THE XRD STUDY OF THE NANOSTRUCTURED TiC/C AND TiN/C COMPOSITES

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Abstract. Nanocrystalline carbides, nitrides and carbonitrides are studied today with the aim to develop hard but non-brittle materials. Carbides and nitrides are materials that have desirable properties for a variety of applications. Their key properties are high hardness and strength along with resistance to heat, corrosion and wear. The nonhydrolytic sol-gel process has been employed successfully for the preparation of the nanocomposites TiC/C and TiN/C in powder form. The paper presents the results of characterization of nanostructured TiC/C and TiN/C composites elaborated by sol-gel method. The phase composition and TiC and TiN crystallite sizes and lattice parameters have been determined by X-ray diffraction (PHILIPS X'PERT). The TiC/C and TiN/C powders were additionally characterized by means of microanalysis (wavelength dispersive and energy dispersive spectroscopies) using IBEX System Noran Instruments and Oxford ISIS 300, scanning electron microscopy (JEOL JSM 6100).

1. INTRODUCTION

Nanomaterials are attractive for various applications because of their enhanced properties. The TiC and TiN particles have high hardness and strength along with resistance to heat, corrosion and wear. Additionally, they exhibit good electrical and thermal conductivity. However, widespread use of TiC and TiN has been limited due to their inherent brittleness and catastrophic failure mode at low temperature. One possibility to improve TiC and TiN mechanical properties might be the reduction of crystallite sizes down to the nanosized range. Nanostructured ceramics show several important mechanical modifications like superplasticity, increased strength, diffusivity, higher thermal expansion coefficient, lower thermal conductivity, reduced density, improved toughness etc. [1,2]. Sintering of nanoparticles indicated depressed sintering onset temperatures (0.2-0.3 Tm) as compared to conventional powders (0.5-0.8 Tm) [3].

The nanocrystalline TiC and TiN can be synthesized by several methods such as syntheses in gas phase and those based on carbothermal reduction in vapour – solid or vapour – liquid phases and sol-gel methods or by mechanical processing e.g. by mechanical milling and mechanochemical synthesis [4-11]. The nanostructures are produced by structural decomposition of coarse grained structures as a result of severe plastic deformations. The sol-gel processing of materials offers advantages over conventional methods. These advantages include energy efficiency owing to low synthesis temperature and simplicity of the equipment necessary to a production scale.

In the present paper, the results about nanostructured TiC and TiN obtained by sol-gel method have been outlined. The crystallite sizes and lattice con-

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stants vs. saturation of gel solution for TiC and heating conditions for TiN have been determined thanks to XRD method by measuring full width at half maximum (F.W.H.M.) and angular position of the TiC and TiN powder peaks.

2. EXPERIMENTAL PROCEDURES

Nonhydrolytic sol-gel process has been applied in order to obtain TiC and TiN nanocrystals [12]. In the present work mixtures of polyacrylonitryle, dimethylformamide and titanium chlorides were used to form gels containing the Ti – C bonds. The mixtures are also the precursors for synthesis of titanium carbide as well as titanium nitride. The dispersed phase of the gel is formed by polymerizing polyacrylonitryle cross linked 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. All the operations and gel precursor preparations were carried out in a glove box under protective atmosphere of argon using the Schlenk technique. 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 in the temperature range 293 to 1273K. The reactions of TiC and TiN phases proceeded at temperatures below 800K. The parameters of manufacturing TiC and TiN with or without carbon as coatings and powders are subjected to the patenting procedure.

The following techniques were applied for the samples characterization: scanning electron microscopy (JEOL JSM 6100), X-ray diffraction (PHILIPS X'PERT), transmission electron microscopy and electron diffraction (JEOL JEM 1200EX). The obtained TiC/C and TiN powders, Ti-C coatings, and TiN/C pumice were additionally characterized by the microanalysis (wavelength dispersive and energy dispersive spectroscopies) using IBEX System Noran Instruments and Oxford ISIS 300. The following parameters of XRD measurements were applied: cobalt X-ray tube, high voltage 40 000V and current 0.020 A. 0.05 degree step and 3 second counting time per step for the purposes of phase analysis were applied. For average crystallite size and lattice constant measurements the step of 0.02 degree in 2θ system and counting time 10 second per step were applied. Average crystallite size was measured according to the Sherrer formula [13]:

$$\overline{D} = \frac{k\lambda}{(B - b)\cos\theta},$$ (1)

where: k – shape factor, λ – wave length of the used X-ray, B – full width at half maximum of reflection (FWHM), b – full width at half maximum of reflection of coarse crystallite standard, D – average size of crystallites, θ – diffraction angle.

The shape factor 0.9 was assumed. The instrumental reflection broadening of TiC was determined by coarse grain standard, commercially available from Sigma-Aldrich Co. In the TiN case the instrumental reflection broadening was determined by coarse grain silver standard by interpolation for angular position of TiN reflection.

Both the TiC and TiN crystallise in face centred cubic system. Based on (220) reflection the lattice constant of TiC and TiN was measured. In order to measure the exact angular position of the reflection an addition of silver standard was introduced to the sample. It was assumed that the lattice parameter of silver standard is 0.40862 nm according to 04-0783 ICDD card (International Centre for Diffraction Data).

The Philips X'Pert HighScore v. 1.0 software was used to determine FWHM and angular positions of diffraction reflections.

3. RESULTS

Five samples of carbon composites containing nanocrystals of TiC or TiN nanocrystals were used in the investigations. X-ray powder diagrams of the investigated samples are shown in Figs. 1 and 2.

The samples marked as (1), (2) and (3) are the TiC/C nanocomposites which were obtained from precursors with a decreasing stoichiometric ratio Ti:C from (1) to (3) respectively. The determined lattice constants and crystallite sizes of the TiC crystals are shown in Table 1.

The samples of TiN/C, marked as (4) and (5), were obtained in different heating conditions using gel precursor with the same composition. The sample marked as (4) contains those TiN nanocrystals which nucleated and grew within carbon matrix. The fifth sample contains those TiN crystals which grew randomly without carbon matrix. The determined lattice constants and crystallite sizes of the TiN crystals are shown in Table 2. The lattice constant of TiC is 0.4327 nm according to 32-1383 ICDD card. Note that the lattice constant of coarse grain TiC sample is practically the same as obtain from the ICDD card. Therefore, low values of the
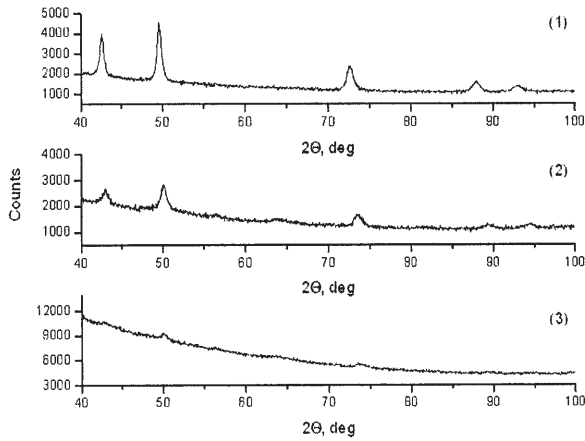
Fig. 1. XRD powder diagrams of the TiC/C composites vs. gel precursor saturation.
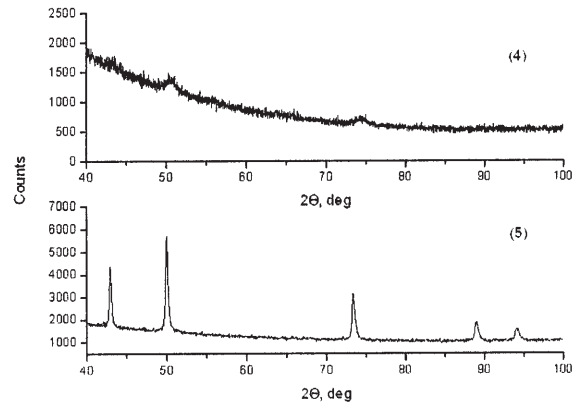

Fig. 2. XRD powder diagrams of the TiN/C composites vs. heating conditions.

Table 1. Crystallite size and lattice constants values of the TiC crystals.

TiC sample	(hkl) reflections	lattice constants,nm	Crystallite size, nm
(1)	(111)	0.4283	24
	(220)	0.4281	17
	(311)	0.4283	15
(2)	(111)	0.4239	13
	(220)	0.4224	12
	(311)	0.4221	12
(3)	(111)	0.4231	5
	(220)	0.4225	13
	(311)	0.4227	12

Table 2. Crystallite size and lattice constants values of the TiN crystals.

TiN sample	(hkl) reflections	lattice constants,nm	Crystallite size, nm
(4)	(111)	0,4206	10
	(220)	0,4191	8
	(311)	0,4186	7
(5)	(111)	0.42417	94.9
	(220)	0.42382	55.6
	(311)	0.42382	54.5

measured lattice constants of nanocrystalline materials can not be explained by an error in measurements. The lattice constant of TiN is 0.4242 nm according to 38-1420 ICDD card.

The saturation of gel solutions was found to influence the average grain size and lattice constant values. Both of them decrease along with a decrease of the gel precursor saturation. The comparison of the lattice parameters and grain sizes of the TiN crystals suggests that the presence of carbon matrix during crystallization process influences these values.

4. CONCLUSION

The TiC and TiN nanocrystals were obtained using the nonhydrolytic sol-gel method. The TiC crystals nucleated and grew within a carbon matrix. The growth of the largest crystals took place in the most saturated gel solution. The measured lattice parameters showed that a decrease of the grain size was accompanied by a decrease of the lattice constants. All the values of the determined lattices constants are smaller than those for the lattice constant of TiC standard according to the ICDD card.

Similarly, the lattice constants of the TiN crystals are smaller than the lattice constant of TiN according to the ICDD card. The lattice constant of the crystals which grew within the carbon matrix are smaller than those which grew randomly. The measured lattice parameters showed that a decrease of the grain size was accompanied by a decrease of the lattice constants.

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