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PROGRESS IN UNDERSTANDING ATOMIC STRUCTURE OF THE ICOSAHEDRAL PHASE

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Abstract

Electron diffraction analysis of the icosahedral phase (i-phase) in AlMn alloys (i-AlMn) is presented which shows clearly that, in addition to the sharp diffraction maxima from the i-phase, there is a considerable amount of diffuse intensity indicating the presence of a certain amount of disorder interspersed within this phase. This result correlates well with previous results from both neutron diffraction and field ion microscopy studies and helps to reduce the number of possible structural models of the i-phase. Analysis of FIM images indicates the presence of a hierarchy of cluster sizes with numerous features which appear to agree qualitatively with recently proposed models. A complete quantitative description of the structure of the i-phase is being pursued by comparing experimentally observed atomic motifs with computer-simulated model surfaces, and preliminary results are presented.

The original (1) and subsequent reports of transmission electron microscopy (TEM) of the icosahedral phase (i-phase) of Al6Mn show electron diffraction patterns with only sharp diffraction maxima, consistent with an atomic structure having long-range orientational (icosahedral) order and no translational symmetry. However, weak-beam dark-field TEM images reveal an assembly of patches with about 5 nm dimensions (2). Field ion microscopy (FIM) has shown atomic structural features which are consistent with these TEM results, and additionally some apparent disorder (3). We present here the results of further TEM studies, some analysis of the FIM micrographs of the i-phase of Al6Mn and our initial efforts to computer simulate the FIM images.
Specimens for this work were prepared as described previously (3,4). Figure 1 shows a selected area diffraction pattern taken along a minor zone axis. In addition to the sharp diffraction maxima, a significant diffuse ring is evident, indicating the presence of disordered material within the i-phase. Dark-field images were obtained using a small portion of the diffuse ring to illuminate the i-phase; this showed that the diffuse scattering originated from very small regions, usually 1 nm or less in dimension, uniformly dispersed throughout the i-phase (M.J. Kaufman and A.J. Melmed, unpublished results). Also, a similar background occurs in diffraction patterns taken along the major 2-, 3- and 5-fold zone axes, as expected from the above results, although it is less intense relative to the intensities of the sharp maxima and therefore ordinarily is not obvious. Further, similar diffuse intensity has been observed for other i-phase materials as well. This correlates well with the FIM observations of disorder (3) and also with evidence for disorder seen in neutron diffraction patterns from the i-phase (B. Mozer, unpublished results).

We are thus led to speculate that only those structural models of the i-phase which consist of building blocks, or structural units, packed together with a profusion of small spaces (that is, interspersed with small disordered regions) are viable. We are aware of two such models which are promising candidates in terms of the degree to which they agree with the TEM observations. These are 1) packing of a Mackay-like 54 atom icosahedron (5) via 3-fold symmetry faces, a model of Cahn and Gratias (CG) and 2) packing of a similar size, but less dense 24 atom icosahedron via octahedral connecting links similar to (but slightly distorted from) the packing of icosahedra in the crystalline α-AlFeSi structure, proposed by Audier and Guyot (AG) (6). The AG icosahedron consists of a small hollow-centered icosahedron of 12 Al atoms, decorated with 12 Mn atoms at the corners. Thus, it can be dissected into planar pentagons normal to any 5-fold rotational symmetry axis, giving large regular pentagons of 5 Mn atoms and smaller regular pentagons of 5 Al atoms. The CG icosahedron has 30 additional Al atoms packed around the outside of the small icosahedron. Dissection of the CG icosahedron into planes, as above, gives small regular Al pentagons, large regular pentagons of 10 (5 Al and 5 Mn) atoms with Mn atoms at the corners, and also a large ring of 10 Al atoms. Thus, the models differ with respect to the structure of the basic icosahedron building block and the manner in which the icosahedra are interconnected. AG also suggest that a larger unit, a triacontahedron, is an integral part of the i-phase. Both of these models are incomplete at present, and the absolute dimensions are uncertain.

We have begun a detailed analysis of FIM image features for i-AlMn; a complete analysis awaits computer simulations of FIM images based on the different models. First, we consider images of the 5-fold rotational symmetry pole; thusfar, we have found essentially three types of atomic arrays in that region. These are (see figure 2) 1) a small incompletely resolved pentagon (P1), aligned with or rotated 36 deg. relative to the overall...
i-phase orientation, 2) a larger pentagon, similarly aligned, which has either a vacant center or an atom in the center (P2) and 3) apparently disordered or non-descript arrays of atoms. We note that the general atom ring system seen around the 5-fold pole is significantly smaller than around the 2- or 3-fold symmetry poles, usually indicating a smaller interplanar spacing perpendicular to the 5-fold pole (7). We have observed also many other completely or incompletely resolved pentagons of various sizes located some distance from the 5-fold symmetry axis.

We can assign dimensions to image features based on magnifications determined from the measured image voltages (7). Due to the uncertainties in this determination and the measurements of image spot positions, we estimate conservatively the possibility of ± 15% uncertainty in these dimensions. The edge-atom spacings for pentagons P1 (estimated by using one half the measured total width of the partially resolved pentagon side) and P2 are 0.35 and 0.78 nm, respectively. These are larger than similar pentagons within the icosahedra of the CG and AG models. Interestingly, however, if we increase the scale of the models by a factor of \((1+\sqrt{5})/2 = 1.62\) (the Golden mean) the small pentagon of the model icosahedra becomes 0.41 nm and the large one becomes 0.83 nm, which agree with the dimensions we have found. However, we have not observed two features of the CG icosahedron, specifically a larger (outer shell) pentagon having five Mn atoms at the corners and five Al atoms, each halfway between the Mn atoms, and a large ring of ten Al atoms.

The next FIM image feature we consider is a larger, seemingly distinct structural unit appearing at the surface as a recognizable patch having a surface cross-section size of about 2-7 nm, and sometimes having a pentagonal, although not necessarily regular, shape (examples of these can be seen in figures 3 and 4). Thusfar, we have identified 20 patches having about 4.5-5.5 nm maximum width. The atomic arrangements or motifs seen at the surface of these units, despite their appearances, are not random. Rather, we have found examples of considerable similarity in the atomic motifs.
The irregular pentagonal array of atoms seen slightly off-center on a 3-fold symmetry pole plane in figure 4 is rather interesting. It is about 5.1 nm across its widest part and has a shape which relates closely to the AG triacontahedron in the three-fold projection of that figure (again, the scales do not agree (even if we scale by about 1.62 as discussed above).

The very ragged edges of the atomic rings seen in the FIM micrographs (3) also is a feature which is explained by a cluster model, such as the two described above. The field evaporation process (6) results in such rings due to the intersection of planes with the nearly hemispherical specimen apex. In terms of a cluster model, such rings would be expected to be discontinuous, or broken up, as the individual building blocks and their interspaces are cut through by field evaporation. Interestingly, in a survey of 21 micrographs, no seemingly continuous ring segment having a chord longer than about 8 nm was found, and most large segments had chords about 4.5-6.5 nm long; many smaller segments were also observed. This observation tends to support a model with a hierarchy of structural units. The segments would result, in such a model, from the disruption of atom chains whenever some separation between building blocks occurred.

Selected scenes of the 3- the 2-fold symmetry regions are shown in figures 4 and 5. Some of these motifs are reproduced approximately in different instances on other similar planes; the analysis of these motifs is not yet complete. We have been using Moore’s computer simulation scheme (8) to simulate FIM micrographs for comparison to the experimental images; thusfar, we have simulated.

Fig. 3 Neon field ion micrographs of selected surface areas, not located on poles or zone lines. The upper and lower left micrographs are original results; the upper and lower right micrographs have outlines added to help the reader locate the large patches. Scale markers represent 2.5 nm.

Fig. 4 Neon field ion micrographs of 3-fold rotational symmetry poles. Scale markers represent 2.5 nm.
small areas corresponding to various single planes. One of the striking features of the computer-simulated field-evaporation of these planes, at least in the CG model which we are computing, is the frequent appearance of locally non-symmetric atomic arrays (fig. 6). This happens also for the 5-fold pole and, of course, results from the lack of short-range symmetry inherent in the model. This computer result agrees qualitatively, at least, with the FIM images (3). Local symmetry is often lost as field evaporation produces consecutive surface cuts through the specimen, because the individual building blocks (icosahedra in both models) are not stacked or arranged periodically in any direction.

![Fig. 5 Neon field ion micrographs of 2-fold rotational symmetry poles. Scale markers represent 2.5 nm.](image)

The direct comparison of FIM images and computer model structures is made difficult by the confluence of several factors. Field evaporation of binary alloys generally is difficult to simulate accurately (8); the field evaporation of binary alloys is often less orderly and less reliably understood than for elemental metals; and aluminum-based alloys are not known to be as well imaged in the FIM, compared to more refractory materials. Here, we note that at present we cannot distinguish images of Al and Mn atoms solely by image contrast. We believe that at least some of the atoms imaged are Al atoms, because atom pair spacings as small as 0.28 nm are seen, and also that at least some of the atoms imaged are Mn atoms, because the i-phase images and field evaporates as a more-refractory collection of atoms than does the excess Al phase (3). Finally, we note that the aperiodicity of the i-AlMn phase makes FIM image analysis non-routine. Thus, it seems reasonable to assume that ternary i-phase materials will present an even greater challenge.

We conclude that the i-phase contains very small regions of disorder interspersed within the phase and that the phase contains a hierarchy of sizes of building blocks. Also, all of the main features of the AG icosahedron have been seen in the FIM images, although there remain dimensional scaling differences, while two major features of the CG icosahedron have not yet been seen. In addition, there is some evidence for the existence of a larger structural unit. The FIM analysis presented here is based on micrographs obtained after random amounts of field evaporation (3). More decisive results, especially with regard to the structure of the basic structural building blocks, should be obtainable in the future from carefully controlled field evaporation and imaging sequences.
Fig. 6 Computer simulations of small areas of FIM surfaces (7).

a: four surfaces normal to a 5-fold pole, b: four surfaces normal to a 2-fold pole, and c: four surfaces normal to a 3-fold pole. A spherical shell of radius 60 nm and thickness 0.156 nm was cut through 5 to 8 icosahedra composed and connected as described in reference 4. Each surface area has a width of about 3 nm, based on the current model (4).

(The surface generating program is due to Jim Sims.)

References