Raman Spectroscopic Investigation of Graphitization of Diamond during Spark Plasma Sintering of UO₂-Diamond Composite Nuclear Fuel

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Abstract

Micro-Raman spectroscopy (MRS) was utilized to investigate the graphitization of diamond particles within a UO₂-diamond composite processed by spark plasma sintering (SPS). While pure diamond gives a sharp Raman peak at 1331.6 cm⁻¹, the graphitized diamond shows broad peaks either at 1350cm⁻¹ (G-peak) or 1580cm⁻¹ (D-peak). The degree of graphitization was quantified by calculating the area beneath the diamond and graphite peaks. It was found that more than 20% of diamond was graphitized on the surface of the UO₂-diamond pellet and only around 10% diamond was graphitized in the interior regions of the pellet. This current study highlights the necessity to review the implications of these results carefully while implementing UO₂-diamond composite nuclear fuel.

Key Words

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1 Introduction

The development of enhanced thermal conductivity and accident tolerant fuels is a major priority in the nuclear industry. In an effort to increase the thermal conductivity of UO_2 , the concept of fabricating UO_2 -based composites by adding a high thermal conductivity second phase has been investigated in recent years. Many materials such as silicon carbide (SiC) [1], carbon nanotubes (CNT) [2] and diamond [3] have been investigated and high density composite pellets have been successfully fabricated utilizing a new sintering technique called spark plasma sintering (SPS). Among these materials, UO_2 -diamond composite pellets are of particular interest due to the extremely high thermal conductivity of diamond [4]. Nevertheless, stability of diamond particles and their properties during the SPS processing remains a concern. It is known that diamond is a metastable allotrope of carbon and it has a propensity to convert to graphite even under normal atmospheric conditions [5]. Although the conversion rate is negligible under room temperature, the rate is expected to increase by orders of magnitude under high temperatures [6]. In order to fulfill the density requirement of a nuclear fuel pellet (at least 96.5% of the theoretical density), a temperature of 1400°C or above is required for the processing of UO_2 -diamond composite pellets using SPS [3]. Under such high sintering temperatures, graphitization of

diamond is expected. The formation of graphite has a huge influence on the thermal and mechanical properties of the composite fuel and therefore, the understanding of graphitization of diamond in UO_2 -diamond composites is of considerable interest.

Due to superior thermal properties, diamond and diamond related materials have been used in many high temperature devices such as light emitters, high temperature electronics and micro-electromechanical systems (MEMS) [7]. In operation of a nuclear reactor, fuel pellets are subjected to high temperatures up to 1600°C [8]. The high temperature stability of diamond is also an important consideration in all these applications.

Micro-Raman spectroscopy (MRS) is a powerful technique for chemical analysis of **ceramics**. Utilizing MRS, phase transformation [9-11] in various ceramics have been effectively studied. Gogotsi et al. [10] characterized various phases of silicon (hexagonal phase, α phase, amorphous phase, etc.) in machined silicon thin films. Ghosh et al. [9] observed the amorphization of B_4C during indentation by the appearance of amorphous carbon peaks in the Raman spectrum. Jannotti et al. [11] studied the compositional change and found a so-called core-rim structure in reaction bonded B_4C ceramics. Diamond and graphite, both of which are also Raman active materials, can be characterized through MRS as well [12].

Unlike other characterization techniques such as X-ray diffraction (XRD), MRS can be used to analyze micro-scale features due to its high spatial resolution. Therefore, the purpose of this study was to utilize MRS and analyze

the phase transformation of diamond particles within a UO_2 -diamond composite pellet. We investigated whether diamond has undergone graphitization during high temperature processing of the composite by noting the appearance of graphitic peaks in the Raman spectra. A quantitative study on the degree of graphitization within the composite pellet was also conducted.

2 Experimental

2.1 UO_2 -diamond Pellet Fabrication

Figures 1(a) and 1(b) show SEM images of the as-received UO_2 and diamond powders, respectively. The uranium dioxide powder, supplied by AREVA Federal Services (Hanford, Washington, USA), was reported to have a mean particle diameter of $2.4\mu\text{m}$. The grain size was determined to be 200-400nm, see Fig.1. The diamond powder was obtained from Advanced Abrasives (Pennsauken, NJ, USA) and had a mean particle size of $3\mu\text{m}$.

Figure 1. SEM image of as-received (a) UO_2 powder and (b) diamond powder.

A SPEX-8000 shaker was used to blend UO_2 and a 5 vol% diamond powder for 1 hour with a blending aid (2,3-Dihydroperfluoropentane). The use of

a blending aid was proven to be effective in the uniform mixing of the two powders and non-contaminative to the final mixture. The mixture was dried in an oven at around 40°C for one hour [13]. Under current mixing/milling condition, a uniform distribution of diamond particles can be obtained [3]. The powder was placed in a graphite die and sintered using a Dr. Sinter® SPS-1030 spark plasma sintering (SPS) system at a maximum sintering temperature of 1400°C at a uniaxial pressure of 36MPa. The heating rate was 100°C/min. After holding for 5 minutes at the maximum sintering temperature, a programmed cooling rate of 100°C/min was applied and the uniaxial pressure was slowly released when the cooling process started. These sintering parameters were chosen in order to minimize the internal stress between UO₂ matrix and diamond particles and possible chemical reaction between UO₂ and diamond [3]. The sintered pellet had a diameter of 12.5 mm and a thickness of 3.5 mm, see Figure 2(a). A more detailed description of this method can be found elsewhere [1, 13-16].

2.2 Raman Spectroscopy

A Raman spectrometer (Renishaw Invia® model, Hoffman Estates, IL) with a 532nm laser was used. The spectral resolution of this system is 0.1 cm⁻¹ and the spatial resolution is 0.38 μm. In order to avoid the influence of laser heating and assure sample integrity, only 10% of the total laser power was used. A Si standard was used for calibration of peak position before testing the UO₂-diamond sample. The fabricated pellet was cut vertically and the cross-section of the pellet was polished by successive smaller grinding medium. Raman scanning

was performed at five locations (A-E) along the centerline of the pellet depicted in Figure 2(b).

Figure 2(a) UO_2 -diamond composite pellets sintered by SPS and (b) schematic showing the cross section of the pellet and the locations of Raman scanning.

3 Results and discussion

The spectrum of the as-received pure diamond powder is shown in Figure 3. Only a sharp peak centered at around $1331.6 \pm 0.3 \text{ cm}^{-1}$ is observed between 900 cm^{-1} to 1700 cm^{-1} range. It is well known that diamond has a triple degenerate peak at around 1332 cm^{-1} due to F_{2g} symmetry and the result here is in good agreement with other publications [17-19]. The spectrum of a pure UO_2 pellet sintered by SPS reveals only one broad characteristic UO_2 peak at around $1150 \pm 0.9 \text{ cm}^{-1}$ in the range of 900 cm^{-1} to 1700 cm^{-1} [20]. The presence of this characteristic peak indicated that no alteration of UO_2 occurred during SPS process.

Figure 3. Raman spectra of as-received diamond powder and pure UO_2 pellet prepared by SPS.

3.1 Characteristic Raman peaks in UO_2 -diamond composite

An image of location A (surface) in Figure 2(b) in the UO_2 -diamond composite is shown in Figure 4. The grey region is the UO_2 matrix while the dark regions are diamond particles. A random size Raman map scan of several tens of microns with a grid interval of $1\ \mu\text{m}$ was performed at this location. Raman spectra of all grids were obtained. Obviously some grids are on the UO_2 matrix and some grids are on the diamond particles. The spectra corresponding to diamond particles were then collected in order to study the phase change of diamond. In order to get sufficient data, several such map scans were performed

on the surface and around two hundred spectra were collected from diamond particles. Similar scans were performed on other locations of the pellet (Location B-E shown in Figure 2(b)).

Figure 4. Image of location A in a UO₂-diamond composite showing UO₂ matrix and diamond particles. The grids illustrate the region of Raman map scan performed on the surface.

It is found that all these scans can be classified into three major types as shown in Figure 5(a)-5(d). Only two peaks are observed in Figure 5(a). The sharp peak at around 1332cm^{-1} is the diamond peak and the broad peak at around 1150cm^{-1} is the UO₂ peak, as shown before. In Figure 5(b), not only the diamond peak, but also an additional peak at around 1580cm^{-1} is seen. This peak is a characteristic peak of graphite and is called G (graphite) peak [21]. In Figure 5(c)-5(d), another peak at around 1350cm^{-1} was also observed. It is also a characteristic peak of graphite which is called D (disordered graphite) peak [21].

The appearance of D peak and G peak clearly indicated that some diamond has been converted to graphite. It should be noted that a variability of UO_2 peak intensity was observed. However, there is no evidence showing a relationship between the UO_2 peak intensity and graphite D and G peaks. With the appearance and increase of D and G peaks, the UO_2 peak intensity could either decrease or increase, see Fig. 5(c) and Fig. 5(d). The variability of UO_2 peak intensity is simply due to the location of the laser beam during the Raman scan. Each point scan can only provide the surface information of a specific location with a spatial resolution of $0.38\text{ }\mu\text{m}$. For the locations where UO_2 dominates, a relatively large intensity of UO_2 peak was obtained. While for the locations where diamond dominates, a relative low intensity of UO_2 peak was obtained. Thus the peak intensity is simply dependent on the composition of the location where the laser was focused.

(b)

(c)

Figure 5. Typical Raman spectra of diamond in UO_2 -diamond composite showing (a) UO_2 and diamond peaks only, (b) UO_2 , diamond peak and graphite G-peak, and (c) (d) UO_2 , diamond peak and graphite G-peak and D-peak.

3.2 Quantification of graphitization of diamond

In order to investigate the degree of graphitization of diamond, a quantitative analysis was performed. Wang et al. [19] studied the relative intensities of diamond and graphite peaks in Raman spectroscopy and derived the following relationship

$$C_d = 100 A_d / (A_d + \frac{\sum A_i}{50}) \quad (1)$$

where C_d is the diamond purity, A_d is the area of the spectrum beneath the 1332cm^{-1} diamond peak and A_i are the areas of peaks corresponding to the graphitic bands. Ferreira et al. [22] later used Eq. (1) and studied the content of diamond film grown on a silicon substrate. Utilizing the method above, the content of diamond in UO_2 -diamond composite can be calculated. In this study, all peaks were curve-fit by mixed Gaussian and Lorentzian functions and the area beneath each peak was calculated using the software WiRE 3.4 supplied by the manufacturer of Renishaw spectrometer.

According to Eq. (1), C_d corresponds to diamond purity, any value less than 100% will imply graphitization. Therefore, we use $(1 - C_d)$ to indicate the content of graphite. It should be noted that the value of $(1 - C_d)$ from a single spectrum is not representative, as it only provides the information at a specific point (a diameter of $\sim 0.3\ \mu\text{m}$). Recall that around two hundred points were measured at each location along the centerline of the cross section shown in Fig. 2(b). It is indicated that within any region, some diamond particles have been fully transformed to graphite while some diamond particles are not graphitized at all. Thus, the values of $(1 - C_d)$ may vary from 0 to 1. For this reason, the degree of graphitization for each location was determined by averaging $(1 - C_d)$ of all spectra at that location on the cross section. The result is shown in Figure 6. It appears that at all measured locations within the pellet, more than 10% of the diamond has been transformed to graphite. However, a large difference in the degree of graphitization was observed between diamond particles on the surface and those within the interior of the pellet. On both top and bottom surfaces, around 22% of

the diamond was transformed to graphite, while in the interior of the pellet, only 12%-14% of diamond was transformed.

Figure 6. Degree of graphitization in UO_2 -diamond composite pellet. Location A & E correspond to the surface of the pellet and B, C, & D correspond to the interior of the pellet.

The graphitization of diamond has been a subject of interest since the 1960s. Davies and Evans [23] showed that under zero pressure and below 1500°C , the transformation of diamond to graphite was not detectable experimentally and the graphitization rate is relatively slow between 1500°C - 1960°C . Below 1900°C , only 5% of diamond was transformed after 40 minutes of exposure. Howes [24] also stated the rate of graphitization would not start to increase rapidly until 2100°C . In our study on SPS processed UO_2 -diamond composites, however, the graphitization of diamond did occur at a maximum

sintering temperature of only 1400°C and a significant amount of diamond has been transformed for a hold time as short as 5 minutes.

The reason for this difference could be explained by the nature of spark plasma sintering process. First of all, the programmed temperature of 1400°C is controlled by a pyrometer, which measures the temperature on the external surface of the graphite die during SPS but not directly on the powder being sintered inside the die. The die wall thickness is around 6 mm. There exist a temperature gradient between the surface of the die and the interior die surface and the temperature difference can be several hundred degrees [25]. Secondly, as UO_2 is a semiconductor, electric current still passes through the UO_2 powder compact during SPS and a significant Joule heat can be generated along the particle interfaces within the powder during the process. Therefore, the actual temperature in the powder being sintered can be significantly higher than 1400°C. Last but not the least, as a field assisted sintering method, the existence of electric field in SPS may also facilitate the phase transformation of diamond to graphite. Francis and Raj [26] observed the phase transformation phenomenon of tetragonal-stabilized zirconia during flash sintering and highlighted the effect of electrical field and current during the process. They stated that the electrical field provides the driving force for nucleation and the current facilitates the growth in phase transformation. But to the authors' knowledge, no literature has reported the effect of electrical field on graphitization of diamond and the assumption above cannot be verified yet. It should also be mentioned that unlike the zero pressure environment in literature [6] which discussed graphitization of diamond,

a uniaxial pressure of 36 MPa was applied during SPS. High pressure may retard the graphitization process based on the pressure-temperature phase diagram of carbon [27]. Davies and Evans [23] studied the transformation of diamond under 4.8 GPa and reported that compared to zero pressure environment, an increase of 90°C-130°C of temperature was required in order to achieve the same graphitization rate. However, the pressure in SPS is two orders of magnitude lower than the above value and hence the effect of pressure should be limited. Despite the above complexities in SPS, graphitization does occur under the current sintering conditions in SPS.

The large variation in the degree of graphitization of diamond within the pellet is also expected to be a result of SPS. Due to the low thermal conductivity of the UO_2 , the temperature on the top and bottom surfaces, which are in contact with the graphite punches, of the powder compact in the die, can be much higher than the temperature in the interior of the powder. Similar result was observed by Ge [14] in sintering of pure UO_2 using SPS where exaggerated grain growth occurred only on the very top surface of the pellet, due to higher temperature than the interior. Thus, it is clear that a temperature gradient existed within the powder compact during SPS. The top and bottom surface of the UO_2 -diamond composite do indeed experience higher temperature during SPS than the interior of the powder compact and give rise to a higher degree of graphitization of diamond. The severe graphitization will have a negative influence on the thermal and mechanical properties of the pellet. Therefore, it is important to carefully

consider the implications of these results on the use of UO₂-diamond composite fuel pellets in nuclear reactors.

4 Conclusion

Micro Raman spectroscopy was utilized to study the phase transformation in diamond particles within a UO₂-diamond composite fabricated by spark plasma sintering. The graphitization of diamond was observed at all locations along the centerline of the pellet. Quantitative analysis was performed to calculate the degree of graphitization. It was found that more than 20% of diamond was graphitized on the surface of the UO₂-diamond pellet and only around 10% diamond was graphitized in the interior regions of the pellet.

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