CaO固硫过程中Ca~(2+)在CaSO_4产物层内扩散的研究

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摘要 应用标记实验技术,研究CaO固硫反应过程中产物层扩散控制阶段的反应机理

。利用扫描电镜和反射式光学显微镜,对压制烧结并带有Pt标记的CaO样品在固硫 反应前后的形貌变化观察,结果表明:经过较长时间的固硫反应后,在Pt标记层外 表面形成一层覆盖物,

XRD分析结果证明该覆盖物是CaSO_4。利用电化学综合测试 仪测量了CaO及CaSO_4在高温下的电导率, 结果表明在1000 ℃时CaSO_4的电导率达 到了10~(-3)数量级,说明在高温下CaSO_4内Ca~(2+) 有较高的离子迁移特性。根据 标记实验、

电导率测试的结果和CaO掺杂体系的固硫动力学数据的分析认为: CaO固

硫反应在后期的扩散层控制阶段的主要反应是Ca~(2+)通过CaSO_4产物层扩散至 CaSO_4外表面与SO_2和O_2进行反应,生成CaSO_4,而不是SO_2和O_2气体通过 CaSO_4产物层向内扩散,在颗粒内部与CaO发生固硫反应。

关键词 氧化钙 硫 离子扩散 电导率 反应机理 扫描电子显微镜 X射线衍射分析 分类号 0612

Ca~(2+) Cation Diffusion through CaSO_4 Product Layer during Sulfur Retained Reaction with CaO

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Department of Chemistry, Tsinghua University **Abstract** Sintered CaO tablets covered with platinum marker on the

Abstract Sintered CaO tablets covered with platinum marker on the surface were exposed to simulated coal gas containing SO_2 at $1200\,^{\circ}\mathrm{C}$ in a tube reactor. The SEM micrograph and reflex optical micrograph were used to observe morphology changes of the tablets. After the CaO tablet covered with platinum marker being reacted for $120\,\mathrm{h}$, a thick layer of product CaSO_4 formed on the surface of the platinum marker. The layer of product CaSO_4 is compact. At high temperature, the conductivity of CaSO_4 reached $3.5*10\sim(-3)\,\mathrm{S\cdot cm}\sim(-1)$. This means that Ca $\sim(2+)$ ions in CaSO_4 have higher mobility. A new reaction mechanism of sulfur retained by CaO is suggested as follows: In the diffusion stages of GaO desulphurization, Ca $\sim(2+)$ ion in CaO diffuses outward through the sulfate product layer to the interface of CaSO_4 and gas to form GaSO_4 with O $\sim(2-)$, O_2 and SO_2, rather than that SO_2, O_2 diffuse through the sulfate product layer into the interface of CaSO_4 and CaO to react with CaO.

Key wordsCALCIUM OXIDESULFURionic diffusionELECTRICAL CONDUCTIVITYREACTIONMECHANISMSEMXRD

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