Supplement to Z. Phys. D 26, S 70–72 (1993)

Atoms, Molecules
Zeitschrift für Physik D and Clusters

Transformations in Quasimelting

D. Narayanaswamy and L.D. Marks

Department of Materials Science
Northwestern University
Evanston, Il 60208
Recieved 16 September 1992

Abstract. The structural fluctuations in small particles in the presence of an electron beam has been investigated using real time video recordings. The acquired images have been analyzed frame by frame in order to probe the exact nature of the quasimolten state. This analysis demonstrates that quasimelting, as experimentally observed in a high resolution microscope is a mixture of rapid rotations of the particle and much slower structural transformations. In addition, no evidence is found for an amorphous state.

PACS: 64.70.KB; 61.16 DI

1. Introduction

The structure of small particles has been a subject of research interest for many years. The observation[1] that such particles fluctuate in structure in a high resolution microscope has led to a fairly broad range of both experimental[2-5] and theoretical analyzes[6-8]. A common element of all the experimental analyses has been that the particles translate, rotate and change structures, the exact order and relative importance of these being, to date, undetermined. Theoretical explanations of these processes have been varied, ranging from transient melting due to inelastic excitations[6,7] to thermodynamic fluctuations in shape/structure[8]. The latter model has received substantial support of late. The model describes the particles as being in a state where they fluctuate between different local equilibria assisted by, but not solely due to, the electron beam. Molecular dynamics calculations by a number of authors[9-12] show the presence of such a state and a number of recent experiments indicate that the electron beam is not critical in perpetuating the state[13,14].

In order to understand the fluctuations in more detail, it is necessary to characterize the state and the factors that contribute to the energetics. Some progress has been made in determining the significant energy terms. For instance, it was first suggested[13] and recently confirmed[14] that the particle substrate adhesion energy plays a critical role. However, beyond a few snapshots of particle shape, little is currently known about the exact character of the morphological transformations in quasimelting.

In this note, we report the results of a detailed, frame by frame analysis of a quasimolten particle using high resolution electron microscopy(HREM). The data has been reduced to show the particle morphology as a function of time. From this data, it becomes apparent that the particle stays in a given structure for relatively long times between structural fluctuations and rotates at a much higher frequency.

2. Experimental Procedure

Small particles of gold were evaporated onto a holey silicon monoxide support. These particles were then examined in a conventional 300KV high resolution electron microscope at an electron beam flux of $25A/cm^2$. A Gatan TV camera was used to observe the images and its output was fed (without processing) into a Sony 8mm videotape recorder. The images were recorded at the rate of 30 frames per second. Single frames of the images were then transferred to an Apollo computer using an Imaging technology 151 framestore bus interface for further analysis using

SEMPER software.

The data acquired by the image recording was analyzed by employing a data reduction scheme. A basis set of good images were selected from the entire recording, and completely characterized. The HREM characterization was done on the lines of earlier workers[15]. Some of these images are shown in Fig 1.

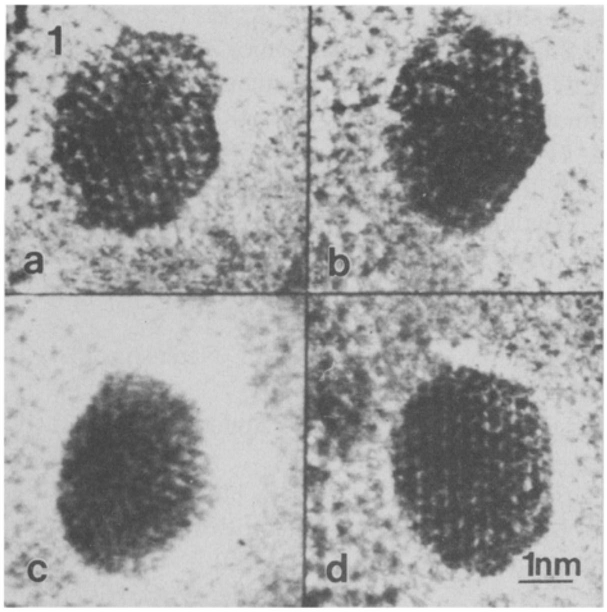

Figure 1: Sampling of the basis set (a) Single twin, (b) Asymmetrical decahedral multiply twinned particle(MTP), (c) Single crystal, (d) Icosahedral MTP.

The basis set was found to consist of four distinct morphologies in various orientations. The morphologies isolated were

1) Single crystal particles in a Wulff-polyhedron shape.

2) Particles with a twin boundary.

3) Decahedral particles.

4) Icosahedral particles.

The tape was then processed frame by frame by matching all the images with the collected basis set. Cross-correlation filtering with a Gaussian[16] Fourier filtering and power spectra of single frame images were used to enhance the visibility of any fringes in the particle. In addition to any lattice fringes, the overall particle morphology and facetting of the surfaces were also used. We should note that we were only able to identify the particles about 50% of the time, and included an undetermined classification in the analysis.

3. Discussion

One breakdown of the morphological analysis is shown in Fig 2.

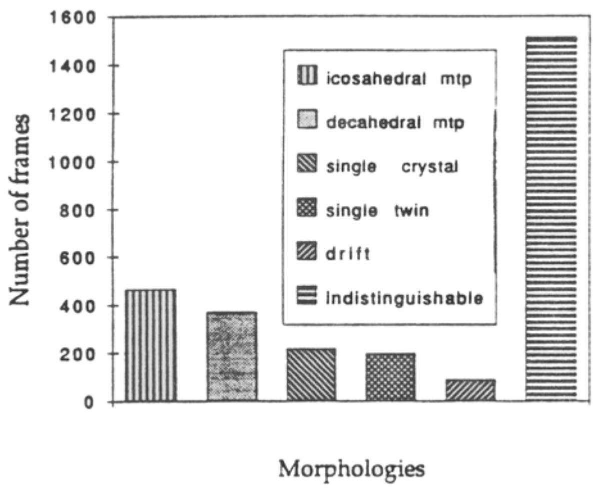

Figure 2: Histograms showing the total time spent by a 3nm particle in a particular morphology.

A total of 2849 frames were used in this analysis, and all the data is for a single particle. From this data each of the morphologies is approximately equally probable. However, the statistics are as yet too poor to be positive about this.

A much better representation of the data is the trajectory of the particle as a function of time. This is illustrated in Fig 3. The data reveals that the particle resides in a clearly identifiable state for some time then becomes unidentifiable and finally reverts to the same identifiable state once again. It is further observed that during the time the particle is identifiable its morphology and orientation undergo very small changes. The interpretation is that the particle stays in essentially the same morphology for extended periods of time, fluctuating slightly and rotating but not transforming.

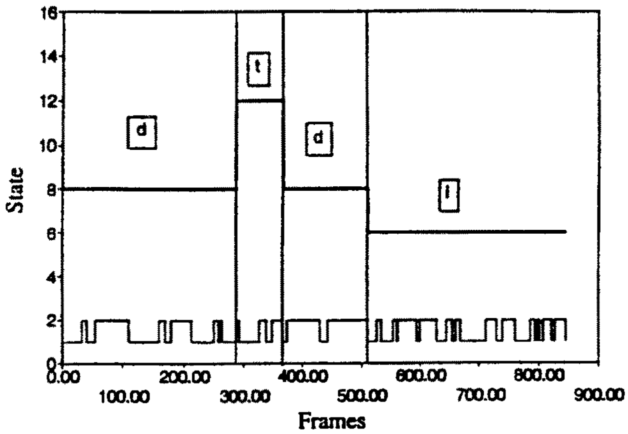

Figure 3: Time sequence comparison of rotational and structural transformations. Arbitrary values have been assigned for the structural states (The labels d,i,t denote decahedral, icosahedral MTPs and single twin respectively) and rotations(1,2 states).

One final point about the experimental data.In the quasimelting regime the particle is decoupled from the substrate and has minimal interaction with the substrate. During this state, the particle exhibits a variety of morphologies. If an amorphous state existed with a stability period of at least the order of 1/30th of a second, it would have been observable as an amorphous "speckle" image. There was no evidence of such a state in this experiment, which puts an upper limit on the stability of amorphous states.

There are still many uncertainties about the exact nature of the quasimolten state. The evidence is now quite strong that quasimelting is assisted by the electron beam in an electron microscope, but does occur in its absence and is therefore intrinsic to small particles. However, the matter remains undecided. The real answers will come when maps of the morphologies of small particles as a function of time become available. Unfortunately, the current limitation to 1/30 second resolution of TV equipment poses a problem.

This work presents a better definition of quasimelting, which can now be clearly broken down into two elements, namely a rapid rotation and a much slower structural transformation. We hope for more experimental refinement in the future.

The work was supported by the National Science Foundation on grant number DMR8911297.

References

[1] S. Iijima and T. Ichihashi. Phys Rev Lett. **56**, 616 (1986).
[2] D. J. Smith, A. K. Petford-Long, L. R. Wallenberg and J. O. Bovin. Science. **233**, 872 (1986).
[3] L. R. Wallenberg, J. O. Bovin, A. K. Petford-Long and D. J. Smith. Ultramicroscopy. **20**, 71 (1986).
[4] J. O. Malm, J. O. Bovin, A. K. Petford-Long and D.J.Smith. Angewandte Chemie. **27**, 555 (1988).
[5] B. D. Hall, M. Flueli, D. Reinhard, J. P. Borel and R. Monot. Rev Sci Instrum. **62**, 1481(1991).
[6] A. Howie. Nature. **320**, 684 (1986).
[7] P. Williams. Appl Phys Lett. **50**, 1761 (1987).
[8] J. Dundurs, L. D. Marks and P. M. Ajayan. Phil Mag. **A57**, 605 (1988).
[9] M. R. Hoare and P. Pal. J Cryst Growth. **17**, 77 (1972).
[10] R. S. Berry, J. Jellinek and G. Natanson. Phys Rev. **A30**, 919 (1984).
[11] J. D. Honeycutt and H. C. Andersen. J. Chem Phys. **91**, 4950 (1987).
[12] S. Sawada and S. Sugano. Z. Phy D. **20**, 259 (1991).
[13] P. M. Ajayan. Phase instabilities in small particles. Phase Transitions. **24**, 229 (1990).
[14] S. Giorgio, C. Chapon, C. R. Henry, G. Nihoul and J. M. Penisson. Phil Mag. A. **64**, 87 (1991).
[15] L. D. Marks and D. J. Smith. J. Cryst Growth. **54**, 425 (1981).
[16] M. I. Buckett, L. D. Marks and D. E. Luzzi. Proc of the 45th annual meeting of EMSA, 752 (1987)