Thermal and collisional history of Tishomingo iron meteorite: More evidence for early disruption of differentiated planetesimals

Jijin Yang, Joseph I. Goldstein, Edward R.D. Scott, Joseph R. Michael, Paul G. Kotula, Ansgar Grimberg, Ingo Leya

Abstract

Tishomingo is a chemically and structurally unique iron with 32.5 wt.% Ni that contains 20% residual taenite and 80% martensite plates, which formed on cooling to between −75 and −200 °C, probably the lowest temperature recorded by any meteorite. Our studies using transmission (TEM) and scanning electron microscopy (SEM), X-ray microanalysis (AEM) and electron backscatter diffraction (EBSD) show that martensite plates in Tishomingo formed in a single crystal of taenite and decomposed during reheating forming 10–100 nm taenite particles with 50 wt.% Ni, kamacite with 4 wt.% Ni, along with martensite or taenite with 32 wt.% Ni. EBSD data and experimental constraints show that Tishomingo was reheated to 320–400 °C for about a year transforming some martensite to kamacite and to taenite particles and some martensite directly to taenite without composition change. Fizzy-textured intergrowths of troilite, kamacite with 2.7 wt.% Ni and 2.6 wt.% Co, and taenite with 56 wt.% Ni and 0.15 wt.% Co formed by localized shock melting. A single impact probably melted the sub-mm sulfides, formed stishovite, and reheated and decomposed the martensite plates. Tishomingo and its near-twin Willow Grove, which has 28 wt.% Ni, differ from IAB-related irons like Santa Catharina and San Cristobal that contain 25–36 wt.% Ni, as they are highly depleted in moderately volatile siderophiles and enriched in Ir and other refractory elements. Tishomingo and Willow Grove therefore resemble IVB irons but are chemically distinct. The absence of cloudy taenite in these two irons shows that they cooled through 250 °C abnormally fast at >0.01 °C/yr. Thus this grouplet, like the IVA and IVB irons, suffered an early impact that disrupted their parent body when it was still hot. Our noble gas data show that Tishomingo was excavated from its parent body about 100 to 200 Myr ago and exposed to cosmic rays as a meteoroid with a radius of ~50–85 cm.

1. INTRODUCTION

The Tishomingo iron meteorite is a particularly interesting meteorite because it has a very unusual composition, a unique structure, and a low temperature thermal history that is constrained by its microstructure. It is an ungrouped iron meteorite with an exceptionally high Ni content of ~32.5 wt.% that is highly depleted in volatile siderophiles and enriched in refractory elements like group IVB irons, which have 16–18 wt.% Ni (Buchwald, 1975; Birch et al., 2001; Corrigan et al., 2005). However the composition of Tishomingo does not fit any plausible extrapolation of group IVB trends to higher Ni concentrations (Corrigan et al., 2005).
Tishomingo lacks phosphides and carbides and concentrations of C and P are exceptionally low; <0.05 wt.% C and P (Buchwald, 1975; Ives et al., 1978). Sulfides are sparsely distributed in the form of small blebs, 20–250 μm across, composed of fine intergrowths of troilite (FeS), daubréelite (FeCr2S4), and metallic Fe,Ni (Buchwald, 1975). Corrigan et al. (2005) report troilite nodules that are up to 6 mm in size, but still much smaller than found in nearly all other irons, and a single grain of stishovite.

In reflected-light, Tishomingo lacks kamacite and appears to be composed predominantly of martensite, unlike other high-Ni irons like Santa Catharina (Zhang et al., 1990). Its microstructure is 80 vol.% martensite, bcc χ2 and 20 vol.% taenite, fcc γ (Buchwald, 1975; Ives et al., 1978). The presence of the coarse martensite χ2 plates, some 20–50 μm wide and up to 1–2 mm long, make Tishomingo a unique iron meteorite. Its closest relative, Willow Grove, contains 27.7 wt.% Ni, and consistent with its lower Ni content contains lath rather than plate martensite (Birch et al., 2001).

Ives et al. (1978) observed Tishomingo in the transmission electron microscope (TEM) and found that the martensite has decomposed to a bcc matrix with taenite (fcc) precipitates. Russell et al. (1991) used the TEM and the atom probe field ion microscope to show the presence of small fcc precipitates, 10–90 nm in size, in the bcc matrix. The composition of the fcc precipitates, measured with X-ray EDS in the TEM, was 51–57 wt.% Ni. Selected area diffraction showed that the particles have a disordered fcc structure. No precipitates were observed in residual taenite, the original fcc structure of the solidified single crystal. From these studies of Tishomingo, Ives et al. (1978) and Russell et al. (1991) proposed that the martensite formed during cooling to temperatures as low as −115 °C and that subsequent reheating to a temperature of more than 200 °C caused the martensite to decompose.

Tishomingo is therefore unique in that no other meteorite has preserved in its microstructure a detailed record of its low temperature history between −100 and 400 °C. However, prior studies were not able to characterize the structure and composition of both bcc and fcc phases, and details of the thermal and shock history of the meteorite and the processes responsible for its remarkable history and composition are still not well understood.

In this paper we use several electron and ion beam microscopy techniques, including electron backscatter diffraction (EBSD), helium ion microscopy (HIM), and TEM, to observe and characterize the metal microstructure and electron probe microanalysis and SEM to characterize the sulfide–metal intergrowths. We also use noble gas measurements to determine the pre-atmospheric radius and the cosmic-ray exposure age of the Tishomingo iron meteorite. Using these data we are better able to understand the time–temperature history including shock and reheating, which were instrumental in the formation of the Tishomingo microstructure. In addition, we integrate this information, with studies of the chemical composition of Tishomingo and Willow Grove to elucidate the origin and impact history of these unique meteorites.

2. METHOD

2.1. Microscopy and microanalysis

A thick section of Tishomingo was obtained from the Smithsonian Institution (USNM 2617b) and prepared for optical microscopy, scanning electron microscopy (SEM), and helium ion microscopy (HIM) by standard metallographic procedures: mounting, grinding, polishing, and etching with 2% nital. The SEM studies were accomplished using a ZEISS EVO 50 at the University of Massachusetts, Amherst and a ZEISS Supra 55VP SEM at Sandia National Laboratories. The HIM study was done using a ZEISS Orion Plus HIM at the Joint School of Nanoscience and Nanoengineering, a joint venture between University of North Carolina at Greensboro and North Carolina A&T State University. The HIM was operated at about 34 kV and 0.5 pA probe current. Secondary electron images were obtained using an Everhart–Thornley detector. Quantitative WDS X-ray measurements of the local bulk composition of the metal matrix and the fine intergrowths in sulfides were carried out using a Cameca SX-50 electron probe microanalyzer in the Geosciences Department at the University of Massachusetts. The Tishomingo thick section was analyzed unetched and with a carbon coating to ensure good electrical conduction. An operating voltage of 15 kV and a beam current of 40 nA were used. Two major elements (Fe and Ni) and three minor elements (Co, S and P) were measured. Pure metals were used as standards for Fe, Ni, and Co. (Fe–Ni)3P and FeS in the Grant meteorite served as the P and S standards respectively.

2.2. EBSD

Electron backscatter diffraction (EBSD) studies were performed using a ZEISS Supra 55VP SEM at Sandia National Laboratories outfitted with an EBSD unit from Oxford Instruments with Channel 5 software (see Goldstein and Michael, 2006). This technique allows the identification of body centered cubic (bcc) and face centered cubic (fcc) Fe–Ni from their electron diffraction patterns as well as the orientation of the bcc and fcc phases with respect to the sample position (x, y, and z directions) in the SEM. In Tishomingo the fcc phase is Ni rich taenite or tetraeute-nite as EBSD cannot distinguish between disordered and ordered fcc phases. The bcc phase is kamacite with <7 wt.% Ni or a non-equilibrium phase, martensite. Martensite forms rapidly from taenite by a diffusionless shear transformation during cooling below Ms, the martensite start temperature (Kaufman and Cohen, 1956). It has a distorted bcc structure and inherits the composition of the taeni-te from which it formed. Similar structures have been described in reheated irons (Yang et al., 2011).

The meteorite samples were prepared for EBSD using standard metallographic polishing procedures followed by a two-step vibratory polishing procedure. The first vibratory polishing step was performed using 0.1 μm Al2O3 for 4 h followed by a second vibratory polishing step using 0.04 μm SiO2 for 2–4 h. Both vibratory polishing steps were carried out on napped cloth. This procedure removed surface...
deformation caused by standard metallographic polishing. Diffraction patterns were obtained using a beam voltage of 20 kV, a beam current of 1–2 nA, and a spot size diameter of less than 2 nm. Orientation information was collected pixel by pixel with a pixel spacing of 0.02 to 0.5 μm. Orientation maps or inverse pole figure maps of the scanned specimen surface were developed using a color scheme to represent the orientation of the bcc and fcc phases with respect to the major poles (111, 100, 110) of the stereographic triangle. Pixels with the same orientation have the same color. Rogue or mis-indexed pixels are removed and then filled using a routine (8 nearest neighbor hole filling) that compares the surrounding pixels and fills in the missing ones. The orientation maps were used to determine local crystallographic orientations, and to provide critical information necessary to understand how the various phases formed during reheating and subsequent cooling. Band contrast images, which resemble SEM back-scattered electron images, were also used to show the quality of the EBSD pattern. Combined band contrast and orientation maps allow the distribution of bcc and fcc phases to be compared.

2.3. STEM-AEM

Scanning transmission-analytical electron microscopy (STEM-AEM) was employed to characterize the chemical composition of phases at the nano-meter scale. X-ray area scans for Fe and Ni were taken in micron and sub-micron sized regions of the thin foil. High angle annular dark field STEM images, which show compositional (atomic number) contrast, were used to locate regions of interest for the X-ray scanning images. The iron meteorite samples used for STEM analysis were thinned using a dual beam FEI DB-235 focused ion beam (FIB)/SEM instrument at Sandia National Laboratories. The STEM samples had a thickness of 50–100 nm and were approximately 10 μm long and 5 μm in width. Thin sections of selected regions were analyzed using a FEI Tecnai F30ST field emission TEM-AEM operated at 300 kV and housed at Sandia National Laboratories. Quantitative Ni gradients in taenite 0.5–2 μm in length were measured in a direction normal to interface boundaries using the stored EDS X-ray scan data. The X-ray data in each pixel were converted to composition using the Cliff–Lorimer method (Cliff and Lorimer, 1975) with a X-ray spatial resolution of 2–4 nm. A \( k_{\text{Ni/Fe}} \) factor in the Cliff–Lorimer method of 1.10 was measured at 300 kV using a 25 wt.% Ni-Fe standard. This technique can obtain composition measurements in regions as small as 1 nm. The chemical information was extracted from the X-ray area scans and used to study the kinetics of the various phase transformations that took place during the thermal events.

2.4. Cosmic-ray exposure measurement

The Tishomingo sample used for the cosmic-ray exposure (CRE) age measurement was purchased from a meteorite dealer. The methods used for the noble gas measurements are standard procedures similar to those described in Ammon et al. (2008, 2011). One Tishomingo sample, weighing 61.94 mg, was cleaned with alcohol and distilled water before loading into the vacuum system. The sample was preheated at about 80 °C for a few days to release atmospheric surface contamination. The sample was degassed in a Mo crucible held at ~1700 °C for about 45 min. A boron-nitride liner inside the Mo crucible prevented corrosion of the crucible. The released gases were cleaned on various Ti getters working in the temperature range 20–700 °C. After cleaning the gas, the He–Ne fraction was transferred to a sector field noble gas mass spectrometer, while the Ar fraction was transferred to a noble gas tandem mass spectrometer. The noble gas analyses were done at the University of Bern, Switzerland. Both instruments were built at the university and work in a static operational mode. During He–Ne analysis, Ar was absorbed on charcoal held at boiling nitrogen temperature. The Ar fraction was further purified of hydrocarbons using an additional cold trap at a temperature of ~50 °C. The gas concentrations were determined by peak-height comparison with signals from known amounts of He, Ne, and Ar, respectively.

For \(^{3}\text{He}, ^{4}\text{He}, ^{21}\text{Ne}, \) and \(^{22}\text{Ne}, \) the blank contributes less than 1% to the sample gas amounts. For \(^{20}\text{Ne} \) the blank contribution is about 5%. For \(^{36}\text{Ar}, ^{38}\text{Ar}, \) and \(^{40}\text{Ar} \) the blanks contribute 1.4%, 0.5%, and almost 100% to the sample gas amounts. The blank subtraction for Ne and Ar is done using the two-component-deconvolution technique assuming that the measured gases are mixtures of cosmicgenic and air.

For most noble gas mass spectrometer the sensitivity and the fractionation factors depend on the pressure of the gas in the spectrometer. Since the gas pressures in the spectrometer during calibrations and sample measurements might differ, the non-linear effect needs to be corrected. For the Tishomingo sample the non-linear effect contributes less about 3% and 1% for He and Ne concentrations, respectively, and about 18% for the \(^{3}\text{He}/^{4}\text{He} \) isotope ratio. For Ar the non-linear effect is about 4% for concentrations and negligible for isotope ratios.

3. RESULTS

3.1. Microscopy and microanalysis

The classic microstructure of the Tishomingo meteorite, martensite plates in a residual fcc taenite matrix, is visible on etching (Fig. 1a, b). At higher magnification, using a high resolution helium ion microscope, HIM, one observes that the martensite plates are decomposed and contain 10–20 nm wide oriented platelets of taenite (fcc) as well as coarse relatively smooth unetched taenite particles 20–100 nm in width, which are not uniformly distributed (Fig. 2b, c). The parent (residual) taenite (fcc) phase (Fig. 2a) has not decomposed. No cloudy zone is observed even though the Ni content is within the range observed for the cloudy zone microstructure (~30 to 42 wt.% Ni). Area measurements of the decomposed martensite and parent taenite matrix were made using SEM images of four regions with a total area of 1 nm². The decomposed martensite area fraction is 78.8–79.9%, with an average of 79.2%.
Fig. 1. Optical and SEM images of the microstructure of Tishomingo. (a) Optical image of a typical region showing martensite plates (dark brown) and residual taenite (light brown) after etching with 2% nital. Field of view is 0.98 mm wide. (b) At higher magnification, a SEM image of several martensite plates containing midribs. The residual taenite regions are structureless. (c) Optical image of unetched region containing a sulfide-metal intergrowth about 100 μm in size. Irregularly-shaped filaments of FeS are intermixed with high Ni FeNi and with low Ni high Co metal and daubre´elite (light gray and indistinct). (d) Optical image after etching of the same sulfide-metal intergrowth as in (c). The low Ni high Co metal, which is concentrated in the rim of the intergrowth, is overetched and appears black. The martensite plates and retained taenite regions around the sulfide intergrowth appear unaffected. However, the sulfide intergrowth appears to extend slightly further into the martensite plates than the adjacent taenite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Helium Ion Microscope (HIM) images of decomposed martensite \( \alpha_2 \) and residual taenite at increasing magnification. In the decomposed martensite, the bcc kamacite phase (dark gray) was etched away and the unetched phase is fcc taenite (light gray). (a) A triangular smooth featureless region of residual taenite surrounded by the decomposed martensite. (b) A decomposed martensite region containing crystallographically oriented particles of taenite. (c) At the highest magnification, the decomposed martensite plates are seen to contain both coarse and fine taenite particles 10–100 nm in size.
consistent with previous measurements of 80% (Buchwald, 1975; Ives et al., 1978).

Tishomingo contains numerous sulfide–metal intergrowths that occur mostly as equant blebs 20–250 μm across (Buchwald, 1975) but also as elongated intergrowths 250 × 10 μm in size (Buchwald, 1975). The intergrowths resemble fizzy-textured shock-melted sulfides in many other irons in that they consist of sub-micrometer irregularly shaped filaments of troilite (FeS) intermixed with Fe–Ni and daubreéelite (FeCr₂S₄) grains (Scott, 1982). However, the intergrowths in Tishomingo are uniformly smaller, and equant-shaped occurrences have a unusual structure, which has not been reported in other meteorites. Etching with 2% nital shows two distinct regions, a core in which the FeS filaments are mixed with taenite and a rim that is predominantly composed of finer grained kamacite and FeS (Fig. 1d). Electron probe analysis shows that in the cores taenite contains 56–57 wt.% Ni and 0.14–0.17 wt.% Co and the kamacite in the rims contains 2.7 wt.% Ni and 2.6 wt.% Co (Fig. 1c). Elongated intergrowths of metal and sulfide also contain kamacite-rich and coarser-grained taenite-rich regions but without any concentric structure. Daubreéelite, which occurs mostly as sub-rounded, 2–5 μm wide grains, tends to be concentrated in the rim of the sulfide–metal intergrowth. However, it also occurs as laths up to 50 μm long, which resemble the normal occurrence of daubreéelite in unshocked irons as lamellae within troilite nodules.

3.2. EBSD

EBSD was employed to display bcc (kamacite or martensite) and fcc taenite regions and to determine the orientation of kamacite and taenite in the Tishomingo. EBSD maps of a large area, 2.1 mm × 0.5 mm, of the meteorite surface are shown in Fig. 3. The band contrast image (Fig. 3a), which resembles a SEM back-scattered electron image, displays two distinct gray levels. The bright gray areas are regions of the residual taenite parent phase, fcc, γ. The fcc orientation map (Fig. 3b) shows that the residual taenite, γ, has the same pink color and therefore the same crystallographic orientation across the entire scanned area. Therefore the entire region was one single crystal of taenite, fcc, before martensite began to form on cooling. The decomposed martensite regions contain relatively thin fcc particles with different orientations as indicated by the multiple colors. The bcc orientation map (Fig. 3c) shows major amounts of bcc kamacite in the decomposed martensite has mainly the same color and orientation. There are also bcc particles that have other colors, indicating different crystallographic orientations.

Higher resolution EBSD orientation maps, Fig. 4a and b, provide more detailed information about the microstructure of the residual taenite and the decomposed martensite regions in Tishomingo. Fig. 4a and b shows fcc and bcc EBSD maps respectively in a 17 × 17 μm region. The corresponding pole figures from the 17 × 17 μm region are displayed in Fig. 4c and d. Fig. 4a shows that the residual
taenite regions, observed in Fig. 3a and b, are single crystal fcc. The decomposed martensite regions contain both fcc and bcc phases. Many of the taenite fcc phases in the decomposed martensite regions are platelike in shape similar to the taenite regions shown in the HIM images, Fig. 2, and also have different orientations. Other taenite regions have the same orientation as the residual taenite. The bcc kamacite regions are a micron or more in width and most have different orientations. In addition, some of the decomposed martensite plates contain parallel kamacite lamellae, for example the martensite plate in the lower right of Fig. 4b. The orientations of kamacite and taenite in the martensite regions of Tishomingo have a Kurdzumov–Sachs (K–S) or Nishiyama–Wasserman (N–W) orientation relationship to each other in which the {111} plane of the taenite (fcc) is parallel to the {110} plane of the kamacite (bcc), see Table 1.

### 3.3. STEM-AEM

Fig. 5a shows the location of a FIB cut taken across a residual taenite region with decomposed martensite plates at both ends of the section. Fig. 5b shows an annular dark field STEM image of the FIB thin section at a boundary between retained taenite and decomposed martensite. A Ni concentration map of a 1 µm² area of Fig. 5b (square labeled 1) is shown in Fig. 5c. Both low Ni kamacite and high Ni taenite regions are present in the decomposed martensite region. A residual taenite-region is present near the top left hand border of the Ni concentration map next to the decomposed martensite boundary. Composition profiles were measured across two two-phase regions in the decom-

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<td>Orientation relationships of kamacite and taenite.</td>
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<td>N–W</td>
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K–S is the Kurdzumov–Sachs (K–S) and N–W is the Nishiyama–Wasserman orientation relationship.
posed martensite (line scans 1 and 2) with a spatial resolution of 8 nm/pixel. Fig. 5d gives the Ni variation in scan 1 across a residual taenite/decomposed martensite boundary and a kamacite particle. The taenite at the kamacite–taenite boundary has a Ni concentration similar to that of FeNi of about 48 wt.% and the kamacite has a Ni concentration of about 4 wt.%. Ni concentration gradients in the taenite surrounding the kamacite particle appear to have developed during kamacite growth. Fig. 5e shows the Ni variation in scan 2 through the decomposed martensite. Several regions have a Ni concentration of ~32 wt.%, the same as the bulk meteorite. The composition of the kamacite regions

Fig. 5. Ni compositional analysis of a decomposed martensite. (a) A SEM image of a region containing residual taenite and decomposed martensite showing where a FIB section was cut. (b) A STEM image of a selected area within the thinned FIB section where a 1 × 1 μm region labeled 1 was selected for chemical analysis. (c) Ni X-ray scan of the 1 × 1 μm region shown in (b) with a resolution of 8 nm per pixel. (d and e) Two Ni X-ray profiles, 1 and 2. The positions of the X-ray analysis traces are shown in (c). The profiles show regions of high Ni taenite (fcc), low Ni kamacite (bcc) and residual taenite (32.5 wt.% Ni).
(<50 nm in width) is less than 10 wt.% Ni. Although composition measurements at phase boundaries are limited by the relatively high 8 nm pixel resolution, several of the kamacite–taenite boundaries contained taenite approaching the FeNi composition of 50 wt.% Ni. We were unable to confirm the presence or absence of tetrataenite, ordered FeNi, using electron diffraction because of the presence of both bcc and fcc spots in the diffraction patterns and the expected low intensity of the fcc ordering spots.

Fig. 6a shows a STEM dark field image of a decomposed martensite plate surrounded by residual taenite. There are many taenite plates present in the decomposed martensite. Fig. 6b shows a Ni X-ray map from the outlined area, 350 × 350 nm, in (a). The X-ray map was taken with 512 × 512 pixels at a spatial resolution of 0.72 nm/pixel. The scan is rotated with respect to the STEM image in a). Ni X-ray profiles were measured along trace 1 and 2 respectively in Fig. 6b and are shown in Fig. 6c and d. The profiles

Fig. 6. High resolution Ni composition analysis of decomposed martensite. (a) STEM image of a decomposed martensite plate containing taenite precipitates. A 350 nm × 350 nm region outlined by the rectangle was selected for analysis. (b) Ni X-ray scan of the 350 × 350 nm region shown in (a). The X-ray resolution is 0.72 nm per pixel. The X-ray map is rotated with respect to the STEM image in (a). (c and d) Ni X-ray profiles measured along traces 1 and 2 respectively. The profiles show Ni compositions approaching 50 wt.% in the taenite plates and in several cases Ni compositions below 10 wt.% consistent with kamacite, α.
show Ni compositions approaching 50 wt.% (FeNi) in the taenite plates and in several cases Ni compositions below 10 wt.% in the surrounding phase, presumably kamacite, x. Other regions show Ni contents below 50 wt.%.

It is probable that many of these regions contain plates that are tilted with respect to the thin film surface and the focused electron beam has also excited X-rays from the surrounding low Ni kamacite. Regions of taenite with uniform Ni concentrations of 32%, the bulk Ni content of Tishomingo, were not observed in either profiles 1 or 2.

To summarize, our studies using HIM, EBSD, and AEM confirm that the decomposed martensite in Tishomingo contains both fcc and bcc phases (Figs. 2–6), as Ives et al. (1978) and Russell et al. (1991) inferred. We identified low Ni kamacite with 4–10 wt.% Ni, residual taenite or martensite with ~32 wt.% Ni, and 10–100 nm wide taenite particles with ~50 wt.% Ni in the decomposed martensite. Analyses of taenite particles by X-ray EDS in the TEM by Russell et al. (1991) gave 51–57 wt.% Ni, similar to our results. Near the edge of the decomposed martensite plates we also found zoned taenite with 30–50 wt.% Ni. In our TEM diffraction studies, we were not able to determine whether the fcc taenite was either ordered (tetraedrite) or disordered. Previous work by Russell et al. (1991) reported that the fcc taenite precipitates in decomposed martensite plates were disordered.

3.4. Cosmic-ray exposure age

The He, Ne, and Ar noble gas concentrations and isotope ratios corrected for interferences and non-linearities before blank correction are given in Table 2. The measured 20Ne/22Ne and 36Ar/38Ar ratios of 0.84 and 0.62 indicate that the measured gas is essentially purely cosmogenic. For partitioning the noble gas concentrations into a cosmogenic (cos) and a trapped (tr) component we assume: 3He = 1He_{cos}, (20Ne/22Ne)_{cos} = 0.83, (26Ne/22Ne)_{tr} = 9.8, (21Ne/22Ne)_{tr} = 0.031. We further assume that all 40Ar is atmospheric contamination and correct 36Ar and 38Ar accordingly. The correction for 21Ne is less than 1%. For 36Ar and 38Ar the corrections are about 1% and a few permil, respectively.

The cosmogenic 22Ne/21Ne ratio for the Tishomingo sample is 1.127. In a systematic noble gas study of the two iron meteorites Grant and Carbo, Ammon et al. (2008) demonstrated that pure meteoritic metal (93 wt.% Fe, 7 wt.% Ni) yields a cosmogenic 22Ne/21Ne ratio between 1.02 and 1.04. This would indicate that some of the cosmogenic Ne in Tishomingo was not produced from Fe but from S- or P-bearing inclusions, although phosphides have not been observed (e.g., Ives et al., 1978). Using the procedure developed by Ammon et al. (2008) such contributions can be corrected. For the end member 22Ne/21Ne ratios we use: 22Ne/21Ne_{metal} = 1.08 and 22Ne/21Ne_{sulfur/phosphorus} = 1.214. The corrected 21Ne concentration of 3.67 ± 0.26 cm3 STP/g is ~35% lower than the measured value (given as 21Ne_{corr} in Table 3). This indicates that about 35% of the cosmogenic 21Ne has not been produced from Fe and Ni but from small traces of sulfur and/or phosphorus. Due to the uncertainties in the endmember ratios used for the deconvolution, the uncertainty of the corrected cosmogenic 21Ne is difficult to estimate. In this case a very conservative estimate is used by adding 50% of the correction, i.e., assuming that the uncertainty due to the correction is 0.5 × (21Ne_{cosmogenic before the correction}) – 21Ne_{cosmogenic, after the correction)}. A slightly higher 22Ne/21Ne_{metal} ratio for Tishomingo was used than for Grant and Carbo because model calculations indicate that the cosmogenic 22Ne/21Ne ratio in Ni-rich iron meteorites is slightly higher than in typical iron meteorites.

If we assume that 35% of the cosmogenic 21Ne was not produced from Fe/Ni but from S and P, and that Tishomingo had a pre-atmospheric radius of about 85 cm and the pre-atmospheric depth of the sample was about 20–40 cm (see below), we can use the model predictions by Ammon et al. (2008) to calculate a S + P content of about 0.4%. This is considerably higher than our estimate given below (Section 4.4). However, considering that the uncertainties for the model predictions for the cosmogenic production of 21Ne from S and P are rather large (Ammon et al., 2011), we consider this agreement as reasonable. For the cosmogenic 3He/38Ar ratio, a ratio of ~11.7 was measured, slightly lower than the ratio of 15–20 measured recently for Grant and Carbo samples (Ammon et al., 2011) and also lower than model predictions, which are between 12–20 for iron meteorites of that size (Ammon et al., 2011, see below). The low 3He/38Ar ratio most likely indicates H and/or 3He diffusive losses of between 3% and 60% (depending on the pre-atmospheric size of Tishomingo, see below). The deficits in 3He are most likely due to diffusive losses of 3He before radioactive decay to 3He. It is not clear if the diffusive losses can be better quantified.

Table 2

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<td>22Ne</td>
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\(^{3}\)He/\(^{4}\)He = 0.228\) with the ratios measured recently for Carbo, which are all between 0.240–0.263 (Ammon et al., 2011). The ratio for Tishomingo is slightly too low and could indicate \(^{4}\)He diffusive losses in the range 5–15\%. However, since the \(^{3}\)He deficits are small and can be explained by \(^{3}\)H losses before radioactive decay, and any \(^{4}\)He losses are only very minor and not well constrained, we assume that the \(^{3}\)He deficits are not accompanied by any \(^{4}\)He deficits and therefore did not correct the measured \(^{4}\)He concentrations.

After correcting the cosmogenic \(^{21}\)Ne for contributions from sulfur and/or phosphorus and after excluding \(^{4}\)He deficits due to diffusion, the pre-atmospheric size of the Tishomingo meteorite and the shielding depth of the studied sample were estimated using the \(^{4}\)He/\(^{21}\)Ne ratio. The (corrected) cosmogenic \(^{4}\)He/\(^{21}\)Ne ratio of 593 ± 178 is within uncertainties the same as the \(^{4}\)He/\(^{21}\)Ne ratio measured recently for the Xinjiang iron meteorite (Ammon et al., 2011). Using the model predictions for \(^{4}\)He/\(^{21}\)Ne (Ammon et al., 2011), the pre-atmospheric radius of Tishomingo is estimated as larger than ~40 cm. However, the high \(^{4}\)He/\(^{21}\)Ne ratio that was determined is only possible in a (pre-atmospheric) depth of more than 20 cm in an object with a (pre-atmospheric) radius between 50 cm and 65 cm and in a (pre-atmospheric) depth of between 20 cm and 50 cm in an object with a pre-atmospheric radius of about 85 cm. Comparing the different possibilities, it appears that the last one is most likely because the shielding range of interest represents the largest percentage of mass compared to the total mass. This suggests that Tishomingo most likely had a pre-atmospheric radius of about 85 cm and our sample was most likely from a depth region of between 20 cm and 50 cm.

After having estimated the pre-atmospheric radius of the meteorite and the shielding depth, the cosmic-ray exposure age can be calculated. The \(^{38}\)Ar production rates for that meteorite size range and the range of shielding conditions are in the range (1.05–2.32) \times 10^{-10} \text{cm}^2\text{STP/g/Myr} with an average of 1.59 \times 10^{-10} \text{cm}^2\text{STP/g/Myr}. The cosmic-ray exposure age is then about 174 Myr, with a possible minimum exposure age of 120 Myr and a possible maximum exposure age of about 260 Myr. If \(^{21}\)Ne is used in the calculation, the production rates (considering the same size and shielding range) are in the range (1.08–3.28) \times 10^{-11} \text{cm}^2\text{STP/g/Myr} with an average value of 1.98 \times 10^{-11} \text{cm}^2\text{STP/g/Myr}. This value gives a cosmic-ray exposure age of 120 Myr (Min = 73 Myr, Max = 220 – Myr). The exposure age calculated via \(^{38}\)Ar would not change much if we would have assumed that the sample comes from the inner part of an object with a pre-atmospheric radius in the range 50–65 cm, which is also compatible with the \(^{4}\)He/\(^{21}\)Ne ratio.

While we consider our result for the cosmic-ray exposure age as relatively robust, the results for pre-atmospheric radius and sample depth depend on how we correct for contributions from S and P. If we assume 600 ppm S and 75 ppm P (see Section 4.4), the contribution of S and P to the cosmogenic \(^{21}\)Ne concentration is about 3%, i.e., much lower than what we determined using the mixing model (35%/a). With a lower correction, we would obtain a higher \(^{21}\)Ne concentration (~3.13 \times 10^{-9} \text{cm}^3\text{STP/g}) and a lower \(^{4}\)He/\(^{21}\)Ne ratio of about 453. From the lower \(^{4}\)He/\(^{21}\)Ne ratio we would deduce a pre-atmospheric radius of about 50 cm (compared to 85 cm, see above) and a pre-atmospheric shielding depth of 20–40 cm. Using these values for pre-atmospheric radius and shielding depth and the higher \(^{21}\)Ne concentration, we calculate a cosmic-ray exposure age of 130 Myr, not much different from the result obtained before.

Here it is worth emphasizing, that due to the lack of radionuclide data, our discussion is based exclusively on noble gas data, making it difficult to decide whether Tishomingo experienced a single or a complex exposure history.

4. DISCUSSION

4.1. Low temperature thermal history of Tishomingo

To understand the phase transformations in the metal phases in Tishomingo, we can use the Fe–Ni phase diagram of Yang et al. (1996) with superimposed martensite

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Fig. 7. Fe–Ni binary phase diagram from 900 °C to ~200 °C (modified from Kaufman and Cohen (1956) and Yang et al. (1996)). \(\alpha\) is low-Ni bcc phase, \(\gamma\) is high-Ni fcc phase, \(\gamma_1\) is paramagnetic fcc phase, \(\gamma_2\) is ferromagnetic fcc phase, \(\gamma^*\) is ordered Ni$_3$Fe, \(\gamma'\) is ordered FeNi tetrataenite. \(M_s\) (dashed line) is the martensite start temperature at which martensite starts to form on cooling from taenite. Transformation is complete at \(M_f\) (dashed line), the martensite finish temperature. \(A_3\) (dashed line) is the temperature at which martensite starts to transform to taenite (austenite) on heating. \(T_C\) is the Curie temperature of the \(\gamma\) phase. \(T''_c\) is the ordering temperature of tetrataenite, FeNi, \(\gamma'^*\). Sp indicates the spinodal region where cloudy taenite intergrowths may form during slow cooling.
transformation temperatures, $M_s$ (martensite start) and $M_f$ (martensite finish) (Kaufman and Cohen, 1956) (Fig. 7). For an alloy with Tishomingo’s Ni concentration of 32.5 wt.%, cooling from $>900\ ^\circ C$ can yield three possible micro-structures depending upon the cooling rate and the concentration of P.

1. At slow cooling rates, 1–10,000 °C/Myr, typical of iron, stony iron, and chondritic meteorites, kamacite plates should form when the alloy crosses the $\gamma/(\alpha + \gamma)$ boundary at about 500 °C, provided that nucleation sites are available. However, Tishomingo lacks the two most important factors which promote nucleation (Reiser and Goldstein, 2003), viz., taenite grain boundaries and the presence of P in the taenite.

2. In the absence of nucleation sites, alloys with 32.5 wt.% Ni that cool slowly at 1–10,000 °C/Myr should form a cloudy zone structure below the spinodal line, Sp, at about 250 °C (Fig. 7). In iron, stony iron and stony meteorites, the spinodal structure forms in the ‘M’ shaped Ni gradient between $\sim 30$ to $\sim 42$ wt.% on cooling. The cloudy zone microstructure in this zone forms in almost pure Fe–Ni meteoritic metal since minor elements, such as S, C, and P have diffused at higher temperatures to their respective exsolved phases, FeS, (Fe–Ni)$_3$C, and (Fe–Ni)$_3$P. At slow cooling rates, we should therefore expect Tishomingo to develop a cloudy zone microstructure as observed, for example, in the Santa Catherina iron meteorite (Zhang et al., 1990), which contains 35.3 wt.% Ni (Buchwald, 1975). We consider it unlikely that subsequent reheating removed cloudy zone taenite. Reheating above 400 °C would remove cloudy taenite; however such reheating would produce a different microstructure containing much lower Ni taenite particles and a decomposed residual taenite of 32.5 wt.% (see Fig. 2). The total absence of any cloudy zone microstructure strongly indicates that Tishomingo cooled $>10,000\ °C$/Myr ($>0.01\ °C$/ yr), even faster than any of the IVA or IVB irons (Yang et al., 2007, 2010).

3. At normal laboratory cooling rates, a bcc martensite structure of the same Ni content as the parent taenite will begin to form after crossing the $M_s$, martensite start line (fcc $\gamma \rightarrow$ bcc $\alpha$), Fig. 7. The $M_s$ temperature measured for an alloy with 32.5% Ni by Kaufman and Cohen, 1956 is $-100\ ^\circ C$ (Fig. 7). However, Ives et al. (1978) estimated the $M_s$ temperature for Tishomingo is $-25$ to $-65\ ^\circ C$. The newly formed bcc martensite $\alpha$, will have either a Kurdjumov–Sachs (K–S) or Nishiyama–Wasserman (N–W) crystallographic orientation, $\{111\}///\{110\}/\alpha$, with the original taenite $\gamma$ (Table 1). More martensite forms on cooling until the alloy is totally transformed to martensite when it crosses the line marked $M_f$ in Fig. 7. The presence of $\sim 80$% martensite in Tishomingo indicates that it cooled to around $-200\ ^\circ C$ according to Kaufman and Cohen (1956) but in the range $-75$ to $-115\ ^\circ C$ according to Ives et al. (1978). Based on these results, Tishomingo cooled to about $-100\ ^\circ C$ or below.

The temperature at which martensite starts to form can be raised by plastic deformation at low temperature (Kaufman and Cohen, 1956). For alloys with 32 wt.% Ni, the temperature at which martensite can form by plastic deformation is about 70 °C. Since Tishomingo was shocked to form stishovite (Corrigan et al., 2005), it is possible that it was deformed plastically at that time or during other impacts. However, as discussed in Section 4.3, Tishomingo was probably shocked after martensite formed. Whether shock can cause martensite to form in Fe–Ni alloys is not certain. Two experiments by Leslie et al. (1965) on a 32 wt.% Ni Fe–Ni alloy indicated that no martensite formed from fcc taenite, $\gamma$, by shock at both 17 and 27 GPa. Although the EBSD map in Fig. 4 does show slight variations in color in the residual taenite single crystal, we concur with the conclusion of Ives et al. (1978) that Tishomingo did not form martensite by deformation as the boundaries between martensite plates and residual taenite are very sharp and straight (see Figs. 1 and 2). In summary the absence of cloudy taenite in the residual fcc taenite shows that Tishomingo cooled through 250 °C at more than 10,000 °C/Myr ($>0.01\ °C$/yr) and the temperature of 80% martensite shows that it cooled to between $-75$ and $-200\ ^\circ C$.

4.2. Decomposition of martensite

4.2.1. Reheating of martensite

The phase compositions of kamacite of $\sim 4$ wt.% Ni and taenite of $\sim 50$ wt.% Ni in decomposed martensite show that Tishomingo was reheated in the temperature range from 200 to 400 °C after martensite had formed (Fig. 7). The details of the reheating can be determined using experimental heat treatment studies of $\sim 32$ wt.% Ni martensitic alloys at low temperature (Section 4.2.2). These studies show that there are two possible scenarios for the decomposition of martensite in Tishomingo. These scenarios are discussed in Section 4.2.3 with the aid of compositional information, provided by analytical electron microscopy, about the microstructure of Tishomingo on the nm scale. In Section 4.2.4 we show that the two scenarios can be distinguished using constraints provided by the crystallographic orientation information using EBSD.

4.2.2. Experimental measurements

Experiments on Fe–Ni alloys with $\sim 30$% Ni have helped to establish the thermal histories necessary to decompose martensite but the results are not completely consistent. Ives et al. (1978) used Tishomingo samples to demonstrate that martensite formed below room temperature and contained residual taenite. Samples of Tishomingo were heated at 350–400 °C for 20 days or more. Fine precipitates were observed within martensite regions. However the precipitate phase was not identified. Zhang et al. (1992) heated a martensitic sample of $\sim 29$ wt.% Ni at 300 °C for approximately 1 year. Plate shaped precipitates with a fcc crystal structure approximately 10 nm in width, similar to precipitates studied in Tishomingo, formed in the martensite plates. The precipitates had a K–S (Kurdjumov–Sachs) orientation relationship with the parent bcc martensite. The Ni
content of the precipitates obtained from atom probe measurements contained as much as 56 wt.% Ni. The L1₀ ordered phase, tetrataenite, was not observed using the TEM. In a further study, Zhang et al. (1994) heated a sample of a binary Fe–Ni alloy containing ~30 wt.% Ni with a plate martensitic microstructure with retained taenite at temperatures between 300 and 400 °C for various times, from 275 to 400 days. As in the previous study, intragranular precipitates of fcc taenite were observed within the martensite plates. The, ordered phase, tetrataenite, L₁₀, was not observed by electron diffraction. Typical precipitate widths were 20 nm at 400 °C and ~10 nm for samples at 350 °C and 300 °C and the precipitates had a K–S orientation with the bcc parent phase. They found that the Ni content of the taenite precipitates increased from about 50 wt.% Ni at 400 °C to ~50 to 55 wt.% Ni at 350 °C, and to ~57 wt.% Ni at 300 °C.

Kabanova et al. (2011) quenched a Fe–32.5 wt.% Ni, low carbon (0.01 wt.% C), alloy in liquid nitrogen, and formed a structure with 80% plate martensite. The alloy was subsequently slowly heated from 240 °C to temperatures between 430 and 500 °C. The microstructure of this heat treated alloy contained taenite rods in kamacite with a Kurdjumov–Sachs (K–S) orientation as in previous studies. After further heat treatment for 5 days below the L₁₀ tetrataenite ordering temperature (320 °C) at 280 °C, taenite precipitates 5–10 nm wide were formed in decomposed martensite with K–S orientations. Contrary to the previous experiments, ordered L₁₀ phase (tetrataenite) was identified by electron diffraction, but the composition of the precipitates was not determined.

In summary, the microstructure, phase compositions, precipitate size, and kamacite–taenite orientation relationships of reheated ~30–32 wt.% Ni–Fe martensitic alloys show remarkable consistencies with those of Tishomingo for reheating temperatures of 300–400 °C. Therefore there is reliable evidence from experimental studies that Tishomingo was reheated for ~1 year or less at temperatures of ~300–400 °C. The Fe–Ni phase diagram (Fig. 7) shows that martensite should decompose at these temperatures into the equilibrium ζ and γ phases. However in addition to this transformation, the martensite can transform directly to fcc taenite of the same composition by a diffusionless shear-type process. The starting temperature for this process (ζ → ζ + γ) is Αₐ, the austenite (taenite) start temperature (Fig. 7). For 32.5 wt.% Ni, Αₐ is ~320 °C (Kaufman and Cohen, 1956; Meyer and Entel, 1998). The proportion of martensite ζ₂ (bcc) that transforms to γ (fcc) taenite of 32.5 wt.% Ni depends on the reheating temperature. The martensite is fully converted to taenite at a temperature of 415 °C, which is called Αₐ, the austenite (taenite) finish temperature and is close to the γ/(ζ + γ) phase boundary (Kaufman and Cohen, 1956). The next two sections discuss whether the reheating temperature of Tishomingo was above or below the Αₐ temperature.

4.2.3. Compositional data

If the reheating temperature is less than Αₐ, the austenite start temperature of ~320 °C for Tishomingo, (Fig. 7), ζ₂ may partly decompose to the equilibrium fcc taenite precipitate (~35 wt.% Ni and bcc kamacite ζ ~4 wt.% Ni (Fig. 7). The orientation of the high Ni taenite is expected to have a K–S or N–W relationship to the bcc martensite and the newly formed low Ni bcc kamacite is expected to inherit the orientation of the bcc martensite. Some of the martensite, ζ₂, will not transform during the reheating process because of the low diffusion rates of Fe–Ni and the available time.

Scenario 1 in Fig. 8 shows the reactions that would occur if Tishomingo had been heated in the temperature range below Αₐ. In Scenario 1, the microstructure of Tishomingo will contain residual taenite (fcc γ) that crystallized at high temperatures (>1000 °C), and decomposed martensite (bcc ζ₂) which contains taenite platelets (γ) in kamacite (ζ), as well as untransformed or retained martensite (bcc ζ₂). AEM X-ray data (Figs. 5 and 6) reveal that Tishomingo contains martensite (bcc ζ₂) of ~32.5 wt.% Ni, a high Ni taenite phase of ~50 wt.% Ni and a low Ni kamacite of ~4 wt.% Ni. These phase compositions are consistent with predicted phase compositions that should form on reheating below Αₐ.

Scenario 2 in Fig. 8, shows the reactions that would occur if Tishomingo had been heated above Αₐ ~320 °C. The proportion of fcc γ taenite of 32.5 wt.% Ni that formed from martensite, bcc ζ₂ with 32.5 wt.% Ni would depend on the reheating temperature between Αₐ and Αₐ (Fig. 7). This reheating scenario was first discussed by Russell et al. (1991) but they were not able to determine the reheating temperature.

On cooling after the reheating event (320–415 °C) in Scenario 2, some of the retained martensite, bcc ζ₂, will partly decompose to bcc with ~4 wt.% Ni and taenite with ~50 wt.% Ni by the reaction ζ₂ → γ + ζ as in Scenario 1. Some of the newly formed taenite, fcc, with 32 wt.% Ni may also transform to equilibrium ζ and γ at the reheating temperature by the reaction γ → γ + ζ. According to the Fe–Ni phase diagram, Fig. 7, γ (45–55 wt.% Ni) and ζ → ζ + γ (4 wt.% Ni) are the equilibrium phases at temperatures of 300–400 °C for a γ phase containing 32.5 wt.% Ni. For reheating temperatures above 400 °C, the Ni content of the equilibrium γ is <40 wt.%, less than the measured Ni content of the taenite γ phase in Tishomingo. Therefore the metal phases in Tishomingo were not heated above 400 °C.

The microstructure of Tishomingo in scenario 2 would contain residual taenite (fcc γ) that crystallized at high temperatures, decomposed martensite (bcc ζ₂) containing taenite platelets (γ) in kamacite (ζ), and untransformed or retained martensite (bcc ζ). This microstructure is similar to that discussed in scenario 1 for reheating below Αₐ ~320 °C. In scenario 2, the microstructure will also contain taenite of 32.5 wt.% that formed during reheating above Αₐ as well as low Ni kamacite and high Ni taenite that formed from this taenite (Fig. 8). Unfortunately, we cannot distinguish, using the X-ray data from the AEM, newly formed fcc taenite from residual taenite crystallized from the liquid since they have the same composition (Fig. 8, Scenario 2).

In summary, we cannot distinguish between the two scenarios on the basis of compositional and microstructural
observation using SEM and TEM. However, we can distinguish between the two scenarios using EBSD data as discussed below because most of the taenite that formed during reheating above $A_s$ will have different crystal orientations.

4.2.4. EBSD data

Reheating scenarios 1 and 2 can be distinguished from each other on the basis of the presence or absence of fcc $\gamma$ and bcc $\alpha$ formed from the decomposition of 32.5 wt.\% Ni fcc $\gamma$ nucleated above $A_s$ (See Fig. 8, Scenario 2). The ideal calculated pole figures of {111} FCC and {110} BCC from a single crystal of $\gamma$, taenite, with a K–S or N–W orientation are shown in Fig. 9a and b. During the decomposition of martensite upon reheating by the reaction $a_2 \rightarrow \gamma + \alpha$, the bcc $\alpha$ phase orientation should be the same as the bcc martensite and should retain its K–S or N–W orientation relationship with the high temperature single crystal fcc $\gamma$ phase. Pole figures of {111} FCC and {110} BCC from the EBSD map in Fig. 4c and d are shown in Fig. 9c and d. These pole figures indicate that most of the {111} poles in the fcc pole figure and most of the {110} poles in the bcc pole figure cluster into distinct groups. The overlap of projected and measured pole figures confirms the K–S or N–W relationship for the fcc and bcc regions in the martensite plates. However, there are additional fcc and bcc phase regions present in the EBSD orientation maps that lie outside the overlap areas as indicated by the arrows in Fig. 9c and d. Further examination of the {110} bcc pole figure, Fig. 9d, indicates that most of the bcc $\alpha$ has a K–S or N–W orientation relationship with the original single crystal fcc $\gamma$ (seven clusters in the bcc{110} projection). However some bcc orientations are outside these clusters, are not associated with the original fcc $\gamma$, and do not have a K–S or N–W orientation relationship with the original single crystal fcc phase. Therefore, decomposition below 320 °C, scenario 1, may not fully describe the observed microstructure.

Fig. 8. Sketch of two possible paths (scenarios 1 and 2) that lead to the formation of phases with the structure and composition of those observed in Tishomingo. In Scenario 1, Tishomingo is reheated to a temperature below 320 °C, the $A_s$ temperature at which martensite with 32.5% Ni begins to transform to taenite. Reheating above the $A_s$ temperature but below 400 °C as in Scenario 2 generates additional orientations of taenite particles which were observed using EBSD.
fcc pole figure. The additional orientations may also be due to the formation of fcc taenite above $A_s$ as well as fcc taenite from the decomposition of $\alpha_2$ in the residual martensite region. No attempt was made to distinguish where newly formed fcc taenite of the same composition as the bcc martensite or fcc $\gamma$ precipitates of high Ni content are located with respect to the scattered dots in the [111]fcc pole figure (Fig. 10c). For scenario 2, the $\gamma$ taenite of 32.5 wt.% Ni formed above $A_s$ (Fig. 8, Scenario 2) transforms to equilibrium $\gamma + \alpha_2$ at the reheating temperature and during cooling by the reaction $\gamma \rightarrow \gamma + \alpha_2$. The bcc kamacite that forms has no specific orientation relationship to the bcc $\alpha_2$ which formed during cooling. The scattered clusters in the measured pole figure of [110]bcc (Fig. 9d) most likely developed from the decomposition of $\gamma$ taenite formed above $A_s$. Therefore, scenario 2 best fits the EBSD data and therefore we conclude that Tishomingo was reheated to temperatures above $A_s$ of 320 °C.

4.3. Origin of troilite–metal intergrowths

Above we have shown that the metallic phases in Tishomingo result from cooling to between −75 and −200 °C to form the martensite and then reheating to 320–400 °C for about a year to partially decompose it. Here we review the properties of the troilite–metal intergrowths and other constraints on the shock and thermal history of Tishomingo.

Tishomingo contains ubiquitous fine-grained metal–troilite intergrowths up to 250 μm in size containing grains and, more rarely, lamellae of daubreelite. These intergrowths clearly formed from preexisting troilite nodules with daubreelite lamellae, like those that are present in many irons (Buchwald, 1975). The small size of the preexisting sulfide nodules in Tishomingo probably reflects an origin by solid-state exsolution from Fe–Ni rather than growth from the liquid, consistent with the experiments of Ives et al. (1978) and the Fe–Ni–S phase studies of Ma et al. (1998), which show that an Fe–28 wt.% Ni alloy can dissolve up to 1100 ± 200 ppm of S at 900 °C. The transformation of the sulfide nodules into sulfide-metal intergrowths probably occurred after the formation of the martensite as the location of the outer edge of some troilite–metal intergrowths appears to depend on the nature of the adjacent phase. For intergrowths that are surrounded by both martensite and taenite (Fig. 1d), the sulfide–metal

Fig. 9. Projected pole figures of [111]fcc (a) and [110]bcc (b) due to the $\gamma \rightarrow \gamma + \alpha_2$ transformation (Goldstein and Michael, 2006) or the phase transformation $\gamma \rightarrow \gamma + \alpha_2$. Measured [111]fcc (c) and [110]bcc (d) pole figures from Fig. 4c and d with projected pole figures from a, and b superimposed. Most of the orientations follow the projected pole figures in (a) and (b) but some poles lie outside the projected positions as indicated by the arrows.
intergrowth appears to penetrate marginally further into the martensite plates than into the taenite.

Fizzy-textured intergrowths of troilite and metal like those in Tishomingo have been described in many other irons and a few chondrites (Buchwald, 1975; Scott, 1982; Bennett and McSween, 1996; Tomkins, 2009; Petaev and Marvin, 1996). Various origins have been proposed for these intergrowths including intrusion of S-rich vapor (Petaev and Marvin, 1996), melting above 850°C during post-shock thermal equilibration (Tomkins, 2009), and localized shock melting of troilite and adjacent Fe–Ni (Buchwald, 1975).

Intrusion of S vapor does not seem plausible for Tishomingo as the intergrowths are contained within a single taenite crystal. If the metal–troilite intergrowths had formed when the whole meteorite was heated above 850–900 °C, as Tomkins (2009) proposed, the martensite would have been transformed to taenite and the microstructure would have recrystallized due to strain energy caused by martensite formation. Fig. 11a and b shows the microstructure after heat treatment of a binary Fe–32.5 wt.% Ni alloy produced in the extraterrestrial materials laboratory at the University of Massachusetts. The alloy was melted using pure Fe and Ni, homogenized to form mm sized taenite grains, and quenched in liquid nitrogen which allowed martensite to form along with retained taenite. The alloy was then reheated to form decomposed martensite which contains taenite particles in a martensite matrix. Fig. 11c shows the microstructure of reheating the alloy containing decomposed martensite to 900 °C for a few minutes. The heat treatment suggested by Tomkins (2009) for the formation of intergrowths of metal and troilite leads to the replacement of the decomposed martensite microstructure with 10–100 µm recrystallized strain-free taenite grains. The high temperature reheated 32.5 wt% Ni alloy no longer retains residual taenite in a single crystal orientation but contains a texture composed of multiple taenite grains of varying orientation. An additional argument against the proposed origin of Tomkins (2009) for the metal–troilite intergrowths is that the Fe–Ni–S melts that would have formed above 850–900 °C would have cooled over minutes to hours, or longer and formed coarse cellular textures (e.g., Fig. 3 of Scott (1982)).

![Fig. 10. EBSD maps from the large decomposed martensite plate in the 17 × 17 µm² area of Fig. 4. (a and b) Show the EBSD fcc and bcc orientation maps from the decomposed martensite plate of Fig. 4. (c and d) Show the [1 1 1]fcc and [1 1 0]bcc pole figures from the EBSD maps in (a) and (b). The color of the fcc and bcc phases in the pole figures relate to the orientation of fcc and bcc regions in the EBSD maps (a and b).](image-url)
The troilite and metal grains in the Tishomingo intergrowths have diverse sizes of $\sim 1-5 \mu m$ and their boundaries are mostly irregularly shaped (Fig. 1c and d). Regions with regularly spaced cellular textures are present but rare. This texture can be attributed to incomplete melting, and the scale of the cellular textures indicates quenching at $\sim 10^4-5^5 \degree C/sec$, not cooling over minutes to hours or longer (see Fig. 9 of Scott (1982) and Scott et al. (2010)). Thus the fine-grained intergrowths are best considered as clast-laden impact melts caused by highly localized shock melting of troilite and adjacent metallic Fe-Ni (Scott et al., 2010).

Buchwald (1975) provides additional evidence that these textures in iron meteorites formed by shock melting. Some intergrowths enclose unmelted blocks of troilite and fragments of schreibersite indicating that melting and crystallization were extraordinarily rapid. In some irons, the sulfides exhibit a complete range of textures ranging from shocked but unmelted troilite, troilite rimmed by fine intergrowths, to complete conversion to metal–troilite intergrowths. This range of textures in a single iron is entirely consistent with the heterogeneous nature of shock heating.

The compositions of the taenite and kamacite grains in the shocked sulfide intergrowths in Tishomingo are similar to those reported in shock-melted intergrowths in Sacramento Mountains, viz., 57–59 wt.% Ni and 2–4 wt.% Ni respectively (Scott, 1982). We infer that these compositions and the high Co in kamacite reflect very low-temperature equilibration between the two phases during post-shock annealing. However, the size of the taenite-rich areas of metal–troilite intergrowth (up to $\sim 50 \mu m$) and the coarser texture of the taenite-rich regions compared to the kamacite-rich regions suggest that low-Ni metal may have crystallized from the melt to form the rims of the intergrowth before high-Ni metal crystallized in the core. Experimental studies of the Fe–Ni–S system (see Ma et al., 1998) show that taenite with $\sim 50$ wt.% Ni can coexist with troilite at 700 $\degree C$. The high-Ni taenite and low-Ni kamacite in the intergrowth probably equilibrated during the reheating event that caused the thermal decomposition of the martensite.

Additional constraints on the shock and reheating history of Tishomingo are provided by stishovite (Corrigan et al., 2005) and the properties of taenite (Ives et al., 1978). Stishovite is the stable silica phase above $\sim 10$ GPa and has also been found in the shocked iron meteorite Muonionalusta (Hollstam et al., 2003). According to the experimental study of Huffman et al. (1993), the survival of stishovite requires that shock pressures do not exceed 30 GPa. They inferred that at higher pressures, post-shock temperatures would exceed $\sim 400 \degree C$ allowing stishovite to decompose to quartz. Assuming that this temperature is an upper limit for stishovite at low pressures, it is plausible that stishovite and the shock-melted sulfides formed during the same impact that caused thermal decomposition of martensite.

Ives et al. (1978) inferred from the twinning, dislocation density and hardness of the taenite that Tishomingo had been shocked to $\sim 17$ GPa after the martensite had formed. We infer that the deformation and twinning in taenite was caused by the same impact event that shock melted the sulfides and formed the stishovite.
4.4. Chemical composition and formation of Tishomingo and Willow Grove

Tishomingo and its close relative, Willow Grove, are both ungrouped irons with unusually high Ni contents, 32.5 wt.% and 28 wt.% Ni respectively (Birch et al., 2001). They have very high Ni contents like Santa Catharina, Twin City, and San Cristobal, which have 25–36 wt.% Ni and are related to the IAB complex irons (Wasson and Kallemeyn, 2002) and NWA 6259, which contains 43 wt.% Ni (Wasson, 2011). However, Tishomingo and Willow Grove have totally different concentrations of all other elements (Table 4). Cobalt concentrations are 0.6 wt.% in the IAB-related irons and nearly double that in Tishomingo and Willow Grove: 1.2–1.3 wt.%.

Refractory siderophiles are also much lower in the IAB-related irons than in Tishomingo and Willow Grove with 0.02–0.3 ppm Ir in the former and 17 ppm Ir in the latter two irons. By contrast, concentrations of volatile siderophiles are much higher in the IAB-related irons compared to those in Tishomingo and Willow Grove: 5–11 ppm Ga vs. 0.2 ppm in Tishomingo and Willow Grove, 2–4 ppm Au vs. 0.1–0.2 in the two irons, and 30–40 ppm As vs. 0.5–0.7 ppm in the two irons.

Tishomingo and Willow Grove are much more closely related to the group IVB irons, which have 16–18 wt.% Ni and are similarly depleted in volatile siderophiles and enriched in refractory siderophiles (Table 4). The two irons are unusually deficient in sulfides, phosphides, and carbides, consistent with their remarkably low volatile contents. Both lack carbides (Buchwald, 1975; Ives et al., 1978). Willow Grove lacks troilite and contains small amounts of schreibersite (<0.1 vol.% in the form of prismatic crystals up to 100 μm long (Birch et al., 2001). In Tishomingo, schreibersite is absent but troilite is present in small amounts.

Our ion probe analysis of bulk P and C in Tishomingo metal gave very low concentrations of these elements, 75 ± 5 ppm P, 2.5 ± 0.8 ppm C, and 20 ± 10 ppm S (Goldstein et al., 2012). We estimate that the total S concentration in Tishomingo including the mm-sized troilite inclusions and smaller metal-sulfide intergrowths is 0.06 ± 0.03 wt.%.

Despite their IVB-like features, Tishomingo and Willow Grove are chemically different from plausible extrapolations of group IVB trends to higher Ni concentrations and are ungrouped (Corrigan et al., 2005). Tishomingo and Willow Grove have chemical compositions that are so similar to each other and so different from other ungrouped high-Ni, IVB-like irons like Chinga (Table 4) Rasmussen et al. (1984) that they probably formed in the same parent body. This group could well be called group IVC when additional irons with their chemical characteristics are discovered. Their exceptionally low concentrations of volatile siderophiles presumably reflect early formation in a hot solar nebula, as for the IVB (Yang et al., 2010) and IVA irons.

If Tishomingo and Willow Grove had been derived from a fractionally crystallized body, we should expect that Tishomingo, which has the higher Ni concentration, would be much richer in Au and As than Willow Grove and poorer in Ir. Since Tishomingo is poorer in Au and As, its IVB-like features must be due to early loss of Au and As.
and has the same Ir concentration as Willow Grove, we can infer that the two irons are not derived from a fractionally crystallized core. This might reflect late accretion when there was insufficient \(^{26}\text{Al}\) to form cores in asteroids, as for IAB complex irons (Schulz et al., 2012). Alternatively, the two irons may be derived from a body that accreted early and formed a molten core but was largely destroyed by an impact so that the residual parts of the core failed to fractionally crystallize. Since their high-Ni concentrations cannot be attributed to fractional crystallization in the dregs of a core, they probably result from condensation processes in the nebula and oxidation of metal in the parent bodies (Campbell and Humayun, 2005; Corrigan et al., 2005).

Tishomingo was initially composed of one or more large taenite crystals and therefore most likely crystallized from the melt. Ives et al. (1978) examined a large polished section of Tishomingo approximately 10 cm long and 3 cm wide with the optical microscope and concluded that the section was originally part of a large single taenite crystal. Our studies of a Tishomingo slice about 1.5 cm \(\times\) 1.5 cm in size, and those of Ives et al. (1978) are consistent with Buchwald (1975) who did not observe any grain boundaries. The very low concentrations of S and P in Tishomingo and Willow Grove indicate that they crystallized at temperatures of \(~1450^\circ\text{C}\), which were higher than for the S-rich IAB-related irons.

The noble gas data indicate that Tishomingo most likely had a pre-atmospheric radius of \(~50–85\text{ cm}\), so the crystals may have been 0.1–1 m in size or larger. An upper limit on the cooling rate during crystallization can be derived from the relationship between dendrite arm spacing and cooling rate (see Scott, 1982). This relationship suggests that a 10 cm wide taenite dendrite (crystal) would have crystallized from a melt that was cooled at \(~0.05\ \text{^\circ\text{C/yr}}\).

### 4.5. Thermal and collisional history of Tishomingo

Fig. 12 summarizes the thermal history that we have inferred for Tishomingo based on our studies, those of Ives et al. (1978), and the experimental studies described above. Tishomingo crystallized slowly from a melt that cooled at \(<0.05\ \text{^\circ\text{C/yr}}\). If Tishomingo cooled in a body that had been partly melted by \(^{26}\text{Al}\), cooling rates at \(~500^\circ\text{C}\) were probably \(<100^\circ\text{C/Myr}\) comparable to the rates experienced by most ordinary chondrites and IAB iron meteorites (Taylor et al., 1987; Scott et al., 2013; Goldstein et al., 2013). However, cooling at 500 \(^\circ\text{C}\) may have been much faster if Tishomingo (and Willow Grove) were derived from a differentiated body that was largely destroyed by an impact. The absence of kamacite that normally forms on cooling through 500 \(^\circ\text{C}\) precludes a more quantitative estimate.

Rapid cooling of Tishomingo through 250 \(^\circ\text{C}\) at \(t_1\) (Fig. 12) is required by the absence of the cloudy taenite. In most irons, cloudy taenite forms at cooling rates of \(<10^4\ ^\circ\text{C/Myr}\) \((<0.01\ \text{^\circ\text{C/yr}})\). Cooling at \(>0.01\ \text{^\circ\text{C/yr}}\) rate is incompatible with a body that was heated and partly melted by \(^{26}\text{Al}\). If Tishomingo was slowly cooling at \(<100^\circ\text{C/Myr}\) at depth in a partly differentiated body, it was disrupted by impact before Tishomingo cooled through 250 \(^\circ\text{C}\). Alternatively, if Tishomingo’s parent body suffered an impact that disrupted the core before it crystallized then it may have cooled through 250 \(^\circ\text{C}\) at \(>0.01\ \text{^\circ\text{C/yr}}\) as a result of this impact. In either case, Tishomingo was disrupted in the first \(~100\ \text{Myr}\) when it was above 250 \(^\circ\text{C}\). Since Tishomingo’s closest relative, Willow Grove also lacks cloudy taenite and contains martensite (Birch et al., 2001), we infer that the parent body of this grouplet, like the parent bodies of the IAB, IVA and IVB irons was disrupted early in solar system history (Yang et al., 2008; Yang et al., 2010; Theis et al., 2013).

As a result of this impact event (or possibly another), Tishomingo cooled to a temperature between \(~75\) and \(~200^\circ\text{C}\) so that 80\% of the taenite was transformed to martensite (Ives et al., 1978; Kaufman and Cohen, 1956). Some time in the last 4 Gyr (at \(t_2\) in Fig. 12), Tishomingo was shocked to \(>10\ \text{GPa}\) on its parent body so that stishovite formed from silica, and sulfides were locally melted. Post-shock temperatures were above \(A_t\) \(~320^\circ\text{C}\), the temperature at which martensite starts to be converted directly to taenite, and below \(400^\circ\text{C}\), the temperature at which the Ni content of the taenite \(\gamma\) platelets (\(<40\ \text{wt.%}\)) is much less than the measured Ni content of the taenite \(\gamma\) phase in Tishomingo. Heating in this temperature range for about a year is consistent with experimentally determined particle sizes of taenite formed in this temperature range. Tishomingo cooled at \(>0.01\ \text{^\circ\text{C/yr}}\) preventing any conversion of untransformed taenite to cloudy taenite. Around 100 to 200 Myr ago (at \(t_3\) in Fig. 12), Tishomingo was excavated and exposed to cosmic rays as a body with a radius of \(~50–85\text{ cm}\) to start its journey out of the asteroid belt to Earth.

Since Tishomingo did not form martensite again after reheating to \(320–400^\circ\text{C}\), it could not have cooled below the \(M_s\) temperature of about \(~50\) to \(~100^\circ\text{C}\) after this reheating event. Tishomingo was therefore warmer when it was exposed in space as an \(~50–85\text{ cm}\) radius body after

![Fig. 12](image-url)
than it was after $t_1$ when 80% of the taenite was converted to martensite below −75°C and possibly as low as −200°C (Kaufman and Cohen, 1956).

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