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Edge dislocations in dicalcium silicates: Experimental observations and atomistic analysis

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ABSTRACT

Understanding defects and influence of dislocations on dicalcium silicates (Ca_2SiO_4) is a challenge in cement science. We report a high-resolution transmission electron microscopy image of edge dislocations in Ca_2SiO_4, followed by developing a deep atomic understanding of the edge dislocation-mediated properties of five Ca_2SiO_4 polymorphs. By decoding the interplay between core dislocation energies, core structures, and nucleation rate of reactivity, we find that γ-C2S and α-C2S polymorphs are the most favorable polymorphs for dislocations in Ca_2SiO_4, mainly due to their large pore channels which take away majority of the distortions imposed by edge dislocations. Furthermore, in the context of edge dislocation, while α-C2S represents the most active polymorph for reactivity and crystal growth, β-C2S represents the most brittle polymorph suitable for grinding. This work is the first report on the atomistic-scale analysis of edge dislocation-mediated properties of Ca_2SiO_4 and may open up new opportunities for tuning fracture and reactivity processes of Ca_2SiO_4 and other cement components.

1. Introduction

Defects such as stacking faults and dislocations, which form and propagate in crystals, significantly impact many chemical and physical properties of materials. For example, material plasticity and crack propagation are markedly influenced by dislocation core structure, dislocation-dislocation interactions, and dislocation mobilities [1]. Similarly, crystal growth can be affected by both screw [2] and edge screw dislocations [3–4]. Although dislocations have been extensively studied in metals [5–8] semiconductors [9–13] and some simple ceramics, [14–21] there have been few attempts in characterizing such defects in more complex compounds such as zeolites, forsterite (Mg_2SiO_4) and dicalcium silicates (Ca_2SiO_4) [22]. The difficulty arises due to the complicated formatting components, heterogeneous nature, and the packing arrangements of several atomic species, which often lead to low symmetry crystals.

Several experimental techniques are used to study dislocations including surface and decoration methods, field ion microscopy, X-ray diffraction, high resolution transmission electron microscopy (HRTEM) and Z-contrast imaging techniques [1,23–25]. While these experiments provide means to observe and infer information about the dislocation structure, distribution and arrangement, they cannot provide precise information on dislocation energetics and mobilities, which often control the dislocations slip, slip-planes and other dislocation-mediated phenomena such as macro scale ductility and crystal growth. From a modeling standpoint, although semi-continuum Peierls-Nabarro models [26–27] are widely used to study dislocations by introducing the energies of generalized stacking faults from density functional theory to continuum model of the dislocations, the significant constraint of planar dislocations limits their applicability [28]. Alternative approaches use atomic scale simulations to calculate explicitly the dislocation core structure. In this group, fully periodic dipole approaches can simulate an infinite array of dislocations (e.g. line defects in silicon [10–11], extended defects in diamond cubic crystals [29], and impurities at edge dislocations [9]). However, this method is less straightforward for complex crystals, due to the correction for interactions between dislocation core fields [30–31], and contributions from core traction in the dislocation formation energy [32]. Recently developed cluster embedded models [33–34], based on one-dimensional periodic boundary conditions, allow to investigate systematically an isolated dislocation with atomic-scale fidelity. The cluster model, employed in this work, has been already highly successful in predicting the core energy and structure of dislocations in different material classes including ionic materials (MgO) [34], zeolites [35], wadsleyite minerals (β-Mg_2SiO_4) [36] and paracetamol (OH-$C_6H_4NHCOCH_3$), a widely used drug known as acetaminophuse [34].

The objective of the present work is to study edge dislocations in structurally complex and low symmetry oxides, which are of both

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scientific and technological importance. As a model system, we focus on five reversible polymorphs of dicalcium silicates (Ca_2SiO_4), key ingredients of industrial cement clinkers where the defect characteristics and integrity of Ca_2SiO_4 crystals' structures play a key role in clinker grinding processes as well as crystal growth mechanisms [37]. The latter is of particular significance in hydration of Ca_2SiO_4 to precipitate semi-crystalline, non-stoichiometric calcium-silicate-hydrate (C-S-H) phase, which is the chief source of strength and durability in cementitious materials [37–38]. Compared to tricalcium silicate (Ca_3SiO_5), the more energy-intensive and dominant ingredient of the cement clinker, Ca_2SiO_4 (also known as belite with shortened notation of C2S in cement chemistry) needs at least ~100 °C lower temperature to produce. However, it requires more energy for grinding it and reacts slower with water, thereby leading to delayed strength development in cement paste [39]. But given the overall economical gain due to lower manufacturing temperature of Ca_2SiO_4 and the augmented need to reduce greenhouse gas emissions from cement plants (currently cement manufacturing is responsible for 5–10% of the worldwide anthropogenic CO_2 emissions), there is an urgent necessity to tune grinding properties and reactivity of Ca_2SiO_4 to make it a more sustainable cement clinker. In this perspective, understanding the defects and edge dislocations in Ca_2SiO_4 can provide important information on how to modulate and promote the salient properties of Ca_2SiO_4.

Ca_2SiO_4 has a crystalline structure that is composed of SiO_4^{4-} tetrahedra and Ca^{2+} ions with a sequence of five reversible polymorphs, namely α, α_H, α_L, β and γ, from high to low temperatures (Fig. 1). X-ray analysis [40] have provided the exact crystal and atomic structure of these polymorphs, which can be transformed from one to another via changing the crystal symmetry, disorder of SiO_4^{4-} groups and slight changes in the position of the Ca^{2+} atoms [41–44]. The α and β polymorphs have monoclinic crystals while α_H, $\alpha_L$and γ polymorphs have orthorhombic crystals [37] (Fig. 2).

Dislocations in Ca_2SiO_4 arise from the growth and cooling processes during cement manufacturing, and presence of impurities [45–47]. Different crystal faces will behave differently during dissolution, etch pit formation, and hydration, depending on the size of the Burgers vector *b* as well as type and density of dislocations [45]. In view of the complexity of low-symmetry cement crystals, very limited experiments are reported so far on the observation of dislocations [47–51], and initiation of etch-pit formation from dislocations [37,52]. In this report, we focus on filling this knowledge gap by providing a clear HRTEM image of formation of edge dislocations in belite, followed by developing a deep atomic-based understanding of the dislocation-mediated properties of Ca_2SiO_4 polymorphs, thus providing de novo insights and strategies for bottom-up engineering of cement clinkers.

2. Methods

2.1. Materials and characterization

Pristine dicalcium silicate (99% purity) was purchased from Sarl Mineral Research Processing Company in France and used as is for characterization. Transmission electron microscopy (TEM) and HRTEM experiments were performed by depositing a small belite sample onto a carbon-coated copper grid. Since the dicalcium silicate was in the powder form, not focused ion beam (FIB) milling was required. The sample was analyzed using a JEOL 2100 Field Emission Gun Transmission Electron Microscope at several different locations until a clear edge dislocation was observed.

2.2. Cluster embedded atom model

For our computational study, we adopted a simulation strategy, so-called cluster embedded atom model, to combine an atomic scale dislocation core with a description of the extended crystal based on continuum linear elasticity [33]. This method takes advantage of the symmetry of Volterra dislocation to create a model using periodic boundary conditions along the dislocation line while only involving a finite cluster of atoms perpendicular to the dislocation line. A convention in this paper is to lay the edge dislocation line along the z axis and its Burgers vector along the x direction. The magnitude of the dislocation is equal to one lattice distance.

We used a three stage approach to create the models of the edge dislocation. The first stage is constructing a charge neutral disk-shape supercell containing the defect–free crystal structure in which the one-dimensional periodicity passes through the central axis of the disk (z axis). The radius of the simulation cell is 90 Å to accommodate relaxation around the core. Typical number of atoms in each simulation cell of the dicalcium silicate is ~15,000–17,000. Charge neutrality of the simulation cells is satisfied by breaking the small extra charge (as the result of cutting a cylinder from the supercell) to all the ~15,000 atoms, hence leading to less than 1% change in the partial charge of each individual atom. We assume this minimal change in partial charges would not affect the accuracy of the force field predictions.

The second stage involves introducing the edge dislocation based on anisotropic linear elasticity [53]. Fig. 3a shows the conceptual model of introducing an edge dislocation in a homogenous linear elastic body, which involved three basic steps: i) identification of the origin of the dislocation, which is a vacant point between the atoms. Note that in continuum (not atomistic) systems, a small part in the center is removed to eliminate the singularity of the original point based on elastic theory. However, this issue is not a concern in our atomic simulation cells since a vacant point between the atoms serves as the origin, ii) a solid line from the perimeter to the center of the cylinder is drawn to represent the "cut". The direction of this "cut", which is along the shortest lattice dimension determines the x axis used in the mathematical formula of anisotropic elasticity, and iii) atoms at opposite sides of the "cut" are displaced horizontally by a Burgers vector to form an edge dislocation.

The dislocated structure of the simulation cell in Fig. 3a is constructed in practice by the elastic displacement field, mapping the location of atoms in the bulk cell to the equivalent point in the dislocated cell. The elastic displacement field is only a function of Burgers vector, atomic positions and elastic properties of the crystals. For the orthorhombic crystals considered in this work, the displacement field is entirely in the plane of Burgers vector ($u_z = 0$) and is given by following equations [53]. If $\lambda^4 < \Lambda^2$, the displacement field corresponding to the *x* component of the Burgers vector reads

$$u_x = \frac{b_x}{4\pi}\left[\arctan\left\{\frac{\sqrt{2\left(\lambda^2-\Lambda\right)}\tan\theta}{1-\lambda^2\tan^2\theta}\right\} - \frac{\Lambda + S_{12}/S_{11}}{\sqrt{\Lambda^2-\lambda^4}}\arctan\left\{\frac{\sqrt{-2\left(-\lambda^2+\Lambda\right)}\tan\theta}{1+\lambda^2\tan^2\theta}\right\}\right] \tag{1}$$

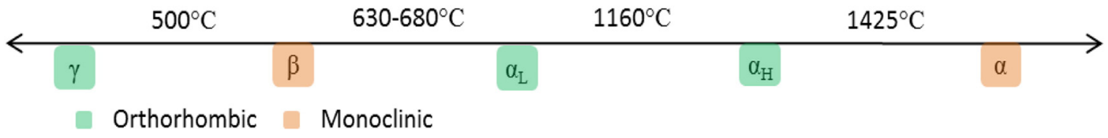

Fig. 1. Five thermodynamically reversible Ca_2SiO_4 polymorphs. The Greek L and H subscripts denote high temperature and low temperature variants.