Thermal histories of IVA iron meteorites from transmission electron microscopy of the cloudy zone microstructure

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Abstract–We have measured the size of the high-Ni particles in the cloudy zone and the width of the outer taenite rim in eight low shocked and eight moderately to heavily shocked IV A irons using a transmission electron microscope (TEM). Thin sections for TEM analysis were produced by a focused ion beam instrument. Use of the TEM allowed us to avoid potential artifacts which may be introduced during specimen preparation for SEM analysis of high Ni particles <30 nm in size and to identify microchemical and microstructural changes due to the effects of shock induced reheating. No cloudy zone was observed in five of the eight moderately to highly shocked (>13 GPa) IV A irons that were examined in the TEM. Shock induced reheating has allowed for diffusion from 20 nm to 400 nm across kamacite/taenite boundaries, recrystallization of kamacite, and the formation, in Jamestown, of taenite grain boundaries. In the eleven IV A irons with cloudy zone microstructures, the size of the high-Ni particles in the cloudy zone increases directly with increasing bulk Ni content. Our data and the inverse correlation between cooling rate and high-Ni particle size for irons and stony-irons show that IV A cooling rates at 350–200 °C are inversely correlated with bulk Ni concentration and vary by a factor of about 15. This cooling rate variation is incompatible with cooling in a metallic core that was insulated with a silicate mantle, but is compatible with cooling in a metallic body of radius 150 ± 50 km. The widths of the tetrataenite regions next to the cloudy zone correlate directly with high-Ni particle size providing another method to measure low temperature cooling rates.

INTRODUCTION

Constraints on the thermal histories of meteorites are invaluable for elucidating the sizes of their parent bodies and their isotopic ages and for understanding their origin (Ganguly and Stimpfl 2000; Trieloff et al. 2003). Although most studies of the thermal history of metallic Fe-Ni grains have focused on the metallographic cooling rates obtained from Ni zoning in taenite that developed during kamacite growth at ~650–400 °C, cooling rates at lower temperatures can be determined from the dimensions of the cloudy zone microstructure observed in residual taenite rims (Yang et al. 1997a).

Figure 1 shows scanning electron microscope (SEM) photomicrographs of the microstructure of taenite rims in the metal of several meteorites. At the high-Ni periphery of the taenite boundary with kamacite, sulfide or silicate, there is a narrow region that appears relatively clear on etching called the outer taenite rim (OTR) or tetrataenite region. The cloudy zone microstructure borders the outer taenite rim and formed by a spinodal phase transformation around 300 °C during cooling of meteoritic parent bodies. A distinct boundary is clearly observed between the OTR and CZ in the metal of the 3 meteorites shown in Fig. 1. The cloudy zone (CZ) has a structure in which high-Ni particles (“island phase”) are enclosed by a low-Ni phase (“honeycomb phase”). The formation of the spinodal is an uphill diffusion process. After initial formation, the phases grow during cooling and the cloudy zone structure coarsens by a diffusion-controlled process. Some of the high-Ni particles grow together and some of the high-Ni particles disappear in the coarsening process (See Figs. 1a and 1b).

Yang et al. (1997a) measured the size of the high-Ni particles at the outer edge of the cloudy zone adjacent to the tetratenite rim in various irons, stony-iron, and stony meteorites by high-resolution SEM. They showed that the size of the high-Ni particles increased with decreasing...
cooling rate. The sizes of the high-Ni particles range from 400–450 nm in the mesosiderites, which cooled very slowly (Fig. 1a) to ~20–40 nm (Fig. 1c) in the rapidly cooled IVA iron meteorites (Yang et al. 1997a). The metallographic cooling rate measured from the growth of the Widmanstätten pattern at temperatures from about 650 to 400 °C ranges from 0.2 °C/Myr for the mesosiderites (Hopfe and Goldstein 2001) to greater than 6,000 °C/Myr for the IVA iron meteorites (Yang et al. 2007, 2008). Since the inverse relationship between high-Ni particle size and metallographic cooling rate is applicable for metal in irons, stony-irons, and stony meteorites, the size of the high-Ni particles in the cloudy zone microstructure provides valuable information on the cooling rates of metal-bearing meteorites at 350 to 200 °C, for example, the anomalous Portales Valley chondrite (Sepp et al. 2001).

Measurements of the size of the high-Ni particles in the cloudy zone of fast-cooled meteorites such as the IVA irons are more difficult to obtain with the SEM as the size of the high-Ni particles approaches the resolution of the SEM (≤10 nm). Specimen preparation becomes more critical. The amount of chemical attack or etching used to reveal the cloudy zone microstructure can affect the measured size of the high-Ni particles and also the visibility of the microstructure in a high-resolution SEM. Too little etching will not produce enough contrast between the high-Ni particles and the low-Ni honeycomb phase to make the microstructure visible in the SEM. Too much etching will dissolve some of the high-Ni particles as well as the surrounding honeycomb phase. Because of their small size, the high-Ni particles in the cloudy zones of IVA irons are especially sensitive to shock. The thermal spike associated with the shock process can cause the high-Ni particles to dissolve rapidly with the formation of single phase taenite and the dissolution of the boundary between tetraenite and the prior cloudy zone. Slow cooling after the reheating process may allow formation of a new generation of cloudy zone by a spinodal reaction or perhaps precipitation of a new phase from the newly formed taenite. It may be difficult to tell which generation of cloudy zone is being observed in the SEM without microchemical data which can be measured using the transmission electron microscope (TEM) equipped with an X-ray (EDS) detector.

The current study was stimulated by the need to understand the low-temperature thermal history of the IVA iron meteorites. The metallographic cooling rates of the IVA irons determined from kamacite growth modeling vary directly with Ni content by a factor of ~60 indicating that the IVA irons formed in a 150 ± 50 km radius metallic body (Yang et al. 2007, 2008). The highest cooling rate of 6,600 °C/Myr allows for the formation of some of the smallest high-Ni particles, ~10 nm in size, in the cloudy zone of any group of meteorites. However, several members of the IVA chemical group have suffered shock reheating (Buchwald 1975), which may have affected the cloudy zone microstructure. In order to
measure the size of small high-Ni particles <30 nm in size, to avoid potential artifacts which may be introduced during specimen preparation, and to determine the microchemistry of the cloudy zone region in reheated IVA irons, we use the TEM, equipped with an X-ray (EDS) detector, to examine the cloudy zone structure.

The purpose of this study is three fold: 1) to measure the size of the high-Ni particles of the cloudy zone as well as the size of the surrounding outer taenite rim or tetrataenite region (Fig. 1) where present in a representative group of IVA irons using the TEM; 2) to use these size measurements to infer cooling rates for the IVA irons at low temperatures and to explain how the IVA irons formed in their parent asteroidal body; and 3) to determine the effect of shock and shock reheating on several moderately to heavily shocked IVA irons by examining the tetrataenite and cloudy zone microstructure using the TEM.

We will show that the widths of the tetrataenite regions correlate directly with cloudy zone particle sizes and indirectly with the cooling rate of the meteorite providing another measurement of low-temperature metal cooling rates. We also document, for the first time, examples of shock reheating in IVA irons that erased the cloudy zone microstructures which formed during initial cooling of taenite. Most critically, our studies of the cloudy zone microstructures in the IVA irons show that IVA cooling rates at 350–200 °C vary by a factor of ~15 and are inversely correlated with bulk Ni concentration. This cooling rate variation is incompatible with cooling in a metallic body of radius 150 µm alumina powder, and 0.05 µm silica. To minimize contamination, the samples were put in a glass container with ethyl alcohol or methyl alcohol and ultrasonically cleaned after each grinding or polishing step. Using this methodology, the kamacite-taenite interface is oriented perpendicular to the surface of the thin section. Figure 2 shows the region of interest and the FIB section formed for the TEM analysis of cloudy zone in a taenite region of the Bristol IVA iron. Three FIB samples were made of kamacite/taenite interfaces for Jamestown, Obernkirchen, and Seneca Township, all moderately to heavily shocked IVA irons that lacked a cloudy zone microstructure. Two FIB samples were made of kamacite/taenite interfaces for New Westville and Chinalauta and one FIB sample was made for the remaining 11 meteorites.

Selected kamacite/taenite interface regions in the thinnest areas of each FIB section were analyzed using a FEI Tecnai F30ST field emission transmission–analytical electron microscope (TEM-AEM) at Sandia National Laboratories or a VG 603 scanning transmission electron microscope (STEM) instrument at Lehigh University, both operated at 300 kV. X-ray scans were taken in micron and sub-micron sized regions of the thin foil. For iron meteorites with a cloudy zone, the size of the high-Ni particles in the cloudy zone next to the cloudy zone/tetrataenite boundary (Yang et al. 1997a) was measured directly from the STEM image or the Ni X-ray scan obtained from the thin foil. The measurement of the size of the high-Ni particles in the cloudy zone was made next to the cloudy zone/tetrataenite boundary since the local Ni content at that position is constant at 40 to 42 wt% Ni (Yang et al. 1997a). High-Ni particles farther away from the cloudy zone/tetrataenite boundary were not measured as the
Table 1. The 16 IV A irons studied by TEM.

<table>
<thead>
<tr>
<th>Meteorite name</th>
<th>Source</th>
<th>Ni(^*) (wt%)</th>
<th>P(^*) (wt%)</th>
<th>Shock level (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jamestown</td>
<td>AMNH88</td>
<td>7.45</td>
<td>0.02</td>
<td>13–40</td>
</tr>
<tr>
<td>La Grange</td>
<td>USNM55</td>
<td>7.57</td>
<td>0.03</td>
<td>13–75</td>
</tr>
<tr>
<td>Obenheimkirchen</td>
<td>USNM189</td>
<td>7.64</td>
<td>0.02</td>
<td>40</td>
</tr>
<tr>
<td>Bishop Canyon</td>
<td>USNM770</td>
<td>7.71</td>
<td>0.05</td>
<td>&lt;13 (13–40)</td>
</tr>
<tr>
<td>San Francisco Mtn</td>
<td>USNM1270a</td>
<td>7.73</td>
<td>0.05</td>
<td>&lt;13</td>
</tr>
<tr>
<td>Bristol</td>
<td>USNM1324</td>
<td>7.92</td>
<td>0.06</td>
<td>&lt;13</td>
</tr>
<tr>
<td>São João Nepomuceno</td>
<td>USNM6881a</td>
<td>8.02</td>
<td>–</td>
<td>&lt;13</td>
</tr>
<tr>
<td>Gibeon</td>
<td>UMass</td>
<td>8.04</td>
<td>0.04</td>
<td>&gt;13 (&lt;13)</td>
</tr>
<tr>
<td>Altonah</td>
<td>UMass</td>
<td>8.36</td>
<td>0.09</td>
<td>13–75</td>
</tr>
<tr>
<td>Seneca Township</td>
<td>AMNH3756</td>
<td>8.41</td>
<td>0.08</td>
<td>13–75</td>
</tr>
<tr>
<td>Bushman Land</td>
<td>USNM2515</td>
<td>8.76</td>
<td>0.1</td>
<td>&lt;13</td>
</tr>
<tr>
<td>Duchesse</td>
<td>UMass</td>
<td>9.28</td>
<td>0.18</td>
<td>&lt;13</td>
</tr>
<tr>
<td>Steinbach</td>
<td>USNM3086</td>
<td>9.40</td>
<td>0.15</td>
<td>&lt;13</td>
</tr>
<tr>
<td>New Westville</td>
<td>USNM1412</td>
<td>9.42</td>
<td>0.14</td>
<td>13–75</td>
</tr>
<tr>
<td>Chinatea</td>
<td>USNM742</td>
<td>9.54</td>
<td>0.17</td>
<td>&lt;13 (13–40)</td>
</tr>
<tr>
<td>Duel Hill (1854)</td>
<td>USNM2748</td>
<td>10.45</td>
<td>0.15</td>
<td>&gt;13</td>
</tr>
</tbody>
</table>

* Wasson and Richardson (2001).
* Buchwald (1975).
* Yang et al. (1997a).
* This study, optical and SEM.

Except for La Grange, Obenheimkirchen, Altonah, and Duel Hill, all the IV A irons listed above were studied using the scanning electron microscope.

The width of the outer taenite rim or tetrataenite region (Fig. 1) was also measured at several points along the kamacite/taenite interface in each TEM section. The widths are measured directly from STEM images or Ni X-ray scans in each meteorite. No correction for orientation effects was necessary for samples examined in the TEM since the kamacite-taenite interface is normal to the thin section (See Fig. 2c).

RESULTS AND DISCUSSION

High-Ni Particle Sizes of the Cloudy Zone

**SEM Data**

Figure 4 shows SEM pictures of 5 low shocked IV A irons. All low shocked irons have clear boundaries between the outer taenite rim (OTR) and the cloudy zone (Fig. 4). The cloudy zone microstructures are similar but not identical to the typical CZ microstructures shown in Fig. 1. Measurement of cloudy zone sizes are difficult to make in some of the SEM pictures and no attempt was made to obtain high-Ni particle sizes. Examination of the original SEM pictures of Yang et al. (1997a) show similar microstructures for the 5 low shocked IV A irons although the samples were usually heavily attacked by the nital etchant. Figure 5 shows SEM pictures of 3 medium to high shocked IV A irons. In these meteorites, the boundary between the outer taenite rim and the cloudy zone microstructure is no longer present. Starting about 100 nm from the kamacite-taenite boundary, there appears to be a microstructure that resembles the normal cloudy zone microstructure where cloudy zone was once present before reheating. This microstructure is, however, more irregular than that observed in the low shocked IV A irons and does not decrease in size systematically with increasing distance from the kamacite interface, as in the cloudy zone. In addition, as discussed below, there is no evidence for separation of high and low-Ni phases as in the cloudy zone. Examination of the original SEM pictures of Yang et al. (1997a) for the Gibeon meteorite show similar microstructures for the medium to high shocked IV A irons. The origin of this microstructure, which appears to have formed after shock heating, is unclear.

**TEM Data**

Eleven of the 16 IV A irons that were studied by TEM have a cloudy zone microstructure. Figure 6a shows a TEM bright field image of the cloudy zone, outer taenite rim and kamacite at a kamacite/taenite interface of the Steinbach IV A iron. This microstructure can be compared with the SEM image of a similar region of Steinbach, Fig. 1c. Figure 6b displays an annular dark field STEM image of the cloudy zone, outer taenite rim and kamacite at a kamacite/taenite interface in the Chinatea IV A iron. The cloudy zone is clearly observed and the sizes of 13 individual high-Ni particles, which were mostly spherical, potato-shaped, or elliptical in shape, were measured in the cloudy zone at the cloudy zone/
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outer taenite rim interface. Figure 7 shows Ni Kα X-ray area scans of the cloudy zone/outer taenite rim/kamacite interfaces at various magnifications from four low shocked IVA irons. The high-Ni particles in the cloudy zone vary in size from one IVA iron to another. Figure 7e gives a Ni composition profile across the kamacite/taenite interface in Fig. 7d. The Ni variation from ~50 to ~40 wt% Ni in the OTR is typical of the boundary region observed between the cloudy zone and kamacite for most low shocked iron meteorites (Yang et al. 1997b). The Ni content of the kamacite, which decreases below 5 wt% within 100 nm of this boundary, is also typical of Widmanstätten pattern formation. In addition, a measurable decrease in Ni content is observed at the boundary between the OTR and the CZ region for low shocked metal. The Ni content in the cloudy zone at this boundary is about 40 wt%. Figure 8 shows Ni Kα X-ray area scans at various magnifications of the cloudy zone microstructure which is present in two moderately to heavily shocked high Ni IVAs, New Westville, and Duel Hill.

The mean sizes of high-Ni particles in IVA irons vary from 10 nm to 32 nm as the Ni content of the meteorites increases from 7.7 to 10.45 wt%. In this Ni composition range, the measured metallographic cooling rate decreases from about 6,600 to 100 °C/Myr. The mean sizes of the high-Ni particles at the OTR/CZ boundary, the number of measured high-Ni particles, and the accompanying one σ measurement error for each of the IVA irons are given in Table 2. Since the typical thickness of a TEM thin section prepared with the FIB instrument is generally 50–100 nm, and the high-Ni particle size in IVA irons is 10 to 32 nm (Table 2), several high-Ni particles are intercepted by the focused electron beam as it passes through the TEM thin section. When the high-Ni particles overlap through the thin section, the contrast in the STEM and X-ray images is degraded, and

Fig. 2. FIB section of the Bristol kamacite/taenite interface. a) SEM photo of kamacite/taenite region of interest. The square indicates the region from which the FIB sample was extracted. b) Higher magnification SEM photo of kamacite/taenite region showing outer taenite rim, decomposed martensite, and plessite in the center of the region. The crosses indicate the position from which the FIB sample was extracted. c) SEM photo of FIB section which is normal to the sample surface. The sample is a wafer about to be cut out of the sample. The kamacite/taenite boundary which intersects the sample surface can be observed in the thin FIB sample.

Fig. 3. Shows a variety of particle shapes that are observed in the IVA irons. For the near spherical particles (Fig. 3a), the size of the particle is measured across the diameter. For the potato-shaped particles (Fig. 3b), the size of the particle is the width along the minor axis. For the egg, banana, and raindrop shapes (Figs. 3c–e), the width is measured along the minor axis which splits the major axis of the particle in two. For amoeba-shaped particles (Fig. 3f), the size of the particle is the shortest distance from one corner to the other side.
it is more difficult to measure the island phase size (see Figs. 7a and 7b, and 8a, 8b). Figures 8c and 8d illustrate how the size measurement of the high-Ni phase was made for the Duel Hill IVA iron. Figure 8c shows the low pass filtered image of Fig. 8b, which in this example helps better establish the interfaces of the high-Ni particles. Figure 8d shows the outline of the 8 high-Ni particles that were measured and the positions where the size measurements were made. We estimate that the measurement errors in the mean high-Ni particle size of each IV A iron are 10 to 20% relative, Table 2.

For most IV A irons, only a single cloudy taenite region was studied, and we cannot exclude the possibility of variations between regions. However, for New Westville and Chinautla more high-Ni particles were measured since two FIB sections were made and several cloudy zone regions were available for measurement. For New Westville the mean high-Ni particle size was 17.6 nm and 17.9 nm for two different cloudy zone regions measured with the FEI instrument and 21.2 nm for one cloudy zone region measured with the VG instrument. The mean high-Ni particle size using all the measurements was $20 \pm 3$ nm (Table 2), and the differences between mean particle sizes measured for 3 separate cloudy zones were within the $1\sigma$ measurement error. For Chinautla, the mean particle size was $30 \pm 4.5$ nm for one cloudy zone.
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region measured with the FEI instrument. In this one case, we were also able to measure a mean high-Ni particle size of $31.2 \pm 3.8$ nm using the annular dark field STEM image (Fig. 3b). The mean high-Ni particle size in the second FIB section of Chinautla was $33.5 \pm 5.4$ nm measured with the VG instrument. The mean high-Ni particle size using all the measurements was $32 \pm 4.5$ nm (Table 2) and the differences in mean particle size measured for 3 separate cloudy zones were well within the $1\sigma$ measurement error.

Figure 9a shows that the high-Ni particle size of the eleven IVA irons with a cloudy zone microstructure is positively correlated with the bulk Ni content. Since the metallographic cooling rate determined from kamacite growth at temperatures between 650 and 400 °C decreases with increasing Ni content (Yang et al. 2008, Table 1), the high-Ni particle size also decreases with increasing metallographic cooling rate, Fig. 9b.

The mean width of the tetrataenite region for one or more kamacite/tetrataenite interfaces of each of the eleven IVA irons that contain a cloudy taenite microstructure is given in Table 2. The error in the width of the tetrataenite region, Table 2, represents the range of tetratenite widths measured for each meteorite but is limited to the length of kamacite/taenite boundaries.
Figure 10 shows that the width of the tetrataenite region is positively correlated with the high-Ni particle size in the cloudy taenite. Therefore, the tetrataenite width also increases with increasing Ni content and decreases with increasing metallographic cooling rate. The measured sizes of the high-Ni particles in the three moderately to heavily shocked IV A irons which contain a cloudy zone microstructure fall below the trend defined by the unshocked IV A irons, Fig. 10. Considering the errors in the measurement of high-Ni particle sizes, it is not clear if this observation is significant.

The Effect of Shock and Shock Reheating

The cloudy zone microstructure was not present in 5 moderately to heavily shocked IV A irons (Tables 1 and 2). Figure 11a
Thermal histories of IVA iron meteorites from transmission electron microscopy shows a STEM image of the kamacite/taenite interface in a thin section of Jamestown, the lowest Ni (7.45 wt%) IVA iron that was studied. The kamacite is recrystallized with grain sizes of ~200 to 500 nm and the kamacite/tetrataenite interface is wavy. No cloudy zone or tetrataenite/cloudy zone boundary is observed. The SEM photomicrograph of Jamestown (Fig. 5) also shows the absence of the outer taenite rim (OTR)/cloudy zone interface. Figure 11b shows a 2 × 2 µm Ni X-ray scan along the kamacite/taenite interface shown in Fig. 11a. Although no cloudy zone is observed, the high Ni taenite region (OTR) can still be observed in most places. Several grain boundaries containing about 20 wt% Ni have formed across the tetrataenite region. The Ni content in kamacite rises somewhat to about 5 wt% (compare to Fig. 7e) during reheating. In addition, a Ni-enriched diffusion zone up to 200 nm in width is observed in the kamacite next to the kamacite/taenite interface. The grain boundaries have formed in the taenite normal to the kamacite/taenite boundary and allow a rapid diffusion path and local removal of the Ni-rich rim. Figure 11d shows two Ni versus distance profiles across the kamacite/taenite interface. The position of the two profiles 1 and 2 are shown in Fig. 11c. Profile 1 shows the Ni distribution well away from the newly formed grain boundaries while profile 2 crosses a kamacite/taenite boundary between two of the newly formed grain boundaries. Diffusion across the kamacite/taenite interface varies from as little as 30 nm (profile 1) to 200 nm (profile 2). In profile 2 we observe that the Ni in the taenite next to the original kamacite/tetrataenite boundary has decreased from about 50 wt% to almost 30 wt% (compare with Fig. 7e) due to diffusion through taenite and along newly formed taenite grain boundaries which form at high shock temperatures. As shown in Fig. 11d, regions beyond about 200 nm from the kamacite/taenite boundary have Ni contents less than about 30 wt% Ni. During cooling after the shock reheating event, new high Ni regions may form, as observed in Figs. 11c, 11d.
This secondary microstructure, developed on cooling after diffusion takes place, is also observed in the SEM images of Gibeon, Fig. 5. This microstructure is probably decomposed martensite in Jamestown.

Figure 12a shows a STEM image of the kamacite/taenite interface in the Obernkirchen IVA meteorite, the third lowest Ni (7.64 wt%) IVA iron that was studied. Shock heating is more limited in this meteorite. Figure 12b shows a 1 × 1 μm Ni X-ray scan along the kamacite/taenite interface shown in Fig. 12a. Although no cloudy zone microstructure is present, the Ni X-ray map shows that there is an intermittent Ni-rich zone remaining with up to ~40 wt%. Profile 1 (Figs. 12c, 12d) shows diffusion across the kamacite/taenite interface extending about 30 nm into kamacite with a decrease in Ni content in taenite at the OTR/kamacite boundary from about 50 to 45 wt%. The Ni content in kamacite rises somewhat to over 5 wt%. In addition, there is no abrupt decrease in Ni content as normally observed at the tetrataenite/cloudy zone boundary (See Fig. 4e). Profile 2 (Figs. 12c, 12d) shows a more extensive diffusion zone of about 150 nm with a decrease in Ni content in the outer taenite region from about 50 to 30 wt%. As in Jamestown, the Ni content in kamacite rises somewhat to about 5 wt%. Altonah (8.36 wt% Ni) is also shock reheated at about the same level as Obernkirchen. Although no grain boundaries are observed, the kamacite/taenite interface is no longer straight with extensive diffusion of up to 400 nm. The Ni content in the outer taenite region decreases from about 50 to about 35 wt%. No cloudy zone is present, and there is no abrupt decrease in Ni content as normally observed at the tetrataenite/cloudy zone boundary (See Fig. 7e).
in Seneca Township, no Ni variation at an X-ray spatial resolution of 2 nm is observed. The fine-scale microstructure in the SEM image, Fig. 5, may have been identified as the cloudy zone by Yang et al. (1997a).

We have made some relatively simple diffusion calculations to put limits on time and temperature during shock reheating which causes the disappearance of the cloudy zone and produces the diffusion profiles across the kamacite/taenite interface (Figs. 11–13). To calculate potential time-temperature scenarios, we used the interdiffusion coefficients $D$ for Fe-Ni in taenite ($\gamma$–fcc) as a function of temperature (Goldstein et al. 1965). To calculate diffusion distances, $X$, we used the approximation that the distance over which diffusion takes place is roughly equal to the square root of the product of the inter-diffusion coefficient $D$ at a given temperature times the reheating time $t$:

$$X \approx (Dt)^{1/2}$$

We calculate that reheating to 1000 °C for two seconds will remove 20 nm sized high-Ni particles and reheating for 40 seconds will cause diffusion zones up to 100 nm in width to develop across kamacite/taenite boundaries. Longer times at lower temperatures are required for the removal of 20 nm sized high-Ni particles in the cloudy zone, for example ~20 s at 900 °C, ~7 min. at 800 °C, and ~4.7 h at 700 °C. Reheating at low temperatures, <550 °C requires times exceeding a year. Grain boundary formation in the taenite will aid the diffusion process decreasing the time necessary for Ni diffusion between kamacite and taenite. Although mild impact heating to low temperatures may require long times to dissolve the cloudy zone, even a few seconds at these low temperatures should be sufficient to disorder the tetraetaenite in the high-Ni particles to form disordered taenite since no diffusion is involved. However, we did not check whether tetraetaenite was still ordered. Impact heating that erases the cloudy zone microstructure and allows diffusion over distances up to 100 nm will not affect the Ni gradient that is measured with the electron microanalyzer since these X-ray data are obtained with micron-level resolution. Therefore the reheating process considered for removal of the cloudy zone in the IVA irons will not affect the Ni gradient and the central Ni content of the taenite which are used to obtain metallographic cooling rates.

It is curious that two high-Ni slow cooled IVA irons, New Westville and Duel Hill, and the fastest cooled low-Ni IVA iron, La Grange, all contain a cloudy zone microstructure even though they suffered moderate to high shock. In the five other moderately to highly shocked IVA irons, features such as grain boundary formation and diffusion at kamacite-taenite boundaries were observed along with the loss of the cloudy
zone microstructure. Apparently, the shock process allowed for local heating of these meteorites but not for New Westville, Duel Hill, and La Grange. It appears that the shock event which removed the cloudy zone in some but not all moderate to highly shocked IV A irons takes place after the IV A irons cool below 300 °C, probably in the event that produced the meter-sized bodies that find their way to Earth. Since shock effects are highly dependent on the direction of the shock wave and the orientation of the sample with respect to the shock wave, it is quite possible that other samples of the same meteorite may have been subjected to a thermal cycle which removed the cloudy zone structure. Another possible explanation for heterogeneous shock heating in IV A irons is that some irons like Gibeon, which contain troilite nodules 2–20 mm in size, were shock melted. The post-shock thermal histories of taenite grains were probably dependent on the distance from the nearest shock-melted troilite nodule and its size.

Comparison with Previous High-Ni Particle Size Measurements

Except for New Westville, the high-Ni particle sizes determined by Yang et al. (1997a) using SEM techniques are 20 to 100% larger than the values we obtained using TEM measurements (Table 2). The difference between the SEM and TEM measurements is larger for the IV A irons with the smaller high-Ni particles. It is probable that the effect of the heavy etching employed in the specimen preparation process by Yang et al. (1997a) to enhance contrast for SEM examination of the high-Ni particles is responsible for these differences in high-Ni particle size. In the etching process, the low-Ni phase in the cloudy zone is preferentially etched away during chemical treatment. The secondary electron signal which is recorded is obtained not only from the high-Ni particles on the flat polished surface but also from high-Ni particles of the cloudy zone which are exposed when the low-

Fig. 11. Jamestown IVA iron. a) STEM image of the kamacite/taenite interface, 2 µm × 2 µm scan area, 256 pixels, ~7.7 nm/pixel. The kamacite/taenite interface is vertical in the image. b) Ni X-ray area scan of 2 µm × 2 µm, color scale gives the Ni content from 5 to 50 wt%. c) Ni X-ray scan of 2 × 2 µm area. The position of the Ni profiles is shown by the dashed rectangles. Two grain boundaries are noted by the heads of the arrows. d) Ni composition profiles across the kamacite/taenite interface 1) well away from newly formed grain boundaries and 2) between two grain boundaries.
Ni phase is etched away. The low kV electron beam employed to view the high-Ni particles is particularly sensitive to surface details and the size of the cloudy zone high-Ni particles may not be accurately represented. This effect is greater as the size of the high-Ni particles decreases since the electron beam interacts with more of these high-Ni particles in 3 dimensions. We did not make any thorough examination of the effect of etching although from Fig. 4 it is clear that the ability to measure small-sized high-Ni particles is very dependent on preparing a sample with just the right etching treatment.

Wasson and Richardson (2001) and Wasson et al. (2006) argue that the 6 high-Ni particle sizes measured by Yang et al. (1997a) indicate constant cooling rates for the IVA irons and interpret this result as evidence that the diverse cooling rates determined from kamacite growth models are flawed. However, except for the New Westville measurement, the Yang et al. (1997) data show a direct variation of high-Ni particle size with Ni content and decreasing metallographic cooling rate (Table 2).

Unfortunately, the original Yang et al. (1997a) data for low Ni IVAs were probably inaccurate because of the effect of the etching treatment in the preparation of the samples for SEM observation with high-Ni particles <30 nm in size as discussed above. As shown in Fig. 5, measurements of cloudy zone sizes are difficult to make using SEM photomicrographs, for example some of the IVA irons that were investigated in this study. Another possible problem with the data of Yang et al. (1997a) is that the microstructure in Gibeon that we observed with the SEM (Fig. 5) was formed during cooling after the major shock event. This shock event removed the original cloudy zone microstructure which developed during Widmanstätten pattern formation. We infer that our measurements of the high-Ni particle size in IVA irons using X-ray images and bright and dark field images from the TEM are more accurate than the SEM data since the high-Ni particles are observed directly without the need to enhance contrast by special specimen preparation techniques and the microchemical effects of shock-induced reheating can be directly observed.
Sizes of High-Ni Particles and Tetrataenite Rims as Cooling Rate Indicators

The inverse relationship between cooling rate and high-Ni particle size for mesosiderites, pallasites, IIIAB and IV A irons is shown in Fig. 14. This diagram resembles that shown by Yang et al. (1997a), but the new data show less scatter for the faster-cooled meteorites. High-Ni particle sizes decrease by a factor of ~30 as the metallographic cooling rate increases by 4 orders of magnitude (0.2 °C/Myr to 6,600 °C/Myr).

Cooling rates and the variation of cooling rate with high-Ni particle size cannot be derived directly because there is no effective model available for spinodal growth (Yang et al. 2007). However, the relative cooling rates of two meteorites, (CR₁) and (CR₂), can be estimated empirically from the ratio of their respective high-Ni particle sizes (PS₂/PS₁):

\[
(CR₁/CR₂) = (PS₂/PS₁)^n
\]

The parameter \( n \) obtained from Fig. 14 equals 2.4 ± 0.4. Given the threefold variation in IVA high-Ni particle size (2.9 ± 0.5; Table 2), Yang et al. (2007) estimate that cooling rates at 300–100 °C varied by a factor of ~15, decreasing with increasing bulk Ni.

We have shown that the width of the outer taenite rim (OTR) or tetrataenite region, which separates the kamacite from the cloudy zone, increases in size with increasing high-Ni particle size (Fig. 10). The measurement of the width of the OTR is a new method that can be applied to obtain relative cooling rates of meteorites. Since high-Ni particle size increases with decreasing metallographic cooling rate, the tetrataenite width also correlates inversely with metallographic cooling rate. The increase in the width of the outer taenite rim and increasing cooling rate is consistent with the fact that the tetrataenite phase nucleates below 350 °C and grows by diffusion control (Yang et al. 1997b). The measurement of the width of the OTR can be made directly on a TEM thin section. However, only one kamacite/taenite interface is usually available for measurement from each FIB prepared TEM thin section. Ultimately, a more thorough investigation is needed using a number of FIB samples for each meteorite to establish the constancy of the width of the OTR. It should be possible, however, to measure the width of the tetrataenite with the SEM on a variety of kamacite/taenite interfaces as long as the orientation of the interface with the polished surface is known.

**IVA Cooling Rates and Impact Histories**

The results of this study of cloudy zone microstructures for group IVA combined with the cooling rates for these iron meteorites based on kamacite growth models show that the IVA irons cooled with very diverse cooling rates that correlate inversely with bulk Ni compositions. Cooling rates varied by a factor of over 50 from ~650 to ~400 °C and most likely by a factor of 15 during cloudy zone formation below 350 °C—ranges that are totally incompatible with cooling in a mantled core. The cooling rates of low-Ni IVA irons from ~650 to ~400 °C are also incompatible with conventional models for igneous differentiation of chondritic asteroids melted by \(^{26}\)Al. To cool a mantled core at 6,600 °C/Myr would have required a body with a radius of only ~2.5 km, according to thermal models of differentiated asteroids (Haack et al. 1990). However, only bodies 10–20 km or more in radius could have been melted appreciably by \(^{26}\)Al (Hevey and Sanders 2006).
The only plausible solution to the IVA cooling rate enigma is that the IVA irons cooled in a metallic body with virtually no silicate mantle so that it had a significant thermal gradient when kamacite nucleated at ~700 °C (Yang et al. 2007).

Yang et al. (2008) infer that the IVA irons are the product of at least three different impact events. The first was the creation of the metallic body with virtually no silicate mantle. Yang et al. (2007, 2008) suggest that a grazing collision between protoplanets created a 150 km radius molten metal body from a differentiated protoplanet 10^3 km in diameter. This body would develop a steep thermal gradient on cooling that could explain the cooling rates of the IVA irons. Inwards crystallization would account for the correlation between Ni content and cooling rate. The second impact occurred after the 150 km body had cooled below ~100 °C, perhaps only ~20 Myr later, and produced a fragment >30 km across or, more likely, a smaller rubble pile body perhaps a few kilometers in size. The third impact 400 Myr ago destroyed this smaller metallic body generating a swarm of meter-sized metallic fragments that are still drifting into a major resonance at the inner edge of the asteroid belt and bombarding the Earth. The medium-to-high shock event that affected many IVA irons probably occurred during the third impact. The second impact is required because demolition of a 150 km radius metallic body 450 Myr ago should have produced a family of metallic asteroids, which are not observed.

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