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Synthesis and Stability of Iron Nanoparticles for Lunar Environment Studies

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Summary

Simulant of lunar dust is needed when researching the lunar environment. However, unlike the true lunar dust, today's simulants do not contain nanophase iron. Two different processes have been developed to fabricate nanophase iron to be used as part of the lunar dust simulant:
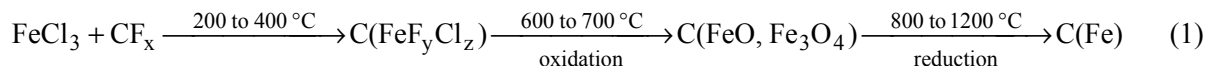
(1) Sequentially treating a mixture of ferric chloride, fluorinated carbon, and soda lime glass beads at about 300 °C in nitrogen, at room temperature in air, and then at 1050 °C in nitrogen. The product includes glass beads that are grey in color, can be attracted by a magnet, and contain α-iron nanoparticles (which seem to slowly lose their lattice structure in ambient air during a period of 12 months). This product may have some similarity to the lunar glassy regolith that contains Fe^0.

(2) Heating a mixture of carbon black and a lunar simulant (a mixed metal oxide that includes iron oxide) at 1050 °C in nitrogen. This process simulates lunar dust reaction to the carbon in a micrometeorite at the time of impact. The product contains a chemically modified simulant that can be attracted by a magnet and has a surface layer whose iron concentration increased during the reaction. The iron was found to be α-iron and Fe_3O_4 nanoparticles, which appear to grow after the fabrication process, but stabilizes after 6 months of ambient air storage.

Introduction

Understanding the physics, chemistry, and toxicity of the lunar dust in the lunar environment is essential for lunar exploration. In order to do research on lunar dust, a few simulants that mimic the lunar dust obtained during the Apollo missions were produced. Although it is noted that the Apollo lunar dust contains chemically reactive iron nanoparticles, none of the current simulants do (Ref. 1). The goal of this research is to produce iron nanoparticles that can be used as a component of lunar dust simulants. Additional efforts were made to investigate the stability of the iron nanoparticles thus produced over a period of several months.

The synthesis of iron nanoparticles in carbon has been performed previously in 1994 and was reported (Refs. 2 and 3). The chemical process includes exposing a mixture of ferric chloride ($FeCl_3$) and graphite fluoride (CF_x) at 200 to 400 °C, followed by oxidation at 600 to 700 °C and reduction at 800 to 1200 °C:

$$FeCl_3 + CF_x \xrightarrow{\text{200 to 400 °C}} C(FeF_yCl_z) \xrightarrow[\text{oxidation}]{\text{600 to 700 °C}} C(FeO, Fe_3O_4) \xrightarrow[\text{reduction}]{\text{800 to 1200 °C}} C(Fe) \quad (1)$$

where C(XX) means nanoparticles of XX embedded in carbon.

Stability of this product was examined by comparing its x-ray diffraction (XRD) data taken 1 week, 1 year, and 14 years after it was produced, adhered to a glass slide by double-sided adhesive tape and stored in ambient air (Fig. 1). This particular sample, $C(Fe, FeO, Fe_3O_4)$, was made according to the above-described reaction (1), where the final reduction did not reach completion. The 1-year and 14-year
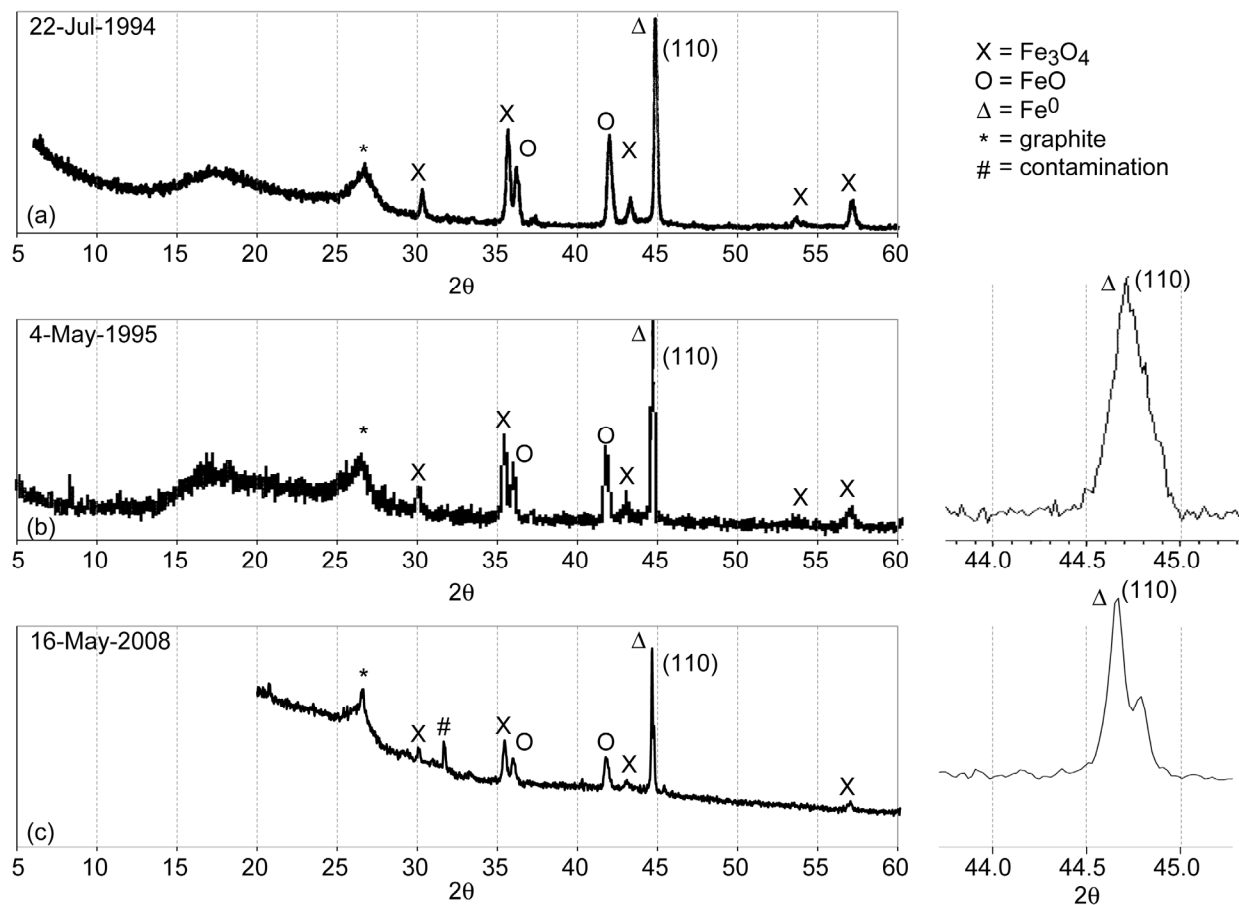
Figure 1.—X-ray diffraction data of iron and iron oxide nanoparticles in carbon obtained according to reaction (1). (a) 1 week old. (b) 1 year old. (c) 14 years old.

data points were taken from the same instrument at the same setting. From these XRD data, no oxidation of the α-iron nanoparticles can be observed during this 14-year period, since the Fe_2O_3 peak continues to be missing, and the FeO and Fe_3O_4 peak height relative to the Fe peak became lower as time progressed. This suggests the iron nanoparticles were well embedded in carbon and well protected from the surrounding ambient air. Additionally, the α-iron nanoparticles appear to become either more ordered or larger in size during the 14-year period, as the width of the α-iron's (110) peak becomes narrower. This sample was not examined by transmission electron microscopy (TEM). However, a TEM image of its precursor, $C(FeF_yCl_z)$, shows the particle size was in the <10 to 100 nm range (Fig. 2). Other TEM images of this precursor show nanoparticles as large as 250 nm.

It was thought that the trace amount of ambient air in nitrogen could be the source of oxygen from which the FeO and Fe_3O_4 nanoparticles in reaction (1) are produced. However, trace amounts of air were later found to be insufficient to prevent the iron halide from evaporation. Alternatively, large amounts of air reacted with iron halide quickly to form large Fe_2O_3 particles separated from the carbon structure. There is evidence indicating that nanosized iron oxide in carbon is best produced if the iron halide nanoparticles in carbon oxidized slowly when exposed to either fused quartz (SiO_2) or nickel oxide powder (Ref. 3). However, the nanoparticles thus produced from oxidation by nickel oxide were not pure iron, but a nickel-iron alloy (Ref. 3).

In this report, two different approaches are used to produce iron nanoparticles for use as a component of lunar dust simulants. Process (1) follows the same approach as that described above, except the oxidation reactions (see reaction (1)), use soda-lime glass as the source of oxygen. Soda lime glass was selected so that the product would have some similarity to the glassy materials in the lunar regolith
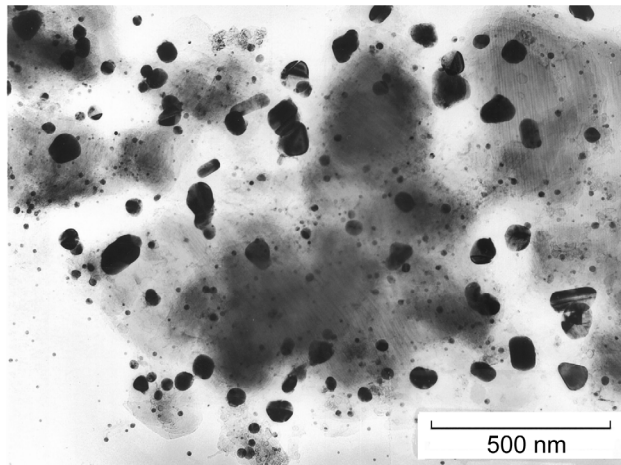
Figure 2.—Transmission electron micrograph of product resulted from $CF_{0.9}$-$FeCl_3$ reactions at 310 °C in nitrogen. Dark globules are compound of iron.
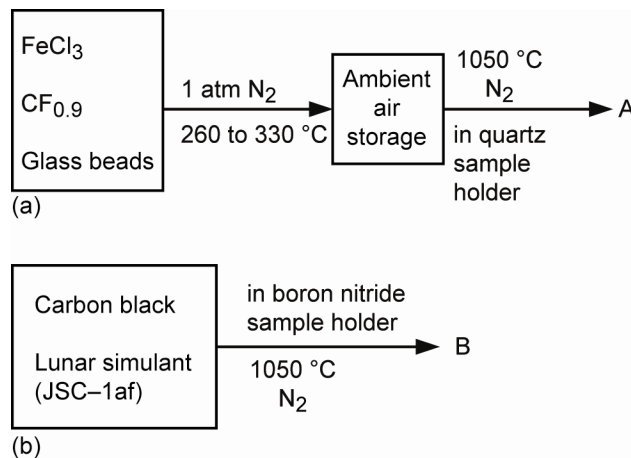

Figure 3.—Iron nanoparticles examined in this report. (a) Product A from process (1). (b) Product B from process (2).

(Ref. 4). Process (2) follows the chemical principles for the above process, but on today's lunar simulant. This process involves reducing iron oxides embedded in a host material by carbon. In this approach, the host material was JSC–1af (Ref. 5), which is a lunar dust simulant candidate and primarily a silicide containing mixed-metal oxides (including iron oxide), and carbon black was used as the reducing agent. This process is designed so that the reaction conditions are similar to what the conditions are believed to be when a meteorite hits the lunar surface, since meteorites contain carbon, lunar dust contains iron oxides, and the high temperature would result from the impact. The fact that carbon is in the meteorites but much depleted in the lunar samples (Ref. 6) suggests the possibility that carbon is at least partly consumed by the mixed-metal oxides in the lunar dusts.

Synthesis

Two of the iron nanoparticle samples that were fabricated according to the two different approaches described above are presented in this report. Synthesis of these samples is summarized in Figure 3.

Product A was produced when a mixture of $FeCl_3$, fluorinated carbon powder ($CF_{0.9}$), and 0.1-mm soda lime glass beads (mass ratio 0.7:1:1.1) was heated under a nitrogen environment in a glass reactor at a temperature range of 260 to 330 °C for 1 h. The product was placed in ambient air for 50 h. It was then placed in a quartz sample holder, which in turn was placed in a quartz reactor and further heated in nitrogen at 1050 °C for 1 h to produce iron nanoparticle products, as described in Figure 3.

Product B in Figure 3 was obtained by placing a mixture of lunar simulant JSC–1af and carbon black (mass ratio 5.3:1) in a boron nitride sample holder, which was then placed under a nitrogen environment in a quartz tube and heated at 1050 °C for 1.3 h.

The XRD, scanning electron micrograph (SEM), and energy dispersive spectrum (EDS) data of these products were examined and analyzed. The stability of these iron nanoparticles in ambient air was also investigated by examining the XRD of the samples several times during a period of 1 year.

Results and Discussions

For either sample made from the reactions described in Figure 3, the EDS data from different sites (probe size 0.5 to 50 µm range) in the sample invariably show the same element distribution with large peaks of many elements including iron. In addition, both products were ferromagnetic (attracted to a regular magnet), and the XRD data indicate the products contain α-iron. This indicates that particles of α-iron smaller than the probe size (0.5 µm) were produced and distributed over the entire samples. Details of the results are described and discussed below.

Process (1): Lunar Glassy Regolith Simulant

The process used in this study to fabricate product A (described in Fig. 3) is similar to the process to fabricate the product described in Figure 1 (from Ref. 2). Both processes follow reaction (1), except the former used 0.1-mm soda lime glass beads as the source of oxygen during the oxidation reaction, whereas the latter used the quartz reactor as the oxygen source. The glass beads had more surface area and are in direct contact with the reactant $C(FeF_yCl_z)$. It therefore was more effective in using its oxygen to burn off carbon and oxidize the mixed iron halide. Consequently, a product of glass beads containing α-iron was formed. Most of these beads were still about 0.1 mm in diameter, but were grey in color and could be attracted to a magnet. This glass-iron nanoparticle composite appears to have some similarity to the lunar glassy regolith, which contains Fe^0. Its EDS data was examined and compared with that of the precursor: the glass beads before the reactions. The results are described in Figure 4. The largest difference between the reactant glass beads and the product glass beads is that the product contains more iron, but less sodium. The iron is believed to be migrated from the reactant $C(FeF_yCl_z)$ to a surface layer on or under the glass bead surface. The sodium, however, is believed to be evaporated after the sodium oxide component in the glass beads released its oxygen for oxidation of iron and carbon as described in reaction (1). The loss of sodium oxide from the soda-lime glass beads may cause its overall bond strength (Ref. 7) and softening point (Ref. 8) to increase. This would explain why the soda lime glass has a softening point of 575 °C, but did not soften at the reaction temperature of 1050 °C used in this research.

The product A in Figure 3 was further examined using XRD to examine its structure 3, 8, and 11 months after the completion of the fabrication reaction (Fig. 5). Comparing this figure with Figure 1, where the sample was made by the same process except without the reactant glass beads, both figures contain α-iron and Fe_3O_4 peaks. Figure 5 (XRD of product A in Fig. 3) has no carbon peaks, though, and no FeO peaks, whereas it has Fe_2O_3 peaks that are absent in Figure 1. The absence of the carbon peaks suggests most carbon reacted with the oxygen in the glass beads and became either CO or CO_2, which agrees with the EDS data: Figure 4 shows a very small carbon peak. Without sufficient carbon in the sample, the iron oxides are more exposed to the surrounding ambient air. This exposure appears to have resulted in the oxidation of FeO into Fe_2O_3 because product A in Figure 3 contains Fe_2O_3, but not FeO.
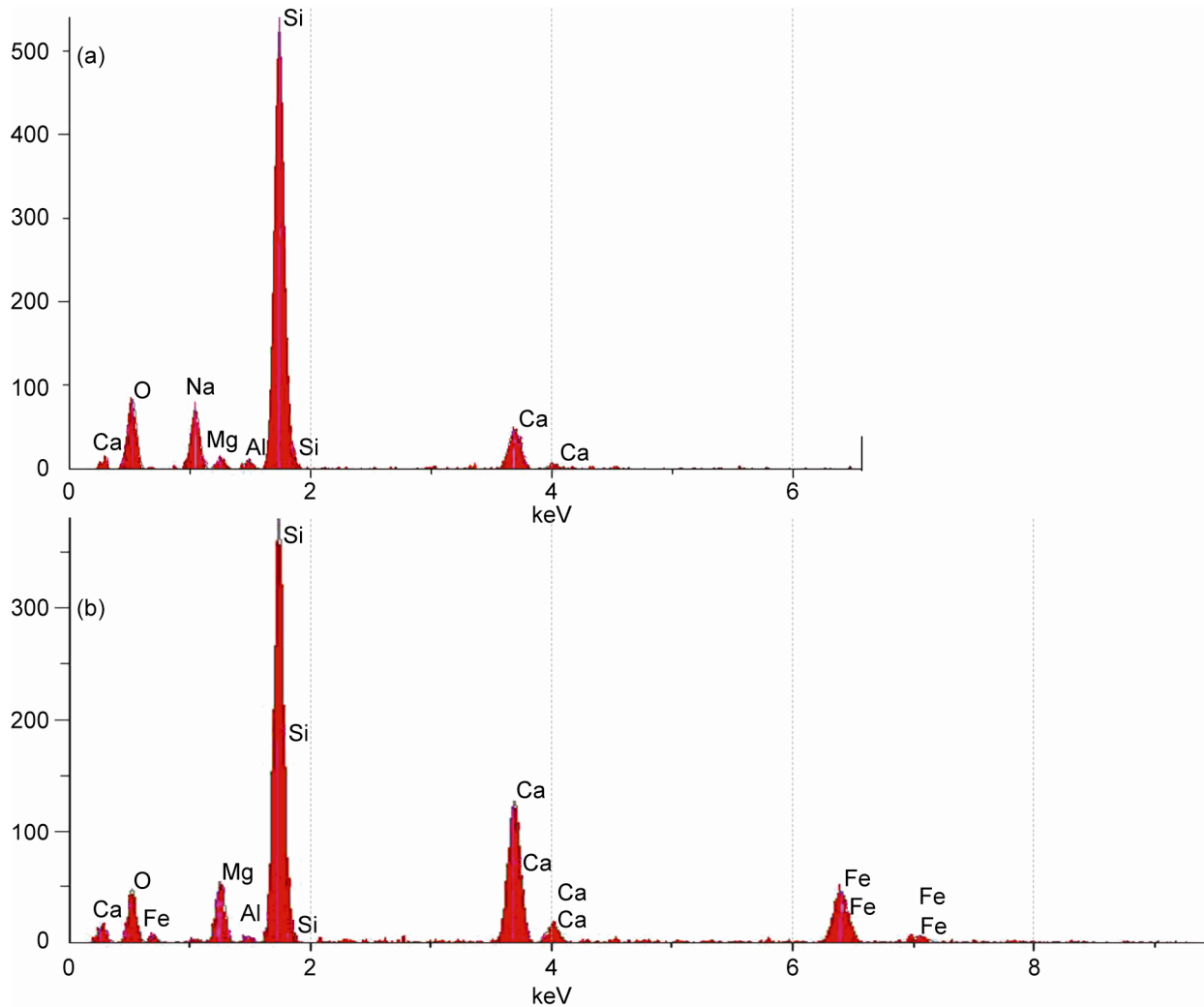
Figure 4.—Energy dispersive spectra of soda-lime glass bead used in process (1) reactions that produced iron nanoparticle product A as described in Fig. 3. (a) Before reaction. (b) 11 months after reaction.

Comparing the 3-, 8-, and 11-month XRD data in Figure 5, the peaks for the iron nanoparticles seem to be slowly decreasing. These small but apparent changes may possibly be the result of experimental error. They may also possibly be true changes caused by the insufficient protection by carbon from the surrounding ambient air and the glass beads. The nanoparticles could slowly react with air or glass beads, lose its lattice structure, and become more disordered during this period.

The α-iron external to the glass beads was removed by further treating product A in Figure 3 with 35 wt% HCl at room temperature for 20 min, rinsed, and heated to 1050 °C in nitrogen. After such treatment, a small fraction of glass beads could still be attracted by a magnet, indicating some α-iron was present in the glass beads and therefore protected from the HCl attack.
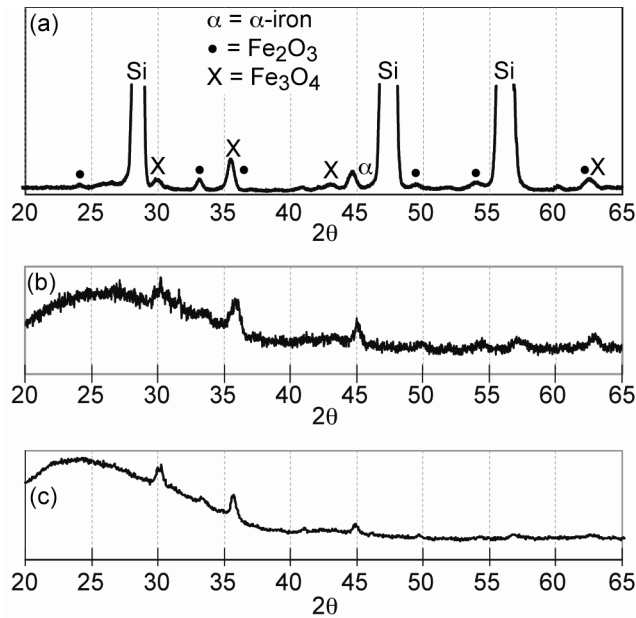
Figure 5.—X-ray diffraction from product A in Fig. 3.
(a) With silicon standard, 3 months after synthesis.
(b) 8 months after synthesis. (c) 11 months after synthesis.

Process (2): Lunar Simulant That Produces α-Iron

The process to fabricate product B described in Figure 3 is a reaction between a lunar simulant and carbon—a reaction of reducing iron oxides embedded in a host material by carbon (see reaction (1)). It is a simulation of a proposed space weathering process where nanophase iron particles on lunar regolith grains are created when carbon-bearing micrometeorites impact lunar regolith.

Figure 6 presents typical EDS data taken from a number of regions included in the accompanying SEM photo of product B in Figure 3. For comparison, the EDS data for the reactant (JSC–1af) is also included. The most notable differences between the reactant and the product is that the product has higher iron and oxygen concentrations near the surface of the JSC–1af particles, the region that was actually probed by the instrument. The oxygen concentration increase could be explained as follows: The carbon-JSA1af reaction would at first remove some oxygen from the mixed oxide, breaking the chemical bonds extensively, resulting in a reactive intermediate product which could then bond to an excessive amount of oxygen when (or if) the product was stored in ambient air after the completion of the process. The increase of iron concentration near the surface of the JSC–1af particles, however, was not expected and cannot be explained satisfactorily. It is suggested that during the reactions immediately after some oxygen atoms were removed by carbon, α-iron would crystallize from the unstable, oxygen-deficient intermediate product. This would cause a reduction of ferrous or ferric iron near the surface and result in diffusion of these ions from the interior to the surface. This suggestion is supported by the fact that the reaction temperature (1050 °C) is only a little lower than the melting point of JSC–1af (1150 °C). Under this condition, the diffusion coefficient of ions in a solid may be high.

That α-iron is present in the product is supported by the fact that the product can be attracted by a magnet immediately after the process is complete and the product exposed to ambient air. However, it is interesting that the α-iron XRD peak (at 2θ near 44° to 45°) was missing when the XRD spectrum was
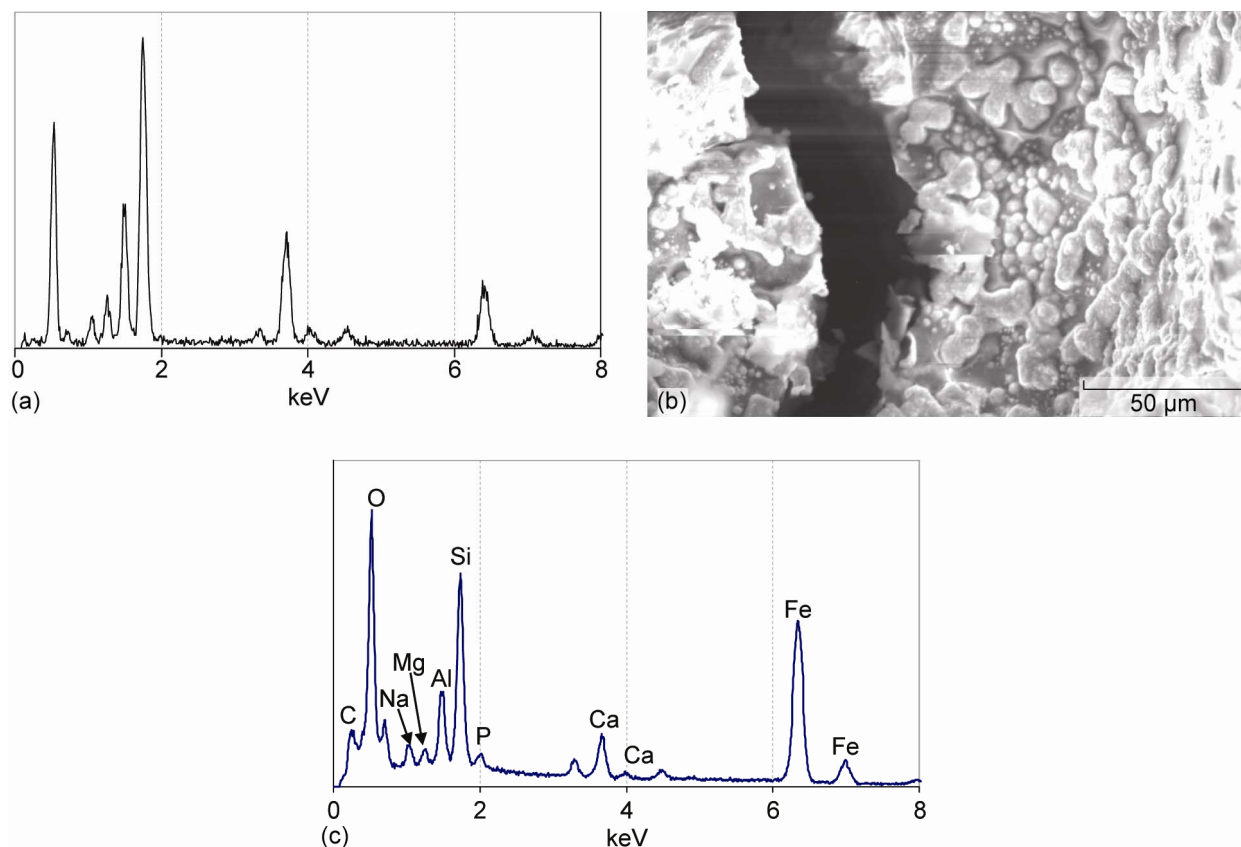
Figure 6.—Energy dispersive spectroscopy (EDS) of reactant and product from process (2) (see Fig. 3) resulting from reaction of JSC–1af lunar simulant and carbon black product. (a) EDS of JSC–1af reactant. (b) Scanning electron microscope image of product B, 1 month after synthesis. (c) EDS of product B taken from areas shown in part (b).

taken the first time, about 1 month after the completion of the process. The α-iron peak did show up in the later scans made 6 and 10 months after the completion of the reactions (Fig. 7). At the beginning, the iron might be present as nanoparticles too small to be detected by XRD. Alternatively, the iron may be present initially in a glassy state after partial melting. In either case the nanoparticles grow in size, resulting in the appearance of the XRD peaks.

For comparison, in previous work nanophase iron particles were found in vapor-deposited olivine produced by pulsed laser irradiation on an olivine sample (Ref. 9). That process involved irradiation, heating, evaporation, and condensation. The research presented in this report, however, shows that iron nanoparticles can be formed by heating a lunar simulant with carbon at 1050 °C in nitrogen. This process involves heating, carbon reactions, and perhaps ferrous or ferric ion diffusion in the lunar regolith grains, but not evaporation or condensation. It simulates the reactions between micrometeorites and the lunar regolith grains that are impacted, heated, and nearly melted, but not evaporated. Both processes result from efforts of trying to simulate the complex "space weathering" phenomena on the lunar surface, but have different focuses. The results suggest that the "space weathering" that produces nanophase iron may have more than one kinetic path.

The process of heating alone cannot produce iron from the lunar dust simulant. In an experiment performed for this study JSC–1af was heated at 1050 °C in nitrogen, without the presence of carbon. The product thus obtained could not be attracted to a magnet and was not further examined.
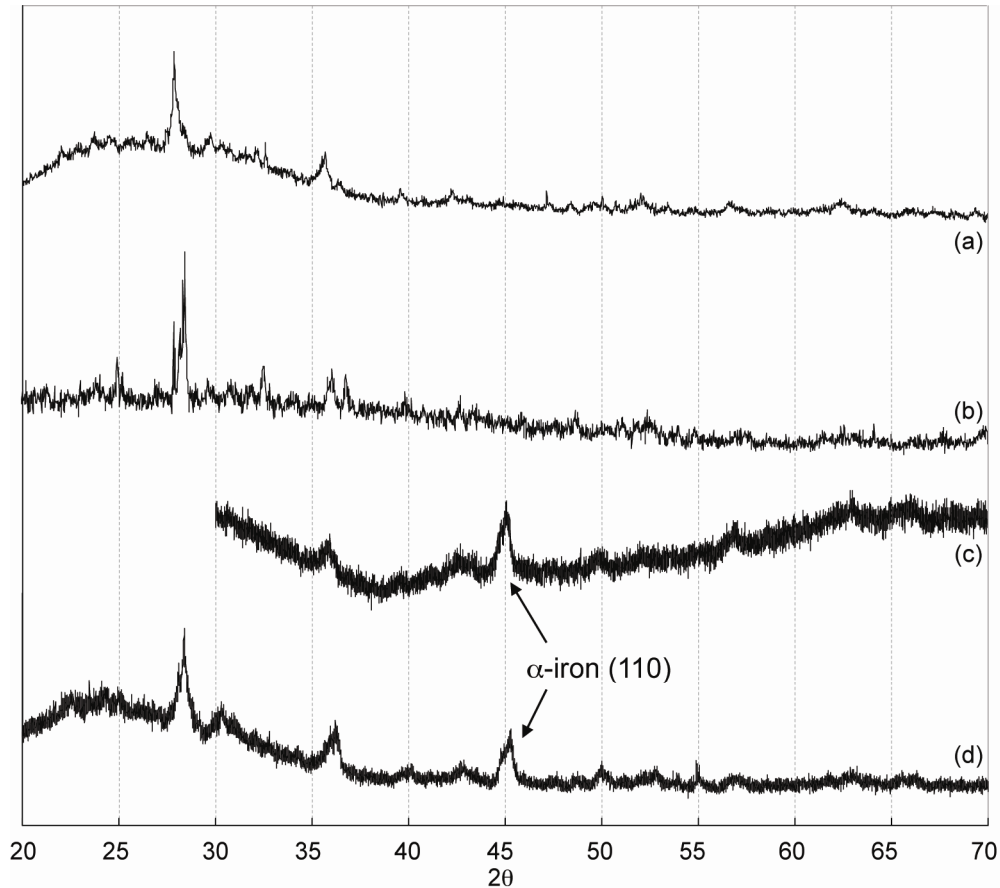
Figure 7.—X-ray diffraction of reactant and product B from process (2) (see Fig. 3) in reaction of JSC–1af lunar simulant and carbon black. (a) JSC–1af reactant. (b) Product B, 1 month after synthesis. (c) Product B, 7 months after synthesis. (d) Product B, 11 months after synthesis.

Conclusions

Two different processes were developed to fabricate nanophase iron that can be used as part of the lunar stimulant. Process (1) produces a simulant similar to the lunar glassy regolith that contains nanophase iron: sequentially treating a mixture of ferric chloride, fluorinated carbon, and soda lime glass beads at about 300 °C in nitrogen, at room temperature in air, and then at 1050 °C in nitrogen. The products include glass beads that are grey in color and can be attracted by a magnet. The x-ray diffraction data indicates it contains α-iron nanoparticles, some Fe_2O_3, and some Fe_3O_4. The lattice structure of the nanoparticles seems to slowly become disordered in ambient air during the 12-month observation period. Process (2) is a reaction that simulates lunar dust reacting with carbon in a micrometeorite at the time of impact: this is accomplished by heating a mixture of carbon black and JSC–1af —a lunar simulant candidate of mixed-metal oxides that contain iron—at 1050 °C in nitrogen. The product contains a chemically modified JSC–1af that can be attracted by a magnet and has a surface layer whose iron concentration increased during the reaction (confirmed by energy dispersive spectrum data). The x-ray diffraction identifies the iron as in the form of nanoparticles of α-iron and Fe_3O_4. The nanoparticles appear to grow after the completion of the fabrication process, but are stabilized after 6 months of ambient air storage.

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14. ABSTRACT
Simulant of lunar dust is needed when researching the lunar environment. However, unlike the true lunar dust, today's simulants do not contain nanophase iron. Two different processes have been developed to fabricate nanophase iron to be used as part of the lunar dust simulant: (1) Sequentially treating a mixture of ferric chloride, fluorinated carbon, and soda lime glass beads at about 300 °C in nitrogen, at room temperature in air, and then at 1050 °C in nitrogen. The product includes glass beads that are grey in color, can be attracted by a magnet, and contain α-iron nanoparticles (which seem to slowly lose their lattice structure in ambient air during a period of 12 months). This product may have some similarity to the lunar glassy regolith that contains Fe^0. (2) Heating a mixture of carbon black and a lunar simulant (a mixed metal oxide that includes iron oxide) at 1050 °C in nitrogen. This process simulates lunar dust reaction to the carbon in a micrometeorite at the time of impact. The product contains a chemically modified simulant that can be attracted by a magnet and has a surface layer whose iron concentration increased during the reaction. The iron was found to be α-iron and Fe_3O_4 nanoparticles, which appear to grow after the fabrication process, but stabilizes after 6 months of ambient air storage.

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