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TRANSPORT PROPERTIES AND MICROSTRUCTURE CHANGES OF ALUMINA COATINGS CHARACTERIZED BY EMANATION THERMAL ANALYSIS*

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Emanation thermal analysis was used to characterize the thermal behaviour of alumina coatings as deposited on EUROFER 97 steel surface by filtered vacuum arc technique. Temperature ranges of the healing of cracks and structure irregularities observed by SEM were determined from the ETA results. Transport properties of the alumina coatings were assessed from the ETA results by the evaluation of radon diffusion parameters in the temperature range from 50 to 300°C. Healing microstructure irregularities of the alumina coatings can be expected in the range 300–700°C as indicated by the decrease of the radon release rate. From the ETA results it followed that the onset of healing the cracks observed by the SEM on the surface of one alumina coating sample can be expected at 430°C.

Keywords: *alumina coatings, emanation thermal analysis, filtered vacuum arc technology, microstructure changes, radon diffusion*

Introduction

It has been observed that alumina coatings deposited on martensitic steel can be used as a diffusion barrier of hydrogen isotopes for future nuclear fusion power reactors [1]. Alumina coatings of a micrometer thickness may efficiently suppress the hydrogen diffusion through a fusion relevant martensitic steel called EUROFER'97 [2]. The coatings of such properties should contain only the α-phase of alumina (α-Al_2O_3) and should not contain open pores or cracks. Alumina exists in many forms depending on preparation conditions. The γ-Al_2O_3 is formed by thermal treatment of mineral boehmite AlOOH. Other alumina phases, such as δ- and θ-Al_2O_3, are formed on further thermal treatment. Each transition alumina phase has the unique crystal structure due to movement of Al atoms into vacancies. The density of these phases is relatively constant at 3.60 g cm^{-3}, since the O atoms remain stationary in the fcc-lattice.

The thermodynamically stable α-Al_2O_3 (corundum) phase with a density of 3.98 g cm^{-3} is formed on heating at elevated temperatures [2]. Therefore, it has been of interest to characterize the thermal behavior of alumina coatings suitable for advanced technology applications.

The aim of this paper is to use the emanation thermal analysis to characterize transport properties and microstructure development on heating of alumina coatings deposited by filtered vacuum arc on the steel surface. The application potential of the emanation thermal analysis has been already demonstrated in the characterization thermal reactivity of ceramic clays, in the micro-structural development of minerals, such as natural and ion exchanged vermiculite, brannerite, etc. [3–5].

Experimental

Samples prepared

The deposition of the alumina coatings was performed by a filtered vacuum arc device, 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 the filtered vacuum arc deposition technique used can be found in [2]. In general, the alumina coatings

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prepared by this technique showed a good adhesion without visible cracks or delamination. Two good quality samples of alumina coatings were investigated, namely: sample I – thickness 4 μm and sample II – thickness 0.5 μm, in the preparation of both samples the substrate temperature during the alumina deposition was 650°C.

In addition, we investigated one sample of the alumina coating that contained visible cracks. This sample, denoted as sample III, was considered as not suitable for further application. It 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 deposition was 730°C.

Methods of characterisation

ETA measurements were carried out by using the modified NETZSCH DTA-ETA 404 equipment. Details of the ETA measurements and data treatment have been described elsewhere [6–8]. Samples for ETA measurements were labelled by radionuclides of ^{228}Th, ^{224}Ra and ^{220}Rn, using the recoil energy of 85 keV atom^{-1}. The specific activity of the sample was 10^5 Bq per gram. Atoms of ^{220}Rn radon were formed by the spontaneous α-decay of the ^{228}Th and ^{224}Ra radionuclides. The maximum depth of ^{220}Rn penetration was 60 nm as calculated with Monte Carlo method using TRIM code [9]. The labelled samples were heated in the temperature range 20–700°C at the rate of 6°C min^{-1} in the argon flow (flow rate 50 mL min^{-1}). The purity of argon gas was 99.9996%. The values of the radon release rate, E, are presented (in relative units) as $E=A_\alpha/A_{\text{total}}$, where A_α is α-radioactivity of radon released in unit time from the labelled 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 for the characterization of surface morphology of the alumina coatings.

Background for the ETA experimental data evaluation

The experimental ETA data were evaluated by using the mathematical model described in [10]. The diffusion in open pores and the inter-boundary space was considered as the main mechanism of radon release from the labelled alumina samples in the temperature range used. Considering this diffusion mechanism, the rate of radon release $E(T)$ can be expressed as

$$E(T) = E_{\text{D}}(T)\Psi(T) \tag{1}$$

where the term $E_{\text{D}}(T)$ is characterizing the radon mobility along structure irregularities that served as radon diffusion paths, and the term $\Psi(T)$ is characterizing the decrease in the number of radon diffusion paths due to healing microstructure irregularities. The radon release rate, $E_{\text{D}}(T)$, is expressed as

$$E_{\text{D}}(T) = A[F(T_0)] - F(T) \tag{2}$$

where $F(T)=\dfrac{1}{k_{\text{D0}}\exp\left(-\dfrac{Q_{\text{D}}}{RT}\right)+\lambda_{\text{Rn}}}$, $A=\lambda_{\text{Ra}}C_{\text{R}}$, and the decay constant of ^{224}Ra is $\lambda_{\text{Ra}}=2.2035\cdot10^{-6}$ [s^{-1}], C_{Ra} is equilibrium concentration of ^{224}Ra, $\lambda_{\text{Rn}}=1.2464\cdot10^{-2}$ [s^{-1}] is the 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 Arrhenius relationship,

$$k_{\text{D}} = k_{\text{D0}}\exp(-Q_{\text{D}}/RT) \tag{3}$$

where k_{D0} [s^{-1}] is radon diffusion rate coefficient, Q_{D} is the activation energy of diffusion, R=8.314 J mol^{-1} K^{-1} is the universal gas constant.

To describe the decrease in the number of the radon diffusion paths on sample heating following temperature dependence was used:

$$\psi(T) = 1 - \frac{\kappa}{2}\left[1 + \operatorname{erf}\frac{1-\dfrac{T_{\text{m}}}{T}}{\dfrac{\Delta T\sqrt{2}}{T}}\right] \tag{4}$$

where erf is Gauss error function, T_{m} is the temperature of the maximal healing rate of the defects serving as radon diffusion paths, ΔT is the temperature interval of the respective solid state process and κ is the parameter describing the contribution of the solid state process to the change in the number of the radon diffusion paths.

Results and discussion

Figures 1a and b depict ETA results characterizing the thermal behaviour of the alumina coatings, namely samples I (a) and sample II (b), on heating in argon from 20 to 700°C. Experimental results are presented as open circles, model curves obtained by fitting the experimental results with the mathematical model are presented as full lines. The increase of radon release rate in the temperature range 20–300°C was due to radon diffusion along structure irregularities of the alumina layers in their surface and subsurface up to 60 nm. It was assumed that in this temperature range the diffusion of radon in the subsurface of the alumina coatings was controlled by

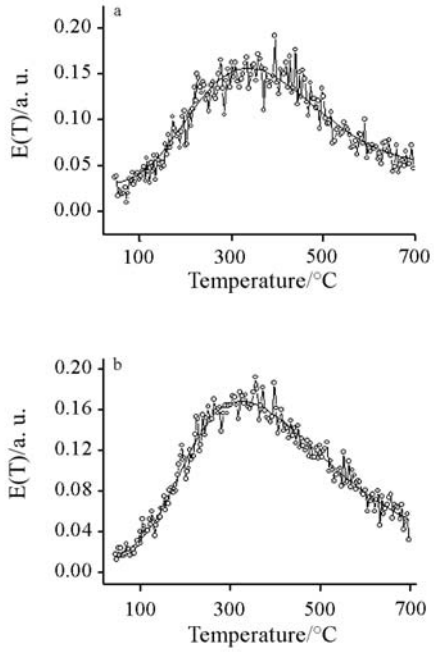

Fig. 1 ETA characterization of the alumina coatings: a – sample I and b – sample II. Temperature dependencies of the radon release rate $E(T)$ was measured during heating of the alumina coatings samples in argon. Experimental results are presented as open circles, model curves obtained by fitting the experimental results with the mathematical model are presented as full lines

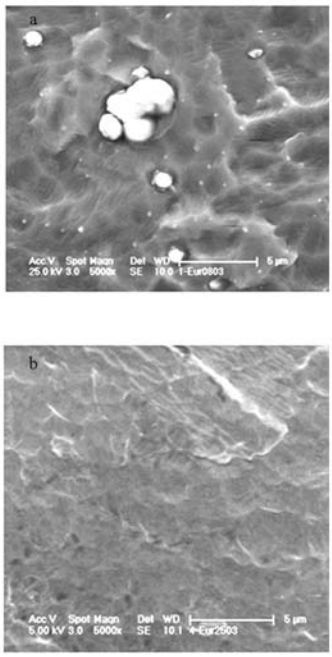

Fig. 2 SEM micrographs of the alumina coatings samples a – I and b – II

a random 'single jump' mechanism and that the break observed at about 300°C and the subsequent decrease of the radon release rate $E(T)$ in the range of 300–700°C was due to healing of microstructure irregularities. Microstructure irregularities of the alumina coatings, cracks, grain boundaries, etc. served as radon diffusion paths in the sample. SEM micrographs that characterized the surface microstructure of these samples are presented in Fig. 2.

ETA results and SEM micrographs of the alumina coating (sample III) that contained visible cracks are presented in Figs 3 and 4, respectively. The onset temperature of healing the visible micro-cracks was expected in the range 430°C, as indicated by the effect on the ETA curve (curve 1, Fig. 3). No such effect was observed on the ETA results of the sample prepared at the same conditions, but containing no micro-cracks (curve 2, Fig. 3). 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 700°C.

Transport properties of the alumina coatings can be assessed from the radon diffusion parameters evaluated by fitting of experimental ETA results with

Table 1 Characterization of radon mobility in alumina coatings as determined from the ETA results measured in the temperature range 50–300°C

Alumina coatings deposited on the EUROFER97 steel substrate	Radon diffusion parameters*	
	Diffusion rate coefficient k_{D0}/s^{-1}	Activation energy Q_D/kJ mol^{-1}
Sample I Substrate temperature 650°C coating thickness 4 μm	8.8	29±3
Sample II Substrate temperature 650°C, coating thickness 0.5 μm	18.9	32±3
Sample III Substrate temperature 730°C, coating thickness 0.5 μm	46.1	34±3

*for the radon diffusion parameters relationship see Eq. (3)

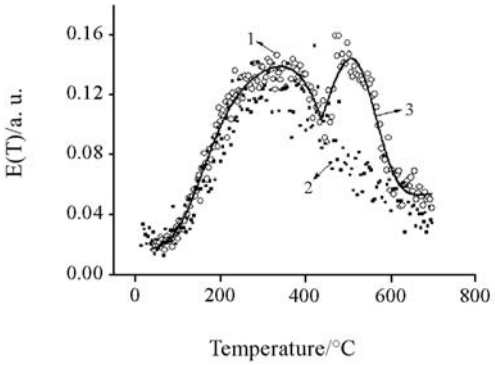

Fig. 3 ETA results of two pieces of alumina coating sample III. The experimental results of the piece that contained surface micro-cracks are shown as open circles (curve 1), whereas the results of the second piece that contained no visible micro-cracks are shown as black points (curve 2). The full line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

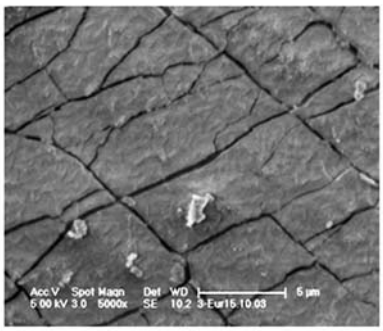

Fig. 4 SEM micrograph of the alumina coating sample III that contained visible micro-cracks

the mathematical model. Equation (3) was used to determine the diffusion characteristics of radon diffusion from the ETA experimental data. Table 1 summarizes the radon diffusion parameters of the alumina coatings namely the activation energy Q_D of radon diffusion and the diffusion rate coefficient k_{D0}. From Table 1 it followed that no significant differences in the values of the activation energy Q_D of radon diffusion in the samples I–III were found. Nevertheless, the values of k_{D0} differed, indicating different amounts of structure irregularities that served traps and diffusion paths for radon atoms in the alumina samples investigated.

Conclusions

Thermal behaviour of alumina coatings deposited on EUROFER' 97 steel surface by filtered vacuum arc technique was characterized by the emanation thermal analysis as follows:

In the temperature range from 50 to 300°C the radon diffused along the structure imperfections, serving as diffusion paths for radon in the alumina coatings. The radon diffusion parameters determined from the ETA experimental results were used to characterize the transport properties of the alumina coatings. Changes in transport properties due to healing microstructure irregularities of the alumina coatings were supposed in the temperature range 300–700°C. It followed from the ETA results that the onset of healing of visible micro-cracks can be expected at the temperature of 430°C.

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