RADIATION-INDUCED EPR SPECTRUM OF INITIAL AND THERMALLY ANNEALED TOOTH ENAMEL POWDERS

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The results of experimental and theoretical studies of the radiation-induced EPR spectrum in tooth enamel powders and its changes at thermal annealing are reported. The increase of the annealing temperature has been demonstrated to result in the low-field shifts of the maximum and one of the minima of the EPR signal, and in the redistribution of the intensity in the spectrum. It has been shown that the central section of the spectrum can be satisfactorily described by a dominant contribution from orthorhombic and axial CO_2^- radicals, and its annealing-induced changes can be explained by a thermal transformation of orthorhombic radicals into axial ones. To describe the low-field section of the EPR spectrum, CO^- and SO_2^- radicals have to be taken into account.

1. Introduction

Although being widely used in application problems (retrospective EPR dosimetry [1–3] and EPR dating [4, 5]), the structure of a radiation-induced EPR signal in dental enamel has no unequivocal explanation. It is well known that this signal has a complicated character. It is considered to be formed by the contributions of different – mainly, carbon – radicals [6]. Those contributions substantially vary depending on experimental conditions; they also depend on a specific specimen and external influences upon it. Therefore, a complete theoretical description of the line shape of the radiation-induced signal is a challenge, and only the first steps have been made to tackle it [7].

In work [8], which has been published recently, the radiation-induced EPR spectrum in dental enamel plates was described – in general outline – as a dominating contribution made by two types of CO_2^- radicals, namely, chaotically oriented orthorhombic and orientationally ordered axial radicals. Variations of the EPR spectrum at annealing have been explained [8, 9] by transformations occurring in the system of those radicals. In order to describe the shape of the EPR signal, two components were used in work [8]. The contribution from orthorhombic radicals was simulated using a theoretically calculated EPR spectrum of the powder, while the contribution made by axial radicals was described by an experimental EPR signal filtered out from the general spectrum due to its orientation dependence in a magnetic field.

It is much more difficult to analyze the shape of the spectrum of tooth enamel powder specimens, because no spectral component can be filtered out experimentally in this case. In powders, orthorhombic and axial CO_2^- radicals produce similar and strongly overlapped EPR signals, so that theoretical models are necessary for their description. At the same time, the comprehension of the spectrum concerned is actual for dosimetric techniques, which mainly use just powder specimens. This work is devoted to the analysis of the EPR spectrum shape in γ-irradiated powders of dental enamel and its variation induced by annealing the specimens.

2. Materials and Methods

Enamel of sound teeth was used for researches. After the dentin had been removed making use of dental tools, enamel was crushed into a powder, until the typical dimensions of granules became equal to 100–300 μm. To excite the radiation-induced EPR spectrum, the powder was γ-irradiated at room temperature using a ^{60}Co source. The absorbed dose amounted to several kGy.

Specimens were isochronously annealed at temperatures up to 360 °C inclusive, in a muffle furnace and in the air environment. The period of annealing was 30 min at every chosen temperature. The temperature was monitored using a thermocouple which provided the accuracy of measurements within ±1 °C.

The EPR researches were carried out on an X-band EPR spectrometer (about 9.5 GHz) at room temperature. The microwave power of about 5 mW and the amplitude of magnetic field modulation of about 0.2 mT corresponded to those conditions, which are most frequently used while solving the application tasks. The powder EPR spectra were calculated with the help of a computer code developed by us; the components of the

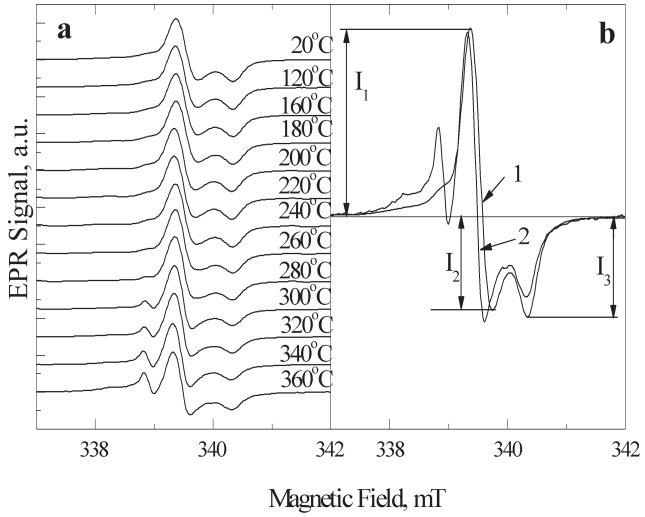

Fig. 1. (a) Modifications of the EPR spectra of γ-irradiated dental enamel powders stimulated by thermal annealing of powder specimens at various temperatures in the range 20–360 °C. (b) A detailed comparison between the EPR spectra of the initial and annealed enamel: *1* – initial enamel, *2* – enamel annealed at 360 °C. For the convenience of comparison, all the spectra were normalized by intensity I_1. Actually, the spectrum of annealed enamel has a considerably smaller intensity than the spectrum of the initial specimen

g-tensor together with the width and the shape of the initial EPR line composed the collection of input parameters for it. The intensities of the EPR spectrum components were fitted making use of a Separator code which is a part of the Visual EPR software package [10].

3. Experimental Results and Their Discussion

The radiation-stimulated EPR signal was shown [8] to change its shape substantially if enamel plates were subjected to annealing. For powder specimens, such variations are less considerable (see Fig. 1,a). Nevertheless, a detailed comparison between the powder spectra of initial and annealed – e.g., at $T_{\rm ann} = 360$ °C – enamels make the variations of the spectrum shape well distinguishable (Fig. 1,b).

For the qualitative analysis of the spectrum modifications, it is convenient to take advantage of the ratio between the spectral amplitudes in their extrema – as was done, e.g., in work [11]. For this purpose, let us introduce the quantities I_1, I_2, and I_3 (see Fig. 1,b). The ratio I_3/I_2 demonstrates most substantial variations in the course of the enamel annealing, so it can be used for the characterization of spectral changes and for the estimations of thermal influence upon the specimen. For initial enamel, the ratio I_3/I_2 is equal to 1.07 ± 0.01. After annealing, this ratio diminishes as the annealing temperature grows, and, for enamel annealed at 360 °C, it amounts to 0.76 ± 0.01. Such a reduction reflects qualitatively the modification of the EPR spectrum shape, which takes place after the enamel powders have been annealed. Another characteristic feature of the annealing influence on the EPR spectra of irradiated enamel is the shifts of the positions of spectral extrema. It is especially notable for peaks I_1 and I_2 with respect to peak I_3, the spectral position of which is not changed within the experimental errors. For example, the distance between peaks I_3 and I_2 was equal to (0.60±0.01) mT for initial enamel, whereas it amounts to (0.74 ± 0.01) mT for enamel annealed at 360 °C. A small low-field shift of peak I_1 approximately equal to 0.02 mT also takes place.

The shape modification of radiation-induced EPR spectra in enamel plates was explained in work [8] by the transformation of orthorhombic radicals CO_2^- into axial ones. Therefore, it is natural to assume that the shape modification of the powder spectra after annealing is also stimulated by this transformation. It is known [8,9] that the radiation-induced EPR spectrum in initial enamel is determined by orthorhombic radicals with a small contribution from axial centers. At the same time, the EPR spectrum of enamel annealed at temperatures above 300 °C is mainly governed by the contribution of axial CO_2^- radicals. In order to calculate the powder EPR spectra, we used the following values for the components of the g-tensor: for axial CO_2^-, $g_\parallel = 1.9970$ and $g_\perp = 2.0027$; for orthorhombic CO_2^-, $g_x = 2.0030$, $g_y = 2.0015$, and $g_z = 1.9970$. The value of 0.33 mT was taken for the width of individual components for both CO_2^- types. The relations between the numbers of axial and orthorhombic radicals at various annealing temperatures were taken from work [8].

Figure 2 examplifies the experimental and simulated spectra of initial enamel and those of enamel annealed at two temperatures, as well as their separate components, which were used in calculations. The description with the engagement of only two components caused by CO_2^- radicals results in a good agreement between the experimental and calculated spectra in their central section and on the high-field side of the radiation-induced EPR signal. For a satisfactory description of the low-field side of the EPR signal, several additional EPR lines had to be introduced. These are a Gaussian-like line (with $g \approx 2.0060$ and the width $\Delta B_{1/2} \approx 0.1$ mT),

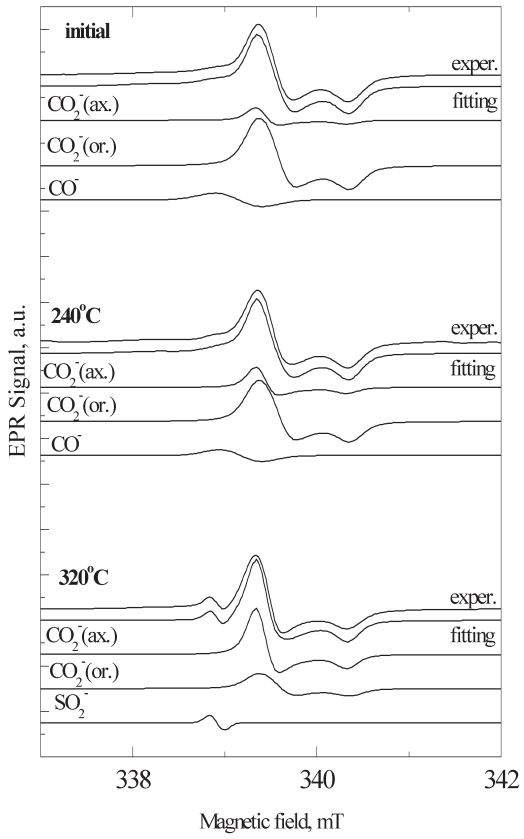

Fig. 2. Experimental EPR spectra and their description for the powder specimens of initial enamel and enamel annealed at most typical annealing temperatures. The components that were included into consideration are depicted below

which has been identified as produced by SO_2^- radicals [12], and a powder spectrum with the parameters $g_x = 2.0061$, $g_y = 2.0039$, $g_z = 2.0018$, and $\Delta B^{\rm G}_{1/2} = 0.6$ mT which correspond to surface CO^- radicals [6]. The latter signal was not observed in enamel plates. Therefore, its occurrence here may be caused by the enhancement of the role of surface centers, occurring due to the crushing of enamel into powder. For the temperatures of enamel annealing above 250 °C, the CO^--signal disappeared.

4. Conclusions

The radiation-induced EPR spectrum in tooth enamel powders and its variations owing to annealing can be satisfactorily described by the dominating contribution from orthorhombic and axial CO_2^- radicals and by the thermally induced transformation of the former into the latter. To describe the low-field section of the spectrum, one should also take into account the less intensive signals from CO^- and SO_2^- radicals. Qualitative variations in the shape of the radiation-induced EPR spectrum at an increase of the annealing temperature manifest themselves as a reduction of the ratio between amplitudes I_3/I_2 and the shifts of the I_1 maximum and the I_2 minimum to the low-field range. The values of those quantities can be used in the EPR dosimetry to reveal whether specimens were subjected to thermal annealing.

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РАДІАЦІЙНО-ІНДУКОВАНИЙ СПЕКТР ЕПР У ВИХІДНИХ ТА ТЕРМІЧНО ВІДПАЛЕНИХ ПОРОШКАХ ЗУБНОЇ ЕМАЛІ

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Р е з ю м е

Експериментально досліджено та теоретично описано радіаційно-індукований спектр ЕПР у порошках зубної емалі та його зміни при термічних відпалах. Виявлено, що зі збільшенням температури відпалу відбувається зсув максимуму та одного з мінімумів сигналу ЕПР в низькопольову область, а також спостерігається перерозподіл поглинання всередині спектра. Показано, що центральна частина спектра задовільно описується домінуючим внеском орторомбічних та аксіальних радикалів CO_2^-, а її зміни при відпалах можуть бути пояснені термічним перетворенням орторомбічних радикалів в аксіальні. Для опису низькопольової частини спектра ЕПР необхідно також враховувати радикали CO^- і SO_2^-.