Acta Materialia 120 (2016) 364–378

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

# Dislocation mediated alignment during metal nanoparticle coalescence

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ARTICLE INFO

*Article history:*
Received 23 June 2016
Received in revised form
10 August 2016
Accepted 23 August 2016

*Keywords:*
Nanoparticle coalescence
Nanoparticle sintering
Dislocations
Twinning
Oriented attachment

ABSTRACT

Dislocation mediated alignment processes during gold nanoparticle coalescence were studied at low and high temperatures using molecular dynamics simulations and transmission electron microscopy. Particles underwent rigid body rotations immediately following attachment in both low temperature (500 K) simulated coalescence events and low temperature (~315 K) transmission electron microscopy beam heating experiments. In many low temperature simulations, some degree of misorientation between particles remained after rigid body rotations, which was accommodated by grain boundary dislocation nodes. These dislocations were either sessile and remained at the interface for the duration of the simulation or dissociated and cross-slipped through the adjacent particles, leading to improved co-alignment. Minimal rigid body rotations were observed during or immediately following attachment in high temperature (1100 K) simulations, which is attributed to enhanced diffusion at the particles' interface. However, rotation was eventually induced by {111} slip on planes parallel to the neck groove. These deformation modes led to the formation of single and multi-fold twins whose structures depended on the initial orientation of the particles. The driving force for {111} slip is attributed to high surface stresses near the intersection of low energy {111} facets in the neck region. The details of this twinning process were examined in detail using simulated trajectories, and the results reveal possible mechanisms for the nucleation and propagation of Shockley partials on consecutive planes. Deformation twinning was also observed *in-situ* using transmission electron microscopy, which resulted in the co-alignment of a set of the particles' {111} planes across their grain boundary and an increase in their dihedral angle. This constitutes the first detailed experimental observation of deformation twinning during nanoparticle coalescence, validating simulation results presented here and elsewhere.

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## 1. Introduction

Solid-state coalescence occurs when two initially isolated particles bond together in order to reduce their surface energies. Coalescence governs the initial stage of sintering when particles have translational and rotation degrees of freedom. It also occurs during crystal growth in solution when small nuclei attach to form larger nuclei [1–4]. Conventional models for coalescence were developed in the context of sintering and describe densification processes by diffusive transport mechanisms (e.g. surface diffusion, grain boundary diffusion, and evaporation/condensation) [5–7]. These models may be used to describe neck growth, but, with the exception of grain boundary diffusion, fail to describe processes by which particles align their crystallographic axes.

Particle alignment processes appear to play an important role during the coalescence of smaller particles (~1–10 nm), for which interfaces and surfaces can greatly influence particle-particle interactions. The thermodynamics of these processes are relatively straightforward – alignment reduces the total energy of the system by removing or reducing strain at the particles' interface associated with a grain boundary. A number of groups observed the rotation of nanoparticles prior to or during attachment using *in-situ* liquid-phase and *in-vacuo* TEM [1–3,8–10]. These rotations corrected

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http://dx.doi.org/10.1016/j.actamat.2016.08.061
1359-6454/Published by Elsevier Ltd on behalf of Acta Materialia Inc.

misorientation and, in some cases, led to perfectly aligned, coherent particles. The driving force(s) for this process, commonly referred to as oriented attachment (OA), are not well understood. Furthermore, the conditions that yield particle alignment or lead to extended defects within the agglomerated crystal have not been realized due to the complexity of this process. Li et al. suggested long range solvation and van der Waals forces may be involved in OA when coalescence occurs in solution [2]. Imperfect OA was observed by Penn and Banfield [11], Li et al. [2], and others, during which particles did not fully correct misalignment during OA and the resulting interface consisted of grain boundary dislocations. It was suggested that subsequent grain boundary migration or dislocation motion could lead to further co-alignment, however the dynamics of these processes, if they occur, remain unclear. Aabdin et al. investigated OA in gold nanoparticles using molecular dynamics (MD) and identified a critical tilt angle (~15°) above which particles did not fully correct misalignment when they had common, adjoining (111) planes [3]. This result suggested that under prescribed initial conditions, sessile dislocations may form at interfaces during coalescence and inhibit further co-alignment. However, the stability of such defects (whether or not they are sessile) and their role in subsequent co-alignment have not been rigorously examined by MD or experiment.

Twins were also observed after coalescence during in-situ TEM experiments involving nanoparticles of iron oxyhydroxide [2], palladium [9], and gold [12]. These twins were often ascribed to preferential particle attachment when the misorientation between particles was consistent with a low energy grain boundary. In MD simulations, however, twins were seen to occur by {111} slip. This raises the question of whether twins form by OA or deformation processes during coalescence. Zhu and Averback, using MD, first observed the deformation of {111} planes parallel to the neck groove during the coalescence of aligned and misoriented ~5 nm copper particles at 700 K [13]. They attributed this deformation to a high surface stress in the neck groove which arises from an imbalance of surface tension at the intersection of the particle surfaces (a dihedral angle smaller than the equilibrium value). Similar deformation behavior involving {111} slip systems parallel to the neck groove was observed during MD studies of aluminum [14], palladium [15], and nickel [16]. Most early MD simulations of nanoparticle coalescence were run for short times (~100 ps) until neck growth terminated. However, coalescence simulations run for longer times (~5 ns) revealed that these deformation modes lead to twins well after the neck is formed. Cheng and Ngan studied these twin structures by simulating the coalescence of particles in the range of 2–4 nm [17]. They found that twinning occurred predominantly by the slip of Shockley partials on consecutive planes. However, the driving force for the observed twinning remains unclear. Furthermore, many details of the twinning mechanism are not well understood such as the source of partial dislocations which glide on parallel {111} planes, the connection between the initial misorientation and the final twin structure, and the high stability of the resulting coalesced, twinned structures. More significantly, no detailed experimental observations of deformation twinning during nanoparticle coalescence have been made to support these *in-silico* results.

In this study, the dynamics of nanoparticle coalescence were systematically studied *in-vacuo* under conditions where dissolution, recrystallization, and solvation effects were eliminated. Particle alignment processes and deformation twinning during the coalescence of gold nanoparticles were identified at low and high temperatures using MD simulations and corroborated by *in situ* TEM heating experiments. Dissociation and glide of grain boundary dislocations after imperfect OA was observed during low temperature simulations, which led to additional co-alignment between particles. Deformation twinning was seen in all high temperature simulations in which the particles had common (100) faces. It was not observed, however, when the particles had common (111) faces. Particle rotation following neck formation was observed during *in-situ* TEM beam exposure experiments, consistent with the simulation results. Deformation twinning was also observed during *in-situ* beam exposure TEM experiments without heating, which resulted in the alignment of the coalesced particles' {111} planes and an increase in their dihedral angle. A model is proposed for the coalescence of faceted particles, which considers the energy cost associated with neck growth. By using a combined simulation and experimental approach, microscopic insights into the dynamics of coalescence were developed which provide a framework for the development of processing strategies for nanocrystalline materials where the formation of metastable defects may limit or enhance their physical properties.

## 2. Molecular dynamics simulations

### 2.1. Methodology

Coalescence events of 5 nm gold nanoparticles with multiple misorientation angles were simulated at 500 and 1100 K. Misorientation is denoted using common grain boundary notation for which rotation angle, rotation axis, and interfacial plane are specified (e.g. 10°[010](100) describes a 10° rotation of one particle about the [010] axis which was initially aligned with its (100) face coincident with the other particle's (100) face). Tilt misorientations of 10°[010](100), 20°[010](100), and 40°[010](100), twist misorientations of 45°[100](100), 45°[111](111), and initially aligned particles, 0°(100) and 0°(111), were analyzed. Prior to simulating coalescence, the particles were thermalized separately by increasing their temperatures at a rate of 4 K/picosecond from room temperature, then annealing at 500 K or 1100 K for 50 ps. Coalescence was simulated for 5 ns with 1 fs time steps under the constant temperature (NVT) ensemble using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). A Nose-Hoover thermostat was used with a 100 time step damping parameter. Interatomic interactions were modeled using an embedded atom model type potential developed by Auckland et al. [18]. The potential was fit to empirical data for the equilibrium f.c.c. lattice parameter, cohesive energy, $C_{11}$, $C_{12}$, and $C_{44}$ elastic constant, the vacancy formation energy, and the stacking fault energy. The cutoff radius for pairwise energy calculations was set to 5 Å, which corresponds to about 1.73 times the separation of nearest neighbors in the equilibrium volume f.c.c. lattice. The potential decays smoothly to zero at the cutoff value. To analyze the microscopic mechanisms, snapshots saved during the coalescence simulations were quenched using a 1000 step steepest decent minimization scheme. Analysis of MD trajectories and dislocations were carried out using OVITO [19] and the dislocation extraction algorithm (DXA) [20], respectively. DXA identifies arbitrary dislocations by integrating over discrete Burgers circuits around displaced regions of the crystal. Although it was used to gain a qualitative understanding of dislocation behavior during coalescence, specific Burgers vectors described in the text were identified by analyzing atomic displacements unless noted otherwise.

### 2.2. Rotation during and immediately following attachment (oriented attachment)

At low temperatures (500 K, or ~0.37$T_m$ where $T_m$ is the melting point of bulk gold), particles *in-vacuo* with tilt misorientations underwent rigid body rotations during attachment (Fig. 1). Rotation during attachment was minimal at high temperatures (1100 K, or