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THERMAL BEHAVIOUR OF ADVANCED COMPOSITE MATERIALS BASED ON SiC FIBRES

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Abstract

Emanation thermal analysis (ETA) was used for characterization of thermal behaviour of SiC_f/SiC composites on heating in argon and air, respectively. Effect of gas environment (argon, air) and helium ions implantation on the microstructure development of the SiC_f/SiC composite prepared by chemical vapour infiltration (CVI) from Nicalon CG fibres was investigated under in situ conditions of heating. The annealing of near surface structure irregularities was observed in the range 280–700°C and evaluated by means of the mathematical model, assuming that the structure irregularities served as diffusion paths for radon. The ETA reflected the formation of amorphous silica and its subsequent crystallization to crystoballite. Morphology of the SiC_f/SiC samples before and after the heat treatments was characterized by means of SEM.

Keywords: annealing, emanation thermal analysis, near surface layers, radon, SiC/SiC_f, structure irregularities

Introduction

SiC_f/SiC composite consists of relatively poor crystalline β-SiC and contains aggregates of uniformly dispersed nano-particles of SiC, SiO_2 and C [1]. This insured the densely bonded structure. The SiC_f/SiC composite manufactured by CVI has excellent resistance to heat and oxidation and maintains strength even up to 1200°C in air. Because of small thermal expansion coefficient the Nicalon based materials have excellent dimensional stability. It has been applied in the field of advanced technologies and space development. It is also a candidate material for fusion technology because of its radiation stability and low activation in the neutron flux.

Thermal stability of Si–C–O fibres (Nicalon CG) has been investigated by several authors [1–7]. Active and passive oxidation mechanisms were proposed for SiC fibres heat treated in oxidizing gas environments with different oxygen partial pressure. The active oxidation mechanism was proposed [3] for the formation of silica layer on the SiC surface heated in the gaseous environment with relatively high oxygen partial pressure

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($2.5 \cdot 10^3$–10^5 Pa). Silica is one of the few oxides, which have extremely low oxygen permeability up to high temperatures. Consequently, the silica formed on the SiC surface serves as the barrier *vs*. further oxidation of the SiC core.

However, there has been a lack of information about the thermal behaviour of the SiC based materials when heated in oxygen containing gas medium in the temperature range below 1200°C. Therefore, the emanation thermal analysis (ETA) [8–10] was used in this study to characterize microstructure changes of SiC_f/SiC composites during heating in the range 30–1300°C. Moreover, the morphology of SiC_f/SiC composite samples was characterized by means of SEM.

Experimental

SiC_f/SiC composite was prepared by chemical vapour infiltration (CVI) from Nicalon CG fibres (Nippon Carbon Co.). Nicalon fibres were produced from polycarbosilane precursor and contained 11.8 mass% of oxygen and excess of C with respect to Si. The typical formula of the CG Nicalon is $SiC_{1.31}O_{0.36}$ [2].

Methods

Emanation thermal analysis (ETA) of the materials was performed by using a Netzsch DTA-ETA apparatus Type 409. Scanning electron microscopy (SEM) micrographs were obtained by means Philips XL 30 CP equipment.

The ETA [8–10] consists in the measurement of radon release rate from samples previously labelled by trace amounts of ^{228}Th and ^{224}Ra radionuclides. Atoms of radon, ^{220}Rn, have been formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra and incorporated into the near surface layers of the sample due to the recoil energy (85 keV atom^{-1}). The specific activity of a labelled sample was 10^5 Bq g^{-1}. It was determined by TRIM code [11] that the maximal penetration depths of ^{220}Rn recoiled atoms into SiC based samples was 84 nm.

ETA measurements

A labelled sample (size 3×3×2 mm) was situated in a furnace (Fig. 3 [10]) and heated in the temperature range 30–1300°C at the rate of 6°C min^{-1} in the flow of argon or air, respectively. The constant flow of the gas (flow rate 50 mL min^{-1}) took the radon released from the sample into the measuring chamber of radon radioactivity. The resulting ETA curve is presented as a temperature dependence of the radon release rate E (in relative units); $E=A_\alpha/A_{total}$, where A_α is α-radioactivity of radon released in unit time from the labelled sample, and A_{total} is the total γ-radioactivity of the labelled sample. The A_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI(T1) detectors were used for the α- and γ-radioactivity measurements, respectively.

Two sets of the the SiC_f/SiC composite samples were investigated. One set of the samples was used for the characterization of the effect of gas environment (argon

and air, respectively) and the second set was used for the characterization of the effect of high energetic helium ions in the microstructure development. The bombardment of the samples with 25 MeV helium ions was performed by using a synchrotron accelerator at the Institute of Nuclear Physics, AS CR Řež (helium ions current was 10 μA, which corresponds to $6 \cdot 10^{13}$ ion s^{-1} cm^{-2}). The calculated penetration depth for helium ions was 236 μm. Both sets of the samples were labelled with ^{228}Th nuclide prior to the ETA measurements.

Results and discussion

Effect of gas environment on thermal behaviour of SiC_f/SiC composite

Figure 1 depicts the experimental ETA results of SiC_f/SiC composite sample on heating in argon and air, respectively. We assumed that the radon release in the range 30–200°C was controlled by the 'single jump' diffusion mechanism along near surface structure irregularities. Consequently, the permeability of the sample can be evaluated from the ETA results observed in this range. The decrease of the radon release rate, *E*, observed in the range 330–595°C characterized the annealing near surface structure irregularities. It is obvious from Fig. 1 that the SiC_f/SiC composite annealing started at 280°C on the heating in air, which is the temperature by 50°C lower than the onset observed during annealing of the sample in argon.

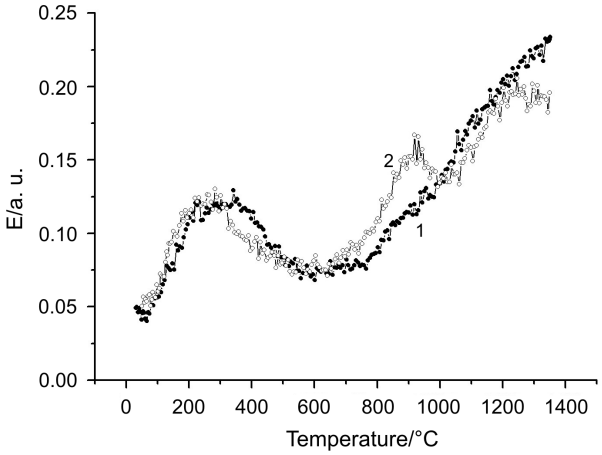

Fig. 1 Emanation thermal analysis results characterising the thermal behaviour of the Nicalon CG based SiC_f/SiC composite during heating in argon (curve 1) and air (curve 2)

We supposed that the enhanced radon release rate, *E*, observed on heating of SiC_f/SiC sample in air in the range 620–920°C was due to SiC oxidation, assuming that the formation of amorphous silica as the SiC oxidation product and the interface boundaries served as additional radon diffusion channels. On the other hand, we as-

sumed that the decrease of E observed above 920°C indicated the formation of crystobalite from the amorphous silica, supposing that the crystallization process led to the decrease of the radon diffusion channels formed previously. This behaviour is in agreement with the results of other authors [3–7] who found that amorphous silica is formed at the beginning of the SiC oxidation and tends to crystallize at longer times and at higher temperatures to crystoballite.

Effect of helium implantation thermal behaviour of SiC_f/SiC on heating in argon

The ETA curves obtained during heating of SiC_f/SiC in argon (Fig. 2) were used for the investigation of the effect of high energetic helium ions (25 MeV) on the SiC_f/SiC composite. It is obvious from Fig. 2 that the implantation of 25 MeV helium ions affected the permeability of radon in the near surface layers of SiC_f/SiC composite. The increase of the slope of the ETA curve was observed in the range 50–200°C on heating of the helium bombarded sample in argon in comparison with non-bombarded sample. This indicated the enhanced permeability of the sample in the range 50–200°C for radon in helium bombarded SiC_f/SiC. A similar enhancing effect of the helium ion bombardment on radon permeability in the SiC_f/SiC composites was observed also in the range 700–1300°C where radon release rate was controlled by bulk diffusion mechanism.

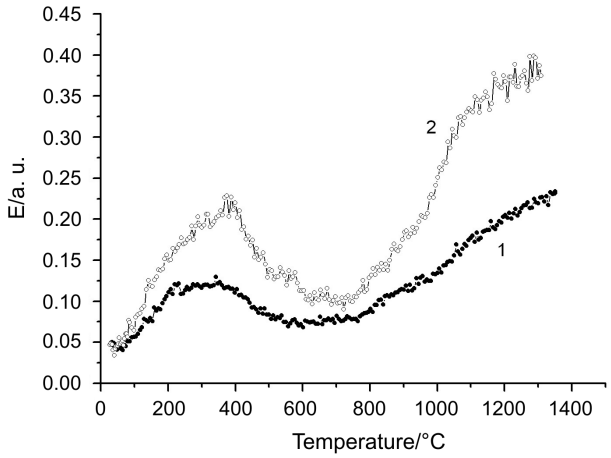

Fig. 2 Emanation thermal analysis results characterising the effect of 25 MeV helium ions on the Nicalon CG based SiC_f/SiC composite during heating in argon. Curve 1 corresponds to non-bombarded sample; curve 2 corresponds to helium-ions bombarded sample

The decrease of E observed at the temperature 380°C for both non-bombarded and bombarded SiC_f/SiC characterized the annealing of structure irregularities in the near surface layers. In order to quantitatively characterize the annealing process, a mathematical model was used supposing that radon migration takes place by diffusion in open pores or interface boundaries.

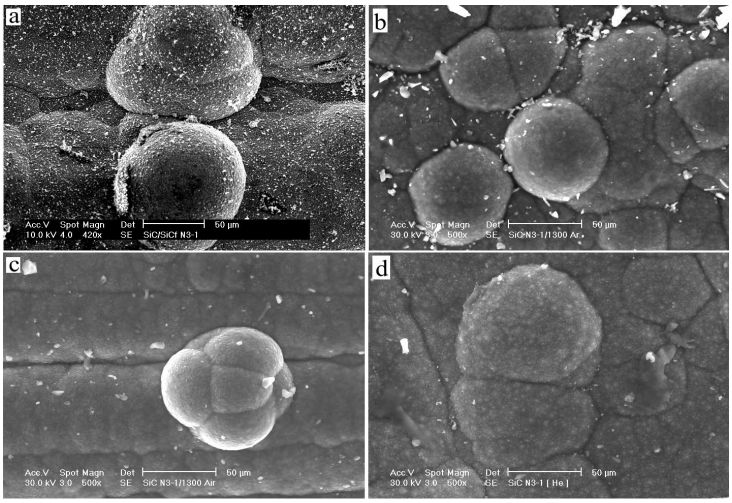

Fig. 3 SEM micrographs of SiC_f/SiC samples before and after heat treatments in argon and air, respectively; a – sample before heat treatment; b – heated to 1300°C in argon; c – heated in air to 1300°C; d – sample before heat treatment bombarded with helium ions

SEM micrographs (Fig. 3) of the samples before and after heat treatments in argon and air respectively were used in order to characterize the morphology of the sample. The SEM results were in accordance with the previous findings by ETA. Moreover, it should be mentioned that processes taking place in the surface and near surface layers on heating of SiC_f/SiC composites have been revealed by ETA under in situ conditions of heating and in a more sensitive way than by SEM.

Modelling and evaluation of ETA results

According to the theory proposed recently by Beckman and Balek [12], the development of the materials microstructure and radon permeability can be characterized by functions E_D and $\Psi(T)$. Radon atoms have been in serving in ETA as microstructure probe of the samples.

The $E(T)$ function can be expressed as

$$E(T)=E_D(T)\Psi(T) \quad (1)$$

where E_D is the radon release rate due to diffusion along structure irregularities, serving as radon diffusion paths, and $\Psi(T)$ is the function which describe the temperature dependence of changes in the number of radon diffusion paths.

The maximal penetration depth of ^{220}Rn recoiled atoms in SiC composite was determined by TRIM code [11] as 84 nm. Taking into account the average diffusion length of radon $L_D=(D/\lambda)^{1/2}$, where D is the radon diffusion coefficient and $\lambda=0.0127\ s^{-1}$ is the radon decay constant, it was supposed, that in the SiC sample heated

to 1000°C contained the atoms of radon to the depths of 130 nm from the surface. It was assumed that radon migrate along several independent paths, such as micropores, intergranular space, as well as interface boundaries. The high amount of ^{220}Rn situated next to the surface ensured the high sensitivity of ETA to microstructure in the near surface layers of SiC based composites.

The following expression was used for the temperature dependence of E_D:

$$E_D = \frac{3}{y}\left(\coth y - \frac{1}{y}\right); \quad y = r_0\left(\frac{\lambda}{D(T)}\right)^{1/2} \tag{2}$$

where r_0 is parameter characterizing the sample size, λ is the ^{220}Rn decay constant.

For $D(T)$ the following temperature dependence was supposed:

$$D(T) = D_0 \exp(-Q_D/RT) \tag{3}$$

where Q_D and D_0 are the activation energy and pre-exponential factor of radon diffusion, resp., R is molar gas constant, T is temperature in K.

Equation (4) was used for $\Psi(T)$ function to describe to annealing of near surface structure irregularities of the samples

$$\Psi(T) = 0.5\left[1 + \mathrm{erf}\left(\frac{1-(T_m/T)}{(\Delta T\sqrt{2})/T}\right)\right] \tag{4}$$

where erf is the sign for the integral Gauss function (error function), T_m is the temperature of maximal rate of the annealing of the structure irregularities which serve as radon diffusion paths, ΔT is the temperature interval of the respective solid state process.

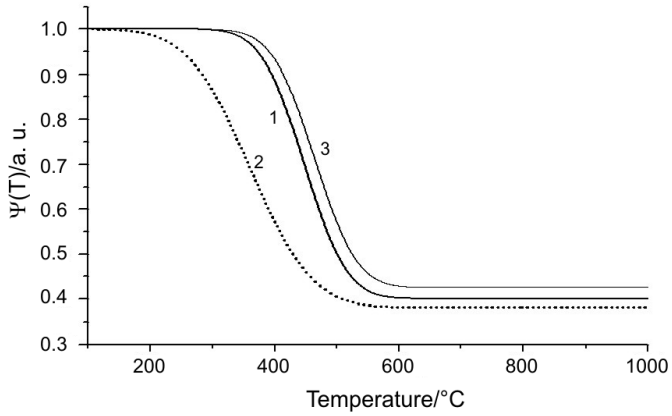

Fig. 4 Temperature dependencies of $\Psi(T)$ functions characterizing of the annealing of near surface structure irregularities in SiC_f/SiC composite sample before and after He ion implantation. Curves 1 and 2 correspond to non-bombarded sample heated in argon and air, respectively, curve 3 corresponds to heating of the helium bombarded sample in argon

Temperature dependencies of $\Psi(T)$ functions, obtained by modelling, which characterized the annealing of near surface structure irregularities, were used for the assessment of the thermal behaviour of samples in the temperature range 280–700°C. Figure 4 depicts the calculated temperature dependencies of the $\Psi(T)$ functions characterizing the annealing of near surface structure irregularities in SiC_f/SiC composite samples. In Fig. 4 the curves 1 and 2 correspond to non-bombarded sample during heating in argon and air, respectively, whereas curve 3 corresponds to heating of the helium bombarded sample in argon. The effect of gas environment can be assessed by comparison of curves 1 and 2, whereas the effect of helium ions bombardment can be assessed by comparison of curves 1 and 3, respectively.

An additional computer treatment was used in order to examine in detail the effects observed by ETA on heating of SiC_f/SiC in various gas environments at the elevated temperatures (Figs 1 and 2). During the computer treatment the model curves, characterizing temperature dependence of the $\Psi(T)$ functions, and the radon diffusion in bulk, respectively were subtracted from the experimental ETA curves. The experimental ETA results obtained on heating in argon and air, respectively are presented in Figs 5a–c along with the results of the computer treatment, corresponding to the three ETA measurements, namely (a) non-bombarded sample heated in argon, (b) non-bombarded sample heated in air, and (c) helium bombarded sample heated in argon.

The ETA experimental data are represented in Figs 5a–c by dots (curves 1), curves 2 are results of modelling by using Eq. (2), curves 3 are model curves characterizing radon diffusion by bulk mechanism, calculated by using Eq. (3) and curves 4 are curves representing the remainders after subtraction of the respective model curves 2 and 3 from the curves 1, for each sample. From Fig. 5b it followed that the formation of crystoballite from amorphous silica layers on heating of SiC_f/SiC sample in air was achieved at the temperature of 1000°C.

Table 1 Characteristics of SiC_f/SiC microstructure annealing and radon permeability of non-implanted and helium implanted SiC_f/SiC samples

SiC_f/SiC samples notation and gas used for treatment	Radon permeability characteristics				Annealing temp. T_{onset}–T_{final} /°C
	50–200°C		700–1300°C		
	D_0/cm^2 s^{-1}	Q/kJ mol^{-1}	D_0/cm^2 s^{-1}	Q/kJ mol^{-1}	
Non-implanted/Ar	$1.3\cdot10^{-6}$	61.5	$2.8\cdot10^{-7}$	158.4	316–560
Non-implanted/air	$1.1\cdot10^{-6}$	58.5	$1.4\cdot10^{-7}$	155.4	250–530
He implanted/Ar	$5.5\cdot10^{-10}$	27.3	$1.8\cdot10^{-3}$	231.6	370–550

Table 1 summarized the quantitative data of radon permeability and microstructure annealing temperatures of the investigated samples which resulted from the evaluation of the ETA results obtained in this study.

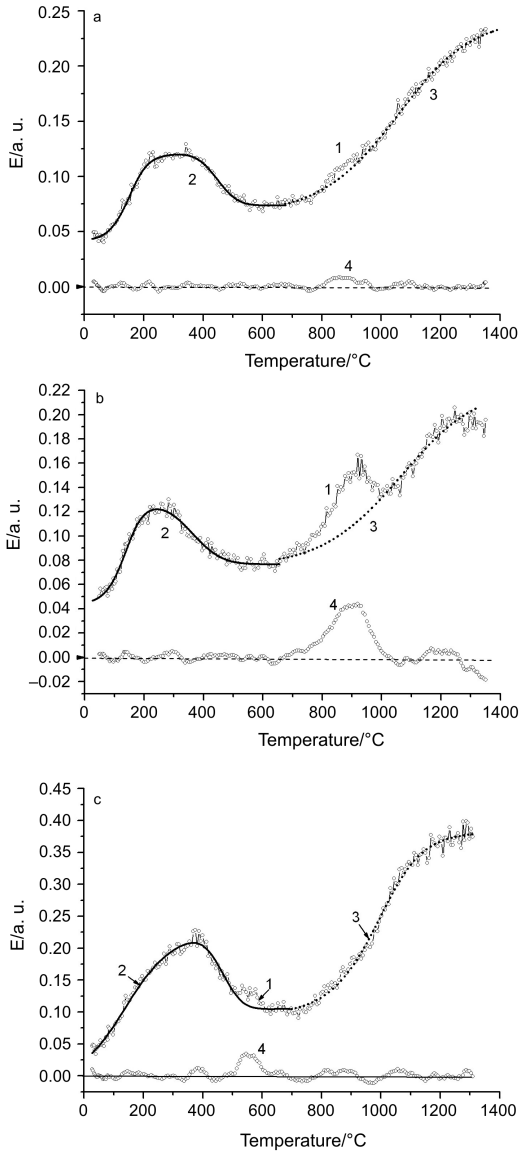

Fig. 5 a–c ETA experimental results and results of the mathematical modelling characterizing thermal behaviour of SiC_f/SiC composite. ETA experimental results are represented by dots (curve 1), curve 2 is model curve obtained by using Eq. (2), curve 3 is model curve calculated by using Eq. (3) and curve 4 is the curve representing a remainder obtained after subtraction of the model curves 2 and 3 from the experimental results, respectively, for each sample a–c.
a – non-bombarded sample heated in argon; b – non-bombarded sample heated in air; c – helium-bombarded sample heated in argon

Conclusions

Microstructure changes taking place in surface and near surface layers of the samples were characterized by means of ETA under in situ conditions of the heat treatment in argon and air, respectively. Effects of gas environments (argon and air) as well as helium ions bombardment on the microstructure development of SiC_f/SiC composite materials based on Nicalon CG fibres were quantitatively characterized.

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