Oxidation Behaviour of Carbon Ion Irradiated IG-110 Nuclear Graphite

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1. Introduction

In the event of an accident causing air ingress, subsequent graphite oxidation results in changes in the physical and mechanical properties of core graphite components.

In this case, understanding the oxidation characteristics of graphite core structural blocks under the high temperature and high neutron fluence operating condition are important for the design and safety of the high temperature gas cooled reactor (HTGR) which are under developing worldwide.

Nevertheless, limited number of publications are having connected with study of irradiated graphite oxidation. This is connected partially with long duration of such experiments on nuclear reactor. The ion accelerators are useful instrument for study radiation effect on graphite oxidation because the large irradiation doses can get for comparatively short time irradiation.

2. Experimental

The specimens of IG-110 nuclear graphite with sizes (10x10x2) mm^3 were irradiated by 3 MeV carbon ions of current 1 μA. The range of ions was 3.2 μm accordingly of TRIM calculation (E_d =25 eV). The peak irradiation doses were 0.26 - 6.15 dpa, at that the irradiation doses were $8.5x10^{-3}$~$2.0x10^{-1}$ dpa in surface layers. The oxidation was performed in the 2.5% air in He environment (flow rate 40 cc/min) at 750 ^{0}C. Differences in the oxidation behaviour between the un-irradiated and irradiated surfaces were detected by optical microscopy, scanning electron microscopy (SEM) and Raman scattering measurements.

3. Results and discussion

SEM photos of oxidized at 750 ^{0}C of un-irradiated graphite specimens after different oxidation times show that the initial surface structure is characterized by presence of open pores and smooth inter-pore surface. The number of open pores on surface increases after oxidizing and the small grooves is observed in inter-pore surface. The big amount of narrow grooves with width smaller 1 μm is appeared on inter-pore surfaces at 120 min oxidation.

The increase of pore amount is observed after irradiation to dose 2.6 $x10^{-2}$ dpa, but the size of pores is not changed visibly. The shallow grooves are revealed on inter-pore surfaces. We can note that the observed grooves at small doses in inter-pore surfaces have preferred direction..

The pore amount and their size decrease after irradiation to dose $2.0x10^{-1}$ dpa. The shallow grooves aren't observed in inter-pore surfaces.

The comparative analysis of surface structure of un-irradiated and irradiated specimens show that ion irradiation intensifies the oxidation processes at low dose irradiation and reduces the oxidation at high irradiation doses.

In order to understand more clearly the causes of such changes of irradiated graphite oxidation we had measured Raman specters of graphite specimens.

Raman spectrum of graphite shows peak at 1580 cm^{-1} (G peak) which correlates with stretch vibration of carbon atoms in graphite crystal. Also, the 1354 cm^{-1} disorder peak (D peak) attributes to defects in the crystal lattice of graphite which have been pointed by authors [1,2]. The value of intensity ratio of D peak to G peak (ratio I_D/I_G) in the spectrum of un-irraidiated graphite is ~ 0.5 and this ratio reaches to~ 0.85 atsurface dose 0.2 dpa. (Fig.1). The full width on half maximum (FWHM) of D and G peaks is remained constant practically to irradiation dose about 0.1 dpa and then FWHM increases sharply.

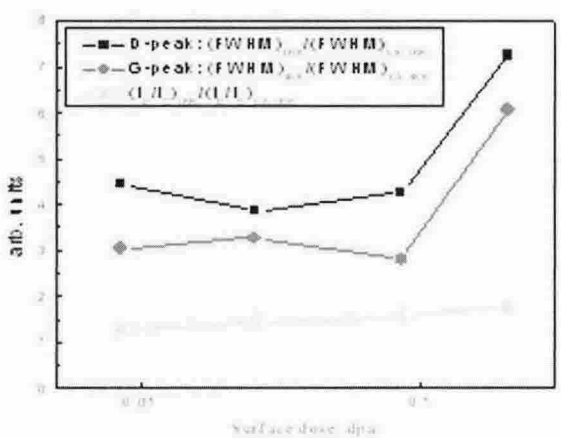

Fig. 1. The relative changes of FWHM and ratio I_D/I_G of Raman peaks on irradiation dose

The optical microscope observation of irradiated specimens surface showed that the visible changes of optical pattern are absent after irradiation to dose about 0.1 dpa, but light reflection grows slightly. Then, when dose increases further, the graphite surface is changed and the areas of rounded form are appeared on surface. We are connecting these surface changes at high irradiation dose with partial amorphization of graphite

structure. Similar effects were observedin pyrographite at ion and neutron irradiation [2.3].

Thus, the results of 3 MeV carbon ion irradiation show that different types of defects are formed at irradiation. At low irradiation dose radiation defects change the ratio I_D/I_G in Raman spectrum at invariable FWHM. The radiation defects appeared at high doses increase sharply FWHM of both peaks. At that the ratio I_D/I_G is increased slowly as well as at low dose.

In order to understand more clearly the causes of such changes of irradiated graphite oxidation we had measured Raman spectrums of oxidized specimens after every time step of oxidation.

The FWHM of D and G peaks in Raman spectrums of un-irradiated specimens isn't changed on oxidation time. The values of FWHM are recovered to initial levels after 15 min oxidation in irradiated graphite by doses to $2.6x10^{-2}$ dpa. Also, FWHM values of these peaks in irradiated by dose $2.0x10^{-1}$ dpa specimen are rapidly decreased after 15 min oxidation and then FWHM values remain invariable practically. However, the FWHM values don't reach of values of un-irradiated specimens.

The ratio I_D/I_G change on the oxidation time have the complex character. The increase of the oxidation time is accompanied with decrease of ratio I_D/I_G in un-irradiated graphite to minimal value and then ratio is increased slightly. The similar behaviour is observed in the irradiated to dose $2.6x10^{-2}$ dpa specimens. The quite other picture is observed in change of ratio I_D/I_G after dose $2.0x10^{-1}$ dpa. The value of ratio I_D/I_G increases slightly after the oxidation time 15 min and then remains invariable to 120 min the oxidation time, but the full recover of ratio I_D/I_G to value of un-irradiated graphite doesn't take place.

So, we see that the oxidation processes at 750 ^{0}C in irradiated graphite depend from irradiation dose.In others words we can select the radiation defects influencing on the oxidation processes after low dose irradiation. This radiation defects are disappeared in beginning time of oxidation and it are observed in graphite irradiated by low doses smaller than $2.6x10^{-2}$ dpa.

The others radiation damage are stable at 750 ^{0}C until long time of oxidation and they are forming at high dose of irradiation.

We suggest that the few types of radiation damage are created under carbon ion irradiation: point defects or theirs complexes and amorphous phase.

The first type of defects is no "un-stable in plane defects", which are annealed at temperature about 300 ^{0}C [4]. Because the oxidation process in our case take place at 750 ^{0}C then these defects can't intensify the oxidation process in the irradiated graphite.

We are proposing that these defects can be complex radiation defects of vacancy or interstitial type such as vacancy clusters, dislocation loops, which have annealing temperature 750 ^{0}C approximately. As we see, accordingly of SEM data such radiation defects can accelerate oxidation in low dose irradiated graphite.

The amorphization of graphite is observed at high irradiation doses therefore the oxidation rate decreases. First it connected with high density of amorphous phase in comparison with un-irradiated graphite. Also, the thermal stability of amorphous phase is more than 750 ^{0}C therefore the oxidation of graphite is reduced till long time oxidation.

The threshold dose of change of oxidation rate of irradiated graphite is about 0.1 dpa for given ion irradiation conditions and the oxidation temperature.

4. Conclusion

1. The radiation damage of different types and thermal stability are generated in graphite at carbon ion irradiation.
2. The study of oxidation of irradiated graphite showed that irradiation can intensify the oxidation at low dose irradiation and oxidation is reduced at high dose of irradiation. Starting from the dose dependence of FWHM change of Raman scattering peaks we can determine the threshold dose as about 0.1 dpa.
3. The acceleration of oxidation at 750 ^{0}C is due by forming of radiation damage of vacancy or interstitial type such as vacancy clusters, dislocation loops. These defects accelerate the oxidation process at beginning time as long as full annealing of these defects take place at 750 ^{0}C.
4. The oxidation process is reduced after the threshold irradiation dose as result of amorphous phase forming in graphite.

References

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