A THREE-DIMENSIONAL STUDY OF METAL GRAINS IN EQUILIBRATED, ORDINARY CHONDRITES

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Abstract. Metal particles in Guareña (H6), Colby (L6), and St. Severin (LL6) were studied by optical microscopy and by electron microprobe analysis. Observations from successive polished sections through the metal particles show that kamacite and taenite grains, which often appear to be isolated particles, are connected directly or by intervening sulfides. Also tetrataenite rims are widest when adjacent to sulfide or kamacite. These observations indicate that transfer of Ni during cooling when kamacite-taenite phase growth takes place does not occur through the silicate phases but proceeds through metal and sulfide phases or along grain boundaries. By utilizing the central Ni content of taenite grains from successive sections, metallographic cooling rates were determined more precisely than by using one arbitrary section. Cooling rates determined in this manner for Guareña, Colby, and St. Severin are 4.3 K m.y. \(^{-1}\), 4.0 K m.y. \(^{-1}\), and 1.0 K m.y. \(^{-1}\), respectively.

Introduction

Metallic structures in chondrites have been studied using optical and electron microscopy by various scientists over the past twenty years [Wood, 1967]. Wood [1967] examined 35 chondrites and presented metallographic descriptions and electron microprobe analyses of metallic grains. Wood proposed that Ni and Fe were able to move effectively from one grain to another through intervening silicates so that isolated kamacite and taenite grains are in effective contact. With this assumption and a modification of the computer program he developed to determine cooling rates in iron meteorites, he was able to deduce cooling rates for the chondrites. Wood's cooling rate technique is based on the premise that the Ni concentration of the center of each taenite particle is a function of taenite radius and cooling rate. Computer calculations of Ni content in the centers of taenite grains versus grain radius for various cooling rates are compared with a set of Ni content-grain-radius data for a particular meteorite. A unique cooling rate is obtained when a good match is found for the measured and calculated data. The fact that the data from a number of meteorites matched well with the computer calculations was cited by Wood [1967] as evidence that the model was correct. However, data sets from some meteorites did not match well and other data sets had much more scatter than could be accounted for experimentally from errors in the microprobe analyses.

Taylor and Heymann [1971] observed that not all the taenite grains are zoned. Clarke and Scott [1980] pointed out that these unzoned or clear taenite grains are new metallic phase, tetrataenite, consisting of ordered FeNi. Tetrataenite occurs in chondrites as massive grains, \(\sim 5\) to \(50\ \mu m\) in size, as a rim phase bordering cloudy taenite, and as \(\mu m\)-sized crystals in the cloudy zone taenite. Current computer programs used in cooling rate studies have not included the growth of tetrataenite since calculations are terminated at \(350^\circ C\), just above the temperature where tetrataenite in proposed to form.

Major questions still remain to be settled concerning the nature of the metallic structures found in chondrites. Among these are, why are metallographic cooling rates a factor of 5 or more slower than those obtained by \(\alpha^{39}Ar-\alpha^{39}Ar\) techniques [Turner, et al. 1978] or \(^{239}Pu\) fission track techniques [Pellas and Storzer, 1977 and 1981], and why do some of the central Ni content versus taenite grain size measurements made by Wood [1967] and Taylor and Heymann [1971] contain excessive scatter and show trends that are not parallel to the calculated trends?

In this paper, we look for answers to these questions by examining the structure of the metallic grains in several chondrites in three dimensions. We report on the interrelationship between kamacite, taenite, tetrataenite, troilite, and silicate phases and show the effects of random sectioning of taenite grains on the measured chondrite cooling rates.

Experimental Procedure

The microstructures of three ordinary chondrites Guareña (H6), Colby (L6), and St. Severin (LL6) were examined in detail. Samples of each meteorite were mounted and polished, then lightly etched with 2% nital. In general, this etch did not affect the tetrataenite phase and caused kamacite to darken slightly. Zoned taenite grains were typically stained with a cloudy (grey) zone adjacent to rim tetrataenite, a narrow, multicolored rim on the inner edge of the cloudy zone and a brownish-white central region. The brownish-white region was observed in those grains in which the Ni content of the center was less than 35 wt % Ni. In some cases the etch did not affect one or two zoned taenite grains even though all other zoned taenite grains were etched. These unetched grains could be stained by prolonged etching.

In the initial microstructural study of a sample 20 to 30 grains were selected as representative of the metal grains in the sample and their positions and shapes recorded. Approximately 10 \(\mu m\) of material was removed from the surface by surface grinding and the sample was repolished and reexamined. In the second section the same grains were identified and reexamined. This procedure was repeated so that six sections in Guareña, two sections in Colby, and four sections in St. Severin were studied. In a number of cases specific metal grains disappeared between sections.
Fig. 1. Sketches representing the range of microstructures observed in the metallic grains of Guarea: $\alpha =$ kamacite, $\gamma =$ taenite, Tt = tetrataenite, and FeS = troilite.

To keep track of the material removed in each successive section, microhardness indentations were made in three or four metal grains. The depth of the indentation was calculated from the diagonal length of the indentation and the angle of the diamond indentor, and was determined for each section. The difference in depth between successive sections represented the thickness of the material removed.

At each stage of the serial sectioning, the samples were carbon coated and the metal grains analyzed for Fe, Ni, and Co with an electron microprobe (ARL-EMX). Pure Fe, Ni, and Co metal and a set of Fe-Ni alloys were used as standards. An energy dispersive spectrometer was used for Fe analyses, while wavelength dispersive spectrometers (LiF crystals) were used for Ni and Co. Operating conditions were 20 kV and 25 nA sample current. The Fe, Ni, and Co contents were calculated from the X ray data using a ZAF correction procedure.

Metallographic Observations

Guarea

The variety of microstructures observed in the metallic grains in Guarea is summarized in Figure 1. Taenite occurs in two modes, either (1) isolated or attached to sulfides; or (2) attached to kamacite. Taenite associated with troilite or as individual grains in silicates is irregularly shaped but has rounded features (Figure 2). A tetrataenite rim surrounds each taenite, generally about 1 to 2 $\mu$m wide adjacent to silicate but up to 5 or 6 $\mu$m wide adjacent to troilite. Inside the rim tetrataenite is a cloudy zone ~10-15 $\mu$m wide, uniform in width and following the contours of the particle boundary. In the particles observed, the zoning consisted of unbroken, concentric rings except in a few cases in which troilite intruded the particle. In these cases, the zoning attempted to surround these intrusions.

There are many examples of taenite and kamacite phases in the same particle. When etched, the taenite acquired the same zoning pattern as described for taenite grains associated with troilite. In most cases, the taenite grains are less than 20 $\mu$m across and are not large enough to display the full range of zoning. From our metallographic observations in Guarea it appears that kamacite nucleated on one side of a taenite sphere and grew across the sphere. Examples of various stages of growth are illustrated in Figure 3. We did not observe any cases in which kamacite appeared either to nucleate in the center of taenite grains or to nucleate around the perimeter of a taenite grain and grow radially inward.

The tetrataenite adjacent to the kamacite and the troilite is wider than the tetrataenite adjacent to the silicate. The high Ni rim and tetrataenite surrounding FeS were developed as Ni left FeS due to decreasing Ni solubility on cooling. Tetrataenite adjacent to kamacite grows with Ni supplied as the kamacite Ni solubility decreases. Because the Ni zoning occurs around each metal particle, one can conclude that some Ni is entering the taenite grain from the taenite/silicate boundary. It is likely that surface diffusion or grain boundary diffusion is sufficiently fast to transport Ni around the perimeter of the taenite grain.

Kamacite grains were observed in three forms,
either associated with taenite, associated with sulfide, or isolated (Figure 1). No zoning or Neumann bands were observed on etching. The kamacite grains were usually polycrystalline with crystal dimensions ranging from submicron to \( \sim 100 \, \mu m \). A few metallic grains are a fine grained mixture of kamacite and taenite (plessite). An example of the microstructure of such a particle is seen in Figure 4.

By observing the metallic grains in three dimensions with our serial sectioning technique, we were able to make the following additional observations. Seventeen zoned taenite grains followed through four or more sections were observed as isolated taenite grains in at least one or more of the sections. Of these 17, five were identified as isolated taenite grains in section 1 and were associated with FeS in a later section. Two taenite grains associated with FeS in section 1 were observed as isolated taenite grains in later sections. Of the isolated taenite grains or the taenite grains associated with FeS, several were also connected to kamacite either in one or more sections. In addition, for 16 apparently isolated kamacite grains, six were attached to taenite in other sections.

These observations suggest that isolated kamacite and isolated taenite grains do not really exist in three dimensions. Taenite grains that appear isolated are attached to troilite grains and/or kamacite grains in a third dimension, not visible in the examined section. The taenite grains may be connected to kamacite directly or are linked to kamacite by troilite (FeS). Kamacite grains that appear isolated are connected to taenite grains through troilite or have taenite crystals on one edge (Figures 1 and 3). Since the taenite region may represent only about 20% of the total metal particle, it may not be observed in many sections.

Truly isolated metal particles are represented by the plessite particles and fine grained kamacite-taenite particles (Figures 1 and 4). These particles exhibit no evidence of having exchanged Ni with other grains and their bulk Ni contents are very close to the bulk Ni content of the metal phases of the meteorite. This evidence, in conjunction with the observations that no single-phase particles are present in the meteorite and that tetrataenite rims are narrowest when adjacent to silicates, indicates that little if any Ni transport takes place through the silicate grains.

Colby

The metallography of Colby is similar to that of Guareña. One difference between the two meteorites is that the kamacite in Colby often contains Neumann lines. Other differences are that a few of the taenite grains in Colby have plessitic centers and that not all the taenite particles have symmetrical zoning patterns. The first of these differences indicates that Colby has undergone a different shock history from Guareña. The other differences suggest that Colby might be populated with metal grains from different sources.
of these spheres had a Ni content of 10 wt %. The result of off-center sectioning is to decrease the apparent cooling rate of the meteorite. Willis and Goldstein [1981] showed that 75% of the data points from a large number of random sections through a sphere will yield cooling rates between 60% and 100% of the actual value.

Nine taenite particles in Guara were analyzed in five successive sections. The data, presented in Figure 8, generally follow the trends predicted in Figure 7. The smaller taenite particles tend to yield slower cooling rates.

One technique for minimizing the effects of off-center sectioning is to analyze the same taenite particles in a set of successive sections, as shown in Figure 8. One selects the best data point for each taenite particle. Presumably the lowest Ni content data point most closely approximates the composition of the center of the sphere. Similar data points from a number of taenite particles are plotted on a central Ni content versus taenite particle size diagram to obtain the cooling rate. Figure 9 shows a composite central Ni content versus taenite radius diagram for Guara using the best data points for each of the taenite particles studied. The cooling rates determined for the six individual sections and for the composite diagram (Figure 9) are given in Table 1.

The composite cooling rate for Guara represents an improvement over the cooling rates from the individual sections. Scatter in the data is considerably reduced. However the data still trend toward slower cooling rates at smaller grain sizes and this may still reflect off-center sectioning in the smaller grains.

Figure 10 contains cooling rate plots for Colby and St. Severin. The plots for Colby and St. Severin are composite diagrams incorporating data from two and four sections, respectively. The measured cooling rates are 4.0 K m.y.\(^{-1}\) and 1.0 K m.y.\(^{-1}\), respectively. The cooling rate obtained for St. Severin is the same as that of Taylor [1976]. The scatter in the Colby data could be reduced by examining additional sections. However, the possibility that the scatter is related to the events that produced the mild shock features in the metallic structures cannot be ruled out.

The scatter in the St. Severin data is more

**St. Severin**

In general, the metal grains in St. Severin are generally highly irregularly shaped with the exceptions of the small (~25 µm) taenite grains. A typical structure for a large metal grain is shown in Figure 5. The metal grain edges are very jagged and the zoning, as indicated by the etch patterns, closely follows these jagged edges. As was observed in Guara, rim tetra-taenite adjacent to kamacite and troilite was wider than tetrataenite adjacent to silicate minerals. No isolated plessite or kamacite particles were seen in St. Severin.

**Cooling Rates**

The procedure for computing metallographic cooling rates of chondrites was first described by Wood [1967]. We recently revised the computer model for the Wood procedure [Willis and Goldstein, 1981] and these cooling rate plots are used in this paper. A potential source of error in the metallographic technique is in analyzing taenite grains which have not been sectioned through their centers. Figure 6 shows an idealized sphere of zoned taenite, sectioned in three planes, and the respective Ni concentration profiles that would result from microprobe scans of each section. The central Ni content-taenite radius data for each of the three sections will not yield a unique cooling rate. Figure 7 shows three such data points plotted for each of two idealized taenite spheres, one of which cooled at 1.0 K m.y.\(^{-1}\), the other at 10.0 K m.y.\(^{-1}\). Both

**Fig. 6.** Ni concentration gradients for three arbitrary sections through a computer modeled sphere. The sphere was assumed to be 10 wt % Ni, to have initially nucleated kamacite around its outer rim. Data from such spheres were used to calculate the cooling rate curves in Figure 7.
Fig. 7. Calculated central Ni content versus taenite radius curves for three sections from each of two idealized taenite spheres (note Figure 6) containing 10 wt % Ni. One of the spheres was assumed to cool at 1.0 K m.y. \(^{-1}\), the other at 10.0 K m.y. \(^{-1}\).

difficult to explain. The irregularity of the grains can account for some of the uncertainty, but examining multiple sections did not significantly reduce the scatter. There is no evidence that the meteorite has been shocked, nor is there evidence for multiple parent body sources for the metal grains, so these mechanisms for inducing scatter can be ruled out. The most likely source of the data scatter is the formation of tetra-taenite during the later stages of cooling. Since St. Severin has a higher Ni content than most chondrites, the taenite to tetra-taenite transformation should play a more important role in establishing the distribution of Ni. The tetra-taenite transformation produces a discontinuity in the Ni zoning between 40 and 50% Ni. The discontinuity will also be reflected in the computed cooling rate curves. Until the effects of this transformation are incorporated into the cooling rate calculations, data from taenite grains and cooling rate curves greater than 40% Ni should be discounted.

New measurements of Fe-Ni diffusivities at low temperatures, \(\leq 1000^\circ C\) have been made [Narayan and Goldstein, 1983]. These measurements are consistent with data used in our computer model assuming no P is present in the metal. If chondritic metal had P exceeding \(0.05\) wt %, Narayan and Goldstein's higher diffusivities for P containing metal would lead to a calculation of faster cooling rates.

**TABLE 1. Cooling Rates for the Individual Sections and for the Composite of Data for Guärëña**

<table>
<thead>
<tr>
<th>Section</th>
<th>Cooling Rate (K m.y. (^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>4.4</td>
</tr>
<tr>
<td>3</td>
<td>4.6</td>
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<td>5</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>2.7</td>
</tr>
<tr>
<td>Composite</td>
<td>4.3</td>
</tr>
</tbody>
</table>
Summary

From our metallographic observations we can make four general statements concerning the metal grains in equilibrated ordinary chondrites: 1. zoned taenite grains are always attached directly or indirectly through troilite to kamacite grains; 2. kamacite grains are always attached to taenite or troilite; 3. tetrataenite grains are always attached to kamacite or tetrataenite forms as a rim around taenite grains; and 4. isolated metal particles contain the bulk Ni content of the meteoritic metal, are not zoned and contain intergrowths of kamacite and taenite.

Ni redistribution during cooling takes place by diffusion through metal and troilite grains or along metal-metal, metal-troilite, metal-silicate, and troilite silicate grain boundaries. In cases where a metal grain is isolated from all other metal or sulfide grains, Ni does not diffuse through silicate grains or along silicate-silicate grain boundaries.

Metallographic cooling rates for chondrites can be improved if data are gathered on two or more successive sections. Scatter in the data was improved using this technique although the actual cooling rate was not significantly altered. Not all of the scatter can be attributed to grain morphology or off-center sectioning. Some of the scatter at high Ni contents is related to the formation of tetrataenite. Because the metallographic cooling rates are not altered significantly by this work, we can offer no new solution to the discrepancy between metallographic cooling rates and Ar or Pu cooling rates.

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