

# REPUBLIC OF AZERBAIJAN

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## ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

### **THE EFFECT OF IONIZING RADIATION ON THE STRUCTURAL AND THERMAL PROPERTIES OF TiC NANOPARTICLES**

Speciality: 2225.01 – Radiation materials science

Field of science: Physics

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The work was performed at the “Radiation Physics of Disordered Solids” Laboratory of the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan.

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## GENERAL DESCRIPTION OF WORK

**Relevance and development of the topic.** One of the fundamental challenges facing contemporary materials science is the development of novel materials that can maintain their stability under extreme conditions, including high temperature, mechanical stress, and ionizing radiation. This necessity becomes particularly pronounced in strategic fields such as nuclear energy, aerospace technologies, military industry, and plasma physics. The effective utilization of materials in such environments requires not only an understanding of their intrinsic properties, but also a systematic investigation of how these properties evolve under different external factors. In this context, titanium carbide (TiC), which belongs to the class of interstitial carbides, has in recent years attracted considerable attention as a promising material. These compounds, in which carbon atoms occupy the interstitial sites of the titanium lattice, are recognized for their outstanding physical and chemical characteristics. TiC is distinguished by its high melting point (approximately 3100 °C), hardness, chemical inertness, resistance to oxidation, and metallic-type electrical conductivity. As such, it has potential applications both as a protective coating and as a functional component in a wide variety of technological systems. These attributes render TiC a candidate material for devices operating under high-temperature and radiation environments. In general, carbides of this type are employed in various nuclear reactors, including gas-cooled fast reactors (GFRs), as well as in BISO (bi-isotropic) and TRISO (tri-isotropic) fuel designs as protective coatings against fission products.<sup>1</sup>

Nanoscale TiC particles, due to size effects and quantum confinement, may exhibit electronic structures distinct from those observed in bulk form. In such cases, the material's band gap may deviate from classical metallic values and, in certain instances, fall within the 2–3 eV range, thereby influencing its semiconducting and thermoelectric properties. The growing interest in nanostructured

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<sup>1</sup> IAEA-TECDOC-1345. Fuel Performance and Fission Product Behaviour in Gas Cooled Reactors. Vienna: International Atomic Energy Agency, 2003, s. 55–60.

TiC stems from the modifications in phase stability, crystalline structure, surface behavior, and functional parameters that occur when particle size is reduced to the nanometer scale. These transformations also directly affect the type and concentration of defects generated under radiation exposure. Consequently, the investigation of the effects of ionizing radiation on TiC nanoparticles is of both fundamental and applied significance.

Current scientific literature has focused primarily on bulk forms of TiC, whereas systematic and large-scale radiation studies on TiC nanoparticles remain limited. Although radiation-induced degradation has been widely examined in materials commonly used in nuclear technologies, the radiation response of TiC and other carbides at the nanoscale has not yet been comprehensively explored. A critical analysis of the existing literature reveals that structural modifications in TiC nanoparticles under ionizing radiation particularly gamma irradiation such as partial loss of crystallinity, formation of oxide phases, and changes in thermal stability, have not been investigated in a systematic manner. This gap highlights the necessity for further research.

Moreover, studying the radiation resistance of TiC not only substantiates its role as a passive protective layer in nuclear technologies, but also opens new possibilities for its use as an active component capable of maintaining functional stability under irradiation. Whereas earlier approaches regarded TiC mainly as a coating material providing protection for other substrates, contemporary studies demonstrate that it retains its functional characteristics even under radiation exposure. This widens the scope of its application in nuclear technologies, supporting its potential deployment as a structural material, heat-transfer element, or sensor component.

Microscopic changes occurring on the surface and within the bulk of TiC nanoparticles such as amorphization, phase transitions, defect accumulation, and localized oxidation directly influence their properties. Analyzing such transformations can yield more comprehensive insights into the long-term stability and durability of the material. Therefore, the study of the structural and thermal

behavior of TiC nanoparticles under ionizing radiation is not only a subject of fundamental scientific interest but also a matter of strategic importance for applied engineering.<sup>2</sup>

**Object and subject of research.** As the object of research, cubic-structured TiC nanopowder with a specific surface area of 50 m<sup>2</sup>/g, a density of 0.08 g/cm<sup>3</sup>, particle size in the range of 40–60 nm, and a purity degree of over 99% was used (US Research Nanomaterials Inc., USA; Stock: US2052, CAS: 12070-08-5). The subject of the research is the investigation of the structural and thermal properties of TiC nanoparticles under the influence of gamma irradiation.

**Goals and objectives of the research.** The research focuses on examining the crystal structure and thermal properties of nanocrystalline TiC particles under the influence of gamma irradiation, investigating possible modifications through various analytical and spectroscopic techniques, identifying trace elements in the chemical composition of the material, and clarifying the mechanisms of gamma irradiation effects on the structural and physical stability of TiC nanocrystals. To achieve this objective, the following tasks were carried out:

- Investigation of the changes in the crystalline structure of nano TiC particles induced by gamma irradiation
- Analysis of the modifications in the functional groups on the surface of nano TiC particles
- Study of the thermal stability and phase transition alterations in TiC samples under irradiation
- Examination of the morphology and elemental composition (EDS) of TiC particles after gamma irradiation using Scanning Electron Microscopy (SEM)
- Determination of trace elements in TiC nanoparticles by neutron activation analysis

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1. <sup>2</sup> Zinkle, S. J.; Was, G. S. *Materials challenges in nuclear energy*. Acta Materialia, 2013, Vol. 61, s. 735–758.

- Clarification of the general mechanism of structural and thermal modifications occurring in TiC nanoparticles under ionizing radiation, based on the obtained experimental results

**Investigation methods:** In the course of the research, a complex set of experimental and analytical methods was employed to investigate the structural and thermal properties of nanoscale TiC particles. The samples were irradiated with different doses using the  $\gamma$ -25 radiation facility based on the Co-60 isotope at the Institute of Radiation Problems.

For the determination of trace elements in the chemical composition of nanocrystalline TiC samples, the ko-INAA method was applied at the TRIGA Mark II research nuclear reactor located in Ljubljana, Slovenia. The crystal structure was examined using a Rigaku MiniFlex 600 X-ray diffractometer (Cu K $\alpha$ ,  $\lambda = 1.54 \text{ \AA}$ ).

The functional groups and chemical bonds of the samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), while their thermal behavior was studied by Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), and Differential Thermogravimetry (DTG). The surface morphology and elemental composition were determined by Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-ray Spectroscopy (EDS).

**The main provisions submitted for defense:**

- Investigation of the crystal structure of nanocrystalline TiC particles after gamma irradiation
- Analysis of radioactive isotopes in TiC samples by neutron activation
- Reduction of crystallite size and increase of microstrain under gamma irradiation
- Examination of the surface morphology, elemental composition, and agglomeration of TiC particles before and after irradiation
- Influence of gamma irradiation on the thermal parameters of TiC nanoparticles
- Formation of oxide phases in TiC nanoparticles as a result of irradiation and investigation of their impact on surface reactivity

**Scientific novelty of the research.** For the first time, the present dissertation has established that:

1. The structural and phase stability of nanocrystalline TiC particles after exposure to gamma ( $\gamma$ ) irradiation was comprehensively investigated, revealing a reduction in crystallite size and an increase in microstrain.

2. Based on XRD analyses, the variations in lattice parameters and the degree of crystallinity of TiC nanoparticles under gamma irradiation were evaluated.

3. FTIR spectroscopy demonstrated changes in the vibrational modes associated with carbon–titan bonds, showing the effect of gamma irradiation on the intensity of functional groups.

4. By applying thermal analysis methods (DTA, DSC, DTG), the thermal stability and phase transitions of nanocrystalline TiC particles were comparatively studied before and after irradiation, and modifications in thermal parameters caused by radiation were identified.

5. Using the  $k_0$ -neutron activation analysis ( $k_0$ -INAA) method, trace elements present in TiC samples were determined, and radionuclide transformations after irradiation were demonstrated.

6. The formation of oxide phases in nanocrystalline TiC samples as a result of gamma irradiation was revealed, and their influence on the surface reactivity of the material was explained.

7. On the basis of the comprehensive experimental results, scientific grounds were established for assessing the stability of nanocrystalline TiC particles in ionizing radiation environments.

**The theoretical and practical significance of the research:**

The nano TiC used in this dissertation is a nanomaterial with high chemical purity and a stable cubic crystal structure. Based on the main scientific results obtained, nanocrystalline TiC, owing to its high chemical purity and stable cubic structure, is considered a promising nanomaterial capable of preserving structural stability under ionizing radiation and high-temperature environments. Due to these properties, TiC is regarded as one of the important materials with potential applications in nuclear technologies, the space industry, radiation-resistant electronics, and sensor systems.

The conducted research has shown that the structural and phase modifications observed in nanocrystalline TiC particles under gamma irradiation are of particular significance for evaluating the radiation resistance of the material. These findings provide a scientific basis for the selection of materials intended for the reliable long-term operation of devices in ionizing environments. The high thermal stability of nanocrystalline TiC particles, the controllability of their surface reactivity, and their resilience under ionizing radiation demonstrate their broad potential for application in nuclear physics, space technologies, energy systems, and micro/nanoelectronics.

### **Approbation and application:**

The scientific results obtained in the dissertation were presented at several international and local scientific events in accordance with the different directions of the research and were brought to scientific discussions. The results of the studies were reported at various conferences and were evaluated by specialists.

✓ Hakhıyeva R.R. Band structure investigation of TiC nanoparticles using FTIR spectroscopy // AL-FARABI International Congress on Applied Sciences – II. Nakhchivan University, Azerbaijan, 2–4 May 2021, p. 138.

✓ Hakhıyeva R.R. Study of nano TiC compounds by infrared spectroscopy // International Asian Congress on Contemporary Sciences – V. Nakhchivan University, Azerbaijan, 1–2 June 2021, p. 242.

✓ Hakhıyeva R.R. FTIR spectroscopy of nano Titanium Carbide (TiC) particles // IX International Conference “Semipalatinsk Test Site: Heritage and Prospects for the Development of Scientific and Technical Potential.” Kurchatov, Kazakhstan, 7–9 September 2021, p. 52.

✓ Hakhıyeva R.R. Investigation of thermophysical parameters of nanocrystalline titanium carbide (TiC) particles by DTA, TGA and DTG methods // 4th International Conference on Innovations in Natural Science and Engineering. Baku, Azerbaijan, 26–30 October 2022, p. 92.

✓ Hakhıyeva R.R. Investigation of thermal parameters of nanocrystalline titanium carbide particles under gamma irradiation // VII International Scientific Conference of Young Researchers. Baku Engineering University, Azerbaijan, 28–29 April 2023, pp. 74–75.

✓ Huseynov E.M., Hakhıyeva R.R. Differential thermal analysis of gamma-irradiated nano titanium carbide particles // 32nd International Conference “Nuclear Energy for New Europe.” Portorož, Slovenia, 11–14 September 2023, p. 91.

✓ Huseynov E.M., Hakhıyeva R.R. Band structure investigation of nanocrystalline titanium carbide (TiC) particles under gamma radiation // NanoteC24 – International Conference on Carbon Nanoscience and Nanotechnology. Nantes, France, August 2024, p. 3462.

**Publications:** The main content and scientific results of the dissertation have been reflected in 3 articles published in international journals and 4 theses included in the proceedings of international scientific conferences, as well as in 4 articles and 4 theses published within the country. In total, the main findings of the dissertation have been published in 15 scientific works, including 7 articles and 8 theses.

**The name of the organization where the dissertation work was performed:** The experiments conducted within the framework of the dissertation were carried out at the Institute of Radiation Problems of the Ministry of Science.

**Personal attendance of the author:** All the main scientific results presented in the dissertation are the outcome of the claimant’s personal research activity. The claimant has substantiated the relevance of the research topic, carried out a comprehensive investigation of the structural, thermal, and surface properties of nanocrystalline TiC samples subjected to gamma irradiation, and provided the processing and scientific interpretation of the obtained results. In addition, the claimant has directly participated in the presentation of the research findings at scientific conferences and in the preparation of the related articles.

**The total volume of the dissertation with a character including a separate volume of the structural units of the dissertation.** The dissertation consists of an introduction, five chapters, a conclusion, a list of references, and abbreviations, covering a total of 163 pages. The main text (excluding figures, tables, and the reference list) comprises 212,516 characters in total. The distribution of characters across the sections is as follows: Introduction – 23,775; Chapter I – 59,675; Chapter II – 49,673; Chapter III – 26,099; Chapter IV – 24,596; Chapter V – 25,503; Conclusion – 2,258. The research work contains 45 figures and 7 tables, and the list of references includes 158 sources.

## **THE CONTENT OF THE DISSERTATION**

**In the introduction,** the relevance of the topic is substantiated, and the research objectives, tasks, object and subject of study, as well as the methods employed, are presented. The importance of investigating the behavior of nanoscale materials in radiation environments is emphasized as one of the priority directions of modern science and technology. It is noted that the stability of nanoscale titanium carbide (TiC) particles against ionizing radiation has wide application prospects in nuclear technologies, the aerospace industry, and other advanced fields. Furthermore, it is justified that the mechanical, thermal, and chemical properties of materials under high temperatures and radiation conditions are of both fundamental and applied significance.

This section also clearly defines the aim of the study, which is to systematically investigate, by means of experimental and theoretical approaches, the structural, thermal, and chemical modifications in nanoscale TiC particles under ionizing radiation.

**Chapter I** provides an extensive review of the fundamental physical properties of nanoscale materials, their application prospects in nuclear sciences, and synthesis methods, based on existing scientific literature. First, size effects are explained in detail as one of the main reasons for the distinct behavior of nanoscale materials

compared to conventional bulk counterparts. As particle size decreases, the increase in surface area and surface energy leads to significant changes in chemical activity and physical parameters. In addition, the potential applications of nanoscale materials in nuclear science and technology are addressed. Particular attention is paid to the importance of materials with radiation and high-temperature resistance for use in nuclear reactors, hard radiation detectors, and radiation-resistant coatings. The role of nanoscale materials in controlling radiation-induced crystal defects and amorphization processes is also highlighted.

Furthermore, Chapter I presents in detail the different synthesis methods of nanoscale TiC particles and their effects on particle size, morphology, and crystalline characteristics. Mechanical milling, physical vapor deposition, chemical vapor deposition, sol-gel synthesis, and other methods are comparatively described with respect to their advantages, limitations, and experimental applications. The key factors influencing particle size, polydispersity, surface functional groups, and crystallinity degree in each method are summarized based on literature data. The chapter also provides a broad scientific discussion of the crystalline structure of TiC, its existing polytypes, and the influence of these structural modifications on its mechanical, thermal, and electrical properties. The role of crystal structure and polytypes in the use of TiC for nuclear technologies, their behavior under radiation, and phase transitions are also emphasized.

**In Chapter II**, the main stages of the experimental studies and the measurement methodologies employed are described in detail. The technical features of the gamma irradiation process and the scientific-methodological basis of the primary methods used to study the physical properties of nanocrystalline TiC particles are presented.

The samples were irradiated in the MRX- $\gamma$ 25 facility at the Institute of Radiation Problems of the Ministry of Science and Education of Azerbaijan, using a Co-60 isotope-based gamma source, within the dose range of 0.05–1.5 MGy. To ensure homogeneous dose distribution, special experimental approaches

were applied, and the absorbed dose rate was calibrated using a high-precision ferrosulfate dosimetry system.

The content of trace elements in the chemical composition of nanocrystalline TiC particles was determined using the  $k_0$ -based instrumental neutron activation analysis (INAA) method. For this purpose, the samples were irradiated with a neutron flux in the JSI TRIGA Mark II research reactor in Slovenia, after which the gamma spectra were analyzed using an HPGe detector. The method enabled the precise and reliable determination of radionuclides with both short and long half-lives. The analyses confirmed the high chemical purity of the TiC nanoparticles, and the quantities of trace elements were evaluated in comparison with international reference materials. The study demonstrated that the  $k_0$ -INAA method is a non-destructive, multipurpose, and internationally recognized approach for determining the elemental composition of nanomaterials, thereby ensuring the reliability of the obtained results.

Structural and phase analyses were conducted using X-ray diffraction (XRD) on a Rigaku MiniFlex 600 diffractometer (Cu  $K\alpha$ ,  $\lambda = 1.54 \text{ \AA}$ ). Based on the XRD results, crystallite size, lattice parameters, and structural modifications induced by irradiation were evaluated. Diffraction peaks were indexed by comparison with the JCPDS database, and crystallite size as well as possible crystal defects were estimated using the Scherrer equation. The increase in the full width at half maximum (FWHM) of diffraction peaks was associated with crystallite size reduction and the presence of internal strains.

The morphological structure of the nanoparticles was investigated by Scanning Electron Microscopy (SEM). SEM technology surpasses the resolution limits of optical microscopy, enabling visualization of nanoscale surface features and aggregation characteristics. The method operates on the principle of the interaction between a focused electron beam and the sample surface. The resulting secondary electrons (SE) and backscattered electrons (BSE) are detected to produce a detailed surface image. Depending on magnification and applied voltage, information about both the

upper surface layers and deeper regions of the sample can be obtained.

The analysis of changes in chemical bonds and functional groups was performed by Fourier Transform Infrared Spectroscopy (FTIR, Varian 600). FTIR spectroscopy is one of the most widely applied analytical techniques for investigating the chemical structure, functional groups, and bonding characteristics of nanomaterials. In this study, a Varian 600 FTIR spectrometer was employed, whose high optical throughput and broad signal-to-noise ratio ensured measurement accuracy. FTIR measurements can be performed in both reflectance and transmittance modes. Reflectance mode is suitable for powder and aggregated samples, while transmittance mode is applied for specimens compressed between KBr pellets. Using both approaches, characteristic absorption bands of TiC particles were recorded in the range of 4000–400  $\text{cm}^{-1}$ .

The thermal properties and phase transitions of the samples were examined using Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (DTG). These methods enabled the determination of thermal stability, heat capacity, activation energy, and the dynamics of oxidation processes. Measurements were performed using a PerkinElmer STA 6000 instrument, and the results were processed with the Pyris Manager software. Variations observed in the temperature and intensity of peaks before and after irradiation made it possible to identify radiation-induced modifications in the thermal stability of the nanoparticles. The chapter also provides the technical specifications of the instruments applied, the accuracy of the measurements, and the methodology for error estimation.

**In Chapter III**, the results of instrumental analyses carried out to examine the structural and chemical modifications in nanoscale titanium carbide (TiC) particles before and after exposure to ionizing radiation are presented in detail. For this purpose, both the chemical purity and quantitative determination of trace elements, as well as the vibrational properties of functional groups on the surface, were investigated using various analytical techniques.

To precisely study the elemental composition of the samples, the  $k_0$ -based instrumental neutron activation analysis ( $k_0$ -INAA) method was applied. The samples were irradiated with a neutron flux in the TRIGA Mark II research reactor in Ljubljana, Slovenia.  $^3\text{Gamma}$  spectra of the radionuclides generated in the samples as a result of  $(n,\gamma)$  nuclear reactions induced by neutron irradiation were recorded using an HPGe detector and processed with specialized software. This analysis confirmed the high chemical purity of the TiC nanoparticles and provided quantitative data on certain trace elements present in their composition. These results made it possible to evaluate the extent and mechanisms of radiation-induced modifications in the elemental composition of the samples. Neutron irradiation led to the formation of new radioactive nuclei in nanocrystalline TiC particles. The decrease of these nuclei over time follows an exponential trend and is expressed by the following equations:

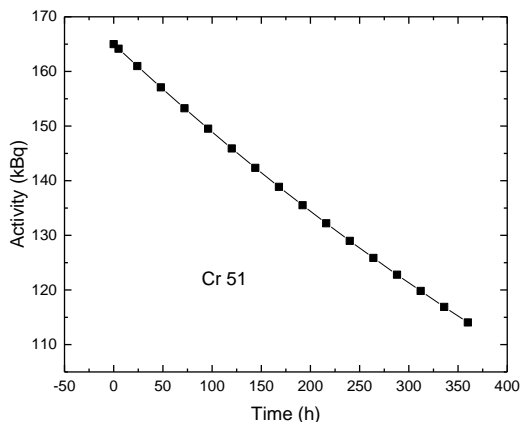
$$\frac{dN}{dt} = -\lambda N \quad (1)$$

As a result of neutron irradiation, the radionuclide  $^{51}\text{Cr}$  (chromium-51) was predominantly formed in the nanocrystalline TiC particles, and an activity level of 170 kBq was recorded. This radionuclide exhibited the highest activity level (Figure 1).

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<sup>3</sup> Žerovnik, G., Kaiba, T., Radulović, V., Jazbec, A., Rupnik, S., Barbot, L., Fourmentel, D., & Snoj, L. (2015). Validation of the neutron and gamma fields in the JSI TRIGA reactor using in-core fission and ionization chambers. *Applied Radiation and Isotopes*, 96, 27–35.

<https://doi.org/10.1016/j.apradiso.2014.10.020>



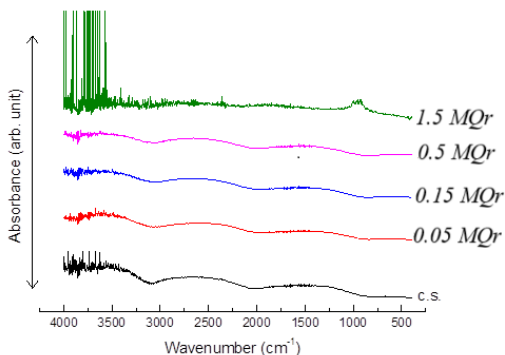
**Figure 1. Activity profile of  $^{51}\text{Cr}$**

In addition,  $^{124}\text{Sb}$  (antimony-124) exhibited a medium activity level (400 Bq), while low-activity radionuclides such as  $^{60}\text{Co}$  (35 Bq),  $^{46}\text{Sc}$  (20 Bq), and  $^{181}\text{Ta}$  (15 Bq) were also identified. These radionuclides play an important role in evaluating the radiation stability of the sample and in assessing its post-irradiation safety.<sup>4</sup>

Subsequently, the surface functional groups and the vibrational modes of Ti–C bonds in TiC particles were analyzed using Fourier Transform Infrared (FTIR) spectroscopy. First, the FTIR spectrum of the synthesized TiC particles before irradiation was obtained and examined. The analysis revealed characteristic vibrational bands corresponding to Ti–C bonds around  $600\text{ cm}^{-1}$ , as well as weak oxygen-containing functional groups in the range of  $1000\text{--}1100\text{ cm}^{-1}$ , and –OH type adsorption bands near  $3400\text{ cm}^{-1}$ . These findings provided preliminary information on the surface functional groups of the nanoscale particles and the strength of their chemical bonding.

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<sup>4</sup> 3.Elchin Huseynov, Anze Jazbec "Trace elements study of high purity nanocrystalline silicon carbide (3C-SiC) using k0-INAA method" Physica B: Condensed Matter 517, 30–34, 2017



**Figure 2. FTIR spectra of nanoscale TiC particles under gamma irradiation at doses of 0.05, 0.15, 0.5, and 1.5 MGy**

The FTIR spectra of TiC particles exposed to gamma irradiation show that certain shifts occur in the vibrational bands corresponding to Ti–C bonds.<sup>5</sup> This indicates the formation of radiation-induced defects, tendencies toward amorphization, and transformations in surface functional groups. In particular, the increase in the intensity of –OH and C–O functional groups, as well as the changes observed in vibrational frequencies, were associated with the acceleration of oxidation processes.

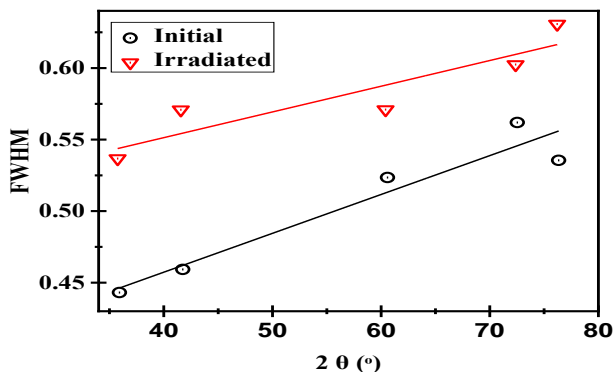
At the end of the chapter, all the experimental results were analyzed collectively and presented in a generalized form. This chapter provided a comprehensive evaluation of the behavior of nanoscale TiC particles in a radiation environment based on the results of complex instrumental analyses, thereby making significant contributions both to fundamental scientific knowledge and to applications in the field of nuclear technologies.

**In Chapter IV**, the modifications in the crystal structure and surface morphology of nanoscale titanium carbide (TiC) particles after exposure to different doses of gamma irradiation were comprehensively investigated. First, X-ray diffraction (XRD) analyses were used to evaluate the changes observed in crystallite

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<sup>5</sup> Kaur, A., et al. “Gamma irradiation effects on nanostructured carbides: FTIR and XRD studies.” *Radiation Physics and Chemistry*, 2018, 152, s. 30–36.

size, lattice parameters, and the broadening of diffraction peaks before and after irradiation. Variations in the shapes of the diffraction peaks were associated with microstrain effects. These changes were found to be related to the increase in lattice parameters according to Bragg's law. The leftward shift of diffraction peaks and the decrease in their intensity indicated the formation of local defects in the crystal structure and an increased degree of amorphization. The results demonstrated that under gamma irradiation, the lattice constant of TiC nanocrystals exhibited a relative increase of approximately 0.35%. This expansion was attributed to local deformations and the formation of point defects within the crystal lattice. The leftward shift of the main (200) reflection peak at  $2\theta = 41.7^\circ$  by  $\Delta\theta = -0.181^\circ$  was regarded as direct evidence of the lattice parameter expansion. The XRD results clearly revealed that the changes in peak intensity and the leftward displacement of diffraction lines before and after irradiation reflected structural modifications in TiC nanocrystals. To assess the local changes induced by gamma irradiation within the crystal structure, the degree of amorphization was determined based on the integration of diffraction peaks. This parameter was considered together with peak shifts, intensity reduction, and weakened symmetry, and the results are presented in Figure 3.



**Figure 3. Williamson–Hall plot based on the X-ray spectra of TiC nanoparticles**

Subsequently, the degree of microstrain and the variations in crystallite size in the crystal structure were separately evaluated using the Williamson–Hall and Scherrer methods. The results obtained from both approaches confirmed a reduction in crystallite size and an increase in microstrain. These findings provided a more comprehensive understanding of the dynamics of the effects of gamma irradiation on the crystal structure. Table 1 presents the values of crystallite size, microstrain, and dislocation density for both the initial and irradiated states.

**Table 1. Structural changes in TiC nanocrystals before and after irradiation**

<b>Parameters</b>	<b>Before irradiation</b>		<b>After irradiation (1.5 MGy)</b>	
<b>A</b>	4.32589 (2)		4.34102 (3)	
<b>V</b>	80.952 (6)		81.804 (9)	
<b>Crystallite size at different lattice planes (Scherrer method)</b>	(111)	(200)	(111)	(200)
	~23.55 nm	21.7 nm	~19.8 nm	17.13 nm
<b>Microstrain (<math>\mu\epsilon</math>)</b>	$30.7734 \times 10^{-4}$		$32.4734 \times 10^{-4}$	
<b>Dislocation density (<math>\delta</math>)</b>	$\sim 39.5 \times 10^{-4}$		$\sim 42.3 \times 10^{-4}$	
<b>Crystallite size (Williamson–Hall method)</b>	27.12 nm $\pm$ 0.045		18.63 $\pm$ 0.047	

The increase in gamma irradiation dose led to a rise in lattice strain and a reduction in crystallite size, while only certain parameters exhibited noticeable changes. This indicates that even when exposed to a high irradiation dose of 1.5 MGy, the overall structural stability of the sample is preserved, and no significant defects are formed.

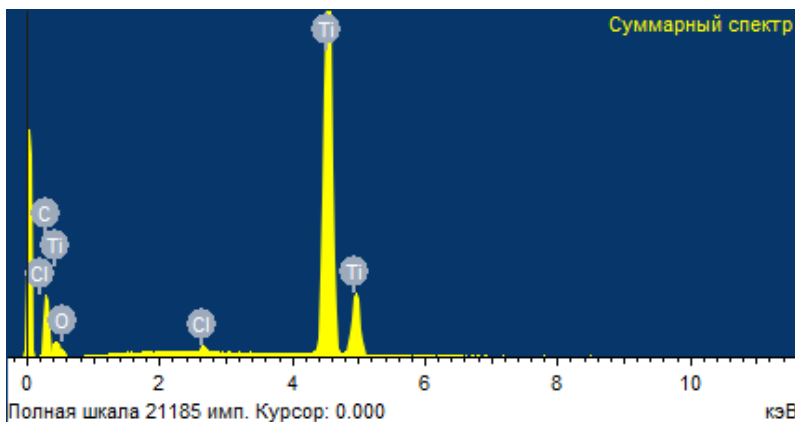
In this chapter, the surface morphology of TiC nanoparticles was also analyzed by Scanning Electron Microscopy (SEM). In SEM technology, the wave properties of the electron beam vary depending on the external electric potential applied within the instrument. The wave characteristics of the electrons are determined by their kinetic properties, which are regulated through the accelerating voltage applied to the electron gun of the microscope. As the applied energy increases, the electron wavelength shortens, allowing higher spatial resolution during imaging. As a result, finer structures can be observed in electron microscopes, particularly in SEM.<sup>6,7</sup>

SEM images taken at different magnifications revealed the aggregation tendencies of the particles, their agglomeration states, and surface defect structures. Under the influence of irradiation, morphological modifications were observed on the surface of the nanoparticles, along with traces of oxidation in certain areas and amorphization phenomena. Furthermore, to investigate the elemental composition of TiC nanoparticles, the energy-dispersive spectroscopy (EDS) module of the SEM instrument was used. The corresponding data are presented in Figure 4.

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<sup>6</sup>Goldstein, J. I., Newbury, D. E., Joy, D. C., et al. *Scanning Electron Microscopy and X-ray Microanalysis*. 3rd ed., Springer, 2003.

<sup>7</sup> L. Reimer, L. *Scanning Electron Microscopy: Physics of Image Formation and Microanalysis*. 2nd ed., Springer, 1998.



**Figure 4. SEM-EDS analysis of the elemental composition of TiC nanoparticles**

Quantitative analysis showed that the sample contained approximately 52% titanium, 38% carbon, and 10% oxygen. This result demonstrates that the TiC nanoparticles possess high purity and a composition appropriate for the intended purpose. The presence of oxygen is most likely associated with a surface passivation layer or minimal surface oxidation that may occur during irradiation or synthesis. Such surface oxidation phenomena are usually limited to local chemical modifications at the surface without significantly affecting the internal crystal structure of the material.

In addition, to study the spatial distribution of elements within the structure of TiC nanoparticles, the mapping technique of the SEM instrument was used, and the corresponding results were presented in this chapter. At the end of the chapter, the obtained findings were generalized, and the effects of gamma irradiation on the crystal lattice, surface morphology, and microstructural stability were interpreted on a scientific basis. These results are of great importance for assessing the performance capability of TiC nanoparticles under high-radiation conditions.

**In Chapter V**, the thermal properties of nanocrystalline titanium carbide (TiC) particles were systematically investigated using differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential

thermogravimetric analysis (DTG). Kinetic and thermodynamic changes under thermal effects, as well as parameters such as activation energy, specific heat capacity ( $C_p$ ), enthalpy, entropy, and Gibbs free energy, were studied comparatively before and after gamma irradiation.

The DSC analyses demonstrated that gamma irradiation leads to an increase in the activation energy of nanocrystalline TiC particles. The activation energy of nanocrystalline TiC was calculated based on the data obtained from the DSC measurements, and for this purpose, the Arrhenius equation was applied.<sup>8,9</sup> The Arrhenius relation is expressed as follows:

$$k = A \cdot e^{-E_a/RT} \quad (2)$$

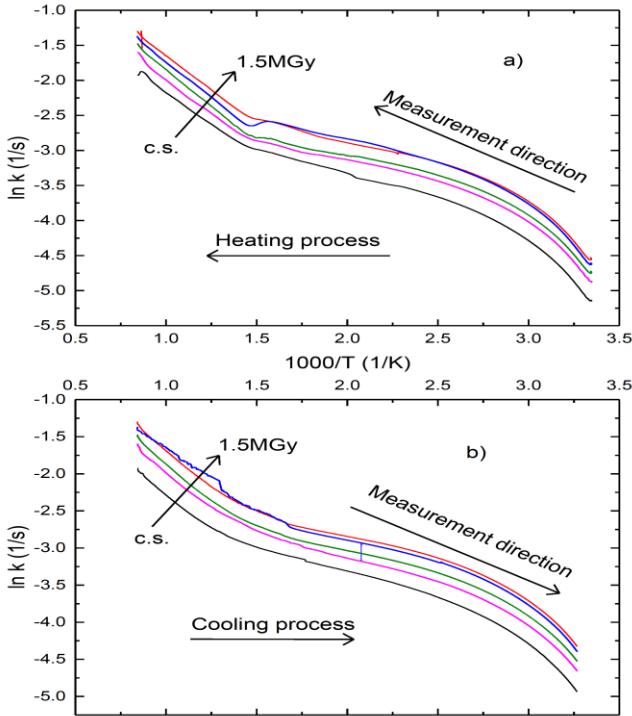
where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy (J/mol or eV),  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), and  $T$  is the temperature (K). This equation was applied to explain atomic mobility and the kinetics of thermal processes with increasing temperature, and it was employed separately for both heating and cooling stages. Based on the dependence shown in Figure 5, three different activation energies were calculated for nanocrystalline TiC: 0.73 eV, 1.65 eV, and 1.9 eV. These distinct values indicate the presence of different thermal processes occurring through various mechanisms within the material. The lowest energy (0.73 eV) is most likely associated with thermal diffusion of atoms retained by weak potential barriers or desorption of adsorbed surface components upon heating. The intermediate energy value (1.65 eV) can be attributed to the migration of local defects and atomic-level lattice reconstruction processes. The highest energy value (1.9 eV) corresponds to more complex thermal phenomena such as local phase transformations and the formation of defect clusters in the crystal lattice. The observation of multiple activation stages confirms the complex thermal behavior of nanomaterials and demonstrates that TiC nanoparticles

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<sup>8</sup> Brown M. E. *Introduction to Thermal Analysis: Techniques and Applications*. – Springer, 2001.

<sup>9</sup> Atkins P., de Paula J. *Atkins' Physical Chemistry*. – 9th ed., Oxford University Press, 2010.

sequentially activate different mechanisms with increasing temperature. Figure 5 shows the  $\ln k$  vs.  $1000/T$  dependences for samples before and after gamma irradiation (0.05 MGy, 0.15 MGy, 0.5 MGy, and 1.5 MGy). It is evident that with increasing irradiation dose, a regular increase in activation energy is observed. This result characterizes the structural stability and thermal resistance of TiC particles under radiation conditions.



**Figure 5. Dependence of  $\ln k$  on  $1000/T$  for nanocrystalline TiC particles during heating (a) and cooling (b) before and after gamma irradiation at doses of 0.05 MGy, 0.15 MGy, 0.5 MGy, and 1.5 MGy**

In this chapter, the temperature-dependent variation of the specific heat capacity ( $C_p$ ) of TiC nanoparticles was also

investigated.<sup>10</sup> The results indicated that at low and medium irradiation doses (0.05–0.15 MGy), no significant changes in Cp were observed, whereas at higher doses (0.5–1.5 MGy) a decreasing trend in Cp was recorded. This reduction was attributed to the formation of defect structures and oxidized phases induced by irradiation within the particles, which weakened Ti–C bonding and thereby affected thermal processes. Thus, the decreasing trend of Cp served as an important indicator for evaluating the radiation stability and high-temperature performance of the material.<sup>11</sup>

To evaluate the thermal stability and structural modifications of nanocrystalline TiC particles, differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential thermogravimetric analysis (DTG) methods were applied. Through these techniques, the thermal reactions, mass changes, and kinetic parameters of the samples were investigated, and the thermophysical properties of irradiated and non-irradiated particles were comparatively analyzed. The analysis of heat flows recorded during heating demonstrated that, after irradiation with different doses, variations in the degree of stability of the samples were observed. At the initial stage, the results obtained from TGA analyses were used to determine the behavioral characteristics of TiC nanoparticles under gamma irradiation. The outcomes of TGA, DTA, and DTG analyses indicated that high-temperature oxidation processes and mass changes occur in the samples.<sup>12</sup> In particular, irradiated samples exhibited mass gain and exothermic reactions, which are important indicators for assessing the stability of TiC particles under radiation conditions. The results obtained from TGA analysis are presented in Figure 6. On the active surface, H<sub>2</sub>O and OH groups absorbed from

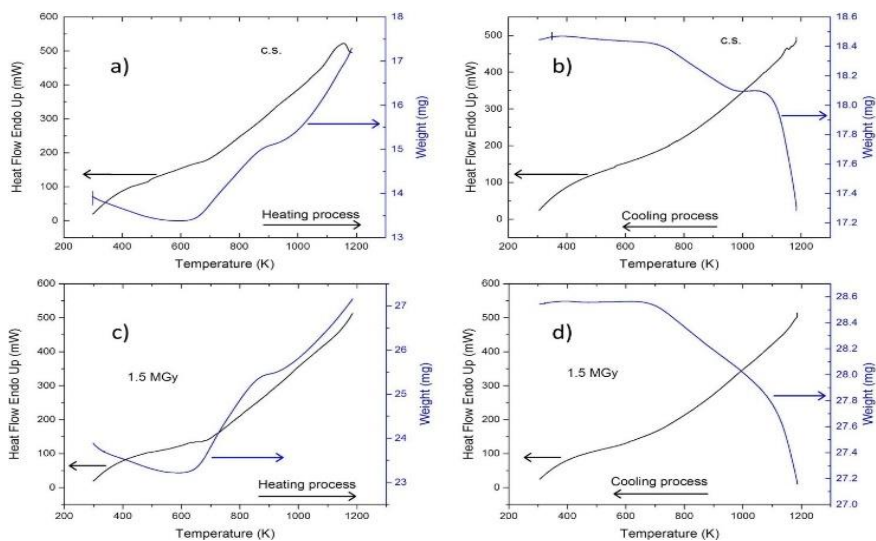
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<sup>10</sup> Huseynov E.M. Thermal stability and heat flux investigation of neutron-irradiated nanocrystalline silicon carbide (3C–SiC) using DSC spectroscopy. *Ceramics International*, 46(5), 5645–5648, 2020.

<sup>11</sup> Rao S. I., et al. Radiation effects in refractory carbides and nitrides // *Journal of Nuclear Materials*. – 2010, Vol. 403, – p. 98–109.

<sup>12</sup> Huseynov E. M., Naghiyev T. G. Study of thermal parameters of nanocrystalline silicon carbide (3C–SiC) using DSC spectroscopy // *Applied Physics A*. – 2021, Vol. 127, №4, – p. 267.

the environment interacted through weak chemical adsorption processes. Based on the thermogravimetric curves, it can be stated that as the temperature increases, the water and other volatile components present in the nanomaterial begin to desorb, and this process is completed at approximately 600 K. At temperatures above 600 K, the TG curves showed that the mass of the nanoparticles continued to increase with rising temperature. In the range of 600–800 K, exothermic reactions occurred, which were associated with partial amorphization and local structural modifications of the nanoparticles. These results are of significant importance for evaluating the stability of nanomaterials at high temperatures.<sup>13</sup>

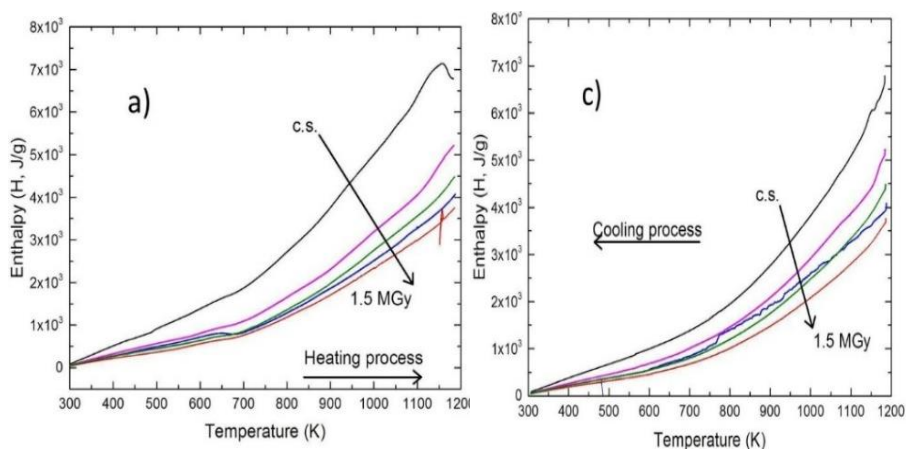


**Figure 6. TGA analyses of nanocrystalline TiC particles before and after gamma irradiation**

The analyses of kinetic and thermodynamic parameters showed that gamma irradiation resulted in an increase in Gibbs free energy ( $\Delta G$ ). With increasing temperature, the value of  $\Delta G$  gradually

<sup>13</sup> Li J., Zhou X., Wang L. *Thermal stability and oxidation behavior of nanocrystalline TiC ceramics*. Journal of the European Ceramic Society, 38(7), 2521–2529 (2018).

decreased and became more negative, indicating the system's tendency to minimize free energy as it absorbs heat and to approach equilibrium. However, in irradiated samples,  $\Delta G$  was characterized by less negative values. This result is interpreted as evidence that after irradiation the system exhibits less spontaneous behavior and becomes relatively more stable in energetic terms.<sup>14</sup> The analyses further revealed that at higher irradiation doses, the system attained a more stable configuration and approached thermodynamic equilibrium. On the other hand, decreases in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) parameters were observed after gamma irradiation (Figure 7).



**Figure 7. Temperature dependence of entropy and enthalpy of nanocrystalline TiC particles before and after gamma irradiation**

According to Figure 7, this behavior was associated with the weakening of energy exchange during thermal processes and an increase in the degree of internal ordering of the system. Similar approaches have also been observed in other carbide-based nanomaterials. In this context, the changes in  $\Delta H$  and  $\Delta S$  were

<sup>14</sup> Chen Y., Gao F., Liu H. *Thermal decomposition and kinetic study of carbide-based nanomaterials using TG/DTG analysis*. *Thermochimica Acta*, 697, 178–185 (2021).

explained in terms of phase stability and the kinetics of thermal processes.<sup>15</sup>

Based on the investigations, the results demonstrate that nanocrystalline TiC particles possess significant potential for use at high temperatures and under radiation conditions, particularly as a promising material for applications in nuclear technologies and aerospace engineering.

## MAIN SCIENTIFIC RESULTS

1. The processing of XRD diffractograms using the Scherrer and Williamson–Hall methods showed that although gamma irradiation caused a reduction in crystallite size (27.1 nm → 18.6 nm) and an increase in microstrain ( $34.8 \times 10^{-4}$  →  $47.9 \times 10^{-4}$ ) in TiC nanoparticles, these changes were relatively minor and the overall crystalline stability was preserved. The 0.35% increase in lattice constant and the leftward shift of diffraction peaks indicated local deformations, but the main lattice symmetry remained intact.

2. The  $k_0$ -neutron activation analysis revealed the formation of  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  radionuclides in TiC nanoparticles. The study demonstrated that even trace elements can exhibit high activity. However, the concentration of radionuclides did not significantly affect the overall structure or stability of the material.

3. SEM and EDS analyses confirmed that the morphological stability of the nanoparticles was preserved under gamma irradiation, with no aggregation observed in the initial 40–60 nm particles. Elemental mapping showed homogeneous distribution of Ti and C, with only slight surface oxidation detected.

4. A comparison of structural and thermal analyses indicated that at high irradiation doses, structural modifications of approximately 10.5% were recorded. Of this, only 1.36% was associated with amorphization, while the remaining changes were attributed to oxidation. Although the formation of  $\text{TiC}_x\text{O}_{1-x}$  phases

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<sup>15</sup> Kumar A., Singh R., Verma N. *TG/DTG analysis of nanostructured transition metal carbides: thermal stability and phase behavior*. Ceramics International, 45(12), 14985–14993 (2019).

was observed in the 1000–1200 K range as a result of oxidation, these modifications did not fundamentally compromise the radiation resistance of the material. The persistence of the main Ti–C bonds after irradiation confirmed the retention of chemical stability in the nanoparticles.

5. Calculations performed using the Arrhenius method based on DSC and DTA analyses indicated that the activation energy increased from 1.9 eV to 1.97 eV. A 3.23% increase in heat flow was recorded, while the specific heat capacity decreased (from 5.73 J/kg·K to 3.21 J/kg·K). The less negative values of Gibbs free energy ( $-4.12 \times 10^4$  J/mol  $\rightarrow$   $-2.24 \times 10^4$  J/mol) indicated a slight weakening of system stability. Nevertheless, the scale of parameter changes remained limited, proving that TiC nanoparticles are a radiation-resistant material under gamma irradiation conditions.

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8. Huseynov E.M., Hakhiyeva R.R. Investigation of Gamma irradiated nanocrystalline titanium carbide particles using thermal methods // Journal of Radioanalytical and Nuclear Chemistry, – 2023, 332(9), – p. 3779–3785.
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The defense will be held on 9 october 2025, at 15:00 the meeting of the FD1.21 Dissertation Council operating under the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan.

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The dissertation is available for review in the scientific library of the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan.

Electronic versions of the dissertation and abstract are posted on the official website of the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan.

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