.

Finally, it is a well-known fact that the femoral ball heads produced from medical-grade alumina (BIOLOX®) or zirconia (ZIOLOX®) are off-white in the as-sintered state. The colour of alumina may be classified as ivory, which changes to a brownish tinge when sterilized by gamma rays [10]. As-sintered zirconia is slightly greyish but changes its colour to a darker purplish-grey on irradiation with both X-rays and γ-rays [14]. While an explanation for the radiation-induced colour change of medical-grade alumina has been given previously [10], that for medical-grade zirconia is still a matter of conjecture. So far there is no information available in the orthopaedic literature that explains the colour change of Y-TZP and, more importantly, proves conclusively that ceramic implants are safe to use even when their colour has changed. Since femoral ball heads made from zirconia (Y-TZP) are new to the orthopaedic community and hence surgeons have little experience with this material, there is a perceived need to investigate the colour of zirconia (Y-TZP) and its changes by analytical methods of solid-state physics. The general objective of such a study is to prove that any radiation-induced colouration of a medical-grade zirconia femoral ball head does not compromise its mechanical and chemical stability and thus its long-term performance in the human body.

3. Irradiation experiments

Standard Y-TZP femoral ball heads of 28 mm diameter, produced by CERASIV GmbH, were irradiated with γ-rays obtained from a ^{60}Co-source with a minimum energy dose of 25 kGy. The fading curves and associated spectral shifts of the colour with time were recorded by optical spectroscopy (OS), electron spin resonance (ESR) spectroscopy, standard thermoluminescence (TL) spectroscopy, and wave length-and-temperature-resolved thermoluminescence (TL) spectroscopy.

The colour of medical-grade Y-TZP samples changed from a slightly greyish hue in the as-sintered state to a purplish-grey colour on irradiation. This colour is not stable and transforms during storage in darkness at ambient temperature to a yellowish-brown colour within two months. Further changes could not be detected so that it is assumed that a stable state had been reached. Increasing the storage temperature to 121 °C speeds up the colour extinction process; after only 30 min exposure to this typical sterilization temperature the stable yellowish-brown colour is obtained.

Investigation of the optical, ESR- and TL-spectra yielded information on the types of lattice defects responsible for the colouration and its changes.

3.1. Optical spectroscopy

After γ-irradiation the residual optical absorption spectrum, i.e. the difference between the spectra of irradiated and as-sintered medical-grade Y-TZP samples shows a broad, weakly structured absorption band in the range 1.5–3.8 eV (Fig. 1). Gaussian deconvolution yielded three individual absorption bands at 2.6 eV (total intensity: 47.7 eV/cm, FWHH: 0.86 eV), 3.2 eV (total intensity: 13.6 eV/cm, FWHH: 0.42 eV) and 3.5 eV (total intensity: 3.5 eV/cm, FWHH: 0.23 eV). The absorption band at 2.6 eV fades rather quickly, and is completely extinct at temperatures above 120 °C.

The colour resulting from the irradiation can be explained by the occurrence of the two main absorption bands. In particular, irradiation with γ-rays and X-rays leads to comparable results. After irradiation with X-rays (MoK$_{\alpha+\beta}$, 40 kV, 25 mA, 100 mm distance) for only 10 min the optical absorption band at 3.2 eV attained a high intensity (13.9 eV/cm) and produced, together with the absorption band at 2.6 eV of comparable intensity (13.7 eV/cm), a yellowish-brown colouration. Increasing the irradiation time to 2 and 4 h, respectively, leads to more pronounced growth of the intensity of the absorption band at 2.6 eV. Hence the composite colour is shifted towards shorter wavelengths (471 nm) and the typical purplish colour of the irradiated zirconia appears. The increase of the intensity of the optical absorption bands during irradiation can be described by an exponential function of the type

$$I(t) = A_1[1 - \exp(-t/k_1)] + A_2[1 - \exp(-t/k_2)] \tag{1}$$

where, for the absorption band centred around 3.2 eV, the pre-exponential factors are $A_1 = A_2 = 15$ eV/cm,

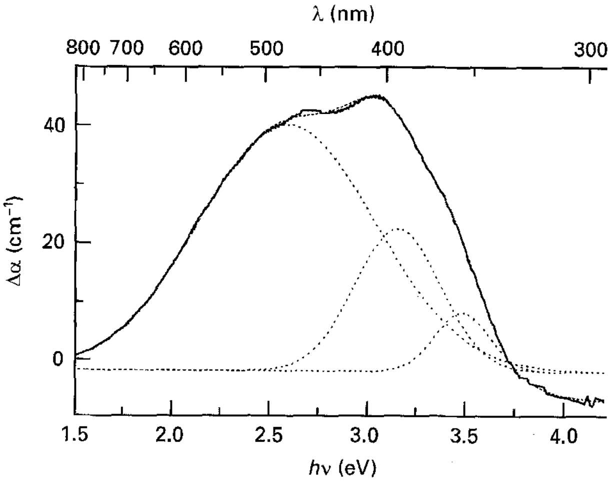

Figure 1 Residual optical absorption spectrum of γ-irradiated sintered medical-grade Y-TZP (—) and Gaussian deconvolution (·····) into three individual optical absorption peaks at 356 nm (3.5 eV), 392 nm (3.2 eV) and 471 nm (2.6 eV).

and the colour decay constants are $k_1 = 220$ min and $k_2 = 15$ min. For the absorption band centred around 2.6 eV the intensity increase can be approximated with $A_1 = 53$ eV/cm, $A_2 = 15$ eV/cm, $k_1 = 200$ min and $k_2 = 15$ min. From this it is obvious that the saturation behaviour of the absorption band at 2.6 eV exceeds that of the band at 3.2 eV, and thus dominates the composite colour.

A similar analysis can be performed to describe the fading of the colour of γ-irradiated medical-grade Y-TZP during storage. In this case the exponential fitting function is of the type

$$I(t) = A_1\exp[-(t - t_0)/k_1] + A_2\exp[-(t - t_0)/k_2] \tag{2}$$

with $A_1 = 0.96$ eV/cm, $A_2 = 11.83$ eV/cm, $k_1 = 0.83$ day, $k_2 = 257.9$ day and $t_0 = 0.45$ day for the absorption band at 3.2 eV, and $A_1 = 8.29$ eV/cm, $A_2 = 32.35$eV/cm, $k_1 = 1.55$ day, $k_2 = 257.1$ day and $t_0 = 0.94$ day for the absorption band at 2.6 eV. Equation 2 indicates that the fading of the colour occurs in a two-step process characterized by a short-time component with decay constant k_1 around 1 day, and a gradual fading over many months with decay constant k_2 of 257 days. The $t_0 > 0$ values point to the fact that between irradiation and first measurement, colour fading has already started. Extrapolation to $t = 0$ yields the initial intensities 61 eV/cm for the absorption band at 2.6 eV and 15 eV/cm at 3.2 eV.

3.2. Psychophysical colour description

The psychophysical colour specification, i.e. unaided eye analysis of the colour of the femoral ball head as the only "tool" available to the surgeon is, of course, highly subjective but nevertheless provides a useful and reliable guide to colour description. There are many colour charts available that could be used for this purpose such as the MUNSELL colour system, the CIE chromaticity diagram, the natural colour system (NCS), the ISCC-NBS system and more [15]. Here the CEC colour shade guide [16] will be used to describe the colours specified by their spectral components as shown above. According to this chart, the colour of the as-sintered zirconia femoral ball heads is A2, i.e. a slightly greyish-white. On irradiation with γ-rays or X-rays until saturation the colour changes to purplish-grey that, however, has no expression in the CEC chart that has been prepared for practical identification of the colours and shades of fired ceramic materials. Subsequent storage at ambient temperature in the dark for two months, or sterilization at elevated temperature leads to a yellow-greenish brown C5 shade that coincides with a CIE 1931 (x_c, y_c, Y_c) colour space with $x_c = 0.356$, $y_c = 0.357$, $Y_c = 56.9$ (DIN 6164 notation: 221). This C5 shade transforms on further storage in daylight for another two months to a light yellowish-brown B3 shade. Subsequent tempering at 550 °C restores the original A2 shade.

3.3. Electron spin resonance (ESR) spectroscopy

This analytical method allows one to detect local electronic defects in solids that possess unpaired electrons. It is therefore tempting to try to associate such electronic defects with the development of the colour of irradiated zirconia. For the correlation of the recorded electronic signals with known types of defects, literature data were used [17–19]. Since, however, these data refer exclusively to fully stabilized, i.e. cubic zirconia, their application to partially stabilized tetragonal zirconia, i.e. Y-TZP, may be problematic. The only slight deviation of the lattice metric of the tetragonal modification of zirconia from the true cubic symmetry, however, may justify this approach.

Fig. 2 shows a simulation of the measured ESR spectrum (thick line) of γ-irradiated medical-grade Y-TZP through summation (dashed line) of individual ESR powder spectra (dotted lines) of the ESR centres X, C [18], and E [19].

The high intensity X centre ($g_x = 1.993$, $g_y = 1.885$, $g_z = 1.853$, line width 3 mT) is related to the slightly altered trigonal T-defect [19]. Centres X and C ($g_x = 1.896$, $g_y = 1.965$, $g_z = 1.975$, line width 1.5 mT) belong to the defect type $\mathrm{Zr_{zr}}'\,\mathrm{O}_{(8-x)}$, i.e. transformation of a four-valent zirconium ion into a three-valent one. The high field flank of centre X is shifted towards the T-defect to higher g-values by 3 mT. The reason for this could be found in lattice defects, tetragonality or the small grain size of the zirconia polycrystals. At the low field flank of centre X the weak center E ($g_x = 2.019$, $g_y = 2.012$, $g_z = 2.004$, line width 0.8 mT) is related to an intrinsic defect type $\mathrm{Y}'_{\mathrm{Zr}}\mathrm{O}^*$, i.e. an electron-hole state cause by an oxygen ion trapped in the neighbourhood of a three-valent yttrium ion.

In addition, trace amount impurities can produce extrinsic defects such as centre B ($g = 4.3$) [18] of defect type $\mathrm{Fe}^{3+}_{\mathrm{Zr}}$ (Fig. 3). Centre G ($g_\perp = 1.96$, $g_\parallel = 1.85$) may be related to microstructural properties such as Y_2O_3 clusters [20].

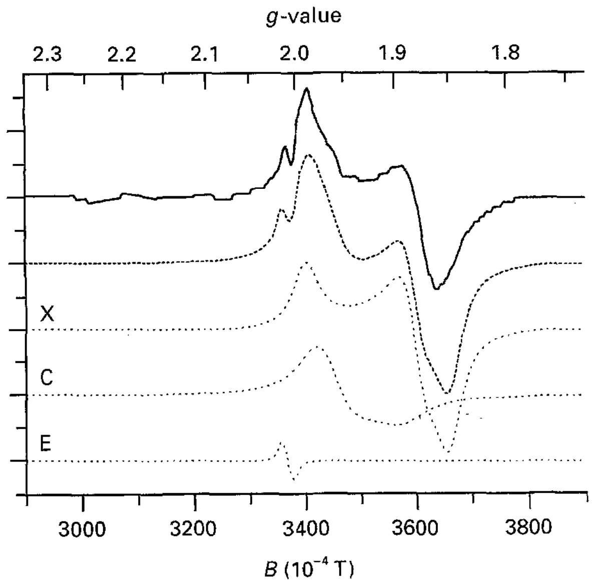

Figure 2 Simulation of the measured ESR spectrum (—) of γ-irradiated medical-grade Y-TZP through summation (– – – –) of individual ESR powder spectra (·····) of the centres X, C and E.

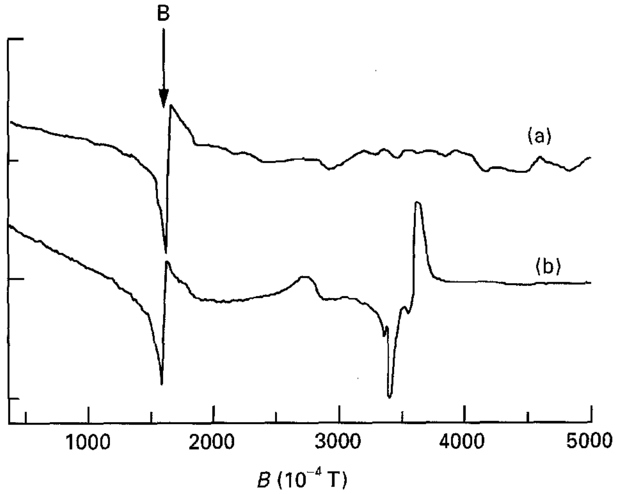

Figure 3 ESR spectrum of medical-grade Y-TZP (a) with centre B ($g = 4.3$) related to a defect type Fe^{3+}_{Zr} and (b) additional centre G ($g_{\perp} = 1.96$, $g_{\parallel} = 1.85$) activated by γ-irradiation.

Some of the defect types detected by ESR spectroscopy can be associated with colour changes as manifest in the optical absorption spectra described above. Paramagnetic defects of the type $Zr^{3+}O_{(8-x)}$ do not appear to cause any optical absorption. This finding contrasts with information found in the pertinent literature [18, 19]. On the other hand, centre E was associated with the optical absorption band at 2.6 eV [19]. According to the measurements described above there is no reason to reject this assignment.

Whereas the optical absorption band at 3.2 eV was described as being related to a cationic defect of the type $Zr_{Zr}'O_6$ [18, 19] there is no evidence in the above analysis to support this assumption. The strong optical absorption band at 3.2 eV may thus be an unknown extrinsic defect related to trace amount impurity ions.

3.4. Thermoluminescence spectroscopy

The principal reason for the appearance of thermoluminescence in irradiated zirconia is the presence of intrinsic oxygen vacancies produced by the incorporation of three-valent yttrium ions into the lattice of four-valent zirconium ions. These double negatively charged (V_0^{**}) defects are ideal traps for electrons. Depending on the configuration of the vacancies and oxygen ions, as well as zirconium ions, yttrium ions and impurity ions a rich variety of new discrete energy states will be created above the valence band and below the conduction band. Fig. 4 shows the energy term scheme of medical-grade Y-TZP with electron sticking terms, i.e. oxygen vacancies or cations with trapped electrons between 0.7 and 1.3 eV, and luminogenic centres caused by electron-holes at intrinsic or extrinsic defects between 1.7 and 2.3 eV. These six energy terms could be recorded in TL spectra. During irradiation electrons will be trapped at sticking terms. Recombination with a luminogenic centre gives rise to thermoluminenscence at 2.2 eV (550 nm), 2.0 eV (623 nm) and 1.7 eV (700 nm) as well as phosphorescence at 1.85 eV. The complex response of the glow curves is shown in a three-dimensional plot in Fig. 5. Electron-hole centres can be related to several defects such as Zr_{Zr}', Y_{Zr}'' or Me_{Zr} but correlation with individual thermoluminescence energies and optical absorption bands is difficult and at this point only tentative.

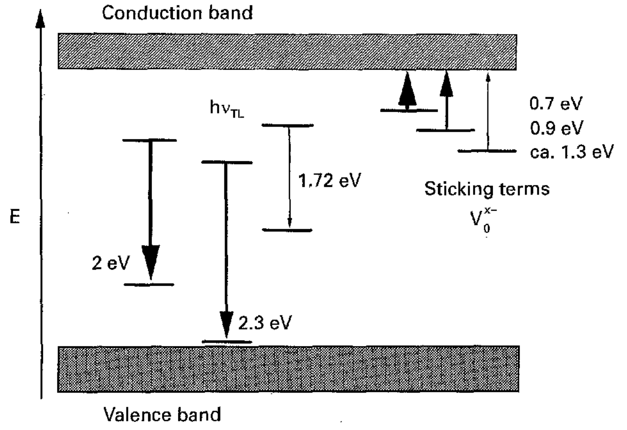

Figure 4 Energy term scheme of medical-grade zirconia with electron sticking terms V_0^{x-} (0.7–1.3 eV) and electron-hole (luminogenic) terms $h\nu_{TL}$ (1.7–2.3 eV).

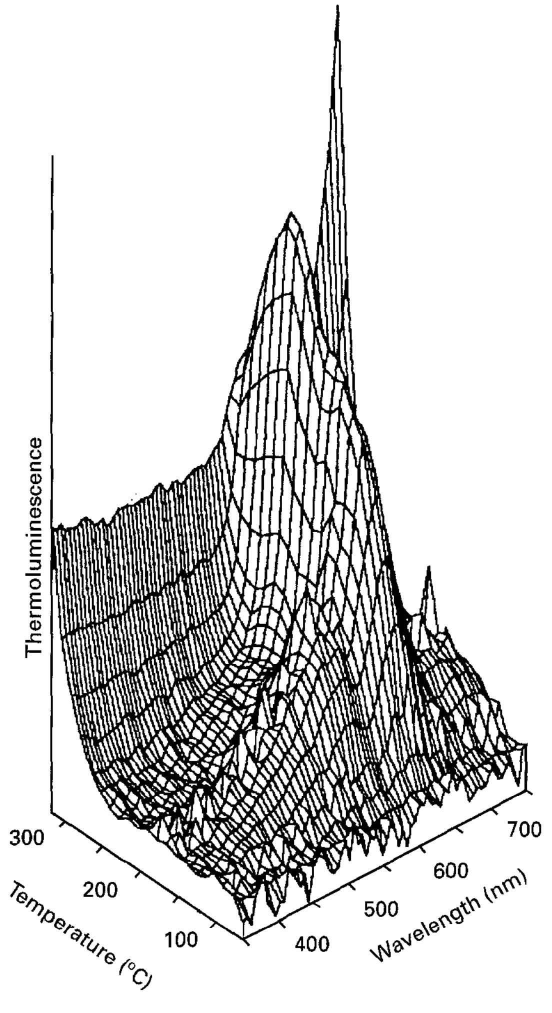

Figure 5 Three-dimensional rendering of the wavelength- and temperature-resolved thermoluminescence spectrum of γ-irradiated medical-grade Y-TZP obtained with a CCD-based TL/OSL spectrometer (Courtesy: Dr M. Krbetschek).

4. Conclusions

The results of the above analyses show that the colour of γ-irradiated medical-grade yttrium partially stabilized tetragonal zirconia polycrystal (Y-TZP) is caused by two electronic transitions at local defects in the crystal lattice. One transition is related to an intrinsic defect of the type $Y_{Zr}'O^*$, i.e. an electron-hole state associated with an oxygen ion trapped in the vicinity of an yttrium ion. This defect is unstable, in particular at elevated temperature and thus decays spontaneously. It can be correlated to an optical absorption band at 2.6 eV (480 nm) and produces the typical purplish-grey discolouration of the γ-ray sterilized femoral ball heads.

A second, presumably extrinsic defect may be the origin of an optical absorption band at 3.2 eV (395 nm). The decay of the band at 2.6 eV is, together with the more stable band at 3.2 eV, the reason for the colour change from purplish-grey to yellowish-brown observed during long-term storage of the irradiated material and, much accelerated, during treatment at elevated temperature as experienced in medical sterilization.

It has been confirmed that the origin of the colour of irradiated medical-grade zirconia is only related to processes confined to the energy terms of the electron shells of the zirconium and yttrium ions constituting the crystal lattice. Therefore the colour changes are in no way related to elevated impurity levels or microstructural changes that may compromise the mechanical and chemical stability of the ceramic material. Thus the local defects associated with colour changes do not influence safety-related mechanical or chemical properties of the ceramic femoral ball heads of hip endoprostheses.

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