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# Chemical and Microstructural Changes at Interfaces between $ZrO_2 \cdot SiO_2$ Glass Fibers Prepared by Sol-Gel Method and Cement Matrices

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Mechanical and chemical tests were performed on $ZrO_2 \cdot SiO_2$ glass fibers manufactured by the sol-gel method and E-glass fibers-reinforced cement composites in order to investigate the interactions between glass fibers and cement matrices. Chemical attack leads to corrosion of the glass fiber surfaces. In the corrosion reactions, the surface of $30ZrO_2 \cdot 70SiO_2$ glass fibers developed a densified concentric layer, which consists of glass corrosion products with much higher Zr and lower Si than the fresh glass fiber. The layer of reaction product is regarded to stiffen the cement matrices and provide a useful improvement to the mechanical properties. The addition of $ZrO_2$ content increases the corrosion resistance of glass fibers in cement by forming a passivating layer on the surface of glass fibers.

***Key words :*** Glass fiber reinforced cement, Alkali resistance, Corrosion, Passivating layer, Sol-gel method, Zirconia

## I. Introduction

Cement pastes can be reinforced with glass fibers to produce a composite with high tensile properties[1] and glass fibers are used as reinforcement material to make thin and complex-shaped cement composites.[2] However, GRC composites tend to lose strength as a consequence of reaction between the highly alkaline cement matrices and the glass fibers.[3] This durability problem is the result of chemical attack on the glass by the alkaline cement environment. The corrosion of silicate glasses in alkaline medium is believed to be due to breaking of the Si-O bonds by hydroxyl ions.[4]

$$\equiv Si\text{-}O\text{-}Si\equiv \; + \; \equiv OH^- \rightarrow \underset{\text{(solid)}}{\equiv Si\text{-}OH} \; + \; \underset{\text{(in solution)}}{O^-\text{-}Si\equiv}$$

Glass fibers used for cement reinforcement must have very high alkaline durability[5]. In order to improve the chemical durability of glass fibers, $ZrO_2$ containing glasses, the so called alkali resistant (AR) glasses,[5] has been developed by Majumdar and Ryder.[7] However, tests of the AR glass fibers as well as GRC composites produced with it have indicated that it is not immune to attack of alkaline ions, although, it can substantially reduce the rate of loss in mechanical properties of the composite, compared to GRC with E-glass fibers. Also, the $ZrO_2$ content is limited to less than a few mol.% owing to increasing melting temperature of the glasses.[8]

Recently, a new method was proposed to prepare the glasses by the sol-gel method using metal alkoxide. Using this method $ZrO_2$ containing glasses with high $ZrO_2$ content have been prepared.[8]

In recent years, different commercial alkali resistant glass fibers have become available.[9] It has been suggested that their improved performance in GRC composite is partly the result of surface treatment of glass fibers.

In the previous reports,[10,11] a preliminary study showed that it was possible to use the drawing method in mixed alkoxide solutions for $ZrO_2 \cdot SiO_2$ glass fibers.

The present work, which is an extension of previous works, describes the results of a study on the behavior of $ZrO_2 \cdot SiO_2$ glass fibers by the sol-gel method and cement matrices in the different curing time and investigates the interactions between the $ZrO_2 \cdot SiO_2$ glass fiber and cement paste.

## II. Experimental Procedure

### *1. The preparation of glass fibers and GRC composites*

In the pervious reports,[10,11] the $ZrO_2 \cdot SiO_2$ glass fibers were prepared from mixed alkoxide($Si(OC_2H_5)_4$ and Zr $(O\text{-}nC_3H_7)_4$)-$C_2H_5OH$-HCl solutions with the mole ratios of $H_2O$/total alkoxides ranging from 1 to 2. mole ratios $C_2H_5$ OH/ and HCl/total alkoxides were 1.0 and 0.3, respectively. The solutions were kept standing at room temperature without cover. The gel fibers were drawn by immersing a glass rod of about 3 mm in diameter into the sol and pulling it up by hand. This step was repeated until the sol gelled into a jelly-like mass. The gel fibers were dried at 25°C for 24h in ambient atmosphere and they were gradually heated at 0.5°C/min., and were calcined in air for 10 h at 800°C.

GRC composites were prepared using a type of Portland cement with the chemical composition (wt.%) 63.8

CaO, 22.1 $SiO_2$, 5.0 $Al_2O_3$, 3.0 $Fe_2O_3$, 2.0 $SO_3$, 0.70 MgO and 0.89 total alkali ($Na_2O+K_2O$). To prepare GRC composites, the $ZrO_2$·$SiO_2$ and E glass fibers were chopped into ~10 mm lengths and mixed with the cement using deionized water to cement ratio of 0.35. The glass fibers content of the mixture were 10 vol.%. The fresh mix was cast into a $50\times10\times10$ $mm^3$ mould and hydrated for 24 h at 25°C. After demoulding, it was sealed in a water bath to prevent evaporation of water and carbonation of the cement paste. GRC composites were cured at 98% relative humidity at 25°C and 50°C for ca. 240 days. The high curing temperature was chosen to accelerate chemical reactions of the glass fibers with the cement.

### 2. *Characterizations of GRC composites*

After having been cured the GRC composites were tested in flexure in three point loading using the computer-controlled servo hydraulic dynamic testing machine (MTS 180) with a span of 20 mm and a crosshead speed of 2 mm/min.

The fractured surfaces and glass fibers were coated with a thin layer of vacuum-deposited gold and examined by SEM (Hitachi X-650) equipped with a Link AN 10000 EDAX system.

## III. Results and Discussion

Fig. 1 shows a SEM micrograph of fresh $30ZrO_2$·$70SiO_2$ glass fibers before immersing them in cement. The surface of glass fibers are very smooth.

Table 1 shows the flexural strength of $30ZrO_2$ $70SiO_2$ glass fibers and E glass fibers reinforced cement (named ZGRC and EGRC) composites. At 25°C, the flexural strength of ZGRC lead to a maximum value of 18.43 MPa after 60 days, before declining to ca. 15.02 MPa after 240 days. The strength reduced to small values and the ZGRC composites became essentially brittle. This is an indication that ZGRC remained strong enough to sustain the stress.

At 50°C, the flexural strength lead to a maximum value at shorter curing time, but the decline of flexural strength was more rapidly than 25°C. At shorter curing time, depending on curing temperature, the glass fibers behave as a continuous reinforcement but the deterioration of glass fibers quickly appear.[7]

This results was confirmed by the examination of fractured surface of GRC composites. A typical fractured surface of ZGRC composite after 60 days of curing at 25°C is presented in Fig. 2. An extensive pull-out is clearly visible on ZGRC with fibers even coming 5 mm out of the surface. Fig. 3 shows SEM micrographs of $30ZrO_2$·$70SiO_2$ glass fiber in the cement matrix(a) and higher magnification of the corrosion products of (a) after 90 days cured at 25°C.

The corrosion production $Ca(OH)_2$ developed on the surface of glass fiber. $Ca(OH)_2$ adjacent to the surface of the glass fiber leads to accelerated local attack, effectively reducing the mean length of the fibers.[5] More general

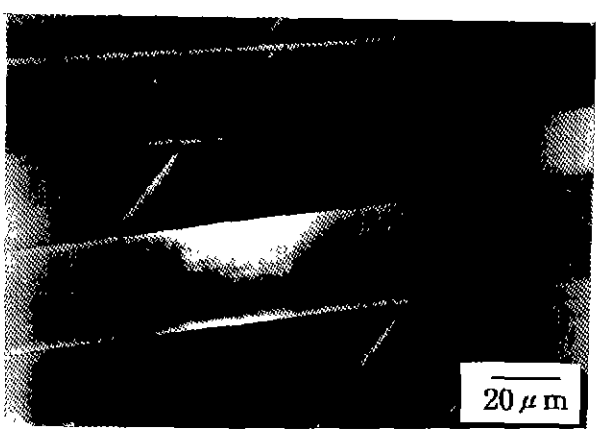


**Fig. 1.** SEM micrograph of $30ZrO_2$·$SiO_2$ glass fibers heated at 800°C.

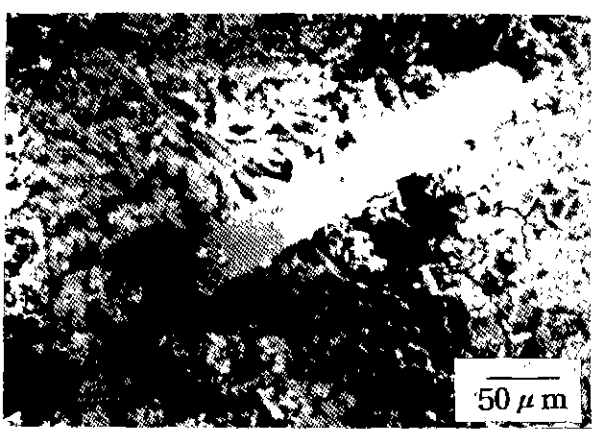


**Fig. 2.** Fibers pulled-out on the fractured surface of $30ZrO_2$·$70SiO_2$ glass fibers reinforced cement after 60 days cured at 25°C.

**Table 1.** Flexural Strength of Cement Paste Samples Reinforced with Aligned Fiber Strands After 240 Days Cured at 25°C and 50°C* (Unit: MPa)

| Samples \ Curing Time (Days) | 30 | 60 | 120 | 150 | 180 | 240 |
|---|---|---|---|---|---|---|
| Cement paste | 9.83 | 11.24 | 10.53 | 9.76 | 8.33 | 8.83 |
| Reinforced with $30ZrO_2$ $70SiO_2$ glass fiber | 16.98 | 18.43 | 15.43 | 15.2 | 15.1 | 15.02 |
| | *18.1 | *14.54 | *14.21 | *13.5 | *13.5 | *13.3 |
| Reinforced with E glass fiber | 15.93 | 11.75 | 11.23 | 10.12 | 10.12 | 9.71 |

surface attack and roughening of the originally smooth fibers occur, and water also migrates into the glass fibers.[2] The ingress of water hydrolyze Si-O bonds and is accompanied by inward diffusion of Ca ions arising from the cement, while Si from the fibers migrate outward into the adjacent paste. The chemical diffusions and accompanying mechanical stresses lead to debonding between cement and fibers.[5] The corrosion products have an amorphous or gel-like appearance (Fig. 3.(b)).

The extent of chemical attack on $30ZrO_2 \cdot 70SiO_2$ glass fibers in the extracted cement paste solutions cured at 25°C after 150 (Fig. 4(a)), 180 days (Fig. 4(c)) and higher magnification of the corrosion products of (Fig. 4(a)) and (Fig. 4(c)) are shown in Fig. 4 (b),(d). The $30ZrO_2 \cdot 70SiO_2$ glass fibers have been deeply eroded with curing time by attack of alkaline ions from extracted cement paste solutions. Needle-like morphology developed surface of $30ZrO_2 \cdot 70SiO_2$ glass fiber at 25°C for 150 days. The longer curing time, the more corrosion products of needle-like morphology developed (Fig. 4(d)). The corrosion products probably consist of Zr and $CaO\text{-}SiO_2\text{-}H_2O$.[6]

Fig. 5 shows microstructures of $30ZrO_2 \cdot 70SiO_2$ glass fibers in cement matrix after 240 days cured at 25°C (Fig. 5(a)), 50°C (Fig. 5(c)) and higher magnification of cor-

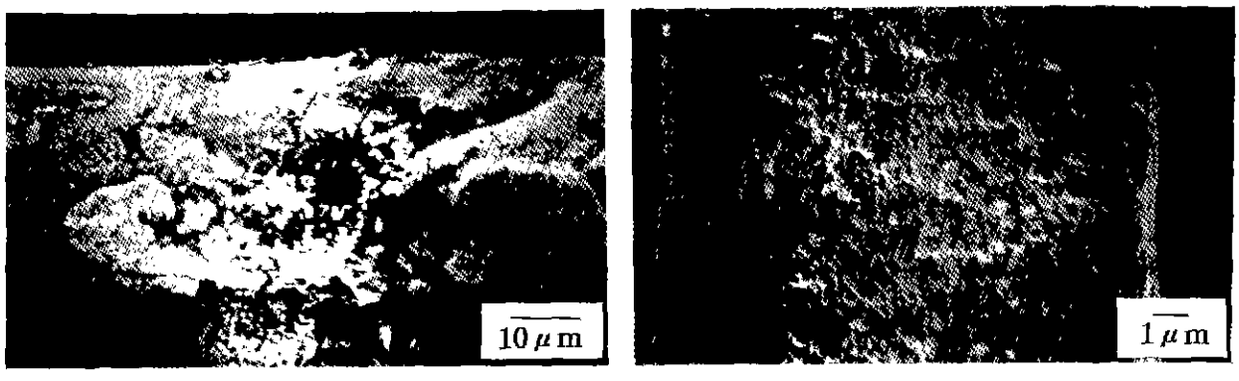


**Fig. 3.** Microstrructures of $30ZrO_2 \cdot 70SiO_2$ glass fiber in cement matrix (a) and corrosion product (b) after 90 days cured at 25°C.

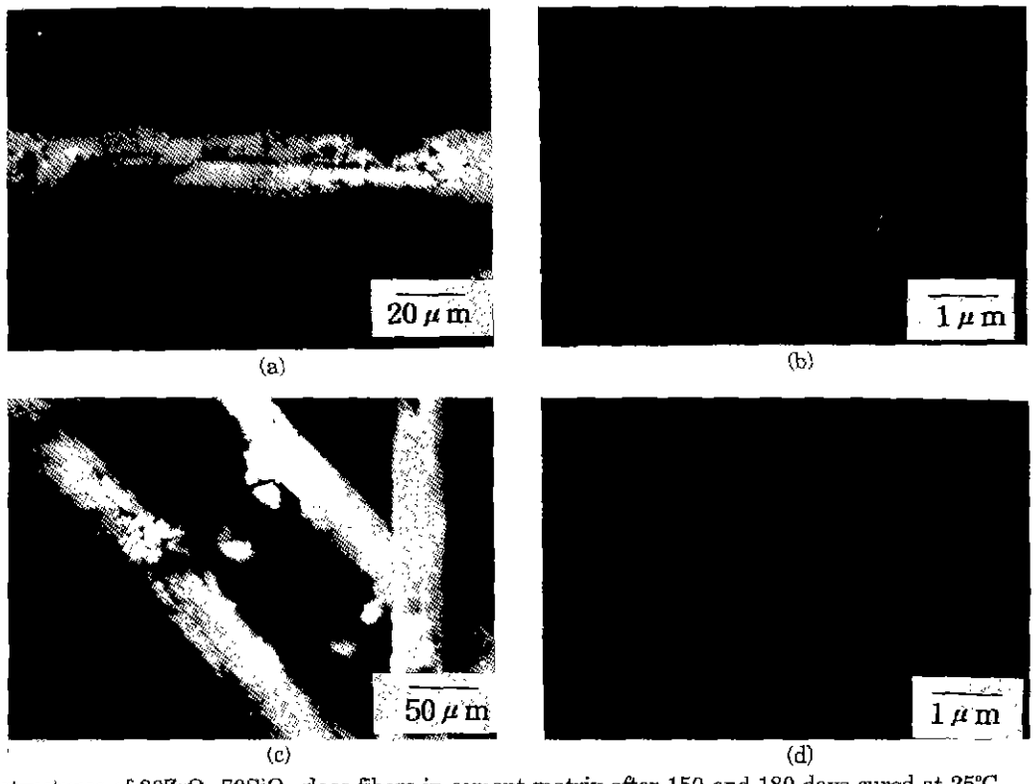


**Fig. 4.** Microstructures of $30ZrO_2 \cdot 70SiO_2$ glass fibers in cement matrix after 150 and 180 days cured at 25°C. (a) 150 days cured at 25°C. (b) corrosion product of (a). (c) 180 days cured at 25°C. (d) corrosion product of (c).

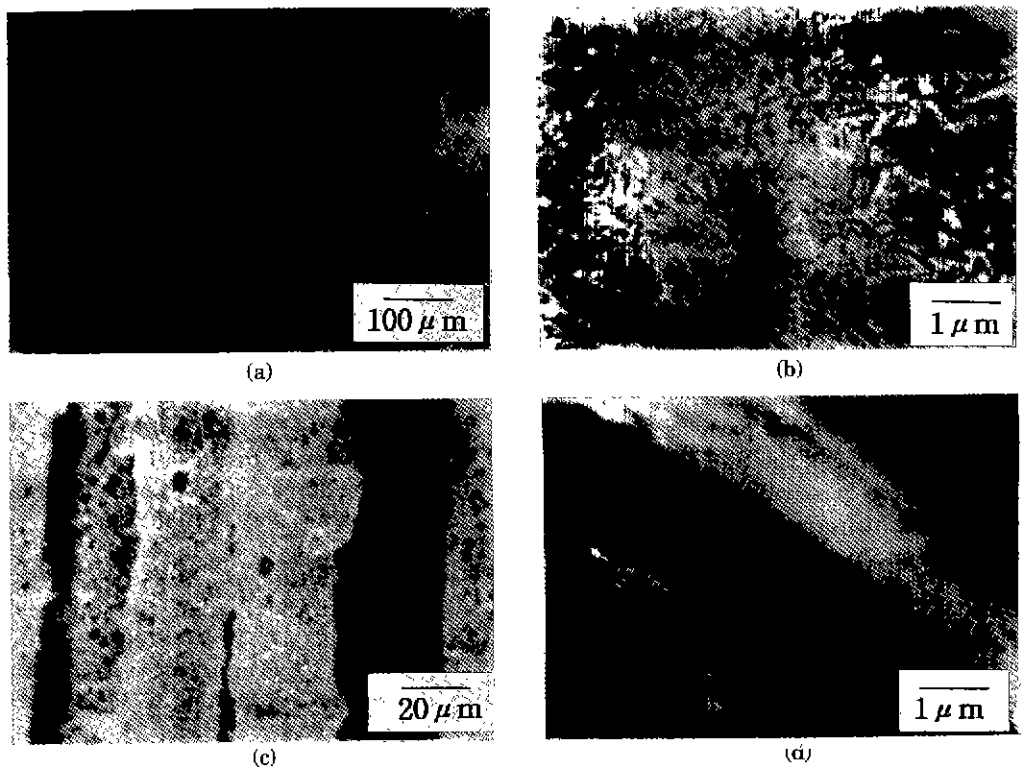


**Fig. 5.** Microstructures of $30ZrO_2$ $70SiO_2$ glass fibers in cement matrix after 240 days cured at 25°C and 50°C. (a) 240 days cured at 25°C. (b) corrosion product of (a). (c) 240 days cured at 50°C. (d) corrosion product of (c).

**Table 2.** Chemical Composition of the Surface of $30ZrO_2 \cdot 70SiO_2$ Glass Fibers and in Hydrated Composites by EDAX (Unit: wt.%)

| | | Curing duration (25°C) | | | | Curing duration (50°C) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 30 | 90 | 180 | 240 | 30 | 90 | 180 | 240 | (days) |
| Si | (45.1) | 45.1 | 42.1 | 40.3 | 38.2 | 43.2 | 41.3 | 38.2 | 37.2 | |
| Zr | (54.9) | 54.6 | 54.4 | 54.1 | 54.0 | 54.2 | 54.0 | 53.9 | 53.8 | |

rosion products (Fig. 5(b)) of Fig. 5(a) and a cross section (Fig. 5(d)) of Fig. 5(c). The $30ZrO_2 \cdot 70SiO_2$ glass fibers have maintained good physical contact with the cement hydration products. At 25°C, the corrosion products of needle-like morphology was gradually replaced by snowflake-like morphology consisting of glass-cement reaction products.

Higher curing temperature, 50°C, accelerated reaction of the glass fibers in cement matrix and resulted densified concentric layer (Fig. 5(d)). A remarkable change in the microstructure of the reinforcement thus occurs at 50°C after 240 days. The darker zone represents the unattacked fraction of the glass fiber and brighter zone around the glass fiber is the corrosion layer of the glass fiber-cement. The needle-like or snowflake-like morphology is gradually replaced by densified layer consisting of glass-cement reaction product. These have relatively hollow cores and low aspect are aptly termed concentric structures. The lowered aspect ratio occurs as a consequence of notching by $Ca(OH)_2$ crystals. The hollow-cylinder or densified concentric layer, together with the adjacent partly densified paste regions, are viewed as contributing to the residual flexural strength.[5]

**Table 3.** Chemical Composition of Corrosion Products of the $30ZrO_2 \cdot 70SiO_2$ Glass Fibers at 50°C by EDAX (Unit: wt.%)

| | Curing duration (50°C) | |
|---|---|---|
| | 90 days | 240 days |
| Si | 35.07 | 32.43 |
| Zr | 42.09 | 41.08 |
| Ca | 20.38 | 23.93 |

The EDAX measurements of the surface composition of $30ZrO_2 \cdot 70SiO_2$ glass fibers in hydrated cements are recorded as a function of temperature and curing time in Table 2. The content of the elements present on the surface of glass fiber is significantly altered as a consequence of chemical attack.[9] The Zr content in glass fiber does not change significantly. Si content of the surface of glass fiber was drastically reduced due to leaching, whereas the Ca content of the surface layer increased during the corrosion process.[2]

Table 3 gives the chemical composition of the corrosion products in $30ZrO_2 \cdot 70SiO_2$ GRC composites hydrated for 90 and 240 days at 50°C. The corrosion products are rich in Zr, Si and Ca. The corrosion products almost certainly consist of hydrous phases, although the EDAX system is not able to analyze hydrogen. Paul[12] pointed out that hydrated $ZrO_2$ is the only stable product in the pH range 0-17. Breaking the Zr-O bonds in the anhydrous glass may lead to the formation of hydrated $ZrO_2$, probably colloidal $Zr(OH)_2$.[12]

The addition of $ZrO_2$ increases the corrosion resistance of glass fibers in cement by forming a thin stable passivating layer on the surface of glass fibers. The pH of the pore fluid extracted from the cement paste is $\geq 13$. The pH value is high enough to break the Si-O bonds in glass fibers. Although a Zr-rich passivation layer was formed at the initial stage of hydration, it did not prevent further depletion of Si and penetration of hydroxyl ions.[5]

## IV. Conclusions

The chemical attack leads to hydroxylation of glass fiber surfaces. These results are related to the measured flexural strength of composites. After 240 days at 25°C fibers still provide a significant degree of reinforcement: flexural strength in 3-point loading do not fall below 15.02 MPa. However, at 50°C, glass fiber deteriorations are much more rapidly occur than at 25°C. Deterioration of glass fibers in cement arises as a consequence of attack of alkaline ions and the glass fibers lose part of their strength with increasing curing temperature and due to growth of hydration products between the glass fibers.

In the course of corrosion reaction, the leaching of Si from the glass fiber surfaces occurs and drives the chemical attack of the glass network. A marked enrichment in the Zr and Ca contents of the corrosion products is observed due to dissolution of silica. Several processes occur competitively, $Ca(OH)_2$ crystals in the cement paste impinge on fibers, causing accelerated corrosion and local notching which leads to overall fiber shortening. But mass attack on the fibers also occurs, leading to their hydroxylation and dissolution. Partial passivation of the fiber allows time for the densified concentric layer to develope properly. This layer of dense reaction product is considered to stiffen the matrix and provide a useful improvement to the flexural strength, relative to cement paste.

### Acknowledgement

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