On micro-level vulnerability of concrete surface layer in process of crystallization of hydrating Portland cement and upon mechanical load

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Abstract. The target of this research is to make a system of data on discontinuity of the cement stone microstructure in concrete. To achieve this, the following issues had to be addressed: a) a justification for the presence of dislocations in cement stone and definition of their type had to be provided; b) the source of the considered material weakness had to be identified; c) an explanation of formation and propagation of micro cracks starting at the surface and going deeper into the concrete had to be given; d) an educated guess had to be made for the opening/depth ratio of micro cracks; e) information about the distances between micro cracks in the capillary walls of the cement stone should be obtained; f) binding energy in the calcium silicate crystalline hydrate has to be determined. The research results show that the mechanical properties of crystals and polycrystals in the cement stone (concrete) depend on the ratio of small-angle ($\theta \leq 10...150$) and large-angle boundaries. Due to a relatively small number of large-angle boundaries, intergranular and plastic flow deformations are dampened under straining, resulting in cleavage in the areas where stress-raisers are found (pores, capillaries, submicrocracks, etc.).

1. Introduction

Vulnerability is a property of a material to accumulate structural discontinuities as affected by the external factors. Depending on the geometry, these discontinuities can be point-like, linear, flat or dimensional. A cement bonding agent, which binds together coarse and fine aggregate, crystallizes during hardening, forming a space lattice. The dimensions of this lattice are limited by the size of crystalline conglomerates (the so-called crystallites) formed from calcium silicate crystalline hydrates [1,2]. They range in size from $10^{-7}$ to $10^{-6}$ cm, and micro-discontinuities in them are vacancies (meaning there is no atom/ion in a site of the lattice) and dislocations (meaning an entire layer of atoms/ions is missing from the lattice), as it was established through physical-chemical methods [3].

The target of this paper is to create a system of data on discontinuity of the cement stone microstructure in concrete. To achieve this, the following issues had to be addressed: a) a justification for the presence of dislocations in cement stone and definition of their type had to be provided; b) the source of the considered material weakness had to be identified; c) an explanation of formation and propagation of micro cracks starting at the surface and going deeper into the concrete had to be given; d) an educated guess had to be made for the opening/depth ratio of micro cracks; e) information about
the distances between micro cracks in the capillary walls of the cement stone had to be obtained; e) binding energy in the calcium silicate crystalline hydrate had to be determined. The research results showed that the mechanical properties of crystals and polycrystals in the cement stone (concrete) depend on the ratio of small-angle (θ≤10°...150°) and large-angle boundaries.

2. Research methods
To solve the problems, we use the analogue method: let us draw parallels between the structural properties of the cement stone and brittle metals. It is understood that ductility of metals results from dislocations in their structure caused by exposure to mechanical stress and temperature. In a cement stone, dislocations are not very mobile (called sessile), and this explains its relatively small deformability. To the authors’ knowledge, there is only one paper on dislocations in the cement stone structure [4] (this question remains understudied). This article attempts to substantiate this fact by referring to partial cement hydration according to the topochemical scheme of clinker particles dissolution in water [5]. In this case, hydration of clinker crystals occurs through the hydrogen bonds of water molecules without fundamental rearrangements within clinker crystals, in contrast to how it happens, for example, in metals during crystallization of melt during cooling or even during chemical interactions in a solid state [1].

The number of dislocations in cement clinker crystals is the following: (C₃S) – 5×(10⁸...10⁹) cm⁻² for Alite, (C₂S) – 0.5...5×10⁸ cm⁻² for Belite [5]. In [4], the possible number of dislocations in crystals calculated theoretically using Kitaygorodsky formula is up to 10¹² cm⁻² (as in work-hardened metals). That said, the following question arises: why are cement stone dislocations not very mobile? As a first approximation, this question could be answered indirectly by referring to the facts of brittle failure of metals with a body-centered close-packed crystal lattice [3]. For example, according to the experimental data for molybdenum, when a relative temperature is approximately 20% of the melting point, the tensile strains appear as cleavages and may lead up to a total dynamic fracture. In contrast, fracture of face-centered metal crystals under tension (in them, the atoms are located at the corners and along the centers of the cube faces) is characterized by ductility [3].

The main minerals of Portland cement clinker are di- and tricalcium silicates, 2CaO SiO₂ (Ca₂SiO₄) and 3CaO SiO₂ (Ca₃SiO₅), which are classified as nesosilicates based on their structure [6,7]. Compared to other silicates, they have the highest energy of the crystal structure, a high melting point, a low thermal expansion coefficient, and high hardness [8]. In these silicates, the vertices of tetrahedrons [SiO₄]⁴⁺ do not connect between themselves. Each oxygen ion belongs to only one tetrahedron. The groups of [SiO₄]³⁻ are interconnected by cations Ca²⁺. The ratio is Si:O=1:4. The bonding force of a Si⁴⁺ cation in the tetrahedron is 1, of Ca²⁺ in the structural emptiness is one quarter [7]. The ionic bonding Ca-O is weak and, in our opinion, breaking of bonds will appear between the cations Ca²⁺, that is, micro cracks will form. To test this hypothesis, it is necessary to undertake special experimental studies, at which point knowledge of a thermodynamically-equilibrium form of cement stone micro crystals should also be acquired. In these conditions, the equilibrium form of macroscopic crystals is, theoretically, determined according to the Wolf’s rule [9].

It was also experimentally established that the cleavage of crystals perpendicularly to the trigonal bond occurs along a longer bond across the planes. The surface is not reconstructed, there is a slight relaxation of the first layer (~1-2.5% of the lattice constant) [10]. A similar situation also occurs in tetrahedral crystals.

According to the experimental data [2], fracture photomicrographs of the cement stone fracture process show cleavage steps, as well as micro cracks near the walls of pores, along the cohesion planes and crystalite grain boundaries. Note that the cement gel, which makes up about 75% of the cement stone volume [11], consists of colloidal sized particles. According to the data of [7], amorphous or micro crystalline colloids can eventually form groups of microscopically sized crystals. Their main structural motives are SiO₂ tetrahedrons.

When studying crystals using experimental procedures, it was found that the defects on the surface or in the surface layer of a crystal could play an important role in determining the physical properties
of the surface. In case of surface adsorption, the region of significant variation in the surface properties is in the submonolayer. When a crystal is opened, there appear micro cracks, steps, vacancies, etc. In charged atoms of defects, the Coulomb interaction, which is weakly screened due to a free half-space outside the crystal, can cause an inhomogeneous charge distribution leading to structural rearrangements [10].

In small-sized crystals (~102 Å) of the cement stone, such as ettringite needles, which are particles of an ultrafine medium, recrystallization can occur during heat treatment in the process of manufacturing [12], which is observed in experiments [13]. This can be explained by the fact that the boundary in this kind of crystals is so complex that it becomes significantly nonequilibrium [14].

It is important to note that there are low-angle and large-angle boundaries in polycrystal grains. The latter include boundary angles of crystals >10...15°. Since the distance between dislocations becomes small, the dislocation centers fuse, and the atomic outline in the large-angle boundaries differs from the small-angle boundaries [15]. Large-angle boundaries weaken the intercrystalline bond (cohesion) to a far greater degree, leading to embrittlement in the area of such a crack. Small- and large-angle boundaries act differently when interacting with intragranular shears. The first rearrange rather intensively under the internal fields of elastic strains generated by dislocation pileups pushed to the boundaries. These rearrangements proceed the more actively, the smaller the disordered orientation angle θ, i.e. the more independently can the dislocations forming the boundaries move in these fields. Due to the absence of lattice dislocations in their structure, the large-angle boundaries are much less susceptible to similar rearrangements [14]. During deformation, the boundaries get fragmented (go through faceting) in places of interaction with their intragranular shears. The faceting intensity varies for the boundaries that differ in disordered orientation. The boundaries with the least disordered orientation are faceted (rearranged) to the greatest extent, and the large-angle boundaries are faceted the least. The more low-angle boundaries there are in polycrystals, the less prone they are to intergranular and plastic deformation at high temperatures (fires).

Due to a high orderliness of their atomic-crystalline structure, delocalization effect is inhibited at the low-angle boundaries, and may not occur at all, therefore the more low-angle boundaries there are in crystals, the less they are susceptible to intergranular and plastic deformation. Considering that the properties of small- and large-angle boundaries are so different, mechanical properties of crystals may depend on the interrelation of the numbers of boundaries of each type. The experiments show that in real polycrystals the number of low-angle boundaries is abnormally large compared to the randomly disoriented ensemble. Understandably, under such circumstances one expects that (with relative dampening of intergranular and plastic deformation) a cleavage will appear in the cement stone grains.

The recently acquired facts suggest the large-angle boundaries appear under tension and compression of the crystal structure of refractory metals [16], when the adjacent crystals are interconnected along complex transitional formations called microbands, but not along large-angle boundaries with the same disordered orientation.

The latter have a width of 2-3 µm and consist of a set of 10-20 small-angle (θ ~ 3°) dislocation boundaries, the combination of which accounts for the observed large-angle disordered orientations of deformation bands. The subsequently accumulated data suggest that along with small-angle boundaries and their complex correlated combinations, which cause large-angle rotations, individual intergranular boundaries are formed in severely deformed crystals.

The boundaries of the deformational origin are not dimensional, but flat [16]. At θ < 3°, the boundaries of the deformational origin have a pronounced dislocational structure. They are generally highly imperfect and are enclosed in the dislocation fringe. Dislocations within the boundaries are irregular. The apparent width of the boundaries is at least 200 Å. Under relatively small strains ε, many boundaries with θ<3° break inside a crystal, creating elastic strain sources of dislocation type along the break line.

In [17], the number of dislocations in the mosaic blocks of the cement stone crystals was theoretically defined as 1.1×1011 ... 1×1012 cm² at the age of 420 days. The number of dislocations in work-hardened metals is 1012. The average internal stresses in a cement stone crystal are sufficient to
trigger slips and initiate a germination of submicrocracks up to 36.375 Å long, and 480 Å long micro cracks [17].

Based on their morphological and crystal-geometric features (large $\theta$, banded contact), strong boundaries of deformational origin bear a resemblance to large-angle grain boundaries in many ways. Their only significant difference from the latter consists in the numerous sources of long-range elastic stresses, which are abundant at the large-angle boundaries of deformational origin [16].

3. Results and discussion
To summarize a statement on the micro-level vulnerability of the cement stone (concrete), the fundamental propositions, which rely on the laws of chemistry and physics, should be mentioned. When a developing or even a formed crystalline structure is exposed to external energy, this structure can be rearranged, and the point-like, linear, two-dimensional and even three-dimensional defects may appear (in the form of small cleavage cracks or a detachment (submicrocracks, micro cracks)).

At the same time, in the process of individual and grouped exposure (in the latter case, for example, an instantaneous group or alternating in time (mechanical load, temperature, humidity, ionic diffusion from the environment...)), one or another type of the listed defects appears in the crystal structure in accordance with the magnitude of the applied energy.

In the ideal crystal structure free of defects (except thermodynamically conditioned), we assume that there are critical cleavage and shear stresses in the microstructure – $\sigma^{**}_{nuw}$ and $\tau^{**}_{nuw}$, respectively (with their averaged determination by unit area and volume).

A defect, depending on its size, increases vulnerability to external energy (by specific area or volume) locally (and with an increase in size – globally).

The effect of the external energy is manifested in the structure of a material in the form of displacements of crystals and crystallites (grains), or local rearrangements with the appearance of point-like, linear, two-dimensional and three-dimensional defects. The influence of defects on strength characteristics of a specific area (volume) could be assessed phenomenologically as functions (before physical and chemical data are accumulated):

$$R_{\sigma_{\mu}} = \sigma^{**}_{\mu} - f(\sigma^{**}_{\mu}, D)$$

$$R_{\tau_{\mu}} = \tau^{**}_{\mu} - f(\tau^{**}_{\mu}, D)$$

where $f(\sigma^{**}_{\mu}, D)$, $f(\tau^{**}_{\mu}, D)$ are tensor quantities for estimating the stress (stress-strain) state of a specific area or volume with regard to the ideal and actual states of a material (considering defects) under certain conditions (temperature, humidity, crystal structure).

Identification of the shape of the $f$ and $f_1$ functions is described below. In this regard, we analyze the experimental data on deformations in concrete prior to formation of cracks with an opening of 0.06÷0.1 mm, measured using photoelastic coatings on the surface of a reinforced concrete beam [18].

The strain distribution before breaking at the edges of a future crack with an opening of 0.1 mm could be described by an exponential or power function. That said, when function matching, it would be right to use three parameters due to a potentially more accurate approximation. Note that the event of maximum peaks in the area near the cracks (in the direction perpendicular to the crack opening) covers a small distance from the edge: no more than 5 mm.

The average distance between shrinkage cracks in the pore walls of 80x77 µm in the “one-day” cement stone sample calculated by the authors on the basis of an experimental sample is 2.6÷43.6 µm (with the ratio of the average crack length, 19.7 µm, to the biggest opening equal to 29.4 [18]). These data and the results obtained by P.P. Budnikov on the linear expansion of cement stone suggest that in the pore walls, micro cracks open along the boundaries of crystalline hydrates C-S-H (1). The average opening of the shrinkage micro cracks on the pore wall surface was 0.67 μm, which is approximately 6740 Å, i.e. several hundred cells of the crystal lattice C-S-H (1). When the crack opening becomes larger than the typical size of the elements of the cement stone microstructure, the energy of the crystal lattice can be calculated using the formula of A.F. Kapustinsky, obtained from the M. Born equation:
\[ U = 256.1 \sum N_i a_k a_a \frac{1}{r_k + r_a} \]  

where 256.1 is a constant factor leading to the dimension of kcal/mol; \( N_i \) is the number of ions; \( a_k, a_a \) is the valence of ions (cations and anions); \( r_k, r_a \) are the ionic radii of cation and anion.

4. Conclusions

1. The mechanical properties of crystals and polycrystals in the cement stone (concrete) depend on the ratio of small-angle \((\theta \leq 10...150)\) and large-angle boundaries. Due to a relatively small number of large-angle boundaries, intergranular and plastic flow deformations are dampened under straining, resulting in cleavage in areas where stress-raisers are found (pores, capillaries, submicrocracks, etc.).
2. A number of dislocations in a cement stone reaches up to \(10^{11}...10^{12}\), which is sufficient to trigger slips and initiate a germination of microcracks up to \(36..480\) Å long.
3. At the angles equal \(\theta < 30\), the boundaries of the deformational origin have a pronounced dislocational structure. Many boundaries break inside a crystal, creating elastic strain sources of dislocation type along the break line.
4. Micro cracks first form on the surface of concrete elements.

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