Structural Changes in IG-110 Nuclear Graphite due to Proton Irradiation and Oxidation

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1. Introduction

In high temperature gas cooled reactor (HTGR) graphite act as a moderator, major structural component so that the dimensional change due to neutron irradiation and the thermal oxidation due to air ingress have been extensively studied [1, 2]. However, little effort has been made for correlation between the microstructure of damaged graphite and the physical or material parameters. In the present work, we have tried to characterize the structural changes of nuclear graphite due to proton irradiation and oxidation by means of positron annihilation lifetime spectrometer and X-ray diffractometer.

2. Experimental

The material used in this study was high density ($1.78 g/cm^3$), isotropic nuclear graphite IG-110 produced by Toyo Tanso Co. Ltd., Japan. The specimens were squares with the dimension of $10 \times 10 \times 1 mm^3$.

3.0 MeV proton irradiation was performed in a Tandetron Accelerator at KIGAM to a dose of $3.4 \times 10^{17}/cm^2$ below 353 K. The depth profile of the displacement damage was calculated with the SRIM code under the assumption of the displacement energy of 40eV [3]. The projected range of the protons is 80μm and the damage peak is at 75μm. The displacement per atom (dpa) of the first 60μm of the proton range is about 3.5mdpa.

Thermal oxidations were performed with a tube furnace and the oxidant was ambient air supplied by the natural circulation. The test temperatures were selected as: 500 (72hr), 700 (3hr), 900°C (25min) to oxidize in the chemical regime, the in-pore diffusion controlled regime and the boundary layer controlled regime, respectively. The weight loss was about 18% regardless of the oxidation conditions.

Positron lifetime and X-ray diffraction were performed. Positron lifetime measurements were performed with a usual fast-fast time spectrometer with a time resolution of about 230 ps (FWHM) and positron source of ^{22}Na (0.8 MBq) sealed with Al foil. The lifetime spectra were analyzed with the PATFIT-88 program.

3. Results and Discussion

The lifetime spectra were decomposed into two components and the results of positron annihilation lifetime measurement are summarized in Table 1. The first component is related to the free positrons annihilated in the perfect lattice if only one type of defect exists. The second component is related to the positrons trapped at the structural defects.

The lifetime of free positrons delocalized in the perfect graphite lattice is reported to be 210±5 ps. As can be seen in Table 1, the second lifetime, τ_2 is about 400±20 ps regardless of the materials conditions. The lifetime of 400 ps, observed in well-crystallized pyrolytic graphite and natural graphite, is interpreted as the lifetime of positrons trapped at the internal surfaces between crystallite [4, 5]. It can be seen that major open volume defects in as-received IG-110 nuclear graphite is the crystallite boundaries.

Generally, the oxidized nuclear graphites show the development of extensive porosity in the binder region but less extensive attack on the filler phase. However, the nanometric texture of graphite remains after oxidation, the positron lifetime parameters of the oxidized graphites are nearly the same to those of the as-received graphite.

It is clearly seen that the first lifetime increases from about 175 ps to 250 ps by proton irradiation. Positrons are considered be trapped at two sites, radiation-induced vacancies (about 40%) and the pre-existing structural defects (about 60%). It is well known that radiation damage occurs due to carbon atoms being displaced from the crystal lattice. The displaced carbon atoms either recombine into vacant position within the graphite crystal lattice or combine with other atoms to form interstitial loop. Likewise, vacant site may join together to form small vacancy cluster. Vacancies do not start to be mobile until irradiation temperature of 650°C is reached.

Table 1 Positron annihilation lifetimes results of IG-110

Material condition	Positron lifetime parameters		
	τ_1 (ps)	τ_2 (ps)	I_2 (%)
As-received	190	405	83
Oxidized at 700°C	188	419	82
Oxidized at 900°C	185	401	81
Proton irradiated	253	405	61

The lattice spacing and the crystallite size measured by X-ray diffraction are summarized in Table 2. For perfect graphite crystals the 'd', or inter-layer spacing has been measured to be 3.3539 Å with an 'a' spacing of 2.46 Å. The lattice spacings of the as-received graphite are comparable to the reported values.

Table 2 X-ray diffraction results of IG-110

Material condition	Positron lifetime parameters			
	c (Å)	a (Å)	Lc (Å)	La (Å)
As-received	3.3573	2.4606	380	560
Oxidized at 700°C	3.3599	2.4596	410	620
Oxidized at 900°C	3.3615	2.4597	370	520
Proton irradiated	3.3702	2.4608	200	310

After the thermal oxidation, the lattice spacing is not changed regardless of oxidation temperature but the crystallite size of the sample oxidized at 700 °C increases about 3% both in 'c' and 'a' directions. In the boundary layer controlled regime (900 °C), the oxidation reactions are concentrated in the superficial layer and generally uniform both in filler and binder phases due to high chemical reaction rate. However, in the in-pore diffusion controlled regime (800 °C), the closed pores are opened and micropores are converted to macropore and the resulting oxidation are nearly uniform through the whole depth of the penetration. In this regime, the oxidation rate is relatively slow and the poorly graphitized binder phases are selectively attacked. It is reported that the graphite made from petroleum coke is composed of larger crystallites than that made from pitch coke under the same graphitization process. The increase in crystallite size after oxidation at 700 °C is attributed to the enhanced contribution of filler phase to X-ray diffraction with the loss of binder phase.

The lattice parameters increase slightly in the 'c' direction. The expansion in the 'c' direction can be explained by the presence of interstitial atoms between the graphite lattice planes. The crystallite sizes decrease significantly in both the 'c' and 'a' directions due to lattice disorder (radiation defects).

4. Conclusion

The positron lifetime technique is very sensitive to point defects which are not easy to detect in TEM and X-ray diffraction easily shows disordering mainly due to interstitial atoms. More detailed understanding of the microstructural changes in nuclear graphite with these techniques would be very helpful in the selection of nuclear graphite for HTGR construction and the evaluation on the degradation mechanism of graphite.

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