Grain Boundary Diffusion

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September 23, 2015

1 Background

Grain boundary diffusion has been a subject of research since at least the early 20th century [1]. In 1951, Fisher published a method of gathering grain boundary diffusion information, with an approximate derivation of the applicable equations [2].It was observed that diffusion along a grain boundary was much faster than diffusion in bulk phases. Unfortunately, Fisher's model incorporated several assumptions to make the derivation more straightforward, and the work has been built upon by Mishin and Yurovitskii [3], as well as Klinger and Rabkin [4], focusing on anisotropy of the grain boundary diffusion and inhomogeneity of the bulk phase, respectively. More work has also been done by Turnbull et al. dealing with orientation effects [5]. It has been noted that Fisher's derivation was very approximate, and that a better theoretical derivation was introduced by Whipple [6], but that Whipple's derivation was unable to be applied to experiment [7].

An attempt has been made to relate overall average grain boundary diffusion effects [8], which has been used in obtaining intergranular diffusion characteristics [9]. Further, the problem of the "Kirkendall Effect" during grain boundary diffusion shows that the physical location of the interface can change, which has been addressed [10]. Much of the research in grain boundary diffusion has been using experimental observation and phenomenological models, but atomistic models have the potential to give insight into the modes of diffusion and the underlying causes [11]. Thanks to work done by Green [12, 13] and Kubo [14, 15], there is a solid framework by which an atomistic model can be tied to transport properties.

Unfortunately, numerically modeling the systems involved in grain boundary diffusion is computationally intensive. Also, the ensemble used to in many MD simulations involves a constant energy assumption, which is less helpful than a constant temperature assumption. This problem was overcome by the Nose-Hoover method [16]. MD simulations for diffusion problems run with timescales on the order of fs, while the diffusion characteristics are determined on the order of ns, so that meaningful simulations need to run on the order of 10^6 timesteps [17]. An effort was made by Sørenson et al. to use a hybrid kinetic Monte Carlo-molecular dynamics approach, which used molecular dynamics to determine the modes by which diffusion can occur, and using kinetic monte carlo to determine the rates of diffusion. This allowed for a smaller, less rigorous molecular dynamics simulation, and because the monte carlo method does not deal with these disparate timescales, computational efficiency was improved [18].

Periclase is one of the most important minerals for understanding the properties of the deep mantle, which could be important in gaining understanding about the formation of the earth [19]. Studies have been done by Lacks and Van Orman dealing with the behavior of diffusion and isotope fractionation in silicate melts [20], as well as diffusion of Al in the bulk of periclase [21]. Viscosity, chemical diffusivity and partial molar volumes of silicate liquids near interfaces were found as a function of pressure through MD Simulation as well [22].

We propose a study of grain boundary diffusion in periclase through experimental methods and through simulation techniques, in order to increase the available information and gain further insight on the mechanism and factors in grain boundary diffusion.

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