Characteristics of Fe Powders Prepared by Spray Pyrolysis from Various Types of Fe Precursors as a Heat Pellet Material

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Aggregated Fe powders comprising elongated and aggregated particles used in the production of heat pellets for application in thermal batteries were prepared by spray pyrolysis. Iron oxide powders comprising dense and hollow particles were prepared by spray pyrolysis from spray solutions containing various types of Fe precursors. Iron oxide powders prepared from iron chloride and iron nitrate precursors were comprised of spherical and micron-sized particles. On the other hand, iron oxide powders prepared from iron oxalate were comprised of large, hollow, and thin-walled particles. The Brunauer-Emmett-Teller (BET) surface areas of iron oxide powders prepared from iron chloride, iron nitrate, and iron oxalate precursors were 17.5, 71.9, and 78.5 m² g⁻¹, respectively. At a low reduction temperature of 550 °C, iron oxide powders prepared from iron oxalate afforded loosely aggregated Fe powders comprised of elongated and loosely aggregated particles, with a BET surface area of 5.9 m² g⁻¹. The heat pellets prepared from Fe powders reduced at 550 °C and composed of fine primary powders had an ignition sensitivity of 0.9 W and a burn rate of 10 cm s⁻¹.

Keywords: energy storage materials, chemical synthesis, oxidation, scanning electron microscopy (SEM), thermal battery

1. INTRODUCTION

Thermal batteries are used in applications where there could be a sudden demand for electric power. These batteries are primary reserve batteries that are in a solid state at normal temperature. For many years, thermal batteries have been the preferred power supply for military equipment such as guided missiles and nuclear weapons. Thermal batteries are thermally activated, hermetically sealed, primary reserve power sources, generally consisting of series or series-parallel arrays of cells. Each cell comprises an anode, an electrolyte-separator, a cathode, and a heat pellet [1-7]. The main role of the heat pellet is to provide the exact amount of heat required to melt the electrolyte. The electrolyte material remains completely inert and nonconductive until the battery is activated, after which it becomes molten and highly conductive.

A wide range of fuels/oxidizing agent combinations have been investigated, and a combination of iron and potassium perchlorate (KClO₄) has been found to be the most suitable for preparing heat pellets. Therefore, heat pellets were prepared using Fe and KClO₄ powders. Mixtures of Fe and KClO₄ powders are easy to pelletize and strong pellets can be obtained. Heat pellets should have a high burn rate, good ignition sensitivity, high thermal output, and sufficient mechanical strength. The morphologies of the Fe powders can have a strong impact on the physical properties of the heat power in which they are used [8]. Aggregated Fe powders comprising elongated particles that were several tens of micrometers in size are mainly used to produce heat pellets. However, methods for the preparation of aggregated Fe powders that can be used to produce heat pellets are not well known.

Fe aggregate powders can be obtained by the reduction of iron oxide powders in a reducing atmosphere. The mean size and morphologies of iron oxide powders strongly affect the characteristics of the Fe powder aggregates. In particular, severe preparation conditions such as high reduction temperature and long heating time, which are required to obtain pure crystals, result in the formation of strongly aggregated Fe powders. Because of the high ductility of Fe, conventional milling processes cannot be used to reduce the size of the aggregated Fe powders [9].
In this study, Fe aggregate powders were prepared by spray pyrolysis. The effects of the morphologies of iron oxide powders on the formation of Fe aggregate powders were investigated. Iron oxide powders comprising dense and hollow particles were prepared by spray pyrolysis from spray solutions containing various types of Fe precursors. These iron oxide powders comprising hollow and porous particles were used to produce Fe powders comprising elongated and loosely aggregated particles at low reduction temperatures. The characteristics of the Fe aggregate powders prepared from various types of Fe precursors were investigated to determine if they can be used in the preparation of heat pellets.

2. EXPERIMENTAL PROCEDURE

The iron oxide powders were prepared by ultrasonic spray pyrolysis. The spray pyrolysis system consisted of a droplet generator, a quartz reactor, and a particle collector. A 1.7-MHz ultrasonic spray generator having six vibrators was used to generate a large number of droplets, which were then carried to the reactor. The length and inside diameter of the tube in the furnace were 1200 mm and 50 mm, respectively. The flow rate of air used as the carrier gas was 60 L min$^{-1}$. A high flow rate was used to improve the hollowness of the particles comprising iron oxide powders. The residence time of the powders inside the hot wall reactor maintained at 900 °C was 0.2 s. FeCl$_3$·6H$_2$O (99%, Junsei), FeC$_2$O$_4$·2H$_2$O (98.5%, Kanto), and Fe(NO$_3$)$_3$·9H$_2$O (98%, Junsei) were used as starting materials. The concentrations of the Fe precursors were fixed at 0.25 M. Iron oxide powders prepared by spray pyrolysis were post-treated in a reducing atmosphere (20% H$_2$/N$_2$ mixture) for 10 h. The reduction temperature was increased from 550 °C to 700 °C.

To produce pyrotechnic heat pellets, the Fe aggregate powders and KClO$_4$ powders were first mixed. The mixing ratio of the Fe and KClO$_4$ powders was 84:16. The mixed powders were pressed into disc-shaped compacts using a uniaxial press; 10000 kg force was applied for 10 min. The ignition sensitivity of the powder compacts was determined by using a solid-state diode laser (Wondar laser, 301-C20), whose output was controlled by a constant-current power supply. The burn rate was measured by a high-speed motion picture camera (Sanyo, Xacti) with a running speed of 60 frames per second (fps).

The morphologies of the powders were investigated by scanning electron microscopy (SEM; JEOL JSM 6060). The crystal structures of the powders were studied by X-ray diffraction (XRD; Rigaku DMAX-33) with Cu-Kα radiation ($\lambda$ = 1.5418 Å). The surface area and pore-size distribution of iron oxide and Fe powders were calculated by the BET and Barrett-Joyner-Halenda (BJH) methods, respectively.

3. RESULTS AND DISCUSSION

The morphologies of iron oxide powders obtained by spray pyrolysis from the spray solutions containing various types of Fe precursors are shown in Fig. 1. The type of Fe precursor used as the source of the metal component in preparing heat pellets affects the morphology of the powders prepared by spray pyrolysis; this is due to the differences in the drying and decomposition properties of the precursors. Iron oxide powders prepared from iron chloride and iron nitrate precursors were spherical and micron-sized. However, some of the powders prepared from the iron chloride precursor fractured and formed fine-sized powders, as shown in the circle in Fig. 1(a). On the other hand, the iron oxide powders prepared from the iron oxalate precursor comprised large, hollow, and thin-walled particles.

In spray pyrolysis, the hollowness of the powders is affected by the gas-penetration properties of the dried or decomposed powders. The powders formed from iron oxalate have poor gas-penetration properties. In addition, a large amount of gas evolves from the decomposition of iron oxalate. Therefore, the iron oxide powders formed from iron oxalate comprised particles that were large, hollow, and had thin walls. Figure 2 shows the pore-size distributions of the iron oxide powders analyzed by the BJH method. The iron oxide powders prepared from the iron nitrate precursor

![Fig. 1. SEM images of the iron oxide powders prepared from various Fe precursors: (a) Chloride, (b) Nitrate, and (c) Oxalate.](image-url)