A major revision of iron meteorite cooling rates—An experimental study of the growth of the Widmanstätten pattern

C. NARAYAN and J. I. GOLDSTEIN
Department of Metallurgy and Materials Engineering, Lehigh University, Bethlehem, PA 18015

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Abstract—In this study kamacite was experimentally grown in taenite grains of Fe-Ni-P alloys containing between 5 and 10 wt% Ni and 0 and 1.0 wt% P. Both isothermal heat treatments and non-isothermal heat treatments at cooling rates of 2 to 5°C/day were carried out. Analytical electron microscopy was used to examine the orientation and chemical composition of the kamacite and the surrounding taenite matrix. The kamacite so produced is spindle or rod shaped and has a Widmanstätten pattern orientation.

The presence of heterogeneous sites such as phosphides is necessary for the nucleation of the intergranular kamacite. During kamacite growth both Ni and P partition between kamacite and taenite with chemical equilibrium at the two phase interface. The growth kinetics are limited by the diffusion of Ni in taenite. Additional diffusion experiments showed that the volume diffusion coefficient of Ni in taenite is raised by a factor of 10 at 750°C in the presence of only 0.15 wt% P.

A numerical model to simulate the growth of kamacite in Fe-Ni-P alloys, based on our experimental results, was developed and applied to estimate the cooling rates of the iron meteorites. The cooling rates predicted by the new model are two orders of magnitude greater than those of previous studies. For example the cooling rates of chemical groups I, IIIAB and IVA are 400–4000°C/10⁶ years, 150–1400°C/10⁶ years and 750–6000°C/10⁶ years respectively. Previous models gave 1–4°C/10⁶ years, 1–10°C/10⁶ years and 3–20°C/10⁶ years. Such fast cooling rates can be interpreted to indicate that meteorite parent bodies need only be a few kilometers in diameter or that iron meteorites can be formed near the surface of larger asteroidal bodies.

INTRODUCTION

The Widmanstätten pattern in iron meteorites is composed of a two phase aggregate of kamacite (α, bcc) and taenite (γ, fcc) that bears a specific crystallographic (Kurdjumov-Sachs) orientation relationship. When a meteoritic body cools through the temperature range 800–500°C, kamacite precipitates in a homogeneous taenite matrix and grows to form the observed geometric pattern. Using the experimentally determined bulk compositions, Ni diffusivities and the Fe-Ni equilibrium phase diagram, WOOD (1964) and GOLDSTEIN and OGLIVIE (1965) developed numerical growth models to simulate Widmanstätten precipitation in Fe-Ni binary alloys. They predicted the thermal histories of meteoritic bodies by comparing the predicted Ni concentration profiles and precipitate sizes with the measured values. Recently, a more sophisticated model of kamacite growth, which incorporates the effects of the third element P, was developed (MOREN and GOLDSTEIN, 1979). Although the numerical growth models have become increasingly sophisticated and the available data more precise, the basic assumptions that go into the models have remained the same. Consequently, the cooling rates of specific iron meteorites determined by these models often agree to within a factor of 5 or less.

GOLDSTEIN and DOAN (1972) have grown intragranular Widmanstätten precipitates in Fe-Ni-P alloys in the laboratory. Instrumental limitations prevented a thorough investigation of the nucleation and growth processes. Nevertheless they found that the amount of precipitate growth was larger than that predicted by the numerical models. This result indicated that the presently available iron meteorite cooling rates may be too low. Independent cooling rate estimates based on radiometric dating techniques (WOOD, 1979), and measured Ag isotope ratios (KAISER and WASERBURG, 1983), also suggest that the metallographic cooling rates are too low.

The purpose of this investigation is to experimentally grow intragranular kamacite in Fe-Ni-P alloys containing between 5 and 10 wt% Ni and 0 and 1.0 wt% P and to examine the nucleation and growth process of these precipitates using analytical electron microscopy (AEM) techniques. An additional objective is to develop a numerical model to simulate the growth of intragranular kamacite in Fe-Ni-P alloys based on the experimental studies and to use this model to revise the existing cooling rate estimates of the iron meteorites.

EXPERIMENTAL TECHNIQUE

The Fe-Ni-P alloys containing between 5 and 10 wt% Ni and 0 and 1.0 wt% P were made from pure elements. Iron and nickel with impurity levels in the ppm range were obtained as 5 mm diameter rods from United Mineral Corporation, New York. Phosphorus with a purity of 99%+ was purchased in the form of a red powder from Mallinckrodt Inc. The required amounts of iron and nickel were cut and weighed and placed in a mullite crucible (Coors Porcelain, Colorado). The crucible was positioned within the induction coils of a RF generator and melted in an argon atmosphere. A predetermined amount of P was then added to the molten metal. The alloys were subsequently sealed in evacuated quartz tubes and homogenized at 1150°C for 4 days.
compositions and homogeneity of the alloys were determined by the electron microprobe. The homogeneity criterion developed by Goldstein and Yakowitz (1975) was used to evaluate the compositional uniformity of the alloys. Tables 1 and 2 list the bulk compositions and homogeneity of the experimental alloys.

Both isothermal and non-isothermal experiments were carried out to grow intragranular kamacite precipitates. The isothermal experiments involved heat treating the alloys in vacuum sealed quartz tubes in the single phase taenite field (900-1000°C) followed by a heat treatment at the temperature of interest in the two phase kamacite plus taenite field. The samples were then quenched to room temperature. The continuous cooling experiments involved treating the alloys in vacuum sealed quartz tubes in the taenite field (900-1000°C) followed by slow cooling through the two phase field in a controlled cooling furnace. The temperature range for the slow cooling extended to 150°C below the equilibrium kamacite nucleation temperature. The samples were then quenched to room temperature. Tables 1 and 2 list the thermal histories of the alloys.

Thin foils for electron microscopy were prepared from bulk heat treated bulk samples by electro-discharge machining a cylinder 3 mm in diameter from the sample followed by slicing the cylinder into discs about 500 μm thick with a diamond wafering saw. Each disc was mechanically ground to a thickness of about 75 μm on 600 grit paper before being electrochemically thinned in a jet polisher. The electrolyte was composed of a solution of 150 ml acetic acid, 15 ml perchloric acid and 15 ml glycerol. The polishing was carried out at room temperature under an applied DC potential of 40 volts. The thin foils were stored in a desiccator to prevent surface oxidation.

**NUMERICAL SIMULATION OF THE GROWTH OF INTRAGranULAR WIDMANSTÄTTEN KAMACITE**

**Model**

A model to simulate the bulk diffusion controlled growth of kamacite in a taenite matrix was developed. A numerical method of lines (NMOL) technique was used for the solution of the system of partial differential equations (Schüssler, 1976). The NMOL technique and the Murray-Landes (1959) variable grid spacing transformation were combined to solve the problem of diffusional growth of kamacite. The numerical model calculates the growth of kamacite in the ternary system Fe-Ni-P during continuous cooling and generates the concentration profiles of Ni and P in the kamacite and taenite phases as a function of temperature and time. The simulation was carried out on a CYBER 720 computer. The computation was based on the following assumptions:

1. The growth of kamacite is controlled by bulk diffusion of Ni in taenite.
2. Interfacial equilibrium of Ni and P occurs at the kamacite/taenite interface at all times during the growth process.
3. Kamacite nucleates and grows as a cylindrical precipitate.
4. There is no P gradient in either phase and no Ni gradient in kamacite.
5. No impingement of Ni diffusion gradients occurs between kamacite precipitates.

The justification for these assumptions is given in the Discussion section of the paper.

**Mathematical formulation**

The theory of diffusion controlled phase growth in ternary and higher order systems has been well developed in the literature (Coates, 1973; Kirkaldy, 1958a-c; Randich and Goldstein, 1975). Based on Fick's first and second laws, the time dependence of the concentration of Ni, in any phase, and for a cylindrical geometry can be expressed as

\[ \frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D_{Ni} \frac{\partial C}{\partial r} \right) \]  

where \( D_{Ni} \) is the major diffusion coefficient for Ni and \( r \) is the radial distance from the center of the cylindrical precipitate. In the Fe-Ni-P system the effect of a P gradient on the Ni flux is negligible (Heyward and Goldstein, 1973).

For the phase growth problem where a rod of kamacite (\( \alpha \)) is growing in a taenite (\( \gamma \)) matrix there is a discrete change in the concentration of Ni and P at the \( \alpha/\gamma \) interface. The composition at the interface in the two phases is given by the \( \alpha/\gamma \) tie line in the appropriate Fe-Ni-P ternary phase diagram isotherm. The movement of the interface is governed by the flux of Ni and P in both phases and can be expressed by the following pair of equations

\[ \frac{d\xi}{dt} = \left( J_{\alpha} - J_{\gamma} \right) \left( C_{\alpha} - C_{\gamma} \right) \]  

and

\[ \frac{d\eta}{dt} = \left( J_{\alpha} - J_{\gamma} \right) \left( C_{\alpha} - C_{\gamma} \right) \]  

where \( \xi \) is the interface position and the radius of the precipitate, \( C_{\alpha} \) and \( C_{\gamma} \) are the concentrations of Ni and P in kamacite and taenite at the \( \alpha/\gamma \) interface and \( J_{\alpha} \) and \( J_{\gamma} \) are the fluxes of Ni and P in the two phases at the \( \alpha/\gamma \) interface. These equations will be satisfied by an unique tie-line in the two phase \( \alpha + \gamma \) field since the interface velocity for both Ni and P in the above pair of equations must be identical.
Numerical formulation

The numerical formulation of the phase growth problem requires setting up a space-composition grid. For a cylindrical precipitate growing inside a cylindrical matrix of finite dimensions, the space axis consists of discrete increments of radial distance from the center of the precipitate. At time $t=0$, a kamacite nucleus of finite dimensions (usually 0.1 nm) is assumed to be present inside the taenite cylinder. At any intermediate time, $t$, there is an unique composition of Ni(C$_{t_{\text{Ta}}}$) associated with each grid point, $i$, at a radial distance of $r_i$. A schematic representation of a typical profile for a precipitate radius of $r_a$ at any time $t$ is given in Fig. 1. A set of $n$ grid points is set up in the matrix $\gamma$ phase. The first point, $i$, is at the $\alpha/\gamma$ interface and the last point, $n$, is at the end of the finite $\gamma$ matrix field.

The growth of the precipitate is defined by the movement of the interface, the velocity of which depends on the concentration of Ni in $\alpha$ and $\gamma$ at the interface and the Ni gradient in $\gamma$ at the interface. Using Eqn. (2a) and assuming $J_{\text{f1}}$ is equal to zero, the velocity of the interface can be expressed as

$$v = \frac{D_{\text{Ni}}(\partial C_{\text{Ni}}/\partial r)(C_{\text{Ni}} - C_{\text{Ta}})}{C_{\text{Ni}} - C_{\text{Ta}}}$$

(3)

As the precipitate grows, the taenite field shrinks and every grid point moves in the direction of the interface motion. Grid point, $i$, at the $\alpha/\gamma$ interface moves with a velocity, $v$, defined in Eqn. (3). Grid point, $n$, has a velocity equal to zero. Assuming that the velocity decreases linearly with distance from the $\alpha/\gamma$ interface the velocity of any point, $i$, within the matrix can be written as

$$dr_i/dt = v_i = (r_\alpha - r_i)/(r_\alpha - r_n) \cdot v$$

(4)

The time dependence of the Ni concentration at grid point, $i$, is given by

$$\frac{\partial C_i}{\partial t} = \frac{\partial C_i}{\partial r_i} \cdot \frac{dr_i}{dt} + \frac{\partial C_i}{\partial t}$$

(5)

Equation (5) can be evaluated by substituting $dr_i/dt = v_i$ from Eqn. (4) and $\partial C_i/\partial t$ from Eqn. (1).

When the above equation is defined for all grid points $i$ through $n$ the resulting set of $n$ differential equations can be solved numerically to yield the concentration of Ni at each grid point for a given time $t$. The concentration of Ni in $\alpha$ and of P in $\alpha$ and $\gamma$, is determined by the tie-line Ni and P compositions. The numerical approximation used for solving the differential equations as well as further details of the numerical calculation technique are given by Narayan (1983).

Initial and boundary conditions

At time equal to zero, the concentration of Ni at all grid points is set equal to the bulk Ni content of the alloy. Since impingement does not occur, grid point $n$ will remain at the bulk Ni content of the alloy. The concentrations of Ni and P at the $\alpha/\gamma$ interface are defined by the appropriate $\alpha/\gamma$ tie-line at each temperature. The tie-line must also satisfy the flux requirements of Ni and P (see Eqn. (2)). For the slow cooling rates employed in this study the numerical technique chose the equilibrium tie-line (the one that passes through the bulk composition). Moren and Goldstein (1979) found a similar result in their numerical growth model.

Fixed parameters for the simulation program

1. Fe-Ni-P phase diagram. The Fe-Ni-P phase diagram was used in the computer model to establish the equilibrium compositions at the $\alpha/\gamma$ interface as a function of temperature (800—300°C). Figure 2 is a typical isotherm for the Fe-Ni-P system showing the two phase ($\alpha + \gamma$) field with the nomenclature as suggested by Moren and Goldstein (1979). In the three letter codes used in the figure the first letter A or G is for the alpha or the gamma phase. The second letter U or L is for the upper or the lower phase, the lower point being on the Ni axis and the third letter N or P refers to nickel or phosphorus. ANI and APH are the interfacial Ni and P concentrations in the $\alpha$ phase and GNI and GPH are the corresponding concentrations in the $\gamma$ phase. ANI, APH, GNI and GPH together constitute the equilibrium tie-line in the two phase field (Fig. 2).

As shown in Fig. 2 the two phase ($\alpha + \gamma$) field can be defined in any isotherm by the following eight variables: ALN, AUN, GLN, GUN, ALP, AUP, GLP and GUP. Fe-Ni and Fe-Ni-P phase diagrams in the temperature range 700° to 300°C have been experimentally determined by Romig and Goldstein (1980). Equations for ALN, AUN, GLN and GUN were developed by Romig and Goldstein (1981) using a least squares polynomial fit through the experimental data points.

In the temperature range, 800°—700°C, a straight line fit was used between the data of Doan and Goldstein (1970) at 750°C and the data of Romig and Goldstein (1981) at 700°C. The concentrations of Ni in wt% as a function of temperature (°C) are given below:

$$\begin{align*}
ALN &= 3.00 + 1.24 \times (750 - T)/50 \\
AUN &= 4.47 + 0.27 \times (700 - T)/50 \\
GLN &= 6.40 + 4.10 \times (750 - T)/50 \\
GUN &= 9.22 + 1.62 \times (700 - T)/50 
\end{align*}$$

(6)

2. Ni inter-diffusion coefficient. The inter-diffusion coefficient of Ni ($D_{\text{Ni}}$) in taenite in Fe-Ni-P alloys controls the growth of kamacite (see Eqn. 1). Moren and Goldstein (1979) developed an empirical relationship for the effect of P on $D_{\text{Ni}}$ based on the binary data of Goldstein et al. (1965) and the high temperature data of Heyward and Goldstein (1973) for P saturated $\gamma$ Fe-Ni, namely

$$D_{\text{Ni}} = (1 + 9.3 \cdot C_p^{0.15}) \cdot (7400 - 11.6 \cdot C_p^2/R)$$

(7)

where $C_p$ and $C_p$ are the P and Ni concentrations (wt%) in taenite, $R$ is the gas constant and $T$ is the temperature (K).
At low temperatures where the solubility of P in taenite is considerably reduced, this expression underestimates $D_{Ni}$. In a separate study (Narayan and Goldstein, 1983a), $D_{Ni}$ was measured at low temperatures ($\leq 800°C$) in the presence of small amounts of P ($\sim 0.15$ wt%). In this temperature range the diffusivity of Ni ($D_{Ni}$) is enhanced by a factor of 10 over that given in Eqn. (7). These $D_{Ni}$ values were used in the computer model.

**Variable parameters for the simulation program**

The independent variables are:

1. Bulk concentrations of Ni and P: Compositions of the experimental alloys or iron meteorites under investigation.
2. Cooling rate: Measured cooling rates of the experimental alloys or the assumed cooling rates of specific iron meteorites.
3. Equilibrium kamacite nucleation temperature: Determined by the simulation program from the bulk composition of the experimental alloys or iron meteorites and the Fe-Ni-P ternary phase diagram.
4. Initial kamacite nucleus radius: Assumed non-zero radius (0.1 nm) of kamacite in the first step of the numerical iterations.
5. Radius of the finite taenite field: Size of the diffusion field chosen so that no impingement of diffusion fields from adjacent precipitates occurs.
6. Total time for kamacite growth: Determined by the cooling rate and the final growth temperature.

**RESULTS**

**Experimental alloys**

Kamacite nucleates and grows as needle-shaped crystals inside taenite grains. Figure 3 is a SEM micrograph showing kamacite needles in alloy N8 containing 5.9% Ni and 0.57% P that was step cooled to 700°C. Both longitudinal and transverse sections of kamacite are visible in the micrograph. The precipitates are essentially cylindrical in shape with pointed ends and faceted cross-sections. This kamacite morphology was typical for all the alloys in which intragranular precipitation occurred.

Only some of the alloys exhibited intragranular kamacite precipitates whereas grain boundary kamacite was present in almost all the alloys. Tables 1 and 2 describe the microstructures in the isothermally heat treated and continuously cooled samples, respectively. Figure 4 is a light micrograph showing the intragranular kamacite precipitates in alloy N4. Grain boundary kamacite is also present. Figure 5 is a TEM micrograph showing needle-shaped intragranular kamacite precipitates in an alloy containing 5.9% Ni and 0.5% P that was step cooled to 700°C. Both longitudinal and transverse sections of the kamacite precipitates are visible.
or along grain boundaries in P free alloys. Intragranular kamagate bears a Kurdjumov-Sachs orientation relationship with the taenite as determined by NARAYAN and GOLDSTEIN (1983b) using electron diffraction techniques.

Two experiments were designed to assess the necessity for undercooling to nucleate kamagate inside austenite grains. In one experiment, alloy 15 containing 8.03% Ni and 0.75% P was austenitized in the taenite field and isothermally held at 25°C below the equilibrium nucleation temperature for 22 days, and quenched to room temperature. In the second experiment, alloy N5 containing 7.24% Ni and 0.75% P was austenitized in the single phase field as before and slow cooled from its equilibrium kamagate nucleation temperature to 40°C below that temperature at a rate of 2°C/day, and then quenched to room temperature. Kamagate crystals were observed inside taenite grains in both samples. Therefore little undercooling is necessary for the nucleation of kamagate.

Intragranular kamagate precipitates were observed in alloys 15, N2, N3, N4, N5, N6 and N8 (Tables 1 and 2). In most of these alloys, concentration profiles were measured across kamagate/taenite interfaces using the AEM. Wherever possible, two independent profiles were measured and superimposed. Figure 6a–d shows Ni profiles that were measured in alloys N8, N4, 15 and N5. The error bars are calculated on a ±3 σ basis, where σ, the standard deviation, is the square root of the total number of X-ray counts detected at an analysis point. Figure 7 shows a typical P concentration profile that was measured across a kamagate/taenite interface in alloy N6. No measurable P gradients are present in either phase. Interfacial α/γ equilibrium was confirmed for the experimental alloys.
Computer models

Computer calculations indicate that rod- or cylindrical-shaped kamacite thickens at a faster rate than plates. Figure 8 shows the calculated growth of a kamacite rod and a kamacite plate in an Fe-6.0% Ni-0.3% P alloy. The radius of the rod and the half width of the plate are plotted as a function of temperature when the alloy is slow cooled at 5°C/day from the equilibrium kamacite nucleation temperature of 773°C. The final size of the rod is 1.7 times that of the plate and is independent of the cooling rate and composition.

Figure 9 shows the calculated radius of kamacite rods as a function of Ni content in alloys containing 0.3 wt% P and cooled at 5°C/day. The precipitate size decreases by almost two orders of magnitude when the Ni content increases from 6 to 14 wt%. The effect of P on the precipitate size is not large. Kamacite radius increases by less than 25% when the P content increases from 0.1% to 0.3 wt%. Beyond 0.3 wt% P the growth kinetics are not affected because P exceeds the solubility limit in taenite.

Applicability of the computer simulation technique

The results of the experimental Fe-Ni-P alloy heat treatments show that kamacite will nucleate with little or no undercooling in taenite with a Widmanstätten pattern morphology. The kamacite precipitates grow with a cylindrical-rod like shape. No Ni gradient was observed in kamacite and no P gradient was observed in either phase. The presence of a Ni gradient in taenite indicates that the growth of kamacite is controlled by the diffusivity of Ni in taenite, $D_Ni$. In addition the measurement of equilibrium Ni and P contents at the $\alpha/\gamma$ interface of the kamacite precipitates indicates that local equilibrium occurs at the $\alpha/\gamma$ interface during the growth process. These experimental results justify the assumptions as described earlier in the paper for the computer simulation technique.

The computer model was applied to alloys N8, N4, 15 and 55 using the bulk compositions of the alloys and the actual cooling rates measured in the laboratory. Figure 6 shows the excellent agreement of the calculated Ni profiles with the measured data.
from the AEM. In summary the computer model accurately simulates the actual experimental results. This computer model should be applicable to study the cooling history of the iron meteorites.

The inter-diffusion coefficient $D_{Ni}$ used in this study was 10 times the value used in previous studies (MOREN and GOLDSTEIN, 1979). Figure 10 gives a comparison between a measured concentration profile and three calculated profiles using a $D_{Ni}$ value 1, 10 and 15 times the value of $D_{Ni}$ given by MOREN and GOLDSTEIN (1979), Eqn. (7). A factor of 10 increase is clearly necessary to obtain good agreement between the measured and calculated Ni diffusion profile. The increased value of $D_{Ni}$ helps to explain why GOLDSTEIN and DOAN (1972) observed larger kamacite precipitates than were predicted by the currently available numerical growth models.

**Applicability of the experimental alloy results to iron meteorites**

Figure 6a–d shows measured Ni profiles where the concentration of Ni decreases to the bulk composition in the matrix. This result indicates that there is no impingement of diffusion fields from adjacent precipitates. A similar situation is observed in meteorites containing more than 15 wt% Ni where the kamacite nucleation temperatures are below 600°C and the Widmanstätten pattern is not well developed. Chinga, Hoba, Trazewell, Wedderburn and San Cristobal are some of the meteorites that fall into this category (BUCHWALD, 1975). These meteorites also have spindle shaped kamacite crystals much like those seen in this study. Meteorites containing less than 15 wt% Ni and more than 6 wt% Ni, on the other hand, normally have a well developed Widmanstätten structure. The kamacite crystals are no longer spindle shaped but exhibit a lath or plate morphology. In these meteorites kamacite accounts for a large volume fraction of the microstructure and the diffusion fields from neighboring crystals overlap considerably.

The experimental results of this study suggest that the intragranular kamacite precipitates are spindle or rod-shaped during their early stages of growth. However when the volume fraction of the precipitate increases and the impingement of diffusion fields from adjacent precipitates becomes significant, the precipitates probably take on a lath or plate shape. When the Ni gradients from adjacent precipitates overlap, the radial growth of these precipitates in

![FIG. 9. The radius of intragranular kamacite rods are plotted against the Ni content in alloys containing 0.3 wt% P. The alloys are cooled from the kamacite nucleation temperature at a rate of 5°C/day. The corresponding half widths of planar precipitates are also indicated.](image)

![FIG. 10. The measured Ni concentration profile across an α/γ interface is compared to Ni concentration profiles predicted by a model using different diffusivities.](image)
those directions is severely inhibited and the precipitates begin to widen preferentially along direction where there is no impingement of diffusion fields. This non-uniform change in the transverse dimensions of the precipitate is probably responsible for the shape change from rod to ath during later stages of growth.

In Fe-Ni-P alloys containing up to 20 wt% Ni and up to 2 wt% P there are two possible sequences for the precipitation of intragranular kamacite.

a. $\gamma \rightarrow \alpha + \gamma$, where kamacite precipitates homogeneously in the taenite matrix when the alloy cools from the single phase field into the two phase $\alpha + \gamma$ field.

b. $\gamma \rightarrow \gamma + \text{Ph} \rightarrow \alpha + \gamma + \text{Ph}$ (Ph stands for phosphide), where on cooling from the single phase $\gamma$ field the alloy enters the two phase $\gamma + \text{Ph}$ field. In this 2 phase region, the excess P precipitates out as phosphides on further cooling into the three phase $\alpha + \gamma + \text{Ph}$ field. Kamacite precipitates inside $\gamma$ grains.

Therefore, depending on the composition of the alloy, kamacite can nucleate either in a two phase or a three phase field. When kamacite nucleates in the three phase field it is always preceded by the precipitation of phosphides. Figure 11 shows four iso-nickel concentration sections from the Fe-Ni-P phase diagram, constructed from the data of Romig and Goldstein (1980) and Doan and Goldstein (1970). On these isopleths are plotted the compositions and heat treatments of the experimental alloys. The continuously cooled and the step cooled alloys are indicated by lines joining two circles representing the initial and final temperatures of the heat treatments. Isothermally treated samples are indicated by circles drawn at the temperature of heat treatment. The expected precipitation sequence in these alloys can be seen. The alloys indicated with filled circles represent those alloys in which intragranular kamacite precipitates were observed and those drawn with open circles refer to alloys that did not have intragranular kamacite. All the alloys had grain boundary kamacite with the exception of alloy N7, a P free alloy, which did not have any ferrite at all. Alloys N8, N4, N5, N2, 15 and N3 containing intragranular kamacite precipitates have heat treatments that start either in the two phase $\gamma + \text{Ph}$ field or in the three phase $\alpha + \gamma + \text{Ph}$ field. The three phase field is approached through the $\gamma + \text{Ph}$ field during slow cooling from the austenitizing temperature as indicated by the arrows. The nucleation of kamacite inside the grains, in these alloys, is preceded by the precipitation of phosphides. Alloys N1, N9, N7, 11, 12, 13 and 14, on the other hand, have heat treatments that go from the austenite field into the two phase $\alpha + \gamma$ field. The absence of intragranular kamacite in these alloys indicates that the reaction sequence $\gamma \rightarrow \alpha + \gamma$ is not effective for the nucleation of intragranular ferrite. That phosphides help nucleate intragranular kamacite is also suggested by Fig. 3 where several intragranular kamacite crystals are associated with phosphides.

Alloy N6, plotted on the 6% Ni isopleth, did exhibit a few intragranular kamacite precipitates although its heat treatment was $\gamma \rightarrow \alpha + \gamma$. As alloy N6 cooled through the $\alpha + \gamma$ field, the grain interiors were all single phase $\gamma$ and remained in this non-equilibrium condition, during cooling. When P reached its solubility limit in $\gamma$ FeNi, phosphides begin to precipitate. For alloy N6 phosphides precipitate at 705°C and act as centers for the nucleation of intragranular kamacite. Therefore if an Fe-Ni-P alloy contains relatively small amounts of P, intragranular kamacite crystals will not nucleate until the temperature has dropped to a point where P can no longer remain in solid solution and is rejected from the matrix as phosphides. Kamacite will then nucleate on these second phase particles. The precipitation of intragranular kamacite in Fe-Ni-P alloys is therefore always preceded by the exsolution of phosphides.

The uniform Widmanstätten structure in iron meteorites suggests that the heterogeneities that served to nucleate kamacite were evenly distributed throughout the entire matrix. Many meteorites contain sulfur and carbon in addition to P and it is possible that sulfides and carbides can also act as sites for nucleation of intragranular kamacite.

The nucleation sequence of intragranular kamacite in the different meteorite chemical groups can be studied using a P solubility curve such as the one in

Fig. 11. Iso-Ni concentration sections from the Fe-Ni-P phase diagram showing the heat treatments used for the alloys investigated.
FIG. 12. The solubility of P in γ taenite as a function of temperature.

Fig. 12. In this figure the maximum solubility of P in γ FeNi is plotted as a function of temperature. The precipitation sequence in a meteorite can be understood by plotting a meteorite kamacite nucleation temperature and P content on this figure. The Ni and P content of the meteorite along with the equilibrium Fe-Ni-P phase diagram will determine the equilibrium kamacite nucleation temperature for that meteorite. Four points representing meteorites 1 through 4 are plotted as examples in Fig. 12. Meteorite 1 lies to the right of the solubility line and kamacite will nucleate on preexisting phosphides in this meteorite at the equilibrium kamacite nucleation temperature. Meteorites 2, 3 and 4 have lower P contents and kamacite will not nucleate in these meteorites until the meteorite has cooled to a temperature below the P solubility curve. The extent of the amount of cooling needed for kamacite nucleation will depend on the position of the equilibrium kamacite nucleation temperature relative to the solubility curve in Fig. 12.

If these 4 meteorites belong to one iron meteorite chemical group they can be represented by a line drawn through the points. Each chemical group can therefore be represented on this plot by a line that encompasses the members of the group. Such a representation is seen in Fig. 13 for the chemical groups of the iron meteorites. The circles on the lines refer to the average P contents of the chemical groups using available meteorite compositions (BUCHWALD, 1975). Most meteorites in groups IIB and IVB and all meteorites in groups IIC, IID, IIIB, IIC and IIID lie on or to the right of the P solubility curve. In these meteorites phosphides will be present before the meteorite cools to the equilibrium kamacite nucleation temperature. Intragranular kamacite can therefore nucleate without any undercooling.

CLARKE and GOLDSTEIN (1978) estimated the P contents of a few group IA members and concluded that the P contents were as much as 4 times greater than the previous estimates. These revised P estimates would put most group IA meteorites to the right of the P solubility curve. Most group IIIA and IVA members, however, lie to the left of the P solubility curve and intragranular kamacite nucleation, via phosphides, requires undercooling. The extent of the undercooling depends on the composition of the meteorite, as seen earlier in this section. Since P and Ni contents are directly related in groups IIIA and IVA (SCOTT, 1972), meteorites having lower Ni contents will also have lower P contents. These meteorites will require a greater undercooling for nucleation of intragranular kamacite. The amount of undercooling required to nucleate phosphide and subsequently intragranular kamacite in a meteorite will influence the estimates of cooling rates for that meteorite.

New cooling rates for the iron meteorites—Application of the computer model

Given a starting meteorite composition and a cooling rate, the computer model can predict the final size of the kamacite phase. Using the model, a band width vs. Ni plot similar to that developed by SHORT and GOLDSTEIN (1967) was constructed to facilitate the predictions of cooling rates of meteorites. The curves were constructed assuming no undercooling, that is the kamacite nucleation temperature is determined by the composition of the meteorite and the Fe-Ni-P phase diagram. Since over 90% of the kamacite growth occurs within 100°C of the nucleation temperature, the morphology change from rod-shaped to plate-shaped crystals, which occurs at low growth temperatures, does not affect the applicability of the cooling rate curves.

FIG. 13. The average compositions of meteorite chemical groups are superimposed on a P solubility curve.
The calculated band width vs. Ni plot is shown in Fig. 14. Based on the observed widths of the Widmanstätten precipitates in different meteorite chemical groups (BUCHWALD, 1975), cooling rate regions which outline the groups were drawn over the cooling rate curves. Each balloon shaped region encompasses the iron meteorites of the chemical group it represents. Since the assumption of no undercooling for kamacite nucleation is justified for groups IA, IIB, IIC, IID, IIB, IIIC, IIID and IVB, the cooling rates encompassed by these groups in Fig. 14 are correct estimates. For groups IVA and IIIA, however, some cooling below the equilibrium kamacite nucleation temperatures is necessary to nucleate kamacite because of the low P levels. The cooling rates for meteorites in these groups would be lower than those predicted by Fig. 14 because kamacite nucleates at lower temperatures and the meteorite would therefore require longer times to grow kamacite crystals of the observed sizes. The undercooling required to nucleate intragranular kamacite in low Ni (low P) members of group IVA is about 200°C and the undercooing for the high Ni (high P) members is about 50°C. Using the new nucleation temperatures in the growth model, the cooling rates for the low Ni members of IVA will decrease by a factor of 8.6 and that for the high Ni members of IVA will decrease by a factor of 1.5. Similarly for group IIIA, the undercooling required for the low Ni members is about 150°C for which the cooling rate will reduce by a factor of 5.3 and no undercooling is necessary for the high Ni (high P) members which means that the cooling rate for these meteorites will remain unchanged. The revised cooling rates for groups IIIA and IVA are shown in Fig. 15 together with the other chemical groups.

Overlapping diffusion fields from neighboring kamacite crystals are observed in meteorites with bulk Ni contents less than 15 wt% Ni. Computer simulations of the effect of overlapping diffusion fields in the taenite phase, which contain ≤20 wt% in the center of the taenite field after the cooling process is complete, show that the final size of the kamacite phase is within 10% of that predicted when no impingement effects are observed. In general the Ni build up in the taenite region between two kamacite crystals is not large (less than 20 wt% Ni in the center of the taenite region) unless 1) the kamacite crystals formed after a significant amount of undercooling or 2) the bulk Ni content of the meteorite is equal to or less than about 7 wt%.

The observed widths of the Widmanstätten precipitates in different meteorite chemical groups (BUCHWALD, 1975) used in this study were measured by selecting the largest kamacite precipitates in each meteorite. Presumably these kamacite bands nucleated
with the smallest amount of undercooling. Group IIB irons and the lower Ni portion of the IA irons have bulk Ni contents less than or equal to 7 wt% Ni. These meteorites might have had larger Widmanstätten precipitate widths if significant impingement had not occurred. In addition these meteorites could have cooled at slower cooling where the effect of impingement does not allow the Widmanstätten precipitate to grow to its full width. Therefore the cooling rates of the IIB irons and the low Ni IA irons may be slower than those given in Fig. 14 where impingement effects are not considered. It may be possible to use measured Ni gradients in the residual taenite of these meteorites to obtain appropriate cooling rates (WOOD, 1964), although practical problems still remain in obtaining appropriate data for such an analysis.

GOLDSTEIN and SHORT (1967), MOREN and GOLDSTEIN (1978, 1979), and WILLIS and WASSON (1978), estimated the cooling rates of a large number of meteorites in several chemical groups. The data reported by different investigators agree to within a factor of five and their combined data are listed in Table 3 under previous models. These data are then compared to the cooling rates predicted by the model developed in this study. The cooling rate ranges for groups IIIA and IVA when undercooling effects are considered are also indicated in the table. The cooling rates estimated in this study are more than two orders of magnitude higher than those previously obtained.

The high cooling rate variations indicated in this study help explain the presence of ratios of $^{107}$Ag/$^{109}$Ag in iron meteorites which are far above the value for normal Ag (KAISER and WASSERBURG, 1983). Such excesses of $^{107}$Ag$^*$ were found in the metal phase of IVB irons (KAISER and WASSERBURG, 1983), IIIAB irons (CHEN and WASSERBURG, 1983) and IVA irons (WASSERBURG and CHEN, 1983). The presence of these excesses, as shown by KAISER and WASSERBURG (1983), call for cooling rates of iron meteorites from the liquidus to $\sim 600^\circ$C of $\geq 100-150^\circ$C/my. It is interesting to note that from the results of this study, Table 3, almost all the iron meteorites have cooling rates which are $\geq 100^\circ$C/my.

The absolute values of the cooling rates obtained in this study are probably in error by up to a factor of 2. This relatively large error is mainly due to the uncertainty in the diffusion rate of Ni in γ-Fe-Ni-P alloys. Only preliminary diffusion data are available (NARAYAN and GOLDSTEIN, 1983a) and experimental Ni concentration gradients can be fit with the computer model using Ni diffusivities which vary up to 50% rd (see Fig. 9). The relative accuracy of cooling rates within a specific chemical group, using the band width vs. Ni plot, are probably no better than a factor of 2. Such a relatively large error is mainly due to the inaccuracies in measuring kamacite band widths and the difficulties in measuring the bulk P content of an iron meteorite. The bulk P contents determine the amount of undercooling, if any, before kamacite nucleation occurs.

The wide variation in trace element concentrations and cooling rates between different meteorite chemical groups led GOLDSTEIN and SHORT (1967) to conclude that each chemical group of meteorites originated from a different parent body. In the same paper the authors also discuss two models for parent bodies. One is the core model where the bodies are assumed to be made up of a metallic core within a silicate shell and the other is a raisin bread model where pieces of metal are believed to be distributed like raisins within a silicate body. It has been argued that the range of cooling rates observed within a chemical group will shed some light on the nature of the parent body (GOLDSTEIN and SHORT, 1967). If the core model is correct then the range of cooling rates within a group will be small because of the high thermal conductivity of the metal. From the discussions of errors above one could use the following framework for classifying cooling rate variations for the chemical groups. For cooling rate variations up to a factor of 4 or 5, one could conservatively consider all the meteorites as having very similar cooling rates—core model. Groups IIIC, IID, IIIA, IIIB, IIIIC, IIDD fall into this category. For cooling rate variations over a factor of 8 in a chemical group, one could conservatively classify these chemical groups by a raisin bread model where the low thermal conductivity of the silicate phase allows for a wide variation in cooling rates with burial depths. Groups I, IVA and IVB fall into this category. If IIIAB is considered as one contiguous group the cooling rate variation of 150 to 1400°C/10$^6$ years indicates a raisin bread process for its development. Further detailed discussion of whether chemical groups form by a core or raisin bread process will depend on the availability of more accurate Ni diffusivity values.

Based on the previous cooling rate estimates, GOLDSTEIN and SHORT (1967) concluded that the maximum radius of a parent body will be of the order of 300 kms. Since this study predicts cooling rates that are more than two orders of magnitude greater than previous estimates, the maximum parent body sizes need only be on the order of 10 kms. A detailed thermal modeling of bodies less than 20 kms
in radius is necessary to predict parent body sizes from the revised cooling rates.

FRICKER et al. (1970) modeled the thermal characteristics of large parent bodies for cases where the radioactive heat sources were evenly distributed through the body (uniform model) and for instances when the source was concentrated in the outerlayer of the body (fractionated model). From these two extreme cases they concluded that for central cooling rate >7°C/Myrs and for bodies <100 km in radius, the nature of the distribution of the radioactive heat source is not important. Since this study predicts very high cooling rates (>100°C/Myrs) for meteorites and very small parent bodies (<10 km in radius) the distribution of heat sources need not be a parameter in future thermal models.

CONCLUSIONS

AEM techniques were employed to study the growth of intragranular kamacite in Fe-Ni-P alloys containing between 5% and 10% Ni and 0 and 1.0 wt% P. The experimental evidence was used to develop a numerical model to simulate kamacite growth and hence predict cooling rates of meteorites from observed Widmanstätten patterns. The conclusions from this study can be summarized as outlined below.

1. Heterogeneous sites like phosphides are necessary for the nucleation of intragranular kamacite in the Fe-Ni-P system.

2. During early stages of growth the kamacite precipitates are spindle shaped. When diffusion fields from adjacent precipitates overlap there is a morphology change from a rod to a lath.

3. During growth, both Ni and P partition between kamacite and taenite and there is chemical equilibrium at the interface in both phases.

4. Under slow cooling rates employed in this study (about 5°/day) the system selects the equilibrium tie-line during growth.

5. The growth kinetics of kamacite are limited by the diffusion of Ni in taenite.

6. Kamagate size depends to a large extent on the bulk Ni content and the cooling rate and to a lesser extent on the P concentration.

7. The volume diffusion coefficient of Ni is raised by a factor of ten at 750°C in the presence of only 0.15 wt% P.

8. The cooling rates predicted by the new model are two orders of magnitude greater than those previously estimated.

9. To accommodate the revised cooling rates predicted by this model, meteorite parent bodies need only be a few kilometers in diameter.

10. Distribution of radioactive heat sources is not important for modeling parent bodies.

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