DEVELOPMENT OF CEMENTING SYSTEMS AND COMPOSITES BASED ON INORGANIC GEL-TO-CRYSTAL TRANSITIONS FOR MILITARY APPLICATIONS

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ABSTRACT

Composite materials (fiberglass, carbon-fiber composites) are considered to be the Army's greatest opportunity to develop a new generation of lighter, stronger materials that will be the basis of new shelters, vehicles and weaponry. While a great deal of effort has gone into examining and refining the reinforcing material (metal, carbon and glass fibers) very little attention has been paid to the cement that will be employed in bonding the elements together. Largely it is assumed that organic resins will be the solution to the bonding problem and often the drawbacks related to combustibility, catastrophic loss of strength at elevated temperatures, embrittlement due to depolymerization, degradation due to exposure to sunlight or ozone are largely ignored. The Army cannot effectively reinforce buildings or develop structural components for vehicles or weapons with materials that will melt, burn and generate toxic gases if the materials going into the structure can be set afire during an attack. In order for the Army to use composites, it will be necessary to produce durable, heat-resistant and fireproof composites made with inorganic cements. Investigators have shown that the key to developing inorganic cements lies in learning to tailor the microstructure to provide the highest strength and the best bonding possible. Performance is tied to making a cement that forms the optimum mixture of amorphous and crystalline solid phases in the proper proportions and geometric distribution to provide a mixture of domains, some of which that are rigidly interlocked (crystalline) and others that can yield (amorphous). Investigations undertaken on these systems have demonstrated that the strength can be directly related to optimizing the density of the finished material. In these cementing materials the solid particulate material behaves as the aggregate and provides the rigid skeleton in the solid. The grain-to-grain contact can transmit stress while the gel provides the cementing paste phase that resists failure in shear. The research undertaken in this project optimized the formulation of systems based on zinc and on aluminum and developed techniques for using inorganic fiber as a tightly bonded reinforcement material.

1. INTRODUCTION

Inorganic cements are the strongest most durable matrices that can be used for composite materials. In the family of inorganic cements the strongest are the acid-base cements. The cements that are the easiest to use and the structurally simplest are the cements that form by reacting orthophosphoric acid solutions and base oxides that result in the formation of compounds formed from simple phosphate tetrahedra. The interesting feature of these cements involves the use of the base oxides as both a solid ingredient in the reaction and the aggregate in the cemented solid (Wilson and Nicholson, 1993). Performance in these cements is linked to making an optimum mixture of amorphous and crystalline solid phases in the proper proportions and with the proper mixture of domains, some of which are rigidly interlocking (crystalline phases) and others that can yield (amorphous phases).

The most important metals in the phosphoric acid solutions are zinc and aluminum. These metal oxides react quickly with phosphoric acid, but in order to form strong solids the metal phosphates must remain in a gel or amorphous state (Williams and Smith, 1971). The metal phosphate reaction products are maintained in an amorphous state by introducing interfering ions or modifiers that can prevent crystallization. These ions are introduced into the system as ions dissolved in the reacting acid or as oxides in the solid phase (Kingery, 1950; Finch and Sharp, 1989). The end result of the stable crystal-gel mixture is a rigid solid that has interesting and useful properties (Table 1).

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Table 1. Properties of Zinc Phosphate Cements (From Wilson and Nicholson, 1993)	
Compressive strength (24 hours)	70 – 131 MPa
Compressive modulus	11.9 – 13.5 GPa
Tensile strength	4.3 – 8.3 MPa
Setting time (37 °C)	5 – 9 minutes

The goal of the present project was to explore the relationship between the ratio of the gel to the crystalline phases and the strength of the hardened cement and to examine the effect of adding tightly bonded reinforcement to the cement to form a composite. The zinc oxide-phosphoric acid system was selected as a model system to explore the optimization of the cement composition and to determine if an effective composite material could be produced by bonding fiber reinforcement elements into the optimized cement.

2. METHOD AND MATERIALS

The zinc oxide-phosphoric acid cement system is unusual in that the respective volumes of the gel phase and the cementing phase can be controlled by varying the amount of phosphoric acid added to a fixed amount of zinc oxide. The unreacted zinc oxide than behaves as aggregate particles in an initially fluid zinc phosphate matrix. Optimum packing of the zinc oxide particles occurs when just enough zinc phosphate is formed to fill the voids between the packed zinc oxide particles.

Commercially available zinc oxide particles were mixed with varying amounts of phosphoric acid solution to change the volume of the gel that was produced. Working from the stochiometry of the reaction it is possible to determine the solid fraction of the zinc phosphate produced and the amount of crystalline zinc oxide remaining. The cement selected for this investigation was zinc phosphate cement produced by Shofu Dental Corporation (San Marcos, CA). The compositions of the liquid and solid components of the cement are given in Table 2.

Samples were prepared by mixing the cold liquid and powder components on a chilled glass plate. The homogeneously mixed fresh cement paste was placed in a split plexiglas cylinder mold. All samples were prepared as cylinders 0.25 in. (6.35 mm) in diameter and 0.50 in. (12.7 mm) in height. The samples were allowed to cure in the forms in a saturated atmosphere for 12 hours and then de-molded and cured under water. The time from casting to strength testing was 7 days.

Table 2. Composition of Powder and Liquid Components for Zinc Phosphate Cement	
Powdered Component	
Compound	Amount (%)
Zinc oxide	90.2
Magnesium oxide	8.2
Silicon dioxide	1.4
Bismuth oxide	0.1
Other oxides (calcium, barium)	0.1
Liquid Component	
Phosphoric acid	54.4
Water	16.2
Zinc	7.1
Aluminum	2.5

(Data are from Charlton, David, undated, Current Status of Dental Luting Cements. http://www.brooks.af.mil/dis/DMNOTES/cements.pdf).

The liquid and solid components are typically mixed in the proportions of 1.7 g of powder to 1.0 g of liquid. For the purposes of this investigation the proportions were varied as shown in Table 3.

Fiber-reinforced samples were prepared by combining cleaned, chopped (4 to 6-mm length) glass (SikaWrap 100 G., Sika Corp., Lyndhurst, NJ) or ceramic fiber (Nextel 312, 3M Corp., Minneapolis, MN) with the cement proportioned with 1 gm phosphoric acid solution to 1.70 grams ZnO powder. Prior to mixing the fibers were sintered in a crucible containing ZnO at 500 ºC for 4 hours to coat the fibers with sublimed ZnO. The final mixture had 0.05 g of fiber in every 1.2 g test cylinder. The test cylinders containing fibers were cured and tested in the identical manner to those without fiber.

The surface morphology and composition of the test samples was characterized as to morphology and chemical composition using the ESEM Model 2020 with a lanthanum hexaboride (LaB_6) electron source and a gaseous

Table 3. Proportions of Liquid and Solid in the ZnO – Phosphoric Acid Cement				
Sample No.	Amount of Liquid Component (g)	Amount of Powder Component (g)	Predicted Unreacted Powder (g)	Predicted Unreacted Powder (% of Original Amount)
1	1.00	3.40	2.73	80.3
2	1.00	2.12	1.45	68.4
3	1.00	1.70	1.03	60.6
4	1.12	1.70	0.95	55.9
5	1.25	1.70	0.86	50.6

secondary electron detector (GSED). The imaging conditions employed an accelerating voltage of 20 KeV and 1.81 mA, and approximately 5 Torr (666 Pa) water vapor in the sample chamber. The environmental gas will be vaporized distilled water supplied via a digitally controlled needle valve assembly contained in a sealed Erlenmeyer flask located outside the sample chamber. Images of these samples were collected over a period of 30 seconds, and stored as 1 MB TIF files. Standardless EDX chemical analysis was be used in this study to assist in identification of the coating. The equipment used is an EDX windowless detector linked to a SUN SPARC station 5 running the IMIX analysis software (Princeton Gamma-Tech, Princeton, NJ) which is attached to the Electroscan 2020 ESEM.

The crystal structure of the coating was determined using the Philips PW1800 Automated Powder Diffractometer system. The run conditions included use of CuKα radiation and scanning from 2 to 65° 2θ with collection of the diffraction patterns accomplished using PC-based Windows 95 versions of Datascan (Materials Data, Inc.) and analysis using Jade.

The unconfined compressive strength (UCS) was determined using a Tinius-Olsen Compression Tester. Samples were all tested after 7 days in a wet condition using the procedure adapted from standard concrete test procedures.

3. RESULTS

3.1 Optimum Strength of the Matrix

The data on the compressive strength of zinc-phosphate samples prepared with varying portions of crystalline material (unreacted ZnO) and gel phase (Zn-phosphate hydrate) are presented in Table 4. The strongest samples were prepared with a proportion of acid and basic oxide that left an estimated 61% ZnO particles by volume in the sample. Much of the work with random close packing of spheres suggests that maximum density that could be expected with a particle density of approximately 63% (Torquato et al. 2000). Although the photomicrograph in Fig. 1, indicates that the ZnO particles could only approximate spheres; the present study suggests that the packing ratio is a good starting point in designing a dense, strong cement with the optimum volume of un-reacted particles.

Table 4 Comparison of Test Cylinder Strengths		
Sample	Unreacted ZnO (% vol.)	Compressive Strength (MPa)
1	80.3	19.27
2	68.4	15.47
3	60.6	40.20
4	55.9	11.00
5	50.6	14.83

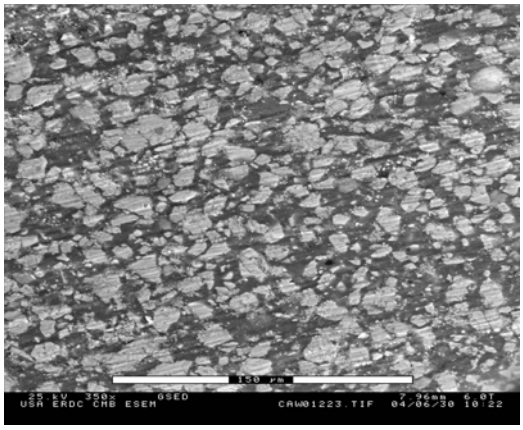

Fig. 1. Photomicrograph of hardened ZnO/Zn-phosphate cement. Note the particles of ZnO embedded in a phosphate matrix.

3.2 Strength of Fiber-reinforced Cement

Table 5 presents the data on the compressive strength of unreinforced, glass fiber-reinforced and ceramic fiber-reinforced zinc phosphate cement. The strongest cylinders are those reinforced with the ceramic fiber. Observations of fracture surfaces suggest that both types of fiber bonded to the cement matrix. The ceramic fibers have far better tolerance to the high temperatures (500 ºC) involved in sintering the fibers and strength loss in the less temperature tolerant glass reinforcement may be related to the loss of strength in the glass fibers.

Table 5. Comparison of Compressive Strength for Reinforced and Un-reinforced Cylinders at 7 Days Curing

Type of Cylinder	Average UCS (MPa)	Maximum UCS (MPa)
Un-reinforced	50.8	53.9
Glass Fiber-Reinforced	34.0	50.2
Ceramic Fiber-Reinforced	76.2	87.9

Fig. 2 shows the surface of a ceramic fiber embedded in the broken surface of a test cylinder. Note that the surface is covered with zinc oxide particles. The fracture surface around the fiber is in the cemented layer adjacent to the fiber.

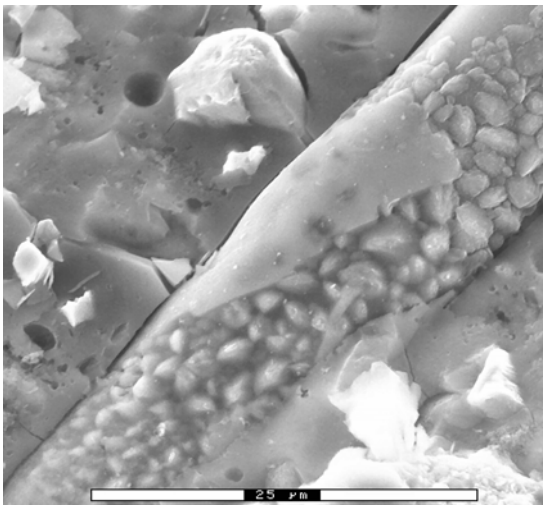

Fig. 2. Photomicrograph showing surface of a ceramic fiber embedded in the zinc phosphate cements.

CONCLUSIONS

The investigation of zinc phosphate cements indicates:

a) The proportion of non-crystalline (gel) phase and crystalline phase in a zinc phosphate cement is critical to obtaining high compressive strengths.

b) Gel-to-crystal proportions that can approximate the close packing of particles are a starting point for designing a cement formulation.

c) Fiber reinforcement with ZnO-coated ceramic fibers can produce an extremely strong material.

d) Glass fiber reinforcement may require use of special high-temperature tolerant glasses or lower coating temperatures.

Inorganic cements such as the zinc phosphate or aluminum phosphate cements can make strong durable composites that should be capable of maintaining their strength without depolymerizing or charring when heated. The zinc oxide-zinc phosphate composites may be useful in the military because they are relatively inexpensive, easy to form, stable materials that are sun-resistant and do not support microbial growth.

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