論　文　内　容　要　旨

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学位論文の 題　　　目	Study on Impurity Partitioning during Colloidal Polycrystallization − effect of grain boundary and morphology of the solid−liquid interface – （コロイド多結晶の成長における不純物分配について－粒界と固液界面形状が与える分配への影響について－）		

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論 文 内 容 要 旨

This thesis focuses on the impurity partitioning during the polycrystallization of colloidal crystals, which investigated the impurity partitioning at grain boundaries (GBs) and revealed the segregation process of impurity and corresponding influential factors. The outline of this thesis is as follows.

In chapter 1, researches about GB segregation were introduced. Though most researches assume that impurity segregation at GBs takes place in annealing process, it was recently reported that GB segregation occurs during solidification. Impurity segregation at GBs during crystal growth is still under debate. To reveal the mechanism of GB segregation, a colloidal crystal is introduced. The growth of colloidal crystals enables us to study the detailed dynamics of crystallization, melting, and nucleation with single-particle resolution in real time.

The colloidal particles and growth cells used in the experiment and the in situ observation technique are described in Chapter 2. The convective self-assembly is applied for growing colloidal crystals in this work, because small density difference between solid and liquid during crystallization is similar to melt growth. Monodispersed polystyrene (PS) particles and red and green fluorescent particles were used in the experiment.

The impurity segregation at GBs are presented in Chapter 3. Impurity partitioning for both grains and GBs were investigated via in-situ observation. A close-packed {111} plane of the face-centered cubic (fcc) structure was observed on the surface normal to the growth direction. The impurities were incorporated into crystals as substitutional impurities. The impurity particles gathered more at GBs than in grains. Impurity partitioning of polycrystalline grains is found to be similar to that of single colloidal crystals, which follows the Burton, Prim, and Slichter (BPS) model. Impurity concentration at GBs (C_{GB}) for various misorientation angles (θ) between adjacent grains and growth rates (V) has been investigated. C_{GB} was found to increase with either increasing θ or V, and also when the size of the impurity is close to that of the host colloid particle. Possible mechanisms for the incorporation of impurities into GBs are discussed. Analysis based on BPS theory indicates that both the incorporation of impurities directly from liquid and impurities that rejected by grain give significant effect on GB segregation.

In Chapter 4, the effect of the solid−liquid interface morphology on the diffusion behavior of impurities in the liquid in the vicinity of the interface is demonstrated. It is observed that GB always has a groove at solid−liquid interface, where GB was exposed to the liquid at the bottom of groove. The time evolution of impurity distribution in the liquid in the vicinity of solid−liquid interface was investigated. The observations revealed that impurities are distributed homogenously at the initial growth stage and are then gradually accumulated at the groove formed at the GB. The impurity concentration of the GB increased with the groove area. For the impurity partitioning of polycrystal colloidal growth, grain orientation was found to influence the energy state of the solid−liquid interface, which determines the groove area and therefore results in different C_{GB}. The influence of the groove area on grain boundary segregation was experimentally demonstrated in this chapter.

The transition of crystal orientation accompanied by the change in the number of layers during colloidal polycrystallization was investigated in Chapter 5. The evolution of packing structure during the change of number of layer from 1 to 2 and that from 2 to 3 was traced. [100]-oriented grains form between [111]-oriented grains when the layer thickness increases. Since the volume fraction of [111]- is larger than that of [100]-oriented grains for the same number of crystal layers in a multilayer region, [111]-oriented grains is more stable, which changes the [100]-oriented grains into [111] after the increase of number of layers is completed.

Chapter 6 is summary of this work. We have successfully clarified the impurity behavior in GB segregation via in situ observations. The detail process of impurity segregation into GBs was observed and it was qualitatively analyzed. We experimentally demonstrated that the groove at the GB contributes to GB segregation. A crystal-orientation transition is associated with change in the number of layers during colloidal polycrystallization. These observations will contribute to the fundamental understandings of GB segregation during polycrystal growth.

論文審査の結果の要旨

コロイド結晶は原子や分子からなる結晶のように相転移を示すため、相転移に関わる様々な物理現象のモデルとして用いられている。様々な材料の結晶成長において、不純物挙動の制御は材料の機能性や高品質化にとり最も重要な要素の一つである。本研究はコロイド多結晶成長中の粒界偏析現象に焦点を当てている。

第 1 章では、コロイド結晶と不純物の粒界偏析について述べている。コロイド結晶成長における不純物挙動について一般的な粒界偏析現象と比較しながら、参考文献を挙げ説明している。

第 2 章では、本研究で用いた結晶育成方法について述べている。コロイド結晶化の原理、特に、本研究で用いた移流集積法について詳述している。

第 3 章では、コロイド多結晶成長における粒界偏析挙動について述べている。粒界に取り込まれる不純物の偏析は、結晶の成長速度、不純物の粒径、粒界をなす粒子間の方位の違いにより支配されることを明らかにした。成長速度と不純物分配の関係を示す通常の BPS モデルはコロイド結晶の粒界偏析に適用できない事を明らかにした。結晶に取り込まれなかった不純物が固液界面を拡散し粒界に到達して粒界に取り込まれる。こうした粒界偏析のプロセスを独自のモデルを立てることにより説明した。

第 4 章では、粒界が固液界面に露出した場所に形成される“凹み”が粒界偏析に与える影響について述べている。固液界面近傍の融液中の不純物分布はこの凹みの影響を受け、凹みの面積が大きいほど粒界の不純物濃度は高くなる事を明らかにした。この凹みの大きさは，粒界をなす結晶間の方位の違い、または結晶の固液界面の異方性で決定されることを示した。

第 5 章では、結晶成長に伴う層の発達に伴う結晶方位の変化について解析している。本研究で用いた成長セルでは、面心立方構造の{111}面と同様の配列をもった 1 層の結晶が成長初期に形成する。その後、セルの厚さの増加に従って結晶を構成する層の数も増加するが、第 *n* 層の形成において直接{111}構造は形成されず、*n*-1 層の{111}面から{100}面の配列をもつ漸移帯を経由して{111}構造が形成されることを明らかにした。

以上の研究成果は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、胡素梦提出の博士論文は博士（理学）の学位論文として合格と認める。