Investigation on the transport properties of chlorides in concrete (I) Identification of ITZ

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Abstract. Concrete is a multiphase composite material, in which the mortar, aggregate and interfacial transition zone (ITZ) have important influence on the chloride ions transport. In this research, the thickness ITZ was measured and the concentration distribution of chloride ions in concrete was obtained through electron microprobe analysis. The experiment results that the thickness of ITZ follows a normal distribution and the size of aggregate shows no clear influence on the thickness of ITZ.

1 INTRODUCTION

Concrete is a multiphase material consisting of aggregate, interfacial transition zone (ITZ) and mortar matrix. Each phase is believed to have significant impact on the chloride ions diffusion. Shah[1] pointed out that the influence of aggregate on concrete permeability included four kinds of effects, the dilution effect, tortuosity effect, ITZ effect and percolation effect. And ITZ has been proved to be of great importance for the chloride ions diffusion in concrete[2]. The thickness of ITZ is a critical parameter for the analysis of chloride ions diffusion in concrete[3]. Although a reasonable range has been provided for thickness of ITZ through different investigation, an appropriate chosen of their values in a specific concrete is still the priority for an accurate analysis of chloride ions diffusion[4].

In this research, the thickness of ITZ in concrete was measured by electron probe technique. And a statistical analysis was conducted to characterize the distribution of ITZ.

2 EXPERIMENT PREPARATION

2.1 Materials

The cement used in this research was normal Portland cement with a grade of P152.5. The sand was natural quartz sand with a fineness modulus of 1.6 and water was tap water. For both concrete and mortar, the water to cement ratio was 0.74 and the mass ratio of sand to cement was 2. For concrete, the volume fraction of coarse aggregates was 39.8%. The ITZ was produced by embedding rod-shaped aggregates into mortar matrix. Rod-shaped aggregates were the core out of a limestone. Three kinds of rod-shaped aggregates were employed in this research with the diameter of 10mm, 7mm and 5mm

respectively. The length of the rod-shaped aggregates was 70mm. The aggregate area at a cross section of a specimen can be characterized through the Fuller aggregate gradation and volume fraction accordingly.

2.2 Electron microprobe analysis

Before electron microprobe analysis, the specimen was placed into a plexiglass pipe with the inner dimension of 60mm×60mm×50mm. Then the high flowable epoxy resin was filled into the gap between specimen and plexiglass pipe. Once the epoxy resin solidified, the specimen was cut transversely by a precision cutting machine. The thickness of the test sample was 5mm. Thereafter, the sample was immersed in a beaker full of alcohol. Then the beaker, as well as the sample, was put in JP-010T ultrasonic cleaner to remove impurities and dust on the cutting surface. The ultrasonic cleaning was totally performed three times, lasting at least 5 minutes at each time. Then the dried sample was coated with carbon film in JEE-420 vacuum coater to finish the sample preparation. Finally, a microscopic observation and element mapping were conducted with JXA-8100 electron microprobe analyzer. The carbon coated sample are shown in Fig.1.

Totally 30 backscattering images of ITZ around the aggregate surface were collected randomly. All images were taken at 250× magnification and the area covered by the images was 480 × 384 μm. A high-resolution backscattering image can precisely reveal the mineral content distribution on the surface of the sample and represent the microstructure in details. As shown in Fig.2, the phases, i.e., the aggregate, sand, pores, unreacted cement and reacted cement paste matrix can all be identified through the grey level. It is also visually recognizable that there exists a dark region, ITZ, lying around the aggregate which implies this region is highly

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porous. In this research, a line scan for element of both Si and Ca was conducted vertically from aggregate to cement paste matrix, covering the ITZ. The length of the scan path was 500 μm , and two line-scans were carried out in each backscattering image. The area scan conducted by electron microprobe analyzer was applied to investigate the two-dimensional diffusion of chloride ions in concrete.

Fig.1 Carbon coated sample

Fig.2 Backscattering image of the sample

3 EXPERIMENT RESULTS

It is well known that ITZ has a higher w/c ratio at the early stage of hydration process. Ions with a relatively high mobility in cement paste solution, such as Ca^{2+} , Al^{3+} and SO_4^{2-} , tend to diffuse into the more porous ITZ due to the higher concentration gradients[5]. Therefore, a noticeable fluctuation of silicon and calcium content is always recognized from ITZ in comparison with cement paste matrix. This phenomenon can be proved by one of the line scans at ITZ, as shown as Fig.3.

Several researchers have used electron microprobe analysis to study the Ca/Si ratio with ITZ and bulk cement paste[6-7]. It is theoretically and experimentally proved that the Ca/Si ratio will settle down gradually at a certain distance from the surface of aggregate in a value about 5 or 6 approximately. While in this research, as there is no Si content in the rod-shape aggregate, so the

Ca/Si ratio will be much higher than its reasonable range. Therefore, the thickness of ITZ is quantitatively assessed from Si/Ca ratio instead of Ca/Si ratio. It should also be emphasized that the measured ITZ prefers to the zone around the rod-shape aggregate. The thickness of ITZ around the sand is much smaller than that around aggregate, as shown as Fig.3(a). Furthermore, the diffusion of chloride in ITZ around sand is considered in the effective diffusion of mortar matrix.

(a) Element content along the line scan path

(b) Si/Ca along the line scan path

Fig.3 Line scan on Ca and Si at ITZ

As shown in Fig.3(b), the Si/Ca ratio is close to 0 before 229 μm along the scan path which corresponds to rod-shape aggregate. Then a slight variation of Si/Ca ratio indicates that some hydration products generate and deposit at the surface of aggregate. So the start point of ITZ can be marked by the small variation. The boundary of ITZ, in previous research, is always determined as an outline paralleled to the surface of aggregate, encircling a region in which the porosity is significantly greater, by a factor of 10% or 5%, than the bulk porosity of cement paste. Analogously, the end point of ITZ is specified as the position at which the Si/Ca ratio is 10% lower than the average value at bulk cement paste. As demonstrated in Fig.3(b), the thickness of ITZ is 40.5 μm which can be

easily calculated through the covered length from start point to end point.

In this research, The ITZs around the rod-shape aggregates with the diameter of 5mm, 7mm and 10mm were all inspected. The measured thickness of ITZs are plotted against the frequency, as represented in Fig.4.

Fig.4 Distribution of ITZ thickness

It can be concluded from Fig.4 that the thickness of ITZ concentrates around 40.5μm and descends gradually on both sides. A statistical analysis implies that the thickness of ITZ generally follows the normal distribution. The mean value of all the measured results are 40.7μm. Actually, different researchers provided different estimations on the range of ITZ thickness, which depends on the experiment technologies and analyzing models. Basheer and Kropp gave a broad assessment as the ITZ ranges from 0 to 100μm[8]. While most of the investigations believed that the thickness of ITZ was more specific between 10 and 50μm[9]. Through SEM techniques, this value was furtherly narrowed down as 40-50μm[10]. It is clear that the measured result using microprobe analysis is in great accordance with previous research. Meanwhile the average ITZ thickness for rod-shape aggregate with the diameter of 5mm, 7mm and 10mm is 40.9μm, 40.6μm and 41.1μm, respectively. There exists no clear difference between the thickness of ITZs for aggregates of different size. This phenomenon is also in well agreement with previous research as the thickness of ITZ is mainly determined by the median size of cement particle rather than the size of aggregate[11].

4. CONCLUSIONS

In this research, an electron microprobe technique was applied to quantitatively characterize the properties of ITZ.

The element analysis indicates that there exists a concentration gradient at the region surrounding the aggregate and the Si/Ca ratio is used to identify ITZ accordingly. A statistical analysis shows that the thickness of ITZ in this specimen follows a normal distribution. Besides, the diameter of rod-shape aggregate has no clear influence on the thickness of ITZ. Based on a parallel diffusion model, the diffusivity of ITZ deduced

from one-dimensional diffusion test is 40.7 times higher than mortar matrix.

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