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Measuring adhesion between steel and early-hydrated Portland cement using particle probe scanning force microscopy

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ABSTRACT

Particle probe scanning force microscopy was used to measure adhesion between steel and early-hydrated cement in the study. Particle probes, created by attaching steel microspheres to microcantilevers, were successfully used to collect adhesive forces between steel and early-hydrated Portland cement in air and in saturated lime water. Mixed Gaussian models were applied to predict phase distributions in the cement paste, i.e., low density calcium silicate hydrate, high density calcium silicate hydrate, calcium hydroxide, other hydrated products and the unreacted components. Consistent correlations were achieved for volume fractions between areas with different adhesion measurements and predictions from the hydration model. Results showed that low density calcium silicate hydrate, high density calcium silicate hydrate and other hydrated products exhibit intermediate adhesion to steel microspheres. Calcium hydroxide exhibits the smallest adhesion, while the unreacted components exhibits the largest adhesion among all groups.

1. Introduction

In reinforced concrete, steel bars are used to improve the tensile performance of concrete. A fundamental assumption of classical reinforced concrete theory is that perfect bonding exists between concrete and steel rebars. A variety factors can lead to the failure of bond between concrete and steel, such as mechanical loads [1], corrosion [2,3] and thermal variations [4]. Significant effort has been devoted to study the bond behavior between concrete and steel rebars using the pull-out test [5–27] and using the pull-off test [28,29]. The bond strength between steel rebars and concrete depends on adhesion, friction and mechanical interlock [30,31]. Despite prior studies, limited research exists to detail the adhesion between steel and different phases of cement paste at microscale, i.e., a fundamental property that determines the performance of reinforced concrete structures at different service conditions. Lack of such knowledge not only hinders us from further understanding the interactions between steel rebars and cement, but also hinders the development of cement and steel that lead to high-performance reinforced concrete composites and structures. Scanning Force Microscopy (SFM) has been used to study adhesion between the probe and different materials [32], such as between glass and silicon [33,34], between stainless steel and polymers [35,36], between ligands and receptors [37,38]. Conventional SFM probes are pyramids usually made from silicon or silicon nitride that include sharp radius on the order of nanometers [32]. Recently, particle probe scanning force microscopy has been used to measure adhesive forces between asphalt binders and mineral microspheres [39–41], such as microspheres of calcium carbonate, silica and alumina. The larger contact between microspheres and substrates leads to adhesive measurements at microscale that are relevant to the characterization of asphalt binders and mixtures in engineering applications.

The objective of this study is to study the adhesion between steel and early-hydrated cement at microscale using particle probe scanning force microscopy. First, particle probes were created by attaching steel microspheres to the free ends of micro-cantilevers. The alkaline environment of concrete provides a service condition (pH of 12–13) to rebars [42–45], in which the presence of calcium hydroxide is critical to maintain the high pH values. To simulate the working condition, adhesive forces were collected between steel microspheres and early-hydrated Portland cement paste in saturated limewater (pH ≈ 12.3). As a comparison, adhesive measurements were collected between steel microspheres and cement substrates in air. Conventional SFM probes were also used to perform adhesion tests in corresponding conditions. Then, mixed Gaussian models were used to deconvolute different phases in the cement substrates based on the adhesion measurements. Volume fractions predicted from a stoichiometry-based hydration model were compared with the experimental data on these groups, including low density calcium silicate hydrate, high density calcium silicate hydrate,

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calcium hydroxide, other hydrated products and the unreacted cement. Finally, adhesive forces between steel microspheres and different phases were analyzed and determined accordingly. This study focuses on the adhesion induced by intermolecular forces [46] between steel and different hydrated cement phases; while interlocking [47,48] and frictions are not studied.

2. Experiments

2.1. Particle probe scanning force microscopy

Scanning Force Microscopy (SFM) has been used to measure different material properties, such as mechanical, magnetic and electrical properties [32] of bi-material interfaces. Conventional SFM probes are pyramids usually made from silicon or silicon nitride that include sharp radii on the order of nanometers. If adhesion tests were performed using these probes and cement substrates, the resulting measurements are not adhesion between the steel and cement. For example, Lomboy et al. [49] studied the adhesive forces between conventional silicon nitride SFM probes and cementitious substrates. Also, conventional SFM probes interacted locally to the substrates because of their sharp probe radii, making it difficult to link the nanoscale adhesion results to engineering applications. However, if a steel microsphere is used to replace the pyramid, the SFM can be used to measure the interactions between the microscale steel spheres and cement substrates.

A schematic of the scanning force microscopy used in this study is shown in Fig. 1. The SFM fluid cell, sealed by an O-ring, is filled with saturated lime water. As the cantilever approaches the cement substrate, the steel microsphere contacts the cement substrate surface. As the cantilever moves away from the substrate after making the contact, the cement paste and steel microsphere sticks together until the restoring force of the deflected cantilever overcomes the adhesion between them. The cantilever is strong enough so that the deflection is linear elastic, in which the adhesive force calculated from Hooke's law is given by

$$F_{ad} = k\Delta x \tag{1}$$

where k is the spring constant of the cantilever, and Δx is the distance between tip-sample contact and the disengage point.

2.2. Cement paste substrates

In this study, the cement substrates were prepared at the water:cement ratio of 0.5 using ordinary Type I/II Portland cement. The compositions were estimated by averaging the component percentages of Type I and II cements, i.e., C_3S (~55%), C_2S (~18%), C_3A (~10%) and C_4AF (~8%) by weight [50]. Cement powders were well mixed with water in a 76.2 mm diameter cylindrical tube, and cured at ambient conditions for 24 h before polishing. After curing, the demolded cement cylinder was cut to blocks of 10 mm × 10 mm × 2 mm and embedded in an epoxy frame as substrates (Fig. 1). Adhesive force measurements require a good contact between the microsphere and a smooth substrate surface, in which the influence of surface roughness is minimized. Specimens were polished using a series of sand papers (3M, Maplewood, MN) ranging from 400, 800, 1200, 1500, 3000 and 5000 grits. After that, polishing cloths (Buehler, Norwood, MA) with oil-based diamond particles (14000, 50000 and 100000 grits) (Reentel International Inc., Westmont, IL) were used to further polish the substrate surfaces. When the polishing process was completed, prepared substrates were cleaned in acetone using the ultrasonic cleaner for ~20 min. Asylum MFP-3D-BIO scanning force microscope with commercial probes (NanoAndMore, Watsonville, CA) was used to characterize the morphology of polished cement substrates in AC mode at the frequency of ~300 kHz.

2.3. Steel particle probes

Steel particle probes used in this study were fabricated by attaching stainless steel microspheres to the microcantilevers. The selection of stainless steel ensures a good control study, based on which the performance of other steels could be compared in the future. Diameters of microspheres were ~10 μm (Cospheric, Santa Barbara, CA). Rectangular and tipless cantilevers (NanoAndMore, Watsonville, CA) of dimensions 3.4 mm × 1.6 mm × 0.315 mm were used. Spring constants of these plain cantilevers ranged from 0.1 to 2.7 N/m. Fig. 2 illustrates the fabrication process of steel particle probes. The movement of the cantilever using a high resolution microtranslation AD-100 system (Newport, Irvine, CA) was guided by an optical microscope (Nikon, Minato, Tokyo). First, the tip was dipped into a wet epoxy on a glass slide. Then, it was moved to touch a target steel microsphere, also on the same glass slide. After that, the probe stayed in air for 24 h to cure the epoxy before adhesion measurements. The thermal tuning method [51,52] was used to measure the spring constants of the particle probes, in which the thermal noise of the cantilever deflection was correlated to the spring constants by the equipartition theorem [51,52]. Commercial silicon SFM probes (NanoAndMore, Watsonville, CA) with nanoscale tip radii were also used to measure the adhesion. The spring constants of these commercial SFM probes ranged from 0.1 to 2.7 N/m.

2.4. Experimental design

In this study, adhesive forces between steel microspheres and early-hydrated cement substrates were measured using Nanoscope E (Bruker Inc., Santa Barbara, CA). All adhesion measurements were collected within 14 days after polishing the substrates. Adhesion measurements were collected in mapping matrices of 10 point × 10 point at the

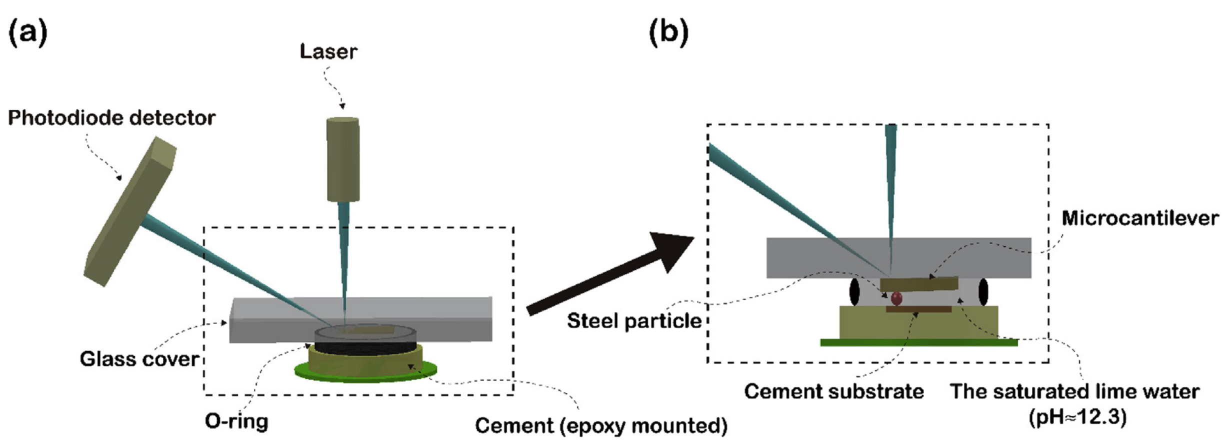

Fig. 1. A schematic of the particle probe scanning force microscopy in saturated lime water: (a) Global view. (b) Side view.