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EXPERIMENTAL DEMONSTRATION OF FORMATION OF IRON-SULFIDE GRAINS WITH Fe-S COALESCENCE TECHNIQUE AND IRON-SULFIDE GRAINS IN CARBONACEOUS CHONDRITE

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Abstract: The coalescence growth process of a joint cloud of fine smoke particles evaporated from Fe and those from S produces fine grains of pyrrhotite, in addition to stoichiometric troilite and marcasite. Pyrrhotite grains exhibited a typical DDSS (diffusion-dependence shell structure) shape produced by diffusion of iron atoms to the surface layer. Various superstructures of pyrrhotites were observed by changing the heater temperature. An outline of the experimental procedures of coalescence growth formation of iron sulfide and the main experimental results are described. Magnetic properties of some carbonaceous chondrites have been summarized and discussed in comparison with the characteristics of the coalescence product.

1. Introduction

Systematic studies of meteorite magnetism, meteorite paleomagnetism in particular, have just started only recently. The first review summary of meteorite magnetism was given by GUS'KOVA (1976), and the first and recent reviews of summaries concerning meteorite magnetism including paleomagnetism were given by NAGATA and SUGIURA (1977) and CISOWSKI (1987), respectively. The most abundant ferromagnetic minerals in meteorites are Fe-Ni metals of various compositions, and iron sulfides which are common minerals in carbonaceous chondrites. The latter often include ferrimagnetic pyrrhotite in addition to the ordinary anti-ferromagnetic troilite (FeS). Since primitive CI, CM, and CV carbonaceous chondrites are the most primordial undifferentiated meteorites, it is believed that their natural remanent magnetization (NRM) was acquired in the early stage of the primordial solar system formation.

In a previous paper (NAGATA *et al.*, 1991b), we showed that chondrites often contain tetrataenite grains of 10 nm or smaller in mean diameter and laboratory experiments can demonstrate the formation of tetrataenite fine grains by coalescence growth at 200°–500°C, from either (a) a joint cloud of evaporated smoke flows of Fe and Ni or (b) an Fe-Ni smoke cloud evaporated from relatively large disordered taenite grains of Fe₅₀Ni₅₀ composition. One of the present authors (T. NAGATA)

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reported recently that the observed coexistence of tetrataenite fine grains with more abundant magnetite and kamacite in Yamato 791717 carbonaceous (CO3) chondrite suggested that the tetrataenite grains were directly formed by a coalescence process of Fe and Ni fine particle smoke in the solar nebula (NAGATA and CARLETON, 1990). Thence, experimental demonstration of formation of fine grains by the use of the coalescence in smoke becomes important in meteorite magnetism.

Stoichiometric FeS (troilite) is antiferromagnetic, but Fe_{1-X}S (pyrrhotite) is ferrimagnetic depending on various values of X in a range of $0.14 > X > 0.11$. In a previous paper (NAGATA *et al.*, 1991a), magnetic properties, NRM characteristics and magnetic minerals of four carbonaceous chondrites (Y-74662, Y-81020, Allende and Leoville) were studied and EPMA analyses of the composition of iron-sulfide grains in these chondrites were done. It became evident that low temperature NRM component was possessed by ferrimagnetic pyrrhotite at temperature below 300°C. These chondrites contain 5–10 wt% of FeS (HARAMURA *et al.*, 1983).

On the other hand, pyrrhotite fine grains are experimentally produced by coalescence of Fe and S smoke streams in inert gas atmosphere of 13 kPa pressure (KAITO and SAITO, 1991). The present study shows the detailed method for the coalescence system of Fe and S smoke streams in inert gas, and detailed discussion on the growth condition of pyrrhotite phase in comparison with other experiments for grain formation, and compares the results with the characteristics of pyrrhotite grains contained in chondrites.

2. Experimental Formation of Iron-Sulfide Grains by Coalescence of Fe and S Smoke Grains

In the previous paper (NAGATA *et al.*, 1991b) it has been shown that formation of tetrataenite fine grains was possible by the gas-evaporation-coalescence technique from Fe- and Ni-evaporated smokes. The coalescence process in smoke has 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 in an Ar gas atmosphere without any substrate. The grains of 10–100 nm can be easily obtained. The gas evaporation-coalescence-system is schematically shown in Fig. 1. Two tungsten V-boats A and B were placed 40 mm apart and parallel to each other in the chamber. Ar gas at 13 kPa was introduced into the chamber and boats A and B were heated at 1700°C and 1400°C, respectively. The arrangement of two B and C boats is different in the case of Fe-Ni system. This method was first applied to evaporate and to produce fine grains of having low melting-temperature materials or of inorganic materials (KAITO and FUJITA, 1986; KAITO, 1987). Boat B was used to create a stationary convection flow and to control atmospheric temperature. The quartz boat C was the evaporation source of sulfur, thence, the temperature at boat C reached about 320°C by the heating of boat B at 1400°C as shown in Fig. 2, which is the temperature distribution curve measured by the specially designed chromel-alumel thermocouple (KAITO *et al.*, 1976). Sulfur smoke appeared from the C. A stream of sulfur smoke rose from boat C riding on the convection flow originated from boat B in Fig. 1. The smoke streams rising straight up from

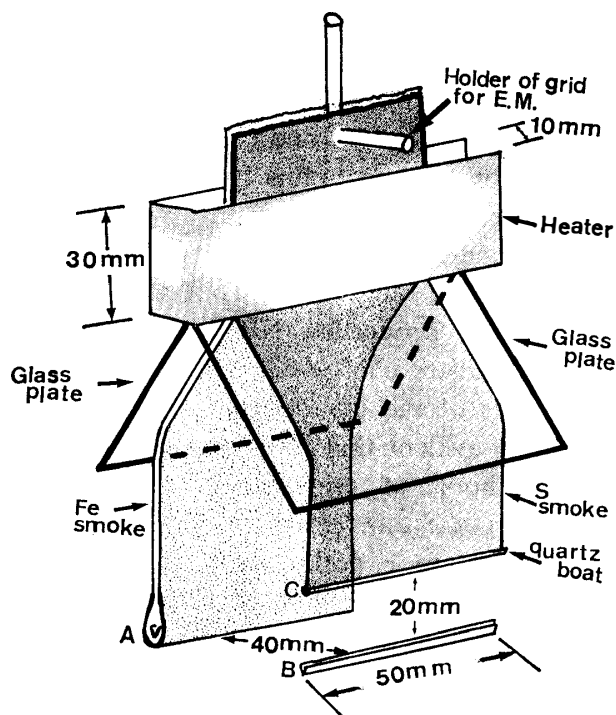


Fig. 1. Schematic illustration of coalescence growth instrument system. Fe and S ultrafine smoke grains are mixed and are passed through a heater.

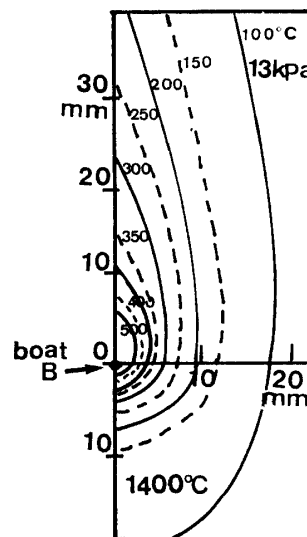


Fig. 2. Temperature distribution around boat B heated at 1400°C in Ar gas pressure at 100 Torr. Boat C was set at 20 mm just above boat B.

the sources flow along the glass plates, and the joined smoke stream at the end of glass plates flows straight upward again. When the joint smoke is not heated up, no coalescence grains of Fe-S are formed. Only Fe and S grains were detected separately.

In the present study, the formation temperature of the iron-sulfide grains due to the coalescence process between Fe and S smoke grains is determined by examining the collected fine grain specimens by an electron microscope HITACHI H-800 and X-ray micro analysis operated with an electron microscope, HITACHI H-9000 interfaced to KEVEX, an energy-dispersive X-ray analysis system. The temperature within the gap of the heater is changed at intervals of every 50°C between 100 and 400°C. In the grain which passed through the heater gap at temperatures higher than 100°C, marcasite, troilite, and pyrrhotite grains were preeminently produced by the coalescence between Fe and S grains in a short time.

Examples of iron and sulfur grains before passing through the heater are shown in Fig. 3. Fe and S grains were α -iron (cubic $a=0.287$ nm) and amorphous, respectively. Most of the fine grains produced by the gas evaporation method were crystals condensed from the vapor phase. Fine amorphous grains produced by the gas evaporation technique were seen in typical glass-forming materials such as selenium, gallium (KIMOTO *et al.*, 1963), SiO (KAITO *et al.*, 1987) and SiO₂ (KATO, 1976). In the sulfur grains, liquid state may be attained above the evaporation source C, because the temperature of the smoke at about 50 mm above the heater

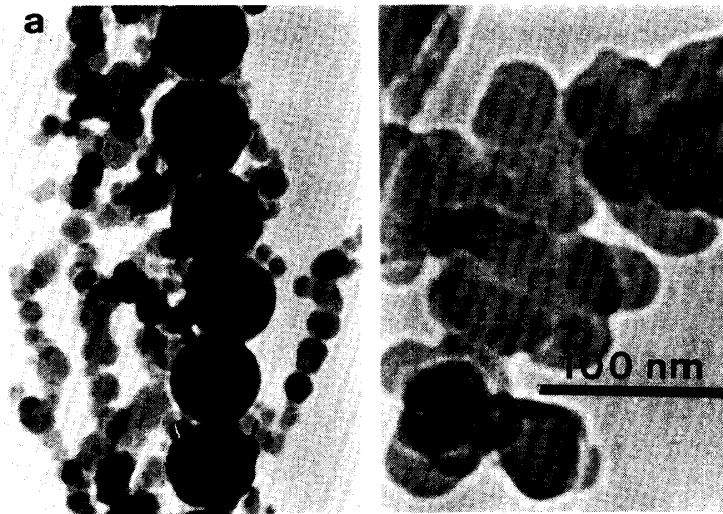


Fig. 3. Typical iron (a) and sulfur grains (b).

C is higher than the melting point of sulfur as seen in Fig. 2, and amorphous solid grains can be obtained at the heater position.

Typical examples of marcasite, troilite, and pyrrhotite grains produced at 300°C in the heater temperature are shown in Fig. 4. The stoichiometric compounds such as marcasite and troilite grains are single crystals of complicated polyhedral shapes. As elucidated in a previous paper (KAITO, 1985), the coalescence phenomena in smoke have been explained by taking into account the two temperature-related processes, *i.e.*, liquid-like coalescence and surface melting coalescence. The appearance of single crystals of troilite and marcasite shows that the liquid-like coalescence took place above 100°C in Fe-S system (KAITO and SAITO, 1991). The central part of the pyrrhotite grains becomes white, as can be seen from the experiment on the oxidation of metallic particles (KAITO *et al.*, 1973), *i.e.*, voids in the original iron grains may be formed by the growth of the sulfur layer. The pyrrhotite which is

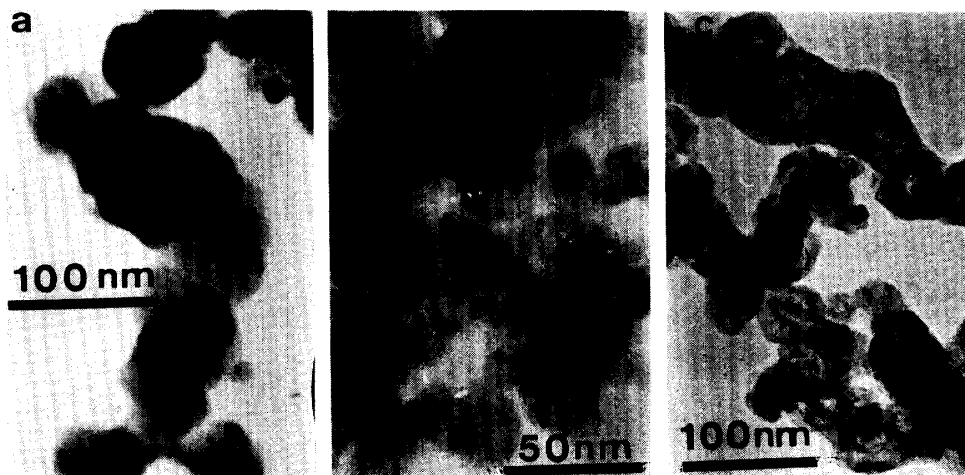


Fig. 4. Typical iron sulfide grains produced in the present experimental system. (a) marcasite. (b) troilite. (c) pyrrhotite.

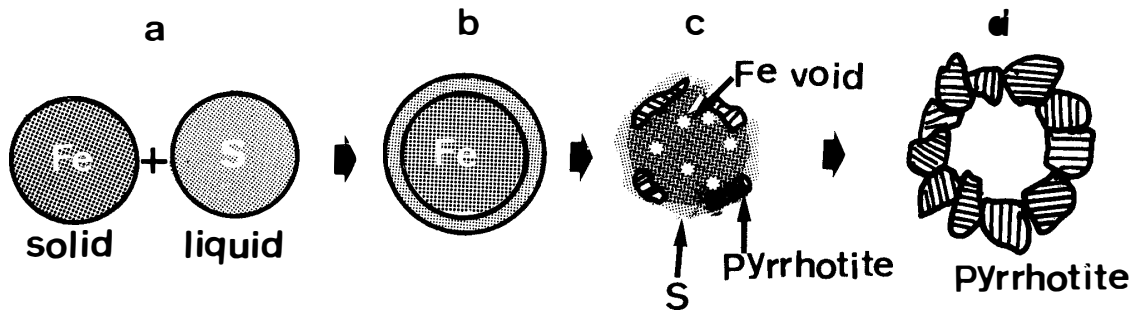


Fig. 5. Schematic representation of the DDSS formation process. By coalescence between solid Fe grain and liquid sulfur grains (a), the grain of Fe was covered with a sulfur layer (b). By the formation of pyrrhotite on the sulfur layer, voids were formed in the Fe grain (c). By the growth of pyrrhotite crystal, DDSS was formed (d).

an important mineral in the paleomagnetic research of the primordial solar system, can be seen as a typical DDSS (diffusion dependence shell structure) shape which was produced by the diffusion of iron atoms to the surface layer as shown schematically in Fig. 5.

The formation mechanism of DDSS was similar to the one elucidated in the oxidation process of iron grains in air (KAITO *et al.*, 1973). In the present case, the reaction speed is about 10^5 times higher than in the case of oxidation, and the growth temperature was lower by a factor of about 1/4. This is because the iron grain was covered with liquidus sulfur layer by the coalescence between solid and liquid grains as shown in Figs. 5a and b. Metallic atoms in the central parts diffuse to the sulfur layer, and sulfides are formed at the interface between the sulfur layer and metallic iron grains. Since the DDSS grains were composed of

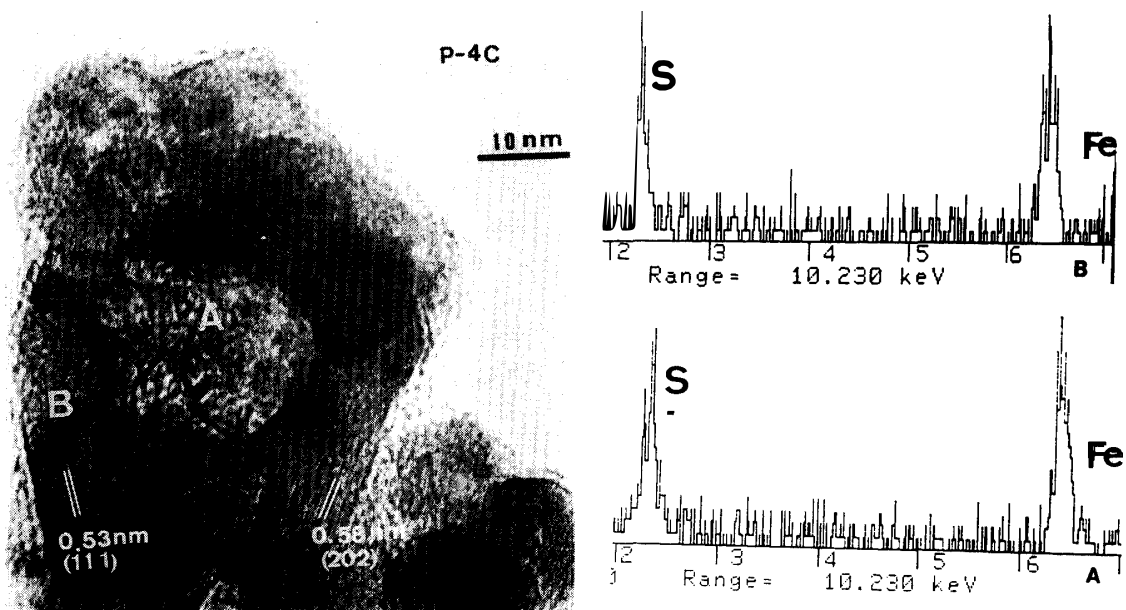


Fig. 6. DDSS grains and X-ray spectra of the central part A and the outer layer B.

pyrrhotite phase, non-stoichiometric sulfide clusters may be formed. Therefore, the structure of the pyrrhotite phase depends on the heater temperature and sulfur fugacity. The sulfides grow at the surface layer and vacancy clusters are left in the iron particle, and then the iron particle forms the shell structure as shown in Figs. 5c and d.

Figure 6 shows a high resolution electron microscopic (HREM) image and X-ray spectrum at the A and B sites of the shell-structure grains produced at 300°C in the heater temperature. The HREM image shows that the outer layer was composed of 4C-type pyrrhotite phase with the size of ~10 nm. Since X-ray spectra at both A and B sites are nearly of a equal height, the particle is composed of the shell structure. If the iron grains remain at the central part, the intensity of characteristic X-ray differs as shown in Fig. 7. Appearance of a white circular layer between the central and outer layers shows the diffusion of iron atoms to the surface layer as elucidated in the previous paper (KAITO *et al.*, 1973).

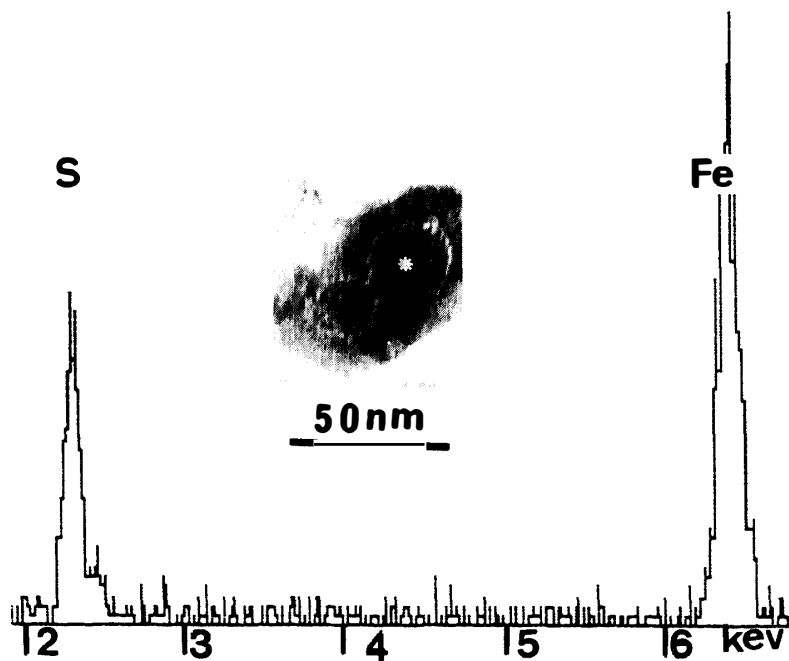


Fig. 7. X-ray spectrum of the DDSS having the iron grain in the central part.

Table 1. Temperature dependence of DDSS. P shows the pyrrhotite phase.

Temperature (°C)	Sulfide
100	P-7C
150	P-7C
200	P-3C
300	P-4C
400	P-1C

The crystal structure of DDSS grains was different in terms of the change in the heater temperature, *i.e.*, high superstructure can be produced at low temperature. The results analyzed are tabulated in Table 1. The morphology of the DDSS was similar by the change of the heater temperatures, but appearing tendency of crystal phases by temperature agrees with the results of the systematic review of sulfide phase relations (RIBBE, 1976). Structures of the grains produced by the reaction of metal vapor and sulfur vapor were different in the present results, *i.e.*, mackinawite (FeS), greigite (Fe_3S_4), and symthite (Fe_3S_4) have been produced in the gas-gas interaction experiment (KAITO *et al.*, 1989). In the present case, the produced sulfides were like those seen in Fig. 4. These results show that the production of sulfides is very difficult and strongly depends on sulfur fugacity. In the case of the ordinary gas-evaporation method, the same compounds of the evaporant cannot be obtained, because decomposition takes place. Therefore, the present method using coalescence of Fe and S smoke grain in inert gas flow is important for production of pyrrhotite grains.

Since the marcasite and pyrrhotite phases contain much more sulfur than the troilite, the amount of sulfur may be important for the formation of DDSS pyrrhotite grains. Another empirical finding is that the DDSS grains were predominately produced by the coalescence between sulfur grains and relative by large iron grains. This indicated that the diffusion process of iron atom to the surface sulfur layer is important for the production of pyrrhotite. As shown in the previous paper (KAITO and SAITO, 1991), if the temperature of the heater in Fig. 1 was below 100°C , the produced sulfide on the iron surface by the diffusion process of iron atom was cubic FeS (ASTM card 23-1123). Therefore, the liquid state of the covered sulfur layer is important for the growth of pyrrhotite grain.

There still remain a number of problems in coalescence phenomena between Fe and S grains. More quantitative studies on these phenomena between thin film of Fe and small spherical particles of S are under way at present.

3. Discussion

Most chondrites possess their own remanent magnetization (NRM). However, the intensity of NRM (I_n) is not always proportional to saturation magnetization (I_s). As shown in the previous paper (NAGATA *et al.*, 1991a), for example, (I_s , I_n) are (1.31, $(0.8-3.5) \times 10^{-4}$), and (1.08, 5.9×10^{-4}) in unit of emu/g, for the Allende and Y-74662 C-chondrites, respectively, while they are (10.3 , 2.1×10^{-4}) and (14.0 , 8.6×10^{-4}) in the same unit for the Leoville and Y-81020 C-chondrites. The above mentioned difference between the first and the second groups is due to the fact that magnetic minerals do not always maintain a stable NRM, but special magnetically coercive minerals only can possess stable NRM.

As discussed in the previous paper (NAGATA *et al.*, 1991a), it was plausible that the NRM low temperature component resided in pyrrhotite (Fe_{1-x}S) and the higher temperature NRM component by taenite (FeNi) and kamacite grains in this chondrite carry only 1% of its NRM.

A simple possible interpretation of the two component structure of C-chondrite

NRM may be that the primordial solar nebula magnetic field was smaller than 0.1 Oe until the nebula temperature cooled down to about 300°C and then the field reached about 1 Oe in the order of magnitude, while the ferri-magnetic pyrrhotite grains were formed at temperatures below 300°C. The growth condition of the pyrrhotite phase by the use of coalescence phenomenon is in agreement with the growth temperature. Another possibility is that the NRM possessed by pyrrhotite grains was originally acquired by small grains with a weaker magnetic field but later the grain size increased keeping the acquired magnetization orientation even in the non-magnetic space, resulting in an enlargement of NRM intensity. This phenomenon actually takes place as a chemical remanent magnetization (CRM) of terrestrial metamorphic rocks. However, a theoretical examination of this process on the basis of Neel's super paramagnetism theory indicates that the NRM intensity magnified owing to the growth of magnetized grains will be larger by less than 30% than the PTRM intensity acquirable in the same original magnetic field by the test sample composed of the already grown-up magnetic mineral grains. It may be provisionally concluded at present, therefore, that the primordial solar nebula had a magnetic field smaller than 0.1 Oe at temperature of 400°–600°C, while it was around 1 Oe at temperature of 0–300°C. However, meteorite paleomagnetism still has various basic problems, particularly with respect to the crystallographic and magnetic properties of the magnetic constituents of meteorites. As it has been proposed that the tetrataenite grains were directly formed by a coalescence process of Fe and Ni fine particle smoke in the solar nebula by the observed coexistence of tetrataenite fine grains with more abundant magnetite and kamacite in Yamato 791917 carbonaceous chondrite (NAGATA and CARLETON, 1990), the pyrrhotite grain in carbonaceous chondrite is within the bounds of possibility. The textural agreement is also necessary between meteorite and coalescence product, but the present result shows one of the possibilities for the formation of pyrrhotite phase on the basis of non-equilibrium growth condition using the characteristics of ultrafine grain. Magnetic properties of the coalescence product grains are being studied way at present.

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