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Widmanstätten structure and kamacite-taenite phase distribution in Toluca meteorite

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Abstract Two types of taenite lamellae were observed, i.e. the clear and the heterogeneous taenite, in the Widmanstätten structure in Toluca iron meteorite. Cooling rate for Toluca meteorite was determined using the central Ni content method, for both types of taenite. The Ni concentration within heterogeneous region (plessite) in taenite was approximated to fit the M-shaped distribution shown by the rim and parts of the central portions. The clear taenite lamellae and the heterogeneous taenite yield similar cooling rates of 100～200℃/Ma. Based on this result, it is supposed that the heterogeneous taenite has been originally homogeneous in composition. As the temperature drops below 400℃ (kamacite nucleation closure temperature), the interior of wider taenite transform into plessite. Textural observations indicate that the harp-like taenite structure is always associated with schreibersite (phosphide). The presence of P in Fe-Ni alloy has a pronounced effect on Ni diffusion and the formation of the Widmanstätten structure. The harp-like taenite may have been formed in high-P concentration regions in Fe-Ni alloy.

Key words: taenite, cooling rate, plessite texture, harp-like taenite, schreibersite

Introduction

Iron meteorite and its classification

Iron meteorites mainly consist of Fe-Ni alloy (primarily kamacite and taenite). In addition, they have inclusions, such as Troilite (FeS), Schreibersite ($(Fe,Ni,Co)_3P$) and so on. Some silicate inclusions are present as well. Iron meteorites also contain trace amounts of siderophile elements such as gold (Au), germanium (Ge), and iridium (Ir) and other elements such as gallium (Ga), silver (Ag), copper (Cu) etc.

There are two classification schemes for iron meteorites viz. structural and chemical characteristics (McSween, 1999). The structural classification is based on the Widmanstätten structure. This structure depends on the bulk nickel content. Table 1 gives the structural classification based upon these two indicators: kamacite band width and bulk nickel content. The iron meteorites are divided into eight groups of which six are octahedrite subgroups. The chemical classification uses nickel and trace element concentrations in the meteorites. Elements such as Ga, Ge, and Ir are used in iron meteorite classification. The chemical classification stand on the hypothesis that the meteorites from the same parent body shows same trend on profile of trace element versus nickel content.

Table 1 Structural classification of iron meteorites (Norton, 2002).

Group	Symbol	Band width (mm)	Nickel (wt%)
hexahedrite	H	＞50	4.5-6.5
octahedrites	O		
coarsest	Ogg	3.3-50	6.5-7.2
coarse	Og	1.3-3.3	6.5-7.2
medium	Om	0.5-1.3	7.4-10.3
fine	Of	0.2-0.5	7.8-12.7
finest	Off	＜0.2	7.8-12.7
plessitic	Opl	＜0.2	Kamacite spindles
ataxite	D	no structure	＞16.0

Widmanstätten structure

Iron meteorites are generally characterized by the intergrowth of two iron-nickel minerals: low-nickel kamacite (α) and high-nickel taenite (β), termed the Widmanstätten structure. This structure can be visible after etching a cut and polished surface with 10%

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nitric acid. Generally, the bright band under reflected light microscope is kamacite and the dark reflecting potion is taenite. Some of the kamacite bands show Neumann lines, especially clear in coarse octahedrites. The higher the meteorite contains Ni, the thicker will be the bands. However, ataxite (highest-Ni) and hexahedrite (lowest-Ni) do not show the Widmanstätten structure.

It is recognized that the Widmanstätten structure is a natural recording thermometer that has recorded the cooling rate for parent body. The formation of this structure is described below.

Fe-Ni phase diagram and Ni diffusion

Figure 1 shows the Fe-Ni stability phase diagram (Yang *et al.*, 1997). The high-Ni taenite is converted to low-nickel kamacite as the meteorite cools. The phase diagram considers the effect of P, because the presence of P in Fe-Ni alloys aid in the kinetics of precipitation of the Widmanstätten structure (Doan & Goldstein, 1970). When the meteorite cools below about 1,400℃, it crystallizes into the face-centered structure of taenite. Between 1400 and 900℃ only taenite is stable. As temperature drops below 900℃, three stability fields (γ, α, $\gamma+\alpha$) appear. If the iron meteorite has less than 5 wt% bulk Ni content, it will convert into kamacite (hexahedrites) as temperature drops. The stability of phase depends on the bulk nickel content in the metal.

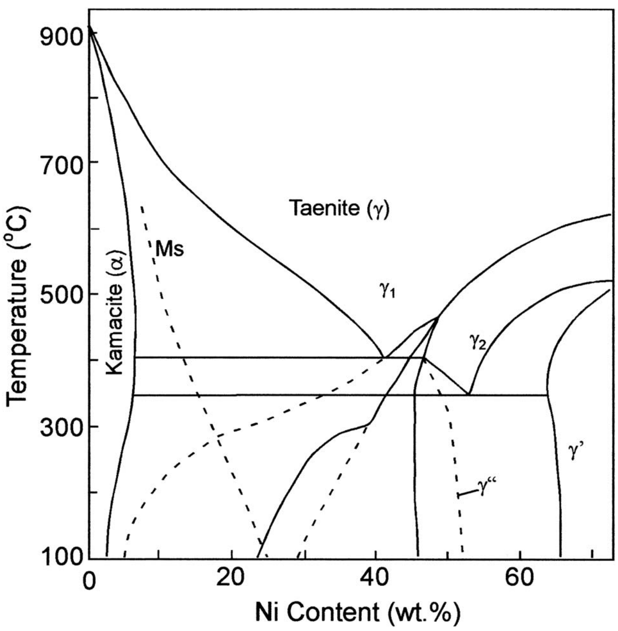

Fig. 1 Fe-Ni phase diagram determined by investigation of meteoritic metal. On this diagram, α represents a low-Ni kamacite, γ represents a high-Ni taenite phase, γ^1 represents a low-Ni paramagnetic bcc phase, γ^2 represents a high-Ni ferromagnetic fcc phase, γ' represents ordered Ni_3Fe, γ" represents ordered FeNi, and Ms represents martensitic transformation starting temperature (Yang *et al.*, 1997).

The diffusion is more efficient at higher temperatures and becomes sluggish and inefficient at lower temperatures. In other words, the slower the cooling rate, the more efficient is the nickel diffusion and therefore the homogenous kamacite and taenite should be formed. Nickel atoms more easily enter the kamacite phase than the taenite. The difference in diffusion rates (D value) of the two phases becomes greater with lowering temperatures. In this case, it is thought that time is the distinguished homogenizer. If the cooling rate was sufficiently slow, the taenite doesn't show M-shaped Ni distribution and becomes homogeneous composition.

In other words, the distribution of nickel in the taenite and kamacite plates is an indicator of the cooling rate of the parent body. A nearly flat nickel profile indicates very slow cooling rate, while steep profile suggests a more rapid cooling rate.

Techniques to determine the cooling rate

Cooling rates are obtained by comparing measured dimensions and Ni contents to computed values using models based on diffusion theory and experimental data on diffusion coefficients (Wood, 1964, 1967; Goldstein & Ogilvie, 1965). Three methods have been developed to estimate the cooling rate. 1) The Kamacite bandwidth method (Goldstein & Short, 1967) is defective because impingement, when overlapping growth fields affect the mutual development of neighboring α-bands, is not taken into account (Saikumar & Goldstein, 1988). 2) The Taenite central Ni content method (Wood, 1964) uses Ni contents at the midpoint of taenite lamellae or grains and half-widths. The cooling rate is computed through superposing the measured data on the cooling rate curves, calculated using numerical model. 3) The Ni profile matching method (Goldstein & Ogilvie, 1965) uses measured Ni concentration across the taenite lamellae. And the gradients are compared to the simulated profiles. These two methods were also verified experimentally by comparing modeled to measured Widmanstätten structure grown in the laboratory at controlled cooling rates (Narayan & Goldstein, 1984a, b). However, because Widmanstätten structure develops in three dimensions, Ni profile shows different gradients depending on crystallographic orientations. Therefore, it is necessary to prepare a section of each meteorite by cutting perpendicular faces of taenite lamellae orientation. On the other hand, the cooling rates determined using taenite central Ni content method shows no difference with face orientation.

Purpose of this study

The purpose of this study was initially to estimate the cooling rate of the Toluca meteorite by central Ni content method. During the course of this study, two types of taenite lamellae were observed the clear and the heterogeneous taenite. Although many investigators have studied to estimate cooling rates of iron meteorites using clear taenite, the estimation using heterogeneous taenite (plessite) have never been attempted. In addition this study also considers the distribution of kamacite-taenite phase in the Toluca meteorite and the mechanism of the heterogeneous taenite nucleation by Ni diffusion.

Toluca meteorite

Toluca meteorite is an iron meteorite found in Mexico in 1776. This meteorite is a coarse octahedrites, and belongs to the IAB group (Fig. 2). The trace element concentration reported by neutron activation analysis (Choi *et al.*, 1995) suggests that the Toluca has typical average trace element contents of IAB group. Cooling rate determination of Toluca meteorite has already been studied by many investigators (Wood, 1964; Goldstein & Short, 1967; Narayan & Goldstein, 1985; Saikumar & Goldstein, 1988). However, the estimated cooling rates are incoherent. Fortunately, most group IAB meteorites show little or no evidence of shock reheating, which can obliterate the previous thermal history. Because of this reason, these meteorites are well suited to estimate cooling rate.

Fig. 2 IAB coarse octahedrite samples studied the Toluca meteorite.

Experimental procedure

Meteorite samples were first cut, polished and observed under reflected light microscope. These meteorites were kept in a vacuum desiccator to prevent rusting. The thin sections of the sample were prepared, polished with diamond paste and carbon coated for electron microprobe analysis. Back Scatter Electron (BSE) images were observed and specific spots selected for qualitative analysis using the JEOL-JXA 733 Superprobe at the Center for Instrumental Analysis, Shizuoka University. A ZAF metal correction was used for metal and metal inclusion analyses. An operating voltage of 25kV and a beam current of 12nA were used. The concentrations of Fe, Ni were measured. JEOL pure Fe and Ni metal standards were used.

The Fe-Ni phase diagrams (Fig. 1) and numerical models of Saikumar & Goldstein (1988) and references therein were used in the estimation of cooling rate using the taenite central Ni content method for Toluca meteorite.

Results

Observations using microscope

Toluca meteorite displays spectacular Widmanstätten structure, having silver kamacite bands, dark taenite lamellae and inclusions (Fig. 3). And several kamacite bands show Neumann lines as well (Fig. 4a, b). Whereas it was reported that group IAB irons are coarse octahedrites with irregular and often angular inclusions of dark silicates, silicate inclusions were not observed in the present sample. However, inclusions were observed.

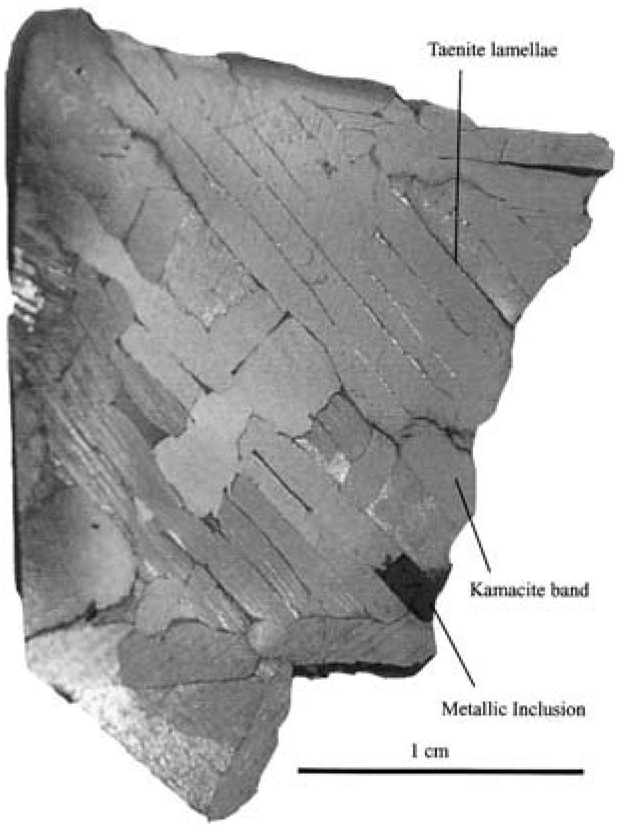

Fig. 3 Widmanstätten structure in the coarse octahedrite, Toluca meteorite.

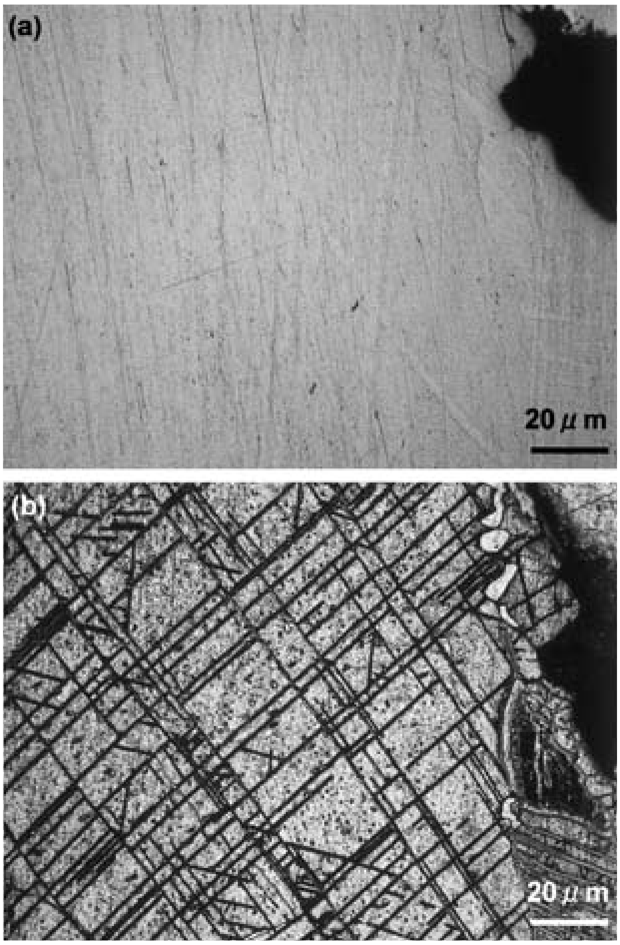

Fig. 4 The kamacite band of Toluca meteorite (a) before etching and (b) after etching, the latter show Neumann lines. Neumann lines are running in several directions through kamacite bands.

BSE images and Fe-Ni contents

BSE image show that the clear taenite lamellae coexist with irregular shaped heterogenous taenites (Plate 1a). Plate 1b displays BSE images of the clear taenite lamellae. The irregular shaped taenite occur in different shapes and sizes (Plate 1c, d). The interior of irregular taenite are heterogeneous in composition, called plessite, which is intergrowth of kamacite and taenite. In addition, harp-like taenites also exist. The rims are homogeneous. Most of the taenite having plessite texture are wider than clear taenite lamellae. The Fe and Ni contents of kamacite and taenite of Toluca meteorite indicate a linear correlation, suggesting absence of other major elements (Fig. 5). Ni composition profiles across the kamacite - clear taenite lamellae - kamacite area in Toluca meteorite show a characteristic M-shape Ni distribution pattern produced by inefficient diffusion (Fig. 6), whereas the profiles across the kamacite - heterogeneous taenite having a plessite - kamacite show an irregular shape (Fig. 7). The Ni concentration of taenite rim shows a smooth gradient, however in the plessite region Ni content varies considerably.

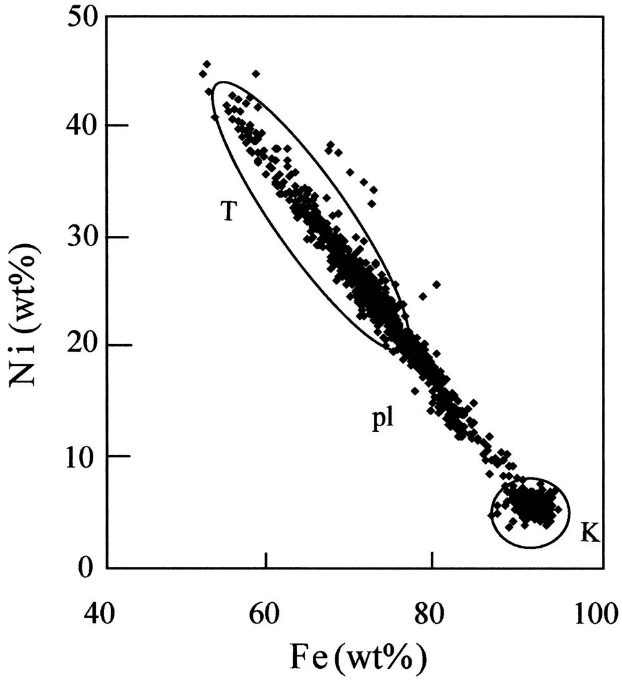

Fig. 5 Fe versus Ni contents for Fe-Ni alloy in Toluca iron. Fe-Ni alloy are composed of K, kamacite; T, taenite; and pl, plessite, which is the intergrowth or interface of kamacite and taenite.

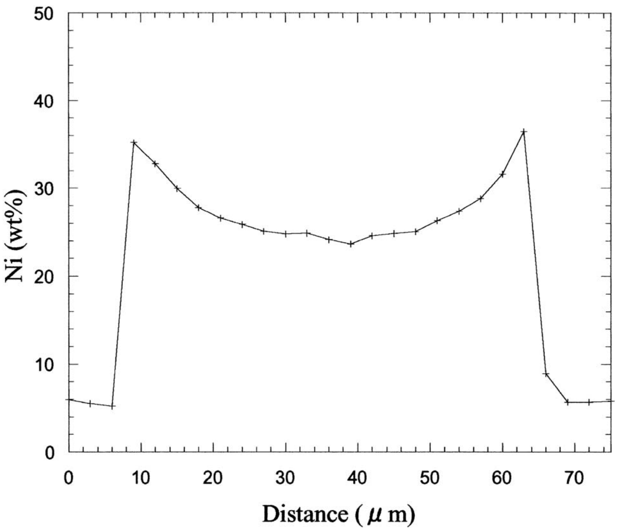

Fig. 6 Ni profile across the kamacite - clear taenite lamallae - kamacite region in the Toluca meteorite.

Determination of cooling rate for Toluca

Plots of taenite central Ni content *versus* taenite half-width were constructed for Toluca meteorite. Measured microprobe data for clear taenite lamellae and heterogeneous taenite were also plotted on the same diagram to estimate the cooling rate for the meteorite. In order to estimate central Ni content for heterogeneous taenite, the dispersion of Ni concentration within plessite region was approximated to that fits

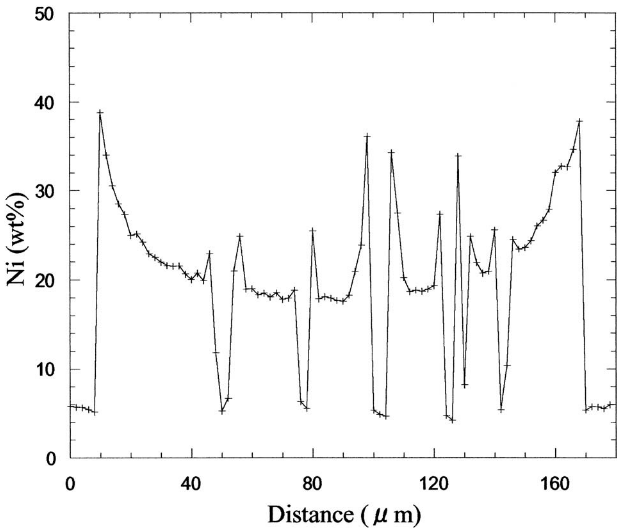

Fig. 7 Ni profile across the kamacite - heterogeneous taenite having plessite texture - kamacite in the Toluca meteorite.

M-shaped distribution shown by the rims and parts of the central portions. The central taenite Ni versus taenite half-width plots for Toluca meteorite is shown in Figure 8. All the results obtained in this study are plotted. The plots of clear and heterogeneous taenite show almost similar tendency. The estimated cooling rate for Toluca, using the taenite central Ni content method, are approximately 100～200℃/Ma.

Discussion

Comparison of cooling rate between clear and heterogeneous taenites

The cooling rates based on the central Ni content method for heterogeneous taenite and clear taenite lamellae were estimated for the Toluca meteorite as a test for consistency. The acquired data have small uncertainties and their position is fixed on central Ni content versus half-width diagram (Fig. 8). Calculated cooling rate curves are superimposed on these data to determine the best match.

The best datasets on the clear taenite lamellae and the heterogeneous taenite yield rates of 100～200℃/Ma. Although determined rates neglect the effect of P content, two datasets show the same trend. Therefore, cooling rate estimated by heterogeneous taenite using taenite central Ni content method can be applied similar to that of clear taenite lamellae.

Cooling rate comparison with other studies

Table 2 compares the cooling rates of Toluca meteorite with those of previous studies. The cooling rate which was determined in this study is faster by a factor of about 100 than the estimates of Wood (1964) and Goldstein & Short (1967). It is considered that there are several reasons for this discrepancy. Firstly, the phase diagrams have been revised to ternary system. Secondly, the role of P on Fe-Ni phase and diffusivities has not been taken into account.

Table 2 Comparison of cooling rates determined for the Toulca meteorite in previous studies and this study.

Cooling Rate (℃/million years)				
Wood (1964)	Goldstein & Short (1967)	Narayan & Goldstein (1985)	Saikumar & Goldstein (1987)	This study
1	2	750	25	100-200

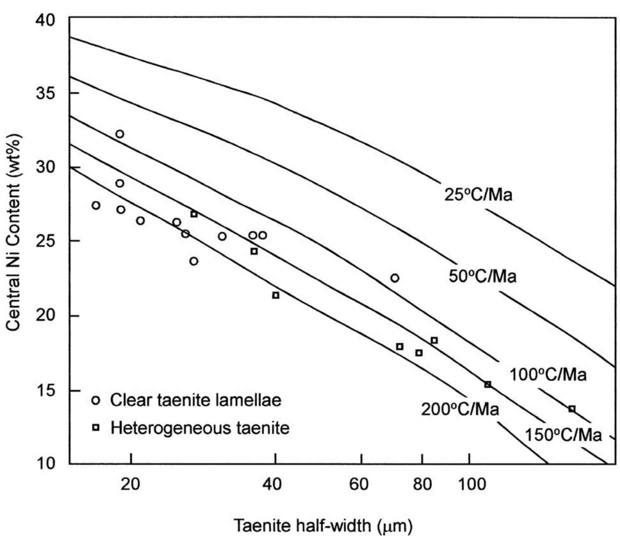

Fig. 8 Cooling rate curves for Toluca meteorite (Siakumar & Goldstein, 1988). Central Ni contents and half-width of clear and heterogeneous taenite in Toluca meteorite fall between calculated 100～200℃/Ma cooling rate curves.

The cooling rate of Narayan & Goldstein (1985) considerably differ, because they used the kamacite bandwidth method and effects of kamacite bands impigement were not taken into account. The results of Saikumar & Goldstein (1988), estimated by central Ni content method, is most plausible in previous studies. They reported a cooling rate of 25±15℃/Ma for the Toluca meteorite (regarding to 8.14 wt% bulk-Ni content). The cooling rate determined in this study (7.86 wt% bulk-Ni; Choi *et al.*, 1995) is greater than that of Saikumar & Goldstein (1988) by more than four times.

Bulk or local Ni and P contents also cause small errors. A change in any of these parameters would manifest itself by a shift in the position of the cooling rate curves. Phosphorus content influences particularly diffusivities and phase relations. Compared to a P-free system, in a P-saturated system Ni diffuses much faster, by factor of 10 in α and 27 in γ, and kamacite nucleates at lower temperatures, depending on when schreibersite forms (Saikumar & Goldstein, 1988). These differences offset each other to some extent; the addition of P increases diffusion rates, but decreases the time available for diffusion by lowering the kamacite nucleation temperature. The increase in diffusion rate dominates. However, a taenite central Ni content method calculated in P-free system can be generated in P-saturated system at cooling rates that are faster by factors of 3-5, depending on Ni and P content (Herpfer *et al.*, 1994).

In other words, the difference of cooling rates determined in this study may be caused by the different bulk Ni concentration (7.86 wt% Ni) and the diffusion coefficient for binary (P-free system). It is thus necessary to quantify again the bulk Ni content and P content to ensure the correction of cooling rates.

Formation of plessite texture in taenite and harp-like taenite

This study confirms that the cooling rate determined by heterogeneous taenite having plessite texture is consistent. Consequently, it can be assumed that the heterogeneous taenite has been originally homogeneous in composition. As the temperature drops below 400℃ (kamacite nucleation closure temperature), the interior of wide taenite transform into plessite by the formation of a stable phase (Fig. 1). In order to recognize the formation process in more detail, a nano-scale investigation is necessary (*e.g.* Zhang *et al.*, 1993; Yang *et al.*, 1997).

Some of the harp-like taenite are observed in Toluca meteorite (Plate 1a). Plate 1e shows a harp-like taenite in Toluca. It can be confirmed that the harp-like taenite always occur together with Schreibersite (phosphide). It is already reported that the presence of P in Fe-Ni alloy has a very pronounced effect on the formation of the Widmanstätten structure (Doan & Goldstein, 1969, 1970). During cooling of a meteorite the reaction could go in one of the following two different paths depending on the bulk P content of the alloy: 1) $\gamma \rightarrow \alpha + \gamma$; when the P content of the alloy was low: 2) $\gamma \rightarrow \gamma +$ phosphide $\rightarrow \alpha + \gamma +$ phosphide; when the P content of the alloy was high. In other words, the harp-like taenite may have been formed in high-P concentration regions by the reaction (2) in Fe-Ni alloy.

Conclusions

Using the central Ni content method (Wood method), the cooling rate of 100～200℃/Ma was estimated for Toluca meteorite by clear taenite lamellae and heterogeneous taenite in this study. The cooling rate estimated by heterogeneous taenite having plessite texture can be applied similar to that of the clear taenite lamellae.

The formation of harp-like taenite was caused by the high P content in the metoerite.

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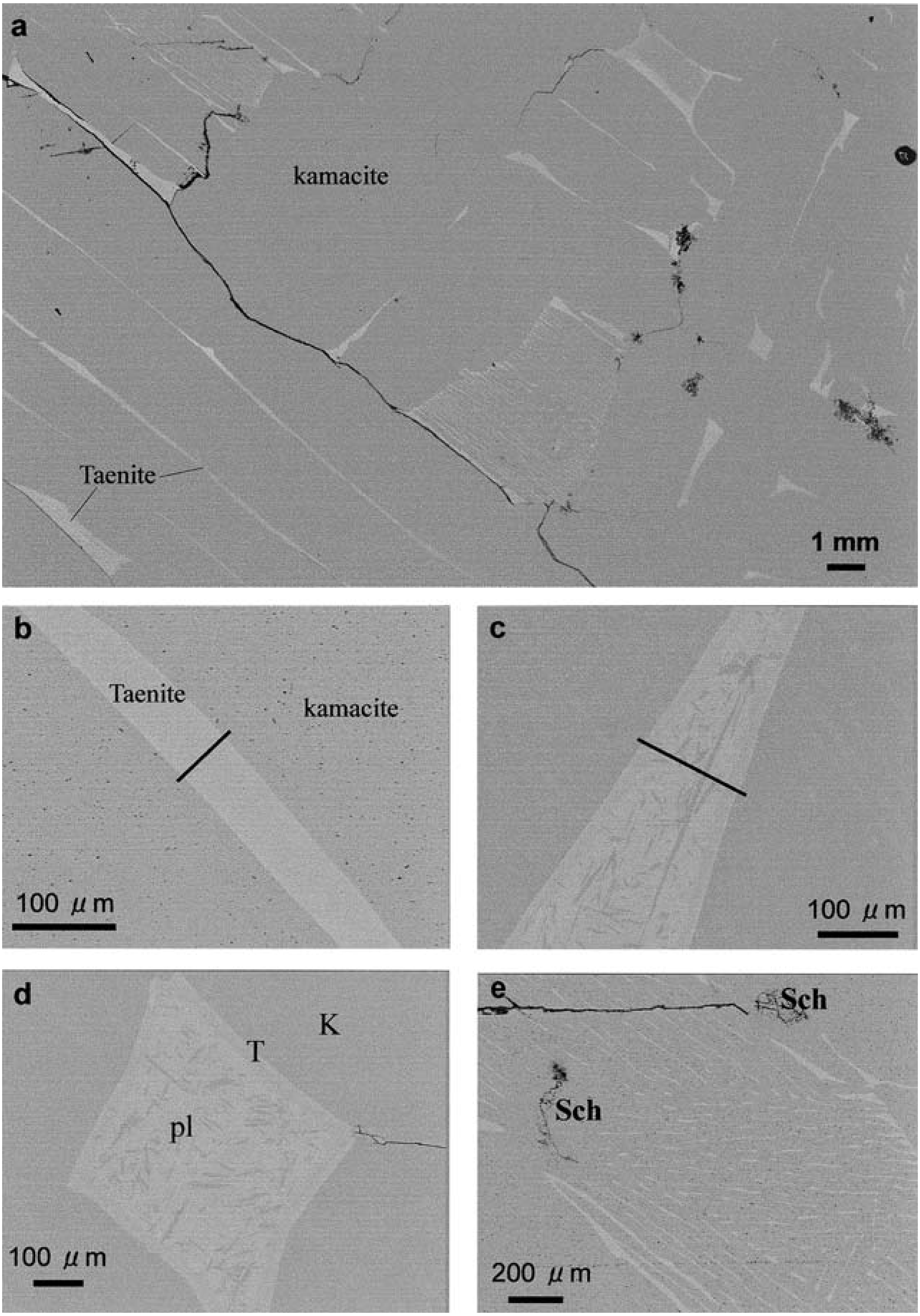
Plate 1 BSE images of Fe-Ni alloy regions of Toluca meteorite.
(a). A composite BSE image for Toluca meteorite. Kamacite and taenite are shown by gray and bright gray, respectively. Clear taenite lamellae coexist with irregular shaped taenite and harp-like taenite.
(b). Clear taenite lamellae has homogeneous interior. The black line in taenite is the traverse of measurement points by EPMA.
(c). This BSE image is showing irregular shaped taenite in Toluca meteorite. The interior and rim of lamellae is heterogeneous (plessite) and homogeneous (taenite), respectively. The black line in taenite is the traverse of measurement points by EPMA.
(d). BSE image showing the interior of irregular taenite shows heterogeneous texture called plessite. The rim of heterogeneous taenite is clear taenite. K, kamacite; T, taenite; pl, plessite.
(e). Harp-like taenite in Toluca meteorite. The metallic inclusion adjacent to the harp-like taenite is schreibersite $(Fe, Ni, Co)_3P$, marked Sch.


a
kamacite
Taenite
1 mm
b
Taenite
kamacite
100 μm
c
100 μm
d
K
T
pl
100 μm
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Sch
Sch
200 μm