Analytical electron microscopy study of the plessite structure in four IIICD iron meteorites

L. S. LIN,* J. I. GOLDSTEIN and D. B. WILLIAMS

Department of Metallurgy and Materials Engineering, Lehigh University, Bethlehem, PA 18015, U.S.A.

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Abstract—Electron optical techniques were employed to investigate the plessite structure and composition of four IIICD fine octahedrites. These meteorites have a similar thermal history and differences in plessite structure can be ascribed to varying bulk Ni content and/or localized differences in carbon content. Microdiffraction patterns from regions as small as 20 nm dia. were obtained for the first time from plessite structures. It was established that transformation twins in clear taenite I have the conventional FCC twin relationship, individual kamacite and taenite cells in the cloudy zone have the Kurdjumov-Sachs orientation and fine γ rods in the decomposed martensite zone display both the Nishiyama and Kurdjumov-Sachs relation with the matrix-α. All the IIICD irons contain cloudy zone and martensitic plessite. Except for Dayton, martensitic plessite shows further decomposition into α + γ at low temperatures. Using STEM X-ray microanalysis with a spatial resolution of ~50 nm, Ni composition profiles in taenite from all the IIICD irons showed a maximum of ~48 wt%, Ni. The structural and compositional data indicate that plessite formation occurs at quite low temperatures (~200–300 °C) during the cooling history of the IIICD irons.

INTRODUCTION

The characteristic microstructure of most metallic meteorites is that of Widmanstätten plates of kamacite (α Fe–Ni) in a matrix of taenite (γ Fe–Ni). Kamacite nucleates and grows on {111} planes of taenite during cooling from the region as shown in the Fe–Ni phase diagram (Fig. 1) (GOLDSTEIN and OGIS, 1965; KAUFMAN and COHEN, 1956). The kamacite and taenite both increase in Ni content as cooling proceeds. By about 500 °C most of the Widmanstätten growth is complete. The regions between the Widmanstätten plates correspond to the original taenite matrix and are enriched in Ni. As kamacite growth continues below 500 °C the taenite borders with kamacite continue to be enriched in Ni. When meteorite specimens are polished and etched these taenite regions show progressive stages of transformation and the decomposed areas are referred to as plessite. Figure 2 shows a plessite region in the Edmonton meteorite. The nonetching zones around the edge of the plessite region are high Ni taenite while the rest of the structure is decomposed taenite. A typical electron probe microanalyzer (EPMA) scan across a taenite region containing plessite will display an Ni profile where the Ni content is highest at the edges (~45 wt% Ni) and lowest in the center (~10–15 wt% Ni). The plessite can be divided into five different zones according to the microstructure shown in Fig. 2b. These microstructural zones may be called: (1) clear taenite I, (2) cloudy zone, (3) clear taenite II, (4) martensite and (5) duplex α + γ mixtures. Typical Ni contents of these 5 zones are (1) > 40 wt%, (2) 30–40 wt%, (3) 25–30 wt%, (4) 15–25 wt% and (5) < 15 wt% respectively.

Figure 1 also shows that, at 500 °C and below, the untransformed taenite can transform in one of two ways: (1) γ → α + γ or (2) γ → α2 (martensite) below the $M_s$ temperature. The second transformation is diffusionless and fcc taenite transforms to distorted bcc martensite below the $M_s$ curve. MASSALSKI et al. (1966) call the γ → α + γ transformation Type I plessite, and the γ → α2 transformation Type II plessite. At high enough temperatures (~200 °C) the martensite may decompose to α + γ through a diffusion controlled process, γ → α2 → α + γ, called Type III plessite (MASSALSKI et al., 1966). Type II and III plessite have very fine structures and are amenable to scanning electron microscope (SEM), transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) studies.

At the high Ni edge of the plessite, a brown rim zone is commonly seen after proper etching (Fig. 2b). This rim zone, called the cloudy zone, because of its appearance in the optical microscope, is separated from Type II or martensitic plessite by a featureless taenite zone (clear taenite II) of roughly similar width and from the kamacite/taenite border by clear taenite (clear taenite I) ~1–2 μm wide. The cloudy zone is always present in irons unless the meteorite has been cosmically or terrestrial reheatcd (SCOTT, 1973). As proposed by SCOTT (1973), this cloudy zone is another variety of plessite, called Type IV. The mechanism for the formation of Type IV plessite is unknown.

In a recent study (LIN et al., 1977) electron optical techniques were employed to study the range of plessite structures observed in the Carlton meteorite, a
METEORITE SAMPLES

Two chemical Group IIIC irons (Carlton, Edmonton) and two chemical Group IID irons (Dayton, Tazewell) were chosen for this study. These meteorites all have well developed Widmanstätten and plessite structures. Table 1 lists the Ni and C contents, structure and cooling rates of these irons. The cooling rates (GOLDSTEIN and SHORT, 1967) are essentially the same so that any observed differences in plessite structure are not a function of thermal history. SCOTT and BILD (1974) proposed that Group IIIC and Group IID irons are related and probably form a single sequence. These irons all contain haxonite, (FeNi)$_{13}$C, and show minimal signs of shock (SCOTT and WASSON, 1975). The carbon contents are \( \sim 0.05 \) wt\% but the bulk Ni contents vary from 12.65 to 17.7 wt\% (Table 1). Thus any differences in plessite structure will probably be due to varying bulk Ni content and/or localized differences in C content.

EXPERIMENTAL PROCEDURES

The procedures for specimen preparation and observation have been described in detail previously (LIN et al., 1977). In summary, meteorite samples were oriented with the Widmanstätten plates normal to the specimen surface and the area of interest selected by optical microscopy. Bulk specimens were observed in an ETEC SEM and composition profiles were determined using an ARL EPMA. Specimens for TEM-STEM analysis were ion beam thinned 3 mm discs, and they were examined in a Philips...

Table 1. Iron meteorites—structure, chemistry and cooling rates

<table>
<thead>
<tr>
<th>Chemical Group</th>
<th>Structure</th>
<th>Ni (wt%)</th>
<th>C (wt%)</th>
<th>Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlton</td>
<td>IIIC</td>
<td>( \sim 17.4 )</td>
<td>( 0.06 )</td>
<td>( 3^\circ/\text{Myr} )</td>
</tr>
<tr>
<td>Edmonton</td>
<td>IIIC</td>
<td>( \sim 17.6 )</td>
<td>( 0.05 )</td>
<td>( 1^\circ/\text{Myr} )</td>
</tr>
<tr>
<td>Dayton</td>
<td>IID</td>
<td>( \sim 17.1 )</td>
<td>( 0.05 )</td>
<td>( 3^\circ/\text{Myr} )</td>
</tr>
<tr>
<td>Tazewell</td>
<td>IID</td>
<td>( \sim 16.9 )</td>
<td>-</td>
<td>( 2^\circ/\text{Myr} )</td>
</tr>
</tbody>
</table>

** BUCHWALD (1975).
\( \triangle \) MOORE et al. (1969).
\( \square \) GOLDSTEIN and SHORT (1967).
Plessite structure in four IIICD iron meteorites

EM300 TEM-STEM instrument operating at 100 kV, equipped with a rear entry solid state X-ray detector.

Quantitative microchemical analyses with a spatial resolution of ~ 30 nm (~ 300 Å) were obtained using the Cliff-Lorimer method (Cliff and Lorimer, 1975) to convert X-ray intensities to wt% composition, with the X-ray values calculated by the method of Goldstein et al. (1977). The precautions necessary for accurate STEM microanalysis outlined by Goldstein and Williams (1977) were used at all times.

Microdiffraction data were obtained using convergent beam diffraction patterns (CBDP) of the type described by Maher (1974) and Warren and Hren (1977). The scanning beam (~ 20–30 nm dia.) was stopped and positioned on the desired region viewed on the STEM image and the CDP was simultaneously observed on the conventional TEM viewing screen. The effective camera length was adjusted using the TEM projector lens control. Maximum exposure time was ~ 32 sec before carbon contamination build-up resulted in sufficient inelastic scatter to obscure the CDP details. In view of the generally low resolution of STEM images subsequent TEM images were recorded to show the exact position from which the patterns were obtained.

EXPERIMENTAL RESULTS AND DISCUSSION

Structural studies

The kamacite (α)-clear taenite I (γ) interface in all the meteorites is well defined as shown for the Tazewell and Dayton meteorites in Fig. 3. The α-γ orientation relationship was obtained using conventional selected area diffraction patterns (SADP) and found in all cases to be that described by Nishiyama, namely \((\{111\}_\alpha/\{011\}_\gamma)\) and \(<(011)_\alpha/\{011\}_\gamma>\). It is obvious in Fig. 3 that the clear taenite region I contains defects. These defects, which were present in all the meteorites studied, have the characteristics of microtwins, namely parallel sides, fine fringe contrast and a clear crystallographic relationship with the γ matrix. An example from the Carlton meteorite is shown in Fig. 4a. The projected width of the twins is ~ 20 nm. Conventional SADP techniques failed to reveal any extra twin spots but use of the CDP technique with a 20 nm spot resulted in direct evidence for twinning as shown by extra spots in Fig. 4b. The pattern is indexed and corresponds to a conventional fcc twin with a twinning plane \(k_1 = (111)\). Further confirmation of twinning is the absence of any composition change in the vicinity of the defects. These microtwins although confined within the γ phase in all the meteorites studied are invariably associated with an α-γ interface. They occur mainly at the Widmanstätten α-clear taenite I interface, but are also observed at the clear taenite I-cloudy zone interface where a well defined band of α invariably exists (see Figs. 3a, b). This fact, combined with the absence of the microtwins in the otherwise structurally identical clear taenite II region (see Fig. 6) implies that they result from transformation stresses at α-γ interfaces.

The possibility of dislocations being associated with the γ-α transformation exists because there is a dense dislocation substructure in both the Widmanstätten α and clear taenite I regions as may be discerned in Figs. 4a and 3b respectively. However any differences in density between α and γ were impossible to determine, and there was no evidence for either preferential localization near the interface, or the presence of confined regions of slip.

All the meteorites studied exhibit the cloudy zone which, as first shown by Scott (1973) using TEM replication and diffraction techniques, is a network of interpenetrating γ and α cells. A typical example from a thin foil showing the relationship of the zone to the rest of the regions is given in Fig. 3 for the Dayton and Tazewell meteorites. As shown in Fig. 3, a thin region of kamacite (α) separates the clear taenite region from the honeycomb structure of the cloudy zone. From SADP data Scott (1973) concluded that the γ and α regions were in fact interpenetrating single crystals. Since SADPs sample at minimum 0.5 μm diameter regions (Edington, 1976) the diffraction pattern will sample the orientation relationships between several hundred cells. Orientation relationships between individual cells can be obtained using CDP techniques as shown in Fig. 5. This is a region of the cloudy zone in the Carlton meteorite. The dark spots (K and T) are the contamination marks showing the position of the 20 nm electron probe on individual α and γ cells, and the resultant CDPs are also shown. The diffraction patterns were taken under the same tilting conditions. The orientation relationship between the two phases was obtained by superimposing the two diffraction patterns, assuming the beam directions are parallel in each case. Thus the Kurdjumov-Sachs orientation relationship of the form: \((\{111\}_\alpha/\{110\}_\gamma)\) and \((\{011\}_\alpha/\{111\}_\gamma)\) is shown in Figs. 5b and 5c. Patterns taken from ~ 20 individual cells of γ and α indicate that this relationship holds true at the individual cell level confirming conclusively both the interpenetrating single crystal model originally proposed by Scott (1973) and the conventional SADP data previously reported by Scott (1973) and Lin et al. (1977).

In the lower Ni clear taenite II region (~ 25–30% Ni) no twins or other microstructural features were observed. Figure 6, taken from the Dayton meteorite, shows a taenite II structure typical of the meteorites studied. The taenite II region merges into the γ cells of the cloudy zone on the high Ni side, and displays a well defined interface with the martensitic regions at the low Ni side as shown in Fig. 6.

In the composition range 15–25% Ni all meteorites show a martensitic region in the optical microscope. Upon investigation at higher resolution the martensite was found to be one of two major types: lath martensite, Fig. 7a or lenticular martensite, Fig. 7b. Figure 6 shows lenticular martensite which has developed at the clear taenite II interface in Dayton. The transition from one type of martensite to another is a sensitive function of Ni content (Speck and Swann, 1965), and both types were often observed in the same meteorite. The lath martensite typically consists of ap-
proximately parallel laths \( \sim 0.1 \) 0.5 \( \mu \text{m} \) wide and several microns long. The laths are separated by low angle boundaries and contain a high dislocation density. No attempt was made to analyze the dislocation arrays as possible clues to thermal or mechanical history.

The lenticular (acicular) martensite is generally on a coarser scale showing characteristic needle-like morphology. According to SPEICH and SWANN (1965), lenticular martensite in FeNi alloys (\( \leq 0.005 \) wt\% C) forms at higher Ni contents often greater than 20 wt\% Ni, consistent with its presence at the clear taenite II interface.

The Tazewell meteorite contains primarily lath martensite. In addition decomposition of the martensite by the reaction \( \alpha_2 \rightarrow \alpha + \gamma \), as described in detail for the Carlton meteorite (LIN et al., 1977), was observed. Figure 8 shows such a region consisting of fine \( \gamma \) rods (\( \sim 20-30 \text{nm} \)) in an \( \alpha \) matrix. Some of the outlines of the original martensite plates can still be observed. Microdiffraction patterns of decomposed martensite in Carlton are shown in Fig. 9 for the \( \alpha \) matrix and \( \gamma \) rods. Two basic orientation relationships were observed, namely (Nishiyama) \( \langle 011 \rangle / / \langle 001 \rangle \gamma \) and Kurdjumov-Sachs \( \langle 011 \rangle / / \langle 111 \rangle \alpha \), in different regions of the same decomposed structure.

Although decomposition of martensite was not observed in our thin sections of Edmonton and Dayton, this may be due to the relatively poor sampling of the structure, a common characteristic of thin foil studies. High magnification SEM photographs (\( \geq 10,000 \times \)) of martensite regions of metallographically prepared specimens of Edmonton did however reveal decomposed martensite structures (\( \alpha_2 \rightarrow \alpha + \gamma \)) with the formation of fine \( \gamma \) rods. Dayton is an unusual meteorite because of the development of pearlitic lamellar platelets of taenite. This specific structure is discussed by BUCHWALD (1975) and the structure is described using TEM by GOLDSTEIN et al. (1976). It is suggested that carbon is responsible for the pearlitic development and that C is mostly in solid solution in taenite (BUCHWALD, 1975). The lack of decomposed martensitic plessite may be due to the effect of carbon on the \( M_s \) temperature. The martensite start temperature (\( M_s \)) is a strong function of carbon content and is decreased \( \sim 50 \) C for each addition of 0.1 wt\% C (BAIN and Paxton, 1966; Nemirovsky, 1968; Payson and Savage, 1944). Therefore localized increases in C content may decrease the \( M_s \) to such low temperatures in high Ni meteorites such as Dayton that decomposition to \( \alpha + \gamma \) is inhibited.

TEM studies of the interior regions of plessite (\( <15 \) wt\% Ni) in the Carlton meteorite (LIN et al., 1977) showed that the duplex \( \alpha + \gamma \) regions must have arisen from a martensitic decomposition (\( \gamma \rightarrow \alpha_2 \rightarrow \alpha + \gamma \)). The plessite is Type III. Figure 10 shows a SEM photo of the fine duplex structure of \( \alpha \) and \( \gamma \) in the Edmonton meteorite. The black matrix is \( \alpha \) and the \( \gamma \) rods are 20-200 nm in width. The blocky regions of fine structure are outlined by the \( \gamma \) phase and within these regions are also \( \gamma \) rods in an \( \alpha \) matrix. The SEM microstructures (Figs. 10a, b) are the same as those of the Carlton. The interior regions of plessite in Dayton and Tazewell contained \( \geq 16.9 \) wt\% Ni (Table 1). Nevertheless this Ni content is only slightly greater than that normally found for duplex \( \alpha + \gamma \) regions and allows for the presence of some regions of decomposed martensite in Tazewell.

### Compositional studies

Compositional studies were restricted to determining the Ni concentration profile across the \( \alpha - \gamma \) interfaces of Edmonton, Dayton, and Tazewell. The use of STEM X-ray microanalysis permits a spatial resolution of \( \sim 50 \) nm (WILLIAMS and GOLDSTEIN, 1978). The change in Ni content at the \( \alpha - \gamma \) interface is abrupt and the composition falls away into the plessite region. Traces from the Edmonton, Dayton, and Tazewell meteorites are shown in Fig. 11. The interface between the cloudy zone and clear taenite I is noted at \( \sim 40 \) wt\% Ni in the figure. In the case of the Dayton meteorite, the composition profile falls smoothly through the clear taenite I (region 1) and there is some evidence for scatter of the readings in Edmonton when the cloudy zone (region 2) is reached. In the Tazewell meteorite however, there is a distinct drop in Ni content upon reaching the cloudy zone, which is considered to result from sampling of the first \( \alpha \) region at the cloudy zone/clear taenite I interface (Fig. 3). Although the drop is not as evident in Edmonton, there is a slight increase in Ni content at the end of region 1 which would be consistent with Ni rejection by the first \( \alpha \) region nucleated in the cloudy zone.

Table 2 lists \( \alpha - \gamma \) interface Ni composition determined using the EPMA as well as the STEM data. The accuracy of the taenite Ni content measurement is \( \sim \pm 0.5 \) wt\% Ni using the electron microprobe while only \( \sim \pm 2 \) wt\% Ni using the STEM. The decreased accuracy using the STEM technique is due to the much lower X-ray counting rates and the uncertainties in the \( k_{\text{NPE}} \) constant used in the Cliff–Lorimer calculation procedure. The large differences between the maximum Ni content in taenite measured with the EPMA by SHORT and GOLDSTEIN (1967) and the data of this study and that of LIN et al. (1977) (Note Table 2) is due to the scan technique employed and the size of the electron probe. In the earlier studies, scans were made at 1 \( \mu \text{m} \) intervals across the \( \alpha - \gamma \) interface and the electron probe size was \( \sim 1 \) \( \mu \text{m} \) at 20 kV operating potential. In the present studies, scans were made at 0.25 \( \mu \text{m} \) intervals across the \( \alpha - \gamma \) interface and the electron probe size was \( \sim 0.2 \mu \text{m} \) at 20 kV operating potential. The diameter of the X-ray excitation area was \( \sim 2 \) \( \mu \text{m} \) in the earlier studies and \( \sim 1 \) \( \mu \text{m} \) in this study. Because of the increased spatial resolution available in the more recent measurements, the maximum Ni content measured in taenite has increased (Note Table 2). In contrast the
Fig. 11. Ni distribution in plessite (regions 1 and 2) as obtained by STEM X-ray analysis for the Edmonton, Dayton, and Tazewell meteorites.

spatial resolution of the 100 kV STEM data is \( \sim 50 \text{ nm} \). The STEM measurements of maximum Ni content in taenite are all higher than the EPMA data, consistent with the improved X-ray spatial resolution.

The temperature of final equilibrium implied from the STEM data by extrapolating the measured Fe-Ni phase diagram (Goldstein and Ogilvie, 1965) (Fig. 1) is approx 400°C, 50°C lower than the temperature obtained from the EPMA data. Clearly the improved spatial resolution using the STEM indicates a lower equilibration temperature than hitherto obtained. Although the 20-fold increase in spatial resolution using STEM is significant, ordered FeNi (\( \sim 52 \text{ wt\%} \)) Ni has been reported in taenite in two octahedrites, Cape York (IIIa) and Toluca (I), (Petersen et al. 1977; Albertsen et al. 1978) by Mössbauer techniques. This discovery indicates that STEM X-ray microanalysis with spatial resolution better than \( \sim 50 \text{ nm} \) should allow one to obtain \( \alpha-\gamma \) interface compositions exceeding \( 50 \text{ wt\%} \) Ni, and therefore even lower equilibration temperatures.

**SUMMARY**

Several microstructural and microchemical observations of plessite in Group IIICD iron meteorites
Table 2. Maximum Ni content in taenite as measured by STEM X-ray microanalysis and electron probe microanalysis

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Maximum Ni Content (wt%) in Taenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edmonton</td>
<td>48 6 48 4 31 40 6 50 6 43 6 43 6 46 6</td>
</tr>
</tbody>
</table>

* This study.
* Short and Goldstein (1967).
* Lin et al. (1977).
* Goldstein et al. (1976).

have been made using electron optical techniques and STEM X-ray microanalysis. Selected area electron diffraction has shown that the kamacite-taenite orientation in the four meteorites studied is that of Nishiyama. Microdiffraction of plessite in the Carlton has shown: (1) transformation twins in clear taenite I have the conventional fcc twin relationship, (2) individual kamacite and taenite cells in the cloudy border have the Kurdjumov-Sachs orientation, and (3) fine γ rods in the decomposed martensite zone display both the Nishiyama and Kurdjumov-Sachs relation with the matrix α.

The clear taenite I zones of the four meteorites contain twins and these probably formed from transformation stresses at α-γ interfaces. All the IIICD irons contain the cloudy border and martensitic plessite structure. Two types of martensite, lath and lenticular, were observed. Except for Dayton the martensitic plessite showed further decomposition by the reaction path α2 → α + γ and the formation of Type III plessite. It is proposed that localized carbon concentrations may lower the martensite start temperature and pearlitic α + γ lamellae may form as a result. The Edmonton and Carlton irons exhibit duplex α + γ plessite which was formed by martensite (α2) decomposition.

Ni composition profiles were measured using STEM X-ray microanalysis with a spatial resolution of ~50 nm. The maximum Ni content in γ was measured as ~48 wt% in all the IIICD irons and indicates an equilibrium temperature 50°C lower than previously obtained by EPMA techniques.

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Fig. 2. Plessite regions in the Edmonton meteorite. (a) Plessite region surrounded by Widmanstätten kamacite. (b) Enlargement of a kamacite (k)-taenite interface region showing four different plessite structures: (1) clear taenite I, (2) cloudy zone, (3) clear taenite II and (4) martensite-α₂.

Fig. 3. Transmission electron micrograph showing kamacite clear taenite I cloudy zone (K/T;C.Z.) in the (a) Tazewell, (b) Dayton meteorite.
Fig. 4a. Transmission electron micrograph showing twins, ~20 nm wide, in the clear taenite I of the Carlton meteorite.

Fig. 4b. Convergent beam diffraction pattern obtained with a 20 nm electron probe diameter from one of the twins in Fig. 4a. The microdiffraction pattern reveals twin spots, which have been indexed, identifying the twins as the conventional fcc variety with the twin plane $k_1 = (111)$. The beam direction is $[110]$. 

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Fig. 5a. Transmission electron micrograph of the cloudy zone close to the clear taenite interface of the Carlton meteorite.

Figs. 5b, c. STEM microdiffraction patterns obtained from the kamacite (K) and taenite (T) constituting the cloudy zone. The regions of the cloudy zone from which they were taken are indicated in Fig. 5a where the carbon contamination peak caused by the fine electron beam is visible.
Fig. 6. Transmission electron micrograph showing the clear taenite II (T_{II}) martensite (M) boundary region in the Dayton meteorite.

Fig. 7a. Undecomposed lath martensite ($\varepsilon_3$) in the Tazewell meteorite.

Fig. 7b. Lenticular martensite ($\varepsilon_2$) in the Dayton meteorite.

Fig. 8. Decomposed martensite in the Tazewell meteorite. Fine $\gamma$ rods, ~20-30 nm wide, are formed in an $\varepsilon$ matrix.
Figs. 9a-c. Microdiffraction patterns from the $\gamma$ rods and $\alpha$ matrix of the Canton meteorite showing the two basic orientations. Figure 9a is a pattern from the $\alpha$ matrix while 9b and c are patterns from $\gamma$ rods in different regions of the decomposed structure. The two orientation relationships are Nishiyama (a/b) $\langle 011 \rangle / / \langle 001 \rangle$, and Kurdjumov-Sachs (a/c) $\langle 011 \rangle / / \langle 111 \rangle$.

Fig. 10. SEM photographs of duplex $\alpha + \gamma$ regions in the Edmonton meteorite. The black matrix is $\alpha$ and the $\gamma$ rods are 20–200 nm in width.


