

The following table gives the values of the widths of the phosphides ( $2\xi$ ) for different nucleating temperatures and cooling rates.

Table 3. Phosphide widths

| Nucleating Temp. |           | Time to cool from 750°C to 350°C       |                             |               |                             |               |                             |               |
|------------------|-----------|--|-----------------------------|---------------|-----------------------------|---------------|-----------------------------|---------------|
|                  |           | $D_{\alpha}$<br>(cm <sup>2</sup> /sec) | 10 <sup>6</sup> years       |               | 10 <sup>7</sup> years       |               | 10 <sup>8</sup> years       |               |
| $T_0$ (°C)       | $2\gamma$ |  | $t_{\text{equiv}}$<br>(sec) | $2\xi$<br>(μ) | $t_{\text{equiv}}$<br>(sec) | $2\xi$<br>(μ) | $t_{\text{equiv}}$<br>(sec) | $2\xi$<br>(μ) |
| 700              | 0.0208    | $1.0 \times 10^{-13}$                  | $2.53 \times 10^{14}$       | 2116          | $2.53 \times 10^{13}$       | 670           | $2.53 \times 10^{12}$       | 212           |
| 650              | 0.0244    | $0.2 \times 10^{-13}$                  | $2.29 \times 10^{14}$       | 1052          | $2.29 \times 10^{13}$       | 332           | $2.29 \times 10^{12}$       | 106           |
| 600              | 0.0228    | $0.3 \times 10^{-14}$                  | $2.04 \times 10^{13}$       | 356           | $2.04 \times 10^{13}$       | 116           | $2.04 \times 10^{12}$       | 36            |
| 550              | 0.0248    | $0.4 \times 10^{-15}$                  | $1.82 \times 10^{14}$       | 134           | $1.82 \times 10^{13}$       | 42            | $1.82 \times 10^{12}$       | 13            |
| 500              | 0.0266    | $0.5 \times 10^{-16}$                  | $1.60 \times 10^{14}$       | 48            | $1.60 \times 10^{13}$       | 15            | $1.60 \times 10^{12}$       | 4.8           |
| 450              | 0.0312    | $0.4 \times 10^{-17}$                  | $1.40 \times 10^{14}$       | 14            | $1.40 \times 10^{13}$       | 4.4           | $1.40 \times 10^{12}$       | 1.4           |
| 400              | 0.0312    | $0.15 \times 10^{-18}$                 | $1.21 \times 10^{14}$       | 2.6           | $1.21 \times 10^{13}$       | 0.8           | $1.21 \times 10^{12}$       | 0.2           |
| 350              | 0.0350    | $0.5 \times 10^{-20}$                  | $1.03 \times 10^{14}$       | 0.6           | $1.03 \times 10^{13}$       | 0.2           | $1.03 \times 10^{12}$       | 0.06          |

The above table shows that schreibersite precipitates the size of those in Fig. 4 ( $500 \mu$ ) must have nucleated between  $650$  and  $700^{\circ}\text{C}$  in order to grow to such a size. The phosphides of a size about  $100 \mu$  in width precipitated between  $550$  and  $600^{\circ}\text{C}$  and the rhabdite particles nucleated between  $450$  and  $500^{\circ}\text{C}$ . These nucleation temperatures are in agreement with the values given by VOGEL and the binary phase diagrams as discussed before. The time that it takes to cool between  $750$  and  $350^{\circ}\text{C}$  fall in the range between  $10^7$  and  $10^8$  years. These times are in agreement with estimates (MASSALSKI and PARK, 1961) for the total time taken for the formation of the Widmanstätten pattern (under conditions of equilibrium and without large pressures), which may be taken to be approximately  $10^7$  years for a  $200 \text{ km}$  radius metallic body and  $10^8$  years for a  $200 \text{ km}$  radius silicate body having a small metallic core.

The non equilibrium composition of the phosphides is due to the reduced flux of Ni into the precipitate at temperatures below  $T_0$ . The composition gradient,  $(\partial C/\partial X)_{x>\xi}$  is decreased greatly as the temperature decreases, and at a lower temperature is inadequate to maintain the growth of the phosphide. Since the phosphide can no longer grow, it retains the high temperature Ni concentration throughout the rest of the cooling period. The phosphide probably stops growing about  $50$  to  $100^{\circ}$  below  $T_0$ . In this temperature range most of the phosphide growth occurs which can be seen from Table 3. Since the Ni content of the phosphide increases with decreasing nucleation temperatures, the rhabdite particles which nucleated below  $500^{\circ}\text{C}$  have the highest Ni contents and the schreibersite particles which nucleated at more than  $650^{\circ}\text{C}$  have the lowest Ni contents. Since the rhabdite particles nucleated at the lowest temperatures, they have the shortest time to grow and therefore the smallest size.

In several meteorites massive schreibersite particles, which have a width greater than  $100 \mu$ , have been found. The phosphorus content of meteorites containing such particles is probably grossly underestimated. This is because most of the phosphorus is segregated in the massive phosphides, which makes it difficult to

obtain an accurate average phosphorus content for the meteorite. The solubility limit of phosphorus in the solid state will be exceeded at high temperatures and the phosphide will nucleate in the taenite phase or possibly the phosphide may form directly from the melt. Even in meteorites where massive schreibersite forms, the phosphorus solubility limit continues to decrease as cooling proceeds and at lower temperatures other phosphides will precipitate in the kamacite phases of the Widmanstätten pattern as described above.

The binary phase diagrams, Fe-S and Ni-S show a sulfur solubility in  $\delta$  iron of 0.18 wt. %, but a solubility of only 0.005 wt. % in nickel (METALS HANDBOOK, 1948). Since the  $\delta$  phase does not form when the Ni content is over 4.5 wt. %, sulfur has very limited solubility in meteorites. As the meteorite cools sulfur in excess of the solubility limit remains in the liquid state until the eutectic temperature at about 985°C. As this temperature a eutectic structure of FeS and  $\gamma$ (Fe, Ni) forms which is in equilibrium with  $\gamma$ (Fe-Ni). Nickel is soluble in the liquid phase, but not in eutectic FeS. The very large sulfide particles found in meteorites are formed in this manner which is in agreement with previous studies (HENDERSON and PERRY, 1958; VOGEL, 1958).

The solubility of sulfur in  $\gamma$ (Fe, Ni) decreases as the meteorite cools below the eutectic temperature. Sulfides are then precipitated in the solid state from the supersaturated  $\gamma$  phase and at lower temperatures from the  $\alpha$  phase. The sulfur solubility in the Grant and Breece meteorites as measured with the electron probe is 0.02 wt. % in kamacite and 0.005 wt. % in taenite. Examples of sulfides which form in the solid state are the Reichenbach lamellae and troilite particles which are of the same general sizes as the phosphides.

The diffusion of sulfur in Fe is much faster than the diffusion of Fe in kamacite;  $D(S, Fe) = (4.8 \times 10^{-6}) \exp(-23,400/RT)$  (BARRER, 1951) versus  $D(Fe, \alpha) = 2.0 \exp(-60,000/RT)$  (BUFFINGTON *et al.* 1961). Therefore the growth of the precipitate in the solid state is controlled by the diffusion of Fe from the sulfide. Both Fe and Ni are rejected from the growing sulfide and since a larger amount of Fe is rejected from the volume occupied by the troilite particle, a build up of Fe in the kamacite immediately surrounding the interface between kamacite and troilite occurs. The area would then contain a depleted zone of nickel. The sulfide shown in Fig. 5 probably nucleated at about 700°C and grew almost to its full size before the phosphide nucleated at its boundaries at about 550°C.

## VI. CONCLUSIONS

It is apparent that schreibersite and rhabdite found in kamacite formed by solid state precipitation. At about 100°C below their nucleation temperature, the phosphides stop growing due to the large depletion of Ni in the region surrounding the precipitate and they retain their high temperature composition during further cooling. The time necessary for the growth of the phosphides is also in agreement with the calculations of MASSALSKI and PARK (1961) for the time of formation of the Widmanstätten patterns in octahedrites. The massive sulfides formed directly from the melt. However, troilite inclusions of smaller sizes formed by solid state precipitation and grew by forming an iron rich region (swathing kamacite) around the sulfide.