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Structural evolution in the crystallization of rapid cooling silver melt

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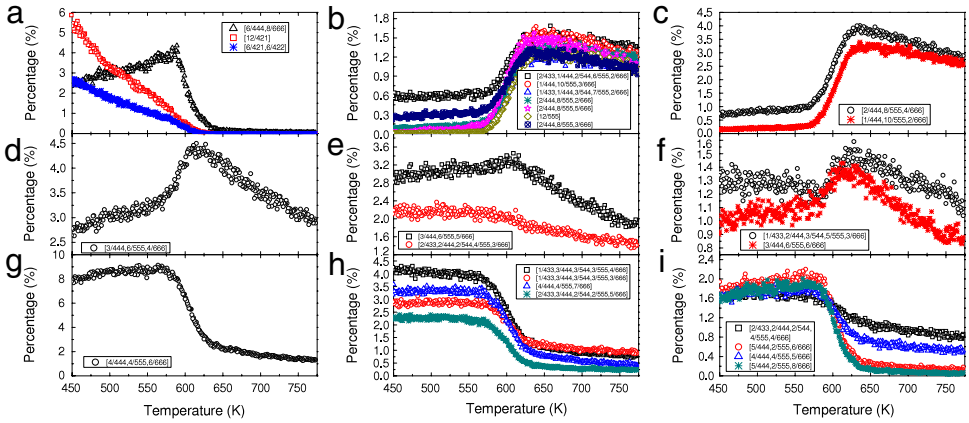
GRAPHICAL ABSTRACT



HIGHLIGHTS

- A comprehensive structural analysis is conducted focusing on crystallization.
- The involved atoms in our analysis are more than 90% for all samples concerned.
- A series of distinct intermediate states are found in crystallization of silver melt.
- A novelty icosahedron-saturated state breeds the metastable bcc state.

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ABSTRACT

The structural evolution in a rapid cooling process of silver melt has been investigated at different scales by adopting several analysis methods. The results testify Ostwald's rule of stages and Frank conjecture upon icosahedron with many specific details. In particular, the cluster-scale analysis by a recent developed method called LSCA (the Largest Standard Cluster Analysis) clarified the complex structural evolution occurred in crystallization: different kinds of local clusters (such as ico-like (ico is the abbreviation of icosahedron), ico-bcc like (bcc, body-centred cubic), bcc, bcc-like structures) in turn have their maximal numbers as temperature decreases. And in a rather wide temperature range the icosahedral short-range order (ISRO) demonstrates a saturated stage (where the amount of ico-like structures keeps stable) that breeds metastable bcc clusters. As the precursor of crystallization, after reaching the maximal number bcc clusters finally decrease, resulting in the final solid being a mixture mainly composed of fcc/hcp (face-centred cubic and hexagonal-closed packed) clusters and to a less degree, bcc clusters. This detailed geometric picture for crystallization of liquid metal is believed to be useful to improve the fundamental understanding of liquid–solid phase transition.

1. Introduction

The properties of metal materials are significantly influenced by the kinetic pathway of the transformation during crystallization. In 1897 Ostwald [1] proposed the rule of stages that an unstable system could transform into another transient state by the smallest loss of free energy, before finally reaching a stable state. Although theoretical basis for this rule is yet to be established [2], there are increasing evidences supporting it in crystallization with slow kinetics, such as colloids [3–5], proteins [6,7], compositions [8], and some simulations based on ideal models, such as the Lennard-Jones fluids [9–13], or 2D square lattice [14]. It is very interesting to find out if this rule holds for crystallization of realistic metals, which have quick kinetics.

An important related question is what intermediate states can be identified for a metal to transform from liquid to crystal? Stranski and Totomanow [15] argued that the phase first formed is the one that has the lowest free-energy barrier of formation rather than the phase that is globally stable under the conditions prevailing. Recent molecular dynamics (MD) studies for Fe, Mo, and V reveal that the solid–liquid interfacial free energy for body-centred cubic (bcc) crystal is lower than that for face-centred cubic (fcc) crystal by 30%–35% [16,17]. Thus bcc structures should probably be formed as an intermediate state from metal liquid to fcc crystal. Some studies have identified the metastable bcc phase at the earlier stage of solidification, but its role is not clearly identified. For example, a simulation for a 10^6-particle L-J system reported that the bcc structures form prior to fcc/hcp ones in a cooling process, with its amount being so small that it is believed to play a very limited role in crystallization [18]. On the other hand, the recent MD simulations for silver melt demonstrate that an intermediate bcc phase is indeed the precursor of the final fcc crystal [19], but for such a small system (only containing 500 atoms) the scale effect is inevitable. Therefore, it is necessary to further investigate the role of the metastable bcc structures during crystallization of metals.

In addition, to explain the phenomena that metal liquids can be supercooled to $0.2T_m$ (the melting temperature) without crystallization [20,21], Frank [22] argued that it is icosahedron (ico) that remarkably stabilizes the supercooled state. Since then, many experiments [23–25] and simulations [26–29] verified that the number of icosahedron is indeed increasing with the decrease of tempera-