CHARACTERISATION OF SIC ELECTRON BEAM IRRADIATED

Yusof Abdullah[1], Mohd Reusmaazran Yusof[1], Megat Harun Al Rashid Megat Ahmad[1], Hafizal Yazid[1], Abdul Aziz Mohamed[2] and Nurazila Mat Zali[1]

[1]*Malaysian Nuclear Agency, Bangi, 43000 Kajang Selangor, Malaysia*

[2]*Universiti Tenaga National (UNITEN), Kajang, Selangor, Malaysia*

yusofabd@nuclearmalaysia.gov.my

ABSTRACT

SiC possesses great potential as a structural or semiconductor material under radiation settings, due to the fact that it has excellent high temperature properties, radiation resistance and chemical stability. The exposure of SiC to radiation causes atomic scale defects via the displacement and the ionizations of target atoms, induced by incident energetic particles. In this work, SiC powder was pressed to form pellets, and was in turn sintered at a heating rate of 6 °C/min to 1400 °C for 2 hours. For irradiation testing, SiC pellets were irradiated (EPS-3000, 3.0 MeV, 10 mA) at a speed of 1.11 ms^{-1}, and total radiation dosage of 200 kGy. After irradiation, the pellets were allowed to cool and sent for morphological analysis using the scanning electron microscopy (SEM) and atomic force microscopy (AFM), X-ray diffraction (XRD) for phase identification, hardness test and thermal expansion characteristics up to 500 °C. The results show that the hardness for post-irradiated samples are capable of withstanding loads of (122.5 HVF), compared to unirradiated samples (118.7 HVF). The amorphous content of the samples increases after irradiation, however, other trace element or phase composition changes were undetected. The results show that the surface roughness of the irradiated samples increased. Furthermore, the morphological analysis of the identified irradiated sample detected the diffusion of surface particles, which was assumed to be the factor that caused the enhancement of the hardness and thermal expansion coefficient.

ABSTRAK

SiC mempunyai potensi besar sebagai bahan struktur atau semikonduktor di bawah tetapan radiasi, kerana ia mempunyai sifat suhu tinggi yang sangat baik, rintangan radiasi dan kestabilan kimia. Pendedahan SiC ke radiasi menyebabkan kecacatan skala atom melalui anjakan dan ionisasi atom sasaran, disebabkan oleh zarah-zarah bertenaga yang bertenaga. Dalam kerja ini, serbuk SiC ditekan untuk membentuk pelet, dan kemudian disinter pada kadar pemanasan 6 ° C / min hingga 1400 ° C selama 2 jam. Untuk ujian penyinaran, pelet SiC telah disinari (EPS-3000, 3.0 MeV, 10 mA) pada kelajuan 1.11 ms-1, dan jumlah dos radiasi sebanyak 200 kGy. Selepas penyinaran, pelet dibenarkan untuk menyejuk dan dihantar untuk analisis morfologi menggunakan mikroskop elektron pengimbasan (SEM) dan mikroskopi daya atom (AFM), X-ray difraksi (XRD) untuk pengenalan fasa, ujian kekerasan dan ciri pengembangan haba sehingga 500 ° C. Keputusan menunjukkan bahawa kekerasan bagi sampel selepas penyinaran mampu menampung beban (122.5 HVF), berbanding dengan sampel tidak beriregrasi (118.7 HVF). Kandungan amorf sampel meningkat selepas penyinaran, bagaimanapun, unsur surih atau perubahan komposisi fasa tidak dapat dikesan. Keputusan menunjukkan bahawa kekasaran permukaan sampel yang diserap meningkat. Di samping itu, analisis morfologi sampel yang disiradiasi mengesan penyebaran zarah permukaan, yang dianggap sebagai faktor yang menyebabkan peningkatan kekerasan dan pekali pengembangan haba.

Keywords: Silicon carbide; Irradiation; Electron beam; Morphology; Thermal expansion

INTRODUCTION

SiC is a potentially suitable material for functional and semiconductor purposes under radiation settings, due to the fact that it possesses excellent high temperature properties, radiation resistance and chemical stability. The exposure of SiC under radiation conditions produces atomic-scale defects via displacement and ionizations of the target atoms; induced by incident energetic particles (Bardeleben et al., 2000). Long-term operations under constant radiation lead to the amorphization of the samples via the accumulation of radiation-induced defects. This will inadvertently cause material degradation, and determine its ultimate performance (Tae Bae, 2006). Research in radiation effects on material is one of the important issues, especially in the context of developing materials for microelectronics devices and nuclear fusion reactors.

Previous studies proved the advantages of SiC over other materials for nuclear applications (Snead et al. 2011; Hermandez et al. 2011). The properties included excellent high-temperature properties, good corrosion resistance, low neutron absorption cross-section, and stability under neutron irradiation. Moreover, the low neutron induced radioactivity inherent to SiC offers economic and potential maintenance benefits. It was found that the degradation of the material is lower for higher irradiation temperatures, indicating that the induced damage is efficiently annealed during irradiation. The hardness of ceramic materials is a property that is of substantial importance, as it is related to the ability of the material to withstand surface penetration via a combination of brittle fracture and plastic flow.

EXPERIMENTAL WORKS

SiC powders were compacted using 13-mm dies made of stainless steel, and pressed by a uniaxial hydraulic press. One metric tonne of pressure was applied on the powder in order to form a pellet with a thickness of about 2 mm. The pellets were then sintered at a rate of 6 °C/min, at a temperature of 1400 °C for 2 hours, and then allowed to cool at room temperature. The samples' characterization was carried to investigate the physical, mechanical and chemical properties of the samples. The characterization of the sample was done to identify phases, microstructure, surface topography, density, hardness and thermal expansion coefficients.

Meanwhile, the ALURTRON plant electron beam facility at the Malaysian Nuclear Agency (EPS 3000, Electron Processing System) was used to irradiate the samples. The electron beam processing facility comprises of an electron beam machine (accelerator) that provides fast irradiation processing with high efficiency and uniformity. The generated electrons are directed towards the target material to impart ionization, degradation, sterilization, irradiation, and radiation dose(s). Irradiation is controlled by regulating the irradiation time, and is evenly achieved over wide areas of materials at room temperature. The plant is equipped with electron beam machine, with a high-energy 1 MeV to 3 MeV, and a current of 0 to 30 mA. In this experiment, irradiation was operated at 3 MeV, 10 mA, and the radiation dose was set at 200 kGray. For characterization purposes, the structural investigation of non-irradiated and irradiated samples was conducted using the X-ray Diffraction (XRD) to confirm their phase formation, while microstructural investigation was conducted using the Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

The particles size analysis is conducted in order to determine particle distribution for SiC powders. The as-received powder has an average particle size of 2.7 µm, as shown in Figure 1, and it is classified as fine powders. Furthermore, the bimodal peaks indicate that the SiC powder contains dual variety sizes and two means different volume sizes at 0.7 and 3.8 µm.

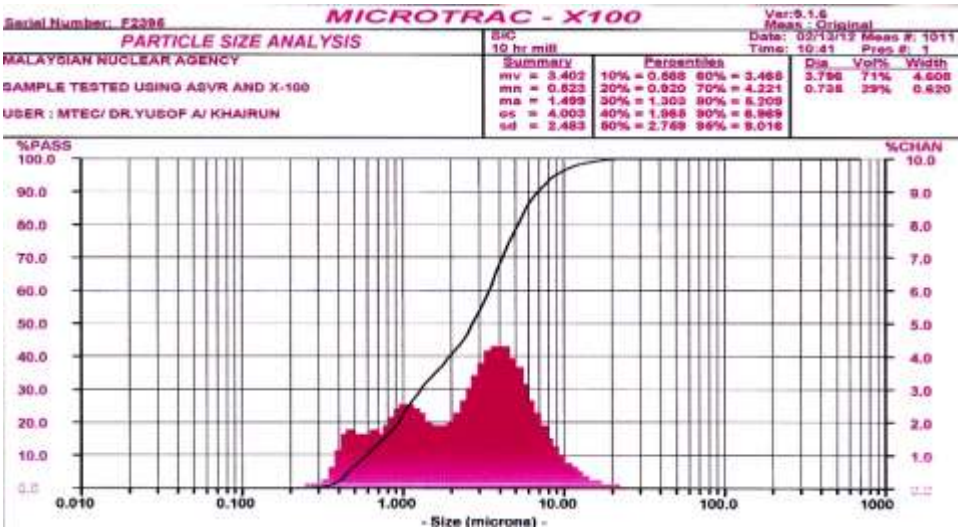

Figure 1: Particle size distribution of SiC after 10 hours mill

Figure 2 shows the XRD pattern of SiC powder pre and post-irradiation, respectively. Generally, both samples display the same XRD patterns. It was verified that the compound present in the samples are SiC. Clear evidence from the figure in which SiC peaks appeared at the 2θ angle are at 34, 37, 36, 60 and 72°. It is also recognized that the position of the peaks are analogous to previous studies, such as that conducted by Gosh and Paradhan (2009). However, the broadness and narrowness of the peaks are not clearly defined in the figure above. Some of the peaks become narrower, while other peaks broaden. These phenomena can be explained by the fact that the X-Ray Diffraction line is influenced by crystallite sizes and internal strains (Lemine, 2009). The results show that after irradiation, the diffraction peaks become broader, and the relative intensity decreases. This phenomenon occurred due to the reduction in crystallite sizes and increase in lattice strains, and the formation of defects during radiation exposure. It was believed that the reaction due to irradiation was assisted in the refinement of particle size, as the reaction is associated with fracture and the particle deformation process (Matsunaga et al., 1991). The fracture was caused by the collision between the incoming radiation and SiC particles, and the effect of this operational technique includes peak broadening of the XRD pattern, as the method introduces high density lattice imperfection.

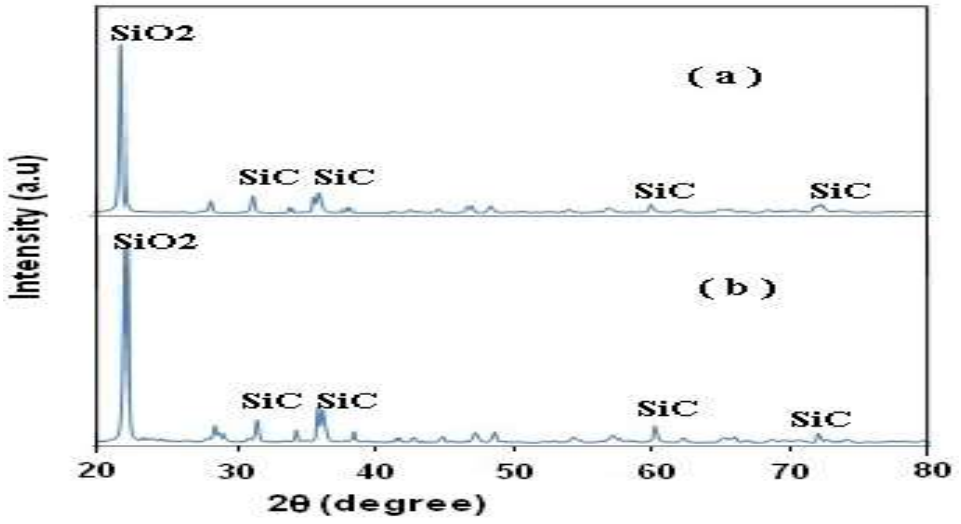

Figure 2: XRD pattern for SiC of a) 0 and b) 100kGy after sintered for set 2

The results presented in Figure 2 are of similar compounds produced in the 0 and 100 kGy samples. Two distinct compounds were detected and identified in the sample, which are SiO_2 and SiC. The SiC peaks are located at 34, 35, 36, 38, 60 and 72°. It was observed that the new formation of compound SiO_2 begin to appear after the sintering process. The presence of SiO_2 is verified using the Energy Dispersive X-ray spectroscopy (EDAX) analysis, which provides elemental maps shown in Figure 3. The existence of SiO_2 is associated with the oxidation of SiC ceramic. Gaseous impurities such as oxygen may be trapped in the powders during the processing, storage or handling stage. Since the size of the powder is categorized as fine, contamination is highly probable due to its large surface area providing a large contact point for impurities. Thus, gaseous impurities may form undesirable oxides at any stage of processing at relatively high temperatures, or get trapped inside porous materials.

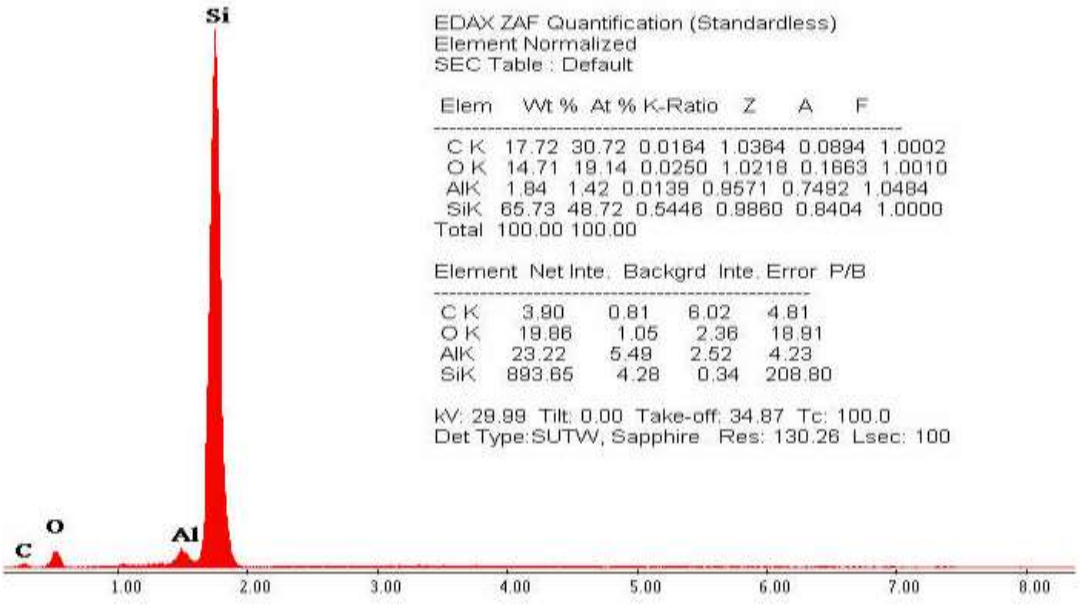

Figure 3: The spectrum of elements present in SiC sample by Energy Dispersive X-ray Spectroscopy (EDAX) analysis

Generally, the shifts in the XRD diffractogram are not observed for both samples. However, intensity reduction was detected for the irradiated sample, which means that after the electron beam are employed on samples, the intensity decreases, particularly for the SiC peaks. The intensity decrease implies a significant loss of crystallinity in the sample. The samples were found to be slightly amorphous, as inferred from the XRD results. The intensity's reduction might be the result of the formation of covalent structure of SiC that are sensitive to radiolysis defects, which controls properties such as conductivity and structure. These changes are noted to occur for low displacement damage to the samples (Hodgson et al., 2011).

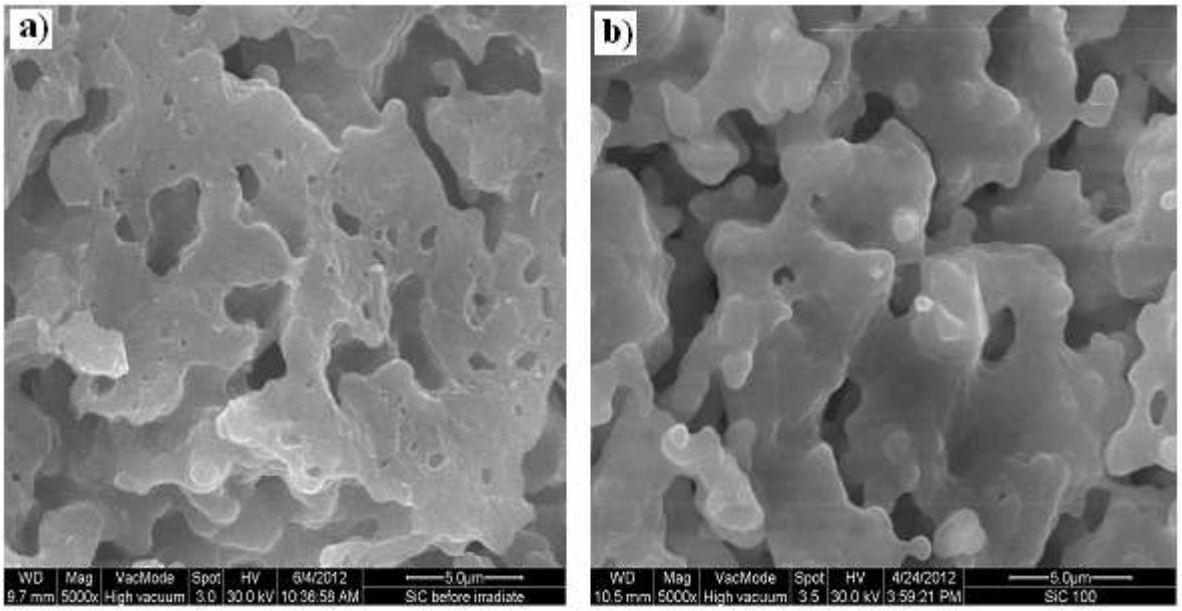

Figure 4: SEM image of SiC for set 2 upon 3 MeV elctron beam irradiation with a flux of a) 0 and b) 100kGy.

The effect of radiation on SiC includes the distortion of crystal sizes, porosity and bonding between the sample's particles. Figure 4 shows the SEM micrographs of unirradiated and electron-irradiated (100 kGy) samples, respectively, after irradiation at room temperature, in air. Unirradiated samples show larger grain sizes and fewer pores, compared to samples irradiated at a dose of 100 kGy. It was assumed that this was due to the atoms from the contacts diffusing into the SiC sample together with the radiation-matter interaction, and the resulting annealing effects that the sample underwent. It seems to be the melting formation for the surface morphology of the electron irradiated SiC sample. The results show the radiation damage due to ionizing effects. The irradiated sample showed that different microstructure behavior may be attributed to changes in the electronic structures by breaking the bond between Si and C atoms, which causes structural distortion derived from electronic excitation. Generally, the covalent nature of SiC makes it extremely sensitive to radiolysis and defects production by ionizing radiation. The XRD result also identified the volume of crystallinity for the unirradiated sample being reduced when it is electron-irradiate with a moderate dose.

The changes in the morphology are clearly seen in the irradiated sample, where there is the deposition of porous sponge on the surface of SiC. The product formed is identified as SiO_2, shown in Figure 3. Vlasova et al. (2009) has found that the formation of silica on SiC ceramic is due to the release of gaseous product via the layer of SiO_2 melt. It shows that the effect of energetic particles, such as electrons, may provide similar result as other types of radiation. It can be concluded that by inducing irradiation, it promotes high temperature and energy, which reforms the grain particles and particle mobility. According to Asaoka et al. (2001), the preferential displacement of carbon atoms and the formation of Si-Si direct bonding with the local crystal structure are still maintained. The irradiated area was slightly fragmented into nano-crystallite, and disoriented to one another. Furthermore, at the room temperature irradiation, the carbon atom must be preferentially displaced in SiC as the lighter elements and diffuse from the displaced area so that the residual Si atom can reconstruct the unsaturated bonds to form a small cluster. Meanwhile, the possibility of a reaction to what happened is the high speed of electron two times the mass of electron bombarded on samples. Since the sample was irradiated at high speeds and longer-timed electron exposure, it will inevitably lead to changes in morphology and structure. High energy induction provides high temperature and shatter particle bondings. Unirradiated sample is more porous compared to irradiated samples. Meanwhile, as the electron beam is imparted on the samples, the grain becomes larger and shuts the pore. The changes can be clearly spotted, since radiation is bombarded with high energy electron, meaning that the bonding between particles is improved and homogeneous. This is because energetic

particles promote high temperature, and provides heat and allow the diffusion of particles, which mechanical contacts induces neck growth, across which atomic bonding is developed. The grain size is increased by local diffusion around the particles' contact. Since the bombardment occurred twice, this means more heat and more diffusion around the particle contact results in larger grains. The effects of grain refinement on microstructural development become significant when the grain size approach the migration distance of a mobile point defect. Besides, as the grain diameter decrease, the total number of defect produced also decreased. The samples after irradiation become more compact after receiving more numbers of strikes. Thus, it can be concluded that 100 kGy electron irradiation sample may have better properties than the unirradiated sample. SEM morphology showed images of SiC (magnification 3000x) after irradiation, indicating better surface structure and even distribution compared before irradiation. The particle shapes of pre-irradiation are irregular, while post-irradiation, it is more spherical. The particle size gets smaller, and the porosity gradually gets smaller, thus resulting in better, smoother images. It was concluded that the radiation effect is the grain diffusing with its neighboring particles.

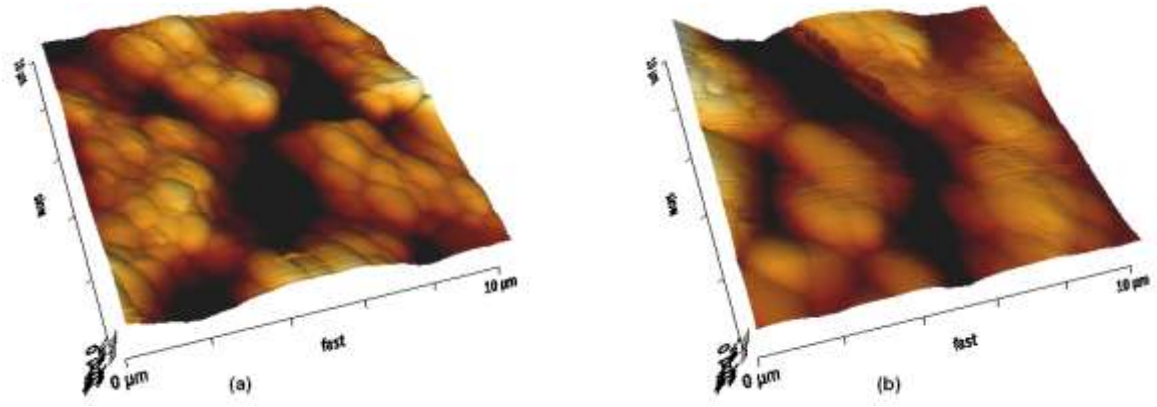

Figure 5: AFM image of SiC for set 1 upon electron beam irradiation with a flux of (a) 0 kGy, Ra= 188.6 nm and (b) 100kGy, Ra=396.4 nm.

The main reason for characterization by AFM is to observe the changes in surface roughness and topography, as shown in Figure 5. It is imperative to do so, due to the fact that surface roughness plays an important role in determining how a real object will interact with environment. For rough surfaces, it is usually associated with wear and tear, and possesses a high friction of coefficient than smooth surface. The performance of the materials can be predicted in terms of mechanical properties. The irregularities on the surface may form nucleation sites of crack or corrosion. The surface topography of SiC before and after electron-beam irradiation can be seen in Figure 4. The results clearly show that the surface roughness increases after irradiation. Hillocks are detected in the unirradiated sample, however, after 100 kGy electron beam irradiation, the number of hillocks decreases, while the surface roughness increased. The result agrees with previous studies, stating that hillocks are the effect of irradiation (Kim et al., 2008). The result reported as the electron beam dose is increased to 100kGy, the number of hillocks increases, which contradicts the obtained result (Kim et al., 2008). It can be concluded that the electron irradiation on SiC increases the surface roughness of the sample due to embedded structural modifications.

The result show that the thermal conductivity was 1.75 W/m.K after irradiation, compared to unirradiated samples (2.85 W/m.K). According to Harris (1995), SiC has high thermal conductivity (4 – 4.5 W/cm.K). This characteristic also allows SiC to be a good superconductor material. The conductivity of SiC in this study were lower, which might be due to the presence of impurities such as iron and chromium in the pellets.

Table 1: Thermal conductivity of SiC before and after irradiated

Sample	Thermal conductivity (W/m.K)
Before irradiate	2.85
After irradiated	1.75

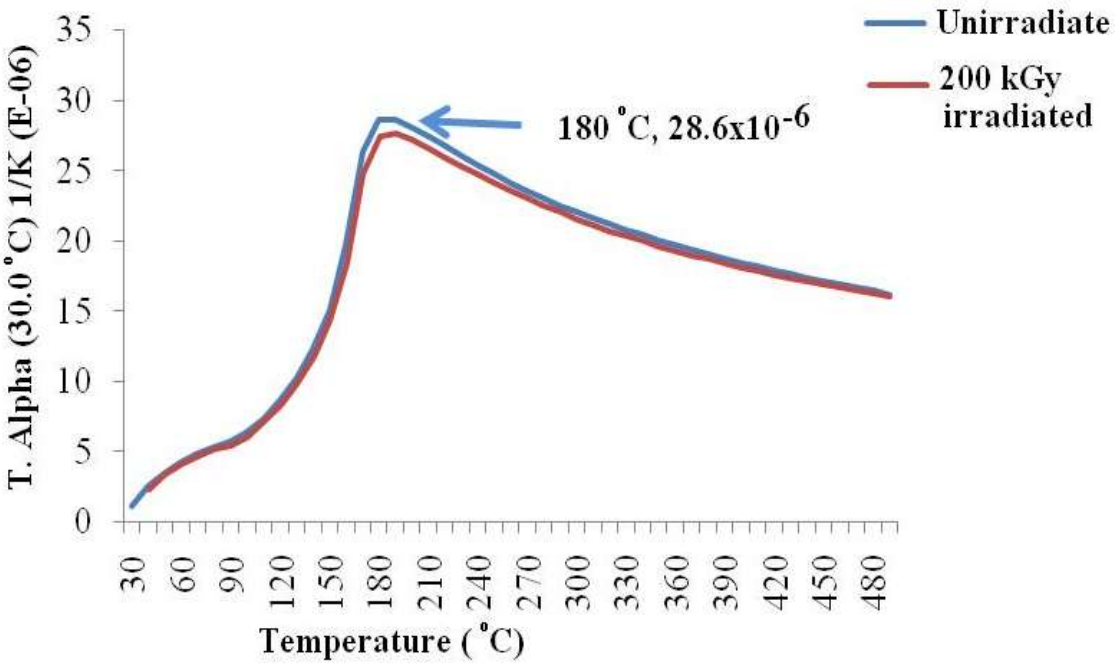

Figure 6: Thermal conductivity measurement of unirradiate and irradiated SiC samples

According to Arpon et al. (2003), the Coefficient of Thermal Expansion (CTE) over a wide temperature range was found to be directly proportional to the particle volume fraction. With varying temperature, the CTE characteristic of SiC is almost constant. Yang et al. (2006) arrived at the same conclusion in their study of the effects of particle size on CTEs of SiC/Al composites, and added that large-sized SiC particles play a more significant role in the decline compared to smaller-sized particles. Thermal expansion coefficient of unirradiated samples posses at maximum temperature 180°C, with a value of 28.6 x 10^{-6} / ^{0}C, and the value after exposure is 27.6 x 10^{-6} / ^{0}C, at a maximum temperature of 190°C (Figure 6). The theoretical value of CTE of SiC is 4.0x 10^{-6} / ^{0}C. Yang et al. (2006) also found that the decline of CTE was much more dependent on the large-size particles. Therefore, the value of CTE for unirradiated samples must have decreased the CTE after exposure.

Compared to the theoretical density, the results obtained are lower. However, the density before and after exposure was 2.49 g cm^{-3} and 2.63 g cm^{-3}, respectively (Figure 7a). After irradiation, the density of SiC increased due to the decreasing pore size of the samples post-irradiated.

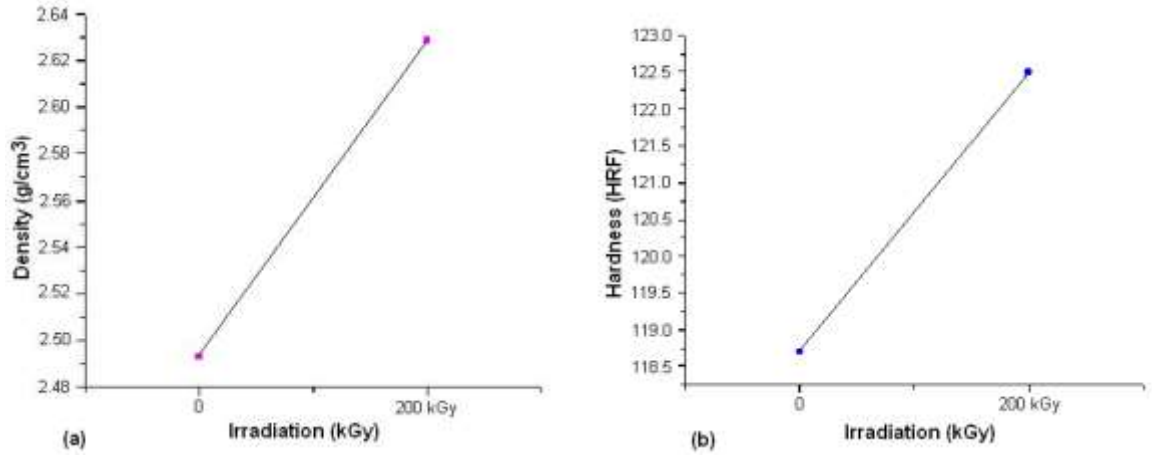

Figure 7: (a) Density of SiC versus radiation dose (b) Hardness of SiC versus radiation dose

Figure 7(b) indicated that the unirradiated SiC samples cannot withstand the load applied during the hardness test compared to post-irradiated samples. Post-irradiated samples are capable of withstanding higher loads (122.5 HVF) than unirradiated (118.7 HVF) samples. From microscopic observations, SiC before irradiation contain more pores. Pores reduce the strength of the ceramics because they reduce the cross-sectional areas, over which a load can be applied and, consequently, lower the stress that these materials can support. This result is parallel to the report by Ju Cheol Oh et al. (2003), who found that on the improvement of hardness and wear resistance in SiC/TiAlV surface composites fabricated by high energy electron beam irradiation, suggested high-energy electron beam irradiation was useful for the increased hardness and wear properties of surface composites.

CONCLUSIONS

Based on the present work, it can be concluded that the effect of electron irradiation changes the SiC's surface morphology and structural properties. It was found that the 200 kGy electron irradiation reduces the SiC crystallite size from 1098.25Å to 829Å. However, the crushing strength was slightly improved from 3696 kgf to 3703 kgf, while the density reduced from 2.4871 g/cm^3 to 2.6183 g/cm^3. Hardness of the samples before exposure was 119.3 HVF, compared to 122.5 HVF for irradiated samples.

ACKNOWLEDGEMENT

This work was supported by the International Atomic Energy Agency Coordinated Research Project (CRP) under IAEA-CRP No. 17087 and PQRD funds from Malaysian Nuclear Agency Project No. NM-R&D-11-20.

REFERENCES

Arpon, R., Molina, J., Saravanan,R. A., Garcia-Cordivilla, C., Louis, E. and Narciso, J., (2003). Thermal expansion behavior of aluminium/SiC composites with bimodal particle distributions, *Acta Materialia* 51: 3145-3156.

Asaoka, N., Muto, S. and Tanabe, T., (2001). Formation of SiC clusters in electron irradiation SiC studied by electron energy loss spectroscopy, *Diamond and Related Materials,* Vol. 10, Issue 3-7: 1251-1254.

Bardeleben, H. J., Contin, J. L., Vickridge, I. and Battistig, G., (2000). Proton Implantation induced defects in n-type 6H and 4H-SiC: An electron paramagnetic resonance study, *Physical Review B,* Vol.62(15): 10126-10134.

Gosh A. and Paradhan, S.K., (2009). Microstructural characterization of nanocrystalline SiC synthesized by high energy ball milling, *Journal of Alloys and Compounds*, vol. 486: 480-485.

Harris, G.L., (1995). *Properties of Silicon Carbide*, Short Run Press Ltd, United Kingdom.

Hermandez, T., Hodgson, E.R., Malo, M. and Morono, A., (2011). Irradiation induced electrical and microstructural degradation at high temperature for HP SiC, *Fusion Engineering and Design*, Vol. 86 (9-11): 2442-2445.

Hodgson, E.R., Malo, M., Manzana, J., Morona, A. and Hernandez, T., (2011). Radiation induced modification of electrical conductivity for three types of SiC, *Journal of Nuclear Materials,* Vol. 417: 421-424.

Ju Cheol Oh, Eunsub Yun, Mikhail G. Golkovski and Sunghak Lee., (2003). Improvement of hardness and Wear Resistance in SiC/Ti-6Al-4V Surface Composites Fabricated by High-Energy Electron Beam Irradiation, *Material Science & Engineering* A351: 98-108.

Kim, K.J., Choi, J., Lee, H., Lee, H.K., Kang, T.H., Han, Y.H., Lee, B.C. and Kim, S., (2008). Effect of 1 MeV electron beam irradiation on Multilayer Graphene Grown on 6H-SiC (0001), *Journal of Physical Chemistry,* Vol. 112(34): 13063-13064.

Lemine, O.M., (2009). Microstructural characterization of α-Fe_2O_3 nanoparticles using XRD line profile analysis, FE-SEM and F-TIR, *Superlattice and Microstructure,* Vol.45: 576-582.

Matsunaga, A., Kinoshita, C., Nakai, K. and Tomokiyo, Y., (1991). Irradiation induced crystal defects in silicon carbide, *Journal of Nuclear Materials,* Vol. 457: 179-181.

Snead, L.L., Nozawa, T., Ferraris, M., Katoh, Y., Shinavski, R. and Sawan, M., (2011). Silicon Carbide composites as fusion power reactor structural materials, *Journal of Nuclear Materials,* Vol. 417(1-3): 330-339.

Tae Bae, Manabu Ishimaru and Yoshihiko Hirotsu, (2006). Structural changes of SiC under electron beam irradiation: Temperature dependence. *Nuclear Instruments and Methods in Physics Research B, Vol. 250, Issue 1-2*: 315-319.

Vlasova, M., Marquez Aguilar, P.A., Resediz Gonzalez, M.C., Kakazey, M., Guzman, J., Bykov, A., Stersenka, V., Tomila, T. and Ragulya, A., (2009). Laser Irradiation of α-SiC ceramics, *Ceramic International,* Vol. 35(6): 2503-2508.

Yang, M.J., Zhang, D.M., Gu, X.F. and Zhang, L.M., (2006). Effects of SiC particle size on CTEs of SiC_p/Al composites by pulse electric sintering, *Materials Chemistry and Physics* 99: 170-173.