JOURNAL OF MATERIALS SCIENCE 33 (1998) 1915–1919

Characterization of ultrafine γ-Fe(C), α-Fe(C) and Fe_3C particles synthesized by arc-discharge in methane

X. L. DONG, Z. D. ZHANG*, Q. F. XIAO, X. G. ZHAO, Y. C. CHUANG
Institute of Metal Research, Academia Sinica, Wenhua Road 72, Shenyang, 110015, People's Republic of China
**E-mail: zdzhang@imr.ac.cn*

S. R. JIN, W. M. SUN, Z. J. LI, Z. X. ZHENG, H. YANG
Laboratory of Ultrafine Particle, Shenyang Polytechnic University, Shenyang, 110023, People's Republic of China

Ultrafine γ-Fe(C), α-Fe(C) and Fe_3C particles were prepared by arc-discharge synthesis in a methane atmosphere. The phases, morphology, structure and surface layer of the particles were studied by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) techniques and X-ray photoelectron spectroscopy (XPS). It was found that the mean particle size ranged from 9.8 to 12.8 nm. The surface of particles mostly consisted of a carbon layer and a little oxide. Phase transformation from γ-Fe(C) to α-Fe(C) was studied by annealing in vacuum and by differential thermal analysis and thermogravimetry (DTA–TGA) measurement. The abundance of γ-Fe(C) was determined by a magnetization measurement to be approximately 30%. Phase transformation occurred between 300 and 500 °C in a flowing argon atmosphere. The Fe_3C particles oxidized to α-Fe_2O_3 and carbon dioxide at 610 °C or so. © *1998 Chapman & Hall*

1. Introduction

Quenched face centred cubic γ(f.c.c.)-Fe particles are of particular interest in fundamental studies of phase transformation and magnetism. Fukano [1, 2] found, though very limited, a finite number of γ(f.c.c.)-Fe particles among body centred cubic α(b.c.c.)-Fe particles produced by gas-evaporation. Another method to obtain quenched γ(f.c.c.)-Fe particles was developed by Kusunoki [3] and Kusunoki and Ichihashi [4]. These authors adopted the technique of furnace heating and subsequent quenching in liquid nitrogen to form fine γ-Fe particles. This led to the conclusion that the mass ratio of γ/α was about 10%, which was determined roughly by comparing the intensity of the (3 1 1) reflection of f.c.c. with that of the (2 1 1) reflection of b.c.c., because the multiplicities of these reflections were the same. Hayakawa and Iwama [5] developed a better technique by applying microwave-plasma processing to the gas-evaporation technique [6]. The result showed that the γ/α ratio was higher, about 40%.

Iron carbides (Fe_3C, Fe_5C_2, Fe_7C_3) have a higher saturation magnetization ($> 100\ \mathrm{A\,m^2\,kg^{-1}}$) [7] than α-Fe_2O_3 ($70\ \mathrm{A\,m^2\,kg^{-1}}$), and a higher resistance to oxidation than iron particles and iron nitrides. Hence, they are good candidates for application to magnetic recording media. Chemical methods [8, 9] and laser pyrolysis [10, 11] have also been used for preparation of iron carbides. However, it is difficult to synthesize a desired iron carbide as a single phase, because most iron carbides are metastable under atmospheric pressure [12].

This work describes a new method of preparing ultrafine γ-Fe(C), α-Fe(C) and Fe_3C particles by adopting arc-discharge-heating [13] in a methane atmosphere. The phases, morphology, structure, surface layer and phase transitions of the resulting particles are investigated by means of XRD, TEM, XPS, DTA, TGA and magnetization measurements.

2. Experimental procedure

Fig. 1 illustrates the experimental apparatus. The pure iron to be evaporated, which is laid on a water-cooled copper stage, serves as the anode. The upper carbon rod, which serves as the cathode, is supported by a copper arm that is also water cooled. After the chamber is evacuated, methane (CH_4) is introduced as a reactant gas to reach the desired pressure. The distance between the two electrodes can be adjusted from outside the chamber, so that the arc can be started and controlled during a continuous operation.

Samples were produced under different methane pressures in the range 13.3 to 66.7 kPa. XRD was then performed to identify the phases in the samples. Micrographs of the powder morphology were taken

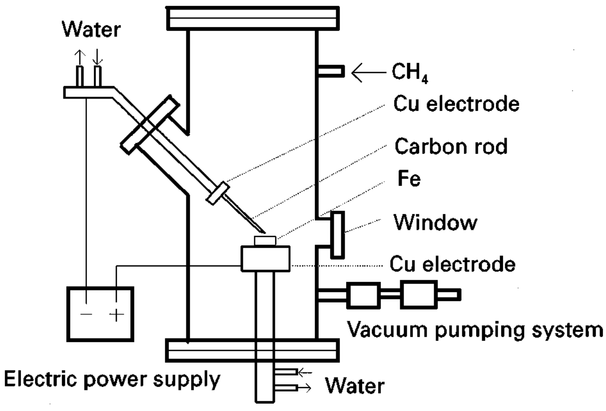

Figure 1 Experimental apparatus for evaporating pure Fe in methane.

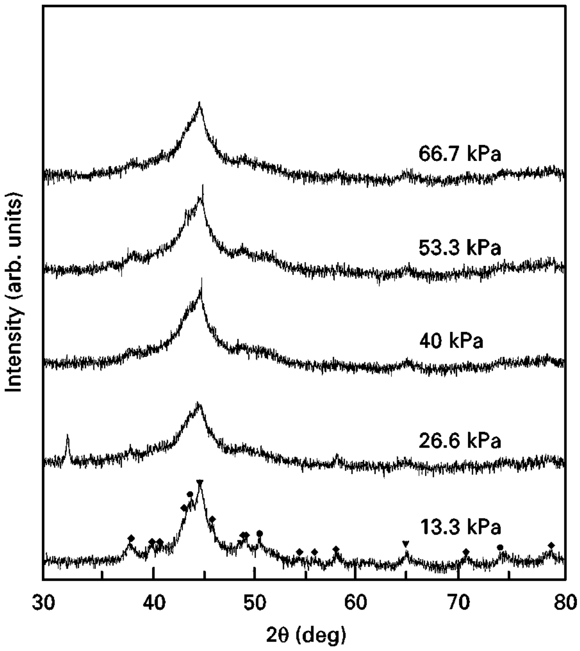

Figure 2 X-ray diffraction (CuK_α) patterns of the samples prepared at methane pressures of 13.3–66.7 kPa: (●) γ-Fe, (▼) α-Fe, (◆) Fe_3C.

using TEM, and the dependence of the mean particle size on methane pressure was determined by image analysis. The microbeam electron diffraction pattern identified the γ-Fe(C) phase as present in the particles.

It is widely realized that the XPS technique has great potential in surface chemistry and physics. The species that cover the surface of fine particles may be detected by analysis of their chemical states. The as-prepared powder sample was compacted into a round plate 10 mm in diameter and about 1 mm thick for measurement with a RIBER LAS-3000 Mk-2 XPS spectrometer; the MgK_α line was used as the X-ray source. The sample was placed in the analysis chamber, which had a base pressure of less than 3×10^{-7} Pa.

The phase transformation from γ-Fe(C) to α-Fe(C) was studied by annealing the sample in vacuum at temperatures from 100 to 800 °C. The starting sample was produced at a methane pressure of 13.3 kPa. Magnetization measurement of the annealed samples, performed in a vibrating sample magnetometer (VSM) in a field up to 0.8 T, was used to demonstrate the phase transformation further. DTA and TGA were employed to determine the temperatures of the phase transformation and dissociation of Fe_3C particles. They were conducted at a heating rate of $10\,^\circ C\,min^{-1}$ in an argon flowing atmosphere.

3. Results and discussion

3.1. Formation of ultrafine γ-Fe(C), α-Fe(C) and Fe_3C particles in a methane atmosphere

During operation, the electric arc can be maintained for several minutes, during which several hundred milligrams of particles can be produced. Fig. 2 shows XRD patterns of the samples generated under various methane pressures of 13.3–66.7 kPa. Three kinds of phases, namely α-Fe(C), γ-Fe(C) and Fe_3C, exist in all samples. Apart from one of the XRD pattern, which corresponds to the sample produced at 13.3 kPa, the peaks for the three phases cannot be separated reliably. This is attributed to the small size of the particles, which can result in peak broadening. Solid solutions of α-Fe(C) and γ-Fe(C) particles with interstitial carbon atoms in the present sample have been verified by the results of Mössbauer spectroscopy [14].

The common synthesis route to generate ultrafine γ-Fe particles is to quench heat-treated ultrafine α-Fe particles at low temperature [3–5]. Evaporating pure Fe from a straight tungsten filament in xenon or argon gas at a pressure of 1.3–0.3 kPa [1, 2], although very limited, can also result in γ-Fe among α-Fe particles. It was concluded that the formation of γ-Fe came from the use of the straight filament heater. Because the heater was small, the γ-phase particles with f.c.c. habits had been retained on cooling to room temperature. In the present work, we can directly obtain γ-Fe(C) particles by evaporating pure Fe in methane. A previous work showed that evaporating pure Fe by arc-discharge in a mixture of an inert gas and hydrogen resulted in only α-Fe particles [15]. Except for the gas, the evaporative conditions in that process are the same as those in our work. It is thought that γ-Fe(C) is easier to retain in a carbonaceous gas on cooling to room temperature. In other words, the Fe–C solid solution of f.c.c. is more easily retained in methane than in the inert gas when cooled to room temperature.

Fig. 3 exhibits the result of XPS measurement for the compacted sample. The binding energy of the $Fe2p_{3/2}$ electron shows that most of the Fe atoms are of free iron (707.26 eV), only a few oxide (710.39 eV) exist. With the above experimental results, it can be concluded that a carbon layer covered the surface of the particles and protected the particles from oxidization; only a little oxide coexisted on the surface due to the rough vacuum or impurity of introduced gases. The methane in the high-temperature arc region must dissociate into an ionic carbon species and hydrogen, the ionic carbon then reacts with vapour iron atoms to form Fe_3C as well as solid solutions of α-Fe(C) and γ-Fe(C) particles, and some of them construct the

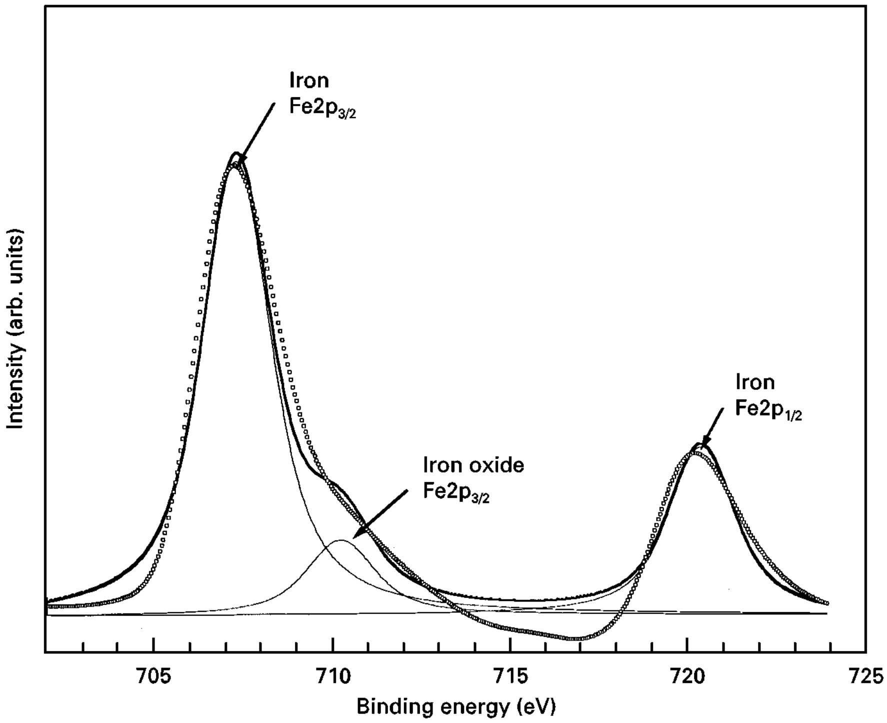

Figure 3 XPS spectra of the particles produced in methane at 13.3 kPa: (···) experimental data, (——) fitted data.

carbon layer on the surface of the particles to protect them from further oxidization. Undissociated methane can act as a condensation gas in the work chamber. The hydrogen obtained from dissociation of methane is also effective in preventing oxidation of the surface of the particles.

3.2. Morphology, electron diffraction pattern of ultrafine γ-Fe(C) and Fe_3C particles

The morphology of the particles generated under various methane pressures is spherical in shape, as shown in Fig. 4. This is due to the carbon layer and to slight oxidation on the surface of the particle. It is inferred that adsorption of active gas molecules homogenizes the surface energy for different crystallographic faces and for this reason no distinct habit forms. The effect of impurities is still recognized even when the amount is estimated to be of the order of 10^{-3} per cent [16].

It is also found that some of the particles form aggregates, like a string of beads. This can be attributed to magnetic interaction among ferromagnetic α-Fe(C) and Fe_3C particles and the tendency for reducing the specific surface energy of the system. The average diameter of the particles was measured by image analysis based on TEM photographs. Fig. 5 shows that the mean size of particles decreases with increasing methane pressure (from 13.3 to 40 kPa), but increases above 40 kPa. The result between 13.3 and 40 kPa is very different from that observed for evaporating metal in an inert gas [17]. This may be due to the fact that below 40 kPa, most methane molecules are dissociated into ionic carbon and hydrogen, and methane acts as a reactant gas. However, methane mostly acts as a condensate above 40 kPa. Fig. 6 shows the electron diffraction pattern of a γ-Fe(C) particle with the incident beam parallel to the $[0\,1\,1]_{\text{f.c.c.}}$ direction.

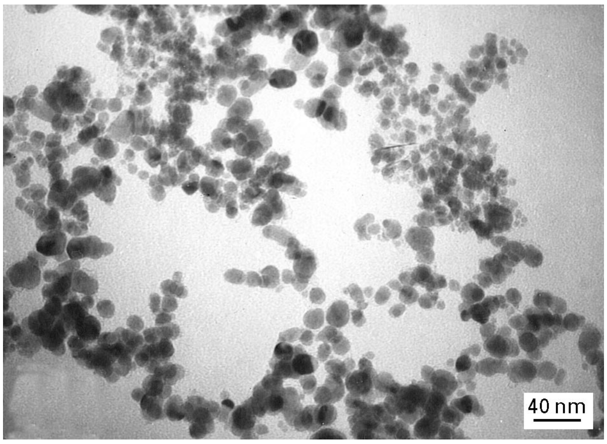

Figure 4 Transmission electron micrograph of the particles produced in methane at 66.7 kPa.

3.3. Phase transformation from γ-Fe(C) to α-Fe(C)

Fig. 7 illustrates XRD patterns of the sample annealed in vacuum from 100 to 800 °C for 20 min. The starting sample was produced under 13.3 kPa of methane. The XRD patterns provide evidence for phase transformation from γ-Fe(C) to α-Fe(C). Nevertheless, even above 600 °C, Fe_3C phase does not decompose. This conclusion apparently differs from that from the DTA–TGA measurements due to differences in the annealing conditions. The DTA–TGA measurements were completed in a flowing argon atmosphere, in which the Fe_3C particles were oxidized into α-Fe_2O_3

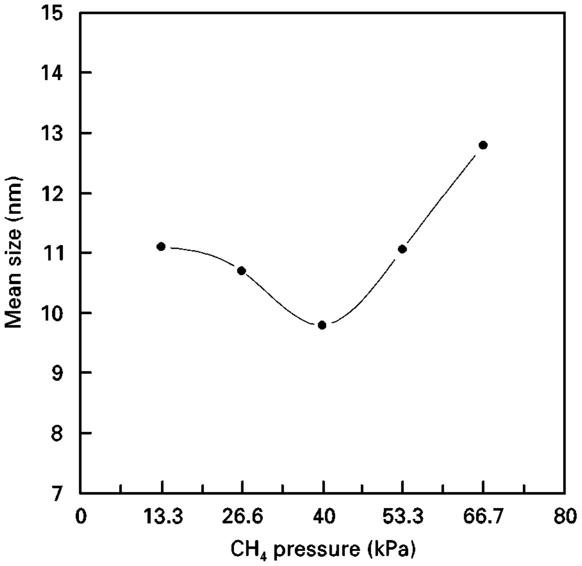

Figure 5 Dependence of mean particle size on methane pressure.

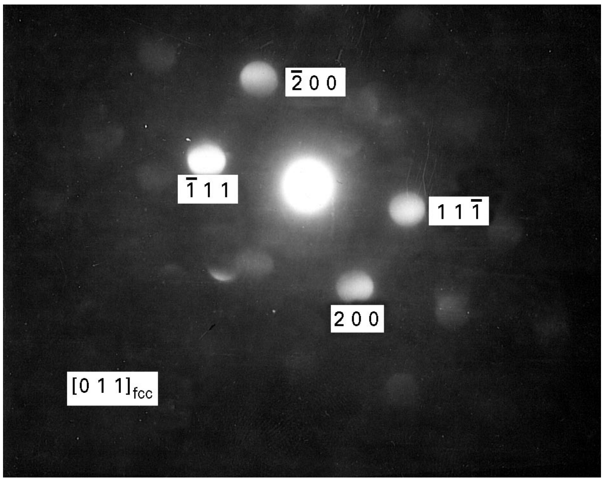

Figure 6 Microbeam electron diffraction pattern of f.c.c. Fe particle (the incident electron beam is parallel to $[0\,1\,1]_{\text{f.c.c.}}$).

and carbon dioxide. Because the argon flowed through an open heater in the DTA–TGA measurements, there was enough oxygen to oxidize Fe_3C and the resulting powders became red due to the presence of α-Fe_2O_3. However, when annealed in vacuum, even above 600 °C, it was difficult to oxidize Fe_3C into oxycarbide or α-Fe_2O_3 due to the lack of oxygen; the colour of annealed sample was still black. It is worth noting that crystal growth of Fe_3C occurs during annealing in vacuum. Phase transformation from γ-Fe(C) to α-Fe(C) results in the enhanced intensity of α-Fe(C) peaks. Although no γ-Fe(C) exists above 600 °C, the intensities of the α-Fe(C) peaks are enhanced in the patterns due to crystal growth. The magnetization of the annealed samples, measured with an applied magnetic field of 0.8 T at room temperature, is shown in Fig. 8. The temperature scale represents the annealing temperature. The minimal value of magnetization is 101.1 $\mathrm{A\,m^2\,kg^{-1}}$, which appears at 400 °C, and the maximum value is 159.3 $\mathrm{A\,m^2\,kg^{-1}}$ at 600 °C. It is thought that the phase transformation from γ-Fe(C) to α-Fe(C) is completed at 600 °C, so that maximum magnetization occurs at this temperature. The minimum magnetization observed at 400 °C is attributed to oxidation that cannot occur above 400 °C in the vacuum. During the annealing in vacuum, the lack of oxygen prevents the sample from oxidizing. By comparing the improvement of magnetization between the starting samples (104.6 $\mathrm{A\,m^2\,kg^{-1}}$) and the annealed sample (159.3 $\mathrm{A\,m^2\,kg^{-1}}$), we can roughly calculate the content of γ-Fe(C) in the starting sample to be about 30%, regardless of the effect of Fe_3C and impurities.

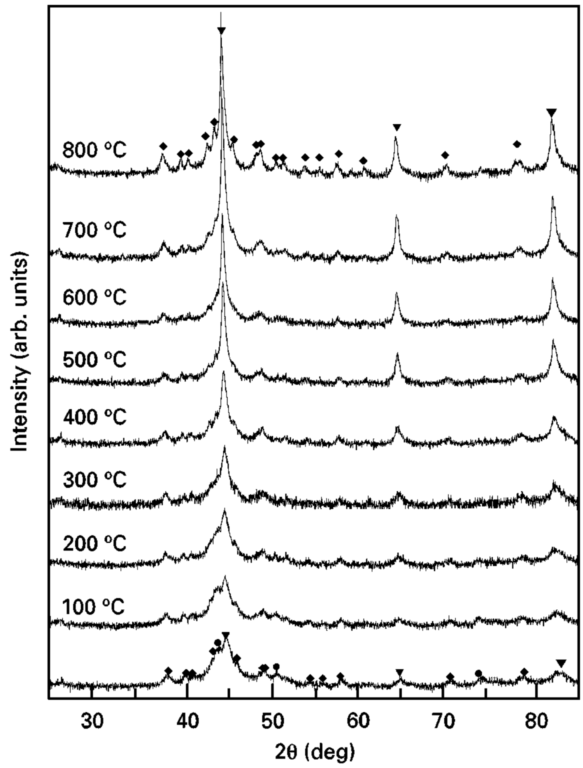

Figure 7 X-ray diffraction (CuK_α) patterns of the samples annealed at vacuum from 100 to 800 °C for 20 min (the starting sample was produced in methane at 13.3 kPa): (◆) Fe_3C, (▼) α-Fe, (●) γ-Fe.

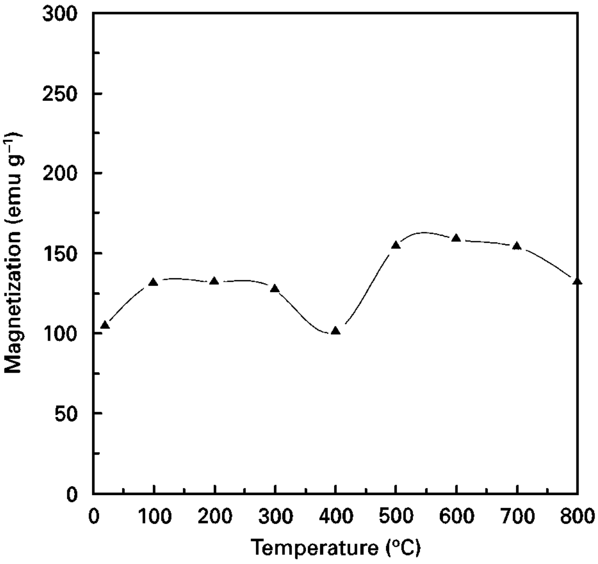

Figure 8 Dependence of magnetization on annealing temperature (magnetization was measured in an applied field of 0.8 T).

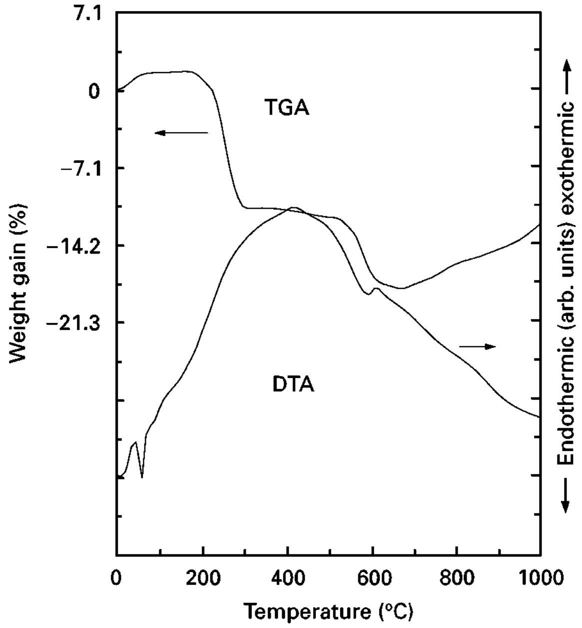

Figure 9 DTA–TGA curves of the samples that compose α-Fe(C), γ-Fe(C) and Fe_3C particles.

3.4. Thermal behaviour of ultrafine γ-Fe(C) and Fe_3C particles

Fig. 9 shows DTA–TGA curves measured at a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ in a flowing argon atmosphere. It is known that the maximum carbon content of γ-Fe(C) may reach 2.11 wt %, while that of α-Fe(C) is only 0.0218 wt %. During the phase transformation of γ-Fe(C) into α-Fe(C), the carbon content is reduced, resulting in a 2.09% weight loss. Assuming 30 wt % for the fraction of γ-Fe(C) mixed in the sample, the whole sample should lose 0.63 wt %. This corresponds to the TGA curve between 300 and 550 °C, which is associated with a slightly exothermic process, but not a sharp peak in the DTA curve. It is thought that the segment from 300 to 550 °C arises from the phase transformation process, in which γ-Fe(C) changes into α-Fe(C). In the next segment from 550 to 660 °C, the TGA curve exhibits an abrupt weight loss, associated with an exothermic peak occurring at about 610 °C. This result suggests that the Fe_3C particles are being oxidized to α-Fe_2O_3 and carbon dioxide. This conclusion is somewhat similar to the result from Fe_5C_2 and Fe_7C_3 [8]. In our DTA–TGA curves, there is a weight gain process in the range from room temperature to 150 °C, which is associated with an endothermic peak. The present authors interpret it to be a chemical reaction of an impurity in the sample, that has not been identified exactly yet. The weight loss occurs in the range 200–300 °C, with no accompanying exothermic and endothermic peaks. This is a process in which particles release absorbed gases and moisture, rather than a chemical process.

4. Conclusions

Evaporating a pure Fe block by arc-discharge under different methane pressures produces ultrafine γ-Fe(C), α-Fe(C) and Fe_3C particles. A carbon layer may cover the surface of the particles. The process of evaporating can be simply expressed as

$$\begin{aligned}\text{Fe (block)} + \mathrm{CH_4} &\rightarrow \alpha\text{-Fe(C)} + \gamma\text{-Fe(C)}\\ &\quad + \mathrm{Fe_3C} + \text{C (surface layer)}\end{aligned}$$

The sample produced at a methane pressure of 40 kPa contains the smallest mean particle size of 9.8 nm. γ-Fe(C) changes into α-Fe(C) at an annealing temperature between 300 and 550 °C, as demonstrated by the results of DTA–TGA measurements. By comparing the improvement of magnetization between the starting sample and the annealed sample, the abundance of γ-Fe(C) is estimated to be approximately 30% in the starting sample. The Fe_3C particles oxidize into α-Fe_2O_3 and carbon dioxide at 610 °C or so.

The particles covered with a carbon layer are very stable in some applications, especially in ferrofluid. The particles' mean size, carbon content, magnetization, etc., can be controlled by adjusting the conditions of operation for different application purposes.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (No. 59421001 and 597 25103) and by the Science and Technology Commission of Shenyang. The authors are grateful to Professor X. K. Sun and Dr H. T. Kim for informative discussions regarding this work. Thanks also go to Dr Y. C. Sui and Mr Z. G. Wang for their kind help in this work.

References

1. Y. FUKANO, *Jpn. J. Appl. Phys.* **13** (1974) 1001.
2. Y. FUKANO, *Nippon Kinzoku Gakkai-ho* (*Bull. Jpn. Inst. Metals*) **15** (1976) 639 (in Japanese).
3. M. KUSUNOKI, in "*Ultrafine Particles*", (eds) C. Hayashi, R. Uyeda and A. Tasaki, in Japanese, Mita Press (1988) pp. 88–91.
4. M. KUSUNOKI and T. ICHIHASHI, *Jpn. J. Appl. Phys.* **25** (1986) 219.
5. K. HAYAKAWA and S. IWAMA, *J. Cryst. Growth* **99** (1990) 188.
6. K. KIMOTO, Y. KAMIYA, M. NONOYAMA and R. UYEDA, *Jpn. J. Appl. Phys.* **2** (1963) 702.
7. J. E. HOFER and E. M. COHN, *J. Amer. Chem. Soc.* **81** (1959) 1576.
8. S. TAJIMA and S. I. HIRANO, *Jpn. J. Appl. Phys.* **29** (1990) 662.
9. S. I. HIRANO and S. TAJIMA, *J. Mater. Sci.* **25** (1990) 4457.
10. X. X. BI, B. GANGULY, G. P. HUFFMAN, F. E. HUGGINS, M. ENDO and P. C. EKLUND, *J. Mater. Res.* **8** (1993) 1666.
11. X. Q. ZHAO, PhD thesis, Institute of Metal Research, Academia Sinica (1995).
12. R. P. ELLIOTT, in "*Constitution of binary alloys*" (eds) M. B. Bever, M. E. Shank, C. A. Wert, R. F. Mehl (McGraw-Hill, New York, 1965) p. 212.
13. R. UYEDA, in "*Ultrafine Particles*", (eds) C. Hayashi, R. Uyeda and A. Tasaki, in Japanese, Mita Press (1988). pp. 46–51.
14. X. L. DONG, Z. D. ZHANG, X. G. ZHAO, Y. S. CHAO, S. R. JIN and W. M. SUN, *J. Mater. Sci. & Tech.* 14 (1998).
15. S. OHNO and M. UDA, *J. Jpn. Inst. Metals* **48** (1984) 640 (in Japanese).
16. R. UYEDA, Crystallography of metal smoke particles in "Morphology of Crystals" (ed.) I. Sunagawa (Terra Scientific, Tokyo, 1987) Ch.6, p. 491.
17. R. UYEDA, *Progress Mater. Sci.* **35** (1991) 34.

Received 24 June 1996
and accepted 5 December 1997