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Observations of Pentagonally Twinned Precipitate Needles of Germanium in Aluminum

U. DAHMEN AND K. H. WESTMACOTT

Unusual pentagonally twinned precipitates were observed in a high-resolution transmission electron microscopy study of needle-shaped germanium particles in aluminum. Although commonly found in small particles formed on substrates, such twinning has not been seen 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 among the most important. The fundamental processes underlying a precipitation reaction have been treated by many different approaches, for example, thermodynamic, mechanistic, kinetic, and elastic continuum methods, all of which illuminate various aspects of the problem. It has recently become clear 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*). In this report we consider a striking example of a precipitate morphology found in an aluminum-germanium alloy and discuss the results of a preliminary analysis on the basis of symmetry considerations.

The aluminum-rich end of the aluminum-germanium phase diagram is particularly simple. A decreasing solubility with decreasing temperature gives it characteristics typical of age-hardening systems. In dilute alloys (1.14 atom percent in the present work) a quench from near the solidus temperature (450°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 (aluminum and germanium have face-centered cubic and diamond cubic crystal structures, respectively, and atomic volumes of 16.6 $Å^3$ and 22.6 $Å^3$, respectively). In the absence of excess vacancies that 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 reflect variations in local vacancy concentration.

Transmission electron microscopy (TEM) micrographs show mainly needle-shaped germanium precipitates; 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 aluminum matrix. As shown elsewhere (*3*), <100> is an invariant line direction in this alloy system, thus constituting a favorable direction for needle growth. The length of the needles 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 germanium 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.

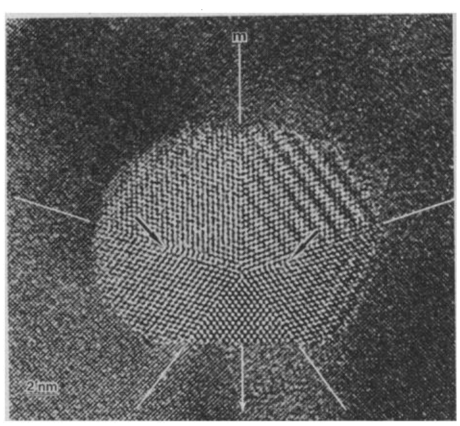

Fig. 1. High-resolution micrograph of a pentagonally twinned germanium precipitate in an aluminum matrix with the beam direction along <110> Ge and <100> Al. The specimen was water-quenched from 450°C and aged for 1 hour at 240°C.

An interesting and unusual example of a multiply twinned germanium particle is shown in the 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 germanium 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 closer inspection reveals that the facet on the lower segment and the notch between the upper two segments are not compatible with a fivefold 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 ***mm*2**, one of the three orthorhombic point groups. This symmetry describes its entire substructure, including the two extra half planes, as well as the shape.

Inspection of the lattice fringe directions in the aluminum matrix indicates 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 a {001} mirror plane and a <110> diad in the matrix, respectively, so that ***mm*2** also represents the symmetry that the particle and matrix have in common,

National Center for Electron Microscopy, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

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 germanium 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 the lower triangular segment, 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 the insertion of two extra planes of atoms. The latter is the more interesting possibility of the two. Bagley (*7*) pointed out that whiskers of diamond and some metals are sometimes found to have pentagonal symmetry. This has usually been interpreted as arising from fivefold 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 its axis, in the manner shown in cross section in Fig. 2. The symmetry of this atomic arrangement is $5/mm2$ (alternatively referred to as $\overline{10}\ 2m$). 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, that is, $m\bar{3}m \cap 5/mm2 = mm2$ (*1*). This is the point symmetry that is in fact observed, a symmetry that remains unchanged even by the addition of two extra half planes in the possible transition from the pentagonal structure with periodicity only along one axis to the face-centered cubic structure. This type of pentagonal twinning is different from that frequently found in small particles of gold and silver (*8–10*) with decahedral and 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*).

There is one substantial difference between the present and earlier examples of fivefold particle symmetry. The symmetry in the germanium particles develops during a solid-state treatment close to equilibrium. In contrast, the decahedral and icosahedral multiply twinned gold and silver 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 aluminum-manganese alloys (*11*) and in other materials (*12*), are formed only under conditions of extremely rapid cooling, for example, splat quenching. Tenfold twin domains similar to the fivefold configuration observed in the present work have been found in nickel-zirconium and iron-aluminum alloys with orthorhombic and monoclinic crystal structure, respectively, but only under conditions of rapid quenching (*13*, *14*).

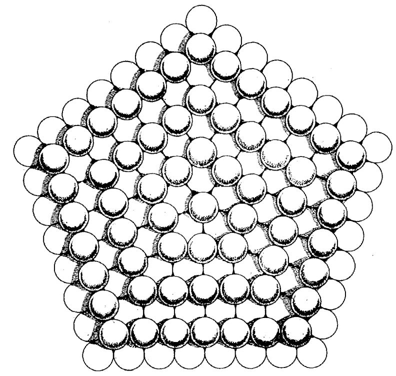

Fig. 2. Close-packing spheres with a fivefold axis of symmetry and translation symmetry only along the axis. [Adapted from (*7*)]

It is expected that further analysis of these particles at various stages in their growth will contribute to a fundamental understanding of underlying atomic mechanisms (*15*).

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A Fossil Grass (Gramineae: Chloridoideae) from the Miocene with Kranz Anatomy

JOSEPH R. THOMASSON, MICHAEL E. NELSON, RICHARD J. ZAKRZEWSKI

A fossil leaf fragment collected from the Ogallala Formation of northwestern Kansas exhibits features found in taxa of the modern grass subfamily Chloridoideae. These include bullet-shaped, bicellular microhairs, dumbbell-shaped silica bodies, cross-shaped suberin cells, papillae, stomata with low dome- to triangular-shaped subsidiary cells, and Kranz leaf anatomy. The leaf fragment extends the fossil record of plants that show both anatomical and external micromorphological features indicating C_4 photosynthesis back to the Miocene. On the basis of associated mammals, the leaf fragment is assigned a Hemphillian age (7 to 5 million years ago).

An intriguing problem in biology concerns the origin and evolution of C_4 photosynthesis, a physiological pathway that involves the formation of C_4-dicarboxylic acids as the initial products of CO_2 assimilation during the early stages of sugar formation in plants (*1*). Especially efficient at high temperatures and light intensities, this pathway is most often found in plants living in warm to hot tropical and subtropical areas. Although generally uncommon among plants, C_4 photosynthesis is

J. R. Thomasson, Department of Biological Sciences, Fort Hays State University, Hays, KS 67601.
M. E. Nelson and R. J. Zakrzewski, Department of Earth Sciences, Fort Hays State University, Hays, KS 67601.