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ELECTRICAL CONDUCTIVITY OF TiC AND (Ti,W)C CERAMIC SAMPLES

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Abstract. Three samples: titanium carbide TiC (sample I), titanium-tungsten carbide (Ti,W)C (sample II), and nanocrystalline TiC dispersed in a carbon matrix (sample III) have been selected for electrical conductivity measurements. The first two samples consisted of micron-size grains, while the third was a nanocrystalline TiC/C composite and was synthesized by a nonhydrolytic sol-gel process. All samples have been characterized by the X-ray diffraction (XRD), scanning microscopy, microanalysis (WDS and EDS), transmission electron microscopy (TEM) and electron diffraction techniques. For sample II the ratio of W:Ti atoms was equal to 0.3. The grain sizes in sample I and II were measured using the Fisher method and mean diameter of the grains was calculated to be below 10 μm. The TEM examination of the TiC particles in the sample III has showed that they were formed with an average crystalline size around 20 nm. XRD measurements of sample III have revealed that the lattice constant is smaller than observed for other titanium carbides TiC_x. dc electrical conductivity studies have been made in the 80-330K temperature range. Samples I and II have shown a metallic behavior but with different slopes of the conductance vs. temperature dependence. Sample III at higher temperatures displayed a pronounced thermal hysteresis in dc conductivity. ac conductivity measurements have not shown any frequency dependence in the 1 kHz –100 MHz range.

1. INTRODUCTION

Titanium materials, especially titanium carbides are one of the most studied groups of compounds, both experimentally and theoretically [1-6]. Titanium carbides, with their high hardness and strength, along with resistance to heat, a very high refractoriness (melting point >3300K), corrosion and wear resistance, are materials with a large variety of applications. A high degree of covalent bonding brought by carbon contributes to bond strength in this structure [7]. Their electrical and thermal conductivities are close to that observed for pure metals. The physicochemical properties of materials containing titanium carbides, especially electrical and thermal conductivities, depend strongly on the way of preparation, doping with other atoms (defects), or the size of particles taking part in their synthesis. Recently, nanocrystalline TiC/C composite was synthesized by the nonhydrolytic sol-gel process that could be an attractive starting point for low-temperature Ti-C coating technologies [8].

The aim of this report is to present the electrical conductivity properties of three carbide titanium compounds. Two examined samples were commercially available and the third sample was synthesized by a new method and consisted of nanoscale-size particles.

2. EXPERIMENTAL

The samples designated as I and II were commercially available, the first from Sigma-Aldrich Co., the second from Baldonit Company. Sample I is crys-

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talline titanium carbide TiC and sample II is titanium-tungsten carbide (Ti,W)C with the ratio of Ti:W=0.3. Preparation of the organotitanium precursor was described in the previous work [9]. Organotitanium compounds, gel precursors were synthesized from mixtures of polyacrylonitrile. Dimethylformamide and titanium chlorides contain the Ti-C bonds and that allows synthesis of titanium carbide at lower temperature, below 800K. The advantages of gel precursors include their higher durability in the air as well as all common benefits of the sol-gel method. Sample III was prepared by using the Schlenk technique in a glove box in a protective atmosphere of argon. The gel sample was heated in a furnace in inert and/or reactive atmospheres depending on the desired products. The reaction of TiC phase proceeded at temperatures lower than 800K. The parameters of TiC manufacturing with or without carbon as coatings and powders are subjected to a patenting procedure.

Phase composition of the samples was analysed using a PHILIPS X Pert XRD diffractometer. Scanning Electron Microscopy (SEM) pictures have been obtained by use of a JEOL JSM 6100 Scanning Electron Microscope. The TiC/C powder was additionally characterized by microanalysis (wavelength dispersive and energy dispersive spectroscopies) using an IBEX System Noran Instruments and an Oxford ISIS 300.

Direct current electrical resistivity measurements were made in the temperature range of 90-320K in small pellets (about 6 mm in diameter, with a thickness of 3-4 mm) prepared under pressure of 70-80 bar using a special dielectric glue at higher temperature. The resistance was measured with a Keithley 181 electrometer according to the two-point geometry, with the highest limit of $2 \cdot 10^{11}$ Ω under the circuitry of the experiment.

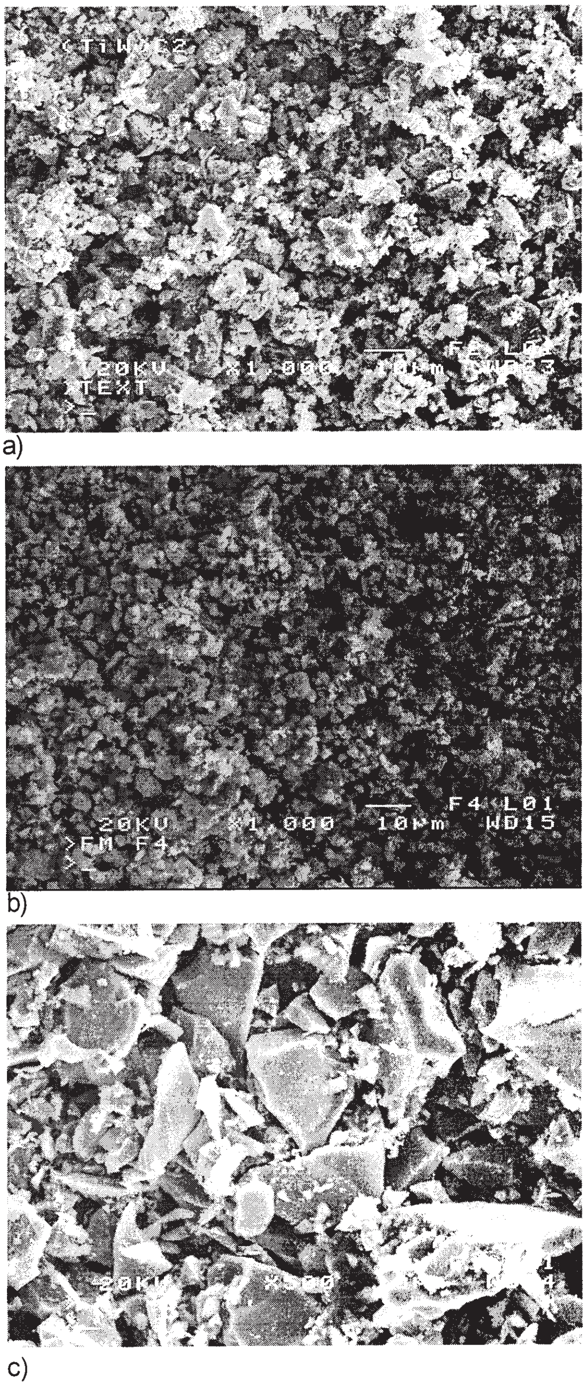

Fig. 1. SEM image for sample I, sample II and sample III.

3. RESULTS AND DISCUSSION

Fig. 1 presents SEM images of the three investigated samples. The SEM pictures obtained show that the sizes of agglomerates differ. It could be seen from Fig. 1a that in the sample I over 95% of contained agglomerates are below 10 μm. Sample II is formed by agglomerates of different sizes, much smaller than 10 μm and larger than 1 μm and almost all of them are dispersed homogeneously in the carbon matrix (Fig. 1b). Fig.1c shows the carbon crystallites in sample III which contained TiC nanoparticle aggregates. TEM investigation of the TiC particles in sample III showed that the nanoparticle aggregates were formed with an average size below 100 nm, dispersed homogeneously in the carbon matrix.

The XRD pattern of sample III is dominated by peaks originating from the titanium carbide crystalline phase (Fig. 2). The broadening of the peaks indicates that the sample is composed of nanocrystallites. Average particle size is near 15

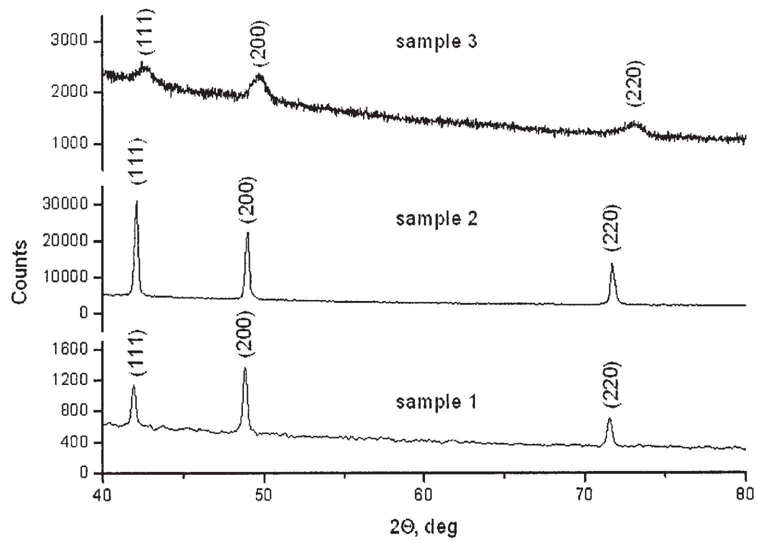

Fig. 2. XRD pattern of TiC (sample I), (Ti,W)C (sample II), and TiC nanocrystals (sample III).

nm, as was calculated by the Scherrer formula. The lattice constant for sample III is 0.423 nm, which is significantly lower than observed for the bulk material (0.43274 nm). A comprehensive structural analysis of the TiC/C powders will be presented in a separate work.

Fig. 3 presents one of the pellets used for the electrical measurements, produced by means of special dielectric glue, stable at higher temperatures, with very good isolating electrical properties. Preliminary measurements have been done to study the influence of the glue on the electrical properties of the sample but the influence was found to be very insignificant.

Fig. 4 gives the temperature dependence of the normalized electrical resistivity for the three samples at higher temperatures. The temperature dependence of electrical resistances shows a linear increase with increasing temperature for samples I and II (Fig. 4a). It suggests the metallic-type behaviour of conductivity. Recently, the temperature dependence of electrical resistances of the Ti-Fe system in the form of thin films displayed a similar behaviour in the high temperature region but with the increase rate two times smaller [2]. The temperature dependence of normalized electrical resistivity (ρ_n) for samples I and II could be well described by the following relation [3]:

$$\rho_n = \rho_{no} + A_n T^N, \qquad (1)$$

where N=1 for samples I and II. Fitting by the least square method gave the following values of ρ_{no} and A parameters: ρ_{no}=0.775(1), A_n=8.94(1)·10^{-4} for sample I, and ρ_{no}=0.892(1), A_n=3.4·10^{-4} for sample II. The results obtained suggest that doping the titanium carbide with tungsten can essentially change the conductivity properties of the sample. Modifications in the microstructure of Ti-W-C obviously can bring about strain effects into transport properties [2]. The random structure of scattering between conduction electrons and the structural disorder lead to a gradual localization of charge carries, hence raising the normalized electrical resistance ρ_{no} and decreasing A_n for sample II [10].

Fig. 4b presents the temperature dependence of electrical resistivity for sample III. The temperature behaviour is drastically different from that ob-

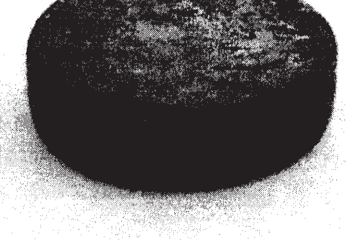

Fig. 3. The obtained pellet of sample III.

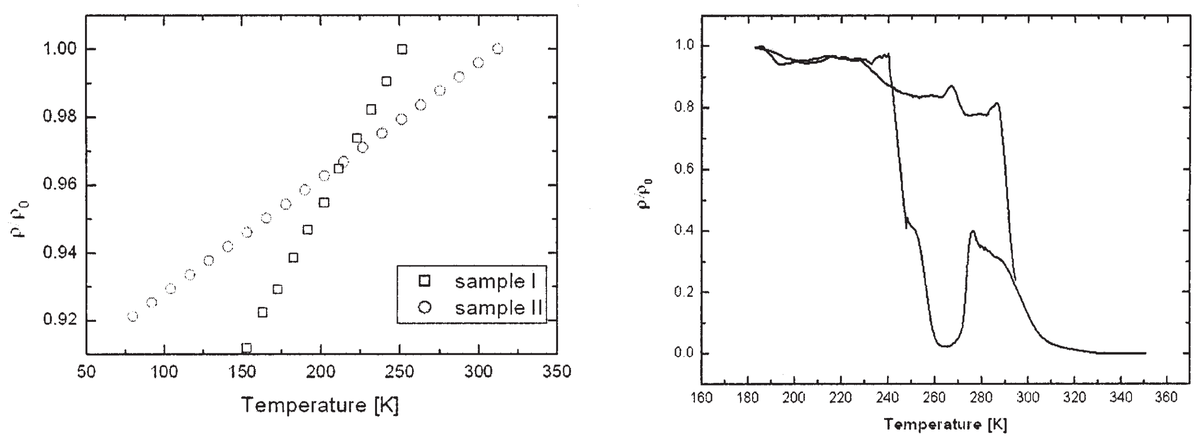

Fig. 4. Temperature dependence of the normalized electrical resistivity for sample I, ρ_0=1.90 Ω·cm (T=250K); sample II, ρ_0=1.34 Ω·cm (T=311K) (a), and sample III, $\rho_0=1.82\cdot 10^{11}$ Ω·cm (T=186K) (b).

served for samples I and II. The electrical resistance shows thermal hysteresis with a tendency to semiconductor (or semi-insulating)-to-metal transition. The hysteresis behaviour of the temperature dependence of conductivity has been previously observed in the Ti-O system [11,12]. The short Ti^{3+}-Ti^{3+} distances can coexist in a disordered phase in titanium oxide system where this disorder can be dynamic [12]. In nanoscale size the disorder phenomena strongly influence the conductivity properties of titanium carbide compounds.

4. CONCLUSIONS

Three different samples: titanium carbide TiC, titanium-tungsten carbide (Ti,W)C, and nanocrystalline TiC dispersed in a carbon matrix have been investigated to resolve their electrical conductivity properties. The first two samples contained grains of micro-scale sizes and the third sample was in the form of nanoparticles. The XRD measurements have shown significantly lower value of the lattice constant for nanoparticles of TiC as compared to bulk material, that suggests, that the disorder phenomena have a major influence on the structural properties of nanoscale titanium carbide. The characteristics of the temperature dependence of electrical resistivity were different for the three samples. Samples I and II showed metallic-type behaviour and the sample doped with tungsten had a lower electrical conductivity. Sample containing nanoscale size TiC grains drastically changed conductivity and structural properties during temperature variation, which could be an effect of the disordering phenomena in the trivalent titanium ions system.

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