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碘化铯负载基体石墨氧化动力学及释放行为研究

摘要

面向未来低碳能源体系，核能在保障能源安全与实现深度脱碳中具有重要战略意义；而核燃料材料服役行为的可靠性，是支撑核能安全高效利用的关键基础。其中，高温气冷堆燃料元件中的基体石墨兼具慢化剂、结构材料和裂变产物滞留屏障等多重功能，其氧化机制及裂变产物释放行为是事故工况安全评价中的核心科学问题之一。一旦高温气冷堆发生进气事故，高温氧化氛围可能导致 TRISO 包覆颗粒破损率升高，使更多裂变产物释放至基体石墨中；与此同时，基体石墨自身也会发生氧化，滞留其中的裂变产物不仅可能改变石墨氧化动力学过程，还可能在氧化过程中发生化学形态转化并进一步释放至一回路中。因此，开展含裂变产物基体石墨的氧化过程及释放行为研究，对反应堆事故状态下释放源项评估和核燃料安全分析具有重要意义。

本研究以稳定碘化铯作为模拟裂变产物，通过溶液浸渍法将其负载于基体石墨中，用以模拟辐照后燃料元件中含裂变产物的基体石墨环境；进一步结合热重-质谱-傅里叶红外联用分析、水平管式炉氧化实验及第一性原理计算，系统研究碘化铯负载对基体石墨高温氧化行为的影响，以及氧化过程中碘、铯元素的释放、迁移与残留特征。

TG-MS-FTIR 结果表明，碘化铯负载显著降低了基体石墨开始氧化阶段的反应活化能，并对石墨氧化生成二氧化碳和一氧化碳的反应过程均表现出明显促进作用；但在本研究所涉及的负载量范围内，碘化铯负载量差异对反应活化能的影响并不显著。水平管式炉氧化实验结果显示，在 600 ℃、700 ℃ 和 800 ℃ 条件下，大部分铯和几乎全部碘均可从碘化铯负载基体石墨中释放，仅少量铯以碳酸盐或氧化物形式残留于氧化灰分中，且随氧化温度升高，灰分中铯残留量进一步降低。释放出的铯中，少部分在石英管近样品端随未燃尽石墨片层共同沉降，大部分则以碘化铯气溶胶形式释放和迁移；碘元素中部分被氧化为气态碘并被碱液吸收，大部分同样以碘化铯气溶胶形式释放和传输。

第一性原理计算进一步表明，在石墨表面尤其是缺陷石墨表面，铯原子相较碘原子具有更低的吸附能，说明负载于基体石墨中的碘化铯可能更倾向于通过铯与缺陷石墨发生相互作用。该相互作用一方面可能增强缺陷石墨的化学活性，从而促进基体石墨氧化；另一方面也可能解释铯相较于碘更易在氧化灰分中残留的现象。上述结果揭示了模拟裂变产物碘化铯对基体石墨氧化动力学及碘、铯差异化释放行为的影响机制，可为高温气冷堆进气事故工况下基体石墨氧化行为分析、裂变产物释放源项评估以及核燃料材料安全性研究提供实验依据和理论支撑。

关键词

高温气冷堆；基体石墨；进气事故；碘化铯；氧化动力学；裂变产物释放；铯碘释放行为；第一性原理计算

Abstract

In the context of future low-carbon energy systems, nuclear energy plays a strategically important role in ensuring energy security and achieving deep decarbonization. The reliability of nuclear fuel materials under service conditions is a fundamental basis for the safe and efficient utilization of nuclear energy. In high-temperature gas-cooled reactors, matrix graphite in fuel elements serves simultaneously as a moderator, structural material, and final barrier against the release of fission products into the primary circuit. Its oxidation mechanism and associated fission product release behavior are therefore among the key scientific issues in accident-condition safety assessment. In the event of an air ingress accident, the high-temperature oxidizing atmosphere may increase the failure probability of TRISO-coated fuel particles, resulting in the release of more fission products into the matrix graphite. Meanwhile, the matrix graphite itself undergoes oxidation, during which retained fission products may not only affect graphite oxidation kinetics but also experience chemical transformation and further release into the primary circuit. Therefore, investigating the oxidation process and release behavior of fission-product-containing matrix graphite is of great significance for source term evaluation and nuclear fuel safety analysis under reactor accident conditions.

In this study, stable cesium iodide was used as a simulated fission product and loaded into matrix graphite by solution impregnation to represent the fission-product-containing matrix graphite environment in irradiated

fuel elements. Thermogravimetry-mass spectrometry-Fourier transform infrared spectroscopy, horizontal tube furnace oxidation experiments, and first-principles calculations were combined to systematically investigate the effect of cesium iodide loading on the high-temperature oxidation behavior of matrix graphite, as well as the release, transport, and retention characteristics of iodine and cesium during oxidation.

The TG-MS-FTIR results show that cesium iodide loading significantly reduces the activation energy at the initial oxidation stage of matrix graphite and markedly promotes the oxidation reactions of graphite to carbon dioxide and carbon monoxide. However, within the loading range investigated in this study, the variation in cesium iodide loading has no significant influence on the activation energy. The horizontal tube furnace oxidation experiments indicate that, at 600 ℃, 700 ℃, and 800 ℃, most cesium and nearly all iodine are released from cesium-iodide-loaded matrix graphite. Only a small fraction of cesium remains in the oxidation ash in the form of carbonates or oxides, and the residual cesium further decreases with increasing oxidation temperature. Among the released cesium, a minor fraction deposits near the sample end of the quartz tube together with unburned graphite flakes, whereas the majority is released and transported in the form of cesium iodide aerosols. Part of the iodine is oxidized into gaseous iodine and absorbed by alkaline solution, while most iodine is also released and transported as cesium iodide aerosols.

First-principles calculations further reveal that cesium atoms exhibit lower adsorption energies than iodine atoms on graphite surfaces, especially on defective graphite. This suggests that cesium iodide loaded in matrix graphite may preferentially interact with defective graphite through cesium. Such interaction may enhance the chemical activity of defective graphite and thereby promote graphite oxidation; it may also explain why cesium is more likely than iodine to remain in the oxidation ash. These results reveal the influence mechanism of simulated fission product cesium iodide on the oxidation kinetics of matrix graphite and the differential release behavior of iodine and cesium, providing experimental evidence and theoretical support for graphite oxidation analysis, fission product source term assessment, and nuclear fuel material safety evaluation under air ingress accident conditions in high-temperature gas-cooled reactors.

Keywords

High-temperature gas-cooled reactor; matrix graphite; air ingress accident; cesium iodide; oxidation kinetics; fission product release; cesium and iodine release behavior; first-principles calculations

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