Ca-Mg 共晶合金の加水分解反応による水素発生

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Hydrogen generation through hydrolysis reaction of Ca-Mg eutectic alloys

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【緒言 Introduction】

In recent years, hydrogen energy has attracted worldwide attention as a sustainable and clean alternative to fossil fuels. Metal hydrolysis presents a low-temperature, on-demand method that circumvents the high energy requirements of conventional electrolysis. Calcium (Ca) and magnesium hydride (MgH_2) are promising candidates due to their spontaneous reactions with water; however, pure Ca reacts too vigorously, posing safety risks, while MgH_2 forms a dense $Mg(OH)_2$ passivation layer that slows reaction rates. To overcome these challenges, Ca–Mg eutectic alloys have been developed, combining the high reactivity of Ca with the stabilizing Mg_2Ca intermetallic phase. Because $Ca(OH)_2$ is more porous and slightly more soluble than $Mg(OH)_2$, sustained hydrolysis is facilitated. This study investigates a gas-atomized Ca–25 at.% Mg eutectic alloy powder designed to achieve a balance between reactivity and operational safety. The gas atomization process produces fine, spherical particles with a globular nanoscale eutectic structure, which enhances water accessibility, suppresses surface oxidation, and promotes galvanic coupling between Ca and Mg_2Ca phases.

【実験方法 Experimental】

In this study, a Ca–25 at.% Mg eutectic alloy powder was produced via gas atomization under an argon atmosphere and sieved to <90 μm. Hydrolysis experiments were performed in triplicate in a 1 L two-neck flask by reacting 1 g of sample with 100 mL of deionized water at 25, 40, 50, and 60 °C. Hydrogen evolution was quantified by the water-displacement method, with real-time mass measurement by a digital balance. Phase analysis was conducted by X-ray diffraction (XRD), and surface and internal structures were examined via field-emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), and energy-dispersive X-ray spectrometry (EDS). Reaction kinetics were modeled using a logistic growth equation, and apparent activation energy was determined from an Arrhenius plot.

【結果 Results】

The Ca–Mg powder achieved a maximum hydrogen yield of 835.6 $mL \cdot g^{-1}$ at 60 °C, with near-complete hydrolysis even at 25 °C. XRD confirmed the formation of $Ca(OH)_2$ and $Mg(OH)_2$. TEM revealed a globular eutectic microstructure with finely distributed Ca-rich and Mg_2Ca phases, enhancing galvanic coupling and diffusion. SEM images displayed uniform spherical particles (6–65 μm), contrasting with the irregular MgH_2 flakes whose passivation hindered reactivity. Kinetic analysis showed that reaction rates increased with temperature, and the apparent activation energy was 36.6 $kJ \cdot mol^{-1}$, indicating a surface-controlled process. Compared with conventional hydrides, the Ca–Mg eutectic powder exhibited superior performance without additives or mechanical activation, demonstrating significant potential for practical, portable hydrogen generation applications.