EXPERIMENTAL DEMONSTRATION OF FORMATION OF MAGNETITE AND WÜSTITE FINE GRAINS

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Abstract: Production method of magnetite and wüstite grains have been introduced. Magnetite and wüstite grains were produced in an Ar gas pressure range of 25 to 100 Torr and 17 to 20 Torr respectively by evaporating FeO powder from a tantalum boat. The growth of these grains has been discussed as the result of oxidation of Fe fine grains and coalescence growth among the oxidized grains.

1. Introduction

The most advanced method for producing grains from a gas phase is the so-called "GAS EVAPORATION METHOD", in which a material is heated in an inert gas atmosphere (Kimoto *et al.*, 1963). The evaporated vapor is subsequently cooled and condensed in the gas atmosphere, *i.e.*, solid grains are attained directly from the gas cloud. By using our developed method (Kaito, 1981), it has been shown that tetrataenite grains, which is a unique metallic mineral in meteorites, can be produced by the coalescence growth process of a joint cloud of fine smoke grains evaporated from Fe and those from Ni (Nagata *et al.*, 1991). A magnetic granulometry analysis of carbonaceous chondrites on the basis of magnetic hysteresis parameters at various temperatures (Nagata and Carleton, 1990) has shown that very fine grains of tetrataenite were contained in the chondrite. It was concluded that the tetrataenite grains in the chondrite were directly formed by a coalescence process of Fe and Ni fine particle smokes in the solar nebula. Thence, analysis of the production condition of grains by the gas evaporation method is regarded as an important field in meteorite physics.

The gas evaporation method extensively began in Japan about 25 years ago (Kimoto *et al.*, 1963) by the stimulation of the Kubo effect (Kubo, 1962). Grains of a few tens of nm in size can be produced easily. A lot of grains produced by this method showed definite crystal habits reflecting the crystal structure of the materials. The coalescence growth is regarded as an important process in the gas evaporation method. Evidence for, and mechanism involved in the coalescence growth of the resulting smoke grains have been elucidated in a series of experiments (Kaito, 1978, 1981, 1984, 1985). The coalescence process takes place during a short period of time such as 10^{-3}–10^{-2} s, and a joint smoke of two different metallic elements and compounds can form alloy grains or compound oxides in an appropriate condition.

The coalescence in the smoke particles (Kaito, 1978) was explained in terms of two stages; a surface melting coalescence and a liquid-like coalescence. These two stages depend on the grain size and its temperature. The morphology, the grain size, and the crystal structure have been controlled by the mass density and the temperature in the smoke, and also by the atmospheric gas and the gas pressure. If the density of the produced material is ρ and grain radius is r, the growth rate of the grains can be presented as follows (Kaito, 1978):

$$dr/dt = mk/4\pi\rho \qquad (1)$$

where m is the mass density which presents the total mass of grains in unit volume of smoke and k is the factor of the coalescence probability which depends on the temperature of the grain. Since m and k become larger with increase of source temperature and gas pressure, the grain size becomes larger. There is a coalescence temperature below which coalescence does not take place. The coalescence temperature of some materials was typically in the range 200–400° (Kaito and Shiojiri, 1982). Since the coalescence is due to intraction among the small solid grains, the coalescence temperature of two different materials such as Fe-Ni system was the confusion temperature. The solid-solid interaction took place at a relatively low temperature in the ultrafine grains in the smoke. Similar terminology of coalescence has been used in the field of the growth of thin film on substrate. In the case of the smoke, there is no substrate, therefore the coalescence in smoke took place in free space accompanying the collision process between grains. Since the interaction between the film and the substrate is very large, the coalescence in smoke predominantly took place more easily than the case of the film growth.

In the growth of smoke particles, the gas pressure effect has been considered as the control factor of the particle size. In the present paper, it is shown that the oxidation state of iron oxide grains can be controlled by gas pressure.

2.   Experimental

The sample preparation chamber is a glass cylinder of 17 cm in inner diameter and 33 cm in height. A tantalum V-boat (length 50 mm, width 2 mm, and depth 1 mm) charged with powder of FeO (99.9%) was placed in the chamber. Ar gas at 10–100 Torr was introduced into the chamber and the boat heated up at about 1800°C. Grains in the produced smoke were collected on thin carbon film supported by an electron microscopic grid and observed with an electron microscope of Hitachi H-800.

3.   Results and Discussion

Typical smokes formed by evaporating FeO in Ar gas at 10 and 100 Torr are shown in Fig. 1. The length-wise direction of evaporation source was almost perpendicular to the photographic plane. The width of the smoke becomes narrow with increase of pressure. The width of the smoke drastically changed below 25 Torr in Ar gas pressure. Since the mean free path of atomic vapor becomes smaller
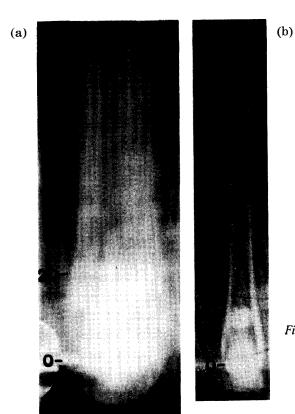
Fig. 1   Typical smokes formed by evaporating FeO powder in Ar gas pressures. The length-wise direction of evaporation source was almost perpendicular to the photographic plane. (a) 10 Torr. (b) 100 Torr.

with increase of the gas pressure, the collision frequency of evaporated vapor becomes larger. The evaporated vapor cooled rapidly near the heat source. The nucleation and growth in the smoke stopped within a few mm around the heater and the temperature of the grains became a few hundred degrees at a point about 10 mm above the evaporation source (KAITO, 1978). The produced grains near the heat source ride on a convection stream of Ar gas produced by the heater. Therefore, we can see the convection flow of the gas as the smoke through the produced grains.

Electron microscopic (EM) images and electron diffraction (ED) patterns of the collected samples in the smokes at about 80 mm above the heat source at 10 Torr and 100 Torr are shown in Figs. 2 and 3, respectively. ED patterns in Figs. 2 and 3 show the formation of iron grains and magnetite grains, respectively. The formation of iron grains shows that the evaporated FeO powder was decomposed, i.e., the direct evaporation of oxides and sulfides did not always give the same component of vapor of the evaporant (KAITO, 1983). The decomposed iron atoms become iron fine grain as seen in a usual smoke. But the decomposed oxygen gas also flowed up riding on the convection stream of the Ar gas. The density of the oxygen gas in the smoke becomes larger in proportion to gas pressure increment, because the width of the smoke becomes narrow. On the other hand, non-evaporation of wet Fe on the boat wall took place. The atmosphere of Ar containing an excess of O_2 may be formed (KAITO, 1983). The oxidation of the small iron grains took place in the nucleation and growth region near the heat source. Therefore, the magnetite fine grains were produced by the oxidation of very fine grains near the
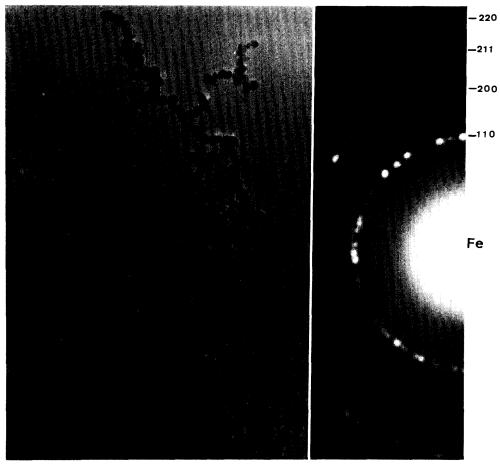
Fig. 2. EM image (left) and ED pattern (right) of the grains produced in Ar gas pressure of 10 Torr. ED pattern is indexed as iron.

evaporation source at 100 Torr. After that, the coalescence growth of the magnetite fine grains becomes predominant (KAITO, 1978).

The external shape of the well-grown magnetite grain was cubic octahedron. As shown in Section 1, the change of the gas pressure has been used to control the grain size. But in the present experiment, the oxidation state of produced iron oxides was also changed by the gas pressure, because oxidation of iron drastically changed by the oxygen gas pressure and atmospheric temperature (IIMORI, 1937, KAITO et al., 1985).

In the present experiment, wüstite grains can be also produced. Figure 4 shows the wüstite grains produced in the Ar gas pressure at 20 Torr. A chemical variation of the produced grains depending on the gas pressure is summarized in Table 1. The magnetite grains were produced at about 25 Torr of Ar gas pressure. At 15 Torr gas pressure, iron grains were covered with a thin wüstite layer. The grain of wüstite predominately appeared at 17–20 Torr of gas pressure. The iron oxide grain formation is concerned with the width of the smoke, i.e., the density of the oxygen gas riding on the gas flow. The width of the smoke at 100 Torr at 10 mm from the evaporation source is about 7 mm as seen in Fig. 1, but the value
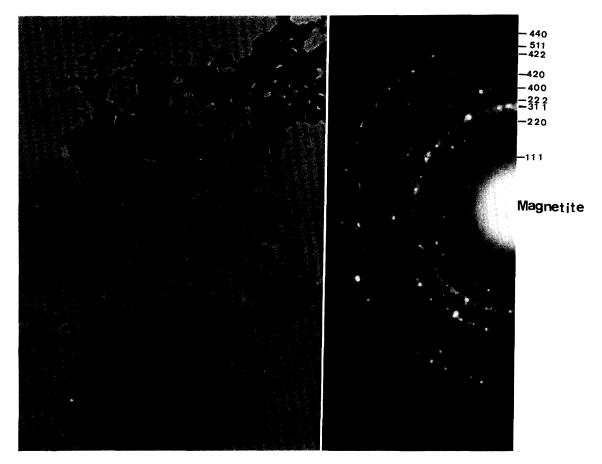
Fig. 3. EM image (left) and ED pattern (right) of the grains produced in Ar gas pressure of 100 Torr. ED pattern is indexed as magnetite (Fe_3O_4).

at gas pressure fo 20 Torr and 10 Torr becomes about 1.7 and 3 times greater. The density of the decomposed oxygen gas in the convection gas stream decreases with decrease of gas pressure. Therefore, the chemistry of produced oxide grains changes due to the gas pressure.

The chemical composition of produced grains was also changed by the use of the tungsten boat, because the solubility of oxygen varies with metal. The solubility of oxygen gas in tungsten is greater than in the tantalum. Therefore, the decomposed oxygen gas pressure in the gas stream became lower by the use of the tungsten boat. Table 2 shows oxygen partial gas pressure effect in Ar gas pressure at 100 Torr. The chemistry of produced oxides also changed by the partial oxygen gas pressure. The iron particles were produced at 0.1 Torr of oxygen gas pressure and Fe_3O_4 grains were produced in the pressure of 0.3 Torr. The number of oxygen gas atoms at 0.1 Torr and 0.3 Torr was estimated by $n = 9.66 \times 10^{18} P(\text{Torr})/T(k)$ at $T = 1800°C$. The ratio of the number of oxygen atoms at the two pressures $n_{0.3}/n_{0.1}$ becomes 3.0. This is coinciding with the width ratio of the 10 Torr to 25–100 Torr width of the smoke. With decrease of the gas pressure, the chemistry of produced oxides changed as shown in Table 1.

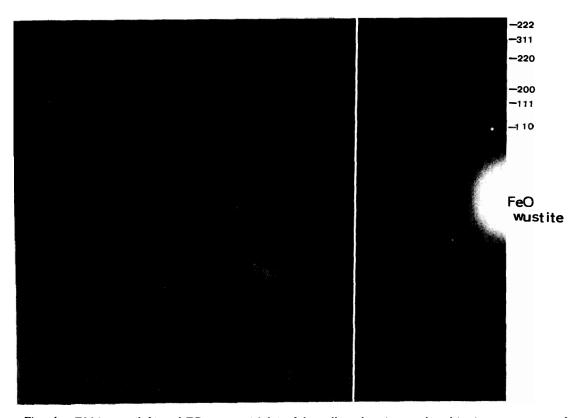Various iron oxide grains produced by the change of heat source, oxygen gas

Fig. 4. EM image (left) and ED pattern (right) of the collected grains produced in Ar gas pressure of 100 Torr. ED pattern is indexed as wüstite (FeO). The index 110 may be due to the existence of grains having superlattice.

Table 1   Results of analysis of iron oxide grains.

Ar Gas Pressure (Torr)	10	15	17–20	25–100
Produced grain	α-Fe	α-Fe (FeO)	FeO	Fe₃O₄

( ) means the oxide produced on the surface of α-Fe.

Table 2   Oxygen partial pressure effect for the production of iron oxidde grain.

Starting	material	FeO	FeO	FeO
Atmosphere	Ar:O₂ (Torr)	100:0.1	100:0.3	100:0.5
Produced	Particle	α-Fe (Fe₃O₄)	Fe₃O₄	α-Fe₂O₃ γ-Fe₂O₃

( ) means the oxide produced on the surface of α-Fe.

pressure and evaporants are shown in Table 3. Typical morphology of the grown crystal is shown in Fig. 5. The crystal shapes differ with the oxides, *i.e.*, crystal structure. It becomes evident that the controlled gas evaporation method can produce the materials seen in meteorites.

Table 3.   Various conditions for producing iron oxide grains.

Starting material	Preparation condition	Produced grain
Fe	Ar 95 Torr, O_2 5 Torr Molybdenum silicide-boat	$FeO^{1)}$
α-Fe_2O_3	Ar 100 Torr W-boat	γ-$Fe_2O^{2)}$
FeO	Ar 100 Torr W-boat	$Fe^{3)}$
FeO	Ar 100 Toor Ta-boat	Fe_3O_4 FeO Fe

1) Kaito et al., 1987. 2) Kaito, 1983. 3) Kaito et al., 1986.

Fig. 5.   Typical EM image of iron oxide particles (a) FeO (wüstite). (b) Fe_3O_4 (magnetite). (c) α-Fe_2O_3 (hematite). (d) γ-Fe_2O_3 (maghemite).

In conclusion, the production of iron oxide grains of magnetite and wüstite in the present experiment is due to the oxidation of iron grains near the heat source and the coalescence growth of oxidized fine grain in the smoke.

Acknowledgments

References

Iimori, T. (1937): Electron-diffraction studies of oxides formed on iron. Nature, 140, 278.
Kaito, C. (1978): Coalescence growth of smoke particles prepared by a gas-evaporation technique. Jpn. J. Appl. Phys., 17, 601–609.

KAITO, C. (1981): Formation of double oxides by coalescence of smoke particles of different oxides. J. Cryst. Growth, 55, 273–280.

KAITO, C. (1983): High resolution electron microscopic study of oxide particles produced by the coalescence of smoke particles of iron and iron oxide. Jpn. J. Appl. Phys., 22, L432–L434.

KAITO, C. (1984): Electron microscopic study of the alloy particles produced by coalescence of Au and Cu smokes. Jpn. J. Appl. Phys., 23, 525–528.

KAITO, C. (1985): Coalescence growth mechanism of smoke particles. Jpn. J. Appl. Phys., 24, 261–264.

KAITO, C. and SHIOJIRI, M. (1982): Structure and coalescence growth of smoke particles of tin oxides and lead oxides prepared by burning the metal in mixture of Ar and O_2. Jpn. J. Appl. Phys., 21, 1404–1408.

KAITO, C., NAKATA, Y., SAITO, Y. and FUJITA, K. (1985): Structure of iron oxide films prepared by evaporating various oxide powder. Appl. Surf. Sci., 22/23, 621–631.

KAITO, C., SAITO, Y. and FUJITA, K. (1986): Electron microscopic studies on the structure of ultrafine particles of astrophysical interest. Proc. XIth Int. Cong. Electron Microscopy, Kyoto, II, 1435–1436.

KAITO, C., SHOJI, R. and FUJITA, K. (1987): Formation conditions of SiO_2 and FeO grains. Jpn. J. Appl. Phys., 26, L965–L967.

KIMOTO, K., KAMIYA, Y., NONOYAMA, M. and UYEDA, R. (1963): An electron microscopic study of fine metal particles prepared by evaporation in argon gas at low pressure. Jpn. J. Appl. Phys., 2, 702–713.

KUBO, R. (1962): Electronic properties of metallic fine particles I. J. Phys. Soc. Jpn., 17, 975–986.

NAGATA, T. and CARLETON, B. J. (1990): Tetrataenite in carbonaceous chondrites. Proc. Jpn. Acad., 66, Ser. B, 183–188.

NAGATA, T., KAITO, C., SAITO, Y. and FUNAKI, M. (1991): Tetrataenite in chondrites and experimental demonstration on formation of tetrataenite fine grains. Proc. NIPR Symp. Antarct. Meteorites, 4, 404–419.