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Study on the microstructure of cement-based piezoelectric ceramic composites

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HIGHLIGHTS

- The interaction of Ti–O and Si–O in cement-based piezoelectric ceramic composites occurs.
- SIMS images provide a direct indication of element spatial distribution in the composite.
- The chemical reaction results in the diffusion of Ti into the cement paste.

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ABSTRACT

In this paper, a study is presented on the microstructure of a cement-based PZT (Lead Zirconate Titanate) piezoelectric ceramic composite. A mechanism is proposed for chemical bonding between piezoelectric ceramic particles and cement material in the composite. The microstructure of the composite, as well as chemical bonding at the ceramic–cement interface is investigated using XRD, IR and XPS. Experimental results indicate that Ti–O in the ceramic particles links to Si–O in the cement paste via bridging oxygen, forming a Ti–O···Si–O bonding. And the change of chemical environment takes place for all of Ti, Si, Ca and Zr for cement-based piezoelectric ceramic composites. One prominent result pertaining to chemical reactions at the interface between ceramic particles and cement paste shows that Ti diffuses into the cement paste via Ti–O···Si–O bonding.

1. Introduction

With the development and application of the "Performance- and Reliability-based Service Life Design" (PRSLD) principle in civil engineering, the importance of health monitoring processes within the PRSLD framework has become clear [1–5]. To facilitate monitoring of targeted functionality, a variety of different sensor types have been developed for use in civil engineering projects. Among the approaches used in the design of sensors and actuators adopted in smart structures, piezoelectricity has proven to be one of the most efficient [6–9], and piezoelectric materials have accordingly received much attention for potential applications in the field of smart materials [10–16]. One such smart material – suitable for structures in civil engineering – is 0–3 type [17,18] cement-based piezoelectric ceramic composite, incorporating lead zirconate titanate (PZT) ceramic powder into the cement paste. Its properties and potential applications in civil engineering have been previously explored by Li et al. [19] However, the microstructure of this new composite, and the relationship between the microstructure and the material's macroscopic properties, are still not well understood.

The present paper focuses on the microstructure of PZT ceramic composite. In particular, attention is given to the interaction of the solid phases (ceramic and cement) [20]. In general, the material properties of a composite, including its piezoelectric, dielectric, and mechanical properties, depend strongly on the microstructure. Therefore, a full understanding of the microstructure of composites is crucial in order to predict the relevant material properties. In addition to the separate material properties of cement paste and piezoelectric ceramic particles, attention should be paid to the interface between the two phases and especially to the bonding behavior between them. The investigation of microstructure can provide a fundamental basis for understanding and predicting the performance of cement-based piezoelectric ceramic composites.

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Table 1
Properties of PZT powder, hardened Portland cement paste, and normal concrete.

	P-85	Cement paste	Concrete
Piezoelectric strain factor d_{33} (10^{-12} C/N)	390	–	–
Piezoelectric voltage factor g_{33} (10^{-3} Vm/N)	23	–	–
Dielectric constant ε_r (at 1KHz)	1700	~56	–
Electromechanical coupling coefficient K_P (%)	58	–	–
Mechanical quality Q_m	2000	–	–
Elastic compliance s_{33} (10^{-12} m^2/N)	–	72	30
Density ρ (10^3 kg/m^3)	7.5	2.0	2.4
Acoustic velocity V(10^3 m/s)	3.40	2.64	3.73
Acoustic impedance ρV (10^6 kg/m^2 s)	–	5.3	9.0

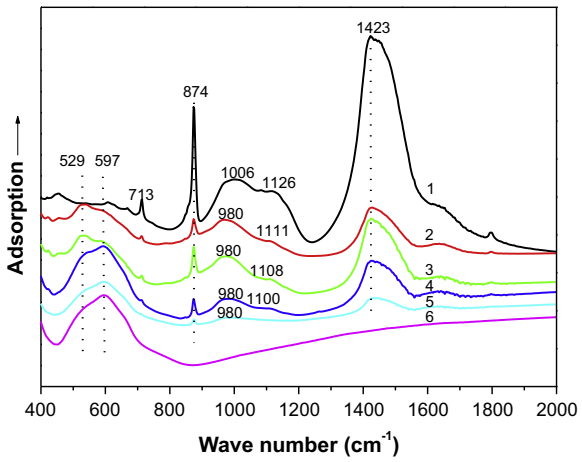

Fig. 1. IR spectra of piezoelectric ceramic, cement paste and cement-based piezoelectric composite with different ceramic/cement volume ratios. 1: White cement, 2: cement-based piezoelectric composite with ceramic/cement ratio = 20:80, 3: cement-based piezoelectric composite with ceramic/cement ratio = 35:65, 4: cement-based piezoelectric composite with ceramic/cement ratio = 50:50, 5: cement-based piezoelectric composite with ceramic/cement ratio = 75:25, 6: piezoelectric ceramic.

2. Experiment

Lead zirconate titanate (PZT) piezoelectric ceramic powder (Hong Kong Functional Ceramic Co. Ltd.) and cement (H.S.L. Enterprises Co. Ltd.) were used to make cement-based piezoelectric composites. The properties of the piezoelectric ceramic and cement paste are listed in Table 1.

Piezoelectric ceramic powder and white cement with various volume ceramic/cement ratios were mixed together to make a 0–3 type cement-based piezoelectric ceramic composite. In order to improving the fluidity of the fresh mixture, a superplasticizer (W19, W. R. Grace) was added. To achieve a uniform mixture, the cement and ceramic particles were first dry-mixed for 2 min. Then water and superplasticizers were added, and mixing continued until a uniform mixture was obtained. The resulting mixture was cast in a 13 mm × 13 mm × 3 mm mould. After casting, the specimens were covered with a plastic plate and rested at room temperature for about 24 h, after which they were removed from the mould. Then the specimens were placed in a curing room at a temperature of 65 °C and relative humidity of 98% for a further 24 h.

The composition of each sample was measured with XRD (High Resolution X-ray Diffraction System, Model PW1825 (Philips)). The bonding structures were analyzed by IR (FT-IR System, FTS 6000). The morphology was observed by optical microscope. The chemical environments of each element were measured by X-ray Photoelectron Spectroscopy (XPS, Surface analysis PHI5600, PHI 5600) and Secondary Ion Mass Spectroscopy (SIMS, Model PHI 7200 (Physical Electronics)).

Table 2
The peak assignment of vibration in IR spectra.

Wave number (cm^{-1})	Assignment
597	TiO_6 octahedron
713, 874	Si–O–H
1423	Ca^{2+}
1006, 1126	Si–O–Si

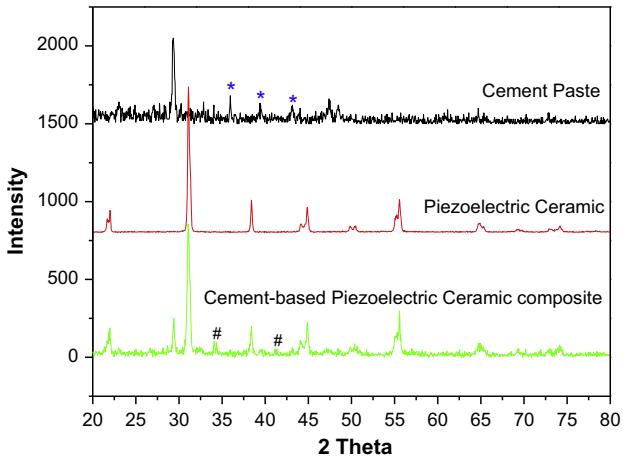

Fig. 2. X-ray diffraction analysis of cement paste, piezoelectric ceramic and cement-based piezoelectric ceramic composite.

3. Results and analysis

It is well known that Si–O chemical bonding occurs during the hardening of Portland cement, leading to the formation of Si–O–Si (siloxane). According to the pioneering work of Damidot et al. [21], silicic acids are unstable after liberation from a silicate. Studies with ^{1}H NMR shows that Si–OH group become detectable immediately after mixing [22]. This indicates the formation of hydroxylated species at the C_3S surface. Ca–OH groups in combination with Si–OH groups, corresponding to C–S–H formation, become detectable during the induction period. Later on, Ca–OH groups belonging to $Ca(OH)_2$ are also formed. At the nanometer scale the C–S–H phase formed by the hydration of C_3S at room temperature seems to be structurally related to the crystalline phase, i.e. 1.4 nm tobermorite and jennite, and also to the poorly crystalline phases C–S–H (I) and C–S–H (II) [23]. Both comprise [SiO_4] square planar units, condensed into linear chains, which are linked so that they repeat at intervals of three [SiO_4] units.

In contrast, PZT ceramic has a perovskite structure with a three-dimensional network of [BO_6−] octahedra; it may be regarded also as a cubic close-packed arrangement of Pb and O ions with Ti (or Zr) ions filling the octahedral interstitial positions (spontaneous polarization will occur when each of the Ti^{4+} ions moves to one side of its octahedron) [24].

Moreover, the experimental analysis was to obtain both qualitative and quantitative clues to elucidate the microstructure and chemical bonding situation in cement-based piezoelectric ceramic composites. Results from IR vibrational spectra were found to be fully consistent with our theoretical predictions. Fig. 1 shows the IR spectra in the wave number range 1300–400 cm^{-1} for cement paste, piezoelectric ceramic, and composite. Interpretations of each peak are summarized in Table 2. IR spectra for silicate compounds exhibit a large absorption between 1200 and 900 cm^{-1}, which corresponds to the asymmetrical stretching vibration (v^3), whereas absorptions at 900 cm^{-1} or below correspond to out-of-plane (v^4) and in-plane (v^2) [24–28] skeletal vibrations. There is a tendency for v^3 to shift to higher wave numbers ("blue shift") as the degree of polymerization or condensation increases. Conversely, for v^3 to shift to lower wave numbers ("red shift") means that the degree of polymerization or condensation decreases. Since $v = 1/2\pi c(f/m)^{1/2}$, as long as the atoms involved are the same,