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AN ATOM PROBE FIELD-ION MICROSCOPY STUDY OF PHASE SEPARATION IN THE TWIN CITY AND SANTA CATHARINA METEORITES

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Abstract - An atom probe field-ion microscopy investigation of the Twin City and Santa Catharina meteorites has revealed that the matrix of these meteorites has an ultra-fine scale two phase microstructure. The results indicate the presence of precipitates with an interparticle spacing of between 7.5 and 20 nm and amplitude fluctuations from 50 at. % Ni to approximately 15 at. % Ni. This evidence indicates that the matrix of these meteorites is a mixture of L1_0-ordered FeNi and a low nickel face centered cubic phase.

INTRODUCTION

The majority of iron-nickel meteorites have nickel contents of approximately 7% and exhibit a characteristic Widmanstätten structure consisting of kamacite and plates of taenite. In addition to these low nickel meteorites, there are two meteorites, Twin City and Santa Catharina, that have higher nickel levels of 30 to 35%. Several characterizations of these meteorites have been reported using a variety of techniques such as optical microscopy, scanning electron microscopy, X-ray measurements, Mössbauer spectroscopy, and transmission electron microscopy to characterize the microstructure. In this paper, atom probe characterizations of these two meteorites are described.

The composition of these two meteorites is close to that of the Invar alloys. In addition to their low expansion coefficient, Invar alloys have shown remarkable resistance to swelling under neutron and heavy ion radiation and are therefore of great technological interest for nuclear applications. Recently, marked composition variations have been reported in the matrix of Fe-Ni and Fe-Ni-Cr alloys that were subjected to high doses of heavy ion and neutron irradiation at temperatures in the range 450 to 650°C. Electron irradiation also affects the Invar behavior below 250°C. Several high temperature properties and parameters including lattice parameter, thermal expansion coefficient, electrical resistivity, magnetization, and elastic moduli show anomalies in Invar alloys. The presence of a low temperature miscibility gap has been suggested to explain these anomalies.

EXPERIMENTAL

The Twin City and the Santa Catharina meteorites used in this investigation have been classified as anomalous. The bulk compositions of these iron-nickel meteorites are given in Table 1. The Santa Catharina meteorite is heavily weathered and varies in composition from one region to another. The Santa Catharina sample used in this study was taken from an unweathered region of the meteorite. X-ray microanalysis in a scanning electron microscope revealed that the average local composition of the taenite matrix of the sample used in this study was 29.5 at. % Ni. The dark areas reported by Danon et al. in back scattered electron micrographs were not apparent in this section of the meteorite. Scanning electron microscopy analysis of the Twin City meteorite revealed an average matrix composition of 26.1 at. % nickel. The majority of the sulphur in these meteorites is contained in troilite, FeS, and does not remain in solution. Both meteorites contained trace amounts of Ga, Ge and Ir.

Table 1. Bulk composition of the Twin City and Santa Catharina meteorites, balance Fe

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Ni</th>
<th>Co</th>
<th>P</th>
<th>Meteorite</th>
<th>Ni</th>
<th>Co</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twin City</td>
<td>30.0</td>
<td>0.5</td>
<td>0.34 wt. %</td>
<td>Santa Catharina</td>
<td>35.3</td>
<td>0.6</td>
<td>0.20</td>
<td>1.8 wt. %</td>
</tr>
<tr>
<td>28.9</td>
<td>0.48</td>
<td>0.62 at. %</td>
<td></td>
<td>33.6</td>
<td>0.58</td>
<td>0.36</td>
<td>3.1 at. %</td>
<td></td>
</tr>
</tbody>
</table>
The primary analytical technique used in this investigation was atom probe field-ion microscopy, although optical microscopy and scanning electron microscopy were also performed to characterize the general microstructure. All atom probe analyses were performed in the ORNL energy-compensated atom probe. The field-ion micrographs were recorded with neon as the image gas, at a temperature of 60K.

RESULTS AND DISCUSSION

The general microstructure of the Twin City meteorite is shown in the optical micrograph in Fig. 1. The meteorite exhibited slip planes, some of which were bent, indicating that the meteorite had been deformed. Small particles decorated these slip planes, particularly at the intersection of two or more slip planes. These 1 μm diameter particles have been previously identified as phosphides. A scanning electron micrograph of the Santa Catharina meteorite, shown in Fig. 2, revealed the presence of larger 10 to 50 μm phosphide inclusions. These phosphide inclusions have been previously identified as Schreiberite, (Fe,Ni)₃P.

A field-ion micrograph of the Twin City meteorite is shown in Fig. 3. Some small brightly-imaging regions are evident. A selected area analysis of one of these brightly-imaging regions revealed a composition of 50.0 ± 2.9 at. % Ni. These brightly-imaging high nickel regions were roughly spherical with diameters of 1 to 2 nm. An atom probe composition profile through the matrix of the Twin City meteorite is shown in Fig. 4. Phase separation into high and low nickel regions was evident. The high nickel regions had a composition of ~50 at. % nickel. The low nickel regions were variable in composition and exhibited a minimum of approximately 15%. The average spacing of the regions was ~7.5 nm.

A field-ion micrograph of the Santa Catharina meteorite is shown in Fig. 5. The two phase microstructure is clearly evident in this micrograph from a high volume fraction of brightly-imaging precipitates in a darkly-imaging matrix. Field evaporation sequences through this microstructure revealed that the precipitates were randomly distributed through the matrix and were roughly spherical with an average diameter of approximately 10 nm and that the interparticle spacing was ~20 nm. Although most of the precipitates were isolated, some precipitates had coalesced due to the high volume fraction. No evidence of crystallographical alignment of the precipitates with a macrolattice was observed. The size and morphology of the precipitates determined in this study is in agreement with that previously reported by Jago from transmission electron microscopy. The isolated nature of the precipitates indicates that the morphology of the microstructure is distinctly different from the isotropic interconnected network of α-α' phases that has been observed in the high chromium FeCr alloys that have undergone spinodal decomposition within a low temperature miscibility gap followed by long aging treatments. However, this difference in morphology may be simply a result of spherosization of an interconnected network due to the much longer aging times.

Preliminary transmission electron microscopy investigations of the field-ion specimens revealed only the presence of ordered face centered cubic reflections in the diffraction patterns. No evidence for a body centered cubic phase was found. From the prominence of the crystallographic planes in the field-ion micrographs, the matrix phase was found to be consistent with a face centered cubic crystal structure (i.e. the (111) plane was more prominent than the (200) plane which was more prominent than the (220) plane).

The ordered nature of the brightly-imaging precipitates was evident by the alternating bright and dim imaging behavior of the (002) planes, as shown in Fig. 6. Atom probe plane-by-plane analysis revealed that these bright and dim (002) planes alternated between essentially pure iron and pure nickel. The lattice matching of the two phases indicated that the precipitates had a cube-on-cube relationship with the matrix. The c-axes of the ordered precipitates were found to be locally parallel to each other. In some of the cases where the precipitates had coalesced, antiphase boundaries were evident from the mismatching of the bright and dim planes across the boundary.

A short section of a random area atom probe composition profile through the Santa Catharina meteorite is shown in Fig. 7. The two phase nature of the microstructure is again clearly evident from the low and high nickel regions. It should be noted that this section of data is not representative of the scale of the microstructure since the centers of the high nickel regions were not intersected. Selected area atom probe analysis revealed that the bright regions in the field-ion micrographs corresponded to the high nickel regions and the darkly-imaging matrix to the low nickel regions. Because of the slightly coarser scale of this microstructure, accurate atom probe selected area analysis of the precipitates and the matrix was possible. Some representative compositions determined from these regions are presented in Table 2. The brightly-imaging regions were close to equiatomic FeNi. The low nickel matrix compositions of between 11 and 15% Ni is in agreement with the electron microscopy study of Reuter et al. These compositions also indicate that the almost 50% volume fraction of the high nickel regions is consistent with the areal fraction determined from the field-ion micrographs. The 50% volume fraction is also in agreement to that previously estimated from Mössbauer spectroscopy by Danon et al.
The microstructure was similar to that reported in a previous atom probe characterization of a 28.0 at.% Ni region of a taenite plate in the Cape York meteorite.\textsuperscript{29}

Table 2. Nickel contents from selected area atom probe analyses of the Santa Catharina meteorite.

<table>
<thead>
<tr>
<th>Low nickel regions</th>
<th>wt.%</th>
<th>at. %</th>
<th>High nickel regions</th>
<th>wt.%</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>region</td>
<td></td>
<td></td>
<td>region</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1)</td>
<td>14.7</td>
<td>14.1 ± 0.4</td>
<td>1)</td>
<td>50.4</td>
<td>49.2 ± 0.1</td>
</tr>
<tr>
<td>2)</td>
<td>11.8</td>
<td>11.3 ± 0.5</td>
<td>2)</td>
<td>52.8</td>
<td>51.6 ± 0.4</td>
</tr>
<tr>
<td>3)</td>
<td>15.8</td>
<td>15.2 ± 0.5</td>
<td>3)</td>
<td>48.4</td>
<td>47.2 ± 4.5</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The two meteorites exhibited the same fine scale microstructure with only minor differences in scale. The microstructure consists of a mixture of roughly spherical equiatomic FeNi precipitates in a matrix phase containing between 11 and 15% nickel. The prominence of the poles in the field-ion micrographs and the electron diffraction patterns both indicate that the low nickel matrix phase is consistent with a face centered cubic crystal structure. The composition, the cube-on-cube orientation relationship with the matrix, the alternating pure iron and pure nickel (002) planar compositions, and the electron diffraction patterns indicate that the high nickel precipitates have an L1\textsubscript{0}-ordered crystal structure (tetrataenite). The diameters of the L1\textsubscript{0}-ordered precipitates were approximately 2 nm in the Twin City meteorite and 10 nm in the Santa Catharina meteorite. The interparticle spacings were 7.5 and 20 nm in the Twin City and Santa Catharina meteorites, respectively. The volume fraction of the L1\textsubscript{0}-ordered precipitates was slightly higher in the Santa Catharina meteorite than the Twin City meteorite, as would be expected from the slightly higher nickel content of the meteorite. The high volume fraction of the two phases and their similar crystal structures is consistent with decomposition within a low temperature miscibility gap.

ACKNOWLEDGMENTS

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REFERENCES

Fig. 1. Optical micrograph of the general microstructure of the Twin City meteorite showing slip planes and small 1 μm diameter phosphide particles.

Fig. 2. Scanning electron micrograph of the Santa Catharina meteorite showing some 10 to 50μm phosphides. X-ray microanalysis of the matrix indicated a composition of 29.5 at. % Ni.

Fig. 3. Field-ion micrograph of the Twin City meteorite showing small brightly-imaging regions.
Fig. 4. Atom probe composition profile through the Twin City meteorite showing high and low nickel regions.

Fig. 5. Field-ion micrograph of the Santa Catharina meteorite showing a well developed two phase microstructure. Atom probe selected area analysis revealed that the brightly-imaging precipitates were approximately equiatomic in iron and nickel. The darkly-imaging matrix was lower in nickel.
Fig. 6. Field-ion micrograph of a brightly-imaging precipitate in the Santa Catharina meteorite showing alternating bright and dim (200) planes indicative of an ordered crystal structure.

Fig. 7. Atom probe composition profile through the Santa Catharina meteorite showing high and low nickel regions.