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Microstructure of ferrospheres in fly ashes: SEM, EDX and ESEM analysis*

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Abstract: Ferrospheres in fly ashes from a coal-fired power plant were extracted by a magnetic separation technique and their microstructure was studied by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and environmental scanning electron microscopy (ESEM). Ferrospheres in fly ashes show significant iron enrichment compared to their respective fly ashes. Iron oxides in ferrospheres mainly occur as minerals magnetite (Fe_3O_4) and hematite (α-Fe_2O_3), which are derived mainly from the decomposition and oxidation of iron-bearing minerals in coal during combustion. EDX data indicate that ferrospheres also contain Si, S, Al and Ca resulting from quartz, mullite, anhydrite and amorphous materials. A large percentage of ferrospheres are commonly 5~50 μm in size. The microstructure of ferrospheres includes smooth, polygonal, dendritic, granular and molten drop characteristics. SEM coupled with EDX provided fast and accurate results of the microstructure and chemical composition of ferrospheres, and helped us to assess environmental issues related to the disposal and utilization of fly ashes.

Key words: Fly ash, Ferrosphere, Microstructure, Scanning electron microscopy (SEM)
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INTRODUCTION

Fly ashes, the solid waste produced during coal combustion, can cause environmental pollution problems. Airborne fly ash particles emitted from a coal-fired power plant are considered to be highly contaminating, since their high surface area gives rise to the enrichment of potentially toxic elements and a mutagenic organic compound. Previous studies revealed the presence of potential toxic elements in fly ashes (Morris *et al*., 1995; Triantafyllou *et al*., 2003; Petaloti *et al*., 2006). Actually, air pollution from airborne fly ash particulate had always been the main pollutant in China over past decades. Mineralogical and morphological properties of fly ashes are well known (Filippidis and Georgakopoulos, 1992; Georgakopoulos *et al*., 1992; Filippidis *et al*., 1992; 1996; Hower *et al*., 1999; Vassilev *et al*., 2003; Goodarzi *et al*., 2006; Jones *et al*., 2006; Koukouzas *et al*., 2006; Zhao *et al*., 2006). Typically fly ashes consist of crystallized phases like quartz, mullite, hematite and magnetite in a mixture of aluminosilicate glass. However, mineralogical, chemical and microstructure studies of fly ashes have been focused on the bulk properties of fly ashes without attention to the details of the properties of the constituents. Previous studies have noted a number of ferrimagnetic component (ferrospheres) in fly ashes, including magnetite, hematite, goethite, Fe^{2+} and Fe^{3+} mixed spinels, Fe^{3+} bearing mullite and Fe^{2+} and Fe^{3+} silicates (Gomes *et al*., 1999; Hower *et al*., 1999; Sokol *et al*., 2002; Vassilev *et al*., 2004). Ferrospheres of fly ashes could be recovered economically by magnetic separation techniques. Depending on the organic, inorganic and intermediate affinity of the trace elements in the coal,

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ferrospheres are mainly associated with heavy metals like Cu, Cr, Pb and Zn (Georgakopoulos *et al*., 1994). Thus, the determination of the characteristics of ferrospheres in fly ashes with a heavy environmental pollution risk is of paramount importance. Otherwise, industrial-grade ferrospheres extracted from fly ashes have some industrial potential, mostly in metallurgy, ore and coal dressing process, and dense concrete production.

The morphology and chemical composition of ferrospheres in fly ashes have been examined using optical microscopes, scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) and other similar techniques (Gomes *et al*., 1999; Chen *et al*., 2005; Kutchko and Kim, 2006; Iordanidis *et al*., 2008). Most of these studies focus on the transformation process of minerals, with little information about the microstructure characteristics of ferrospheres. There is still a lack of systematic interpretation of the morphology of ferrospheres in fly ashes, especially for the fly ash in China's power plants. The purpose of this investigation was to use SEM, EDX and environmental scanning electron microscope (ESEM) to characterize the microstructure of ferrospheres of fly ashes. Knowledge of the mineralogy, chemical composition and morphology of ferrospheres in fly ashes can be helpful in interpreting the environmental processes and the multi-utilization of fly ashes.

MATERIALS AND METHODS

Samples

The fly ash samples were collected from the electrostatic precipitators of two coal-fired power plants in China. The ferrospheres in fly ashes were extracted by the wet magnetic separation method. About 20 g of fly ashes were dispersed in 250 ml water. The slurry flow in a continuous-loop flow driven by a pump and the magnetic particles in fly ashes were obtained by a high-gradient magnet. This procedure was run repeatedly for about 2 h until no more magnetic material adhered to the magnet. Separated magnetic particles were oven-dried at 50~60 °C, weighed and digested with aqua regia. The concentrations of Fe ions in the digestive solution were analyzed with a flame atomic absorption spectrometer.

Analytical techniques

The mineralogy of ferrospheres was identified using an X-ray diffractometer (XRD). XRD studies were carried out on a power X-ray diffractometer (Rigaku D/Max 2550pc, Rigaku Corporation, Japan). The accelerating voltage was 40 kV and the current was 300 mA. Diffraction patterns were collected at 2º~80º θ using Cu K_α radiation. An SEM (Hitachi S-5701) equipped with an EDX was used for the morphology and chemical composition characterization of the ferrospheres. A Philips XL30 ESEM was used to analyse the image of ferrosphere particles. Ferrosphere particles were examined within the ESEM without any form of preparation (i.e., there is no gold or carbon coating, and samples were placed directly onto the ESEM stub). The operational voltage of the ESEM was 20 kV.

RESULTS AND DISCUSSION

Morphology of bulk fly ashes and content of ferrospheres

SEM is one of the best and most widely used techniques for the identification and characterization of mineral phases and morphology of fly ashes (Gomes *et al*., 1999; Vassilev and Vassileva, 2005; Zhao *et al*., 2006). The morphology of bulk fly ashes is shown in Fig.1. The size of the fly ash particles observed ranges from less than 1 μm to greater than 100 μm. The majority of the particles range in size from approximately 10 μm to 50 μm and consists of solid spheres (cenospheres) and amorphous materials (Figs.1a and 1b). Figs.1c~1f are typical morphology of cenospheres in fly ashes. A large percentage of ferrospheres are commonly 5~50 μm in size. The amount of ferrospheres separated from two fly ash samples is 3.0% and 10.2%, the Fe contents in ferrospheres are 16.62% and 27.13%, and the iron enrichment factors in ferrospheres are 6.97 and 4.23, respectively. Iron shows significant enrichment in ferrospheres when compared to their respective fly ashes.

Mineralogy and chemical composition of ferrospheres

Bulk fly ashes are mainly composed of amorphous alumino-silicate materials and a smaller amount of crystalline phases. XRD patterns (Fig.2) show that the ferrospheres consist mainly of iron oxides, quartz, mullite and amorphous materials, while anhydrite is present in minor amounts. The iron oxides observed, collectively referred to as spinel, are identified as magnetite and hematite, which is consistent with (Gomes *et al*., 1999; Zhao *et al*., 2006). Iron in coal is associated with sulfur pyrite (FeS_2), and non-sulfur-bearing minerals such as ankerite ($CaFe(CO_3)_2$), siderite ($FeCO_3$), and Fe^{2+}-illite (clay mineral). Iron oxide minerals in fly ashes are derived mainly from the decomposition and oxidation of pyrite, siderite, and ankerite in feed coals during the combustion process. Hematite is formed from the decomposition and oxidation of pyrite during combustion and hematite is dissolved by molten silicates and then precipitates as crystalline magnetite. The amorphous materials may be amorphous inorganic materials resulting from the combustion of the coal and/or unburned organic matter (Kantiranis *et al*., 2005; 2006). Anhydrite can be formed by a pyrite-calcite reaction (Filippidis *et al*., 1996). As determined by EDX (Fig.3), the predominant elements in the ferrospheres were iron, silicon, sulfur, aluminum and calcium. In Figs.3 and 4, a dense ferrosphere is mainly composed of iron with small amounts of Si, S, Al, and Ca. A higher silicon element composition in a small sphere adhered to the ferrosphere is observed by EDX (Fig.4).

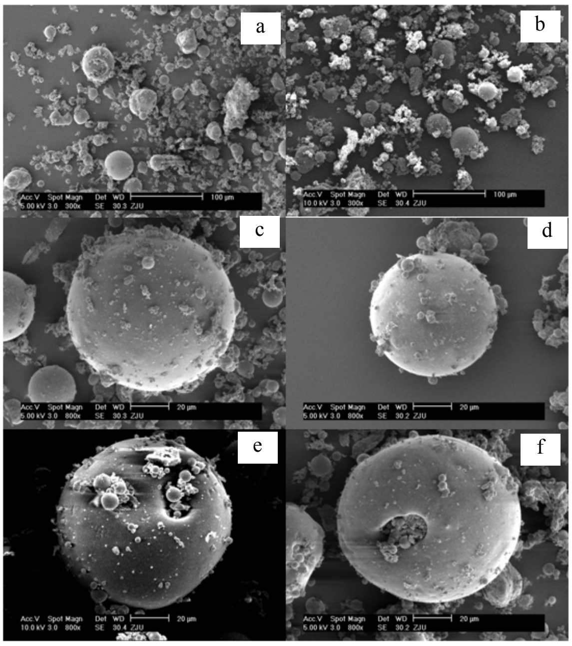


Fig.1 ESEM images of bulk fly ashes. (a) and (b) Bulk fly ashes; (c) and (d) Cenospheres with small sphere adhered to the surface; (e) and (f) Hollow cenospheres

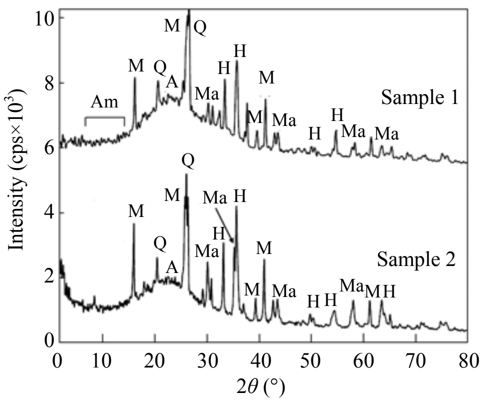


Fig.2 XRD patterns of ferrospheres extracted from fly ashes. A: anhydrite; Am: amorphous materials; H: hematite; Ma: magnetite; M: mullite; Q: quartz

Microstructure of ferrospheres

A general view of the microstructure of ferrospheres is shown in Fig.5. The morphology of ferrospheres is varied (Fig.5a). Most of the ferrospheres have rough surfaces, and their shapes are close to an ideal sphere. The ferrospheres exhibit various textures on the surface and often show a surface

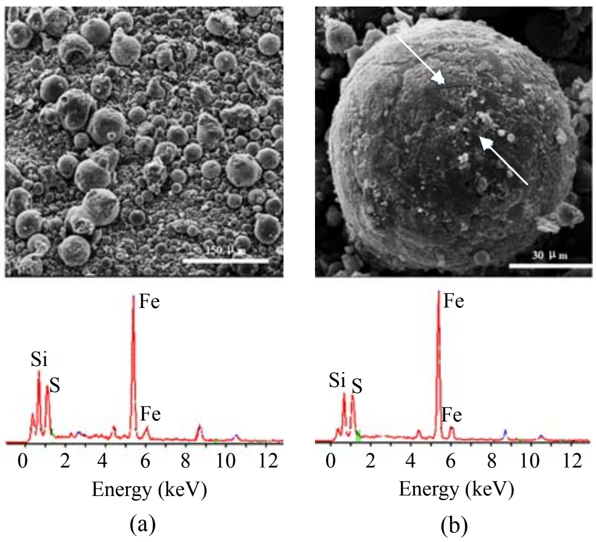
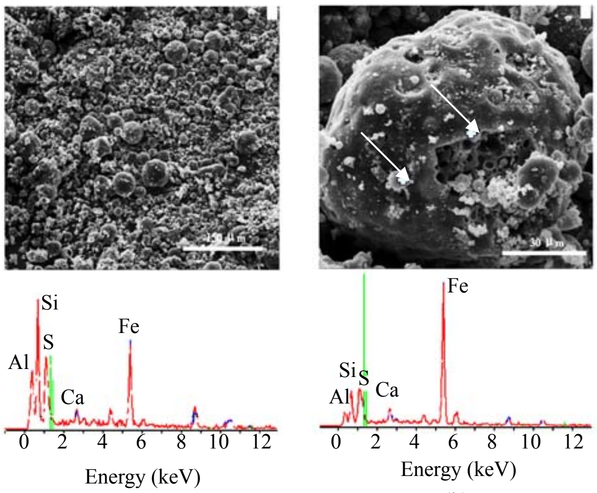


Fig.3 SEM images (top) and EDX (bottom) spectra of ferrospheres in fly ash sample 1. (a) General view of the agglomeration of spherial and irregular ferrospheres; (b) Ideal spheric ferrosphere composed of Fe and of small Si and S. Arrows indicate the points of EDX analysis

melting point. There are often a number of microspheres adhering to their surface. According to the microstructure characteristics identified by ESEM (Fig.5), the ferrospheres in fly ashes can be divided into several types, namely smooth ferrospheres, polygon ferrospheres, dendritic ferrospheres, granular ferrospheres and molten drop ferrospheres. The diameter of smooth ferrospheres often varies from 40 μm to 60 μm (Fig.5b). Lower Fe content is detected in these ferrospheres. Polygon ferrospheres (Fig.5c) often exhibit blocky surface crystallites of iron oxides. A granular ferrosphere is a rough, porous and granular surface structure, and often complicated by the additional presence of small granular crystals (Fig.5e). The granular crystals on the surface of the ferrospheres are predominantly a result of iron oxide crystallization when the temperature decreases. The dendritic ferrospheres with a lot of iron oxide crystals arrayed as stripes on the surface are illustrated in Fig.6. The detailed ESEM observations show that iron oxide crystals on dendritic ferrospheres form trigonal morphology with smaller spheric grains



(a) (b)

Fig.4 SEM images (top) and EDX (bottom) spectra of ferrospheres in fly ash samples 2. (a) General view of ferrospheres, showing a variety of sizes and shapes of spheres; (b) Ferrosphere composed of Fe and of small Si, S, Al, and Ca. Arrows indicate the points of EDX analysis

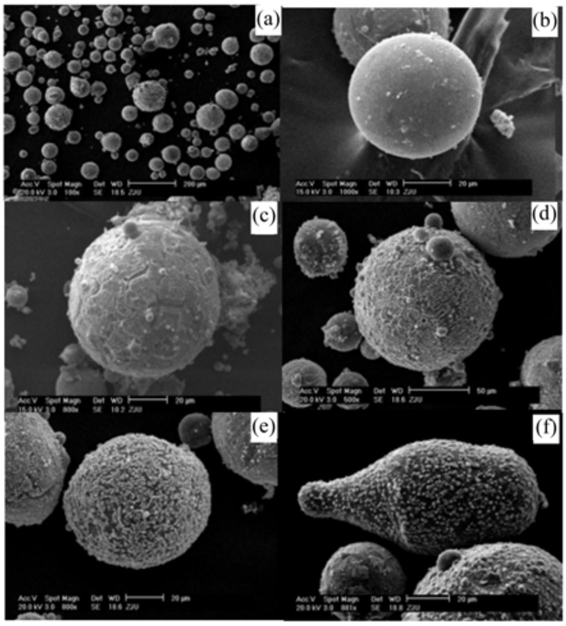


Fig.5 ESEM images of ferrospheres. (a) General view of ferrospheres; (b) Smooth ferrosphere; (c) Polygonal ferrosphere; (d) Dendritic ferrosphere; (e) Granular ferrosphere; (f) Molten drop ferrosphere

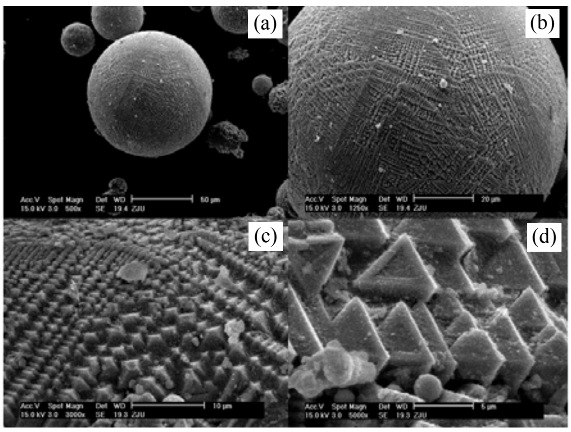


Fig.6 ESEM images of microstructure [(a) and (b)] and detailed structure of iron oxide crystallization on surface of dendritic ferrosphere [(c) and (d)]

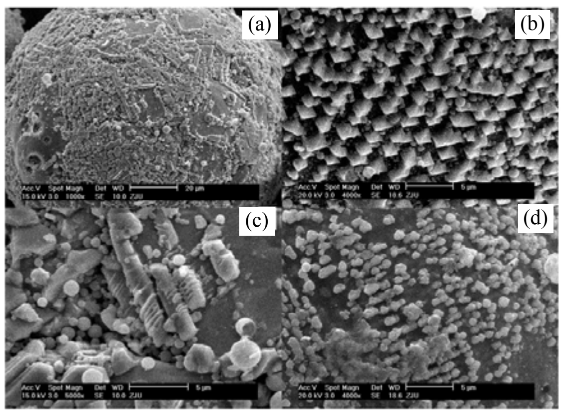


Fig.7 ESEM images of microstructure (a) and detailed structure of iron oxide crystallization [(b), (c) and (d)] of molten drop ferrosphere

attached to the surface of the ferrosphere (Figs.6c and 6d). Fig.7 shows the molten drop ferrospheres with a great deal of globlet and granular particles on the surface. The molten drop ferrospheres may be the crystallization of iron oxides and from the liquid melt of the inner particles.

Different causes are given for the formation of these different types of microstructure in ferrospheres. The surface microstructure of ferrospheres and the size of the crystallites depend on the temperature and duration time of coal combustion, as well as the exact combination of iron-bearing minerals and other minerals or the coal matrix (Hower *et al*., 1999; Vassilev *et al*., 2003; Zhao *et al*., 2006). Iron oxide crystallilization on the surface of ferrospheres could also come from the vaporization of inherent minerals. The major source responsible for the formation of ferrospheres is the minerals found in raw coal, namely iron-bearing sulfides, sulfates, carbonates, and so on. The microstructure of ferrospheres in fly ashes can be used for identification of fly ashes emissions and the analysis of fly ash particulate pollution in local pollution sources and on a wider regional scale.

CONCLUSION

Different amounts of ferrospheres in fly ashes can be extracted by a magnetic separation technique. A large percentage of ferrospheres are commonly 5~50 μm in size. The mineralogical composition of ferrospheres includes quartz, mullite, magnetite, hematite, anhydrite and amorphous materials, and are mainly composed of Fe, Si, S, Al and Ca. The ferrospheres in fly ashes exhibit different surface microstructure characteristics. Several different microstructures of ferrospheres are identified: smooth ferrospheres, polygonal ferrospheres, dendritic ferrospheres, granular ferrospheres and molten drop ferrospheres. The iron oxide crystallites in ferrospheres are mainly derived from the decomposition and oxidation of iron-bearing minerals in coal during combustion. SEM coupled with EDX analysis was capable of providing fast and accurate results on the morphology, chemical composition and microstructure of ferrospheres and helped us to understand environmental issues related to the disposal and ultilization of fly ashes.

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