Bull. Chem. Soc. Jpn., 66, 1536—1541(1993) [Vol. 66, No. 5

Thermal Decomposition of the Iron(III) Hydroxide and Magnetite Composites of Poly(vinyl alcohol).
Preparation of Magnetite and Metallic Iron Particles

Hiroshi YOKOI* and Teruyuki KANTOH
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432

(Received November 10, 1992)

Upon the precipitation of iron(III) hydroxide ($Fe(OH)_3$) and magnetite in the presence of poly(vinyl alcohol) (PVA) at $R<3$, PVA is bound to the precipitates in very high yields, where R=[PVA polymer residue]/[Fe ion]. The thermal decomposition of the $Fe(OH)_3$–PVA composite at $R=1.0$ by heating at ca. 700 °C in nitrogen for 10 min or more affords almost pure iron metal particles of ca. 200 Å in diameter; almost no residues originating from the PVA remain. Before formation of the metallic iron, magnetite particles are produced as its precursor in the 250—650 °C temperature range, where the particle size increases with increasing temperature from ca. 80 up to ca. 350 Å in diameter, although these iron and magnetite products are not uniform, but are agglomerate or sintered particles. In these processes, the initially bound PVA effectively functions as a reducing agent during its own decomposition.

Iron(III) ions interact with various organic compounds, such as carboxylic acids, to form complexes in aqueous media.[1] Iron(III) citrates under alkaline conditions have been reported to exist as a polymer sphere comprising an iron(III) hydroxide ($Fe(OH)_3$) core with citrate ions bound to the surface.[2] When the $Fe(OH)_3$ precipitate is prepared in the presence of organic compounds, the precipitate generally contains varying quantities of those compounds, as has been demonstrated with organic dyes.[3] Iron(III) acetate hydroxide was also prepared as such in the presence of acetic acid.[4,5] The thermal decomposition of this iron(III) compound under a nitrogen atmosphere has been reported to be an interesting procedure for the synthesis of magnetite (Fe_3O_4).[4,5]

Iron(III) ions can interact with poly(vinyl alcohol) (PVA) to form a water-soluble complex,[6,7] as well as copper(II) ions.[8] We have previously shown that these complexes are of an inclusion type in which metal hydroxide is included by PVA.[7,8] This fact suggests that the $Fe(OH)_3$ precipitate prepared in the presence of a small amount of PVA must contain PVA. This is the same for the magnetite precipitate, since very stable colloidal dispersions of Fe_3O_4 are readily prepared in the presence of PVA.[9] This paper describes the thermal behavior of the $Fe(OH)_3$ and Fe_3O_4 composites of PVA, with special interest concerning the syntheses of Fe_3O_4 and metallic iron particles.

Experimental

Materials. Hydrolyzed (97.5—99.5%) PVA with an average molecular weight of 22000 was purchased from the Fluka Chemical Co. Hydrated iron(III) and iron(II) chlorides of guaranteed grade were used without further purification as sources of Fe(III) and Fe(II) ions, respectively. In this work, the concentration of PVA was expressed as PVA polymer residue in terms of monomeric residues; R is defined as the ratio [PVA polymer residue]/[Fe ion], where the Fe ion denotes both the Fe(III) and Fe(II) ions. Easily filterable precipitates were obtained under the conditions of $R\leq 2$ and pH>3 for $Fe(OH)_3$ and of $R\leq 2$ and pH≅10 for Fe_3O_4, where [PVA polymer residue]=0.083 mol dm^{-3}. An examination of the thermal behavior was carried out for samples prepared by drying the above-mentioned precipitates at 50 °C in air. The compositions of many samples as well as their thermal decomposition products were determined by elemental analysis for C and H and by atomic absorption spectrometry for Fe. Elemental analysis data for some of the $Fe(OH)_3$–PVA composite samples at various R values are as follows: C, 8.72, 11.93, and 14.09; H, 2.59, 3.05, and 3.29; Fe, 33.8, 34.3, and 35.7% for the samples at $R=0.625$, 1.0, and 1.5, respectively. At present, however, it is difficult to determine possible chemical formula of the samples from these data alone.

Measurements. Thermal analyses (TG and DTA) were recorded on a Shinku-Riko TGD-1500 RH-P differential thermobalance under dynamic atmospheres of nitrogen and air. Electron spin resonance (ESR) measurements were carried out at room temperature and at 77 K for thermal decomposition products diluted with KBr by using agate mortar and pestle. X-ray powder diffraction measurements were carried out on a Rigaku Geigerflex D-3F diffractometer using Cu $K\alpha$ or Co $K\alpha$ radiation: the JCPDS file was utilized to identify substances from their X-ray diffraction data. The thermal decomposition products for which physical measurements were carried out were prepared by using the above-described thermobalance under various specific conditions. Scanning electron micrographs were taken with a JEOL JSM-T330A scanning electron microscope (SEM). A BET surface-area determination was made on a Quantachrome Quantasorb Jr.

Results and Discussion

PVA Content in the $Fe(OH)_3$ and Fe_3O_4 Precipitates. The $Fe(OH)_3$ and Fe_3O_4 precipitates prepared under the conditions described in the above experimental section contain PVA. In order to estimate the content of PVA in the precipitates dried at 50 °C in air, thermal analyses in air were attempted, as exemplified by Fig. 1. Exothermic reactions in the 170—520 °C and 160—500 °C temperature ranges in air for

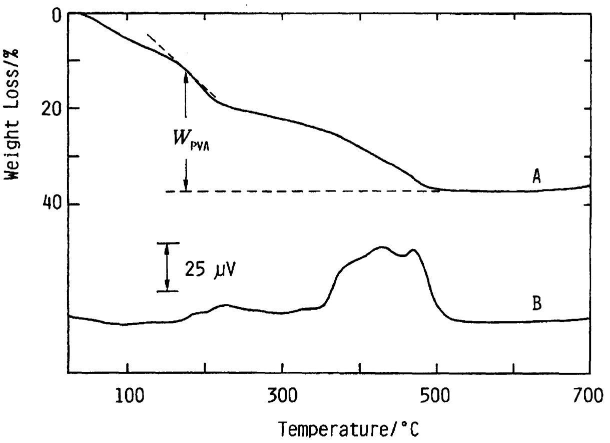

Fig. 1. Thermal analyses of the $Fe(OH)_3$ precipitate with PVA at $R=1.0$ in air: A, thermogravimetric analysis; B, differential thermal analysis. The amount of PVA in the precipitate was estimated from the value of W_{PVA} in the figure (see text, as to details of W_{PVA}).

the $Fe(OH)_3$ and Fe_3O_4 precipitates, respectively, and no weight losses are observed above 520 and 500 °C, respectively. The final decomposition products of the iron species were α-Fe_2O_3, as evidenced by gravimetry and X-ray diffraction. The above-mentioned exothermic reactions are attributed to the combustion of the PVA involved. On the other hand, ca. 10% of the first weight loss below 200 °C for the $Fe(OH)_3$ precipitates is due mainly to the dehydration of the $Fe(OH)_3$.[10] All of these facts indicate that the content of PVA in every sample can be approximately evaluated from such a W_{PVA} value, as shown in Fig. 1.

Figure 2 shows plots of the amount of PVA removed from the solution vs. the R value at which Fe ions and PVA are mixed in the initial solution. Nearly 100% of the PVA are removed from solutions at smaller R values by the precipitation of $Fe(OH)_3$, as well as by the precipitation of Fe_3O_4. Almost the same results were also estimated from elemental analysis data concerning the wt% C. These facts demonstrate that $Fe(OH)_3$ and Fe_3O_4 can be used as excellent reagents for the recovery of PVA from aqueous solutions. For this purpose, however, these precipitates must be prepared in the presence of PVA. If PVA is added after the formation of the precipitates, the recovery of PVA becomes very low, as suggested by the fact that, under the same condition, Fe(III) ions do not effectively interact with PVA to form stable complexes, even at $R \gtrsim 8$.[7] Accordingly, Figure 2 gives evidence for the existence of a fairly strong interaction between PVA and $Fe(OH)_3$ or Fe_3O_4 particles.

Thermal Behavior of the $Fe(OH)_3$ and Fe_3O_4 Composites with PVA in Nitrogen. The $Fe(OH)_3$ and Fe_3O_4 precipitates prepared in the presence of PVA are composites with PVA. Representative thermal analyses under an atmosphere of nitrogen for the $Fe(OH)_3$–PVA composites are shown in Fig. 3. There are weight losses due mainly to the cracking of PVA below 600 °C. The sharp endothermic reactions accompanied by substantial weight losses in the temperature range 650—700 °C are attributed to the reduction of Fe_3O_4 to metallic iron by carbonaceous residues, as will be shown later. All, or part of, the carbonaceous residues disappear by gasification during the reduction. When the atmosphere is changed from nitrogen to air at a constant temperature of 800 °C, the metallic iron is oxidized to α-Fe_2O_3, being accompanied by a corre-

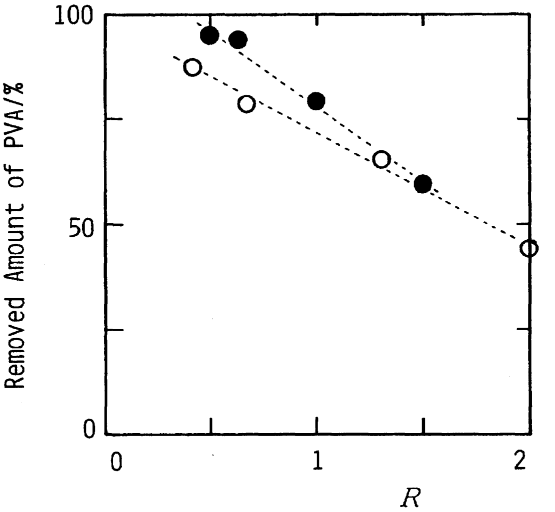

Fig. 2. R dependence of the amount of PVA removed from the solution by the precipitation of $Fe(OH)_3$ (●) and Fe_3O_4 (○) at room temperature (initial PVA concentration: 0.083 mol dm^{-3}).

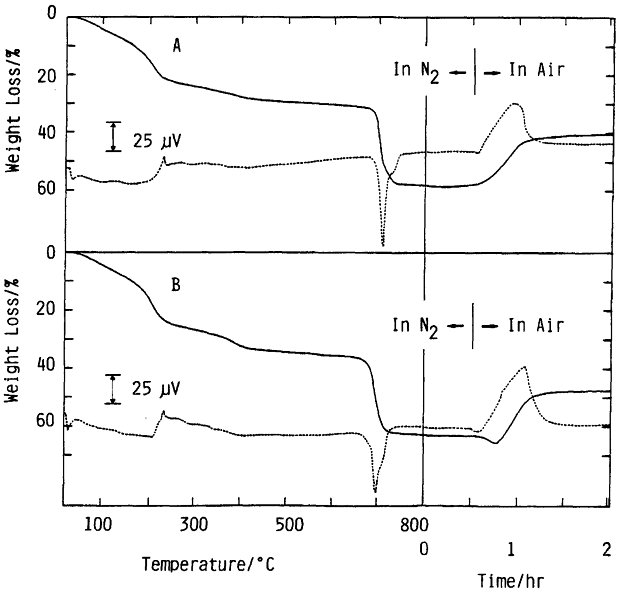

Fig. 3. Thermal analyses of the $Fe(OH)_3$–PVA composites at R=1.0 (A) and 1.5 (B) below 800 °C under an atmosphere of nitrogen, followed by the analyses in air at a constant temperature of 800 °C.

sponding weight gain. In the case of $R=1.0$ (Fig. 3A), the weight gain was found to be in agreement with the calculated one, based on the assumption that the decomposition product at 800 °C in nitrogen is only pure metallic iron. On the other hand, in the same experiments on samples at $R=1.5$ and 0.63, no such agreement was found. For the sample at $R=1.5$, there remained some carbonaceous residues in the decomposition product at 800 °C in nitrogen, in conformity with the observation of a small weight loss curve at 800 °C in air just before a considerable weight gain (Fig. 3B). For a sample at $R=0.63$, the reduction of all Fe_3O_4 particles to metallic iron was not complete. These facts suggest that the amount of PVA in the $Fe(OH)_3$–PVA composite at $R=1.0$ is just enough to reduce all of the Fe ions to metallic iron, as supported by elemental analysis (Found: C, 0.62, 15.30; H, 0.01, 0.36% for the decomposition products of the sample at $R=1.0$ at 800 and 700 °C respectively in nitrogen). In other words, the PVA of the composite disappears without any degradation products, leaving almost pure metallic iron.

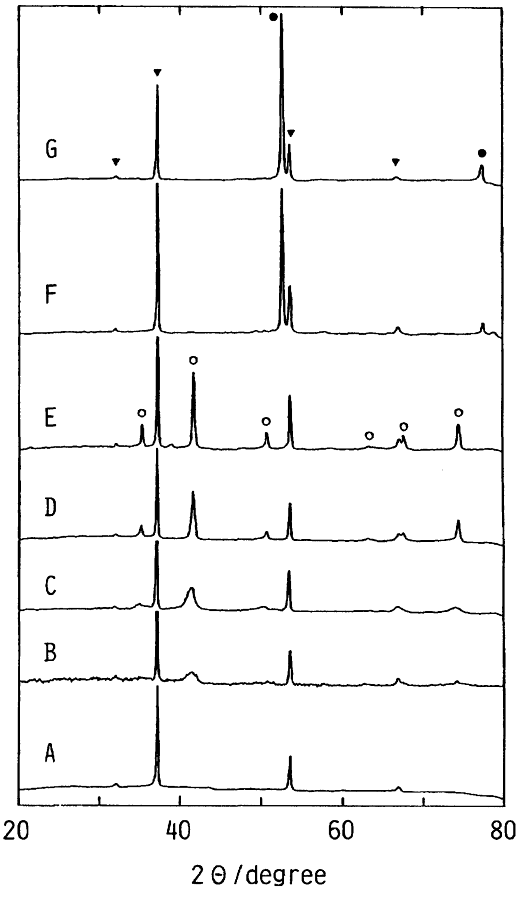

Fig. 4. X-ray diffraction patterns (Co $K\alpha$; 10 kV; 40 mA) of the samples prepared from the $Fe(OH)_3$–PVA composite at $R=1.0$ by thermal decomposition in nitrogen at the following temperature (10 min heating after temperature elevation at a rate of 20 °C min^{-1}): A, without heating; B, 250 °C; C, 300 °C; D, 500 °C; E, 700 °C; F, 750 °C; G, 800 °C. Peaks with the marks of ○, ●, and ▼ are due to Fe_3O_4, α-Fe, and NaCl crystals, respectively.

Figure 4 shows the X-ray diffraction patterns observed for samples prepared from the $Fe(OH)_3$–PVA composite at $R=1.0$ by thermal decomposition by 10 min heating at various desired temperatures after increasing the temperature at a rate of 20 °C min^{-1} under a nitrogen atmosphere. NaCl crystals always appear as an impurity in the thermal decomposition, because iron(III) chloride and sodium hydroxide are used as starting materials for the synthesis of the composites in solutions. However, this NaCl impurity is easily eliminated by washing the sample with distilled water at any stage or by dialyzing the composites before drying and heating. Although unheated $Fe(OH)_3$–PVA composites show no X-ray diffraction peaks (Fig. 4A), but weak and broad peaks due to Fe_3O_4 appear upon heating at 250 °C in air. These diffraction peaks become stronger and sharper with increasing temperature below 700 °C. This fact indicates that the Fe_3O_4 crystals grow at higher temperatures, even in the solid phase, and that the formation of Fe_3O_4 goes to completion upon heating up to 300 °C, judging from its diffraction line intensity (Fig. 5). It is to be noted that, in this Fe_3O_4

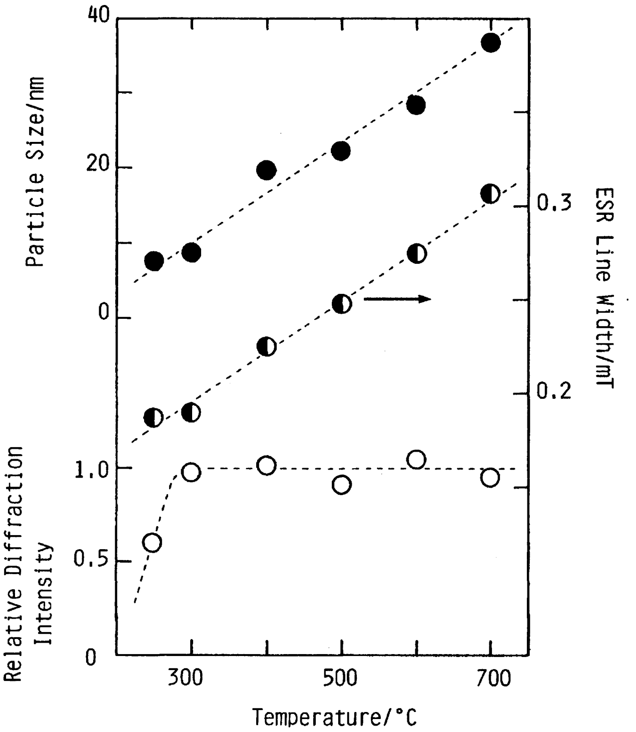

Fig. 5. Plots of the size (●), the relative intensity of X-ray (311) diffraction peak (○), and the ESR line width (◐) of Fe_3O_4 particles prepared by thermal decomposition against the temperature of heating in nitrogen for the $Fe(OH)_3$–PVA composite at $R=1.0$ (see Fig. 6 and its caption, as to the ESR line width (ΔH)).

formation, one-third of the iron(III) ions are reduced to iron(II) ions in the decomposition process of PVA, and that the stable species of iron in the temperature range 300—700 °C in nitrogen for this kind of sample is Fe_3O_4. Figure 5 also shows a plot of the particle size of Fe_3O_4 in this sample against the temperature of heating, where the size was evaluated from the line width of the (311) diffraction peak for Fe_3O_4 crystals by using the Scherrer equation.[11] The size of Fe_3O_4 particles increases linearly with temperature. The ESR spectra of the samples prepared in the same way for the composite at $R=1.0$ are shown in Fig. 6. All of these spectra exhibit very broad line widths and remarkably temperature dependent line shapes. The line width (ΔH) determined by room temperature ESR measurements is also plotted against the temperature of heating, as shown in Fig. 5. There is a correlation between the ESR line width and the particle size of Fe_3O_4. This results suggests that the particle size can also be approximately estimated by the ESR method. The above-mentioned correlation, however, is in conflict with the prediction made by Galembeck et al.,[5,12] although the reason for the correlation is not understood.

Figure 4 also shows the sudden appearance of new peaks attributed to α-Fe at 750 °C. It is interesting to us to investigate in more detail the dependence of the production of α-Fe on the thermal decomposition conditions. First of all, it has been revealed that there is an R-dependence of the temperature at which α-Fe particles appear. The temperatures were approximately 725 and 750 °C for the samples of $R=1.5$ and 1.0, respectively. This is consistent with a general belief that the temperature becomes lower as the quantity of reducing organic compounds becomes greater in the system. Figure 7 shows X-ray diffraction patterns which focus attention on the temperature at which α-Fe is formed for the sample with $R=1.0$. This figure demonstrates that hematite and some iron carbides are formed as intermediates during the transition process of Fe_3O_4 to α-Fe due to temperature elevation, and that the transition takes place over a very narrow temperature range. From the line width of the (100) X-ray diffraction peak, the α-Fe crystals observed in Fig. 7D have been estimated to be ca. 200 Å in diameter. X-Ray diffraction measurements for sample with $R=1.5$ showed that iron carbides were much more abundant at 800 °C, followed by a low yield of α-Fe. The sample with $R=1.5$ also exhibited more intense peaks due to iron carbides than that with $R=1.0$; the latter peaks were very weak in intensity, as shown in Fig. 7D. This is another kind of R-dependence in the thermal decomposition for these composites. It

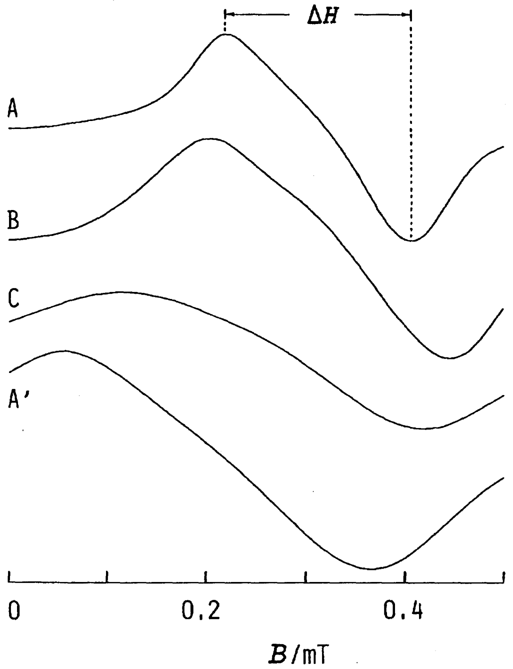

Fig. 6. ESR spectra of the powder samples prepared from the $Fe(OH)_3$–PVA composite at $R=1.0$ by heating in nitrogen at the following temperature: A, 300 °C; B, 500 °C; C, 700 °C (A, B, and C, measured at room temperature); A′, 300 °C (measured at 77 K). ΔH in the A spectrum expresses its line width.

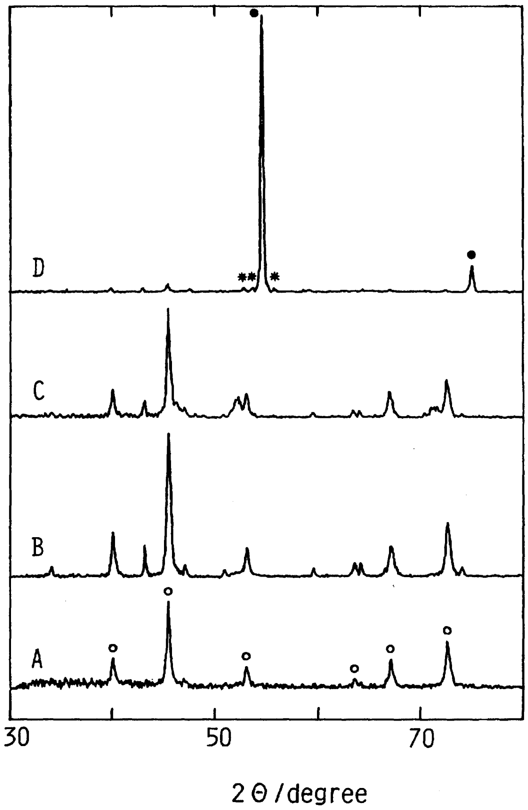

Fig. 7. X-Ray diffraction patterns (Cu $K\alpha$; 15 kV; 35 mA) of the samples prepared from the $Fe(OH)_3$–PVA composite at $R=1.0$ by thermal decomposition under the same conditions as in Fig. 4: A, 675 °C; B, 700 °C; C, 725 °C; D, 750 °C (see the caption of Fig. 4, as to ○ and ● in the figure; weak signals with asterisks in D are due to iron carbides).

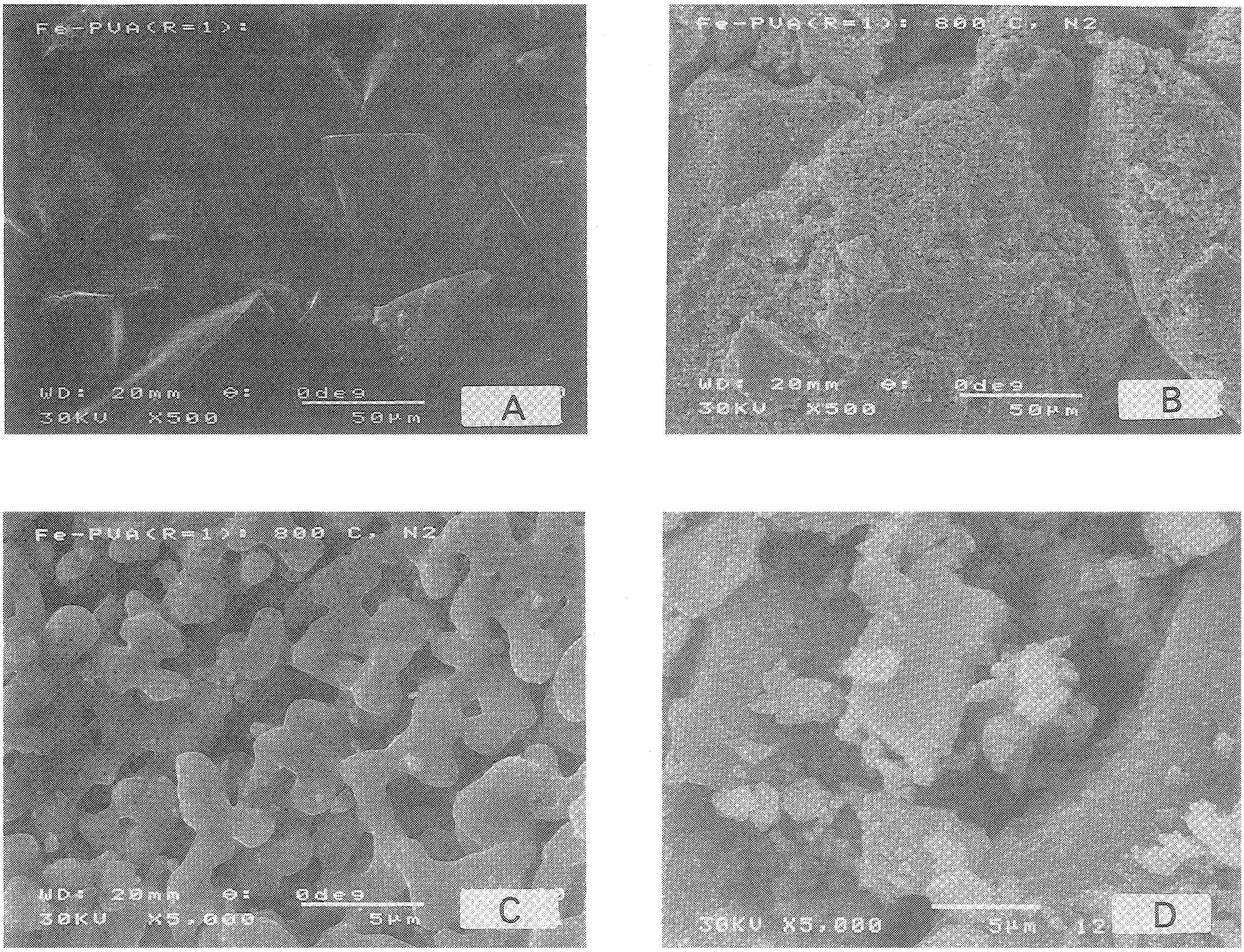

Fig. 8. SEM photographs of the $Fe(OH)_3$–PVA composite at $R=1.0$ (A) and its derivatives prepared by thermal decomposition in nitrogen at 800 °C (B) and (C) and at 500 °C (D).

has also been revealed that the thermal decomposition reaction is dependent on the heating time. In the case of the sample with $R=1.5$, the formation of α-Fe was not only observed upon heating at 725 °C for 10 min, but also upon heating at 675 °C for 2 h. All of the facts described above point out that the thermal decomposition of $Fe(OH)_3$–PVA composites and related ones is a new and interesting method to prepare ultrafine metallic iron particles, even though these particles are in an agglomerate and sintered state.

On the other hand, the Fe_3O_4–PVA composites dried at 50 °C in air show X-ray diffraction peaks inherent in Fe_3O_4 crystals. From the width of the (311) diffraction line, the crystals were estimated to be ca. 170 Å in diameter, which seems to be a little larger than that for Fe_3O_4 colloids.[9] These crystals in the composites grew to ca. 350 Å in diameter in the solid phase upon heating to ca. 700 °C, in a similar way as shown in the case of $Fe(OH)_3$–PVA composites. Furthermore, there was almost no difference between these two composites in the transition process of Fe_3O_4 to α-Fe due to temperature elevation.

Figure 8 shows SEM photographs of the $Fe(OH)_3$–PVA composite ($R=1.0$) dried at 50 °C in air and then powdered with agate mortar and pestle as well as its thermal decomposition products prepared by heating at 500 and 800 °C in nitrogen. This demonstrates that all samples do not comprise uniform crystalline particles, but agglomerate or sintered particles. The starting composite, itself, has a quite smooth surface, as shown in Fig. 8A. However, its decomposition product, obtained by heating at 800 °C in nitrogen, has a porous structure at the surface (Fig. 8B). At higher magnification, the coalescene of many particles of 1—2 µm diameter and neck formation between the particles are clearly seen in Fig. 8C. All of these particles appear to be covered with a continuous, smooth, and unstructured skin. Since the BET surface area of this product was found to be ca. 10 $m^2 g^{-1}$, its apparently porous surface structure is not directly linked with a large surface area. The surface of the thermal decomposition products similarly obtained from composites with $R=1.5$ and 2.0 were quite different and irregular in appearance. Such a particle morphology and a smooth skin (as shown in Fig. 8C) may be characteristic of almost pure metallic iron particles thus prepared by thermal decomposition. Just for information, a SEM photograph of the thermal decomposition product obtained by heating at 500 °C is shown in Fig. 8D. A main iron compound in this product is Fe_3O_4; its surface looks quite different from any of the above-mentioned ones.

The metallic iron product, the surface SEM photographs of which are shown in Figs. 8B and 8C, was found to be considerably stable in air. The stability was checked by monitoring the X-ray diffraction peak intensity due to α-Fe. The intensity was slowly reduced to ca. 60% of its initial value three weeks after.

Thanks are given to Mr. K. Ikeda for his assistance in the experimental work.

References

1) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Spec. Publ., Chem. Soc., (a) 1964, No. 17; (b) 1971, No. 25.

2) T. G. Spiro, L. Pape, and P. Saltman, *J. Am. Chem. Soc.*, **89**, 5555 (1967); T. G. Spiro, G. Bates, and P. Saltman, *J. Am. Chem. Soc.*, **89**, 5557 (1967); T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils, and P. Saltman, *J. Am. Chem. Soc.*, **88**, 2721 (1966).

3) M. -H. Cheng and S. -D. Hung, *J. Colloid Interface Sci.*, **126**, 346 (1988); G. -L. Sheu and S. -D. Hung, *Sep. Sci. Technol.*, **22**, 2253 (1987).

4) P. P. de Abreu Filho, E. A. Pinheiro, and F. Galembeck, *React. Solids*, *Proc. Int. Symp. 10th, Part A-B*, **3**, 241 (1987).

5) E. A. Pinheiro, P. P. de Abreu Filho, and F. Galembeck, *Langmuir*, **3**, 445 (1987).

6) H. Shirai, Y. Nio, A. Kurose, S. Hayashi, and N. Hojo, *J. Chem. Soc. Jpn.*, **1978**, 117.

7) H. Yokoi, Y. Mori, T. Mitani, and S. Kawata, *Bull. Chem. Soc. Jpn.*, **65**, 1898 (1992); H. Yokoi and Y. Mori, *Bull. Chem. Soc. Jpn.*, to be published.

8) H. Yokoi, S. Kawata, and M. Iwaizumi, *J. Am. Chem. Soc.*, **108**, 3358 (1986); H. Yokoi, S. Kawai, A. Kadowaki, and S. Ikoma, *Nippon Kagaku Kaishi*, **1989**, 872.

9) H. Yokoi, K. Yagishita, and Y. Nakanishi, *Bull. Chem. Soc. Jpn.*, **63**, 746 (1990), and references cited therein.

10) S. C. F. Au-Yeung, G. Denes, J. E. Greedan, D. R. Eaton, and T. Birchall, *Inorg. Chem.*, **23**, 1513 (1984).

11) P. Scherrer, *Göttinger Nachrichten*, **2**, 98 (1918).

12) F. Galembeck, N. F. Leite, L. C. M. Miranda, H. R. Rechenberg, and H. Vargas, *Phys. Status Solidi A*, **60**, 63 (1980).