Crystallization of TiC and TiN from a colloidal system

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The sol-gel processing of materials offers several potential advantages over conventional methods. The most important are improved properties thanks to the specific microstructural features. The paper presents the synthesis of TiC and TiN powders and coatings by the sol-gel method. Parameters of the processes were found to influence the structures, chemical compositions and morphologies of TiC and TiN, which were examined using the following analytical techniques: SEM, TEM, XRD, EDX and WDS.

Key words: *titanium carbide; titanium nitride; sol-gel method; composites; coatings*

1. Introduction

The utilization of 'soft' chemical methods of activation of chemical reactions in liquids or in sol-gel precursors are modern directions of material engineering. These methods enable the design of materials starting from well-defined clusters or molecules to complex architectures of final products [1, 2]. Reactions proceed in such systems at lower temperatures in comparison to conventional methods (such as syntheses in gas phases or those based on solid-state reactions) and require lower energies.

Carbides, nitrides and carbonitrides are materials that have properties desirable for a variety of applications. Their key properties are high hardness and strength along with resistance to heat, corrosion and wear. A common feature of the methods already developed for the preparation of titanium carbide in the form of powders, fibres and coatings is the application of energy to activate the chemical processes. Thermal energy, low-temperature plasma and ionizing radiation are, for instance, utilized in the CVD, PACVD and PAPVD processes [3, 4].

The sol-gel based processes utilize chemical methods of activation yielding continuous forms of matter organization. Organotitanium compounds containing a carbon-titanium bonds are characterized by a low durability and an extreme sensitivity to

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the air and humidity [5–7]. Higher stability of the Ti–O–C bonds makes it easier to prepare, store and use such compounds than compounds containing only the Ti–C bonds. A higher affinity of titanium towards oxygen at temperatures below 1000 K prevents their conversion to titanium carbide and nitride. The conversion of titanium oxides or the systems with Ti–O–C bonds to carbide and titanium nitride proceeds under conditions of the carbothermal reduction at elevated temperatures [8]. Thin films of titanium carbide have been obtained by the polymerization process using transesterification of titanium tetraizopropylate with α,α′-diacetateorthoxylene, followed by thermal conversion of the polymer obtained [9]. With regard to the systems with Ti–O–C bonds, the conversion of these precursors to titanium carbide proceeds under conditions of the carbothermal reduction, i.e. above 1073 K. Similar compounds have been obtained as a result of the polymerization of titanium alcoholates with polyalcohols, hydroxylated polymers, resins and cellulose as well as with dicarboxylic acids [10–13].

In the present work, mixtures of polyacrylonitrile, dimethylformamide and titanium chlorides were used to form gels containing Ti–C bonds and being precursors for the synthesis of titanium carbide as well as titanium nitride. According to the hypothesis formulated in [14], the dispersed phase of the gel is formed by polymerizing polyacrylonitrile crosslinked with titanium chlorides, which initially form connections with the polymer chains as a result of intermolecular interactions and chemical bonds. Dimethylformamide acts as the dispersing agent in the system.

2. Experimental

The preparation of the organotitanium precursor was described in the previous papers [14, 15]. All the operations were carried out in a glove box in the protective atmosphere of argon using the Schlenk technique. The gel was applied onto substrates based on sintered aluminum oxide and on nitrided Armco iron surfaces. Before the coating, the substrates were polished and washed with an organic solvent. Armco iron samples were nitrided at 843 K in the ammonia atmosphere for 1h. The dissociation degree of ammonia was equal to 49%. The samples covered then with the gel and the gel samples were heated in a furnace in inert and/or reactive atmospheres depending on the desired products. The heating was carried out in gas atmospheres which contained argon and/or nitrogen, hydrogen and ammonia, under the atmospheric pressure at temperatures ranging from 293 to 1273 K. The reactions of TiC and TiN phases proceeded at temperatures lower than 800 K. The parameters of manufacturing of TiC and TiN with or without carbon as coatings and powders are subjected to the patenting procedure.

The following techniques were applied for the sample characterization: scanning electron microscopy (JEOL JSM 6100), X-ray diffraction (PHILIPS X'PERT), transmission electron microscopy and electron diffraction (JEOL JEM 1200EX). The TiC/C and TiN powders, Ti–C coatings, and the TiN/C pumice were additionally

characterized by the microanalysis (wavelength dispersive and energy dispersive spectroscopies) using an IBEX System Noran Instruments and an Oxford ISIS 300.

3. Results and discussion

Organotitanium compounds being the key precursors for obtaining the TiC and TiN materials have already been described in the literature, e.g. $Ti[N(C_2H_5)_2]_4$ [16, 17], $Ti(bipy)_3$ [5], $Ti[CH_2C(CH_3)_3]_4$ [6] and others. They all allow us to lower the temperature of the TiC and TiN syntheses in comparison to temperatures of conventional syntheses and also enable the achievement of unique microstructural properties. The compounds containing carbon-titanium bonds are characterized by a low durability and an extreme sensitivity to the air and humidity.
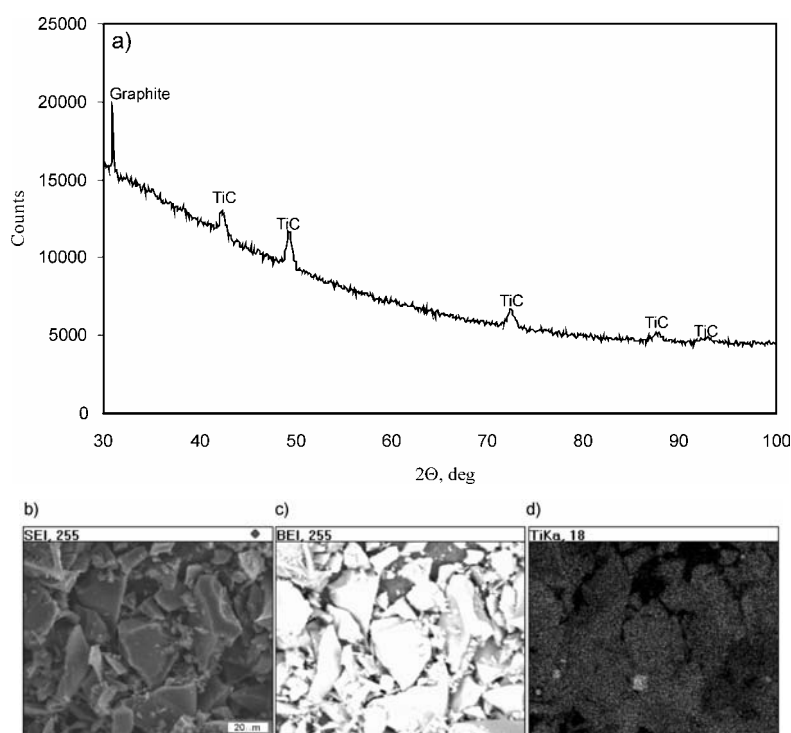

Fig. 1. X-Ray powder diagram (CoK_α) of the TiC/C powder (a),
SEI image (b), BEI image (c), and mapping of the Ti distribution in the powder (d)

Similarly to the above-mentioned organotitanium compounds, the gel precursors which were synthesized from mixtures of polyacrylonitrile, dimethylformamide and titanium chlorides contain the Ti–C bonds and allow to synthesize titanium carbide as well as titanium nitride at lower temperatures, i.e. below 800 K. The advantages of the gel precursors include their higher durability in the air as well as all the common benefits of the sol-gel method.

The X-Ray powder diagram and the SEM images of the TiC/C composite powder prepared by the sol-gel method are presented in Fig. 1. As can be clearly seen, the powder contains two crystalline phases: graphite and titanium carbide. The microscopic and microanalysis results suggest that TiC is homogeneously dispersed in a carbon matrix (Fig. 1b, c, d). The same results have been obtained for the TiN/C system (Fig. 2). Saturation of the solution influenced the rate of the nucleation of TiC and TiN (Fig. 3). The TEM investigations of the TiC and TiN particles showed that they were formed with the average grain size below 100 nm.
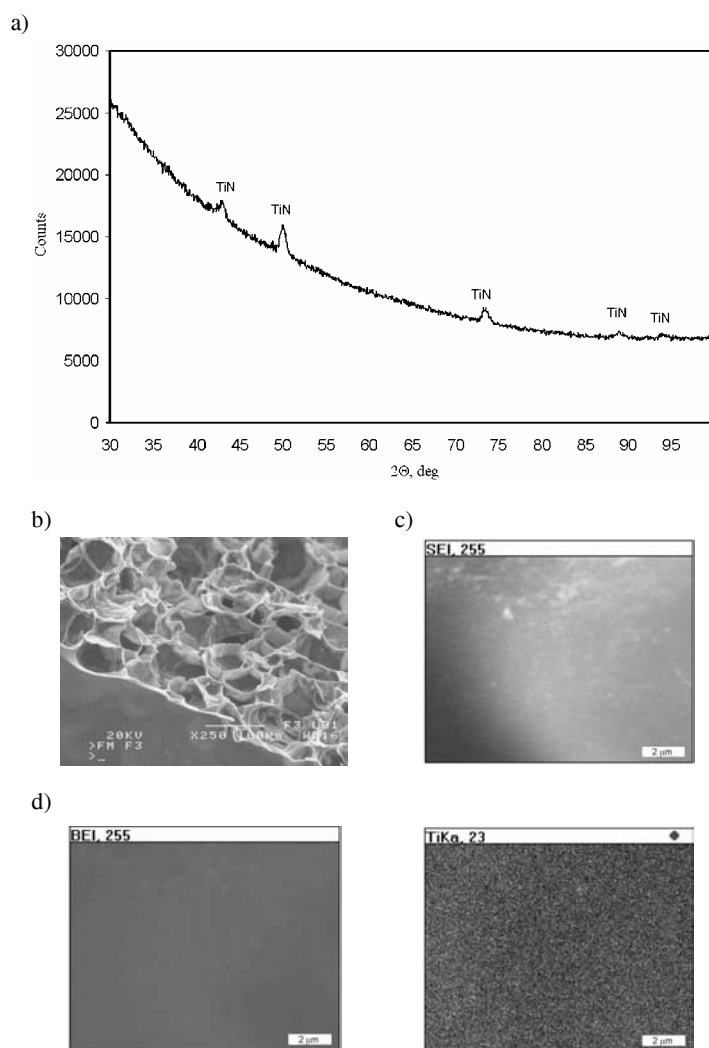
Fig. 2. X-Ray powder diagram (CoK_α) of the TiN\C pumice (a),
SEM image of TiN\C (×250) (b) and EDS images: SEI (c), BEI (d) and mapping
of the Ti distribution in the TiN-amorphous carbon pumice (×10 000)

Two competitive reactions ran during the syntheses of the Ti–C–N materials, i.e. the synthesis of titanium carbide or nitride and the formation of carbon, as becomes evident upon comparing Figs. 1 and 4. Figure 1 shows the X-Ray diagram of the crystalline TiC/graphite powder and Fig. 4 shows the crystalline TiC/amorphous carbon powder. They were obtained under various heating conditions. The conditions such as the temperature, time, heating rate and chemical composition of the gaseous atmosphere influence the form (powder or pumice) and the phase compositions of the products (Figs. 1, 2, 5).
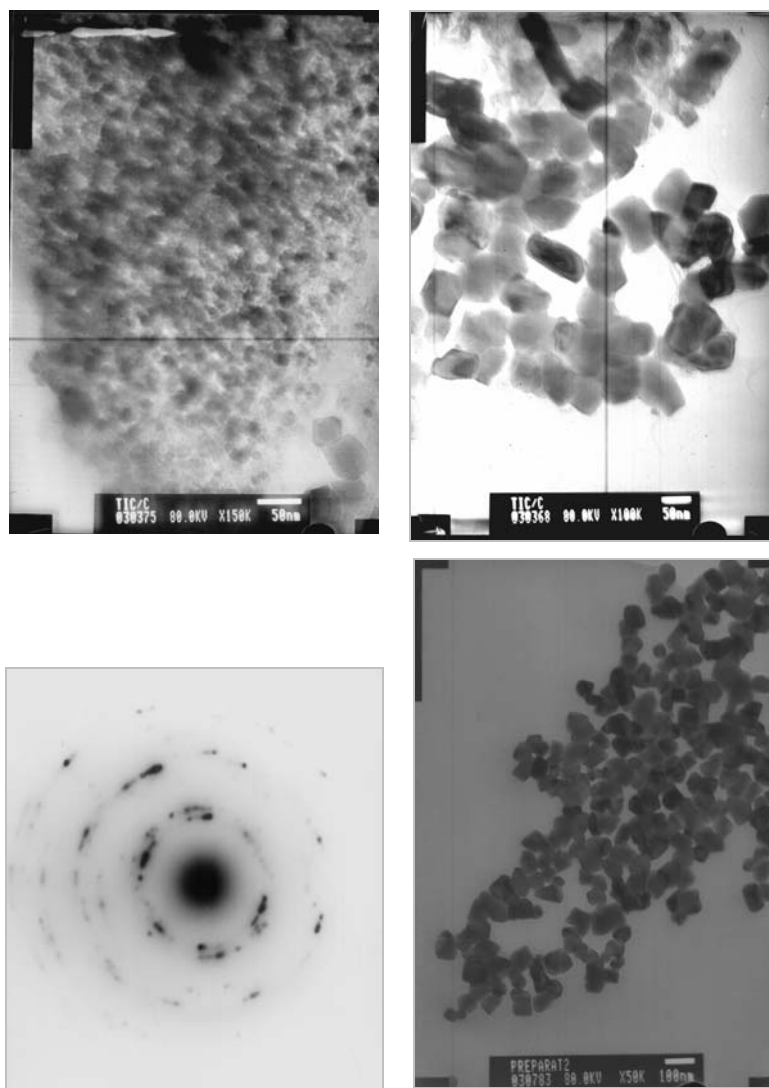
Fig. 3. Transmission electron micrographs and electron diffraction pattern
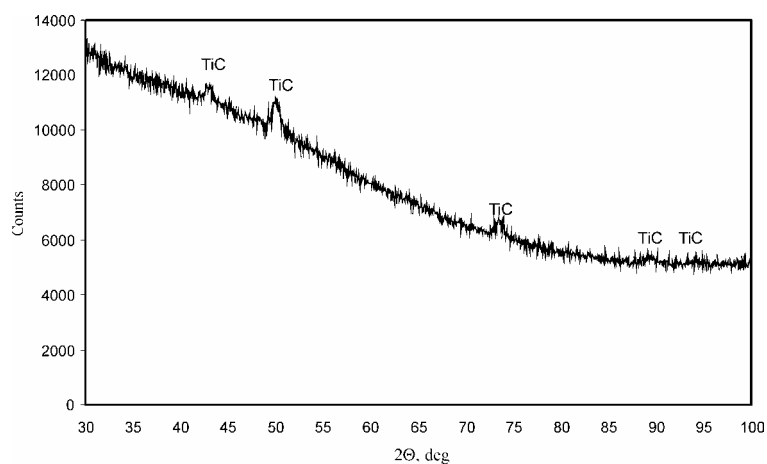of the nanocrystalline TiC particles obtained from differently saturated precursors

Fig. 4. X-Ray powder diagrams of the products obtained
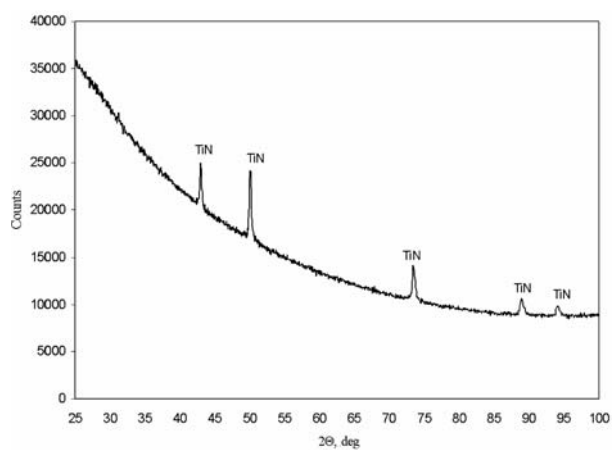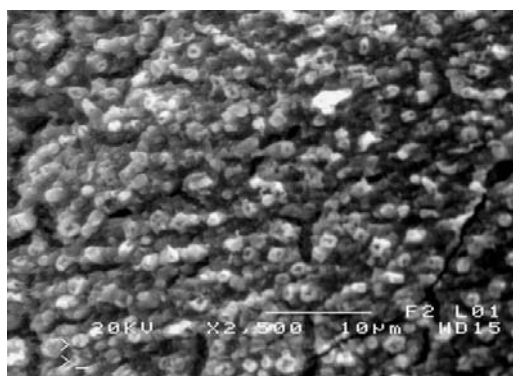during the synthesis of the TiC/C powders (CoK$_\alpha$)

Fig. 5. SEM image and X-Ray
powder diagram (CoK$_\alpha$) of the TiN powder
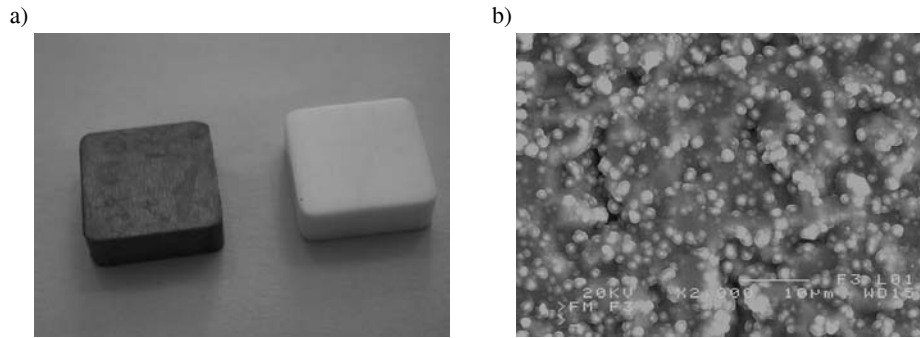
a)
b)

Fig. 6. Photographs of the cutting tools: a) sintered aluminium oxide with the Ti–C coatings,
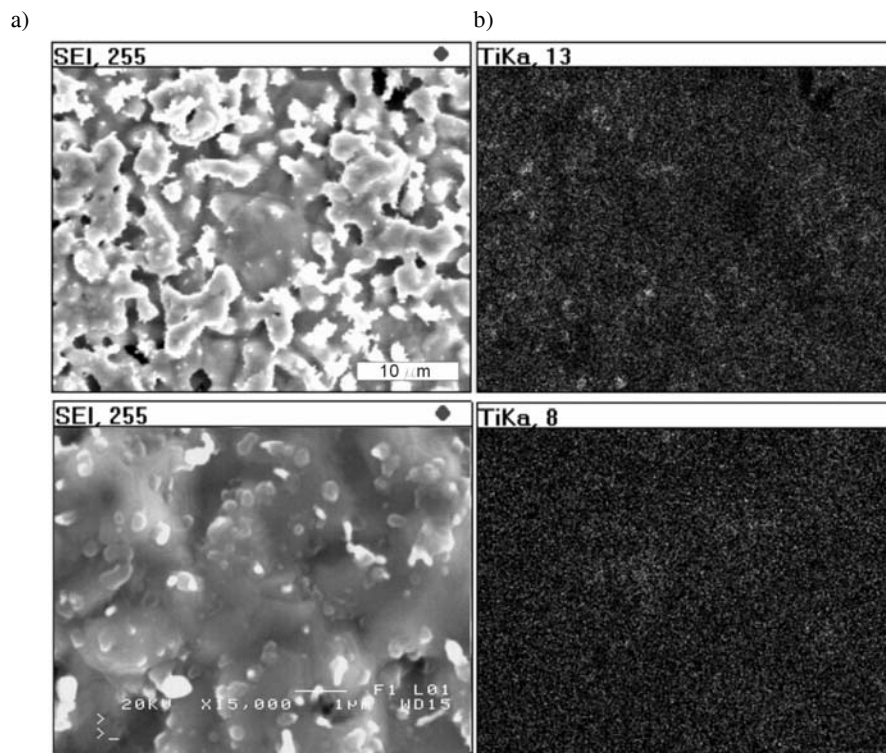and without the coating (white), b) SEM image of the surface of the Ti–C coating

a)
b)

Fig. 7. SEM images of the surface of the Ti–C coatings on nitrided
Armco iron surface (a) compared with mappings of the Ti distribution (b)

It has been observed that the substrate altered the conditions of the crystallization and the nucleation rates during the processes of coating production in which the gel precursor was used. The Ti–C coatings were deposited on the sintered aluminum oxide (Fig. 6) and nitrided Armco iron (Fig. 7a) substrates using the same parameters as those applied during of the process of the TiC/graphite composite synthesis. The

WDS chemical analysis indicated the ratio of C : Ti > 1. These coatings are amorphous, with titanium being homogenously dispersed in the carbon matrix as is illustrated in Fig. 7b.

4. Conclusions

The results of the investigations of the titanium carbide and nitride nanocomposites are presented. The materials were fabricated using organotitanium precursors. During the synthesis of Ti–C–N materials, two competitive reactions take place, i.e. the synthesis of titanium carbide or nitride and the formation of carbon. Saturation of the solution influences the size of the crystallites of TiC and TiN. The parameters of the TiC and TiN manufacturing with or without carbon as powders, pumice and coatings are subjected to patenting procedure. The sol-gel synthesis of the Ti–C–N materials may be an attractive starting point for low-temperature Ti–C–N coating technologies.

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