Recent Development on the Graphene Reinforced Geopolymer Composites

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Outline

1. Introduction
2. Preparation process
3. *In situ* reduction mechanism of graphene oxide (GO)
4. The microstructure and mechanical properties of rGO/geopolymer composites
5. Thermal evolution of and the mechanical properties of ceramic composites derived form rGO/KGP
6. Conclusions
1. Introduction

**Geopolymer**

- **Empirical formula**
  \[ M_n\{-(\text{SiO}_2)_{z}\cdot\text{AlO}_2\}n \cdot w\text{H}_2\text{O} \]
  
  - \(M\) - alkali metallic ion;
  - \(n\) - degree of polymerization;
  - \(z\) - Mole ratio of SiO\(_2\) to Al\(_2\)O\(_3\);
  - \(w\) - Water of crystallization.

- **Structure**

Schematic of the description of metakaolin geopolymerisation by a coarse-grained Monte Carlo model

Sketch of the geopolymerization process
1. Introduction

Graphene

- One-atom-thick carbon material, with carbon atoms packed densely in a hexagonal honeycomb lattice.
- A basic building block for graphitic materials of all other dimensionalities.
- It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite.

Excellent performance

- Thermal property
- Electrical property
- Mechanical property

Difficult to disperse

Graphene oxide (GO)

Hydrophily

Easy to disperse
1. Introduction

Graphene oxide (GO)
- Water solubility
- In-situ reduction:
  - Alkaline reduction
  - Thermal reduction

Geopolymer
- Aquous environment
- Alkaline environment
- In-situ convert into advanced ceramics

In-situ synthesis:
Graphene/Geopolymer composites

High temperature treatment:
Graphene/ceramic matrix composites
2. Preparation process

**Reduction mechanism**

<table>
<thead>
<tr>
<th>GO (wt%)</th>
<th>Reduction reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>1</td>
<td>RT</td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

**Geopolymerization mechanism**

<table>
<thead>
<tr>
<th>GO (wt%)</th>
<th>Geopolymerization reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 1</td>
<td>0, 0.5, 1, 2, 3, 6, 12, 24, 72, 120, 168</td>
</tr>
</tbody>
</table>

**rGO/Geopolymer Composites**

<table>
<thead>
<tr>
<th>GO (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0.05, 0.1, 0.3, 0.5, 1</td>
</tr>
</tbody>
</table>

**reduced graphene oxide (rGO)**

Schematic illustration of preparation procedure for rGO/geopolymer composite
3. In situ reduction mechanism

3.1 Effects of reduction temperature

Optical photographs of GO suspension (a) in deionized water and GO after being reduced under alkaline solution at different temperatures: (b)-(e) RT, 40 °C, 60 °C and 80 °C, respectively.

FT-IR spectras of GO and rGO obtained after being reduced under alkaline solution for different temperatures.
3. In situ reduction mechanism

3.1 Effects of reduction temperature

Values of C/O atomic ratios and peak area ratios of oxygen-containing bonds to C-C bonds obtained by XPS analysis of GO and rGO reduced for 3h at different temperatures:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C/O Ratio</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>2.48</td>
<td>0.67</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>RT</td>
<td>2.74</td>
<td>0.5</td>
<td>0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>40</td>
<td>2.85</td>
<td>0.31</td>
<td>0.1</td>
<td>0.07</td>
</tr>
<tr>
<td>60</td>
<td>3.06</td>
<td>0.4</td>
<td>0.08</td>
<td>0.1</td>
</tr>
<tr>
<td>80</td>
<td>3.36</td>
<td>0.48</td>
<td>0.07</td>
<td>0.06</td>
</tr>
</tbody>
</table>

High resolution C_{1s} X-ray photoelectron spectra for GO and rGO reduced for 3h at different temperatures:
(a) GO, (b) RT, (c) 40°C, (d) 60°C, (e) 80°C
3. In situ reduction mechanism

3.1 Effects of reduction temperature

Typical TEM images and selected area electron diffraction (SAED) patterns of rGO reduced at different temperatures:
(a) GO, (b) GO, (c) RT, (c) 40°C, (d) 60°C, (e) 80°C

SEM micrographs of GO and rGO reduced for 3h at different temperatures:
(a) GO, (b) RT, (c) 40°C, (d) 60°C, (e) 80°C
3. In situ reduction mechanism

3.2 Effects of reduction time

Optical photographs of GO suspension and GO after being reduced under geopolymeric solution at 60°C for different times: (a) GO suspension, (b) 0.25h, (c) 3h, (d) 6h, (e) 72h

FT-IR spectras of GO and rGO reduced at 60°C at different times
3. In situ reduction mechanism

3.2 Effects of reduction time

Values of C/O atomic ratios and peak area ratios of oxygen-containing bonds to C-C bonds obtained by XPS analysis of GO and rGO reduced at 60°C for different times:

<table>
<thead>
<tr>
<th>Samples</th>
<th>C/O Ratio</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>2.48</td>
<td>0.67</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>0.25h</td>
<td>3.03</td>
<td>0.39</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>3h</td>
<td>3.06</td>
<td>0.40</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>6h</td>
<td>3.19</td>
<td>0.66</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>72h</td>
<td>3.75</td>
<td>0.53</td>
<td>0.01</td>
<td>0.09</td>
</tr>
</tbody>
</table>

\[ \text{R-COOH + KOH} \rightarrow \text{RH} + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \]

High resolution C1s X-ray photoelectron spectra for GO and rGO reduced at 60°C at different times:

(a) GO, (b) 0.25h, (c) 3h, (d) 6h, (e) 72h
3. In situ reduction mechanism

3.2 Effects of reduction temperature

Typical TEM images and the selected area electron differentiation (SAED) patterns (insets at upper right corner) of GO and rGO: (a) GO, (b) rGO for 72 h

SEM micrographs of rGO reduced at 60°C for different times: 

a) 0.25 h, (b) 3 h, (c) 6 h, (d) 72 h
3. In situ reduction mechanism

3.3 Thermal reduction

GO $\rightarrow$ rGO + CO$_2$ + CO + H$_2$O

High resolution C1s X-ray photoelectron spectra of GO and rGO obtained after high temperature treatment at 1000°C for 0.5h: (a) GO, (b) rGO

Peak area ratios of C-C bond and oxygen-containing bonds obtained by XPS analysis of GO and rGO

<table>
<thead>
<tr>
<th>Bond</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>0.53</td>
<td>0.36</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>rGO</td>
<td>0.87</td>
<td>0.13</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
3. In situ reduction mechanism

Alkaline reduction: decarboxylic reaction

\[ R\text{-COOH} + KOH \rightarrow RH + K_2CO_3 + H_2O \]

Thermo reduction:

\[ GO \rightarrow rGO + CO + H_2O + CO_2 \]
4. rGO/geopolymer composites (rGO/KGP)

4.1 Phase composition

The photographs of rGO/KGP composites with different rGO contents (wt%), (a) 0, (b) 0.05, (c) 0.1, (d) 0.3, (e) 0.5 and (f) 1

XRD patterns of rGO/KGP composites with different rGO contents(wt%), (a) 0, (b) 0.05, (c) 0.1, (d) 0.3, (e) 0.5 and (f) 1
4. rGO/geopolymer composites (rGO/KGP)

4.2 Microstructure

Typical surface microstructure of rGO/KGP composites with different GO contents:
(a) 0wt.%, (b) 0.05wt.%, (c) 0.1wt.%, (d) 0.3wt.%, (e) 0.5wt.%, (f) 1wt.%
4. rGO/geopolymer composites (rGO/KGP)

4.4 Fracture morphology

Fracture morphology of rGO/KGP with different GO contents: (a) 0wt.%, (b) 0.05wt.%, (c) 0.1wt.%, (d) 0.3wt.%, (e) 0.5wt.%, (f) 1wt.%
4. rGO/geopolymer composites (rGO/KGP)

4.4 Fracture morphology

Detailed observation of interface microstructure of the rGO/KGP5 composites: (a)-(b) deflected crack, (c) bonding between KGP and rGO, (d) rGO pulling out

TEM images of rGO/KGP5, insets display selected electronic diffraction patterns: (a) wrinkled rGO with matrix, (b) bonding between rGO and matrix
4. rGO/geopolymer composites (rGO/KGP)

4.1 Phase composition

Mechanical properties of rGO/KGP composites with different GO contents
5. Thermal evolution of rGO/KGP

5.1 Crystallization kinetics

\[
\frac{dx}{dt} = K(1-x)^n
\]

\[
K = K_0 \exp\left(-\frac{E}{RT}\right)
\]

\[
\ln\left(\frac{\beta^2}{T_p^n}\right) = -\frac{E}{RT_p} + C
\]

Summary of the crystallization kinetics parameters of the KGP and rGO/KGP

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate (°C/min)</th>
<th>Crystallization peak $T_p$ (°C)</th>
<th>$\Delta T$</th>
<th>$n$</th>
<th>Activation energy (kJ/mol)</th>
<th>Average value $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGP</td>
<td>5</td>
<td>1020</td>
<td>25</td>
<td>5.32</td>
<td>248</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1049</td>
<td>35</td>
<td>4.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1075</td>
<td>38</td>
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<td>1095</td>
<td>40</td>
<td>3.95</td>
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<td></td>
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<tr>
<td>rGO/KGP</td>
<td>5</td>
<td>1011</td>
<td>33</td>
<td>4.31</td>
<td>240</td>
<td>3.5</td>
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<td>1048</td>
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<td>1073</td>
<td>45</td>
<td>3.52</td>
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</tr>
<tr>
<td></td>
<td>20</td>
<td>1086</td>
<td>55</td>
<td>2.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DTA curves of (a) KGP and (b) rGO/KGP at different heating rates

Kissinger plots of the KGP and rGO/KGP
5. Thermal evolution of rGO/KGP

5.2 Phase composition and microstructure

XRD patterns of rGO/KGP composites after high temperature treatment at different temperatures:

- ▲ Leucite, tetragonal, 38-1423
- • Quartz, low, 65-0465

2theta, degree

Relative intensity, a.u.

20 40 60 80

Leucite, tetragonal, 38-1423
Quartz, low, 65-0465

•••

1100°C
1050°C
950°C
1000°C
900°C
800°C
rGO/KGP
metakaolin

TEM images of the rGO/KGP1000 sample:
- (a) low magnification
- (b) HAADF STEM image
- (c) high magnification
- (d) HRTEM of rGO and geopolymeric matrix
- (e) high magnification of the matrix
- (f) SAD pattern of area A
5. Thermal evolution of rGO/KGP

5.2 Phase composition and microstructure

SEM images of (a) KGP1000 and (b) rGO/KGP1000
(etching in 3 wt% HF for 30s)
5. Thermal evolution of rGO/KGP

5.3 Fracture morphology

Typical microstructure of fracture surface of rGO/KGP composites after high temperature treatment:
(a) rGO/KGP, (b) rGO/KGP800, (c) rGO/KGP900, (d) rGO/KGP1000, (e) rGO/KGP1050, (f) rGO/KGP1100
5. Thermal evolution of rGO/KGP

5.3 Fracture morphology

High magnification SEM images of fracture surface morphologies of rGO/KGP composites after high temperature treatment: (a) rGO/KGP800, (b) rGO/KGP900, (c) rGO/KGP1000
5. Thermal evolution of rGO/KGP

5.4 Mechanical properties

Mechanical properties of (a) KGP and (b) rGO/KGP samples after high temperature treatment

2.01 Pa·m$^{1/2}$/41.3 Mpa/56.3 GPa

2.04 Pa·m$^{1/2}$/91.1 Mpa/60.5 GPa
6. Conclusions

◆ GO is easily reduced in situ under alkaline conditions, and exhibits long-term stability and well dispersion in the geopolymeric solution. *In-situ reduction* occurs as a consequence of reducing/eliminating C=O and C–O bonds. Meanwhile, The reduction degree of rGO increased with the increasing temperatures. The C/O ratio increased from 2.48 (GO) to 3.36 (rGO, 80°C) with the elevated temperatures.

◆ The introduction of GO has no obvious effects on the global structure of amorphous geopolymer matrices, and following reduction, the rGO sheets which dispersed homogeneously in the geopolymer matrix showed well bonding state to the matrix, resulting in the improvement of mechanical properties.
6. Conclusions

◆ rGO/KGP could fully transform to rGO/leucite composites after heat treatment at 1000°C for 30 min. The presence of rGO in KGP matrix leads to the refinement of leucite grains but has no obvious effect on the lattice parameters of leucite. rGO sheets with scrolled and fold features disperse homogeneously in the leucite matrix, showing no interface reaction between rGO and matrix.

◆ Much more remarkable improvement in mechanical properties was achieved due to the introduction of rGO sheets into the matrix. The high-temperature treatment significantly improves the hardness of both rGO/KGP and pure KGP. Compared with those of the leucite sample (KGP1000), the mechanical properties of rGO/leucite (rGO/KGP1000) reach their own peak values, respectively, indicating the significant strengthening and toughening effect from graphene.
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Thank You for Your Attention