# USE OF EMANATION THERMAL ANALYSIS IN THE MICROSTRUCTURE DIAGNOSTICS OF ALUMINA COATINGS

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*Emanation thermal analysis (ETA), based on the radon release measurements, was used to characterize the microstructure development of alumina coatings on heating. The alumina coatings were deposited on EUROFER' 97 steel surface by using the filtered vacuum arc technique. Healing of microstructure irregularities that served as radon diffusion paths in the alumina coatings was characterized as a decrease of the radon release rate in the range 300-700°C. The healing of surface microcracks observed by SEM micrographs on the alumina coating sample was characterized as the break on the temperature dependence of radon release rate in the temperature range 430 -660°C. From the ETA results it followed that healing of the microstructure irregularities in the range of 300-700°C was depending on the conditions used for the alumina coatings preparation. A higher intensity of this process can be expected with the alumina coating of 4 μm thickness in comparison with the alumina coating of 0.5 μm thickness.*

## INTRODUCTION

Alumina attracts an interest of researchers since many years. As it follows from the database search by using the key words "alumina" or "$Al_2O_3$" the amount of about 58 000 works was published in the period of 1970-2006. It has been stated e.g. in [1] that the most important and common polymorphs of alumina are γ-, δ-, θ-, κ- and α-$Al_2O_3$. The α-$Al_2O_3$ phase is thermodynamically stable polymorph and occurs naturally as corundum or sapphire minerals, while other phases are meta-stable in bulk forms. The thermodynamic stability, chemical inertness and hardness of α-alumina makes it the most suited phase for use in many high temperature applications. The α- alumina films have found applications as e.g. wear resistant [2] and high temperature diffusion barriers [3]. Moreover, alumina has been used in electronics e.g. as an insulator, due to the wide band gap of 8.8 eV, and in optics, as a completely transparent ceramics [4]. The meta-stable phases, like γ-$Al_2O_3$, δ- and θ-$Al_2O_3$, find applications as catalysts or catalyst supports.

The α-$Al_2O_3$ can be prepared e.g. by the thermal treatment above 1050°C of the meta stable phases δ- and θ-$Al_2O_3$ or by heating boehmite or gibbsite minerals.

Moreover, the hard α-alumina thin films can be prepared by the pulsed DC sputtering [5], by plasma assisted chemical vapor deposition [6], by using the RF magnetron sputtering [7] or by using the vacuum arc techniques [8].

It has been found that alumina coatings prepared by the vacuum arc deposition technique can be used as a diffusion barrier of hydrogen isotopes for future nuclear fusion power reactors [9]. Alumina coatings of a micrometer thickness may efficiently suppress the hydrogen diffusion through a fusion relevant martensitic steel [8]. The coatings of such properties should contain only the α-$Al_2O_3$ and should not contain open pores or cracks.

Thermal behavior of the alumina based materials differing in the preparation technology as well as in the purpose of their applications was characterized since decades e.g. [10] by using various methods, such as X-ray diffraction, porosity measurement, differential thermal analysis, emanation thermal analysis, surface morphology characterization by electron microscopy and others.

The emanation thermal analysis was already used in the thermal characterization of γ-$Al_2O_3$ or α-$Al_2O_3$ alumina, respectively [11,12] in the thermal behavior of alumina based aerogels [13,14] as well as in the study of the alumina phases formation by heating synthetic minerals of boehmite [15 ] or gibbsite [16].

In this paper the emanation thermal analysis was used for the microstructure diagnostics of the alumina coatings deposited a steel surface.

## THEORETICAL

Emanation thermal analysis [17-19] is based on the measurement of radon release rate from samples. In general, the increase in the radon release rate, $E$, may characterize an increase of the surface area of interfaces, whereas a decrease in $E$ may reflect processes like closing up structure irregularities that serve as paths for radon migration, closing pores and/or a decrease in the surface area of the interfaces .

The temperature dependence of the radon release rate $E(T)$, can be expressed [20] as

$$E(T) = E_{25} + E_D(T) \cdot \Psi(T) \qquad (1)$$

where $E_{25}$ is radon release rate measured at the room temperature, mainly due to the recoil, $E_D(T)$ is the part of the radon release rate due to radon diffusion along structure irregularities that served as radon diffusion paths, $\Psi(T)$ is the function characterizing changes in the number of the radon diffusion paths.

The temperature dependence of the radon release rate obtained by ETA measurements of solids can be used to characterize the transport properties and microstructure development of the solids.

Following equations were used to evaluate the ETA experimental data. The radon release rate due to diffusion, $E_D(T)$, can be expressed [20] as

$$E_D(T) = A[F(T_0) - F(T)] \qquad (2)$$

where $F(T)$ - $1/k_{D0}$ exp$[-(Q_D/RT)] + \lambda_{Rn}$, $A = \lambda_{Ra}C_{Ra}$ is corresponding to a change in $^{224}$Ra concentration, where $\lambda_{Ra} = 2.2035 \cdot 10^{-6}$ [s$^{-1}$], $C_{Ra}$ is the equilibrium concentration of $^{224}$Ra, and $\lambda_{Rn} = 1.2464 \cdot 10^{-2}$ [s$^{-1}$] is decay constant of $^{220}$Rn; $T_0$ is the initial temperature of heating, $k_D$ is rate constant of radon diffusion, depending on temperature according to the Arrhenius relationship $k_D = k_{D0}$ exp$[-(Q_D/RT)]$ ,where $Q_D$ is the activation energy of radon diffusion, $R = 8.314$ [J/molK] is universal gas constant. Changes in the number of radon diffusion paths during heating of the sample can be described by the $(T)$ function

$$\Psi(T) = 1 - \frac{\kappa}{2} \cdot \left[ 1 + \mathrm{erf} \frac{1 - \dfrac{T_m}{T}}{\dfrac{T\sqrt{2}}{T}} \right] \qquad (3)$$

where erf is Gauss error function, $T_m$ is the temperature of the maximum rate of the healing defects serving as radon diffusion paths, $\Delta T$ is the temperature interval of the respective solid state process and $\kappa$ is the parameter describing the contribution of the respective solid state process to the change in the number of the radon diffusion paths.

## EXPERIMENTAL

### Samples

The deposition of the alumina coatings was performed by a filtered vacuum arc technique, using a solid aluminium cathode and plasma, that was guided through a toroidal magnetic filter to the main chamber and mixed there with oxygen. More details about the filtered arc deposition technique used can be found in [8]. In general, alumina coatings prepared by this technique showed a good adhesion without visible cracks.

Two good quality samples of alumina coatings were investigated, namely: sample I-thickness 4 μm and sample II-thickness 0.5 μm, the substrate temperature of 650°C was used in the preparation of both samples. In addition, one sample, denoted as sample III, of the alumina coating, that contained visible cracks, was investigated. This sample, considered as not suitable for further application, was taken from the edge of the alumina coating deposited by filtered vacuum arc technique on the steel surface. The sample thickness was 0.5 μm and the temperature of the substrate during the alumina coating deposition was 730°C.

### Methods of characterization

ETA measurements were carried out by using modified NETZSCH DTA-ETA Equipment Type 404. Details of ETA measurements have been described elsewhere [16,18].

Before the ETA measurements the samples were labeled by $^{228}$Th as described in [19,20]. The specific activity of the sample was $10^5$ Bq per gram. Atoms of radon, $^{220}$Rn, were formed by spontaneous α-decay of $^{228}$Th and $^{224}$Ra and were incorporated into the sample using the recoil energy of 85 keV/atom. The maximum depth of the $^{220}$Rn incorporation into the alumina samples was 60 nm from the surface as calculated with Monte Carlo method using TRIM code [21]. The samples situated in an alumina crucible were heated at the rate of 6°C/min in an argon flow (flow rate 50 mL/min, argon purity 99.9996 %) and the rate of the radon release from the samples was measured .The values of the radon release rate, $E$, are presented (in relative units) as $E = A_\alpha/A_{total}$, where $A_\alpha$ is α-radioactivity of radon released in unit time from the labeled sample, and $A_{total}$ is total γ-radioactivity of the labeled sample. The $A_{total}$ value is proportional to the rate of radon formation in the sample.

Scanning electron microscope (SEM) equipment by PHILIPS, Type 3020 was used to characterize surface morphology of the samples.

## RESULTS AND DISCUSSION

In this paper the emanation thermal analysis (ETA) was used to determine the temperature ranges of healing microstructure irregularities and to characterize thermal behavior of the alumina coatings deposited on EUROFER' 97 steel surface.

Figure 1 depicts ETA results characterizing the thermal behavior of the alumina coatings, namely sample I (a) and sample II (b),on heating in argon from 20 to 700°C. The experimental results( points) are compared with model curves( full lines)obtained by fitting the experimental results with the mathematical model presented in Theoretical of this paper.

The temperature range used for the ETA measurements of the alumina coating samples was limited by the thermal stability of the steel support used for their deposition.

The increase of radon release rate in the temperature range 20-700°C observed with both samples I and II was due to radon diffusion along structure irregularities of the alumina coatings. Taking into account that radon atoms were introduced during the labeling of the samples to the maximum depth of 60 nm, it was assumed that the radon diffusion in the alumina coatings subsurface in the used temperature range was controlled by a random "single jump" diffusion mechanism. This is in agreement with the statement of other authors [22,23].

The break observed at about 300°C and the decrease of the radon release rate $E(T)$ in the range of 300-700°C indicated the healing of the microstructure irregularities that served as radon diffusion paths in the sample. Figure 2 depicts SEM micrographs that characterized the surface morphology of the samples I and II. ETA results of the alumina coating that contained visible cracks (sample III) are presented in Figure 3,

curve 1 and compared with ETA results of the same alumina coating sample that contained no micro-cracks (curve 2, Figure 3). The SEM micrograph of the surface morphology of the sample III is presented in Figure 4.

The healing of the micro-cracks was indicated by an effect observed in Figure 3, curve 1 in the temperature range 430-650°C. No such effect was observed on curve 2, Figure 3, corresponding to the sample that contained no micro-cracks. From the ETA results it can be expected that the microstructure irregularities of the alumina coatings were healed out after sample heating in argon up to 650°C. By this way, temperature intervals of the microstructure changes were determined from the ETA data measured during heating of the samples in argon.

Moreover, the ETA results were used to evaluate the radon mobility in the samples. The theoretical model (see Theoretical of this paper) was used for fitting the experimental data. A good agreement of the model curves and the ETA experimental data is obvious from Figure 1.

It was of interest to compare the model curves of the temperature dependences of radon release rate $E(T)$ obtained by fitting with the experimental ETA data of the alumina coatings. Figure 5 depicts temperature dependences of the $E(T)$ in the range 50-300°C characterizing the radon mobility in the alumina coatings denoted as samples I and II.

Temperature dependences of the $\Psi(T)$ functions that characterized the decrease of the amount of radon diffusion paths during heating of the samples I and II are presented in Figure 6. As it followed the from the steeper decease of the $\Psi(T)$ function (see Figure 6, curve 1) a higher healing rate of the radon diffusion paths can be expected for the alumina coating - sample I in comparison to the sample II (see Figure 6 ,curve 2).
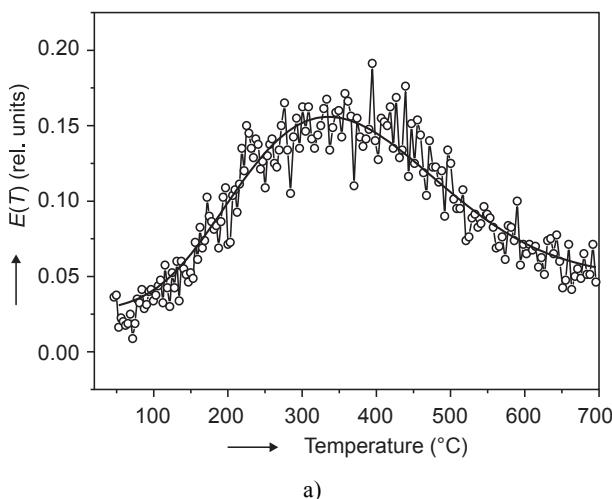


a)
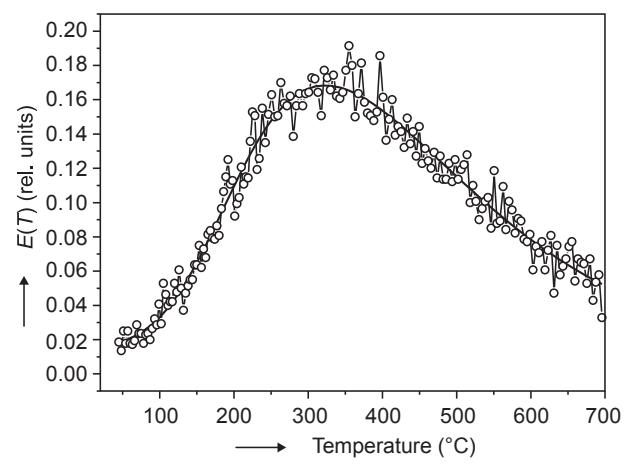


b)

Figure 1. ETA results of the alumina coatings measured on heating in argon. (a) sample I, (b) sample II. The experimental results (points) are compared with the model curves obtained by fitting the experimental results with the mathematical model.
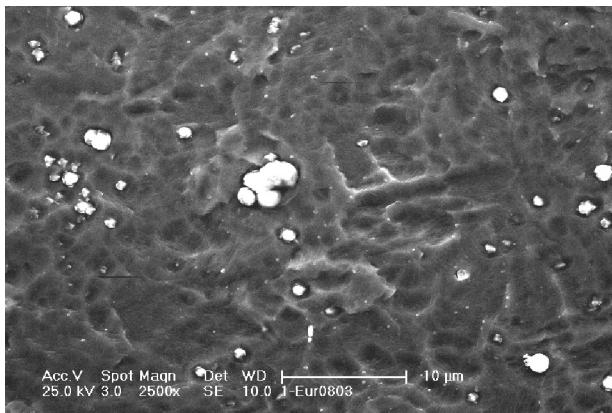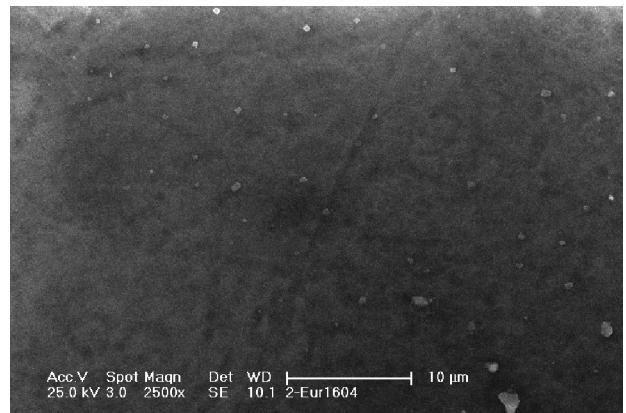
Figure 2. SEM micrographs of the alumina coatings - samples I (a) and II (b).
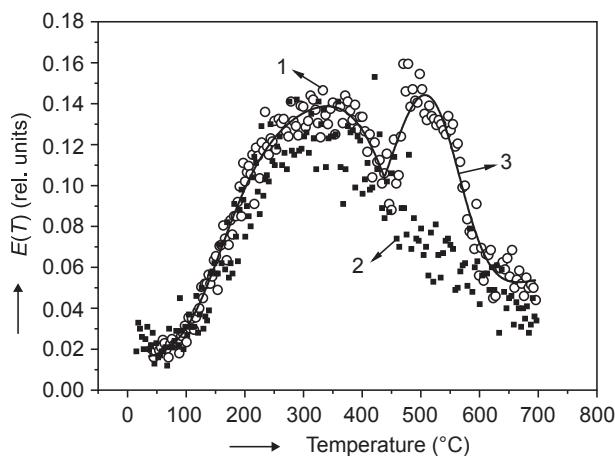


Figure 3. ETA results of two pieces of alumina coating sample III. The experimental results of the piece that contained surface micro-cracks are shown as open circles (curve 1), whereas the results of the second piece that contained no visible micro-cracks are shown as black points (curve 2). The full line in curve 3 was obtained by fitting the experimental ETA results in curve 2 with theoretical model.
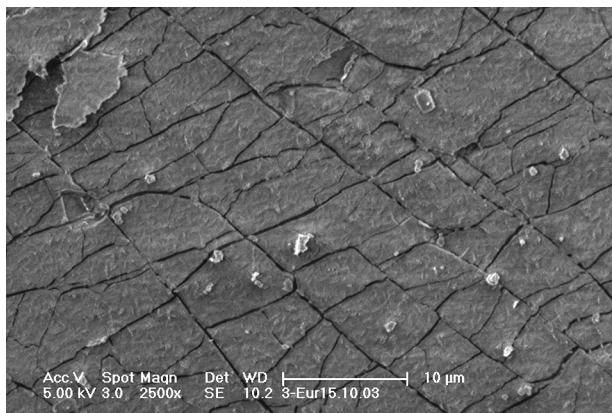


Figure 4. SEM micrograph of the alumina coating (sample III) that contained visible micro-cracks.
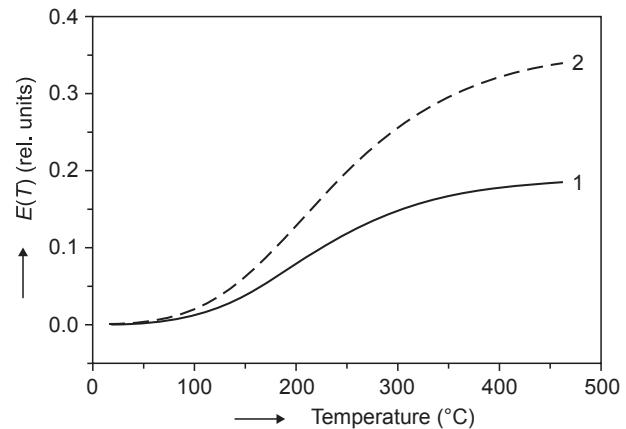


Figure 5. Temperature dependences of the model curves of radon release rate, $E(T)$, characterizing the radon mobility in alumina coatings. Curve 1 corresponds to sample I (thickness 4 µm), curve 2 corresponds to sample II (thickness 0.5 µm).
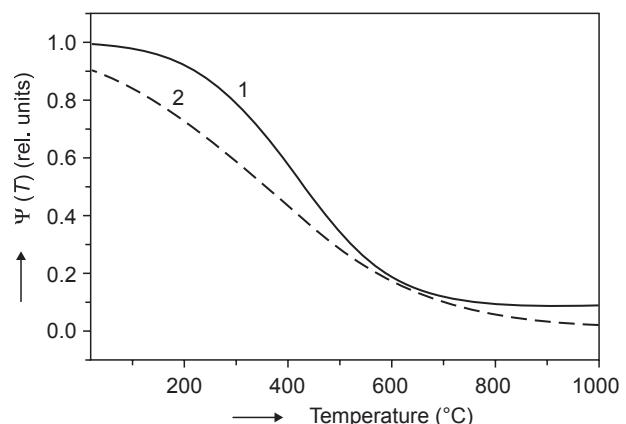


Figure 6. Temperature dependences of the model functions $\Psi(T)$ used for the characterization of the decrease in the number of radon diffusion path due to healing microstructure irregularities of the alumina coatings. Curve 1 corresponds to sample I (thickness 4 µm), curve 2 corresponds to sample II (thickness 0.5 µm).

## CONCLUSION

Temperature intervals of the microstructure changes taking place in the alumina coatings deposited on EUROFER '97 steel surface were determined from the ETA data during heating of the samples in argon.

The decrease of the radon release rate observed in the temperature range of 300-700°C was ascribed to healing microstructure irregularities of the alumina coatings. The healing of surface micro-cracks observed by SEM on the alumina coating surface was characterized by the break on the temperature dependence of radon release rate in the temperature range of 430-660°C. It followed from the ETA results that healing of the microstructure irregularities accompanied by the decrease of radon release in the range 300-700°C depend on the conditions used for the preparation of the alumina coatings: it can be expected more intense with the alumina coating sample of 4 μm thickness as compared to the sample of 0.5 μm thickness.

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## POUŽITÍ EMANAČNÍ TERMICKÉ ANALÝZY V DIAGNOSTICE MIKROSTRUKRURY VRSTEV OXIDU HLINITÉHO

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Emanační termická analýza, založená na měření rychlosti uvolňování radonu, byla použita k charakterizaci vývoje mikrostruktury vrstev oxidu hlinitého během ohřevu. Vzorky vrstev oxidu hlinitého byly připraveny na povrchu oceli EUROFER' 97 metodou filtrovaného elektrického výboje. Pokles rychlosti uvolňování radonu ze vzorků oxidu hlinitého pozorovaný pomocí ETA v oblasti teplot 300-700°C byl přisouzen procesu vyhojování defektů mikrostruktury vrstev oxidu hlinitého během ohřevu v argonu. Kromě toho vyhojování mikrotrhlin pozorovaných pomocí metody SEM na povrchu modifikovaného vzorku bylo charakterizováno na teplotní závislosti rychlosti uvolňování radonu jako efekt v oblasti teplot 430-660°C. Rozdíly v intensitě vyhojování defektů mikrostruktury a změnách mobility radonu byly vyhodnoceny na základě výsledků ETA teplotních závislostí difuse radonu. Z výsledků ETA plyne, že intensita vyhojování defektů mikrostruktury závisí na podmínkách přípravy vrstev oxidu hlinitého. Větší intensitu tohoto procesu během ohřevu v teplotní oblasti 300-700°C lze očekávat u oxidu hlinitého o tloušťce 4 μm ve srovnání se vzorkem oxidu hlinitého o tloušťce 0,5 μm.