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The influence of the pyrolysis process on mechanical parameters and tightness of the black glasses layers on titanium substrates

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ABSTRACT

Black glasses are amorphous materials in which structure Si–O bonds coexist with Si–C bonds. The substitution of divalent oxygen ions by tetravalent carbon ions causes the change of properties, especially mechanical ones. The materials were obtained from the sol-gel synthesized ladder-like polysilsesquioxane organosilicon precursors. After deposition on titanium substrates and ceramization, continuous and hermetic layers were obtained. Adhesion, Young's modulus, hardness, roughness and corrosion resistance were examined as the most relevant mechanical properties of the obtained layers. Nanoindentation, surface mapping, electrochemical, SEM and confocal microscope measurements results are discussed in relation to the pyrolysis temperature of the black glasses layers.

1. Introduction

Mechanical properties of a silica glass (v-SiO_2) can be substantially improved by appropriate cationic and/or anionic substitutions. Partial substitution of divalent oxygen ions by tetravalent carbon ions leads to the obtainment of the so-called black glasses (SiOC - silicon oxycarbide). Black glasses are materials of amorphous silica structure in which two O^{2-} anions are substituted by one C^{4-} anion. Such anionic substitution causes the local increase in the bonds density and, consequently, leads to a significant glass network strengthening. This results in the sharp increase in the mechanical properties of the glass. Silicon ions tetrahedrally bonded with both carbon and oxygen ions are characteristic structural units of black glasses. The ideal structure of black glasses contains only Si–O and Si–C bonds without Si–Si, C–O and C–C bonds. It is expected that mechanical properties of the glass will be improved as the amount of carbon incorporated into the glass structure increases. The literature data show that black glasses with an overall amount of carbon ions reaching 45% can be prepared with the use of appropriate precursors [1]. Therefore, such glasses almost always contain also the so-called free carbon (phase separation). This free carbon is responsible for the color and, hence, the name - black glasses [2,3]. The amount of free carbon and the amount of carbon bonded in the black glasses structure depend mainly on the type of the used precursors.

The first attempts to introduce carbon into the silica glass structure were done by classical melting of dry raw mix e.g. [4–6]. However, obtaining black glasses in this way is very difficult (or impossible) due to the loss of carbon (oxidation) and the decomposition of the material to crystalline SiC and SiO_2. For the black glasses preparation many methods have been proposed: pyrolysis of organosilicon resins or sol-gel structures e.g. [7–13], chemical vapor deposition (CVD) e.g. [14], sputter deposition e.g. [15], oxidation of silicon carbide e.g. [16,17] and even mechanical alloying e.g. [18]. A review of the literature as well as our experience shows that, the simplest and most effective way to obtain black glasses is to use the sol-gel method with appropriate polymeric precursors containing Si–C bonds. These bonds are characterized by high durability and are retained in both the xerogel and the glass obtained after drying and pyrolysis.

Unique mechanical properties of black glasses arouse growing interest of the industry. The literature proposes the use of black glass in many areas of technology, often very distant from each other. They have been proposed for a variety of applications, such as high-temperature structural application materials, and protective coatings [7,19,20]. This is possible due to the control of their properties in a very wide limit by changing the structure of the network and the amount of free carbon.

In our opinion, currently the main problem in the preparation of black glasses with pre-planned mechanical properties is the lack of control over the amount of carbon introduced in the silica structure, resulting in obtaining the materials with uncontrolled quantities of free

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carbon. In some of our earlier works, we showed that the control over the amount of introduced carbon (and at the same time the amount of free carbon) can be provided by using as precursors the well-defined polysilsesquioxanes with ladder-like structure obtained via the sol-gel process [21]. Besides the type of the used precursors, the temperature of the ceramization process has a crucial impact on the structure and microstructure (and thus mechanical properties) of the obtained glasses.

The main objective of this work was to determine the influence of the pyrolysis temperature on mechanical properties and tightness of the black glasses layers on titanium substrates.

2. Material and methods

Based on our previous experience in the preparation of the black glasses layers we concluded that ladder-like silsesquioxanes are the best precursors for their obtainment. Ladder-like silsesquioxanes were synthesized by the hydrolytic polycondensation of methyltriethoxysilane (the so-called T units) and dimethyldiethoxysilane (D units) in the 2:1 ratio [22].

Compounds were mixed in ethanol as the solvent. To initiate reactions of hydrolysis and polycondensation, water pH 4 set by hydrochloric acid was added dropwise. Sol was homogenized for 120 min at ambient temperature. Properly prepared titanium surfaces [23] were coated by the obtained sol using the dip-coating method. Titanium samples were immersed in the sol, maintained per particular time and resurfaced with the precisely defined velocity. The procedure was established to samples speed 20 cm/min and 3 repetitions. Also, reference xerogels were prepared by pouring the sol on Petri dishes. It was essential for the process to perform pyrolysis to transform preceramic polymeric precursors into the ceramic material. The protective atmosphere of the inert gas was needed to avoid oxidation and the carbon ions loss from the structure of black glasses [2]. After 7-day long aging, layers and xerogels underwent high-temperature heat treatment in the atmosphere of argon at temperatures selected based on thermogravimetric analysis.

X-ray diffractograms were obtained with the use of X'Pert Pro Philips (PANalytical) using CuKα1 radiation in Bragg-Brentano geometry with step of 0.008°, Θ-2Θ setup and 5–90° 2Θ range with the use of classic DSH (xerogels) method and GID (Grazing Incident X-ray Diffractometry) - layers.

Thermogravimetric analysis was performed with the use of NETZSCH STA 449 F3 thermal analyzer at a rate of 5 °C/minute up to 1200 °C in the atmosphere of inert gas (argon).

Scanning Electron Microscopy (SEM) of the obtained layers was performed by NOVA NANO SEM 200 (FEI EUROPE COMPANY) apparatus. The samples were not sputtered with any conductive layer.

Surface state examination was performed with the use of Laser Confocal Microscope OLYMPUS LEXT 4000 and the magnification 50x. The scanned area was of approximately 4.68 mm^2. To establish the surface roughness of black glasses on titanium substrates the Ra parameter was calculated from 10 linear measurements on the surface of each sample (5 linear measurements perpendicular to each other). Subsequently, mean values with the confidence intervals were calculated. Two- and three-dimensional (2D and 3D) images were taken.

Nanomechanical properties, such as Young's modulus and hardness, were measured using nanoindentation technique. NanoTest Vantage® (platform 3) system provided by MicroMaterials Laboratory MML were used. Berkovich-shaped, diamond indenter was used for all nanomechanical investigations. Each experiment has been repeated at least 8 times (except surface mapping test). Before the experiment, equipment was calibrated and Diamond Area Function (DAF) of the indenter tip was determined. This procedure was done by performing a series of indentations carried out with different loads on Fused Silica (standard material). Calculated for each load, DAF's were used at every stage of result analysis. In this research, the indents were made by using 10 and 5 mN loads in two types of experiments.

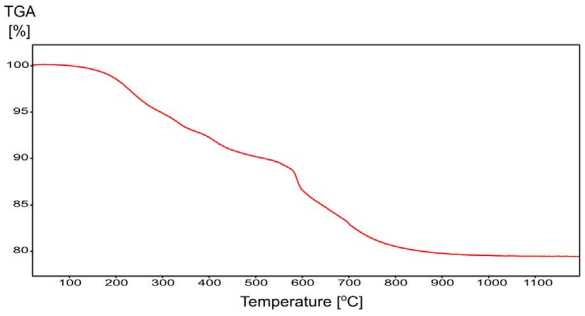

Fig. 1. Thermogravimetric curve of the 2/1 xerogel.

In the first case, dedicated to global mechanical response of the sample measurements were performed by using Load Partial Unload (LPU) test mode. Conducting experiment in such a way provides insight into material mechanical properties as the depth function, which is particularly interesting for multiphase and multilayer materials and coatings [24]. It is also particularly convenient when one wants to judge surface quality of the sample and investigate impact of the ISE – Indentation Size Effect (explained in the next part).

In the second case, the mapping experiment was performed by forming 100 × 100 μm rectangular matrix (i.e. 100 measurement points) through indentations with 10 μm spacing. Depending on the experiment, the applied load corresponded to 50 – 450 nm indentation depth depending on the analyzed material. In order to eliminate creep of the sample, in each measurement, the maximum load was held constant for 2 s. Loading and unloading curves were recorded at 10 and 20 s, respectively. Afterwards, the load-unload curves were fitted by using the Oliver-Pharr method [25]. Finally, one should remember that nanoindentation test produces the Reduced Young's Modulus (E_r) values. Results presented in this work, concern Young's modulus (E) values and were obtained from the following eq.:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

where E_i and vi are the Young's modulus and the Poisson's ration of the indenter (E_i = 1140 GPa and vi = 0.07), respectively. According to the literature, the Poisson's ratio of Ti is 0.32 [26], and that of black glass is 0.11 [27]. These values were used in our calculations.

Nanomechanical parameters are obtained based on analysis of the portion of unloading curve. In our work, this is done by using Oliver-Pharr approach. It is known that other approaches, such as Doerner and Nix [28] or Field and Swain [29] exist. However, classical Oliver-Pharr is the most commonly used in the society. In addition, it is compliment with ISO 14577 standard. For this reason, this approach has been used to estimate nanomechanical properties of studied specimens.

The corrosion resistance of the specimens was evaluated by the use of electrochemical measurements. The experiments were realized using a potentiostat/galvanostat galvanostat (PARSTAT 4000, Ametek, USA) in a 250 mL corrosion cell fitted with three electrodes. The sample served as a working electrode, the auxiliary electrode was platinum mesh, while the reference electrode used throughout the measurements was the saturated calomel electrode (SCE). The corrosive environment of the human body was simulated by conducting measurements in the Ringer's solution (8.6 g dm^{-3} NaCl, 0.3 g dm^{-3} KCl and 0.48 g dm^{-3} $CaCl_2{\cdot}6H_2O$; Baxter, USA) at 37 °C. To determine the effect of surface modification of titanium on its corrosion resistance the following procedure was adopted: a) first the open-circuit potential (E_{OC}) of the untreated Ti sample (Reference) was measured for 3600 s; the measurement time was increased to 7200 s for the coated Ti specimens b) then a short-range polarization (± 0.025 V vs. E_{OC}, 0.1 mV s^{-1}) of the specimens was realized to find a linear region in the current