A New Method for Automated Shape Measurement of Embedded Nanoparticles

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INTRODUCTION

The accurate measurement of particle or inclusion shapes is important because these shapes are related to physical properties such as growth rates or surface energies. For example, the equilibrium shape of an inclusion in a two-phase material is determined by the interfacial energy between the phases. If the interface energy $\gamma$ as a function of orientation is known ($\gamma$-plot), the equilibrium shape can be obtained via the Wulff construction [1]. Conversely, if the equilibrium shape is known, it is possible to derive information about the interface energy [2]. Although it is usually not possible to derive the complete $\gamma$-plot from the equilibrium shape, the shape provides information about the most important surface orientations.

Experimentally, equilibrium shapes are not easily obtained for large particles because equilibration is limited by the rate of diffusion. For example, if surface diffusion is rate limiting, the time to reach equilibrium scales with the fourth power of particle size [3]. Thus, the smallest particles are most likely to reach equilibrium, but the accuracy of shape measurements becomes more difficult at smaller sizes. This article is concerned with the equilibrium shape of small liquid Pb particles (50-200 nm in diameter) in a solid Al matrix. By monitoring the particle shape at different temperatures we aim at understanding the temperature dependence of the interfacial energy between liquid Pb and solid Al. In the past, shapes of liquid particles were mostly observed ex-situ by optical microscopy, scanning electron microscopy (SEM) or transmission electron microscopy (TEM) after quenching from elevated temperatures. However, it is questionable whether the shapes observed after cooling were the ones present at elevated temperatures. These doubts can be removed by the application of in-situ TEM, which allows direct observation of the particle shape at temperature [4,5]. A detailed description of the experimental procedure for alloy preparation, and a full analysis of the results has been given elsewhere [5]. Here we introduce the automated method we developed in order to make objective and accurate shape measurements on large numbers of particles.

The routines of existing computer software programs for stereological analyses proved unsuitable for our specific requirements. A basic problem of such programs is that the particle shape is often altered when the image is made binary (thresholding, "leaking contrast"). Since all subsequent measurements count the number of pixels on lines in different directions across the particle or in the particle area or its perimeter, the results of these measurements are affected. The two most commonly used measures for particle shapes are the aspect ratio $c/a$ and the formfactor $F$ [e.g. 6]. The aspect ratio $c/a$ is the ratio between two characteristic distances of the particle, and for an equilibrium shape, this is directly proportional to the ratio of the corresponding interfacial energies [7]. For a cubic-hedral particle, $c/a$ is the ratio of the distances between the (100) and (111) facets. However, image analysis programs usually define the aspect ratio as the ratio between the longest and the shortest distance measured across the particle. These distances are measured in each of 16 directions (every 11.25 degrees) on the feature. Therefore it is not guaranteed that really the shortest and longest distances are determined and the application of a correction factor to obtain the ratio of distances between (100) and (111) facets is not possible.

The formfactor is the ratio between particle area and perimeter and is generally a good measure of the deviation from an isotropic, spherical shape. However, the artifacts created on the particle perimeter after thresholding (leaking contrast) have a strong impact on this measure. In addition, the formfactor does not distinguish between vastly different shapes that deviate from a sphere by the same amount. As a result the formfactor is not useful for automated measurements of equilibrium shapes.

Our method overcomes these problems by...
treated the particle shape as a mathematical curve that is related to its physical properties and can be described by a number of different parameters.

**ALLOY SYSTEM AND THERMAL BEHAVIOR**

Pb-Al is a good model system for the study of the solid liquid interface. The two metals have widely separated melting points (Pb: 327°C, Al: 660°C) and negligible mutual solubility even at high temperatures (<2% Al in Pb at 660°C, just below the melting point of Al). Both phases have fcc lattices that are aligned parallel. In the solid state Pb precipitates take on a cubic-tetrahedral equilibrium shape. The aspect ratio of distances between the (100) and (111) planes is a measure of the ratio between the interfacial energies $\gamma_{100}/\gamma_{111}$ [7].

During heating above the melting point of Pb the following behavior is observed. Upon melting the (100) facets are replaced by spherical caps while the (111) facets remain initially unchanged, but recede with further increase in temperature until they disappear above a critical temperature, allowing the particles to round off. The critical temperature for rounding depends on size. During cooling a much smaller anisotropy of the particle shape is observed than during heating, and this smaller anisotropy is independent of size. These observations are the same particle shapes are depicted schematically. The aspect ratio $c/a$ is clearly different for the two shapes. However, the contact angle between the spherical cap and the (111) facets remains immobile. The eight (111) faces of the particle may thus be considered rigid boundaries that contain the melted Pb within a limiting octahedron. This is the kinetically limited particle shape.

**MODEL AND METHOD**

The observed discrepancies can be resolved when the kinetics of shape change are taken into account [see 5]. For a given temperature, a particle can change its shape easily at all facets that are above their roughening transition temperature [8]. Facets that are below their roughening temperature are limited by the need for ledge nucleation at the interface. While the (100) facets round off easily above the melting point of Pb the (111) facets are kinetically limited up to the (111) roughening temperature of 540°C. Below this temperature it was found that a size dependent barrier to ledge nucleation on (111) facets prevents the particle from attaining its full equilibrium shapes. While all surface orientations are free to minimize their surface energy, the (111) facets remain immobile. The eight (111) faces of the particle may thus be considered rigid boundaries that contain the melted Pb within a limiting octahedron. This is the kinetically limited particle shape.

Figure 1 gives a comparison of the kinetically limited particle shape during heating (Fig 1a) with the equilibrium shape of the same particle during cooling (Fig 1b). In Fig 1c and Fig 1d the same particle shapes are depicted schematically. The aspect ratio $c/a$ is clearly different for the two shapes. However, the contact angle between the spherical cap and the (111) facet is identical in both cases [5]. For the simple model of a spherical particle truncated by flat facets, it can be shown that the contact angle $\theta$ is directly related to the $c/a$ ratio characteristic of the equilibrium shape.

We developed a computer program that automatically measures the contact angle and the particle aspect ratio. The program is written in C++ and runs on a Unix workstation. Images of the particles are imported into the program as Tiff files. Figure 2 shows the parameters used to compute the equilibrium contact angle and the aspect ratio $c/a$ of the particles. These parameters are: the distance $D_1$ and $D_2$ between the (111) facets, the radii of curvature of the spherical caps, the coordinates of the circle centers $O_1$ and $O_2$ of the spherical caps and of the center of gravity of the particle $O$.

**Program Steps**

1. **Thresholding**
   A curve for the particle outline is obtained by thresholding the image. The threshold value is determined from a contrast histogram in which the intensity of each data point and the contrast to its neighboring points is determined. The intensity that has the highest sum of contrast counts is the threshold intensity.

2. **Hough transformation**
   The curve for the particle outline is sectioned into straight lines belonging to (111) facets and rounded parts belonging to the spherical caps. This is done by applying a Hough transformation based on the particle geometry, i.e. the 70.5° crystallographic angle between the two sets of (111) facets and the parallelism of each pair of (111) facets. A prerequisite for this step is the knowledge of particle orientation in the image to guarantee that the straight lines fitted to the particle curve are parallel to the facets.

3. **Least squares fit**
   The radius of curvature of the rounded segments is determined by a least squares fit to the data points $(x_i, y_i)$ of the particle outline. The general equation for a circle $(x-a)^2 + (y-b)^2 - r^2 = 0$ is fitted to the curve. The error of a fit for a particular radius $r$ is determined by the equation
   \[ \sum_{i=0}^{m} (|x_i - a|^2 + |y_i - b|^2 - r^2)^2 \]
   with $m =$ number of data points on the curved segment. The fit with the smallest error gives the solution for $a$ and $b$ which are the coordinates of the circle center $(a, b)$ and the radius $r$ of the circle fitted to the rounded end cap. The output of the program is an image of the particle into which the best fit for the circles and the parallel lines are drawn (Fig 3) and a table of spacings and coordinates.

**DISCUSSION OF ERROR SOURCES**

Before applying the program to experimental data we estimate the errors due to image acquisition, image processing and digital evaluation. Errors during image acquisition in the TEM and during image processing using the software program Adobe Photoshop are evaluated by comparing deliberately wrong conditions to more exact ones using our automated procedure. We will discuss the effect of the program itself first and then estimate the impact of experimental conditions in the TEM and of image manipulation in Photoshop.

**DIGITAL EVALUATION**

**Image resolution**

The accuracy of the measurement increases with the number of pixels in the object, making large image files desirable. On the other hand computing time and storage space limit the size of manageable files. So the first parameter to be determined is the minimum number of pixels required for an acceptable accuracy of the measurement. Test objects of known geometry were saved in image files with varying resolutions and evaluated by the program. The test objects were a circle representing the spherical particle and a circle truncated by two pairs of facets oriented at an angle of 70.5° with respect to each other, representing the faceted equilibrium shape. The objects were drawn using the program Canvas and saved in EPSF format. Upon opening the file in Adobe Photoshop the object size and image resolution can be selected. For the test objects the object size was kept constant at 1 cm while the image resolution was varied between 300 and 1500 pixels/inch. The reference aspect ratio $c/a = 1.322$ of the faceted particle was determined manually in Photoshop from the number of pixels in the spacings between the spherical caps and the (111) facets.

A comparison of the image output files obtained for different image resolutions shows that at low resolutions the two circles fitted to the object have widely separated centers and much too small diameters. With increasing resolution the circle diameters approximate that of the test object and the circle centers approach each other. The fact that always two circles are fitted to the object is a limitation of the current program leading to a difference between the measured values for the aspect ratio and that calculated from the contact angle $\theta$. However, as shown in Fig 1d these two measures are identical for equilibrium shapes. A comparison of the numerical data obtained for circles measured at different image resolutions shows that at 500 dpi the error due to aliasing is smaller than 1% for both measurements with 0.82% for the aspect ratio $c/a$ and to 0.35% for the contact angle $\theta$. For the faceted particle a comparison between the different image output files shows that a resolution of 800 dpi or more is required to correctly describe the contact angle $\theta$ of the spherical ends with the (111) facets. At this resolution the value calculated for the aspect ratio is 1.323 compared to 1.22 obtained for the contact angle. The deviation from the manually determined value amounts to +0.74% for $c/a$ and -0.49% for the contact angle. From the results obtained for different image resolutions for both test objects we decided to work with a resolution of 800 dpi corresponding to 320 pixels on the particle diameter. This guarantees errors smaller than 1% due to aliasing.

**Particle orientation in image**

A prerequisite for the Hough transformation
carried out by the program is knowledge of the particle orientation in the image. This guarantees that the straight lines fitted to the particle curve are parallel to the (111) facets. Even though the program works for any particle orientation in the image the result of the measurement depends strongly on the orientation of the particle with respect to the (110) zone axis. The errors caused by both variables can be kept below 1% by choosing an image resolution corresponding to 320 pixels on the particle diameter and by keeping the particle orientation constant in all images. The effect of experimental errors such as particle misalignment in the TEM, intensity variations around the particle outline and variation of image contrast was estimated using the evaluation program. It was found that the deviation from the exact orientation of the <110> zone axis has the strongest impact on the results. A continuous control of the particle orientation throughout the experiment is therefore necessary. The effect of intensity variation at the spherical (820) caps is stronger for underexposure than overexposure while variations of the image contrast have a negligible contribution.

The application of the program to monitor the shape changes of small liquid Pb particles in solid Al at different temperatures during a heating and cooling cycle enabled us to resolve the controversy about the anisotropy of the interfacial energy in the system Pb-Al [5]. From the results of a large number of measurements we established the hysteresis in shape between heating and cooling and obtained the true equilibrium shape. The concept of this new method, i.e. to treat the particle outline as a mathematical curve and to exploit the particle geometry to derive a measure for the particle shape, has the potential to be adapted to similar problems concerning the measurement of shape and physical properties.

REFERENCES
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