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Study of the entropy and enthalpy of gamma irradiated TiC nanoparticles

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Abstract

The thermal characteristics of nanocrystalline titanium carbide (TiC) particles were systematically compared before and after gamma irradiation through the application of Differential Scanning Calorimetry (DSC) spectroscopy. Utilizing experimental findings, the Gibbs energy of titanium carbide nanoparticles was ascertained within the temperature range spanning from 300 to 1270 K. The investigation of potential phase transitions in nanoparticles and the amorphization processes induced by gamma radiation was investiagted employing the Differential Thermal Analysis (DTA) methodology. The enthalpy and entropy of the system comprising nanocrystalline 3C-SiC particles were computed both before and after exposure to gamma irradiation, with theoretical calculations corroborated through comparison with experimental outcomes. The values derived from experimental results for all thermophysical parameters were compared both before and after exposure to gamma radiation.

***Keywords*:** nanocrystalline TiC, nanomaterial, thermal parameters, entropy, gamma irradiation.

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1. Introduction

In recent times, a diverse range of modifications to titanium carbide compounds has been extensively utilized across multiple sectors of modern technological devices [1-7]. The exceptional physical properties and elevated temperature resilience inherent in these compounds have propelled the broadening of their applications [8-14]. Titanium carbide is recognized as an economically advantageous material for devices and tools employed in high-temperature operational settings. The exploration of the thermal stability of these composites at varying temperatures during practical applications is of significant interest.

Nanomaterials display specific physical properties associated with their significantly increased specific surface area (SSA) at the nanoscale. Titanium carbide, like other materials at this scale, showcases unique functional attributes and distinctive physical properties [15-17]. Considering these inherent characteristics of nanomaterials, our research endeavors encompass a comprehensive investigation into the effects of ionizing irradiation on diverse types of nanomaterials [18-29]. The considerable specific surface area of nanomaterials can give rise to a discernible difference in surface heat transport, influencing various physical processes, and particularly exerting a noteworthy impact on thermophysical phenomena.

Within nano dimensions, distinct phenomena are observed, diverging from classical thermodynamics and thereby giving rise to the formulation of a novel interdisciplinary theory recognized as nanothermodynamics [30-33]. Presently, the theory of nanothermodynamics encompasses several models. In a broad context, this theory appears to serve as a bridging

mechanism between macroscopic and nanoscopic theories. In recent times, the nanothermodynamics theory has proven instrumental in enabling thorough investigations into size-dependent alterations in thermophysical properties within nanomaterials. In the presented study, a kinetic analysis of diverse thermal processes occurring in nanocrystalline TiC particles has been undertaken, utilizing parameters such as thermal treatment rate and temperature. The thermal parameters of nanocrystalline TiC particles were examined by analyzing the thermal treatment rate across the temperature range of 300-1270 K.

2. Experiments

The study specifically revolved around nanocrystalline TiC particles featuring a cubic modification. These particles exhibited dimensions of 40 nm, a specific surface area (SSA) measuring 50 m^2/g, a nano-state density of 0.08 g/cm^3 (with a real density of 4.93 g/cm^3),and a purity exceeding 99%, in accordance with US2052. The investigation involved samples subjected to irradiation at room temperature, utilizing a Co-60 source with an activity of 1.8627Gy/s at the Irradiation Center of the Institute of Radiation Problems. The samples underwent irradiation at different doses, including 50 kGy, 150 kGy, 0.5 MGy and 1.5 MGy. In the initial phase of the presented study, experiments were carried out employing the "Perkin Elmer" STA 6000 apparatus. The operational temperature span of the "Perkin Elmer" STA 6000 apparatus ranges from 290 K to 1273 K, and a uniform heating rate of 5 K/min was applied across all experiments. Separate experiments were conducted for each sample both before and after gamma irradiation, with subsequent comparisons drawn between the results. The determination of kinetic parameters was carried out utilizing the "Pyris Manager" software. Nitrogen gas was employed to eliminate combustion products from the system and prevent the condensation process. It was introduced into the system at a rate of 20 ml/min. In the experimental setup, a standard pan made of aluminum oxide, weighing 177.78 mg, was utilized. The electron recording device, situated on the thermocouple, automatically records the sample mass with a precision of 10^{-6} g. All values obtained during the experiments, as well as those calculated theoretically, were graphically represented using the 'OriginPro 9.0' software.

3. Results and discussion

The presented study investigates nanocrystalline TiC particles before and after gamma irradiation, examining both melting and cooling processes within the temperature range of 300 K to 1200 K. The enthalpy and entropy of nanocrystalline TiC particles were theoretically calculated based on the experimental results obtained. Figure 1 illustrates spectra corresponding to gamma irradiation, depicting the initial state (c.s.) and the condition following a dose of 1.5 MGy. The temperature-dependent dependencies of entropy and enthalpy for nanocrystalline TiC particles before and after gamma irradiation during the melting processes are depicted in figure1. As indicated by the figure, the absolute value of enthalpy consistently decreases proportionally with the gamma irradiation dose across the entire temperature range (figure 1). However, in the melting process, the enthalpy exhibits a direct proportionality to temperature both before and after gamma irradiation.

The calculated entropy of nanocrystalline TiC particles exhibited a parallel behavior to enthalpy, as observed in the experimental results. As seen from the temperature dependence of the of the entropy of the system, the entropy of the system decreases with an increase in the dose of gamma radiation, following the trend observed in enthalpy. An analogous trend is observed in the temperature dependencies of tentropy and enthalpy of the system before and after gamma irradiation during the annealing process (figure 2). The temperature-dependent dependencies of entropy and enthalpy for nanocrystalline TiC particles before and after gamma irradiation during the cooling processes are depicted in figure 2.

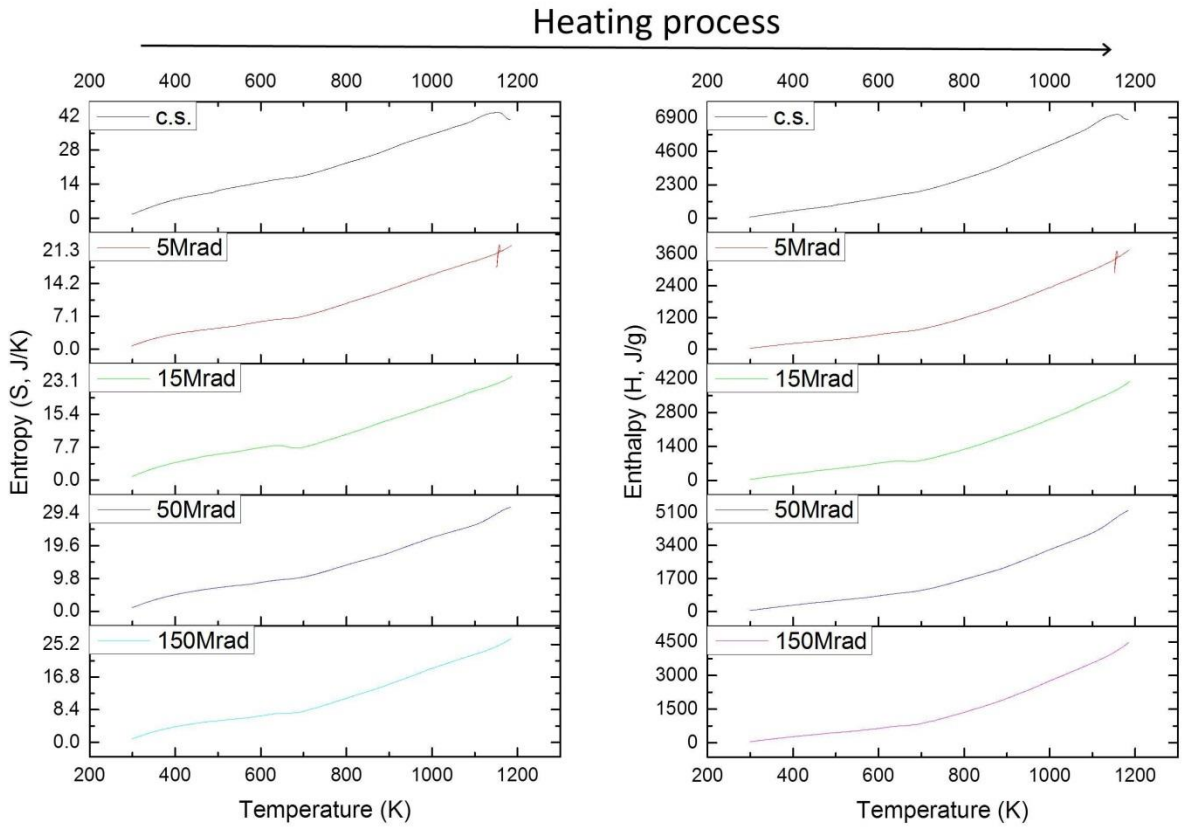

Figure 1. The temperature dependencies of entropy and enthalpy of nanocrystalline TiC particles before and after gamma irradiation in the heating process

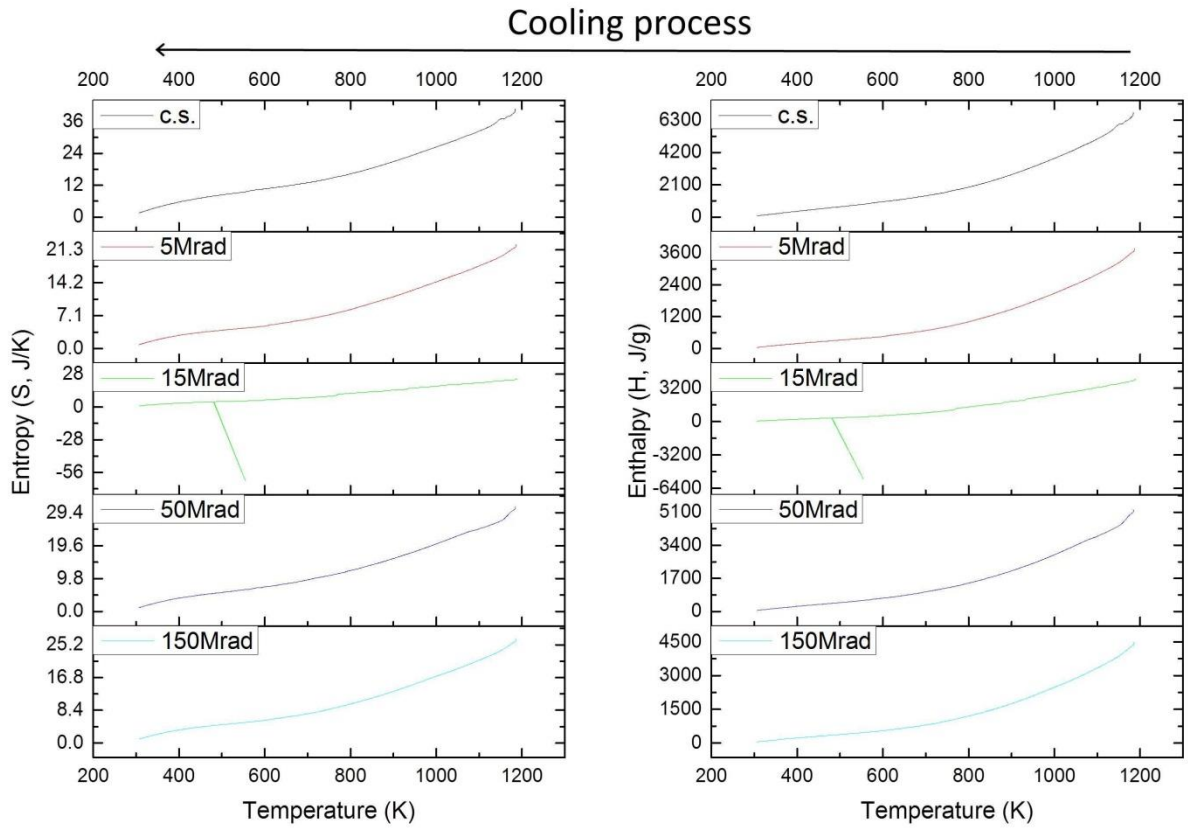

Figure 2. Temperature dependences of entropy and enthalpy of nanocrystalline TiC particles before and after gamma irradiation in the cooling process

The observed increase in the entropy and enthalpy of nanoparticles at temperatures above 600 K can be attributed to the influence of temperature on the oxidation process. The observed stabilization in mass at around 1000 K indicates a correlation with a phase transition occurring in the TiC_xO_{1-x} compound at this temperature [34-38]. Based on the experimental results, an analogy between the entropy and enthalpy has been observed in the designated system for nanocrystalline TiC particles. The system entropy has been observed to decrease with an increasing gamma radiation, corresponding to the temperature dependence of enthalpy.The potential phase transitions and amorphization in nanocrystalline TiC particles resulting from gamma irradiation can be explained with the assistance of Differential Thermal Analysis (DTA) spectra. The noted deviations in the spectra are commonly attributed to a slight amount of amorphization or the existence of stronger interactions with existing groups (such as OH groups or others) in the nanomaterial induced by gamma irradiation. Furthermore, no phase transition associated with the formation of TiC_xO_{1-x} compounds is observed in the nanomaterial within the temperature range of 1000-1200 K. It is crucial to acknowledge that accurate identification of the phase transition linked to the formation of TiC_xO_{1-x} compounds requires additional analytical experiments. The observed difference before and after heating in the 1000-1200 K range could serve as an alternative indicator of amorphization in the nanomaterial influenced by gamma irradiation. As evident from the cooling process, no additional groups depart from the nanomaterial across the entire temperature range. This suggests that the observed deviation in the 600-800 K range can be directly attributed to groups with stronger interactions. In other words, the variance in DTA spectra in the 600-800 K range cannot be attributed to the amorphization of the nanomaterial resulting from gamma irradiation.

4. Conclusion

The conducted experiments reveal that the oxidation process occurs in TiC nanocrystals within the temperature range of 600 K < T < 1200 K. A phase transition arising from oxidation was observed in the TiC_xO_{1-x} compound within the temperature range of 1000 K to 1200 K. It has been established that the entropy and enthalpy of nanocrystalline TiC particles exhibit a direct proportionality with temperature. The conducted research revealed that, across the entire temperature range, the enthalpy and entropy values of the system consistently remain positive.

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