

**NUCLEATION AND GROWTH OF IRON SULFIDE ON METALLIC IRON PARTICLES UNDER LOW-PRESSURE PROTOPLANETARY DISK CONDITIONS.** S. Tachibana<sup>1</sup> Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan (tachi@eps.s.u-tokyo.ac.jp).

**Introduction:** Sulfur is a major volatile element in the solar system. The abundances of sulfur in chondrites shows various degrees of depletion, reflecting elemental fractionation of sulfur and other volatile elements in the early solar system. The fractionations of volatile elements may be attributed to incomplete condensation of volatiles into solids due to coagulation of earlier condensates and/or dispersal of disk gas.

Such incomplete condensation of volatiles should be understood in the context of reaction kinetics, and, in the case of sulfur, sulfidation kinetics of metallic iron should be determined. Experimental studies on sulfidation of metallic iron and alloy were made in order to investigate sulfidation behavior in the early solar system [1-3]. However, no sulfidation experiment was carried out under low-pressure plausible disk conditions. I performed sulfidation experiments of metallic iron in the mixture of He-H<sub>2</sub>S gas with the solar S/He ratio at the total pressure of 1 Pa [4]. In the experiments, sub- $\mu\text{m}$ -sized iron sulfides nucleated sporadically on the surface of Fe metal chip (~20 grains in 400  $\mu\text{m}^2$  area) after 24-hour reaction with He-H<sub>2</sub>S gas, and grew to the size of  $>1 \mu\text{m}$  after ~140-hour reaction. The reaction accompanying the formation of a reaction product on a pre-existing solid could be controlled by diffusion through the reaction product, which was observed in [1] for a sulfide layer with thickness of  $>10 \mu\text{m}$ . However, the grain size of sulfide increased linearly with time, suggesting that the supply of H<sub>2</sub>S from vapor controls the growth rate. The growth rate of sulfide was compared with the supply rate of H<sub>2</sub>S, and it was found that the sulfidation reaction was not effective and only 2 % of incoming H<sub>2</sub>S flux was used for sulfidation. This estimated reaction efficiency was comparable to that predicted in [1].

Another important kinetic process for gas-solid reaction is heterogeneous nucleation of the reaction product on the surface of the pre-existing solid. If the nucleation of iron sulfide proceeds much faster than the subsequent growth, all the metallic iron dust particles may possibly react with sulfur to form iron sulfide. However, if the nucleation is much more sluggish than the growth, only a part of metallic iron particles is converted to iron sulfide. In this study, in order to investigate both nucleation and growth rates of iron sulfide for sulfidation of metallic iron, the sulfidation experiments of metallic iron particles (sub- $\mu\text{m}$  to 1  $\mu\text{m}$  in size) were performed in this study.

**Experiments:** Metallic iron particles condensed from Fe vapor onto substrates of forsterite or corundum at ~1300 K in vacuum were used as starting materials of sulfidation experiments. The vacuum furnaces with a tungsten-mesh heater [5] and with an infrared heating system [6, 7] were used for condensation of metallic iron particles with sub- $\mu\text{m}$  to 1  $\mu\text{m}$  in size.

The sulfidation experiments of metallic iron particles were performed using a vacuum gold furnace (Fig. 1) [4]. The heating unit of the furnace consists of a resistance metal heater and a surrounding gold mirror tube that reflects infrared light from the heater effectively to heat a sample in the chamber. The vacuum chamber of the furnace, connected to a turbomolecular pump, is made of a silica glass tube. The He-H<sub>2</sub>S gas with the solar S/He ratio was flowed into the chamber after evacuation of the chamber down to  $<3 \times 10^{-5}$  Pa. The total pressure inside the chamber was kept at ~1 Pa during experiments by adjusting the flow rate of the mixed gas. The heating temperature was ~770 K, and the heating duration ranged from 21-80 hours. After the desired reaction duration, the heater was turned off for rapid cooling. In order to avoid oxidation of Fe metal, a titanium rod was placed in the chamber. The run products were examined with field-emission scanning microscopy (FE-SEM; JSM 7000F) and energy-dispersive X-ray spectroscopy (EDS).

**Result and Discussion:** An example of the secondary electron images of run products is shown in Fig. 1, and the composite EDS maps of Fe ( $K\alpha$ ) and S ( $K\alpha$ ) of run products reacted for various durations are shown in Fig. 2.

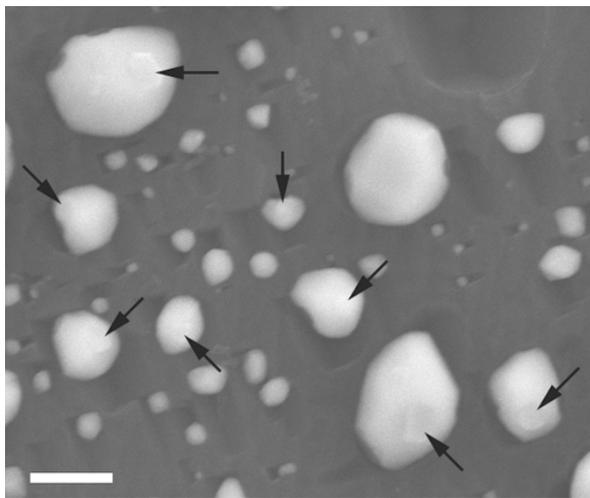
Most of metallic iron particles reacted with the He-H<sub>2</sub>S gas for 21 hours seem to have a nucleus of sulfide on each of grain surfaces (Fig. 2a), roughly corresponding to the nucleation rate of 1 nucleus/10  $\mu\text{m}^2$ . This nucleation rate is consistent with that observed for the experiments for Fe metal chip [4].

The sulfides further grew to ~0.2-0.5 and ~0.5-1  $\mu\text{m}$  after the reaction durations of 45 and 80 hours (Figs. 1, 2b and 2c). Further nucleation of iron sulfide also occurred on the surfaces of metallic iron particles, and sulfides grown from multiple nuclei can often be observed on the surface of each metallic iron particle. Although the interior of the reacted metallic iron particles has not been observed, the growth rate of iron sulfide on the surface of metallic iron is estimated to

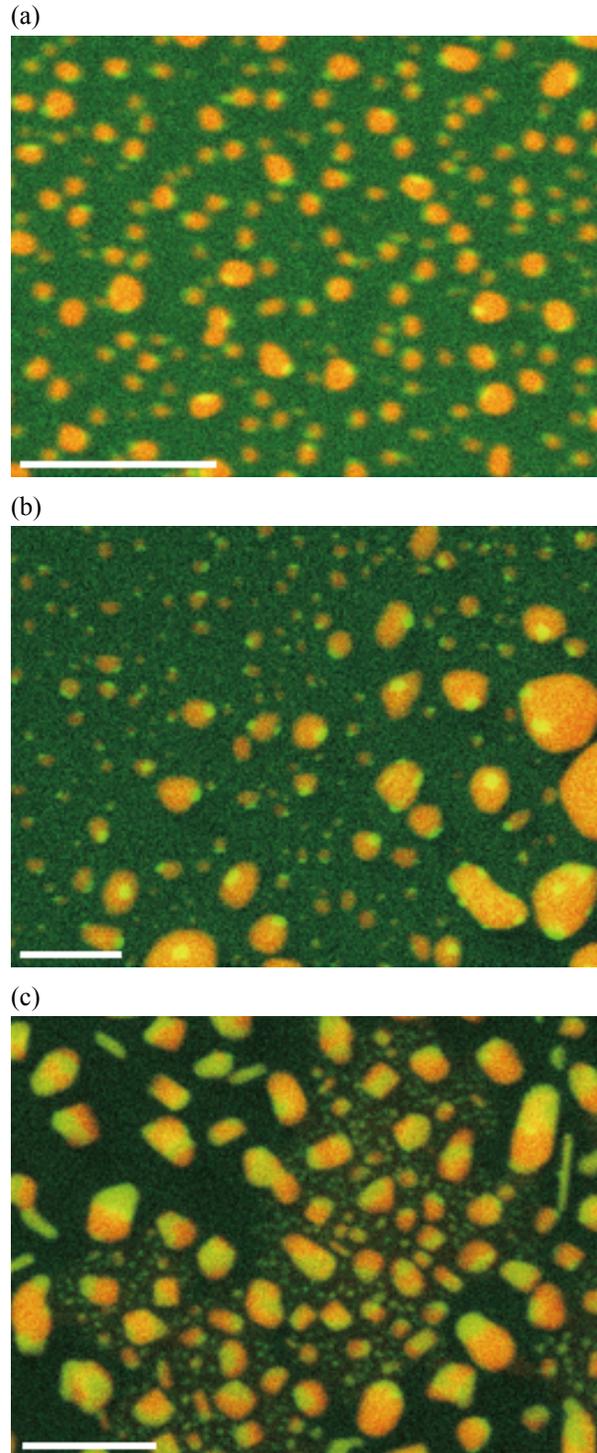
be  $\sim 1.5 \times 10^{-12}$  m/s, which is also consistent with the previously measured growth rate on the surface of Fe metal chip [4].

The present experiments suggest that heterogeneous nucleation of iron sulfide occurs simultaneously on the surfaces of 1  $\mu\text{m}$ -sized metallic iron particles and that further grain growth proceeds at the rate controlled by the supply of  $\text{H}_2\text{S}$  and the surface reaction kinetics (the reaction efficiency of  $\sim 0.02$ ) at 1 Pa and 770 K. If this is the case, most of the metal particles in the protoplanetary disk would experience almost the same degree of sulfidation during cooling. This seems not to be consistent with the observation of metal and iron sulfides in planetary materials, where various degrees of sulfidation seem to have occurred (e.g., Fe-Ni metals and iron sulfides in GEMS). This could be attributed the fractionation processes of Fe-Ni metal at temperatures higher than the formation temperature of iron sulfide. Alternatively, the present experiments were done in the absence of hydrogen gas, i.e., highly supersaturated conditions for iron sulfide, and the nucleation rate shown here could not be the representative for the early solar system. The nucleation rate in the presence of hydrogen will also be reported at the meeting.

**References:** [1] Lauretta D. S. et al. (1996) *Icarus* 122, 288-315. [2] Lauretta D. S. (2005) *Oxid. Metals* 64, 1-22. [3] Schrader D. L. and Lauretta D. S. (2010) *GCA* 74, 1719-1733. [4] Tachibana S. (2010) *Meteor. Planet. Sci.* 73, #5341 (abstract). Supported by Grant-in-Aid for Young Scientists (A) (20684025).



**Fig. 1.** A secondary electron image of metallic iron particles reacted with the  $\text{He-H}_2\text{S}$  gas at 770 K and 1 Pa for 45 hours. The iron sulfide grains are indicated by arrows. A scale bar is 1  $\mu\text{m}$ . The substrate is forsterite.



**Fig. 2.** Composite EDS maps Fe ( $K\alpha$ ) and S ( $K\alpha$ ) of run products reacted with the  $\text{He-H}_2\text{S}$  gas at 770 K for (a) 21 hours, (b) 45 hours, and (c) 80 hours. The reddish color represents metallic iron particles, and greenish to yellowish colored regions represent iron sulfides. The background (dark green to black) is the forsterite (a, b) or corundum (c) substrate. Scale bars are 2  $\mu\text{m}$ .