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Thermodynamics kinetics of boron carbide under gamma irradiation dose

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In this paper, high purity boron carbide samples were irradiated by ^{60}Co gamma radioisotope source (0.27 Gy/s dose rate) with 50, 100, 150 and 200 irradiation hours at room-temperature. The unirradiated and irradiated boron carbide samples were heated from 30°C to 1000°C at a heating rate of 5°C/min under the argon gas atmosphere of flow rate 20 ml/min. Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) were carried out in order to understand the thermodynamic kinetics of boron

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carbide samples. The weight kinetics, activation energy and specific heat capacity of the unirradiated and irradiated boron carbide samples were examined in two parts, $T \leq 650°C$ and $T \geq 650°C$, according to the temperature. The dynamic of quantitative changes in both ranges is different depending on the irradiation time. While the phase transition of unirradiated boron carbide samples occurs at 902°C, this value shifts upto 940°C in irradiated samples depending on the irradiation time. The activation energy of the unirradiated boron carbide samples decreased from 214 to 46 J/mol in the result of 200 h gamma irradiation. The reduction of the activation energy after the irradiation compared to the initial state shows that the dielectric properties of the irradiated boron carbide samples have been improved. After the gamma irradiation, two energy barrier states depending on the absorption dose of samples were formed in the irradiated samples. The first and second energy barriers occurred in 0.56–0.80 and 0.23–0.36 eV energy intervals, respectively. The existence of two energy levels in the irradiated boron carbide indicates that the point defects are at deep levels, close to the valence band.

Keywords: Boron carbide; gamma irradiation; thermodynamics kinetics; heat flow rate; activation energy.

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1. Introduction

In recent years, there has been an increasing interest in boron compounds such as boron carbide, silicide hexaboride and boron nitride. Boron carbide compounds have been widely used in nuclear technology due to its low density, high melting temperature and high neutron absorption cross-section of the boron isotope ^{10}B.[1–7] Boron carbide materials have extremely good hardness, high mechanical properties, and also highly resistant to chemicals.[8,9] Boron carbide compounds are widely used in advanced technology such as neutron absorber and ballistic armor materials.[10–15] Boron carbide compounds retain its basic structure when formed in interaction with a different energetic neutron flow in processes.[16,17] Boron carbide compounds have the ability to repair the radiation defects when interactions with ionizing radiation at low- and high-temperatures in the structure.[18] Different boron compounds have been formed to improve the thermal stability of boron carbide compounds.[19,22] Depending on the external factors, the amorphization of the boron carbide changes the structures in the small parameters. This makes some changes to the properties of the compound. Gamma irradiation is applied to determine the change mechanism of the structural parameters of boron compounds. Although boron carbide composites were studied in the literature, the detailed characterization regarding weight kinetics and heat flow rate of gamma-irradiated boron carbide samples is quite limited. In this work, it is believed that the thermodynamic characterization of boron carbide samples after gamma irradiation will be helpful to understand the process of the thermodynamics properties of gamma-irradiated boron carbide. In this study, the high purity boron carbide samples were irradiated by ^{60}Co gamma radioisotope at different irradiation times. The weight kinetics depending on temperature, activation energy, specific heat capacity, oxidation rate and weight loss of unirradiated and irradiated boron carbide samples are investigated. The weight

kinetics and heat flow rate characterization of boron carbide samples are carried out using Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC).

2. Experimental

Boron carbide (B_4C) compound with a density of 1.8 g/cm^3 (bulk density), particle size 3 μm and a purity of 99.9% (US Research Nanomaterial, Inc., TX, USA) was used in the experiment. The properties of boron carbide samples can be seen in Table 1. Boron carbide samples were irradiated with ^{60}Co gamma source with energies of 1.17 and 1.33 MeV at different irradiation times (50, 100, 150, 200 h) dose rate $D = 0.27$ Gy/s under the statistical conditions (at room-temperature and atmospheric pressure) at a K-25 radiation-chemical facility in High Technologies Centre, Azerbaijan National Academy of Sciences. The thermophysical properties were carried out in the temperature range of 30–1000°C at a heating rate of 5°C/min under the argon atmosphere at flow rate 20 ml/min using the STA 6000 Simultaneous Thermal Analyzer manufactured by Perkin Elmer. The error of weight and heat flow rate kinetics did not exceed 1.5% at 300°C, and 1% at 1000°C, respectively. After heating the boron carbide samples, the cooling process was achieved using the PolyScience analyzer and cooling system and digital temperature controller.[16,17,23–26]

Table 1. Chemical composition.

Boron carbide (3 μm)									
Purity 99.9%		Density 1.8 g/cm^3		Specific surface area 2–4 m^2/g			Making method plasma CVD		
Atom	B	C	N	O	Ca	Al	Fe	Na	Mg
wt.%	77.5	22.4	<0.001	<0.04	<0.002	<0.001	<0.001	<0.001	<0.001

3. Result and Discussions

Boron carbide samples were heated from 30°C to 1000°C at a heating rate of 5°C/min under the argon gas atmosphere of flow rate 20 ml/min. The weight kinetics and heat flow rate of unirradiated boron carbide samples are shown in Fig. 1. The weight kinetics and heat flow rate of unirradiated boron carbide samples were divided into four and five regions, respectively. The regions for weight kinetics and heat flow rate are as follows:

For weight;

- $30 \leq T \leq 110$°C intensity decrease range
- $110 \leq T \leq 623$°C decrease range
- $623 \leq T \leq 674$°C constant range
- $674 \leq T \leq 950$°C increase range (oxidation reaction).

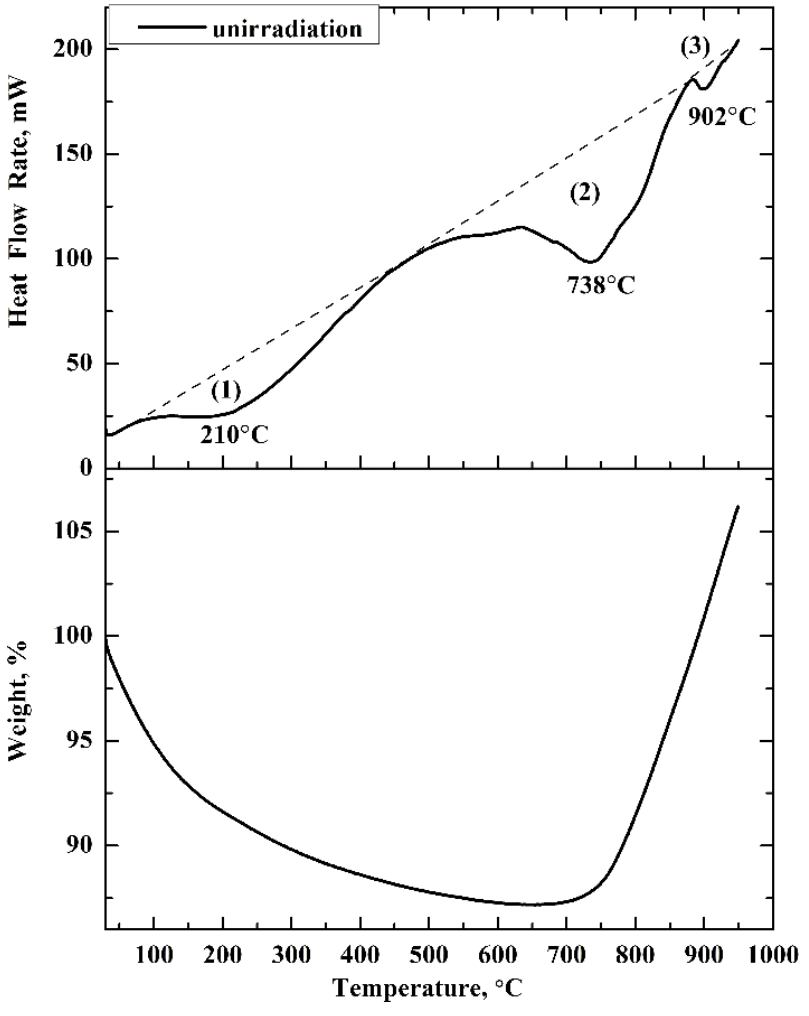

Fig. 1. Weight and heat flow rate kinetics of unirradiated boron carbide samples depending on temperature.

For heat flow;

- $30 \leq T \leq 95°C$ small endoeffect
- $95 \leq T \leq 530°C$ expanded endoeffect
- $530 \leq T \leq 632°C$ small phase transition
- $632 \leq T \leq 883°C$ oxidation reaction
- $883 \leq T \leq 930°C$ phase transition.

All thermophysical parameters were calculated based on the heat flow rate. The weight kinetics of unirradiated boron carbide samples upto $T \leq 623°C$ have been divided into two parts: decreasing rapidly to $T \leq 110°C$, and comparatively slightly

Table 2. Thermophysical parameters of boron carbide $T \leq 631°C$ temperature range (part 1).

Irradiation time (h)	Activation energy (J/mol)	Energy of area (J)	Specific heat capacity (J/g·°C)	Weight loss (%)
Unirradiation	2186	41.8	19.5	11.3
50	2130	39.7	17.9	1.7
100	2062	37.6	16.4	2.4
150	1947	36.9	14.2	3.1
200	1858	35.5	12.2	9.1

decreasing to $110 \leq T \leq 623°C$. The average weight loss ratio for each part is 11.3%. In experimental studies conducted in the vacuum atmosphere, the weight reduction and oxidation of samples have small values.[27–29] While the weight kinetics of boron carbide samples decreased sharply at the temperature range of $30 \leq T \leq 110°C$, the heat flow rate showed a tendency to increase slowly. As can be seen from Fig. 1, it can be mentioned that there is an inverse relationship between the weight kinetics and the heat flow rate of unirradiated boron carbide samples in the range of $T \leq 623°C$. The weight of the unirradiated boron carbide samples has shown an increase of 10% in the temperature range of $674 \leq T \leq 950°C$. This increase is based on the occurrence of the oxidizing of boron carbide due to the chemical reaction between B_4C and oxygen at the interface of B_4C/B_2O_3. Oxidation mechanism with temperature effect is applied in ceramics and their various combinations.[27] For $674 \leq T \leq 950°C$ temperature interval where the oxidation reaction took place, the overall effect width was calculated to be 72.7 mW, which this value is the maximum value taken for the unirradiated material. The large effect depth indicates that the oxidation reaction occurred in the range of $650 \leq T \leq 950°C$. At the same time, the central peak in the heat flow slope is an inherent structural transition with the nature of phase transition decreasing at 902°C. This internal phase transition is also confirmed by a lack of change in weight kinetics graphic, which can be seen in Fig. 1. After the irradiation of the boron carbide samples, the internal phase transition of the boron carbide changes depending on the irradiation time. Figure 2 shows weight kinetics and heat flow rate of irradiated boron carbide samples at different irradiation times (50, 100, 150 and 200 h) depending on temperature. The weight kinetics of 50 h irradiated samples showed that two stages decline at the temperature range of $30 \leq T \leq 631°C$. The total weight loss at this range was calculated to be 1.7%. The first small effect in linear decrease was observed in the range of $30 \leq T \leq 88°C$ and the central peak was at 43°C. The second effect occurred in the central peak 224°C and its width at 87 mW of heat flow slope. Table 1 (part 1) shows the values of activation energy, specific heat capacity, the energy of area and weight loss for all unirradiated and irradiated boron carbide samples in the temperature range of $T \leq 631°C$. The weight increase of 50 h irradiated boron carbide samples was determined at 9% due to the oxidation reaction in the temperature range of $686 \leq T \leq 950°C$. The width of endoeffect

was calculated to be 103 mW in this range. For the irradiated samples (50 h), the phase transition was observed at 933°C. In Fig. 2, other phase transition values can be also shown for different irradiation times. Thermophysical parameters (activation energy, energy of area, specific heat capacity and oxidation reaction)

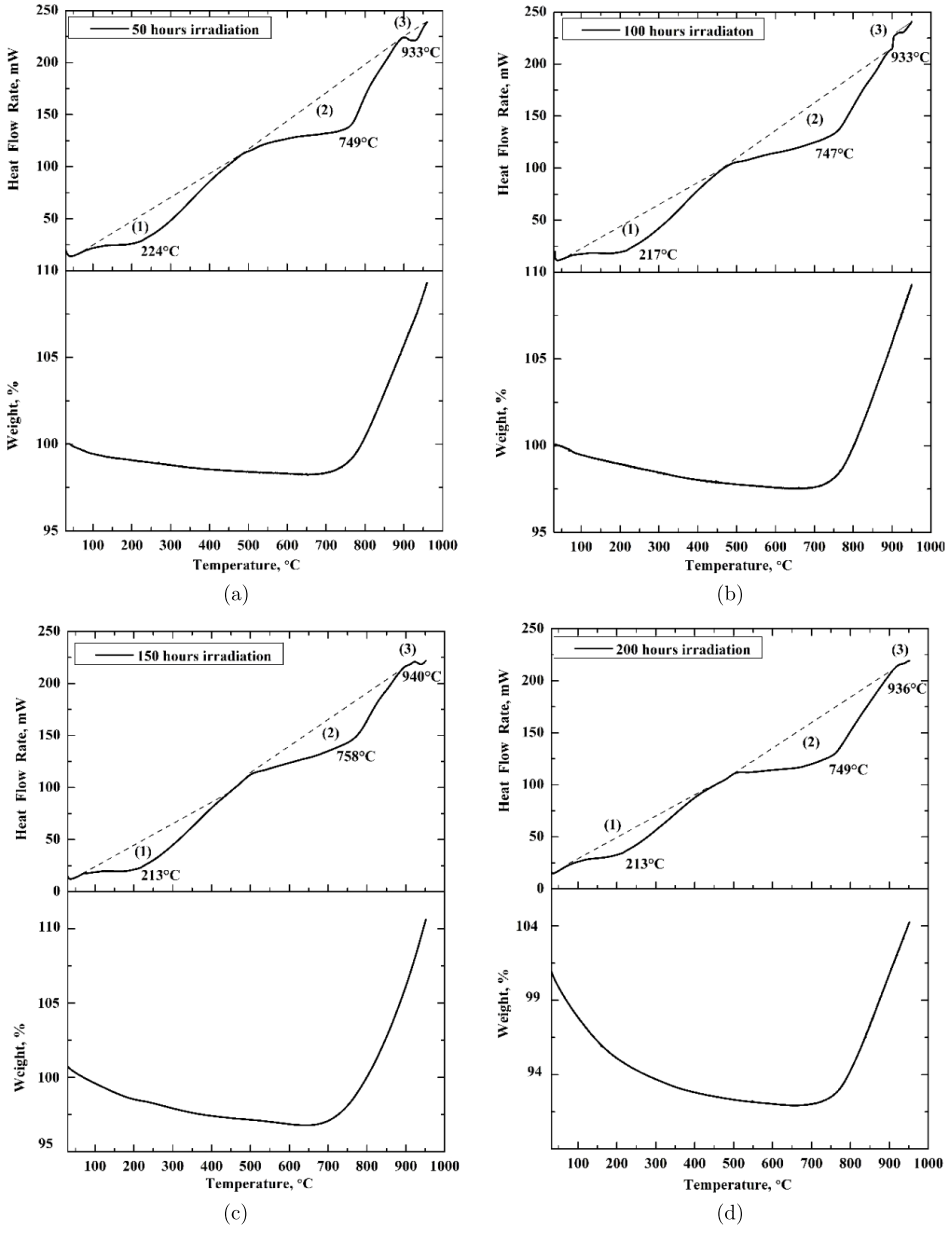

Fig. 2. Weight and heat flow rate kinetics of irradiated boron carbide samples with (a) 50 h, (b) 100 h, (c) 150 h, (d) 200 h irradiation time depending on temperature.

Table 3. Thermophysical parameters of boron carbide $T \geq 631°C$ temperature range (part 2).

Irradiation time (h)	Activation energy (J/mol)	Energy of area (J)	Specific heat capacity (J/g·°C)	Oxidation weight (%)
Unirradiation	3918	58.3	29.6	10
50	3817	53.4	26.5	9
100	3336	49.3	24.7	10.5
150	3218	48.6	22.9	10
200	3156	47.4	21.4	12

Table 4. Thermophysical parameters of phase transition in the boron carbide $903 \leq T \leq 940°C$ temperature range (part 3).

Irradiation time (h)	Activation energy (J/mol)	Energy of area (J)	Specific heat capacity (J/g·°C)
Unirradiation	196.4	2.81	7.26
50	185.6	2.62	7.06
100	152.4	2.33	6.45
150	97.4	2.02	6.05
200	46.8	1.86	5.97

for unirradiated and irradiated boron carbide samples upto 940°C are shown in Tables 3 and 4. The weight kinetics were examined for the irradiated and unirradiated materials as shown in the following. The weight kinetics were divided into two and three parts, for upto 150 h and in 200 h of irradiation, respectively. The weight kinetics of the irradiated samples for different irradiation time in the decreasing regions pass to the steady state at different temperatures, which vary from 547°C to 631°C. This temperature interval is a thermal stable region for irradiated boron carbide samples. The maximum decrease in the stable weight interval of the unirradiated boron carbide samples was 11.3%. The weight loss of the irradiated samples was obtained as 1.7%, 2.4%, 3.1% and 9.1% for 50, 100, 150 and 200 h irradiation time, respectively. The calculations show that the weight loss of irradiated boron carbide samples has increased 5.35 folds with increasing irradiation time (from 50 to 200 h) in $T \leq 650°C$. The effect of temperature and gamma irradiation time on the oxidation mechanism in weight kinetics of the boron carbide is quite a complex process. However, the activation energy, energy field and decreasing and increasing effects of a portion of the mass give a good opinion in order to understand the nature of the mechanisms of boron carbide associated with gamma irradiation. For this reason, it should be noted that experimental data were not obtained during gamma irradiation. However, measurements were carried out after irradiation at room-temperature. The energy of the area of irradiated specimens was examined in the two regions according to the temperature. The calculations showed that for $T \geq 650°C$, the energy area of irradiated materials increased 1.56 times. It also increased 1.85 times for $T \leq 650°C$ because of 200 h of irradiation. The activation energy of the endoeffects that produced $T \leq 650°C$ of the irradiated samples at

different irradiation times decreased 4.4 times and the specific heat capacity felt down by 1.58 times. As a result of the irradiation of the materials, it can be concluded that the activation energy is reduced and the irradiated samples have better dielectric properties after gamma irradiation. For $T \geq 650°C$, the activation energy and specific heat capacity for unirradiated boron carbide samples decreased 3.1 and 2.66 times, respectively. Depending on the irradiation time of irradiated boron carbide samples, the internal phase transition temperature of boron carbide samples changes upto from 902°C to 940°C. The degradation of thermophysical properties is based on the internal phase transition, activation energy and specific heat capacity of the irradiated boron carbide samples. During this process, the activation energy and specific heat capacity of irradiated materials decreased 4.65 and 4.01 times, respectively, compared to the unirradiated boron carbide samples. Experimentally, there are many sub-lattice structures in the boron carbide and these structures are greatly degraded by gamma rays. The weight kinetics of boron carbide have been given using the approach by Arrhenius for $T \geq 650°C$ temperature interval. The energy area of irradiated boron carbide samples was decreased with increasing irradiation time. The weight kinetics in the graphs are located in a linear fall zone of the mass and can be explained by two approaches. Firstly, when boron carbide samples are cooled, surface defects and active centers are formed. These active centers on the surface are more active than the active centers at the depths. It can be said that the kinetically active surface in weak interaction from the environment with the water vapor undergoes reaction in the region upto 150°C linear decrease and this reaction is called chemisorption. Secondly, a defect concentration depends on the absorption dose of the gamma irradiation. Therefore, an increase in the gamma absorption dose leads to an increase in the defect concentration. In addition, depending on the temperature, the recombination of the defects will have a different value. Using the Arrhenius approach, the energy of active centers in two energy levels for unirradiated and irradiated samples relevant to absorption dose was determined. At high-temperatures, point defects migrate within the solid. The diffusion of the defects can be expressed as thermally activated splashes of atoms from one crystal lattice structure to another lattice site. Boron carbide samples, which are gamma irradiated with different irradiation doses, formed two different energy levels. Defects were determined between 0.56 and 0.80 eV in the first energy case and in the second case 0.23 and 0.36 eV. In Fig. 3, depending on the irradiation process of the materials, the defects at the energy levels of 0.23–0.36 eV shift to the upper values of the temperature and this difference is 300 K between the irradiated and unirradiated boron carbide samples. The change in the energy level of the boron carbide samples after irradiation is the result of experimentally settling the point defects in the sample to smaller energy levels and being closer to the conductive area. Under the influence of gamma radiation, energetic transitions in boron carbide are directly proportional to temperature. The linear reduction of kinetic parameters in the same kind of phase transition depending on the radiation duration is a result of not distributing the temperature equally to all atoms accord-

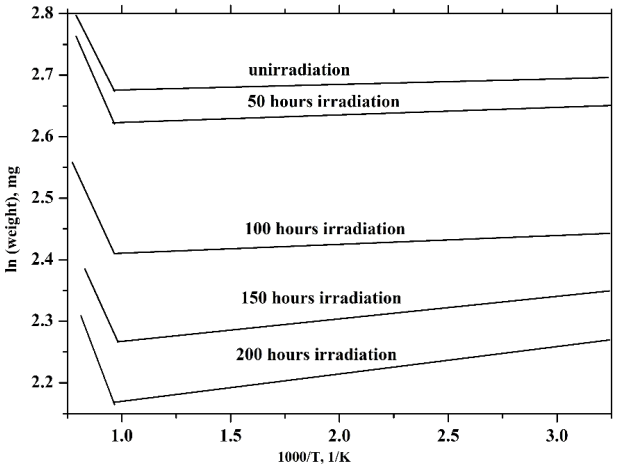

Fig. 3. Arrhenius plots of the unirradiation and irradiated boron carbide samples.

ing to Fermi–Dirac statistics. Experimental results showed that the weight kinetic and heat flow rate of boron carbide were faster at low-temperatures and slower at high-temperatures.

4. Conclusions

TG and DSC were carried out in order to understand the behaviors of the thermodynamic kinetics of boron carbide samples. All thermophysical parameters were determined based on the heat flow rate. The weight kinetics of unirradiated boron carbide samples were investigated in the two temperature intervals as $T \leq 623°C$ and $674 \leq T \leq 950°C$. The inverse relationship is obtained between the weight kinetics and heat flow rate for unirradiated boron carbide samples in the range of $T \leq 623°C$. The weight loss was observed in this temperature interval due to chemisorption reactions. The weight loss was obtained around 11.3% for unirradiated samples. In addition, the weight loss of irradiated boron carbide samples increased upto 9.1% with increasing irradiation time. On the other hand, the weight of the unirradiated boron carbide samples showed an increase of 10% in the temperature range of $674 \leq T \leq 950°C$. This value reached 12% of the maximum with 200 h gamma-irradiated boron carbide samples. It is considered that this increase is dependent on the occurrence of the oxidizing of boron carbide due to the chemical reaction between B_4C and oxygen at the interface of B_4C/B_2O_3. The experimental results showed that the activation energy of the irradiated boron carbide samples decreased 4.65 times compared to the initial state in the result of 200 h gamma irradiation. It can be concluded that the dielectric properties of the irradiated boron carbide samples have been improved after gamma irradiation. The specific heat capacity and energy of area in irradiated boron carbide samples increased with increasing irradiation time and temperature. The phase transition of unirradiated

boron carbide sample was determined to be 902°C. Depending on the irradiation time of irradiated boron carbide samples, the phase transition temperature of irradiated boron carbide samples ranges from 933°C to 940°C. After the gamma irradiation, two energy barriers are formed in the irradiated samples depending on the absorption dose of the samples. The first and second energy barriers emerged at 0.56–0.80 and 0.23–0.36 eV energy ranges, respectively. The presence of two energy levels in the irradiated boron carbide indicates that the point defects are close to the valence band at deep levels.

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