JOURNAL OF Materials CHEMISTRY Communication

Coating nanosized iron oxide particles on submicrospherical alumina by a sonochemical method

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Recieved 23rd June 1998, Accepted 22nd July 1998

Iron oxide which adhered strongly to an amorphous alumina core has been prepared by a sonochemical method; the phase transformation of maghemite to haematite was greatly retarded in the coating.

The coating of metals and metal oxides on substrates and the interaction between coated metallic elements and substrates have long been of interest to materials scientists[1,2] and catalysis chemists.[3,4] Conventional methods such as evaporation, impregnation, precipitation and sputtering usually yield a coated polycrystalline product. As reported by Suslick *et al.*[5] the sonochemical method can be used as a tool to prepare nanosized amorphous metals. The formation of the amorphous metals is due to the extreme conditions, such as the highest transient temperature, which exceeds 5000 K at localized hot spots, and the ultrafast cooling rate of $>10^{10}$ K s^{-1}, that can be obtained in sonication. Recently, sonication has been further developed as a tool to drive the deposition of iron oxide, nickel and cobalt on the surface of silica particles.[6–8] However, for materials scientists, since silica can form impurity phases with many coated magnetic materials,[9–11] Al_2O_3 is a superior substrate and a better matrix material. This is the reason why developing a general and efficient coating method for Al_2O_3 is an important objective. Here, we report the coating of nanosized iron oxide particles on submicrospherical alumina by employing sonication. We also report the new finding that the known transformation of maghemite (γ-Fe_2O_3) to haematite (α-Fe_2O_3) is greatly retarded owing to a strong interaction between the coated iron oxide and the amorphous alumina.

Submicrospherical alumina was prepared by hydrolysis of a dilute solution of aluminum *sec*-butoxide in a mixture of octan-1-ol, butan-1-ol and acetonitrile.[12] The precipitate was washed thoroughly with acetone and dried in vacuum. Crystallized γ-alumina was obtained when the precipitate was heated to 1000 °C. Sonochemical coating of nanosized iron oxide particles on alumina spheres was carried out under 1.5 atm of argon at 0 °C for 3 h (Ti-horn, 20 kHz, 100 W cm^{-2}). In the sonication cell, 400 mg of pre-prepared alumina submicrospheres, 1 ml of iron pentacarbonyl, and 40 ml decalin were mixed together. Prior to sonication, argon gas was bubbled for 1 h, preventing possible oxidation of iron carbonyl from air. The sonication product was then washed thoroughly with hexane.

Fig. 1 shows the XRD patterns of as-prepared alumina and its iron oxide-coated products. It clearly indicates that as-prepared alumina and its as-prepared sonication product are formed in the amorphous state [Fig. 1(a)]. This amorphous nature was further confirmed by electron diffraction measurements, which showed only a diffuse ring pattern. However, the as-prepared coated sample heated at 400 °C developed the characteristic patterns of γ-Fe_2O_3 or Fe_3O_4 (magnetite). Differentiating between γ-Fe_2O_3 and Fe_3O_4 by XRD is somewhat difficult, because their XRD patterns are almost identical (ASTM card 19–629 for Fe_3O_4 and 24–81 for γ-Fe_2O_3). However, Mössbauer spectroscopy results show the product to be a mixture of γ-Fe_2O_3 (18%) and Fe_3O_4 (72%). Additionally, we can not completely exclude the possibility that γ-Fe_2O_3 was produced from Fe_3O_4 in the process of sample handling, since Fe_3O_4 is very sensitive to air. For crystallized alumina, a γ-Al_2O_3 structure was confirmed by its XRD pattern [Fig. 1(d)] compared to ASTM card-10–425. The weakening of γ-Al_2O_3 peaks in the XRD pattern for coated samples is due to the fact that the alumina surface was covered by iron oxide. When the sonication was carried out with the submicrospherical crystallized γ-alumina and the product heated to 400 °C in argon, γ-Fe_2O_3 (or Fe_3O_4) was observed by XRD [Fig. 1(e)].

Fig. 2 shows the TEM images of two samples heated to 400 °C in argon. Fig. 2(a) shows the TEM image of iron oxide coated on amorphous alumina, and Fig. 2(b) that on crystallized γ-alumina. It is observed that the alumina substrate has a particle size ranging from 180 to 300 nm and a regular spherical shape. Most of the Fe_2O_3 particles coated on amorphous alumina are resolved, and separated from each other and possess a relatively regular spherical shape. Moreover, they are strongly adhered to the alumina core and have a radius of 10–20 nm, whereas the Fe_2O_3 coated on crystallized γ-alumina is an agglomerate of small particles with a size distribution of 1–10 nm, resembling a dense cloud. Most of Fe_2O_3 coated on crystallized alumina is not adhered to the substrate. This result indicates that the deposited materials are strongly influenced by the reactivity of the alumina surface.

Fig. 3 shows DSC curves of two as-prepared sonication products. Fig. 3(a) shows the DSC curve of as-prepared iron oxide coated on amorphous alumina, and Fig. 3(b) that on crystallized alumina. The endothermic peak at *ca.* 150 °C in both Fig. 3(a) and (b) is attributed to the desorption of con-

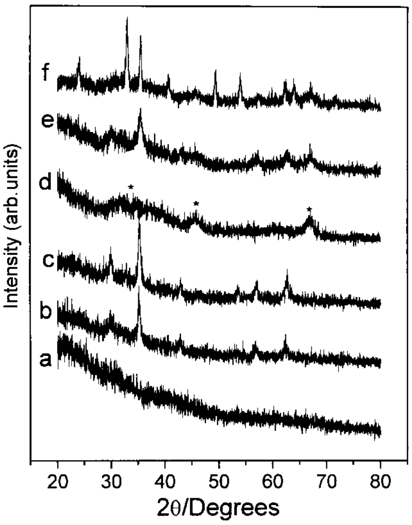

Fig. 1 XRD patterns of (a) the as-prepared material obtained by sonicating $Fe(CO)_5$ and amorphous alumina(the alumina is denoted as A); (b) iron oxide coated on A and heated at 400 °C in argon; (c) iron oxide coated on A and heated to 550 °C; (d) the as-prepared material obtained by sonication of $Fe(CO)_5$ and crystallized γ-alumina (the alumina is denoted as B and marked with an asterisk); (e) iron oxide coated on B and heated at 400 °C in argon; (f) iron coated on B and heated to 550 °C.

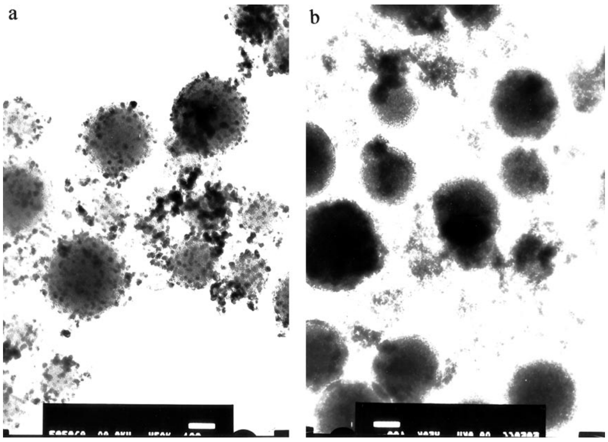

Fig. 2 TEM micrographs: (a) iron oxide coated on A alumina and heated to 400 °C in argon; (b) iron oxide coated on B alumina and heated to 400 °C in argon.

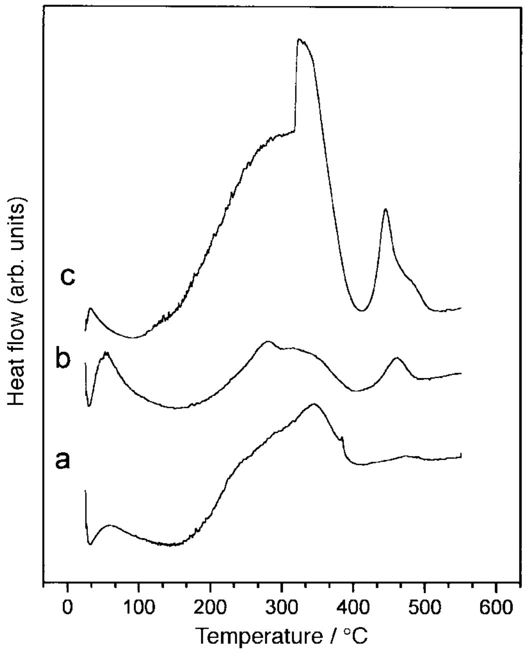

Fig. 3 DSC curves of (a) as-prepared sample of iron oxide coated on A alumina; (b) as-prepared sample of iron oxide coated on B alumina; (c) iron oxide prepared by the sonication of $Fe(CO)_5$ under air.

taminants such as solvent molecules from the surface of the product. The large exothermic peak in the range 200–350 °C corresponds to the crystallization of amorphous γ-Fe_2O_3. This is consistent with our previous results,[13,14] as well as with the above XRD results. On the other hand, it is of particular note that in contrast to Fe_2O_3 coated on amorphous alumina, which shows an almost featureless curve in the range 400–550 °C, a comparatively large exothermic peak was observed for Fe_2O_3 coated on crystallized γ-alumina [Fig. 3(b)]. It is proposed that transformation of γ-Fe_2O_3 to α-Fe_2O_3 occurs in this temperature region[15,16] (The above observation of a mixture of γ-Fe_2O_3 and Fe_3O_4 in the sample heated at 400 °C in argon does not influence our analysis, since, it is known that, for Fe_3O_4 particles smaller than 300 nm, the transformation to α-Fe_2O_3 includes an initial formation of γ-Fe_2O_3[15]). To confirm this, two investigations were carried out, First, a pure amorphous Fe_2O_3 sample was prepared following the method of Cao *et al.*[13] Its DSC curve is shown in Fig. 3(c) from which it is seen that a similar but larger exothermic peak is observed. Secondly, the above two as-prepared coated samples were heated to 550 °C under argon, and XRD measurements carried out. The XRD patterns are shown in Fig. 1(c) (iron oxide coated on amorphous alumina) and Fig. 1(f) (iron oxide on crystallized alumina), respectively. It is clearly seen that Fe_2O_3 coated on amorphous alumina remains as a γ-Fe_2O_3 phase even after heating to 550 °C, while the Fe_2O_3 on crystallized alumina is converted to α-Fe_2O_3. The absence of the 450 °C exothermic peak is a result of a strong interaction between the adhered iron oxide and the amorphous alumina, which results in the elevation of the phase transition temperature of γ-Fe_2O_3. At the same time, unadhered Fe_2O_3, when coated on crystallized alumina, shows a similar phase transformation behaviour to bulk Fe_2O_3. The mechanism of the $\gamma \rightarrow \alpha$ phase transformation is known to be dependent on the particle size and the mechanism of this transformation for small particles (<15 nm) is a chain mechanism[15] which involves recrystallization of up to 100 particles to form single α-Fe_2O_3 flakes of *ca.* 40–70 nm. Obviously, the strong interaction between coated iron oxide and alumina can hinder this type of gathering and recrystallization of iron oxide particles on an alumina surface. In addition, we can not rule out the involvement of trace Al^{3+} ions, which are known to replace Fe^{3+} ions in the unit cell, in elevating the transformation temperature.[17] If this phenomenon is indeed responsible for the higher transformation temperature, it should occur mainly with the amorphous alumina, where the interaction is stronger.

A. Gedanken thanks the Ministry of Science and Technology for supporting this research through the grant for infrastructure. Dr. Yuri Koltypin thanks the Ministry of Absorption for his Giladi scholarship. Dr. Ziyi Zhong and Dr. Yanming Zhao thank the Kort Scholarship fund for supporting their postdoctoral fellowships. The authors thank Professor M. Deutsch, Department of Physics, for extending the XRD facility, and Dr. Shifra Hochberg for editorial assistance.

References

1 D. Segal, *Chemical Synthesis of Advanced Ceramic Materials*, Cambridge University Press, 1989.
2 H. Yanagida, K. Koumoto, M. Miyayama, *The Chemistry of Ceramics*, John Wiley & Sons, New York, 1996.
3 A. A. Tsyganenko and P. Mardilovich, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4843.
4 D. A. Hucul and A. Brener, *J. Phys. Chem.*, 1981, **85**, 496.
5 (a) *Ultrsound: Its Chemical, Physical and Biological Effects*, ed. K. S. Suslick, VCH, Weinheim, 1988; (*b*) K. S. Suslick, S. B. Choe, A. A. Cichowlas and M. W. Grinstaff, *Nature*, 1991, **353**, 414.
6 S. Ramesh, R. Prozorov and A. Gedanken, *Chem. Mater.*, 1997, **9**, 2996.
7 S. Ramesh, Y. Koltypin, R. Prozorov and A. Gedanken, *Chem. Mater.*, 1997, **9**, 546.
8 S. Ramesh, Y. Cohen, R. Prozorov, K. V. P. M. Shafi, D. Aurbach and A. Gedanken, *J. Phys. Chem. B*, submitted.
9 J. L. Dormann, C. Djega-Mariadasson and J. Jove, *J. Magn. Magn. Mater.*, 1992, **104**–**107**, 1576.
10 C. Djega-Mariadasson, J. L. Dormann, M. Nogues, G. Viller and S. Sayouri, *IEEE Trans. Magn.*, 1990, **26**, 1819.
11 D. L. Leslie-Pelecky and R. D. Rieke, *Chem. Mater.*, 1996, **8**, 1770.
12 T. Ogihara, H. Nakajima, T. Yanagawa, N. Ogata, K. Yoshida and N. Matsushita, *J. Am. Ceram. Soc.*, 1991, **74**, 2263.
13 X. Cao, Y. Koltypin, R. Prozorov, G. Kataby and A. Gedanken, *J. Mater. Chem.*, 1997, **7**, 2447.
14 X. Cao, R. Prozorov, Y. Koltypin, G. Kataby, I. Felner and A. Gedanken, *J. Mater. Res.*, 1997, **12**, 402.
15 R. M. Cornell and U. Schwertmann, *The Iron Oxides–Structure, Properties, Reactions, Occurrence and Uses*, VCH, Weinheim, 1996.
16 F. del. Monte, M. P. Morales, D. Levy, A. Fernandez, M. Ocana, A. Roig, E. Molins, K. O. Gray and C. J. Serna, *Langmuir*, 1997,**13**, 3627.
17 P. S. Sidhu, *Clays Clay Miner.*, 1988, **36**, 31.

Communication 8/04759F