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Review

Understanding the reaction of nuclear graphite with molecular oxygen: Kinetics, transport, and structural evolution

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HIGHLIGHTS

- Critical review of graphite oxidation relevant to a high-temperature gas-cooled reactor.
- Assesses oxidation in terms of microstructure and its evolution.
- Model is applicable to all nuclear graphites by using a grade independent kinetics model for the graphite-O_2 reaction system.

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ABSTRACT

For the next generation of nuclear reactors, HTGRs specifically, an unlikely air ingress warrants inclusion in the license applications of many international regulators. Much research on oxidation rates of various graphite grades under a number of conditions has been undertaken to address such an event. However, consequences to the reactor result from the microstructural changes to the graphite rather than directly from oxidation. The microstructure is inherent to a graphite's properties and ultimately degradation to the graphite's performance must be determined to establish the safety of reactor design. To understand the oxidation induced microstructural change and its corresponding impact on performance, a thorough understanding of the reaction system is needed. This article provides a thorough review of the graphite-molecular oxygen reaction in terms of kinetics, mass and energy transport, and structural evolution: all three play a significant role in the observed rate of graphite oxidation. These provide the foundations of a microstructurally informed model for the graphite-molecular oxygen reaction system, a model kinetically independent of graphite grade, and capable of describing both the observed and local oxidation rates under a wide range of conditions applicable to air-ingress.

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Nomenclature

All symbols are listed in order of appearance.

Symbol	Description	Units/Value	Equation(s)
ϕ_n	Thiele modulus: ϕ_n^2 relates the ratio of surface reaction rate to an effective rate of diffusion through a porous material.	Unitless	NA
k_0	A rate constant used for a semi-empirical fit of experimental data to a rate law.	Varies	1,2
E_A	Activation energy	$\frac{kJ}{mol}$	1,2
R	Universal gas constant	$8.3145\ \frac{J}{mol\ K}$	1,2
T	Temperature	K or °C	1,2,12,13,25,30
n	Reaction order	Unitless	1,2
P_{O_2}	Partial pressure of molecular oxygen gas	*Varies*	1
$[O_2]$	Concentration of molecular oxygen gas	$\frac{mol}{m^3}$	2,11–13,19,21–23,25
x	Stoichiometric coefficient of $CO(g)$. Purposely expressed as seen in Eq. (5) to represent the fraction of $CO(g)$ gaseous product	Unitless	3,21–23,25
C_e	Carbon edge atom at a {100} and {110} surface	NA	4,5,7,8
$C_e(O_2)$	Surface dioxyranyl reactive intermediate	NA	4,5,7
$C_e(O)$	Surface semiquinone reactive intermediate	NA	4,5,7
C_b	Carbon atom within basal plane, (001) surface	NA	5,6,8
$C_b(O)$	Stable/mobile surface intermediate, epoxy bridge	NA	5–7
k_{A1}	Reaction rate constant for Eq. (4a)	Kane et al. [29]	4a,11,13
k_{A2}	Reaction rate constant for Eq. (4b)	Kane et al. [29]	4b,11,13
$k_S \cdot k_S^*$	Reaction rate constant for Eq. (5)	Kane et al. [29]	5,11,13
k_{Hop}	Reaction rate constant for Eq. (6)	Kane et al. [29]	6
$k_{D1} \cdot k_{D1}^*$	Reaction rate constant for Eq. (7a)	Kane et al. [29]	7a,10,11,13
$k_{D2} \cdot k_{D2}^*$	Reaction rate constant for Eq. (7b)	Kane et al. [29]	7b,10,11,13
$k_{D3} \cdot k_{D3}^*$	Reaction rate constant for Eq. (7c)	Kane et al. [29]	7c,10,11,13
k_{NSD}	Reaction rate constant for Eq. (8)	Kane et al. [29]	8
θ	Surface coverage as defined in Eq. (9)	Unitless	9
N_C	Carbon molar flux towards the graphite surface	$\frac{mol}{m^2 s}$	10–12
$[C_e(O_2)]$	Surface density of dioxyranyl reactive intermediate	$\frac{mol}{m^2}$	10
$[C_e(O)]$	Surface density of semiquinone reactive intermediate	$\frac{mol}{m^2}$	10
Γ_e	Surface density of ASA	$\frac{mol}{m^2}$	11,13
k''_{eff}	Effective reaction rate constant for graphite-oxygen reaction normalized to ASA	$\frac{m}{s}$	12,13,19,2123,25
$N_A,\ N_B,\ N_i$	Gaseous flux of arbitrary gaseous species A or B or specific gaseous component i	$\frac{mol}{m^2 s}$	14-16,20–24,
C_T	Total gas phase concentration	$\frac{mol}{m^3}$	14,15,20
D_{AB}	Binary gaseous diffusion coefficient for arbitrary species A and B	$\frac{m^2}{s}$	14,15,31