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Authors
Dahmen, U.
Westmacott, K.H.

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U. Dahmen and K.H. Westmacott

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Unusual pentagonally-twinned precipitates were observed in a high-resolution transmission electron microscopy (TEM) study of needle-shaped germanium particles in aluminum. Although commonly found in small particles formed on substrates, such twinning has not been seen before in precipitates grown in the solid state. The morphologies and orientation relationships are consistent with symmetry principles.

The morphology of a precipitate forming in a solid matrix is determined by many factors. Strain energy, interfacial energy, formation temperature and prior history are amongst the most important. The fundamental processes underlying a precipitation reaction have been treated using many different approaches; for example, thermodynamic, mechanistic, kinetic, elastic continuum, all of which illuminate various aspects of the problem. It has recently become more appreciated that considerable understanding of a precipitation process might be deduced from an analysis of the precipitate morphology and orientation relationship in terms of crystal symmetry operations. (1-3) The present note gives a striking example of a precipitate morphology found in an Al-Ge alloy and a discussion of a preliminary analysis based on symmetry considerations.

The aluminum-rich end of the Al-Ge phase diagram is particularly simple. A decreasing solubility with decreasing temperature gives it characteristics typical of age-hardening systems. In dilute alloys (1.14 at% in the present work)
a quench from near the solidus temperature (550°C) followed by an aging treatment below 320°C leads directly to the precipitation of the pure germanium equilibrium phase. However, in contrast to its metallurgical simplicity, the precipitation process is by no means facile. This is a consequence of large disparities in the crystal structures and atomic volumes of the parent and product phases (Al and Ge have face-centered-cubic and diamond-cubic crystal structures respectively, and atomic volumes of 16.6 Å³ and 22.6 Å³ respectively). In the absence of excess vacancies which fulfill both structural and volume accommodation roles in the transformation(4), germanium precipitates cannot readily nucleate and grow in the aluminum matrix. This effect manifests itself in a variety of morphologies(5) which presumably reflects variations in local vacancy concentration.

TEM micrographs show mainly needle-shaped Ge precipitates, and when the foil is viewed along an <001> zone axis it is apparent that these needles lie along the three crystallographically equivalent <100> directions of the Al matrix. As shown elsewhere(3) <100> is an invariant line direction in this alloy system, thus constituting a favorable direction for needles to grow. Their length typically ranges from 100 to 500 nm. Until recently their cross-sectional shape was unknown. In the course of the present study, high resolution images of many needle cross-sections have shown that the needle axis is always parallel to a <110> direction of the Ge precipitate.(3,5) However, at least three major orientation relationships were found within the confines of <110> Ge || <100> Al. All precipitates contained twins along the needle axis, and often complex multiply-twinned particles were observed.
An interesting and unusual example of a multiply-twinned Ge particle is shown in the high-resolution image in Fig. 1 which was taken on the 1 MeV JEOL Atomic Resolution Microscope. Five wedge-shaped sections radiate from a common center of a precipitate that is roughly circular in cross-section. The five sections meet along planar twin boundaries indicated by lines drawn on the image. The \{111\} twin planes in the diamond cubic structure of Ge enclose an angle of 70.5°. Five such sections are therefore insufficient to fill a complete circle. The closure failure of 7.5° is taken up by two extra lattice planes inserted radially and ending at the arrow marks. A slight relative rotation between adjacent segments results from these extra planes and these defects are perhaps more appropriately described as wedge disclinations(6). Note the step in the left boundary at the end of the extra plane, and the stacking fault from there to the center. The particle appears to have pentagonal symmetry, but on closer inspection the facet on the lower segment and the notch between the upper two segments are not compatible with a five-fold rotation axis. It is also apparent that the center of the fivefold star is not at the centroid of the particle. However, the particle does possess mirror symmetry with respect to the twin plane marked m and with respect to the image plane, as well as a twofold rotation axis along the intersection of the two mirror planes. Hence the morphological symmetry of this precipitation is mm2, one of the three orthorhombic point groups. This symmetry describes its entire substructure including the two extra half planes as well as the shape.

By inspecting the lattice fringe directions in the Al matrix it can be seen that the \{110\} mirror plane in the matrix is parallel to the mirror plane marked \(m\) in the particle. The other mirror plane and the twofold axis are parallel to an \{001\} mirror plane and a \langle110\rangle diad in the matrix respectively, so that mm2 also represents the symmetry that the particle and matrix have in common,
referred to as their intersection group or the symmetry of the Wulff plot\(^{(1)}\).

Further examination of the symmetry elements common to the matrix lattice and that in each individual twin section of the precipitate reveals that four sections share only the 2/m monoclinic symmetry common to \(<110>Ge\) and \(<001>Al\). However, the fifth is of higher symmetry. In addition to the 2/m symmetry along the needle axis the Ge lattice in the lower segment also shares with the matrix 2/m symmetry along two further orthogonal axes, resulting in orthorhombic 2/m 2/m 2/m symmetry.

The observed symmetry points to two alternative mechanisms for the nucleation of this particle; i) the nucleus is a single crystal, most likely in the orientation of segment 1 which then forms several twins during subsequent growth, or ii) the nucleus is a pentagonal prism that changes to a pentagonally twinned crystal during growth by inserting two extra planes of atoms. The latter is the more interesting possibility of the two. It was pointed out by Bagley\(^{(7)}\) that whiskers of diamond and some metals are sometimes found to have pentagonal symmetry. This has usually been interpreted as arising from five-fold twinning of the crystal. However, another possibility is that growth occurs from a common axis of a close packed arrangement of atoms with pentagonal point symmetry but translation symmetry only along it axis, in the manner shown in cross-section in Fig. 2. The symmetry of this atomic arrangement is 5/mm2.* The equilibrium shape of such a particle in a cubic matrix must conform to the intersection of the point symmetry groups of matrix and precipitate, i.e. \(m3m \cap 5/mm2 = mm2\)\(^{(1)}\). This is the point symmetry that is in fact observed, a symmetry that remains unchanged even by adding two extra half planes in the possible transition from the pentagonal structure with periodicity only along one axis to the face-centered-cubic structure. Note that this type of pentagonal twinning is

*This group is also referred to as \(\overline{10} 2 m\)
different from that frequently found in small particles of Au and Ag\(^{(8-10)}\) with decahedral or icosahedral morphology. The multiple twinning in these particles is due to an anisotropy in surface energy: when twinned in a decahedral or icosahedral configuration the particle surface consists of low-energy \{111\} facets only. The savings in surface energy more than offsets the energy of the additional twin boundaries necessary for this morphology above a critical particle size of about 5 to 10 nm\(^{(10)}\).

One significant difference exists between the present and earlier physical science examples of 5-fold particle symmetry. The germanium particles appear to be the first in which the symmetry develops during a solid state treatment close to equilibrium. In contrast the decahedral and icosahedral multiply-twinned Au and Ag particles which have been produced by vapor deposition onto various substrates, are grown under conditions far from equilibrium. Similarly, the recently discovered quasi-crystals, which exhibit icosahedral point symmetry, but no translational symmetry, observed in Al-Mn\(^{(11)}\) and now in other materials\(^{(12)}\), are formed only under conditions of extremely rapid cooling e.g. splat quenching. Tenfold twin domains similar to the fivefold configuration observed in the present work have been found in Ni-Zr and Fe-Al alloys with orthorhombic and monoclinic crystal structure, respectively, but again only under conditions of rapid quenching \((13, 14)\).

It is expected that further analysis of the present particles at various stages in the growth will contribute to a fundamental understanding of underlying atomic mechanisms. A more detailed account of this work will be given elsewhere.

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References

Figure Captions

Fig. 1. High-resolution micrograph of pentagonally-twinned Ge precipitate in Al matrix with beam direction along $<110>_{Ge}$ and $<100>_{Al}$. Specimen water-quenched from 540°C and aged 1h at 240°C.

Fig. 2. Close packing of spheres with a fivefold axis of symmetry and translation symmetry only along the axis (after Bagley (7)).
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