THERMAL ANALYSIS OF ACICULAR SHAPED MAGNETITE. H. V. Lauer Jr.[1], D. W. Ming[2], and D. C. Golden[3], [1]LMSO , 2400 NASA Rd1, Houston, TX 77058 (howard.v.lauer1@jsc.nasa.gov); [2]SN2 NASA/JSC, Houston, TX 77058 (douglas.w.ming1.@jsc.nasa.gov);[3] Hernandez Engineering Inc., Houston, TX 77058 (d.c.golden1@jsc.nasa.gov)

Introduction: We are in the process of developing a database on the thermal properties of well-characterized Martian analog materials in support of future Mars surface missions. The database contains the thermal behaviors of these analog materials under reduced and Earth ambient pressures [1]. Magnetite in planetary materials has received considerable attention in recent years since the identification of fine grain single-domain magnetite in Martian meteorite ALH84001 and their possible link to past life on Mars (i.e., possible biominerals of magnetotactic bacteria). Because of its possible importance to Mars science, we report here the thermal properties of magnetite particles with acicular morphology, i.e., needle-shaped magnetite.

Acicular shaped magnetite can be commercially produced from goethite (FeOOH) as the starting material via a H_2 reduction process. However, instead of using this process or procedure, we report here on the thermal characterization of acicular magnetite formed under reducing conditions from well-characterized needle-shaped goethite [2] at low temperature in controlled CO-CO_2 1-bar atmosphere gas mixing furnaces.

Materials and Methods: Two samples of well-crystalline goethite were used in this study as starting materials [2]. Approximately 150 mg of one starting material was gently crushed into a fine powder, placed in a Pt crucible and suspended in the hot zone of a controlled atmosphere gas-mixing furnace. The crushing was done to insure that all of the material had "good contact" with the furnace atmosphere. The reducing gas mixture was set at 95% CO_2 – 5% CO. At the temperatuers we are operating, higher concentrations of CO will result in carbon precipitation on the sample [3] and therefore were not used for magnetite formation.

The FeOOH sample was slowly heated (50 °C/hr) in the "reducing" gas mixture to a given set temperature, held for 1 hr at the set temperature, and then cooled to ambient temperature (200 °C/hr). The set temperature that goethite was heated for 1 hr is subsequently referred to as T_{MAX}. As a result of this heating process, we formed a set of acicular magnetite particles (i.e., needle-shaped particles) whose thermal heating history is known. This set of material forms the basis of this study to determine the thermal properties of acicular magnetite.

Thermal properties of acicular magnetite were determined by a differential scanning calorimeter (DSC) interfaced with a quadrupole mass spectrometer (QMS). In order to correctly analyze the thermal properties of magnetite in a DSC enough of O_2 must be present in the carrier gas to convert all of the magnetite to maghemite. We have therefore used pure O_2 as the carrier gas. However, in one experiment, magnetite was heated in O_2 from 30 °C to 700 °C under an Ar/O_2 carrier gas to clearly demonstrate oxygen consumption or lack there of during the exothermic reactions. The amount of O_2 in the DSC carrier gas is detected by the QMS on the output side of the DSC in the Ar/O_2 carrier gas, which is not possible in a pure O_2 carrier gas.

Results and Discussion: The thermal reactions for acicular magnetite are illustrated in Figure 1.

Figure 1

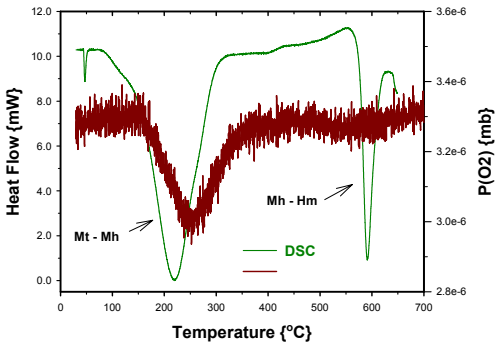

Figure 1. DSC plot of an acicular magnetite together with the partial pressure of oxygen in the carrier gas as a function of the DSC heating temperature.

The DSC heat flow curve (green curve) has been corrected for baseline and the partial pressure of O_2 in the carrier gas (red curve) shows O_2 consumption during heating. The first exothermic reaction (~225 °C) is the conversion of magnetite (Mt) to maghemite (Mh) and the second exothermic reaction (~590 °C) is the conversion of maghemite to hematite (Hm). In the first reaction O_2 is required to complete the reaction (i.e. transformation of magnetite to maghemite), but the second reaction is a phase transformation only from maghemite to hematite. This interpretation is clearly supported by depletion in O_2 during the magnetite to maghemite transition but not during the maghemite to hematite transition. These phases were confirmed by X-ray diffraction (XRD) analysis in the DSC runs that were stopped at either 450 °C or 650 °C.

Figure 2 shows a plot of the measured DSC peak temperature for the magnetite to maghemite transition for magnetite previously formed as a function of the growth formation temperature T_{MAX}. There is a clear increase in the DSC peak temperature for magnetite with an increase in growth formation temperature (T_{MAX}).

Figure 2

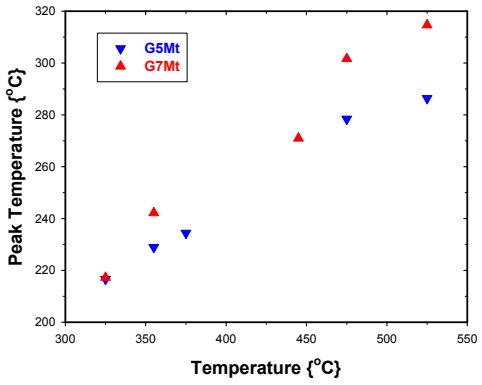

Figure 2. DSC measured peak temperature for the magnetite to maghemite transformation vs. magnetite formation temperature T_{MAX} for acicular magnetite.

Figure 3

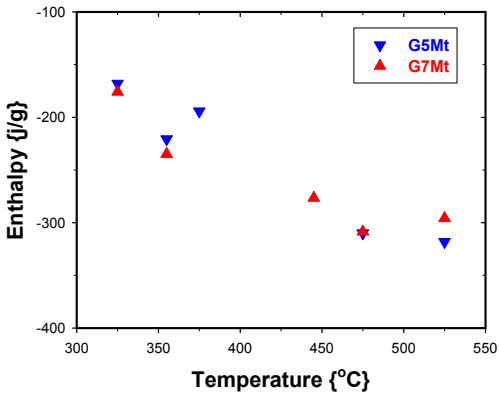

Figure 3. Plot of the measured DSC enthalpies for the magnetite to maghemite transformation vs. magnetite formation temperature T_{MAX} for acicular magnetite

Figure 3 shows the measured enthalpy for magnetite to maghemite transformation. Again, it should be pointed out that there is a smooth trend of increasing enthalpy with increasing formation temperature T_{MAX}.

Figure 4 shows the XRD full half width (FWHM) of the 2.52 Å d-spacing ([311]) for maghemite, which has formed after heating the acicular magnetite sample to 400 ºC. The measured half width of the [311] peak for a well crystalline "standard" maghemite [2] that has been heated in air for 100 hrs was measured to be 0.215 degrees. Our data show that the maghemite formed from magnetite, which had been produced at higher temperatures, approached this value. This suggested that formation temperature of magnetite plays an important role in the crystallinity of magnetite and the subsequent crystallinity of maghemite that forms after heating the magnetite in the DSC.

Figure 4

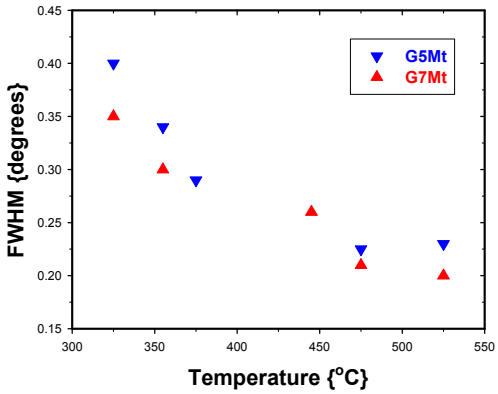

Figure 4. Plot of the measured XRD full-width-at half-maximum intensity of the 2.52 Å [311] maghemite peak as a function of the acicular magnetite T_{MAX} temperature.

Summary: The formation temperature of acicular magnetite plays an important role in the thermal properties of magnetite. Crystallinity of acicular magnetite improves at higher formation temperatures as shown by the XRD analysis. This is further supported by the increasing DSC onset temperatures and enthalpies for the acicular magnetite formed at higher temperatures.

Reference: [1] Lauer Jr. H.V. et. al. (2000) **LPSC XXXI CD-ROM.[2]** Morris R.V. et.al. (1985) **JGR 90 #B4** 3126-3144 [3] Jurewicz A J.G. Private communication.