Ceria-based ceramic composites for high temperature thermochemical applications

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Among thermochemical conversion processes, the production of fuels such as H_2 via solar thermochemical cycles is potentially more efficient and more economical than the use of electric energy to electrolyze water. The principle of solar thermochemical cycles is based on the remarkable properties of some oxides, which can be reduced and oxidized cyclically (redox cycles), i.e., releasing and absorbing oxygen under certain temperature (or pressure) regimes. These redox cycles can be efficiently used to convert H_2O (or CO_2) to H_2 (CO). Thermochemical redox cycles avoid the problematic step of fuel / O_2 separation and allow operation at more moderate temperatures (~ 1500 K) **[1]**. In this work, a new material concept for the separation of high temperature H_2O based on porous ceramic composites composed of an ultra-high temperature ceramic phase (UHTC) and doped cerium oxide is proposed. UHTC usually exhibit extremely low mass diffusion rates and excellent thermomechanical properties for high temperature applications **[2]**. Gadolinium-doped ceria (CGO) presents unique processes at low oxygen partial pressure ($pO_2 < 10^{-12}$ atm) and high temperatures (T > 800 °C) such as faster mass diffusion, which are not observed in conventional sintering under ambient air conditions. In CGO/Al_2O_3 composites the resulting effects driven by such mass diffusion are low viscosity flows and high reactivity between phases, indicated by the formation of $CeAlO_3$**[3]**. In this work, a comparison is made between sintering CGO/Al_2O_3 under ambient air and reducing condition, focusing on densification, viscosity and the evolution of the microstructure. The redox process of CGO/Al_2O_3 is investigated using dilatometry, microscopy, and electrochemical impedance spectroscopy. The preliminary results evidenced that new phases with remarkable microstructure can be obtained at reducing atmosphere depending on the temperature of reoxidation during cooling. FAPESP, CNPq, CNEN.