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KINETICS OF THERMO HETEROGENEOUS PROCESS UNDER NON-ISOTHERMAL TERMS ON THE TITANIUM CARBIDE: A STUDY ON THE DIFFERENT IRRADIATION CONDITIONS

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Abstract. We have used confocal to study the defects introduced in the nanoparticle titanium carbide by different irradiation conditions. In the work used nano TiC powder with a purity of 99.9 %, bulk density of 0.16 g/cm^3 to 4.93 g/cm^3 (true density of 4.93 g/cm^3), specific surface area (SSA) of 35 m^2/g. The heat capacity value increases to 51.6 J/K×mol in titanium carbide nanoparticles subjected to 10^{15} n/cm^2 neutron flux and 500 kGy gamma irradiation. The non-irradiated sample is up to 58.6 J/K×mol, and it is equal to 60 J/K×mol for the sample exposed to 10^{15} n/cm^2 neutron flux.

Keywords: *Calorimetry, Thermodynamics, Heterogeneous process, Titanium carbide.*

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1. Introduction

Titanium and titanium ceramic-based materials are widely used in detectors, coatings, nuclear technology, solar energy, the production of optical materials and the application for ceramic armor (Agayev *et al.*, 2020; Alekperov *et al.*, 2019; Demir *et al.*, 2019, 2020). Firstly, titanium carbide is used as the many functional materials, such as the neutron absorber with large neutron cross-section of ^{10}B in a nuclear reactor, the anticorrosion and refractory material at high temperature with high hardness (Subramanian *et al.*, 2010). In addition, TiC and its composite have been expected as the

thermoelectric materials, which transform thermal energy directly to electrical energy at high temperatures (Gunjishima *et al.,* 2001; Arita *et al.,* 2000). Secondly, hexagonal titanium carbide a wide bandgap semiconductor known for its deep ultraviolet photonic application has emerged as an outstanding neutron detector material due to the fact that the isotope has a large capture cross section (3840 barn) for thermal neutrons (Maity *et al.,* 2018, Mirzayev *et al.,* 2020, 2021).

The fact that these materials are resistant to variable temperature ranges further increases the demand for them. High melting point, thermal diffusivity and thermal conductivity of sample at the 30-1000 °C temperature range were decreases from 0.065 cm^2/sec to 0.011 cm^2/sec, and from 0.30 W/cm·K to 0.05 W/cm·K, respectively (Mishra *et al.,* 2015). Other way round, the heat capacity increases from 2.1 J/g·°C to 2.7 J/g·°C at the temperature range 30-1000 °C in the titanium carbide. Thermal conductivity of titanium carbide of 29 W/m·K to 96 W/cm·K, respectively. The specific heat capacity various from 1.1 J/g·°C to 1.6 J/g·°C in titanium carbide at the 440 °C to 580 °C. The lattice parameters of hexagonal graphite-like titanium carbide have been measured in the temperature range from 300 to 1800 K up to 7 GPa using energy-dispersive powder diffraction of synchrotron radiation. From the obtained p-V-T relation for TiC, the temperature dependence of isothermal bulk modulus (B0[GPa] = 32.06(4) + 4.47(9)·e−(T[K] − 298)298) and pressure dependence of thermal expansion coefficient ($\beta \times 106$[K−] = 40.9(8) − 1.6(2)·p[GPa]) have been derived (Zhi *et al.,* 2011; Solozhenko *et al.,* 1997). In addition, the thermophysical properties of composite boron carbide (TiC-SiC) compounds are keeping as in free carbide (Perevislov *et al.,* 2020). Abenojar et al, were studied during the curing reaction the influence of TiC on the kinetic parameters and activation energy of TiC/epoxy sample (Abenojar *et al.,* 2014). The thermal conductivities of the SiC–TiC composites, on the other hand, showed a decreasing trend from that of the base-line specimen. The reduction of the thermal conductivity for the composites indicates that the presence of the SiC/TiC interface hinders efficient phonon transport. Typical electrical resistivity, thermal conductivity, flexural strength, fracture toughness, and hardness of the SiC-2 vol% TiC composites were 6.9×10^6 Ω cm, 99.7 W/m K, 554 MPa, 2.4 MPa m1/2, and 26 GPa, respectively (Kim *et al.,* 2015). In this research paper main aim, we study the thermodynamic properties of nano titanium carbide samples after degradation and amorphization mechanism under gamma and neutron irradiation.

2. Experimental methods

2.1. Materials and structural characterization

TiC nano powder with a purity of 99.9 %, bulk density of 0.16 g/cm^3 to 4.93 g/cm^3 (true density of 4.93 g/cm^3), specific surface area (SSA) of 35 m^2/g, Zeta potential 25 mV, chemical composition (free O< 0.9 %, Mg<3ppm, Al<60ppm, Cu<3ppm, Si<40ppm, Fe<35ppm and Ni<5.5ppm) (US Research Nanomaterials, Inc., TX, USA), respectively (Mirzayev *et al.,* 2019, 2020). The TiC belongs to the cubicspace groups (D_{3d}^5 - R$\bar{3}$m) with lattice constants are a = 0.519 nm, α = 66º18′ and hexagonal lattice constants are a = 0.560 nm and c = 1.212 nm, respectively (Clark *et al.,* 1943). R.S. Pease showed unit cell dimensions of hexagonal boron nitride sample space groups ($P6_3/mmc$) at the 35.3ºC of a = 2.5038 Å and c = 6.660 Å (Pease *et al.,* 1950). The lattice parameters and space groups of the titanium carbide are consistent with the references results (Mirzayev *et al.,* 2018, 2020).

2.2. Differential scanning calorimetric technique

The low temperature DSC measurements were carried out using the DSC3 STAR^e Systems manufactured by METTLER TOLEDO. The standard adiabatic calorimetry (no vacuum) was performed in the temperature range of 77 up to 300 K at a heating rate of 5 K/min in argon atmosphere at flow rate (20 ml/min and which was previously calibrated with indium) (Mirzayev *et al.,* 2018, 2019). High temperature DSC measurements were carried out using the standard adiabatic calorimetry STA 449 F3 Jupiter®, which was performed in the temperature range of 300–1400 K with a heating rate of 5 K/min in an argon atmosphere (Mirzayev *et al.,* 2022).

2.3. Irradiation techniques

The samples were enveloped with aluminium foil and then irradiated at different doses. Neutron irradiation was conducted at the IBR–2 high–flux pulsed reactor at Frank Laboratory of Neutron Physics (JINR, Dubna, Russia). The samples were irradiated at normal conditions 293.15 K and 1 atm at fluencie of 10^{15} n/cm² (neutron energy E > 0.1 MeV) (Mirzayev *et al.,* 2020; Darziyeva *et al.*, 2021; Neov *et al.,* 2022; Jabarov *et al.*, 2021). The γ dose rate was ~ 500 kGy which is about 85 % of the total dose.

3. Results and Discussion

The heat capacity of a sample is one of the most important thermophysical parameters and characterizing the material at the termodinamic profile. The complex heat capacity of the sample is divided into two real and imaginary main parts. In recent years the determination of the value of heat capacity (real and imaginary) for thermodynamic reversing and non-reversing processes has been widely studied by researchers (Simon *et al*., 2001; Reading *et al.,* 1994; Hemminger *et al.,* 2003; Clark *et al.,* 1943).

$$C_{p,reversing} = \frac{A_p}{mA_{\dot{T}}}$$

$$C_{p,\ non-reversing} = \frac{1}{m}\left(\frac{W}{\beta} - \frac{A_p}{A_{\dot{T}}}\right)$$

The A_p amplitude of heat flow calculated from temperature difference between of research sample and reference sample in the calorimetric spectra of DSC. The $A_{\dot{T}}$ calculated to the temperature profile of the heat flow rate curve and calculated from sinusoidal or sawtooth temperature profile (Simon *et al*., 2001). The sinusoidal profile may be calculated from equation $T = T_0 + \beta t + \sin(\omega t)$, β: heating rate, T and T_0 initial and after temperatures of the sample in time t and t = 0. The weight of sample measurements was made using a digital balance (M/s Sartorius, model BP221S, USA) and accuracy in the measurement of weight was ±0.00001 mg.

In addition, it is possible to switch to thermodynamic functions with a specified heat capacity. With the given values of temperature-dependent functions for thermophysical properties, it is possible to determine the heat flow, calibration factor and heat capacity. Figure 1 shows the temperature dependence of the specific heat capacity under the influence of neutron and gamma radiation in the temperature range of 77≤T≤2000 K in the sample of nano titanium carbide. It is known that the temperature dependence of the heat capacity characterizes the temperature dependence kinetics of the heat flow. It is clear from the dependence of heat capacity on temperature that the temperature range of 0-674 K K can be called the "quantum region of heat capacity" in

the non-irradiated, 10^{15} n/cm^2 neutron flux and 500 kGy gamma radiation sample. At this time, the heat capacity value increases to 46.5 J/K×mol in the specified interval. However, the heat capacity value increases to 51.6 J/K×mol in titanium carbide nanoparticles subjected to 10^{15} n/cm^2 neutron flux and 500 kGy gamma irradiation. However, starting from the temperature of 674 K, the heat capacity for the non-irradiated sample is up to 58.6 J/K×mol, and it is equal to 60 J/K×mol for the sample exposed to 10^{15} n/cm^2 neutron flux and 500 kGy gamma radiation at different intervals.

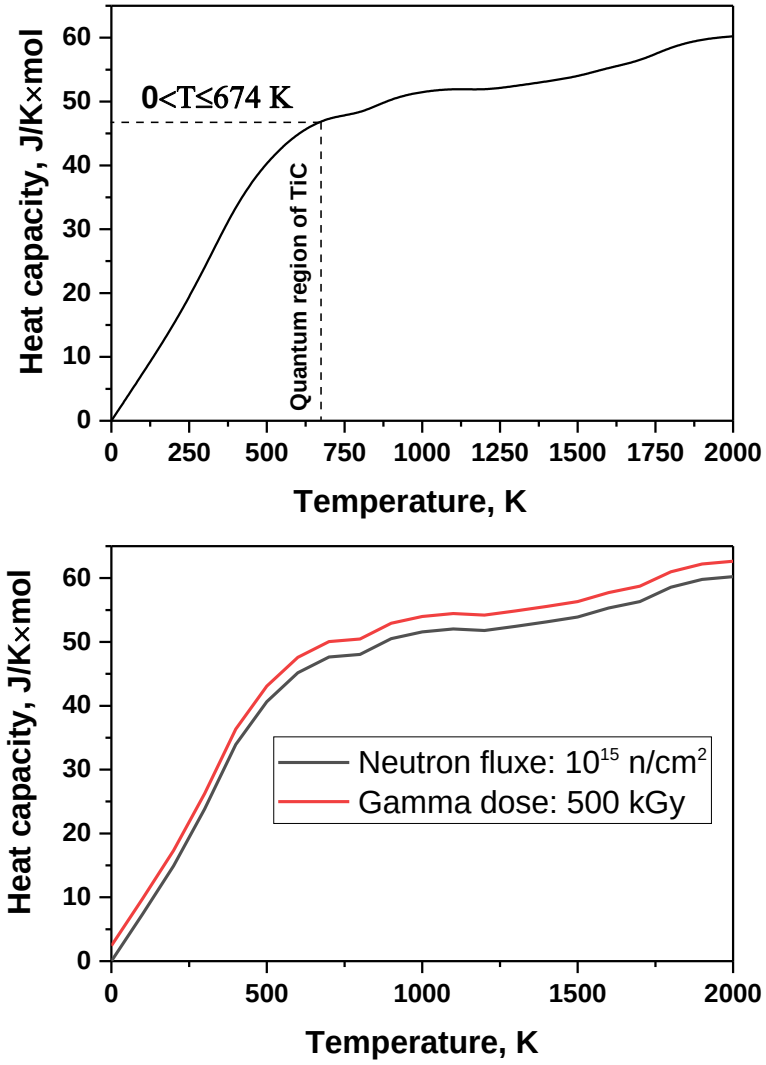

Fig. 1. Specific heat capacity of nano titanium carbide samples of unirradiation and the neutron and gamma irradiation at the $0 \leq T \leq 2000$ K temperature ranges

4. Conclusions

We have used DSC spectroscopy to study the defects introduced in the titanium carbide by 10^{15} n/cm^2 neutron flux and 500-kGy gamma irradiation dose. The heat capacity value increases to 51.6 J/K×mol in titanium carbide nanoparticles subjected to 10^{15} n/cm^2 neutron flux and 500 kGy gamma irradiation. From the temperature of 674 K, the heat capacity for the non-irradiated sample is up to 58.6 J/K×mol, and it is equal to

60 J/K×mol for the sample exposed to 10^{15} n/cm^2 neutron flux and 500 kGy gamma radiation at different intervals.

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