The Defect Structure Changes of Graphite Manufactured by Isostatic Molding Method under Ion Irradiation

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1. Introduction

The properties of graphite depend on micro- and macrostructure which are determined by method of graphite synthesis. The best properties possess graphite with isotropic macrostructure. In order to get isotropic microstructure the methods of isostatic pressing or molding are used in technology cycle. In previous paper a data for fine grained nuclear graphites IG-110 and IG-430 manufactured by the isostatic pressing method were presented [1]. The isostatic molding method is widely used in production of isotropic graphite because it's less laborious than method of isostatic pressing.

The ion irradiation effects on defect structure of graphite manufactured by isostatic molding method have been studied in this work.

1. Experimental

The isotropic graphite NBG-18 (from coal raw) and NBG-25 (from petroleum raw) manufactured by SGL, Germany as possible candidate graphite for HTGR were selected for study.

The graphite plates of dimensions (10×10×1) mm^3 were ultrasonic cleaned in acetone. All specimens were annealed after drying for 2 hours in air at 110 ^{0}C.

The Raman spectrums were recorded by a LabRamHR with a LN2 cooled CCD multichannel detector at room temperature in a conventional backscattering geometry. The spectrums were excited with the 514.5 nm line of an Ar-ion laser. The laser beam power was 2 mW on a specimen. The Raman parameters of the spectrum peaks were obtained by a Lorentzian fitting.

The ion irradiation was presented by 3 MeV carbon ions at a beam current density 6.25×10^{12} ions/cm^2. Irradiation temperature was ≤ 60 ^{0}C.

2. Results and discussion

The Raman spectrum of ideal structure graphite with threefold coordinated bonding has peaks at 1310 and 1591 cm^{-1} [2].

The positions of peaks and ratio I_D/I_G in Raman spectrums of un-irradiated graphite are shown in Table 1. The calculated values of crystallite sizes were: 19.1 nm for NBG-18 and 29.3 nm for NBG-25.

It's clear that the structure of un-irradiated graphite is partially disordered.

Table 1.
Parameters of Raman peaks for un-irradiated graphite

Graphite	Peak position, cm^{-1}		I_D/I_G
	D peak	G peak	
Ideal	1310	1591	
NBG- 18	1356	1585	**0.23**
NBG- 25	1356	1583	**0.15**

Fig. 1 shows dose dependencies of the relative changes of FWHM D of peaks and ratio I_D/I_G.

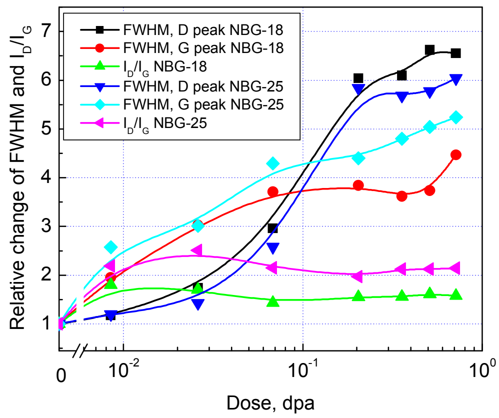

Fig. 1. Dose dependencies of relative changes of FWHM of the peaks and ratio I_D/I_G. A relative change of FWHM is: $(FWHM)_{IRR}/(FWHM)_{INIT}$ and the relative change of ratio is: $(I_D/I_G)_{IRR}/(I_D/I_G)_{INIT}$

As fig.1 shows the relative growth ratio I_D/I_G is observed at the beginning doses. A ratio reaches some maximal value at minimal used dose 0.0085 dpa and then a ratio decreased slightly. It can note that the relative change of ratio is larger for NBG-25 graphite.

The increase of FWHM of G peaks was observed for both graphite but a saturation stage of the relative changes of G peak's FWHM was revealed for graphite NBG-18 in dose range (0.8– 5)×10^{-1} dpa.

A multistage dose dependency was observed for the relative change of FWHM of D peaks. In the first stage (up to ~ $1\text{-}2\times10^{-2}$ dpa) the insignificant increase of FWHM value was observed, then the FWHM noticeably increased up to dose ~ 2×10^{-1} dpa and a tendency to saturation was observed after dose ~ 2×10^{-1} dpa (fig. 1).

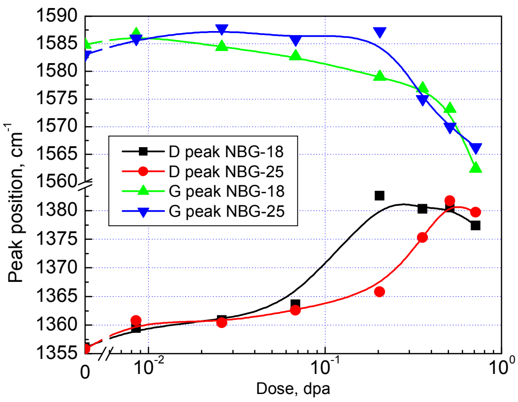

Fig. 2. Dose dependencies of D and G peaks positions

Fig. 2 shows changes of D and G peaks position at ion irradiation. It can see some stages are revealed in dose dependencies. The position of G peak in NBG-25 was practically constant up to dose ~ 2×10^{-1} dpa and then downward shift was observed. The first downward shift of G peak position was already revealed at dose ~ 8.5×10^{-3} dpa in NBG-18 and then, the second fall was observed at dose ~ 2×10^{-1} dpa.

The position of D peaks for both graphite in the first stage of irradiation was slightly changed up to dose $2\text{-}4\times10^{-2}$ dpa and then a fast shift to large wave numbers took place (fig. 2). Besides the dose of the fast shift of D peak position was smaller for NBG-18.

The maximal values of wave numbers for peak's positions were observed at ~ 2×10^{-1} for NBG-18 and ~ 5×10^{-1} for NBG-25.

A complex character of dose dependencies of the Raman parameters can explain by disordering of graphite structure. It is known that radiation damage transfer structure of graphite in disordered state with following amorphization [3].

Position of peak and FWHM characterize the energy state, therefore a shift of peak can be explained by introduce of defects and creation of defect carbon rings at irradiation [2, 4]. Moreover, an increase of intensity of D peak and FWHM is due by growth of defect concentration and transformation of point defect to complex.

Analysis of dose dependencies of Raman parameters of peaks showed that it can select three main stages:

a) *beginning stage of the point defects accumulation up to ~1×10^{-2} dpa* – growth of ratio I_D/I_G without change of FWHM of D peak, FWHM of G peak is increased, positions of D and G peaks aren't changed noticeable.

b) *stage of defect transformation and disordering (from ~1×10^{-2} dpa up to ~$2\text{-}3\times10^{-1}$ dpa)* - accumulation of defects are continued, part of defects are transformed to complex and FWHM of D peak increases sharply. Structure graphite is being disordered (increase of FWHM of G peak and shift of positions of G peaks in NBG-18). Although a change of position of the G peak isn't observed for NBG-25, the increase of FWHM shows disordering of structure in this dose range.

c) *stage of graphite amorphization (above $2\text{-}5\times10^{-1}$ dpa)* - it is accompanied with sharp downward shift of the G peak position and continuation of disordering (an increase of FWHM of G peak). Above dose $2\text{-}5\times10^{-1}$ dpa a decrease in both G and D peaks position is observed and it is possible connected with creation of fourfold-coordinated bonds [4].

3. Conclusion

a) The analysis of dose dependencies of Raman parameters revealed multistage process of disordering of graphite structure at ion irradiation.

b) The processes of structure disordering at irradiation takes place at smaller dose in graphite NBG-18 then NBG-25 due to larger initial disordering of NBG-18 graphite.

4. References

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