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Influence of heating temperature on structural properties of sol-gel materials

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In this paper, the influence of heating temperature on the properties of sol-gel materials was investigated . The aim of the study was to examine the production repeatability. All samples were made with factor $R = 15$, denoting the ratio of the number of precursor (TEOS) moles to solvent (water) moles. The samples were prepared in acid hydrolysis route on water, whereas two groups were considered: in one group the hydrolysis was terminated by addition of $NH_3 \cdot H_2O$ and in the other there was no addition of base. The samples were stored for 1 month at room temperature and then exposed to high temperatures: 1000, 1200 and 1350°C. They were examined by means of scanning electron microscopy (SEM). The electron microphotographs were recorded, digitized and analyzed. The Fisher linear discriminant analysis for evaluation of the microscopic images was exploited. It was shown that the repeatability varied between 83.24% and 95.48%. The analysis demonstrated that the best results were achieved for neutralized samples made at 1000°C.

Keywords: sol-gel, scanning electron microscopy (SEM), repeatability, Fisher linear discriminant analysis.

1. Introduction

The sol-gel process for production of inorganic or hybrid organic-inorganic amorphous materials made at ambient temperatures, relies on hydrolysis of the silica based precursors (*e.g.*, TEOS, $Si(OC_2H_5)_4$) mixed with alcohol or water and subsequent polycondensation to glass-like form. The technology allows organic or inorganic additives to be incorporated into the silica network at room temperature. Based on the sol-gel process a large number of sophisticated materials have been prepared and studied [1, 2].

Sol-gel materials are classified as porous materials. A porous material is simply some kind of solid material with holes, also called pores. Generally, porous materials

have the porosity of 0.2–0.95 [3]. The porosity means the fraction of pore volume to the total volume [4]. Porosity of silica based sol-gel materials depends on the factor R, defined as the ratio number of the of solvent moles number to the of precursor moles.

Many porous materials have been used for various applications [5, 6]. They are classified by many different criteria such as pore size, pore shape, material composition and production methods. Classification by pore size and by distribution of pores is useful while considering the applications of porous materials.

The pore size of porous material ranges widely from atomic size to the order of millimeter. Different pore sizes are required for different applications of porous materials. Most porous materials do not have uniform pores. Pore size distribution is also an important property. Narrow pore size distribution, *i.e.*, uniform pore size, is required, for instance, for filters and bioreactor beds. Methods of evaluating exact pore size are important for manufacturing and applying porous materials. There are many methods of evaluating pores size in porous materials. Mercury porosimetry and gas adsorption methods are commonly used to measure pores size and pore distribution. Also the microscopic images, both optical [7] as well as from electron microscope of porous materials can be analyzed in order to obtain information about the material structure.

Recently, ceramic materials are in the focus of attention as potential candidates for producing various coatings with tailored features, especially in the field of biomedicine. They can act as protective and simultaneously bioactive compounds used, for example, to enhance the performance of prostheses. The preparation in many cases requires that the layer should be dense and adherent, which can be obtained by exposing the materials to high temperatures [8].

The results obtained from material examinations should give better understanding of the correlation between material preparation process and microstructure. Recently, we have shown that statistical pattern recognition method may be used for evaluation of sol-gel materials reproducibility [9]. Furthermore, we proved that these materials may be produced with high repeatability rate. The examination was based on analysis of optical microscopic images of sol-gel matrices.

To examine the sol-gel material properties the scanning electron microscopy (SEM) is often used [10]. SEM can reveal the finest details of internal structure of sol-gels. The aim of our study was to check how the exposure to high temperatures influences the surface structure, especially whether is it possible to obtain materials with high degree of reproducibility.

2. Preparation of materials

The silica sol-gel materials for the present study were prepared by acid based hydrolysis from the silica precursor – TEOS (tetraethyl orthosilicate, 98% from Aldrich) mixed at room temperature with double distilled water with molar ratio $R = 15$. As a catalyst hydrochloride acid (HCl, 36% from Polish Chemicals) was used.

T a b l e 1. Silica sol-gel materials.

Sample groups (class)	Heating temperature	Factor *R*	Neutralization with NH_4OH	Solvent
1	1000°C (1273.15 K)			
2	1200°C (1473.15 K)	15	No	H_2O
3	1350°C (1623.15 K)			
4	1000°C (1273.15 K)			
5	1200°C (1473.15 K)	15	Yes	H_2O
6	1350°C (1623.15 K)			

The substrates were mixed for 4 hours by means of magnetic stirrer (speed 400 rot/min). The final pH of the liquid obtained was equal to 2. Cylindrical plastic containers were filled with 10 ml of sol. Half of the samples were neutralized with suitable amount of ammonia solution ($NH_3 \cdot H_2O$, 25% Polish Chemicals) and all of them were left at room temperature. All the samples were stored for one month, until they were solid and dry.

Next, the bulk samples were exposed to higher temperature in a special laboratory furnace. The temperature increase rate was 1°C/min (or 274.15 K/min, or 4.57 K/sec) up to the moment when desired temperature was reached. The samples were exposed to final temperature for 2 hours. The following cooling process was run at approximately the same rate of temperature decrease 1°C/min. The various maximal temperatures were chosen 1000, 1200, and 1350°C (1273.15, 1473.15 and 1623.15 K). Each group of samples was heated and cooled separately. A detailed description of materials prepared is presented in Tab. 1.

3. SEM examination

The optical microscopic methods can provide some information about the structure of the silica based materials obtained by sol-gel method [11, 12]. Electron microscopy is an important tool for performing microstructural analysis [13, 14]. For example, transmission electron microscopy (TEM) method allows the distribution and the size of the dopant particles to be determined [15], which can be the compared with the distributions of pores and silica network in sol-gel materials.

In the SEM technique an electron beam scattered and reflected from the sample forms an image of the material structure. The image, formed by the interaction of the electron beam with the structure, magnified and focused is observed on a fluorescent screen and can be captured by camera.

In recent years, digital image processing has evolved to the point where it is now possible to exploit more fully the high resolution potential of the SEM [16]. In this study, pictures were obtained using the digital scanning microscope DSM950 from LEO – Carl Zeiss Company.

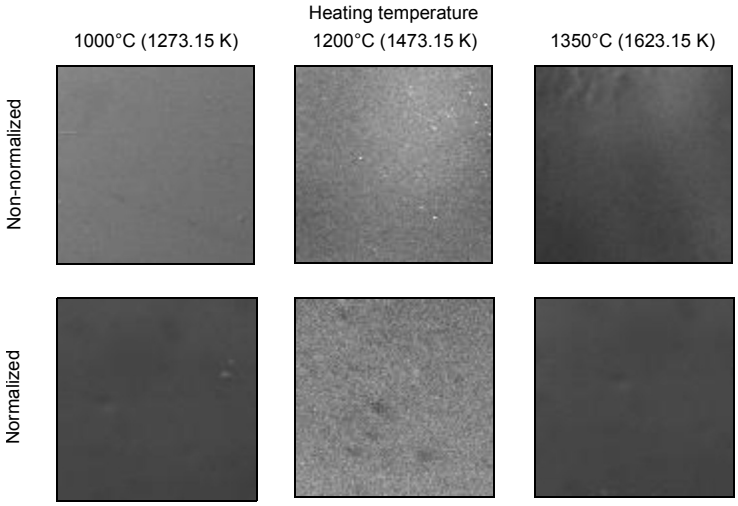

Figure. Examples of original SEM images.

The samples for SEM investigation were prepared by the following method: the sol-gel material was immobilized on carbon material and then placed on microscopic supports. In order to visualize the structure of materials all samples for the SEM were covered by a suitably thick layer of gold. The supporting metal plate served as a holder in SEM equipment. Some examples of SEM images are presented in the Figure.

4. Image analysis

The microphotographs obtained during SEM investigation were analyzed by use of statistical pattern recognition method, namely by Fisher linear discriminant analysis (FLDA) (also called Fisher's mapping). The FLDA is frequently used in statistical signal detection, estimation theory and pattern recognition for extraction of most expressive features and dimensionality reduction of the data [17, 18].

In the experiment, all the materials under examination were divided into six classes, depending on heating temperature and kind of hydrolysis (with or without addition of $NH_3 \cdot H_2O$, as is shown in Tab. 1). The data set comprised 180 images of sol-gel samples, 30 for each kind of material. In the first step, the learning and test database were prepared. The learning base included 60 randomly selected images (10 for each sol-gel material) and test database contained 120 remaining images (20 for each material).

Then, the Fisher linear discriminant analysis (FLDA) was applied. The FLDA uses the Fisher criterion as a general separability measure. First, the within-class scatter and the between-class scatter matrices were calculated. Based on those matrices the separation matrix was obtained. The first few eigenvectors of separation matrix,

associated with the largest eigenvalues, for the maximization of Fisher criterion were taken. The new data base was generated. This base spanned a lower dimensional subspace than the original one and simultaneously had most specific features for each analyzed matrices.

Next, the classification based on 1-NN method (nearest neighbour) was performed. As a distance measure between objects in the reduced subspace, the Standardized Euclidean metric was used.

The above procedure, including selection of new databases , was repeated 50 times. Finally, the average correct classification rates, standard deviations, upper and lower limits for confidence level 0.99 were estimated.

5. Results

In the examinations described here, the correct classification rate (CCR) was taken as a measure of heating temperature influence on the structural properties of sol-gel materials. The CCR coefficient is defined as the percentage of well classified objects and can also be treated as a degree of material repeatability. This corresponds to the material properties pointing out the degree of intraclass similarity between the samples examined.

In both analyzed cases, with and without addition of $NH_3 \cdot H_2O$, we found to be highly similar the sol-gel matrices produced. Generally, the samples which were not neutralized, had slightly better homogeneity. The mean CCR in this case reached 90.78% (see Tab. 2).

The detailed data for neutralized sol-gel samples are shown in Tab. 3. The mean CCR value in this case is 89.15%.

We noticed that there are differences in materials, depending on the applied heating temperature. The best results, independent of the neutralization, were observed for

T a b l e. 2. Results of analysis for the non-neutralized materials (confidence interval $P = 0.99$).

Heating temperature	CCR [%]	Std. dev.	CCR (lower limit) [%]	CCR (upper limit) [%]
1000°C (1273.15 K)	95.48	1.06	92.75	98.21
1200°C (1473.15 K)	83.24	1.32	79.84	86.64
1350°C (1623.15 K)	88.73	1.58	84.66	92.80
Mean CCR [%]	90.78			

Table 3. Results of analysis for the neutralized samples (confidence interval $P = 0.99$).

Heating temperature	CCR [%]	Std. dev.	CCR (lower limit) [%]	CCR (upper limit) [%]
1000°C (1273.15 K)	93.14	0.95	90.69	95.59
1200°C (1473.15 K)	87.82	1.05	85.12	90.52
1350°C (1623.15 K)	91.37	1.37	87.84	94.90
Mean CCR [%]	89.15			

the samples heated at a temperature of 1000°C (1273.15 K) and the worst for 1200°C (1473.15 K).

6. Conclusions

The heating temperature influences structural properties of sol-gels. In our examination, the highest repeatability was found for the samples heated at 1000°C (1273.15 K). The acceleration of condensation by addition of base slightly decreases the reproducibility of sol-gel materials. It was shown that generally the repeatability varied between 83.24 and 95.48%. The performed analysis demonstrated that the best results were obtained for neutralized samples made at 1000°C (1273.15 K). When considering the production of adherent dense samples we can state that it is possible to produce heated materials with high degree of repeatability.

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