

THERMODYNAMIC PROPERTIES AND ORIGIN OF METEORITIC MINERAL. III. HEIDEITE, FeTi_2S_4 . M.I. Petaev (1), K.S. Gavrichev (2), V.M. Gurevich (1), E.G. Osadchyy (3), T.A. Stolyarova (3), V.E. Gorbunov (2), I.L. Khodakovsky (1); (1) Vernadsky Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences, Moscow, USSR; (2) Kurnakov Institute of Chemistry of the USSR Academy of Sciences, Moscow, USSR; (3) Institute of Experimental Mineralogy of the USSR Academy of Sciences, Chernogolovka, USSR.

Physico-chemical study of meteoritic minerals provides useful information on origin of meteoritic mineral assemblages, i.e. a meteorite as a whole. The most valuable data may be obtained from the investigations of exotic accessory meteoritic minerals, i.e. nitrides and sulfides of Si, Ti, Cr, etc.

To these minerals also belongs heideite found only in aubrite Bustee. According to Keil and Brett [1], the Bustee enstatite achondrite consists predominantly of enstatite and diopside with minor amounts of other silicate minerals. Small quantities of metallic nickel-iron, osbornite, troilite, ferroan alabandite and daubreelite are also present. Heideite occurs as rare, discrete, anhedral grains at the grain boundaries of silicate minerals. Grains range in diameter up to $100\mu\text{m}$, but most are of the order of $40\mu\text{m}$ in diameter. Heideite is nowhere in contact with any other opaque mineral in the sections examined.

The Bustee meteorite contains several Ti and Fe-bearing minerals while these are not in contact with each other. This may be used for estimates of gas fugacities equilibrated with these minerals. These estimates are derived from the analysis of phase relations in the Ti-Fe-S-N-O system. Though oxides of Ti and Fe are not found in Bustee, the minerals, i.e. ilmenite and rutile are observed in other meteoritic types [2]. To carry out this investigation we determined the thermodynamic properties of synthetic FeTi_2S_4 .

Synthetic FeTi_2S_4 is a powder with the grain size of $50-100\mu\text{m}$. The phase was prepared by dry synthesis at 850°C from elements in evacuated silica tubes. X-ray analysis was used for identification of synthetic FeTi_2S_4 . Impurities in synthetic FeTi_2S_4 were determined by semiquantitative spectral analysis: $\text{Ni} < n \times 10^0$ ppm, $\text{Mn}, \text{Cu}, \text{Zn}, \text{Mg}, \text{Si}, \text{Al}, \text{Cr}, \text{Ca} < n \times 10$ ppm.

Using the adiabatic calorimeter the low temperature heat capacity of synthetic FeTi_2S_4 was measured over the $4.75-345\text{K}$ temperature range. Heat capacity curve has 2 anomalous region. One region is observed over the $90-155\text{K}$ temperature range. This anomaly corresponds to magnetic transition [3]. Its energetic characteristics are: $T_{\text{max}} = 135 \pm 2\text{K}$, $\Delta S_{135} = 1.4 \pm 0.1 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $\Delta H_{135} = 170 \pm 10 \text{J} \cdot \text{mol}^{-1}$. The second anomaly is observed over the $2-14\text{K}$ temperature range. It has a complex configuration. The λ -form peaks are observed at the beginning and at the end of anomalous region. Maximums of peaks correspond to 8.3K and 12.8K . Its energetic characteristics are: $\Delta S_{8.3} = 0.41 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $\Delta H_{8.3} = 2.29 \text{J} \cdot \text{mol}^{-1}$, $\Delta S_{12.8} = 0.05 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $\Delta H_{12.8} = 0.73 \text{J} \cdot \text{mol}^{-1}$. The standard thermodynamic properties at 298.15K are: $C_{p,298} = 208.62 \pm 0.12 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $S_{298} = 226.97 \pm 0.40 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $H_{298} - H_0^0 = 35890 \pm 30 \text{J} \cdot \text{mol}^{-1}$. The coefficients of Maier-Kelley equation were computed by least squares analysis using heat capacity data over the $250-345\text{K}$ temperature range: $C = 68.68 + 453.99 \times 10^3 T - 3.998 \times 10^5 T^2$.

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The reaction $\text{FeTi}_2\text{S}_4(\text{s}) + 4\text{Zn}(\text{s}) = 4\text{ZnS}(\text{s}) + \text{Fe}(\text{s}) + 2\text{Ti}(\text{s})$ (1) was chosen for determination of the standard enthalpy of heideite formation. This reaction proceeds completely at ca 1000C in evacuated (10^{-4} torr) silica tubes during 5-6 minutes. According to X-ray analysis the products of the reaction are: β -ZnS (wurtzite) and metallic Fe and Ti. The calorimetric investigation of the possibility of the reaction between Fe and Ti ($\text{Fe} + 2\text{Ti}$) under conditions similar to those for the reaction (1) was also carried out. According to X-ray analysis and due to the absence of thermal effect the initial state of the mixture remains unchanged throughout the experiment. Using a vacuum-bloc calorimeter [4] the heat of the reaction (1) was measured. The inner space of calorimetric bomb is filled with argon ($P \approx 30$ atm). During the experiment the thermostat temperature was 25.00 ± 0.01 C. The completeness of the reaction is tested by reheating of tubes. No additional thermal effect is observed. The enthalpy change of the reaction (1) is -112.7 ± 3.8 kJ \times mol $^{-1}$. This value and the standard formation enthalpy of wurtzite [5] was used for the calculation of the standard formation enthalpy of heideite. $\Delta H_f^{\circ 298}(\text{FeTi}_2\text{S}_4)$ is -666.7 ± 3.8 kJ \times mol $^{-1}$.

Thermodynamic properties of FeTi_2S_4 and other meteoritic minerals [6, 7] were used for estimation of heideite origin conditions. The analysis of phase relations in the Ti-Fe-S-N-O system was made. The sulfur fugacities were calculated from the Fe-FeS buffer. The results are shown in Fig. 1. As seen Fig. 1, the heideite

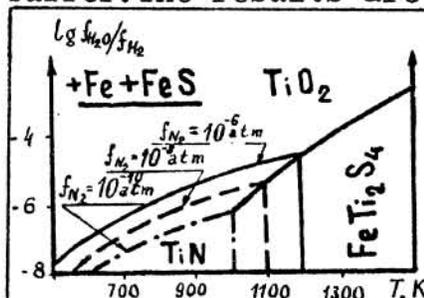


Fig. 1. The phase relations in the Ti-Fe-S-N-O system.

formation is promoted by high temperatures and low nitrogen fugacities. Here the equilibrium temperature of osbornite-heideite assemblage is reciprocal in respect to nitrogen fugacity value. Taking into consideration the breccia structure of Bustee and discrete grains at the grain boundaries of silicates we may suggest that heideite and osbornite were formed at a different time. Furthermore, they resulted from different formation process. If so, Bustee in its further evolution process was not heated to temperatures higher than the osbornite decomposition temperature and

did not contact with the gases of relatively high nitrogen fugacities (Fig. 1).

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