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EMANATION THERMAL ANALYSIS OF SiC BASED MATERIALS

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Abstract

Results of emanation thermal analysis (ETA) characterizing microstructure changes of SiC based materials during heat treatment in argon are demonstrated. This method made it possible to reveal fine changes of the texture of SiC nano-sized powders, SiC micro-sized powders and SiC whiskers under *in situ* conditions of the heating. ETA curves can serve as 'fingerprints' of the respective samples.

Keywords: emanation thermal analysis, SEM, SiC nanocomposites

Introduction

The aim of this study is to demonstrate the use of emanation thermal analysis (ETA) [1–3] as a tool for the characterization of microstructure changes of SiC based materials. This method made it possible to reveal fine changes of the microstructure of SiC based composites, such as SiC/Al_2O_3 [4]. The thermal behavior characterization of SiC nano-sized powders, SiC micro-sized powders and SiC whiskers under heating in argon are presented in this paper. ETA results presented in this paper will be discussed in comparison with the electron micrographs of the respective samples.

The advantage of the characterization by means of ETA consists in the possibility to indicate fine changes of the texture taking place in the surface and near surface layers of the samples with various texture. The measurement of the release of radon atoms, previously incorporated into the near surface layers, reflects the changes of surface area and open porosity serving for the radon migration. The temperature dependence of the radon release rate give information about the changes of the surface area and porosity.

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The recoil energy of radon atoms produced by spontaneous alpha decay of ^{224}Ra has been used for the introduction of radon atoms in the near surface layers of the samples [1]. The recoil depth ^{224}Ra and ^{220}Rn ions implanted by the recoil energy (85 keV per atom) into SiC was calculated by means of TRIM code [5] as: 37.7 nm (3.9 nm straggling) and 38.2 nm (straggling 3.8), resp. Therefore, we can suppose that radon atoms penetrate into the near surface layers of SiC to the maximum depth of 83.6 nm. In this study the parent isotopes ^{228}Th and ^{224}Ra served as 'recoil ion implantators' of the radon atoms.

It can be supposed that the solubility of radon atoms in SiC, is negligible. The inert gases are trapped at lattice defects, vacancy clusters, grain boundaries and pores. The defects in the solid can serve both as traps and as diffusion paths for the inert gas. A survey of the influence of various factors on the migration of inert gases in solids is given in [1]. The diffusion in the matrix is the main mechanism for the radon release from the samples. We considered the radionuclide of ^{228}Th as a quasi-permanent source of ^{220}Rn.

Experimental

Materials studied

SiC ultrafine powder (particle-size 20 nm), SiC submicro-sized powder (0.5 μm), SiC whiskers. The texture of the materials was characterized by SEM.

Samples labelling

The atoms of ^{228}Th were adsorbed from acetone solution on the sample surface, serving as a quasi-permanent source of ^{224}Ra and ^{220}Rn. The specific activity of the labelled sample was 10^5 Bq per gram. The labelled samples were stored at least three weeks prior to ETA measurements in dry condition to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established. We suppose that the surface layer to the depth of 83.6 nm was labelled by ^{220}Rn recoiled atoms (as calculated by the TRIM code [5]).

Method used

ETA measurements were carried out at the Nuclear Research Institute Ře using modified Netzsch DTA-ETA 404 equipment.

The ETA apparatus consisted of the sample holder situated in a furnace, the detector of α-radioactivity, the counts-meter and the carrier gas system. The labelled sample was heated at the rate of 6 K min^{-1}, overflowed by the constant flow of the carrier gas (argon: flow rate 50 mL min^{-1}), which took the radon released from the sample into the measuring chamber of radon radioactivity. The resulting ETA curve is presented as temperature dependence of the radon release rate E (in relative units) [2].

For microstructure characterization the Scanning Electron Microscope Philips XL 30 CP equipment was used at the Institute of Inorganic Chemistry, Ře .

Results and discussion

Microstructure changes taking place during heating of the finely dispersed SiC samples were characterized by means of ETA under *in situ* conditions of the heat treatment in argon up to 1300°C.

It was demonstrated in our previous papers [6–8] that the early stage of sintering and the annealing of surface roughness can be reflected by ETA. Consequently, the annealing of the surface roughness of the SiC samples of different size and shape revealed by ETA can characterize in a unique way the thermal behavior of the samples with the specific thermal history and technological processing.

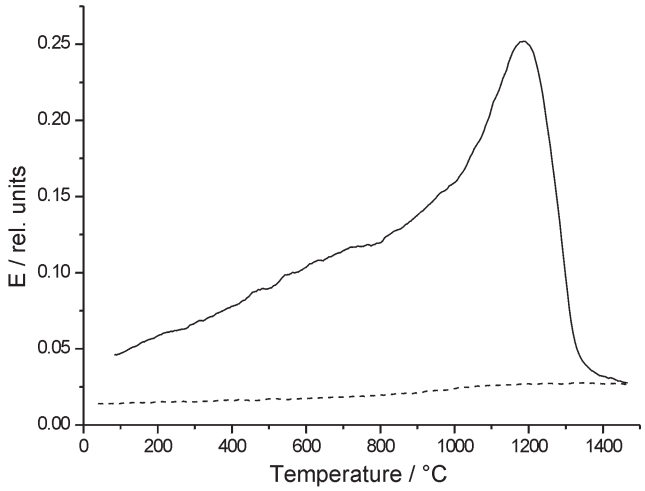

Fig. 1 Temperature dependence of radon release rate, *E*, from SiC nano-sized sample during heating (full line) and cooling (dashed line) in argon at the rate 6 K min^{-1}

Figure 1 shows the ETA curve of ultrafine SiC powder (size 20 nm), which was measured during heating in argon. The sample was prepared by means of laser-assisted synthesis from silane-hydrocarbon mixture [9, 10]. It was found by Cauchetier *et al*. that the surface of SiC nano-sized powders was covered by a layer of SiO_2 thin layer (thickness approximately 4 nm). From the ETA curve we can suppose that thin layer of SiO_2 can melt at about 1180 C, therefore the break observed on the ETA curve in the temperature range 1180–1350°C can be ascribed to the densification of the nano-sized SiC powder due to the interaction of the melted silica surface layer. As it follows from the ETA curve measured during subsequent cooling, the sample was perfectly densified. Character of the cooling curve corresponds to the very low diffusion of radon which is characteristic for the sintered solid covered with the fused silica layer. From the ETA curve it follows that in the range 100–800°C the diffusion of radon in the intergranular space of the sample is the controlling mechanism of the radon release from the sample. SEM micrographs (Fig. 2) characterized the texture of

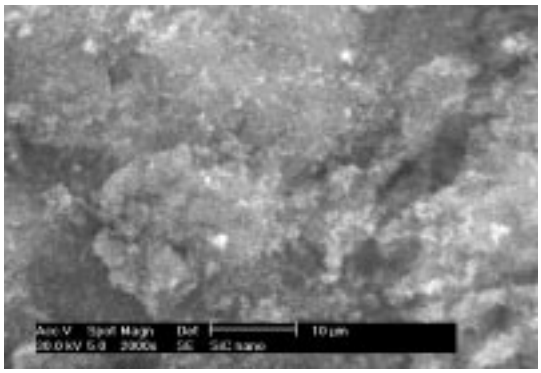

Fig. 2 SEM micrograph of SiC nano-sized sample

the nano-sized powder as a very fine powder forming agglomerates of the size approximately 10 μm.

Figure 3 corresponds to the ETA curves of the SiC submicro-sized sample. From Fig. 4 it follows that the size of the powders is not uniform. The main part consists of the particles sized 0.3 μm. The ETA curve characterizes the thermal behavior of all parts of the sample. Consequently, we can suppose that the annealing (compactization) by surface sintering of the sample takes place on heating above 750°C. The next effect observed on the ETA curve at 1200°C could be ascribed to the interaction of silica layers formed on the surface of SiC particles. Obviously this effect is not so intense as observed for SiC ultrafine particles where in total a larger amount of SiO_2 is present. The ETA curve reflected the overall behavior of the sample composed of the grains of various size.

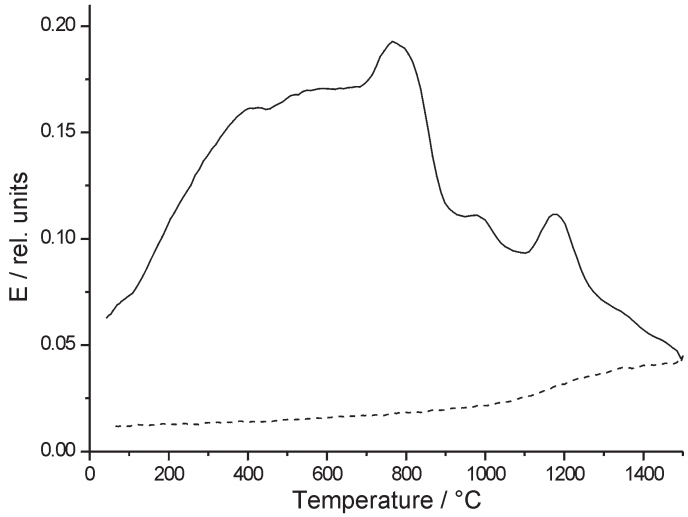

Fig. 3 Temperature dependence of radon release rate, *E*, SiC submicro-sized sample during heating (full line) and cooling (dashed line) in argon at the rate 6 K min^{-1}

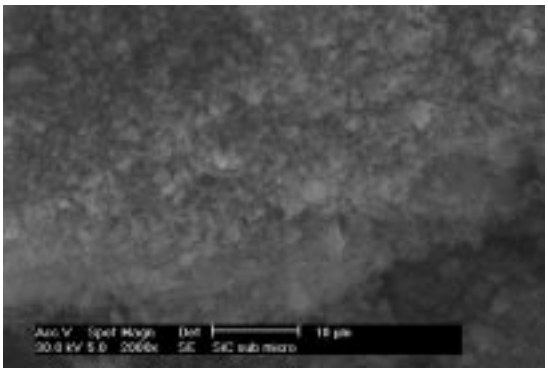

Fig. 4 SEM micrograph of SiC submicro-sized sample

Figure 5 represents the ETA curve of the SiC whiskers. From the ETA curve it is evident that in the range from 300 to 500°C annealing of the SiC whiskers takes place resulting in the decrease of the intergranular space between the whiskers. The effect observed in the ranges 800–900 and that starting at 1250°C indicated the processes, which led to the decrease of the number of diffusion paths for radon. Such processes are the annealing of open porosity, grain growth or the interaction of SiO_2 based layers covering the micro-sized SiC sample. From the ETA curve measured during cooling it follows that by previous heating a complex material involving strains was formed. The effect observed on the ETA curve measured during ample cooling in argon corresponded to the release of the strains.

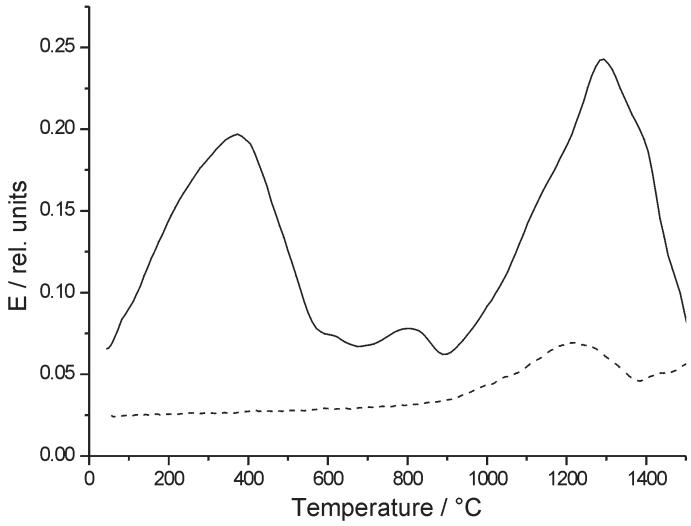

Fig. 5 Temperature dependence of radon release rate, *E*, SiC whiskers during heating (full line) and cooling (dashed line) in argon at the rate 6 K min^{-1}

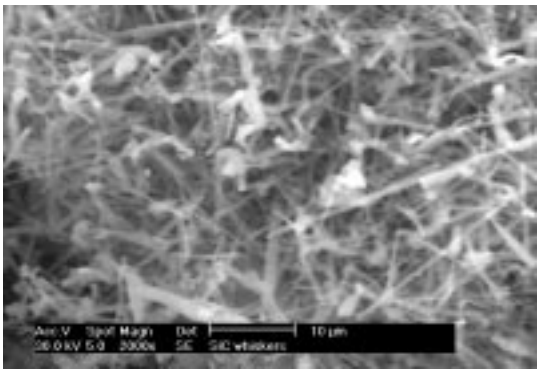

Fig. 6 SEM micrograph of SiC whiskers

Conclusions

ETA can be used as a sensitive tool to reflect texture and microstructure changes in the near surface layers of SiC samples submitted to the heating in the selected atmosphere (argon). ETA results characterized thermal behavior of SiC nano-sized and submicro-sized powders and whiskers, respectively. ETA curves can be used as 'fingerprints' for checking their thermal behavior in requested gas medium. ETA can be recommended a tool, giving information about the dynamic behavior of the samples, additionally to the electron micrographs. A more detailed evaluation of the ETA curves from the viewpoint of the diffusion mobility of radon will be given in the next paper.

ETA can be recommended as non-common method to obtain additional information about microstructure (microporosity) changes taking place during thermal treatment of the precursors of the SiC based composites, materials for joints etc. The Nuclear Research Institute Řež possesses the equipment for ETA and offers collaboration to other laboratories investigating SiC based materials.

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