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DIAGNOSTICS OF INORGANIC MATERIALS BY DIFFUSION STRUCTURAL ANALYSIS

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ABSTRACT

In this paper the principle of diffusion structural analysis (DSA), based on the measurements of inert gas migration in solids, is given. The potential of this method and various applications are demonstrated . e.g. the determination of inert gas mobility in metals, ionic crystals and ceramics, characterization of non-crystalline solids and their changes, checking and control of solid state processes taking place during preparation of advanced technology materials, the quality testing of intermediate and final products of these technologies, testing the oxidation and corrosion stability of the materials, etc.

INTRODUCTION

The inert gases can be used as a probe for the defects of solids, such as non-uniformity of the structures, the presence of various types of structure defects and changes of their concentration, etc. The radioactive nuclides of inert gases (e.g. ^{24}Ne, ^{39}Ar, ^{85}Kr, ^{133}Xe, ^{220}Rn), applied as the diffusion probe of solids, enabled us to make diagnostics of various defects in solids. Inert gases of "smaller size" such as He, Ne (the atomic radius of Ne is 0.112 nm) can be applied in the study of the single point defects, whereas the "large sized" inert gases, such as Kr, Xe, Rn (atomic radius of Rn is 0.214 nm) can be used in the complex defects mobility assessment, in the investigation of the morphology formations of solids and their changes.

PRINCIPLE OF THE METHOD

Diffusion structural analysis (DSA) is based on the study of the migration of inert gas traces in the solid samples during their thermal, mechanical and other treatment [1]. The high sensitivity of radioactive nuclide detection enabled us to use very low concentrations of the inert gases, so that no mutual interaction of the inert gas atoms can be expected .This method makes it possible to gain information about the defects and irregularities of the structure of solids, which is complementary to the information given by other methods, i.e. X-ray diffraction, conventional thermal analysis methods, etc. In this paper an overview of the application of DSA to the diagnostics of inorganic materials is given, aiming to promote further use of this method.

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Inert gas labelling of solids.

The inert gas atoms may be incorporated into the solid samples by several techniques [2] , e.g. by the diffusion of the inert gas intoa solid at higher pressure and temperatures. The implantation of accelerated inert gas ions can be also used for labelling of solids, the concentration profile of the inert gas being dependent on the energy of the inert gas ions, on the structure and composition of the solids. In some cases it is advantageous to produce the inert gas atoms within the solid to be studied by nuclear reactions, e.g. in alkali-metal-or alkaline earth metal halides Ar, Kr and Xe are formed by means of (n,α) and (n,p) reactions, resp. Nuclear fission reactions have been used for the incorporation of the radionuclides of ^{133}Xe and ^{85}Kr into the solids. Radon atoms can be formed by spontaneous α-decay of thorium or radium nuclides, e.g. according to the schemes: $^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn$; $^{226}Ra \xrightarrow{\alpha} {}^{222}Rn$.

There is an advantage in using the radon parent nuclide ^{228}Th for labelling solid samples, as ^{228}Th serves as the permanent source (the half life = = 1.9 y) of ^{220}Rn (the half life = 55 s).

The inert gas parent nuclides can be introduced into solids by coprecipitation during the sample preparation or by adsorption on the sample surface. In the latter case the inert gas atoms are incorporated into the surface layers of several tens of nanometers, due to the recoil energy (85 keV/atom) which every ^{220}Rn atom gains in the moment of its formation by the ^{224}Ra decay.

Trapping and mobility of inert gases in solids.

The inert gas atoms incorporated into solids are situated on the structure defects, such as vacancies, vacancy clusters, dislocations, grain boundaries and pores. The mobility of the inert gases in solids is strongly dependent on the structure and its changes. An important role in the gas migration is played by impurities of various kinds and by natural and artificially induced defects. The defects of the solid can serve both as traps and as diffusion paths for the inert gas.

In cases whereinert gas atoms were incorporated directly into solids the diffusion controls the inert gas release. When the inert gas atoms are formed by the decay of the parent nuclides within the solids, the recoil mechanism of the inert gas release should be taken into account in addition to the diffusion. The recoil plays an especially important role at temperatures where the inert gas diffusion in the solid is negligible and with solids of large surface area.

Theoretical concepts given by Kříž and Balek [3,4] , Beckman and Shviryaev [5] and other authors [6] can be used for evaluating diffusion parameters of inert gas migration in solids from the experimental data.

In the case of direct inert gas labelling an asymmetric peak-like curve is obtained for the temperature dependence of the inert gas release rate during the sample heating at a constant rate. Supposing the single jump diffusion mechanism the peak temperature T_{max} increases with the activation energy Q of the inert gas diffusion and with the heating rate. In the case of sample labelling by the inert gas parent as a relatively stable inert gas source, an S-like curve is obtained for the temperature dependence of the inert gas release rate, the exponential part of the curve depending on the activation energy Q of the inert gas diffusion [2] .

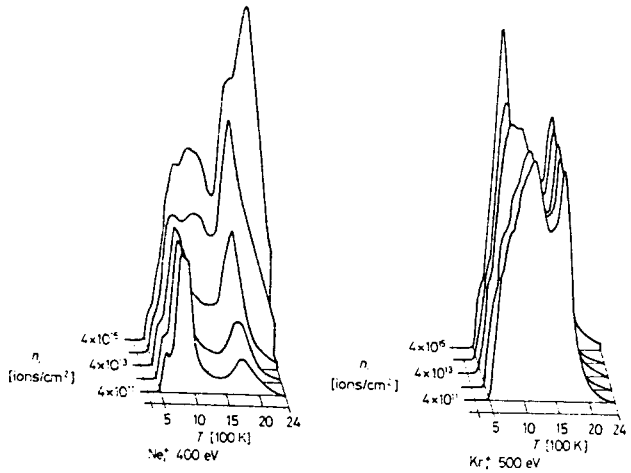

Fig. 1 Temperature dependence of the neon and krypton release rate from polycrystalline tungsten labelled by ion bombardment at various ion doses. Heating rate 10 K min^{-1}.

POTENTIAL OF DIFFUSION STRUCTURAL ANALYSIS IN DIAGNOSTICS OF INORGANIC MATERIALS

Defectoscopy of crystalline and non-crystalline solids:
defect state estimation in ionic crystals as well as of the non-crystalline solids, i.e. gel-like, glassy and other materials
defect concentration changes in the bulk structure and in the solids surface
thermal annealing of the structure defects, surface smoothening
crystallization of glasses and gel-like materials
study of structure defect creation by mechanical treatment, irradiation, etc.

Assessment of the sinterability and reactivity of solids:
influence of thermal, chemical and mechanical history
effect of the presence of impurities and admixtures, etc.

Determination of the temperature intervals of surface changes, phase changes and chemical transformations, accompanied by the changes of defect concentration in the bulk and in the surface.

Investigation of the interaction of solids with gases, liquids and solids: the differences in reaction mechanisms and kinetics can be revealed by a suitable choice of sample labelling technique.

EXAMPLES OF DIFFUSION STRUCTURAL ANALYSIS APPLICATION

Mobility of inert gases in metals, ionic crystals and ceramics.

The influence of the ion energy and dose during ion bombardment inert gas release was studied during thermal treatment of polycrystalline tungsten [7] and is demonstrated in Fig. 1 for Ne and Kr.

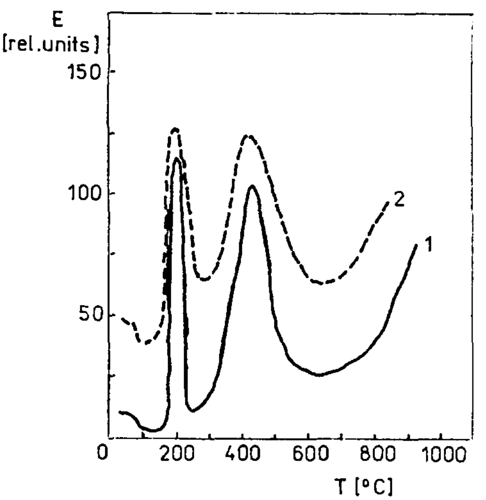

Fig. 2 Temperature dependence of helium release rate from BeO ceramics neutron irradiated by 6 • 10^{20} n/cm^2- curve 1; and by 7 • 10^{20} n/cm^2- curve 2. Heating rate 4K min^{-1}.

The helium mobility in BeO is characterized in Fig. 2 by two peaks indicating two kinds of structure defects where He is trapped, those of the energies 23.2 kJ /mol and 116 kJ/mol. [8]

The temperature dependence of ion implanted ^{85}Kr release from KCl, KBr and KI is demonstrated in Fig. 3. The shift of the peak temperatures towards lower temperatures with increasing anion size was observed [9]. The peak temperatures correspond to the activation energy values 184, 160 and 147 kJ/mol, resp.

The annealing of the radiation damage in ion bombarded oxides - ferric oxide, alumina, zirconia, urania, etc. was studied by several authors using the inert gas probe [2,10].

The mobility differences of Ar, Kr and Xe in CsCl crystal during heating in the temperature range of the phase transition of NaCl lattice type to the CsCl lattice type revealed new information about this phase transition. In the low temperature range Ar, Kr, and Xe have practically the same mobility, but above 469 °C a tremendous separation of Ar, Kr, Xe takes place (Ar mobility being 200 times higher than Xe mobility) [11].

It was shown by several authors [11,12] that different crystal faces gave different release rates of inert gases. The crystal orientation effect is emphasized in the case of the ion bombardment and fission recoil techniques [12,13].

Characterization of non-crystalline solids and their changes.

The inert gas diffusion can be used for the assessment of the changes in non-crystalline solids, as glasses and gel-like materials. The glassy material of the composition 2 $PbO.SiO_2$ was characterized in this way during heating at the constant rate 5 K min^{-1}. The ground sample was labelled by radon parent nuclide ^{228}Th, using the impregnation technique. An enhanced radon release rate was observed above the glass transition temperature T_g = 340 °C. The DTA results determine the glass crystallization intervals, the radon release rate effects proved the differences of the character of crystallization processes in the temperature ranges 410 - 430 °C (formation of $[Si_2O_7]^{6-}$ and $[Si_4O_{12}]^{8-}$ ions), and 470 - 610 °C (transformation of tetrameric anions into polysilicate chains $[PbO]\,[SiO_3]^n$), resp. [14]. The DSA enabled us to characterize the kinetics of the structure changes during the crystallization of the glass in the above temperature intervals.

The Ge-Te-Se chalcogenide glasses of various composition were characterized [15,16] by means of diffusion structural analysis using ^{220}Rn incorporated by surface impregnation of ^{228}Th. The changes of the disorder degree of the glassy samples and the changes from glassy to crystalline stage were characterized. In the crystallization temperature range the enhanced radon release rate was observed. The decrease of the radon release rate was observed at the pre-melting temperatures, indicating the changes in the sample surface. The melting in the bulk is indicated by the increase of the radon release rate from the sample.

The Ge-Se-Te samples of various chemical compositions were studied by DSA, representing four types of materials of different thermal behaviour. This method enabled us to characterize the differences in the defect degree of the glassy samples prepared by cooling from the melt at different cooling rates. The differences in thermal behaviours of powdered and compact samples were evaluated by means of this method.

Gel-like materials. Voluminous precipitates and gel-like materials are characterized by high inert gas permeability. When the samples are labelled by ^{228}Th, the ^{220}Rn release rate can be used as the indicator of the morphology changes. In Fig. 4 the changes of radon release rate are compared with the sample size measurements of the UO_2 xerogel droplets prepared by the sol-gel technique. The DSA results are especially valuable in the temperature ranges where common thermoanalytical techniques do not indicate any changes of material, as e.g. in the temperature range 750 - - 1000 °C, where the recrystallization of UO_2 xerogel is demonstrated by DSA. By further heating above 1000 °C, when the shrinkage of the sample takes place, the radon release is at first enhanced (due to the radon thermal diffusion) and afterwards drops (when the densified structure hinders the radon release)[17].

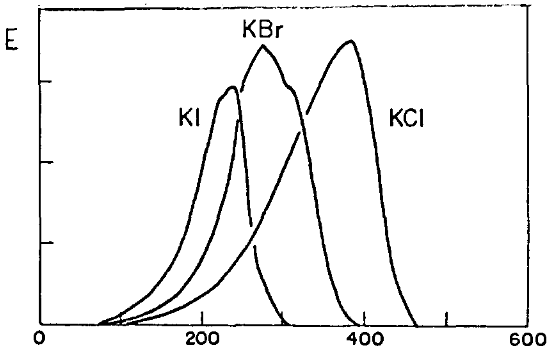

Fig. 3 Temperature dependence of Kr ion bombarded release rate from KCl, KBr and KI. Heating rate 10 K min^{-1}. ^{85}Kr ions energy: 10 keV/at.

Various UO_2 xerogels prepared under different conditions (gelation additives concentration, washing, drying, aging, etc.) were characterized by means of the DSA. The radon diffusion probe indicates sensitively the changes of xerogel morphology, enabling us to reveal even very fine changes which may be caused by varying technological conditions in the preparation of the intermediate products of UO_2 ceramics. Fig. 5 demonstrates the dif-

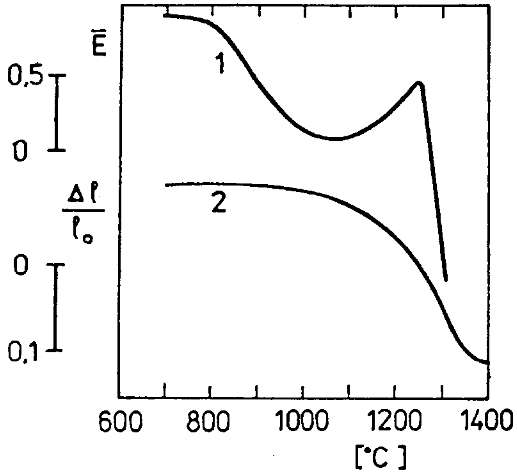

Fig. 4 Temperature dependence : of radon release rate (curve 1) and of the length changes (curve 2) of the UO_2 xerogel droplet during heating in argon + 5 % H_2 at the heating rate 5 K min^{-1}.

ferences in thermal behaviours of the fresh gel-like sample (curve 1) and of the water aged sample (curve 2) during heating in reducing atmosphere. The DSA was advantageously used in the study of thermal behaviours of other gel-like materials, such as silicagel, etc.

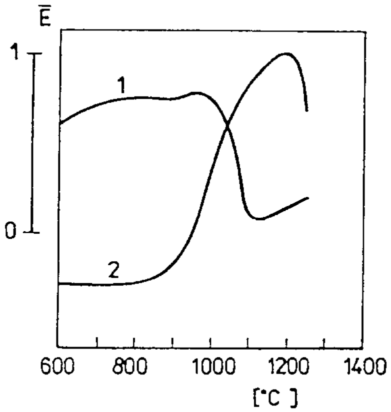

Fig. 5 Temperature dependences of the radon release rate of UO_2 gel-like samples obtained during heating in argon + 5 % H_2 at the heating rate 5 K min^{-1}. Curve 1 - freshly prepared gel; curve 2 - the sample after 30 days aging under wet conditions.

Checking processes taking place in preparation of advanced technology materials

The inert gas probe can be advantageously used for checking microstructure changes accompanying the advanced technology materials preparation processes. In the technology of ferrites the thermal behaviour of Fe_2O_3 feed component in the reaction mixture with ZnO was checked [18]. The differences in the activity and the microstructure changes were observed, caused by various activity of the mixture components. The recommendations for the technology optimization were given on the basis of these results.

For rutile pigments technology raw materials obtained by ilmenite hydrolysis are used. The minor impurities present in the feed hydrolyzate have to be washed out or suppressed by suitable admixtures aiming to produce a pigment of perfect quality . The diffusion structural analysis was used for the investigation of processes during heat treatment of the raw material (see Fig. 6). The DSA results enabled us to ascertain the microstructure changes taking place during heating of the differently treated samples (washing intended to remove the residual SO_4^{2-} ions and adding various cations). It is obvious that the diminution of SO_4 anion content leads to the decrease of the anatas recrystallization temperature from 600 to 400 °C the admixture of 0.5 % ZnO leads to enhanced rutile formation above 900 °C. [19]

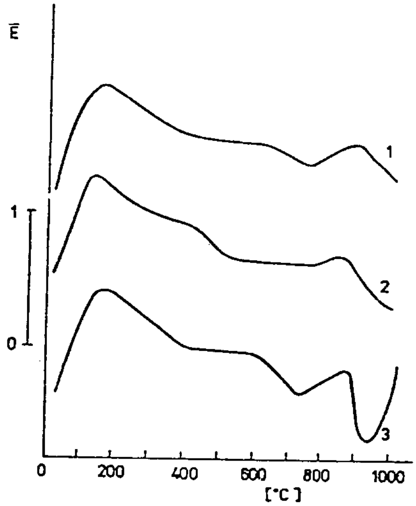

Fig. 6 The temperature dependence of radon release rate from ilmenite hydrolysis product used as feed material for rutile production.
curve 1 - hydrolysis product as received containing 0.3 % SO_4^{2-}
curve 2 - residual sulphate ion removed from sample 1 by ammonia
curve 3 - sample 1 containing 0.5 % ZnO admixture

The thermal decomposition of various iron salts (sulfate, Mohr's salt, oxalate, carbonate) in air was studied in order to check the process of hematite preparation used as pigment or as the feed material for ferrite production [20,21] .

Most recently, the DSA was used as a powerful tool for checking the preparation of Y-Ba-Cu-O ceramics with supperconducting properties [22] . The solid state reaction taking place in the synthesis of the ceramics of required properties is indicated by increased radon release rate. The microstructure changes taking place in these ceramics, being caused by oxygen desorption and adsorption and by O-T transition, are indicated by the changes of the radon release rate.

Quality testing of the intermediate products of advanced technology ceramics

The production of the advanced technology ceramics necessitates the quality control of the intermediate products. The DSA can be recommended as a method for this purpose as it reflects the microstructure of the materials which plays an important role in attaining the required properties. By means of the inert gas probe the sinterability and reactivity of ceramics powders such as Fe_2O_3, Al_2O_3, ZrO_2 etc. were evaluated [23].

The effect of the mechanical treatment (pressing, milling) on the sinterability of powders was determined by DSA [23]. The reactivity of Fe_2O_3 was tested directly in the reaction mixture used for the ferrite production. It was found that the surface area used so far as the parameter for reactivity testing is not sufficient to describe the reactivity of the materials at elevated temperatures. It does not reveal the presence of impurities and other defects which may play an important role in the reactivity of solids.

The defect state of solids can be characterized by the value of apparent activation energy Q of radon diffusion. Fig. 7 demonstrates the temperature dependence of radon release rate for ferric oxide samples prepared by thermal decomposition of various iron salts and heated to 1100 °C in air. The values Q of the apparent activation energy of radon diffusion were evaluated from the slope of the dependence log E_d vs. $1/T$ (see Fig. 7b) in the temperature range 600 - 800 °C where the radon diffusion in ferric oxide is controlled by the non-equilibrium structure defects.

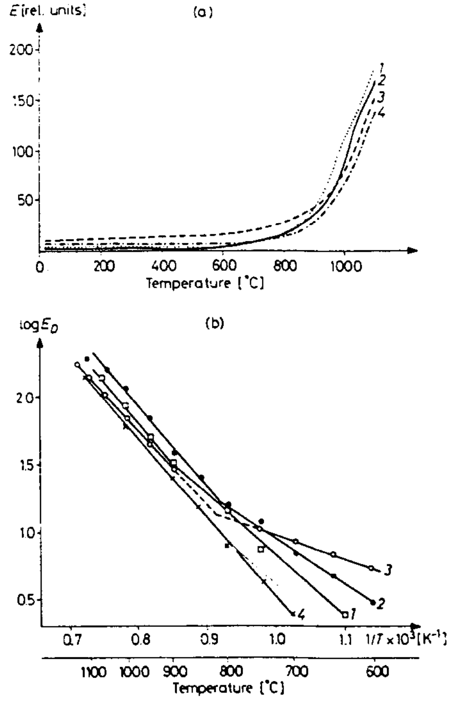

Fig. 7 Curves of iron(III) oxide prepared by heating various iron salts to 1100 °C: iron(II, III) carbonate (Curve 1); iron(II) sulphate (Curve 2) Mohr's salt (Curve 3) and ferrous(II) oxalate (Curve 4); (a) as dependence of E vs. T; (b) as dependence of log E_D vs. $1/T$

The values Q = 46, 80, 120 and 126 kJ/mol were obtained for ferric oxide samples from Mohr's salt, iron(II) sulphate, iron(II) carbonate and iron(II) oxalate, resp. The Q values enabled us to predict the reactivity of the ferric oxide samples. The smaller value of the activation energy of radon diffusion is, the higher reactivity can be expected . An excellent agreement of the reactivity tests was found [21] .

For rutile sample prepared by the calcination of ilmenite hydrolysates up to 1100 °C in air, the Q values were evaluated from the cooling curves. The Q values characterize the structure disorder of the rutile samples obtained by this technology. Following values were determined for non-washed feed hydrolysate Q = 172 kJ/mol, for ammonia washed feed hydrolysate Q = 306 kJ/mol, for hydrolysate with 0.5 % ZnO additive Q = 373 kJ/mol. The higher value of the activation energy Q of radon diffusion is, the more perfect structure of rutile can be expected. These conclusions are in good correlation with the technological tests [24] .

Endurance testing of inorganic materials.

An important task of the materials technology in the objective and rapid estimation of the thermal stability during oxidative heating and estimation of the materials endurance towards aggresive gaseous and liquid media.

We have used DSA for evaluation of the oxidation stability of BN samples. The oxidation of BN gives rise to B_2O_3 during heating above 800°C , the B_2O_3 melts , which is indicated by the decrease of the radon release rate above 850°C [25] .

The inert gas diffusion probe was successfully applied for indication of the chemical attack of aggressive gases (SO_2, HF) on the surface of stones, minerals, glasses, etc. The high sensitivity of this method makes it possible to reveal the very beginning of the SO_2 interaction with marble surface in humid atmosphere, the corrosion of concrete and of natural stone by liquid aggressive media [26,27] .

CONCLUSION

The family of methods used for the diagnostics of inorganic materials was enriched by the diffusion structural analysis. This method can find wide application in various fields of the materials technology and research, in the environmental science and technology and in other branches.

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