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Parking simulation of three-dimensional multi-sized star-shaped particles

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Abstract

The shape and size of particles may have a great impact on the microstructure as well as the physico-properties of particulate composites. However, it is challenging to configure a parking system of particles to a geometrical shape that is close to realistic grains in particulate composites. In this work, with the assistance of x-ray tomography and a spherical harmonic series, we present a star-shaped particle that is close to realistic arbitrary-shaped grains. To realize such a hard particle parking structure, an inter-particle overlapping detection algorithm is introduced. A serial sectioning approach is employed to visualize the particle parking structure for the purpose of justifying the reliability of the overlapping detection algorithm. Furthermore, the validity of the area and perimeter of solids in any arbitrary section of a plane calculated using a numerical method is verified by comparison with those obtained using an image analysis approach. This contribution is helpful to further understand the dependence of the micro-structure and physico-properties of star-shaped particles on the realistic geometrical shape.

Keywords: star-shaped particle, inter-particle overlapping algorithm, parking, sectional plane analysis, microstructure

(Some figures may appear in colour only in the online journal)

1. Introduction

On meso-/microscopic scales, particulate composites, such as ceramic, glasses, polymer and cementitious composites, can be considered the packing system of particles with irregular shape [1]. The evolution of the interior structure of particulate composites is, to a certain extent, relevant to the initial packing state of particles. Since the physico-properties of particulate composites are directly related to their meso-/micro-structure, the packing structure of particles can give us insights about the effects of various geometric characteristic parameters on the structures of interfacial transition zones (ITZs) and the matrix, as well as on the physical/mechanical/thermal/hygral properties [2–4]. Over the past decades, scientific attention has broadened the study of the meso-/micro-structure of particulate composites through computer simulation of the packing of particles with regular geometrical shapes, such as spherical [5], ellipsoidal [6], cylindrical [7, 8], polyhedral [9, 10], hyperspherical and hypercubic [11], etc. It is helpful to understand the effect of the regular geometrical shape of particles on the meso-/micro-structure as demonstrated by these prominent works. However, since the grain shape of most particulate composites in nature is irregular, simulating the influence of an arbitrary-shaped particle packing structure on the meso-/micro-structure is still a challenge.

To establish the packing model of an arbitrary-shaped particle, the geometrical shape of the particle, which is close to the realistic shape in particulate composites, should first be constructed. Currently, there have been several attempts to quantify the realistic geometrical shape of grains. For instance, employing a digital image-based method, an arbitrary-shaped particle can be characterized by a coherent collection of pixels for the two-dimensional (2D) case or voxels for the three-dimensional (3D) case using professional image equipment techniques [12], such as scanning electron microscopy (in back-scattered electron mode), x-ray computer tomography (x-ray CT) and magnetic resonance tomography (MRT) [13] etc. Hall *et al* [14] have developed a so called original grain-scale volumetric digital image correlation method that permits the characterization of real sand grains in a specimen. Unfortunately, this requires a huge memory to store the pixels/voxels of all of the particles in a specimen.

Either a Fourier series (2D case) [15, 16] or a spherical harmonic series (3D case) [13, 17, 18] is employed in the literature to characterize the particle shape. In this situation, a particle must be star-shaped (or star-like). For a shape to be star-like, any line segment whose one endpoint is in the kernel of the star-shaped particle and the other endpoint is on the surface must be totally contained in the shape itself, that is, each ray from the kernel of the star-shaped particle must have one and only one intersection with the surface [17, 19, 20]. The kernel of the star-shaped particle is usually a convex set of points that contains all of the points that can be used as the one fixed point in the star-shaped particle.

The key issue for hard particle packing in a given cell is detection of inter-particle overlapping. Approximate collision detection schemes always use a series of bounding boxes, spheres or voxels to solve the collision detection problem [21]. In many applications of computer graphics [22, 23] and game development [24], a fast and robust collision detection algorithm is required to decompose a complex object into simpler pieces [25, 26]. Since polygonal meshes are extensively used in computer graphics, one method for intersection detection is based on ‘ray shooting’ using polygon meshes (triangulations) [27]. For a regular-shaped particle system, there are many well-known algorithms for detecting inter-particle overlap. For instance, Perram and Wertheim [28] presented a contact potential function to check inter-ellipsoid overlapping based on the work of Vieillard-Baron [29]. The contact potential function has also been applied extensively to simulate ellipsoid packing structure [30, 31]. Additionally, to precisely judge inter-ellipsoid overlapping, Xu *et al* [32, 33] developed a novel

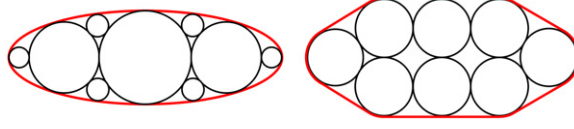


Figure 1. Two particles are defined by the spheres assembly method.

golden section searching algorithm. Recently, Jiao *et al* [9] and Xu *et al* [34] used the classical separation axis algorithm to check overlapping between regular convex particles. Garboczi and Bullard [35] made an additional outstanding contribution by detecting overlap between two star-shaped particles using an efficient numerical search process. Qian [36] has proposed a method to determine whether two particles overlap by solving contact equations. Nevertheless, these algorithms only apply to star-shaped particles. It is still unclear whether or not these algorithms can extend to arbitrary-shaped particles. It is worth noting that a spheres assembly method has been used to determine overlapping between two arbitrary-shaped particles [8, 37]. In the spheres assembly method, the profile of a particle is supposed to be composed of a series of mono-/multi-sized spheres, and the overlapping detection of two arbitrary-shaped particles is shifted to judge inter-sphere overlap (see figure 1). However, the accuracy of this method is restricted by the number of spheres imposed on the profile of an arbitrary-shaped particle. The main idea of this paper is to develop an algorithm to quickly and effectively detect overlapping of star-shaped particles.

As a more suitable approximation for real grains, the star-shaped particle will be described in this paper by the spherical harmonic series. Subsequently, an overlapping detection algorithm for arbitrary-shaped particles is introduced. Afterwards, based on the classical random sequential parking algorithm, star-shaped particle parking structures are presented. In addition, a serial sectional plane of such a parking system is visualized in order to verify the reliability of the developed overlapping criterion.

2. Description of a 3D star-shaped particle

The profile of a star-shaped particle has commonly been described by spherical harmonic analysis in the literature [13, 17–19, 38, 39]. In this section, we will briefly explain how the spherical harmonic analysis is used to describe the profile of a star-shaped particle.

2.1. Spherical harmonic analysis

A star-shaped particle surface can be composed of a set of controlling points, lines and triangles. The points are described as a series of spherical coordinates $(r(\theta, \varphi), \theta, \varphi)$ in a spherical coordinate system (see figure 2(a)), or Cartesian coordinates (x, y, z) , which can be retrieved from the spherical coordinates using equation (1)

$$\begin{cases} x = r(\theta, \varphi) \sin \theta \cos \varphi & r \in [0, \infty) \\ y = r(\theta, \varphi) \sin \theta \sin \varphi & \theta \in [0, \pi] \\ z = r(\theta, \varphi) \cos \theta & \varphi \in [0, 2\pi], \end{cases} \quad (1)$$

where $r(\theta, \varphi)$ is the radial distance from the particle centre to the point with spatial angle (θ, φ) on the surface of the particle, the polar angle θ is measured from the zenith direction and the azimuthal angle φ is measured from the azimuth reference direction to the orthogonal projection of the line segment on the reference plane xoy , as shown in figure 2(a).

A point $P_{jk}^{sp}(r_{jk}(\theta_j, \varphi_k), \theta_j, \varphi_k)$ on the particle surface in the spherical coordinate system is equivalent to a point $P_{j,k}(x_{j,k}, y_{j,k}, z_{j,k})$ in the Cartesian coordinate system, as shown in

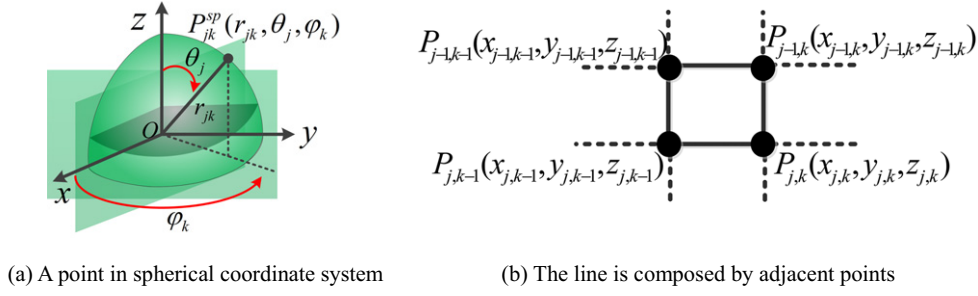


Figure 2. Point and line of the particle surface.

figure 2(a). The location of surface point P_{jk}^{sp} can be determined based on the polar angle θ_j , the azimuthal angle φ_k and the radial distance r_{jk} , which is a distance from the particle centre to the surface point P_{jk}^{sp} .

$$\begin{aligned}\theta_j &= \frac{j-1}{m-1}\pi \quad (j = 1, \dots, m) \\ \varphi_k &= \frac{2(k-1)}{n-1}\pi \quad (k = 1, \dots, n),\end{aligned}\quad (2)$$

where m and n are the number of points evenly spaced in $[0, \pi]$ and $[0, 2\pi]$, respectively. Note that θ_j and φ_k are angle periodic functions with periods m and n , i.e. $\theta_{j+m} = \theta_j$ and $\varphi_{k+n} = \varphi_k$.

By considering three additional points, $P_{j,k-1}$, $P_{j-1,k-1}$, $P_{j-1,k}$, in figure 2(b), it can be seen that a line is composed by connecting two adjacent points on the particle surface, i.e., the line $P_{j-1,k-1}P_{j-1,k}$ or $P_{j-1,k-1}P_{j,k-1}$, and the diagonal line is connected by default from $P_{j-1,k-1}$ to $P_{j,k}$. Three adjacent lines may construct a triangle (for instance, $\Delta P_{j-1,k-1}P_{j,k-1}P_{j,k}$, or $\Delta P_{j-1,k-1}P_{j-1,k}P_{j,k}$). The particle surface can be approximately reconstructed by seamless tessellation of all adjacent non-overlapped triangles. The accuracy of the reconstructed surface depends on the number of points imposed on the particle surface.

The radial distance r_{jk} is the key component in the spherical harmonic series and can be described as

$$r(\theta, \varphi) = \sum_{s=0}^{\infty} \sum_{h=-s}^s a_{sh} Y_s^h(\theta, \varphi), \quad (3)$$

where a_{sh} and $Y_s^h(\theta, \varphi)$ are the coefficient and the spherical harmonic series with degree s and order h ($-s \leq h \leq s$), respectively.

The coefficient a_{sh} in equation (3) is calculated from the surface points by choosing each angle according to the Gaussian quadrature procedure as shown in equation (4). The radial function $R(\theta, \varphi)$ in equation (4) is the distance from a particle centre of mass to the surface voxel with angular coordinate (θ, φ) , and the surface voxel is obtained from x-ray CT data of the particle. The details on how to obtain $R(\theta, \varphi)$ can be found in [40]. The coordinates of the points are the coordinates of the voxels of a particle surface relative to the centre of mass of the particle (see figure 3). In this article, a_{sh} is provided by Garboczi at the National Institute of Standards and Technology (NIST) [17]. Table 1 shows an example of a coefficient a_{sh} from the particle shape database.

$$a_{sh} = \int_0^{2\pi} \int_0^\pi \sin(\theta) R(\theta, \varphi) Y_s^{h*} d\theta d\varphi, \quad (4)$$

where the asterisk (*) denotes the complex conjugates.

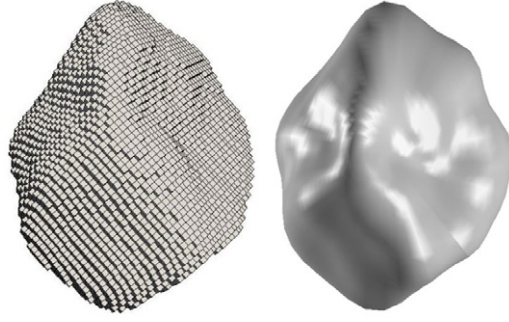


Figure 3. Comparing the digital image generated by the open-source software ParaView (51 486 voxels) of a particle with the particle obtained by spherical harmonic series.

Substituting a_{sh} and $Y_s^h(\theta, \varphi)$ into equation (3), we can reconstruct the particle surface as shown in figure 3. Table 1 shows an example of the spherical harmonics series $Y_s^h(\theta, \varphi)$ from $s = 0$ to $s = 3$.

2.2. Data structure of a single particle

Before developing the inter-particle overlap algorithm, a suitable data structure should be constructed to store the information for each particle. In this study, a mesh data structure is presented in equation (5) and in figure 4(a). In this mesh data structure, three matrices, i.e. $X_{m \times n}$, $Y_{m \times n}$, $Z_{m \times n}$ (m rows and n columns, the subscripts are in (row, column) order), will be defined and used to store separately the x -, y - and z -coordinates of all of the points $P_{j,k}(x_{j,k}, y_{j,k}, z_{j,k})$ on the particle surface:

$$\begin{aligned} X_{m \times n} &= \{x_{j,k}, j = 1, 2, \dots, m; k = 1, 2, \dots, n\} \\ Y_{m \times n} &= \{y_{j,k}, j = 1, 2, \dots, m; k = 1, 2, \dots, n\} \\ Z_{m \times n} &= \{z_{j,k}, j = 1, 2, \dots, m; k = 1, 2, \dots, n\}. \end{aligned} \quad (5)$$

To guarantee that a particle surface is seamlessly covered by the triangles without any overlaps or gaps, the three matrices described in equation (5) should satisfy the following requirements.

- (1) All elements in the first and last rows of the three matrices should have the following features: $x_{1,1} = x_{1,k}$, $y_{1,1} = y_{1,k}$, $z_{1,1} = z_{1,k}$ and $x_{m,1} = x_{m,k}$, $y_{m,1} = y_{m,k}$, $z_{m,1} = z_{m,k}$ ($k = 1, 2, \dots, n$), which are two points $P_{1,1}(x_{1,1}, y_{1,1}, z_{1,1})$ and $P_{m,1}(x_{m,1}, y_{m,1}, z_{m,1})$ on the particle surface, as shown in figure 4(b).
- (2) The first columns of the three matrices are equal to those in the last columns, i.e., $x_{k,1} = x_{k,n}$, $y_{k,1} = y_{k,n}$, $z_{k,1} = z_{k,n}$ ($k = 1, 2, \dots, m$). All of the elements in these columns are shown as a red curve on the particle in figure 4(b).

In order to determine whether or not inter-particle overlap exists, the particle surface will be tessellated up with small triangle meshes in figure 2(b); this process is called particle surface triangulation. Figure 4(b) shows a tetrahedron that is composed of one triangle with the particle centroid.

After the particle surface is tessellated into many triangles with seamless connection, the data structure of the triangle is presented and the three point coordinates $A_j(a_{xj}, a_{yj}, a_{zj})$, $B_j(b_{xj}, b_{yj}, b_{zj})$, $C_j(c_{xj}, c_{yj}, c_{zj})$ of each triangle $\Delta A_j B_j C_j$ ($j = 1, 2, \dots, NT$) are stored in the 3×3 matrix, as shown in figure 5. Herein, $NT = 2(m-2)(n-1)$ is the total number of triangles tessellating the whole surface of a particle,

Table 1. List of spherical harmonic series from $s = 0$ to $s = 3$; a_{sh} is the coefficient of a particle.

List_ID	s	h	a_{sh}	$Y_s^h(\theta, \varphi)$
1	0	0	20.523 994 + 0i	$\frac{1}{2}\sqrt{\frac{1}{\pi}}$
2	1	1	0.079 608−0.041999i	$\frac{-1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\varphi}$
3	1	0	0.189 590 + 0i	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
4	1	−1	−0.079 608−0.041999i	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\varphi}$
5	2	2	−0.368 958−0.000794i	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{2i\varphi}$
6	2	1	0.030 733 + 0.345538i	$\frac{-1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{i\varphi}$
7	2	0	−2.499 989 + 0i	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
8	2	−1	−0.030 733 + 0.345538i	$\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{-i\varphi}$
9	2	−2	0.368 958 + 0.000794i	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{-2i\varphi}$
10	3	3	−0.950 525−0.344 838i	$\frac{-1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta e^{3i\varphi}$
11	3	2	0.727 578−0.004 410i	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta e^{2i\varphi}$
12	3	1	0.199 042 + 0.320 090i	$\frac{-1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{i\varphi}$
13	3	0	1.085 789 + 0i	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
14	3	−1	−0.199 042 + 0.320 090i	$\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{-i\varphi}$
15	3	−2	0.727 578 + 0.004 419i	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta e^{-2i\varphi}$
16	3	−3	0.950 525−0.344 838i	$\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta e^{-3i\varphi}$

and the value of $m \times n$ is defined as the ‘grid density’, with a higher grid density meaning a greater value of m and n .

The numerical surface area of the particles can be calculated by summing the area of all of the triangles via Heron’s formula. Furthermore, there are totally NT tetrahedrons that are composed of each triangle and the particle centroid, see figure 4(b). The numerical volume of the particle is summed up by the entire volume of the tetrahedrons as shown in equation (6).

$$V_{\text{Tetrahedron}(j)} = \frac{|\overrightarrow{OA_j} \cdot (\overrightarrow{OB_j} \times \overrightarrow{OC_j})|}{6}. \quad (6)$$

The accuracy of the particle shape obviously depends on how many points (or triangles) are set on the particle surface, i.e. the value of the parameters m and n in equation (2) should be considered. For example, the exact value of the surface area and volume of a sphere with radius $r = 1$ is 4π and $4\pi/3$, respectively. The numerical results for the surface area and volume

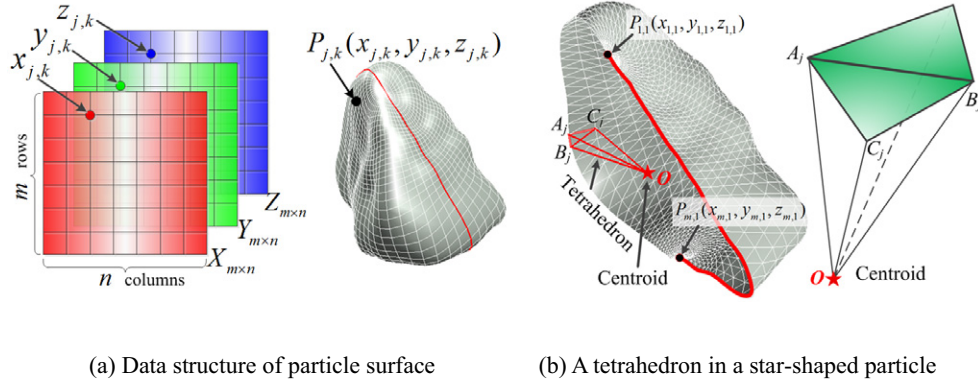


Figure 4. Data structure of a particle surface and the particle surface triangulation.

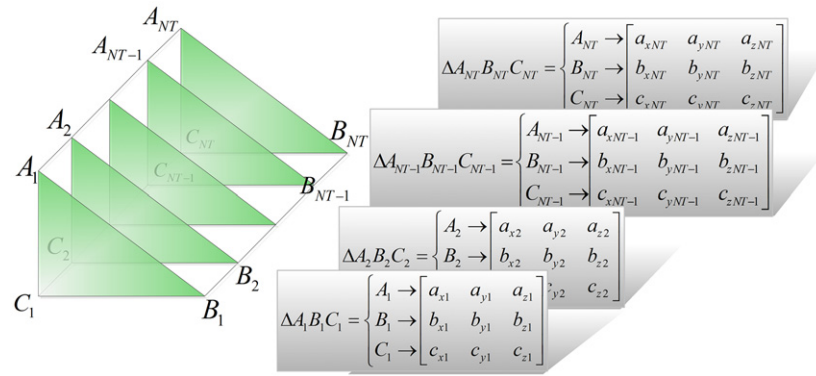


Figure 5. Data structure of triangles.

of the sphere with different values of m and n can be calculated using the above methods and are given in table 2. Apparently, the numerical accuracy will increase with the increasing grid density, i.e. the value of m and n . When the values of m and n reach 50, both of the relative errors are less than 0.5%.

Table 2 shows that the deviation from the exact value at $m = n = 500$ is very small, and therefore the numerical value at $m = n = 500$ will be assumed in this article to be the 'exact' value for a particle from the particle shape database. This particle is represented by its spherical harmonic series with degree $s = 12$. Table 3 shows the difference between the numerical values of the particle (as shown in figure 3) at different grid densities and the value at $m = n = 500$. It can be seen that the relative error for both the surface area and volume are less than 0.5% when $m = n = 60$. So, $m = n = 50$ or 60 is advisable for a particle.

3. Inter-particle overlapping detection algorithm

Two-particle overlap detection is the key algorithm in the parking procedures. Garboczi and Bullard [35] proposed comparing d with the distance d_1 from the centre of particle 2 to the particle 2 surface point in the direction given by spherical polar angles. Here, d is the distance from a point on the surface of particle 1 (inside the extent overlap box) to the centre of particle 2.

Table 2. The relative error of the numerical surface area and volume of a sphere with unit radius are computed at different grid densities.

$m (= n)$	The numerical surface area	The relative error of the surface area (%)	The numerical volume	The relative error of volume (%)
10	12.0096	4.430 64	3.8227	8.739 76
20	12.4250	1.124 99	4.0949	2.241 46
30	12.5034	0.501 10	4.1468	1.002 44
40	12.5309	0.282 27	4.1652	0.563 18
50	12.5437	0.180 41	4.1737	0.360 25
60	12.5506	0.125 50	4.1783	0.250 44
100	12.5607	0.045 13	4.1850	0.090 48
200	12.5649	0.011 70	4.1878	0.023 64
300	12.5657	0.005 34	4.1884	0.009 32
500	12.5661	0.002 15	4.1886	0.004 54

Table 3. The difference between the numerical value of a particle from the value $m = 500$ with degree $s = 12$ at different grid densities.

$m (= n)$	The numerical surface area	The relative error of the surface area (%)	The numerical volume	The relative error of volume (%)
10	12.5143	12.155 36	3.4879	16.732 48
20	13.7962	3.156 97	4.0156	4.135 66
30	14.0470	1.396 75	4.1110	1.857 48
40	14.1342	0.784 05	4.1451	1.041 89
50	14.1749	0.49847	4.1611	0.662 19
60	14.1971	0.342 70	4.1696	0.457 16
100	14.2289	0.119 42	4.1821	0.159 47
200	14.2422	0.025 96	4.1874	0.033 41
300	14.2445	0.010 38	4.1883	0.010 63
500	14.2459	0	4.1888	0

If $d < d_1$, then the point on the surface of particle 1 is also contained inside particle 2, so overlap exists. If $d > d_1$, then overlap does not exist at this point, so we go on to the next point of particle 1 that is in the angular range. If all the points on particle 1 do not fall inside particle 2, then the particles do not overlap. Qian [36] assumes that there is a contact point $C(x_c, y_c, z_c)$ at their local coordinates $(\theta_{c1}, \varphi_{c1})$ and $(\theta_{c2}, \varphi_{c2})$ by solving contact equations to determine whether two star-shaped particles overlap. However, the equations have four unknowns $\theta_{c1}, \varphi_{c1}, \theta_{c2}, \varphi_{c2}$, but only three equations, which makes them unsolvable. They fix one of the four unknowns at preselected values in the range $[0, 2\pi)$ and then try to solve the three equations with the three unknowns. If a solution is found, then the contact point exists and the two particles overlap, otherwise there is no overlap between the two particles.

These spherical harmonic particle contact algorithms only apply to star-shaped particles, rather than arbitrary-shaped particle. In this paper, the purpose of using the surface triangulation approach is to expand the capacity of the previous contact detection methods to the arbitrary-shaped particle systems by decomposing the surface of a particle into a set of non-overlapping seamless triangles. Then, a tetrahedron can be formed by linking each triangle with the particle centroid (as shown in figure 4(b)). We can then further use the separation axis theorem to quickly detect inter-particle overlap.

3.1. Separation axis theorem

The separation axis theorem is often used to check for collisions between two convex hulls. Geometrically, two convex hulls (an object is convex if for every pair of points within the object, every point on the line segment connecting them is also within the object) do not overlap in a 3D space if and only if there exists an axis onto which the projected line segments of these two convex hulls do not overlap. If we find an axis along which the particles do not overlap, then we do not have to continue testing the rest of the axes. Otherwise, if the particles overlap along all of the possible separating axes, then they definitely overlap with each other. This method is named the *separation axis theorem* [10, 23, 34]. For two convex polyhedrons in 3D space, the set of vectors normal to the faces of the two polyhedrons and the set of vectors generated by cross-products between the two edges which form each polyhedron have to be checked for a separation axis [41]. The separation axis theorem can be used to determine whether or not two stationary convex polyhedrons overlap. For example, figure 6 shows their projected line segments (MN , PQ , respectively) between a pair of tetrahedrons. It can be seen from figure 6(a) that there is a separation axis on which the two projected line segments (MN , PQ) do not intersect when the normal vector of the tetrahedral face is taken as the separation axis. Therefore, we can conclude that these two tetrahedrons do not overlap. However, it is not clear whether the two tetrahedrons overlap, even though figure 6(b) shows that all of the projected segments are overlapped along the vectors normal to the faces of the two tetrahedrons. The set of vectors generated by cross-products between the two edges from each tetrahedron should be checked for a separation axis, as shown in figures 6(c) and (d). Figure 6(d) shows that two tetrahedrons definitely overlap because no single separation axis is available for their projected line segments of the two tetrahedrons.

For a 3D particle, the projected segment of the particle is the particle projecting its shape onto an arbitrary vector, as shown in figure 7. The projected segment is parallel to the vector $\mathbf{n}$. For example, we select an arbitrary point $P_{j,k}$ on the star-shaped particle surface that lies on the projected segment of the particle MN , where M and N are the minimum and maximum values of all of the projected points along the direction of the vector $\mathbf{n}$, respectively. The length of the line segment $MP'_{j,k}$ is $|\overrightarrow{MP_{j,k}}| = |\overrightarrow{MP_{j,k}}| \cos \theta$.

3.2. Overlap detecting of two star-shaped particles

In our implementation, a star-shaped particle is characterized by all of the vertices relative to its centroid, representing the position of the particle. Although the star-shaped particle is never a convex polyhedron, many independent triangles are obtained after the surface of the star-shaped particle is triangulated in 3D space, and a tetrahedron can be formed by linking each triangle with the particle centroid (see figure 4(b)). Suppose that P_1 (m_1 rows and n_1 columns) and P_2 (m_2 rows and n_2 columns) are a set of vertices of two star-shaped particles with centroids O_1 and O_2 , respectively, i.e.

$$P_1 = \{(X, Y, Z)_{m_1 \times n_1}\}, P_2 = \{(X, Y, Z)_{m_2 \times n_2}\}. \quad (7)$$

Then the sets of corresponding triangles of particles surface (see figure 5) are

$$\begin{aligned} P_{\Delta 1} &= \{\Delta_1 A_j B_j C_j, j = 1, 2, \dots, 2(m_1 - 2)(n_1 - 1)\} \\ P_{\Delta 2} &= \{\Delta_2 A_j B_j C_j, j = 1, 2, \dots, 2(m_2 - 2)(n_2 - 1)\} \end{aligned} \quad (8)$$

The sets of corresponding tetrahedrons are

$$\begin{aligned} P_{T1} &= \{O_1 - \Delta_1 A_j B_j C_j, j = 1, 2, \dots, 2(m_1 - 2)(n_1 - 1)\} \\ P_{T2} &= \{O_2 - \Delta_2 A_j B_j C_j, j = 1, 2, \dots, 2(m_2 - 2)(n_2 - 1)\}. \end{aligned} \quad (9)$$

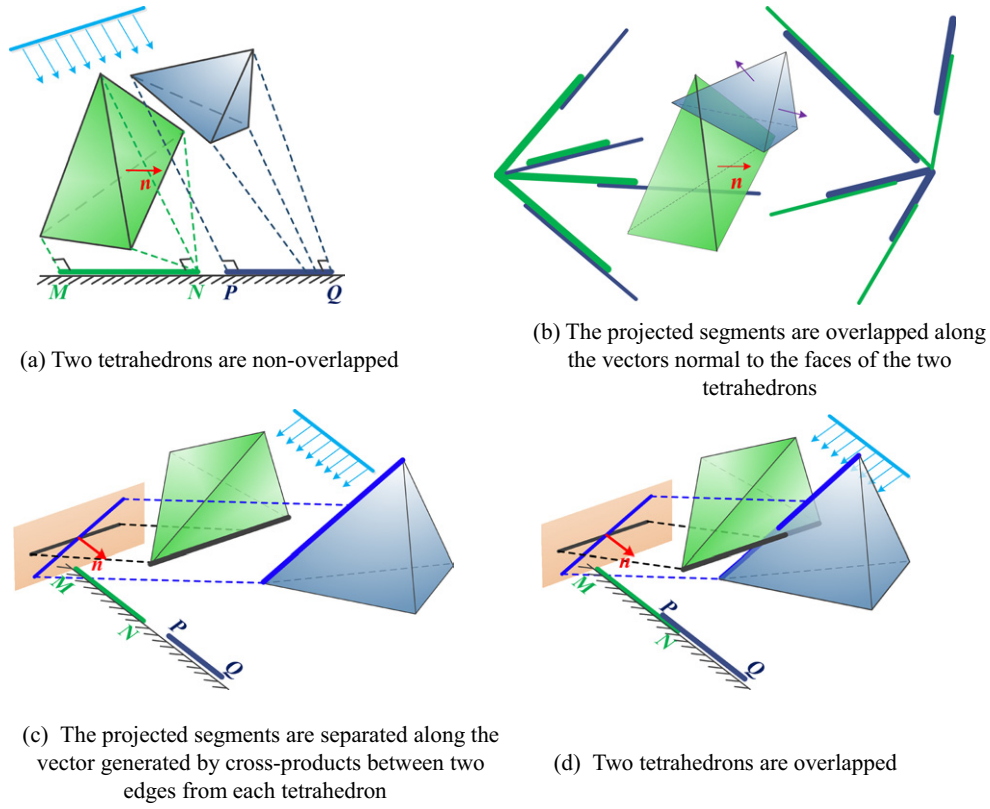


Figure 6. Positional relationships of two tetrahedrons are determined using the separation axis method.

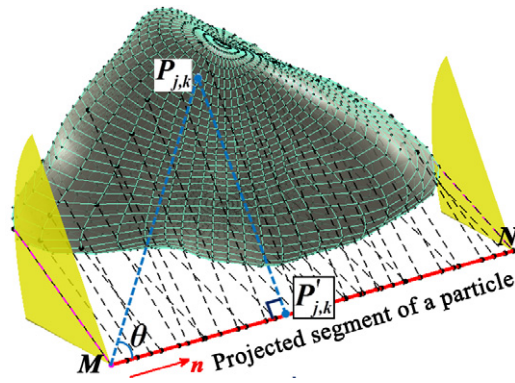


Figure 7. Projected segment of a star-shaped particle.

Consequently, the overlapping problem between particle P_1 and particle P_2 can be transformed into checking the overlap between two sets of tetrahedrons, P_{T1} and P_{T2} . As is known, the greater the number of tetrahedrons in each set, the more time-consuming it is to perform simulations.

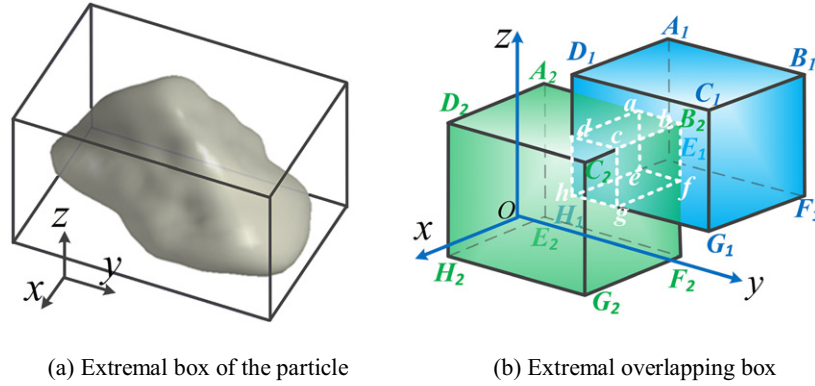


Figure 8. Extremal box and extremal overlapping box.

For the purpose of reducing how much time is consumed, an extremal box (EB) [35] is introduced in figure 8(a) to surround each particle for a preliminary check of inter-particle overlap. The extremal box is defined as a rectangular parallelepiped (or cuboid), of which three orthogonal edges are the projected segments of the particle (as shown in figure 7) onto the x , y and z axes, respectively. The potential overlapping portion of two extremal boxes in the global coordinate system is called the extremal overlapping box (EOB) [35]. Notably, EOB is essentially an EB. If an EOB exists, then an EOB is contained in the EB. If an EOB does not exist, then we may demonstrate that these two particles do not overlap.

Two EBs ($A_1B_1C_1D_1E_1F_1G_1H_1$ and $A_2B_2C_2D_2E_2F_2G_2H_2$, see figure 8(b)) and an EOB ($abcdefgh$) can be composed of a point e and three lengths eh , ef , ea of the EOB, which can be derived using the following strategies.

Point e of the EOB is determined by $e = (\max(E_{1x}, E_{2x}), \max(E_{1y}, E_{2y}), \max(E_{1z}, E_{2z}))$, and the three lengths of the EOB can be accessed by paralleling the x -axis with $eh = \min(H_{1x}, H_{2x}) - \max(E_{1x}, E_{2x})$, the y -axis with $ef = \min(F_{1y}, F_{2y}) - \max(E_{1y}, E_{2y})$ and the z -axis with $ea = \min(A_{1z}, A_{2z}) - \max(E_{1z}, E_{2z})$, respectively.

Actually, the overlapping portions of the two particles occur only in a partial region of the particles; it is not necessary to assess all the surface points on the particles. For two star-shaped particles, the overlapping portion inevitably occurs in a 3D region (EOB) located between planes 1 and 2; the two planes are perpendicular to the line passing through the centroids of the two particles, see figure 9. Therefore, locating these key points on the particle surface can greatly reduce the computational complexity. In this section, a selection procedure will be presented that can efficiently discard most of the triangle (or tetrahedron) elements but which will not interfere with the target element, so that only a fraction of the total number of elements have to be evaluated for their relationship with the target element. Now we will present how to efficiently detect overlap between two star-shaped particles.

Consequently, the operating details of the overlapping algorithm for the star-shaped particles can be developed using the following procedure [35].

- (1) If an EOB does not exist, as shown in figure 10(a), then the two particles do not overlap.
- (2) If an EOB exists, then the following cases should be considered.
 - (2a) One of the particles is not inside the EOB, as shown in figure 10(b), and therefore the two particles are non-overlapping.
 - (2b) When two particles are in the EOB, then we should consider the two projected line segments that the portions of the two particles inside the EOB project onto the line

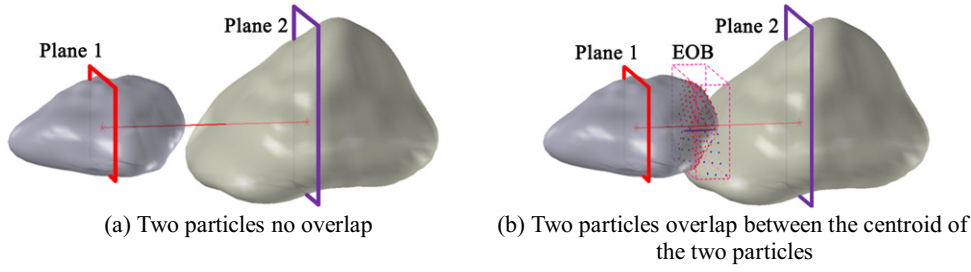


Figure 9. Test overlapping of two particles between their centroids.

connected with two centroids. If these two projected line segments do not overlap, then the two particles must not overlap; see figure 10(c). Otherwise, the two projected line segments will intersect (we labelled this as a projected intersected line segment). We can map these points to their own particle surface while projecting them onto this projected intersected line segment, as shown in figure 10(d). In this figure, the tetrahedrons can be tracked by these points between the two particles and need to be evaluated further by the tetrahedron overlap criterion introduced above.

- (3) If overlap exists between any two tetrahedrons coming, respectively, from the two star-shaped particles, then the two star-shaped particles definitely overlap, as shown in figure 10(e). Otherwise, the two particles are separated; see figure 10(d).

Obviously, the computational time is associated with the grid density. For two particles with grid density $m \times n$, the number of tetrahedrons for a particle is $NT = 2(m-2)(n-1)$. In the algorithm, the overlap region occurs in the EOB. Meanwhile, we only need to consider those tetrahedrons which project onto the projected intersected line segment. In other words, it is not necessary to compare $(NT)^2$ times tetrahedron overlap criterion before one can conclude that there is no overlap between the particles [35]. Thus, the algorithm will greatly reduce computation time.

3.3. Verification

Now the various regularly shaped particles (here a sphere, ellipsoid and octahedron are used as examples) will be used to verify the reliability of the above inter-particle overlapping algorithms. Figure 11(a) shows three spheres where the radius is 1 and the surface of the spheres has been tessellated (undoubtedly, the detecting accuracy is determined by the grid density). Three spheres can be described by the equations S1: $x^2 + y^2 + z^2 = 1$, S2: $(x-2)^2 + y^2 + z^2 = 1$ and S3: $(x-3.5)^2 + y^2 + z^2 = 1$. Obviously, the centres of spheres S1, S2 and S3 are (0, 0, 0), (2, 0, 0) and (3.5, 0, 0), respectively. Meanwhile, we take three ellipsoids as an example, as shown in figure 11(b). The standard equations of three ellipsoids are E1: $x^2/4 + y^2 + z^2 = 1$, E2: $(x-3)^2 + y^2 + z^2/4 = 1$ and E3: $(x-5)^2/4 + y^2 + z^2 = 1$.

According to the overlapping detection algorithm, spheres S1 and S2 (externally tangent), and S1 and S3 (separation) are non-overlapping because there are no EOBs between them, however, sphere S2 overlaps with S3 due to the overlap that exists in the EOB between the two tetrahedrons belonging to spheres S2 and S3, respectively. These conclusions are consistent with the geometric theory. Similar to the spheres, ellipsoids E1 and E2 (externally tangent), and E1 and E3 (separation) are non-overlapping, while ellipsoid E2 is overlapping with E3.

For a pair of octahedrons O1 and O2, figure 12 shows eight possible overlapping detection configurations: (a) vertex–vertex contact, (b) vertex–edge contact, (c) vertex–face contact,

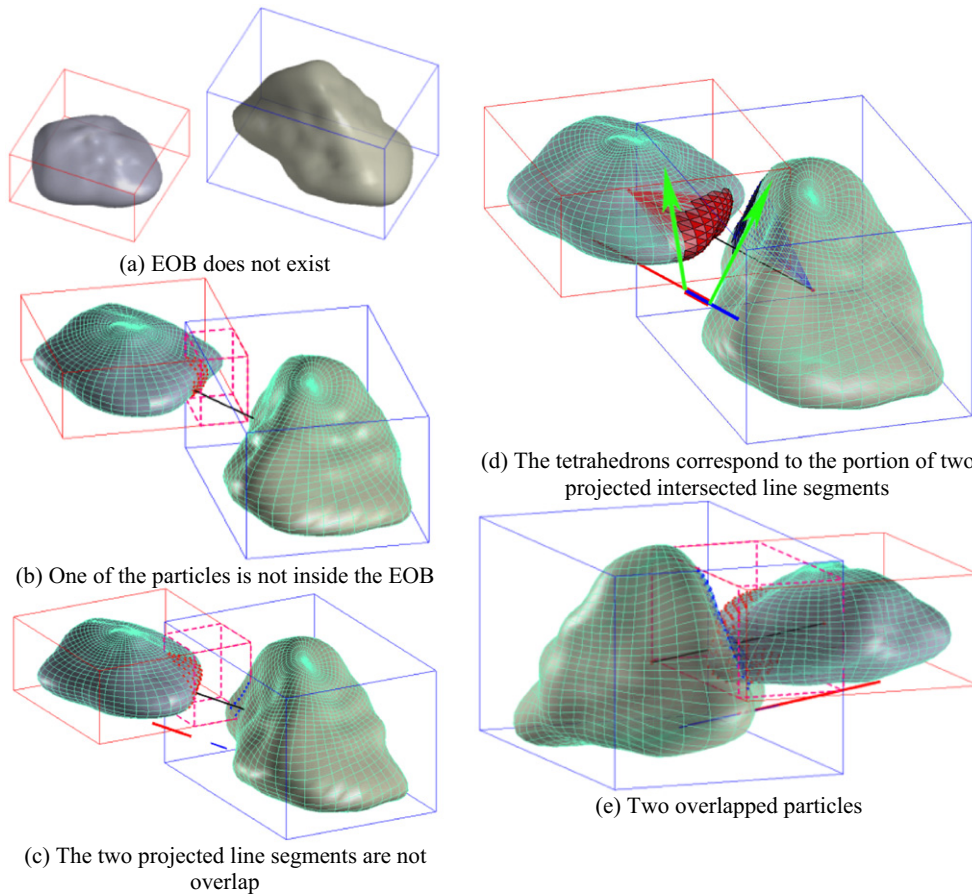


Figure 10. Overlap detecting for two star-shaped particles.

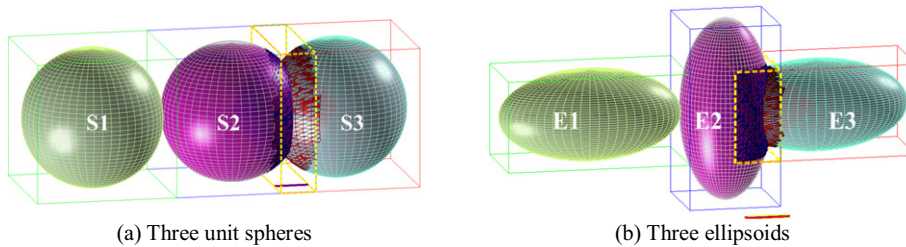


Figure 11. Schematic view of the overlapping detection between three spheres.

(d) edge–edge contact, (e) edge–face contact, (f) face–face contact, (g) overlap and (h) separation. Since there are no EOBs for octahedrons O1 and O2 in cases (a), (b), (d) and (h), non-overlaps are the conclusions of the overlapping detection algorithm. In particular, octahedron O1 is touching O2 in cases (a), (b) and (d); these cases will occur with a probability of measure zero and so do not need to be considered. For cases (c) and (e), O1 is touching O2, even though an EOB exists, however, the two projected line segments obtained by the separation axis theorem are non-intersecting. When the two projected line segments are intersecting in

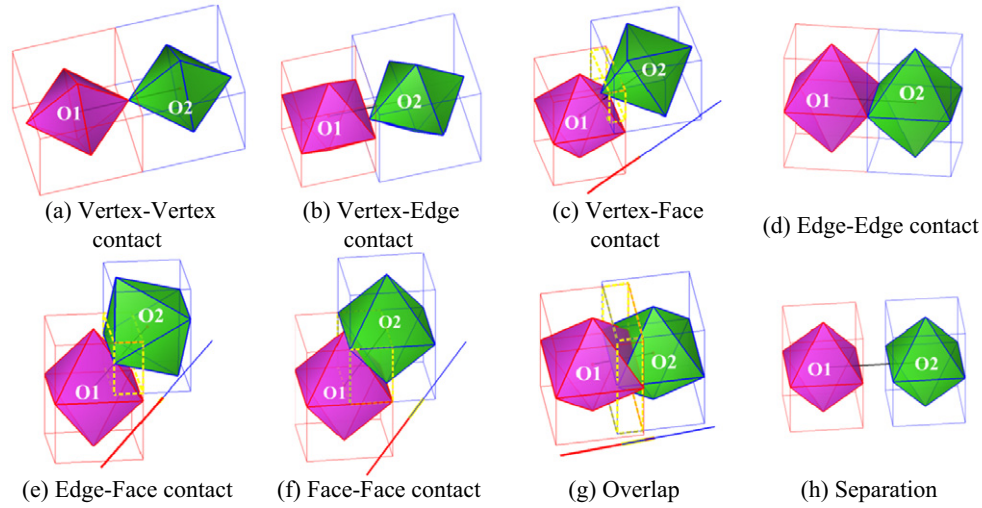


Figure 12. Schematic view of the overlapping detection of two octahedrons.

case (f), then O1 is non-overlapping with O2, because if any two tetrahedrons belong to the octahedrons, then O1 and O2 are not overlapped. However, when O1 is overlapping with O2, it means that two tetrahedrons are overlapped, as shown in figure 12(g).

It can be seen from figures 11 and 12 that the overlapping detection algorithm is accurate and effective.

3.4. Random parking of particles

A large collection of non-overlapping solid objects (particles) in d -dimensional Euclidean space R^d is called packing [10, 42]. Packing problems are a class of optimization problems in mathematics that involve attempting to pack particles together (often inside a container) as densely as possible. The packing makes sure that there are no overlaps between any two hard particles or any particles and the container wall. In this paper, parking is different from packing. Particle packing is at least locally jammed, that is, each particle cannot be translated or rotated while fixing the positions and orientations of all the other particles [10]. Particle parking [36, 43] presents a container that would be occupied by particles, with particle size distribution and inter-particle non-overlap that are placed or created randomly in the space until no more can be placed under certain conditions. The essential difference is that particles that are parking are suspended in the container with no overlap. However, particle packing has contact between particles and particles or the container but no overlap. The main aim of this study is to detect inter-particle overlap.

After the inter-particle overlapping detection algorithm is finished, we can park a number of particles in a container with a given particle shape and size. Here, a given random sequential parking algorithm from [34, 44, 45] is applied. The particle shapes are from the shape database and the particle size can be controlled by multiplying each coefficient by a scale factor $s = W_a/W_b$, where W_a is the particle width after scaling and W_b is the width before scaling [17, 36]. All the particles are randomly placed by uniformly distributing their positions and directions in the container. If a newly generated particle does not overlap with the others, then the particle is valid. Otherwise, the position and direction of the particle are rearranged. After a predefined number of trials, if the particle has not found a place to stay

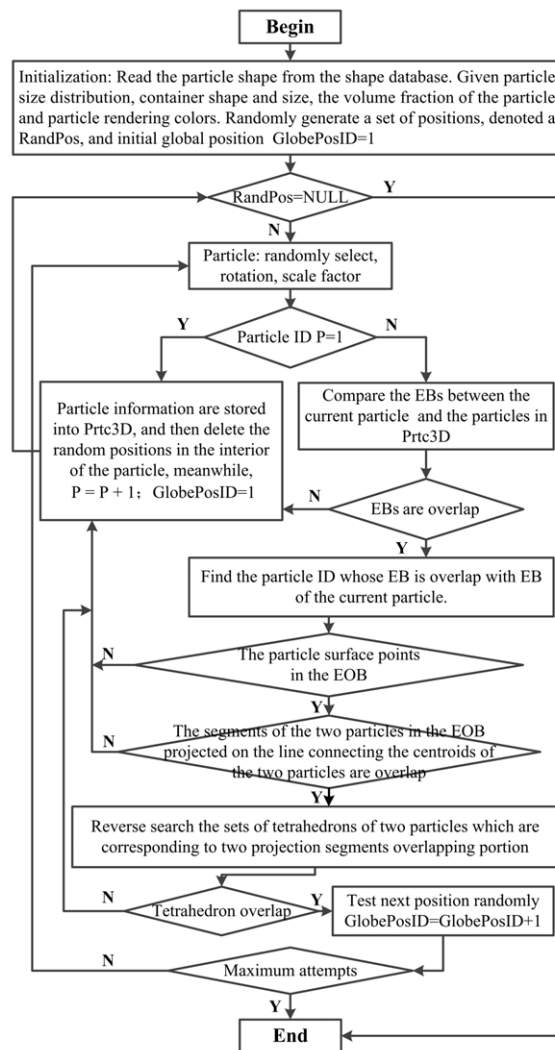


Figure 13. Flowchart of parking procedures.

yet, then this particle is discarded and another particle will be selected and tried by following the same procedure. The flow chart of the particles random parking algorithm [36] is shown in figure 13.

Parking structure is generated by the above random sequential parking algorithm in a cube (container) with its width equal to eight times of the unit size of particles, as shown in figure 14. In this case, the volume fraction of the solid is 0.5006.

4. Sectional plane analysis

4.1. Methodology

When the particle parking structure is generated, we need to check whether or not the neighbour particles overlap. In this section, because the inter-particle overlap in 3D space may be reflected

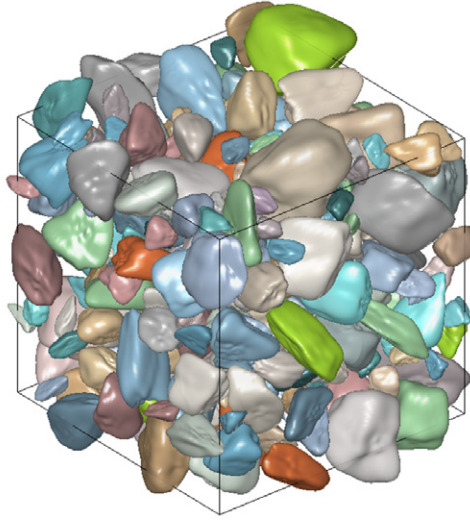


Figure 14. 3D illustration of parking structure.

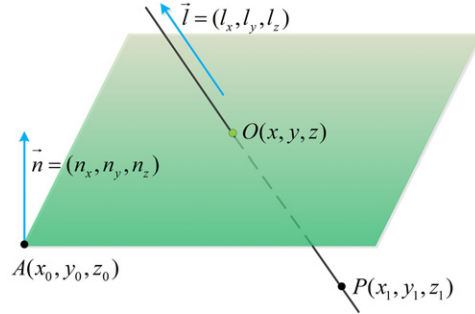


Figure 15. Intersection point of a line and a plane.

in the sectional plane, a sectional plane analysis (or sectioning analysis) method is employed to verify the reliability of the inter-particle overlapping algorithm developed above. In addition, the interior details of the parking system can be visualized through any cross section. Also, we may further calculate the area and perimeter of the intersecting area of each particle with the given sectional plane. In order to develop a sectional plane algorithm for such star-shaped particle parking systems, a case of the intersection between a plane and a line in a 3D space (see figure 15) is first introduced.

For the intersection of a line with a plane, there are three potential possibilities, i.e. an empty set, a point, or a line. For instance, in the 3D space, a plane with a nonzero normal vector $\vec{n} = (n_x, n_y, n_z)$ through the point $A(x_0, y_0, z_0)$ is

$$n_x(x - x_0) + n_y(y - y_0) + n_z(z - z_0) = 0. \quad (10)$$

The parametric equation for a line passing through a given point $P(x_1, y_1, z_1)$ and parallel to the nonzero vector $\vec{l} = (l_x, l_y, l_z)$ can be expressed as

$$\begin{cases} x = x_1 + l_x u \\ y = y_1 + l_y u \\ z = z_1 + l_z u. \end{cases} \quad (11)$$

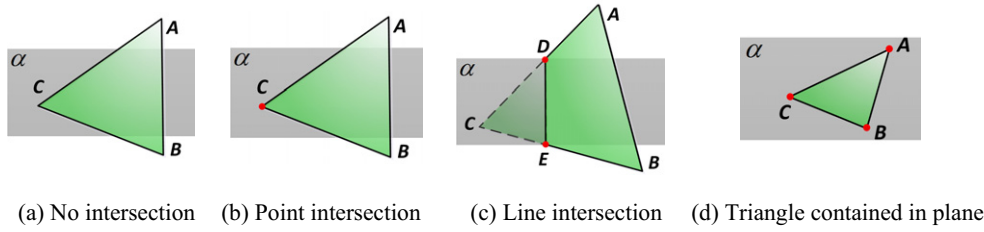


Figure 16. Four possible cases of triangle-plane intersections.

Combining equation (10) with equation (11), we can get

$$u = \frac{n_x(x_0 - x_1) + n_y(y_0 - y_1) + n_z(z_0 - z_1)}{n_x l_x + n_y l_y + n_z l_z}. \quad (12)$$

If the denominator in equation (12) is zero, then the line will be parallel to the plane.

Substituting the value u in equation (12) into equation (11) yields the intersecting point $O(x, y, z)$ of the line with the plane.

Similarly, the above approach may also be used to determine the intersection of a line segment with a plane. First of all, the intersecting point of the plane with the line where the line segment is located can be obtained, then determine whether the intersecting point is within this line segment. If the intersecting point belongs to the segment, the line segment passes through the plane. Otherwise, the line segment and the plane do not intersect.

Furthermore, for three line segments composed of a triangle, figure 16 shows the intersecting relationship of a triangle with a given plane. Apparently, the number of intersecting point may be 0, 1, 2, 3, which corresponds to figures 16(a)–(d), respectively. There are no line segments in figures 16(a) and (b), and figure 16(c) shows only one line segment composed by two intersecting points D and E . When the triangle is contained in the plane as shown in figure 16(d), there will be three line segments formed by the three edges of the triangle. Thus, when a sectional plane passes through a star-shaped particle, a series of intersecting points or line segments can be generated from the sectional plane with the triangles composed of the particle surface, as shown in figure 17. The sectional morphology of the sectional plane with the particle surface triangulation can be determined as follows.

- (1) We tessellated a particle surface into many triangles; the data structure is shown in figure 17.
- (2) We calculated intersecting points between all of the triangles in step (1) with a given plane defined by equation (10).
- (3) We ensured that the intersecting points were unique without repetitions and were labelled according to the order of natural number. Then, these indexes were mapped to line segments, as shown in figure 18.
- (4) We connected these line segments in turns to create a closed region, which is defined as the sectional morphology.

Figure 18 shows that one endpoint may appear twice. In terms of graph theory terminology [46, 47], this is similar to a degree of vertex, which is defined as the number of edges associated with a vertex. Therefore, the degrees of the endpoints may be 0, 1, 2, 3, 4, etc; see figure 19(a). We have to search for every endpoint and connect them in turn. In order to improve the searching efficiency for endpoints, a bidirectional searching strategy is proposed. In this method, an entry point is randomly selected at first, and then two paths are formed from this point to both sides,

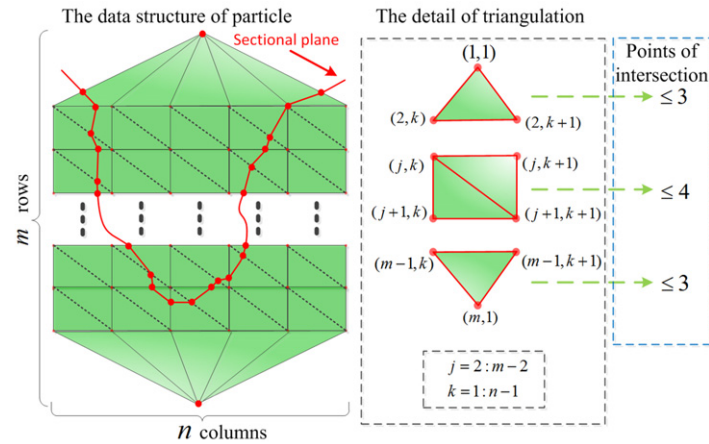


Figure 17. The data structure of sectional plane.

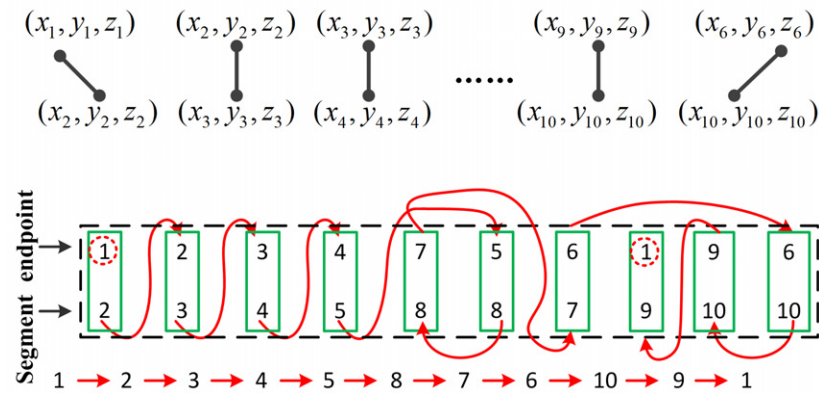


Figure 18. Connecting line segments in order.

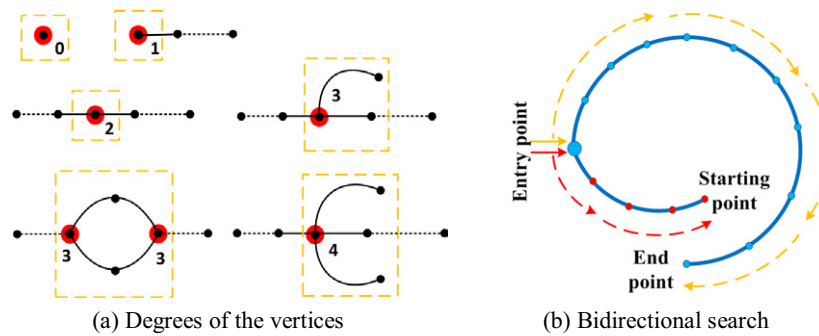


Figure 19. The degrees of the vertices and bidirectional searching are defined.

as shown in figure 19(b). Finally, a closed path can be formed by joining these two paths together.

The sectional morphology will be very complicated when a sectional plane cross through an undulating particle surface, as shown in figure 20. This situation contains many closed

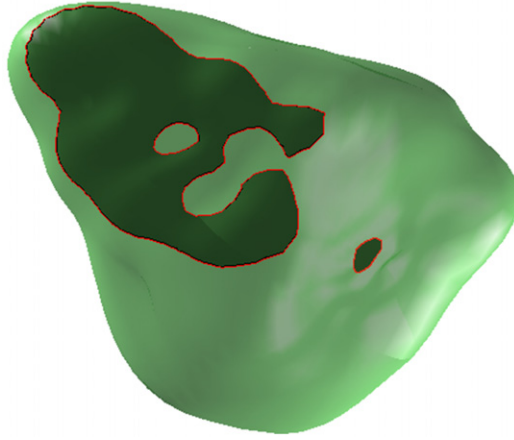
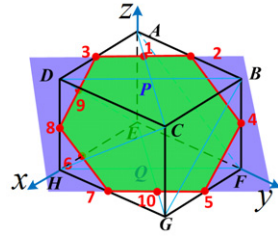
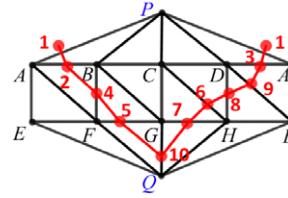


Figure 20. A complicated morphology.



(a) A sectional plane cross a cube



(b) The points and line segments on the particle surface

Figure 21. Sectional plane across a cube and the line segments in the cube surface.

regions. We should pay attention to embedded regions when seeking the area of the sectional morphology.

4.2. Benchmark test

In order to verify the validity of the above sectional plane analysis, we consider a cube with eight vertices A, B, C, D, E, F, G, H and we suppose that the local origin is vertex E , with edges parallel to the axes and with an edge length of 1. This unit cube and a sectional plane equation $(x - 0.5) + (y - 0) + (z - 1) = 0$ with a normal vector $(1, 1, 1)$ through a point $(0.5, 0, 1)$ can be taken as an example (shown in figure 21(a)). In terms of the data structure of a particle described in section 2.2, the expression in the form of particle surface meshes is

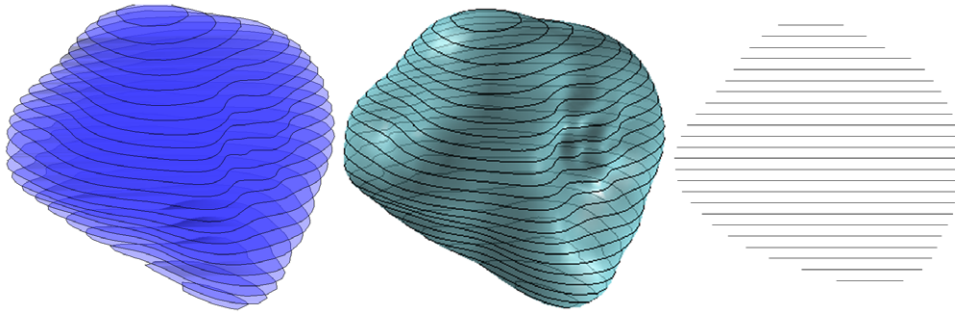
$$\begin{bmatrix} P & P & P & P & P \\ A & B & C & D & A \\ E & F & G & H & E \\ Q & Q & Q & Q & Q \end{bmatrix}, \quad (13)$$

where P and Q are the midpoints of the line segments AC and EG , respectively.

This sectional plane crosses the cube through each of the triangles on the cube surface, a lot of intersecting coordinates and line segments can be obtained as shown in figure 21(b) and table 4.

Table 4. The intersection coordinates and line segment of the sectional plane with the cube surface.

No	Intersection coordinates		Triangle	Line segment
	Numerical result	Theoretical result		
1	(0.25, 0.25, 1)	(1/4, 1/4, 0)	$\triangle ABP$	1—2
2	(0, 0.5, 1)	(0, 1/2, 1)	$\triangle ABF$	2—4
3	(0.5, 0, 1)	(1/2, 0, 1)	$\triangle BFG$	4—5
4	(0, 1, 0.5)	(0, 1, 1/2)	$\triangle FGQ$	5—10
5	(0.5, 1, 0)	(1/2, 1, 0)	$\triangle GHQ$	10—7
6	(1, 0.25, 0.25)	(1, 1/4, 1/4)	$\triangle CGH$	7—6
7	(1, 0.5, 0)	(1, 1/2, 0)	$\triangle CDH$	6—8
8	(1, 0, 0.5)	(1, 0, 1/2)	$\triangle DEH$	8—9
9	(0.75, 0, 0.75)	(3/4, 0, 3/4)	$\triangle ADE$	9—3
10	(0.75, 0.75, 0)	(3/4, 3/4, 0)	$\triangle ADP$	3—1

**Figure 22.** Serial sectional planes of a single particle are shown from different viewpoints.

It can be seen from table 4 that the numerical results of the sectional plane analysis are consistent with the theoretical values. Meanwhile, the sectional plane can be obtained after connecting the endpoints of the line segments in turn: 1—2—4—5—10—7—6—8—9—3—1. This example demonstrates the validity of the sectional plane algorithm developed in section 4.1.

4.3. Sectional plane analysis in a star-shaped particles parking system

For a single particle, the results of equidistant parallel sectional planes are visualized in figure 22.

The sectional plane analysis of the parking system given in figure 14 is visualized in figure 23. The overlap between any particles in different directions can be observed in the series of sectional planes.

5. Microstructural analysis

In order to verify the reliability of the sectional plane algorithm in 2D space, the entire area and perimeter of star-shaped particles on an arbitrary sectional plane are derived and compared with

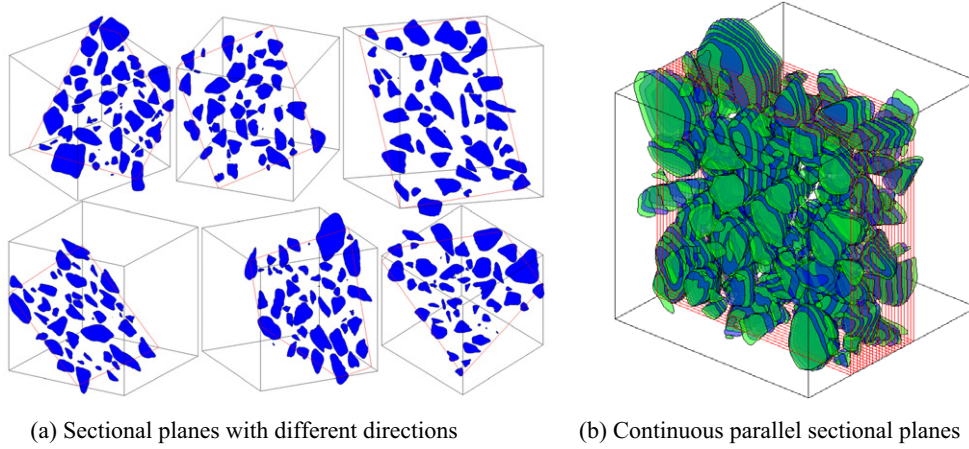


Figure 23. Sectional plane on the particle parking system.

those from the commercial image analysis software. However, the whole area and perimeter of sectional polygons (it is that supposed all sectional polygons are simple polygons) need to be first solved by an ear clipping algorithm [48], for which the details are introduced as follows.

We can see that the perimeter is easily determined from the above line segment. In addition, the area of a sectional polygon can be calculated by decomposing the simple polygon into a set of non-overlapping seamless triangles [49] and by summing up the area of these triangles in terms of Heron's formula.

In geometry, a simple polygon is defined as a shape consisting of non-intersecting line segments or 'edges' that are joined pair-wise to form a closed path. If the edges intersect, then the polygon is not simple. Obviously, all intersecting polygons of particles with a given sectional plane are simple. In this article, we establish that the polygon is ordered counterclockwise so that as we traverse the edges, the interior is to our left.

An ear of a simple polygon is a triangle formed by three consecutive vertices, V_{j-1} , V_j and V_{j+1} (e.g. vertex 2, 3 and 4 in step 1 of figure 24), for which no other vertices of the polygon are inside the triangle. The line segment between V_{j-1} and V_{j+1} is a virtual diagonal of the polygon, and the vertex V_j is called the ear tip, see figure 24. In order to find the ear of a polygon, we need to distinguish the vertex into two categories. The reflex vertex (or concave vertex) is one for which the interior angle formed by the edges sharing it is larger than 180° (figure 25(b)). The convex vertex is one for which the interior angle is smaller than 180° , as shown in step 1 of figure 24 and figure 25.

Equation (14) and figure 25 show the procedure to assess whether a vertex is the convex vertex or the reflex vertex by using a method that is similar to the cross product in mathematics.

$$\begin{aligned}\Delta x_j &= x_j - x_{j-1}, \Delta y_j = y_j - y_{j-1}, \\ \Delta x_{j+1} &= x_{j+1} - x_j, \Delta y_{j+1} = y_{j+1} - y_j, \\ \text{flag} &= \Delta x_j \Delta y_{j+1} - \Delta x_{j+1} \Delta y_j.\end{aligned}\quad (14)$$

If $\text{flag} > 0$, then the interior angle is smaller than 180° ; (x_j, y_j) is a convex vertex. If $\text{flag} < 0$, the interior angle is greater than 180° ; (x_j, y_j) is a reflex vertex. Otherwise (i.e., $\text{flag} = 0$), the interior angle is equal to 180° .

The following example shows how the algorithm is described, and is demonstrated in figure 24. In step 1, the set of convex vertices is $C = \{0, 1, 3, 4, 5, 7, 9, 11\}$, the set of reflex vertices is $R = \{2, 6, 8, 10\}$ and the set of ears is $E = \{3, 4, 5, 7, 9, 11\}$. The ear at vertex 3 is

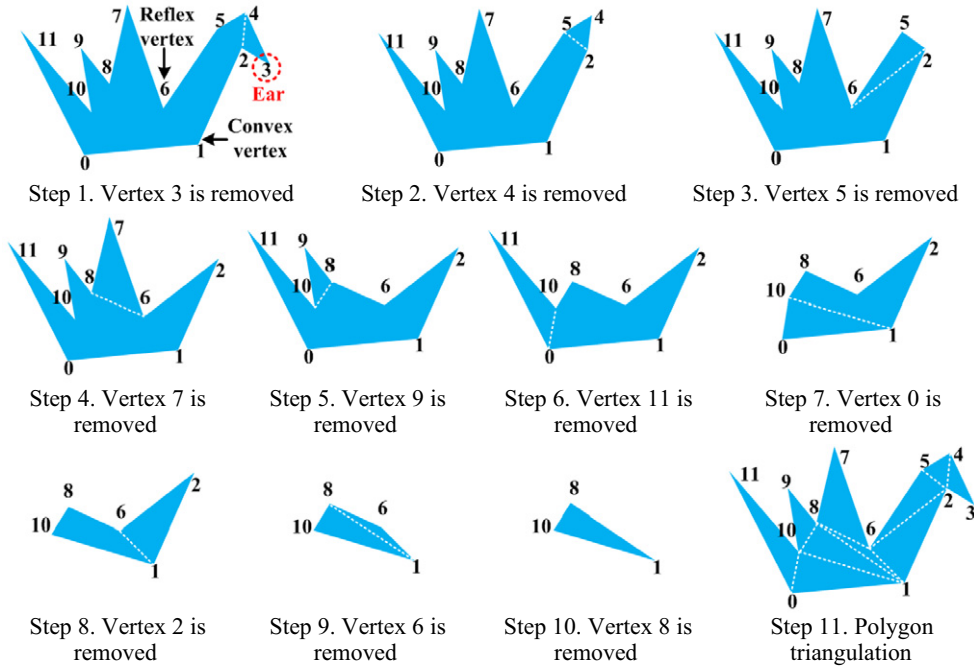


Figure 24. The polygon shows an ear and the triangulation of the polygon.

removed, so the first triangle in the triangulation is $\text{Tri} = \{2, 3, 4\}$. The adjacent vertex 2 was reflex, but now is convex, and it is tested to be an ear. Therefore, we update the sets in step 2: $C = \{0, 1, 2, 4, 5, 7, 9, 11\}$, $R = \{6, 8, 10\}$, $E = \{4, 5, 7, 9, 11, 2\}$. Vertex 4 is an ear in step 2, so vertex 4 is removed. The triangle in the triangulation is $\text{Tri} = \{2, 3, 4\}, \{2, 4, 5\}$, and the sets are updated in step 3: $C = \{0, 1, 2, 5, 7, 9, 11\}$, $R = \{6, 8, 10\}$, $E = \{5, 7, 9, 11, 2\}$. We follow the same procedure until there are only three vertices remaining (step 10). The full triangulation is shown in step 11.

In the ear clipping algorithm, since one triangle consists of a single ear, we need to iterate over the vertices and find the ears. A triangle is decomposed after we find one ear, then the ear is removed and the edge configuration can be changed. Finally, we get the full triangulation of the original polygon. Also, the area of the polygon can be calculated by summing the area of all the triangles, as shown in figure 26(a).

The area and perimeter of a sectional plane (see figures 26(b) and (c)) obtained with image analysis can be calculated by the following formulas:

$$\left(\frac{b}{a}\right)^2 = \frac{\text{Area of pixel}}{\text{Area of particle}} = \frac{B^2 \times \text{Pixel area fraction}}{A^2 \times \text{numerical area fraction}} \quad (15)$$

$$\frac{b}{a} = \frac{\text{Length of pixel}}{\text{Perimeter of particle}}, \quad (16)$$

where the area of the pixels is the number of pixels. To solve the perimeter from image analysis, the commercial, open-source code software *ImageJ* can be used. The perimeter is calculated using the total length of the ROI (region of interest) boundary and subtracting $2 - \sqrt{2}$ for each non-adjacent corner. The algorithm counts edge pixels as 1 and corner pixels as $\sqrt{2}$ from the source file. For example, a 1×1 pixel ROI has a boundary length of 4 and 2 non-adjacent

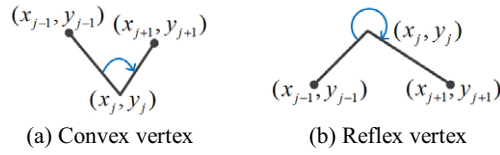


Figure 25. Convex vertex and reflex vertex.

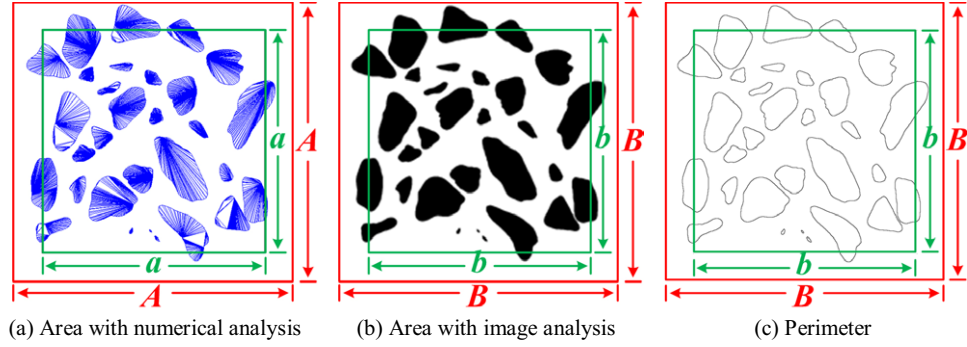


Figure 26. Calculation of the area and perimeter of a solid by numerical analysis and image analysis.

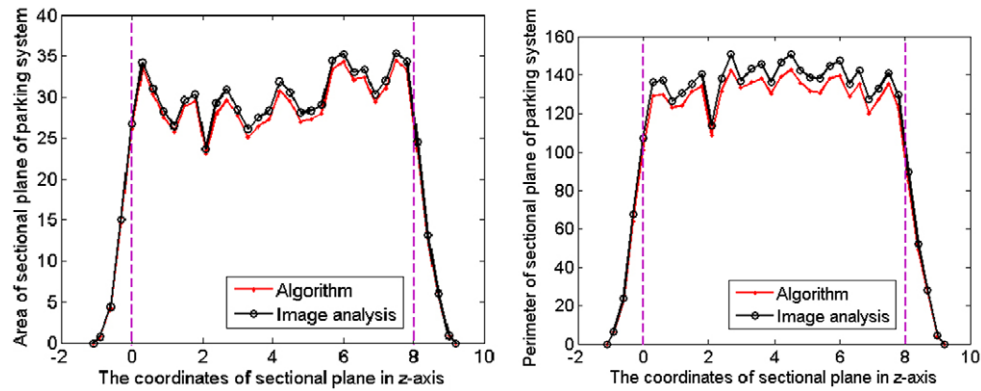


Figure 27. Comparison of numerical analysis with image analysis.

edges so that the perimeter is $4 - 2 \times (2 - \sqrt{2}) \approx 2.83$. A 2×2 pixel ROI has a boundary length of 8 and 4 non-adjacent edges so the perimeter is $8 - 4 \times (2 - \sqrt{2}) \approx 5.66$.

For the sake of simplicity, we assume a series of sectional planes perpendicular to the z -axis. Figure 27 presents the comparison of the areas and perimeters obtained by the above algorithms with those from traditional image analysis technology.

From figure 27, it can be seen that the numerical results are in good agreement with those from the image analysis. Therefore, these findings indicates the validity of the present algorithms.

6. Conclusions

In this study, a star-shaped particle has been reconstructed based on the spherical harmonic analysis. With the assistance of a triangle mesh algorithm, a separation axis theorem and an Extremal Box, an overlapping detection algorithm for star-shaped particles has been developed. In the algorithm, to reduce the amount of time consumed, we have proposed that the overlapping parts of any two particles that occurred in a 3D region (EOB) located between two planes that are perpendicular to the line pass through the centroids of two particles. Additionally, a sectional plane analysis algorithm for such a star-shaped particle parking system has been presented to validate the reliability of the developed overlapping detection algorithm. Furthermore, the areas and perimeters of the star-shaped particles on the sectional planes have been derived and compared with those from image analysis. The verification procedure indicated the reliability of the algorithms in the present work.

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超高性能钢纤维增强水泥基复合材料的力学性能及微结构分析

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摘要: 本文系统研究偏高岭土对超高性能钢纤维增强水泥基复合材料力学性能的影响规律, 并采用 XRD、纳米压痕、SEM 等现代分析测试手段揭示该材料具有超高性能的微观机理。结果表明, 掺加偏高岭土比不掺的试件在相同养护龄期、相同纤维掺量等条件下显示出更加优异的力学性能; 超高性能钢纤维增强水泥基复合材料由于具有极低的低水胶比, 其 90d 水泥水化程度仅有 65% 左右, 硬化水泥浆体中存在大量未水化的水泥颗粒, 且绝大部分水化产物为 UHD C-S-H 凝胶; 偏高岭土中存在大量的活性 SiO_2 和 Al_2O_3 , 可以促进水泥的水化, 进一步填充了复合材料内部的空隙, 使得材料整体的密实度得以提高, 界面得以强化, 从而使复合材料呈现出优异的力学性能。

关键词: 偏高岭土; 超高性能纤维增强水泥基复合材料; 钢纤维; 微结构; 纳米压痕

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Mechanical Properties and Microstructure Analysis of metakaolin Ultra High Performance Steel Fibre Reinforced Cementitious Composite

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Abstract: The effects of metakaolin on the mechanical performance of ultra-high performance steel fiber reinforced cementitious composite were studied in this paper. The microstructure evolution of the material was also investigated via XRD, Nanoindentation, SEM and other different analysis testing methods in this paper. The results indicate that the mechanical performance increases due to the addition of metakaolin at the same curing age and volume fraction of steel fiber. The hydration degree of the composites is only 65% at the curing age of 90 days because of the very low water-binder ratio. There is large amount of unhydrated cement in the hardened composite and UHD C-S-H is the most hydrated product. As the active components (SiO_2 and Al_2O_3) in metakaolin can promote the hydration process and can also fill in the micro pores inside the cementitious composite further, the structure gets denser and the interface is strengthened. So the composite has excellent mechanical performance.

Key words: metakaolin; ultra-high performance cementitious composite(UHPCC); steel fiber; microstructure; Nanoindentation

随着人类生活环境的进一步恶化以及开发和利用未知空间需求的亟需, 基础工程的建设越来越向高层、大跨的方向发展, 且越来越多地面临着严酷环境的威胁, 传统的普通混凝土材料已越来越难满足这种需要, 而超高性能水泥基复合材料 (Ultra High Performance Cementitious Composites, UHPCC) 以其优异的力学性能和耐久性能的特殊优势成为目前学术界研究的热点, 且广泛用于土木、建筑、水利、交通、隧道、桥梁、国防防护等对结构及性能有特殊要求的诸多领域领域^[1-5]。

目前, 国内外制备超高性能混凝土材料已越来越多的采用粉煤灰、硅灰、磨细矿渣等工业废渣取代水泥熟料, 走生态环保之路, 但随着这些矿物掺合料的需求增大, 如何开发利用其他具有活性组分的掺合料成为解决资源枯竭、保持社会可持续发展的必由之路。偏高岭土中含有大量的活性 Al_2O_3 和 SiO_2 , 能迅速与水泥水化生成的 $\text{Ca}(\text{OH})_2$ 反应, 促进水泥的水化。已有的实验研究表明^[6-10], 偏高岭土能显著提高普通混

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凝土的抗拉、抗压和抗弯强度等力学性能。为此，本文尝试研究偏高岭土对超高性能水泥基复合材料力学性能的影响规律，此外，拟采用多种分析测试手段以期揭示此超高性能水泥基复合材料的微观结构形成机理。

1.材料制备

1.1 原材料

水泥：P•II 52.5R 硅酸盐水泥，密度 3.1g/cm³，化学组成见表 1 所示；
超细粉煤灰：南京热电厂 I 级超细粉煤灰，密度 2.1g/cm³，比表面积 400m²/kg，化学组成见表 1 所示；
硅灰：埃肯公司生产的微硅粉，比表面积 22000m²/kg，SiO₂ 含量 94.48%，密度 2.2g/cm³，化学组成见表 1 所示；
偏高岭土：平均粒径 10.9μm，化学组成见表 2 所示；
细集料：最大粒径 2.36 mm 的普通黄砂，细度模数 2.26，连续级配，堆积密度 1.4g/cm³，表观密度 2.4g/cm³；
高效减水剂：西卡公司生产的聚羧酸高性能减水剂，减水率≥40%；
钢纤维：微细镀铜钢纤维，直径为 0.175 mm，长度为 13mm，抗拉强度为 2310Mpa，弹性模量为 200GPa，断裂伸长率为 3.5%。

为揭示偏高岭土对 UHPCC 材料力学性能及微观结构形成的影响规律，本文制备了掺与未掺偏高岭土的水泥基复合材料，其配合比见表 3 所示：

表1 水泥、粉煤灰及硅灰的化学组成 (%)

原材料	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	N ₂ O	L.O.I
水泥	20.4	4.70	3.38	64.7	0.87	1.89	0.49	0.33	3.24
粉煤灰	53.98	28.84	6.49	4.77	1.31	1.16	1.61	1.03	0.72
硅灰	94.48	0.27	0.83	0.54	0.97	0.8	---	---	1.04

表2 偏高岭土的化学组成 (%)

原材料	NaO ₂	MgO	Al ₂ O ₃	SiO ₂	TiO ₂
偏高岭土	1.13	2.42	43.72	49.96	1.12

表 3 UHPFRCC 的配合比

编号	水泥 (%)	粉煤灰 (%)	硅灰 (%)	偏高岭土 (%)	砂胶比	水胶比	外加剂 (%)	钢纤维体积率 (V _f)
MK00	55	35	10	0	1:1	0.17	2.5	0
MK01	55	35	10	0	1:1	0.17	2.5	1
MK02	55	35	10	0	1:1	0.17	2.5	2
MK03	55	35	10	0	1:1	0.17	2.5	3
MK10	49	35	10	10	1:1	0.17	2.5	0
MK11	49	35	10	10	1:1	0.17	2.5	1
MK12	49	35	10	10	1:1	0.17	2.5	2
MK13	49	35	10	10	1:1	0.17	2.5	3

1.2 试验方法

1.2.1 成型工艺 超高性能钢纤维增强水泥基复合材料制备工艺为：成型过程中先将称量好的粉体原材料

和细集料干拌均匀，之后在搅拌过程中均匀地撒入钢纤维，继续搅拌2min以利于钢纤维的均匀分散，然后在搅拌过程中将称量且混合均匀的水和外加剂缓慢地倒入搅拌机内，湿拌3min。当混合料进入粘流状态后，继续搅拌3min。之后在模具中浇铸成型，并适当加以振动（1min）以增进密实，标准养护1d后拆模，放入养护设备（ $20\pm 2^{\circ}\text{C}$ ， $\text{RH}>95\%$ ）中到不同龄期后取样进行力学性能及微观分析测试。

1.2.2 力学性能测试 根据标准GB17671-1999进行力学性能测试，抗折试件尺寸为 $40\text{mm}\times 40\text{mm}\times 160\text{mm}$ 的棱柱体，每组3个试件，采用三点弯曲，跨距100mm，试验设备为深圳新三思公司生产的CMT5105电子万能试验机，加载速度为1.5 mm/s；抗压试件尺寸为 $40\text{mm}\times 40\text{mm}\times 40\text{mm}$ 的立方体，每组3个试件，实验设备为无锡新路达仪器设备有限公司生产的TYA-2000型电液式压力试验机，加载速度为5kN/s。

1.2.3 XRD定量分析测试 将养护至规定龄期的样品切割取样后在无水酒精溶液中浸泡1d后取出以终止水化，然后放入玛瑙研钵中研磨（在无水酒精环境中），直至全部粉末通过0.08mm筛，再将粉末样品置于 50°C 的真空干燥箱中干燥1d，再于密封袋中慢慢冷却至室温，之后称取一定量同样过 $80\mu\text{m}$ 方孔筛的标准 $\alpha\text{-Al}_2\text{O}_3$ 粉末，与样品粉末以1:9的质量比混合后，在玛瑙研钵中与适量无水乙醇一起混研约1h以混合均匀，混匀后的所有样品置于真空干燥器中以待测试。

XRD测试仪器采用配制了LynxEye阵列探测器的Bruker-Axs D8 DISCOVER X射线衍射仪，靶材为Cu靶，室温环境（ $T = 298\text{ K}$ ），设置工作电压为40 kV，工作电流为30 mA， 4.0° 索拉狭缝，步长step size = $0.02^{\circ} 2\theta$ ，扫描速度0.30 s/step，扫描角度范围 $5^{\circ} \sim 80^{\circ} 2\theta$ 或 $7^{\circ} \sim 80^{\circ} 2\theta$ 。

1.2.4 纳米压痕测试分析 首先，将养护至规定龄期的样品切割成边长2cm左右的小块，用无水乙醇浸泡48h以终止其水化；其次采用环氧树脂将试样进行冷镶嵌，待树脂固化后，将试样切割成5~10mm的薄片并将试样切割面在磨样机上依次用180、600、1200目的碳化硅砂纸打磨，之后用 $9\mu\text{m}$ 、 $3\mu\text{m}$ 、 $0.5\mu\text{m}$ 、和 $0.05\mu\text{m}$ 的抛光液分别进行超过2h的抛光，得到平整、光洁的观察表面；最后，将抛光处理后的试件采用超声波清洗15min，以清除表面吸附的抛光剂颗粒。

试验仪器采用Micro Materials公司的纳米力学性能测试系统NanoTestTM，选用棱锥形Berkovich 压头。在试样界面区附近选取 10×10 的点阵，相邻2点的间距为 $20\mu\text{m}$ 。试验采用位移控制模式，材料的最大压痕深度设定为300nm，当压头接触到样品表面时按照0.25mN/s 的速率线性加载至设定压痕深度，恒载30s，之后按照0.25mN/s 的速率线性卸载。依次对每个测试点进行加载—卸载循环，并记录其荷载—位移曲线。

1.2.5 扫描电镜（SEM）分析 SEM分析所用仪器为Sirion场发射扫描电镜。样品制备过程如下：取尺寸为 $8\text{mm}\times 8\text{mm}\times 5\text{mm}$ 的样品，在无水酒精溶液中浸泡1d后取出，并在 $60\pm 2^{\circ}\text{C}$ 温度下干燥48h后取出，在测试表面喷金后放入扫描电镜中观察。

2. 结果及分析

2.1 力学性能测试与分析

本文对不同养护龄期条件下的超高性能钢纤维增强水泥基复合材料的静态力学性能进行了测试分析，其结果如图1和图2所示。

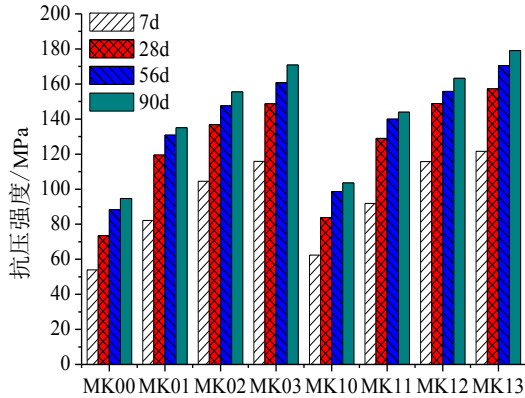


图 1 不同龄期对 UHPCC 抗压强度的影响

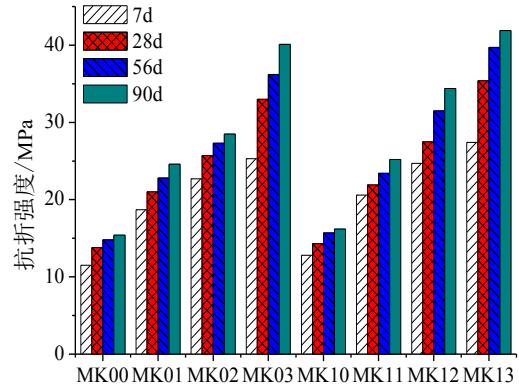


图 2 不同龄期对 UHPCC 抗折强度的影响

从图 1 可以看出,不同系列的超高性能纤维增强水泥基复合材料的抗压强度随着龄期的增长而增大,在相同养护龄期条件下,随着纤维掺量的提高,其抗压强度大幅提升,尤其是掺加了 3% 体积率的钢纤维后,其抗压强度提升幅度十分明显,90d 抗压强度可达到 180MPa 左右。相对于未掺加偏高岭土的材料而言,掺加 10% 的偏高岭土取代水泥之后,材料在不同龄期条件下的抗压强度不仅没有明显的下降趋势,反而有所增加,这主要在于偏高岭土中存在大量的活性 SiO_2 和 Al_2O_3 ,可以促进水泥的水化,且与水泥的水化产物进一步反应生成 C-S-H 凝胶,进一步填充了复合材料内部的空隙,使得材料整体的密实度得以提高,从而使复合材料呈现出优异的力学性能。

从图2中可以看出,不同系列的超高性能纤维增强水泥基复合材料的抗折强度呈现出同抗压强度相似的变化规律,未掺高岭土偏的UHPCC基体的90d抗折强度为15.4MPa,随着钢纤维掺量的提高抗折强度也不断提高,掺入3%钢纤维后UHPCC的抗折强度提高到基体混凝土的2.6倍,这是由于复合材料中均匀分散的微细钢纤维充分发挥出了阻裂和增强作用,从而使UHPCC的抗折强度随着纤维掺量增大得到不断的提高。此外,可以看出,在相同龄期条件下,掺加偏高岭土的复合材料的抗折强度比未掺的试件略有提高,但其提升幅度比抗压强度的提升幅度要小。复合材料中掺入了45%的超细工业废渣,随着养护龄期的延长,其火山灰效应不断发挥,可以进一步提高复合材料的密实度和纤维/基体间的界面粘结力,因此可以推测该材料的力学性能将随着龄期的进一步延长而提高。

2.2 XRD 定量分析

传统的常用于定量分析物相组成的X射线衍射方法对于单一的、结晶程度较好的物相具有很好的分析效果,但对于所含物相数目繁多、衍射谱图中无定形相的水泥基复合材料的样品而言,存在的严重的谱峰重叠、择优取向效应等会给定量分析带来很大的困难。Rietveld 全谱拟合法在X射线衍射图谱分析中的应用,有可能改变这一不足,其原理在诸多文献中都有仔细阐述^[11-13]。

本文首先对粉末样品的XRD图谱物相定性分析,尽可能多的找出所有的物相;然后利用TOPAS软件进行定量分析。

本文对不同养护龄期(7d、28d、90d)的掺与未掺偏高岭土的基体试件(未掺入细集料)水化产物进行定量分析,表4列出了主要矿物相的定量分析结果,图3为标准养护90d掺偏高岭土试件的分析结果。

表4 不同养护龄期下的掺与未掺偏高岭土试件的XRD定量分析结果

类别	龄期 (d)	物相					
		C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Ca(OH) ₂	amorphous phase
MK00	7	5.94	8.36	1.89	3.28	4.81	47.22
	28	4.46	8.54	1.63	2.89	4.38	48.22
	90	4.44	7.71	1.14	1.92	4.03	50.52
MK10	7	5.67	7.33	1.68	1.54	2.82	54.89
	28	5.43	6.00	1.42	1.41	1.76	55.25
	90	4.39	6.85	1.01	1.33	1.17	57.98

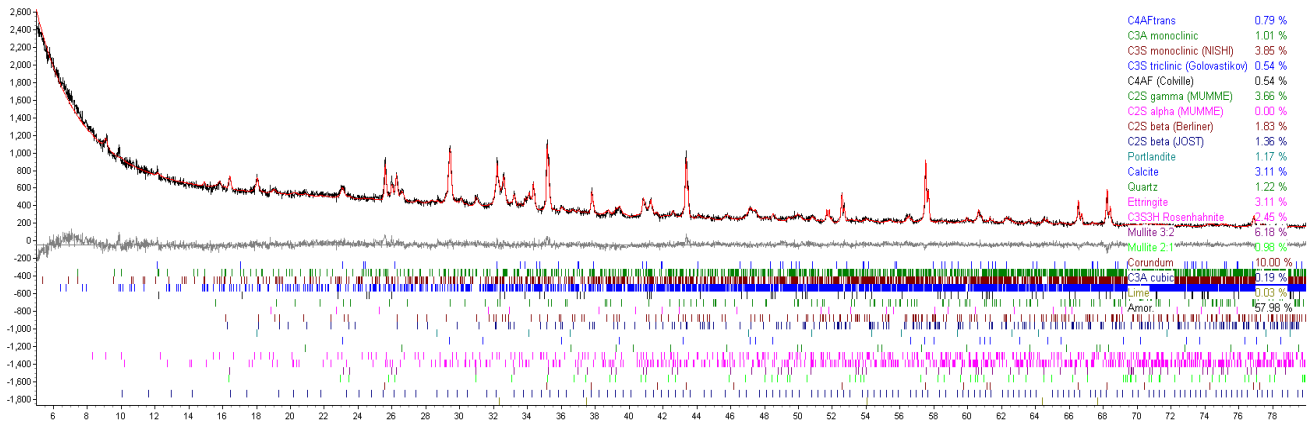


图3 标准养护 90d MK10 的 XRD 定量分析结果

从表 4 的分析结果可以看出，随着养护龄期的延长，水化反应不断进行，未水化水泥相（C₃S、C₂S、C₃A、C₄AF）不断减少，水化产物的无定形相（C-S-H 凝胶等）不断增多，但由于 UHPCC 材料的水胶比极低(w/b=0.17)，水泥不可能完全水化，其 90d 的水化程度仅有 65%左右。此外还可以看出，水化生成的 Ca(OH)₂ 相却不断减少，且掺加偏高岭土试件的水化产物中 Ca(OH)₂ 含量明显少于未掺的试件，这主要是由于材料中的工业废渣的火山灰反应消耗了大量的 Ca(OH)₂，且偏高岭土中的活性 SiO₂ 也与 Ca(OH)₂ 反应生成 C-S-H 凝胶，使得 Ca(OH)₂ 未在界面区大量的排列生成，因此本文制备的 UHPCC 材料的界面微观结构得到了明显的改善与强化。

2.3 纳米压痕结果及分析

根据2.2节XRD的分析结果来看，UHPCC硬化水泥浆体组分中主要含有水化凝胶相、氢氧化钙(CH)以及未水化水泥颗粒。普通混凝土C-S-H凝胶相主要以高(低)钙硅比凝胶以及高(低)密度水化硅酸钙凝胶(LD C-S-H 和HD C-S-H)为主，而根据文献研究结果显示^[14-15]，在低水灰比条件下大量存在高密度C-S-H凝胶（UHD C-S-H），其具有更高的力学性能。

本文对标准养护56d的掺加偏高岭土的试件进行纳米压痕测试，根据表3中XRD的分析结果来看，Ca(OH)₂相在材料中的比例极少，因此作者在分析时忽略了Ca(OH)₂相。其力学性能参数的大致分布图如图4所示，从图4中可以看出，试件中都存在大量的未水化水泥颗粒及UHD C-S-H相，HD C-S-H相被水化产物UHD C-S-H相所包围，未见明显的界面过渡区。

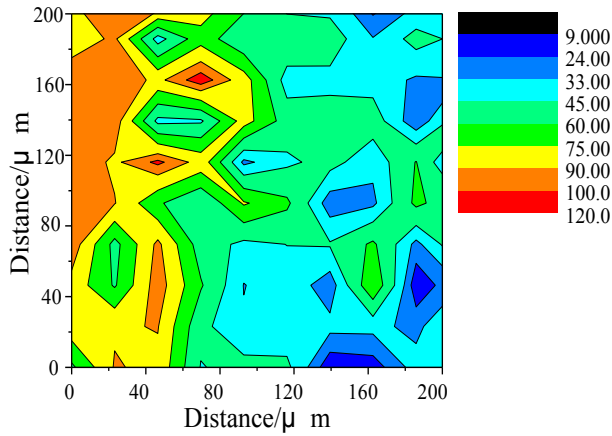


图 4 MK10 样品表面弹性模量分布图

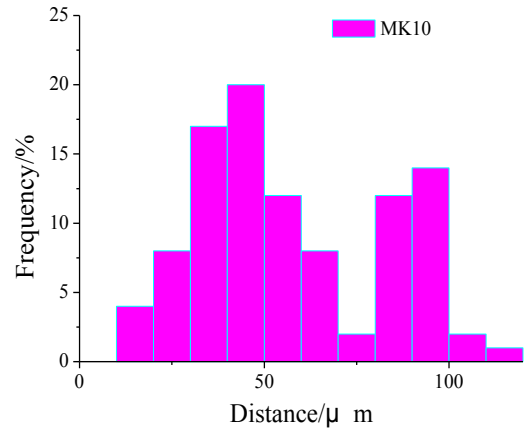


图 5 MK10 样品弹性模量的频率分布图

对试验所得的弹性模量的数据进行统计分析, 获得频率分布图如图 5 所示, 从图中可以看出, 其弹性模量峰值在 35~50GPa 以及 80~100GPa 之间, 分别为 UHDC-S-H 相及未水化水泥颗粒相, 从数据结果来看, 未发现 LD C-S-H 相, 试件中存在少量的 HD C-S-H 相, 因此, 对本文制备的超高性能纤维增强水泥基复合材料而言, 其水化产物与普通混凝土存在明显的不同, 除存在大量的未水化颗粒外, 其水化产物主要由 UHDC-S-H 相组成, 界面区结构得到了充分强化, 正是由于其水化产物具有较高的力学性能, 才使得材料宏观上表现出优异的力学性能。

2.4 SEM 结果与分析

本文对标准养护 56d 龄期下的 MK10 试件进行了 SEM 分析测试, 其结果如图 6 所示。

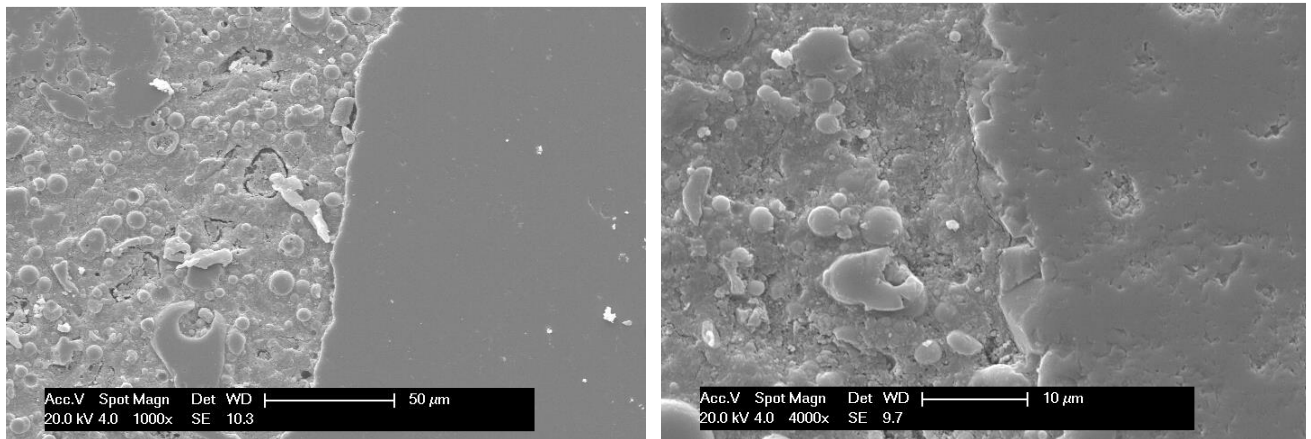


图 6 标准养护 56d 龄期下 MK10 试件的 SEM 图

从图 6 中可以看出, UHPCC 材料结构比较致密, 细集料与硬化水泥浆体之间没有明显的缺陷。复合材料中存在着大量的未水化水泥基颗粒、部分团聚的偏高岭土颗粒、未反应的粉煤灰颗粒等, 这些颗粒被水泥水化产物所包裹着, 形成非常致密的微观结构。随着养护龄期的延长, 这些未水化颗粒可以进一步水化生成凝胶产物, 填充更加微细的孔隙结构, 从而使得复合材料整体结构更为致密, 使复合材料的力学性能进一步提升。

3. 结 论

(1) 采用偏高岭土、粉煤灰、硅灰组成复掺活性掺合料,有利于超高性能水泥基复合材料力学性能的提升,掺加偏高岭土比不掺的试件在相同养护龄期、相同纤维掺量等条件的显示出更加优异的力学性能。

(2) 偏高岭土中存在大量的活性 SiO_2 和 Al_2O_3 ,可以促进水泥的水化,且与水泥的水化产物进一步反应生成 C-S-H 凝胶,进一步填充了复合材料内部的空隙,使得材料整体的密实度得以提高,从而使复合材料呈现出优异的力学性能。

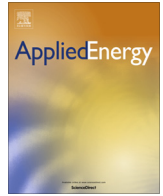
(3) 超高性能钢纤维增强水泥基复合材料由于具有极低的低水胶比,其 90d 水泥水化程度仅有 65%左右,硬化水泥浆体中存在大量未水化的水泥颗粒,且绝大部分水化产物为 UHD C-S-H 凝胶,未发现类似普通混凝土材料中的 LD C-S-H 凝胶,正是由于水化产物 UHD C-S-H 凝胶具有超高的密度、硬度和弹性模量,使得材料在微观结构上不存在类似于普通混凝土的界面薄弱区,此外,由于材料中的工业废渣以及偏高岭土中的活性组分的消耗了大量的 $\text{Ca}(\text{OH})_2$,使得 $\text{Ca}(\text{OH})_2$ 未在界面区大量的排列生成,从微观形貌来看亦可断定其界面区微观结构得到了改善及强化,使得材料整体呈现出异常密实的微观结构,因此 UHPCC 才显示出优异的力学性能。

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Development of thermal energy storage composites and prevention of PCM leakage



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HIGHLIGHTS

- PCM leakage during fabrication of thermal energy storage composite was prevented.
- The prevention mechanisms of different modifiers were analyzed.
- Influences of modifiers on thermal energy storage composite were investigated.

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ABSTRACT

Thermal energy storage composites were developed by incorporating granular phase change materials (PX25 from Rubitherm[®]) into cement paste. Without prevention, however, a significant amount of phase change material (paraffin) leaked from the PX25 during the fabrication process. To prevent paraffin leakage during fabrication, three types of nano-SiO₂ powder (hydrophilic fumed silica (fs1), hydrophobic fumed silica (fs2), and precipitated silica (ps2)) were chosen to modify PX25. The influence of dosage of these modifiers was investigated with reference to PCM leakage during fabrication. Paraffin leakage was eliminated when hydrophobic fs2 or ps2 was used in a 2.3% and 9.0% mass fraction (relative to PX25), respectively. However, hydrophilic fs1 did not prevent leakage of paraffin. Microstructural and mechanical analyses of the thermal energy storage composites were used to analyze the prevention mechanism of hydrophobic nano-powder against paraffin leakage.

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1. Introduction

Phase change materials (PCMs) are widely used in latent-heat thermal storage systems for saving energy. Many PCMs (organic, inorganic, and eutectic) are available for any required transition temperature range [1]. Paraffin, alkane, and fatty acids are commonly used latent-heat storage materials [2–4]. Perlite, diatomite, expanded graphite, and silica fume [5–9] are commonly used supporting materials that provide structural strength and prevent the leakage of liquid PCMs. Leakage of PCM occurs not only during the solid–liquid change process but also during the mixing process with cement mortar or other binder materials when water is added.

PCMs may be incorporated into cement paste, mortar, or gypsum as thermal energy storage materials [3,10,11]. They have been used in solar domestic hot water (SDHW) systems, heat sinks,

and building structures to increase practicality and energy efficiency [12–15]. Incorporating suitable PCMs into the walls or floor of a building can reduce indoor temperature swings, thus reducing the building's energy consumption. Cement paste that is produced by mixing Portland cement and water has wide applications in buildings, such as for creating smooth wall surfaces. The incorporation of PCMs in cement paste can improve the thermal mass and thermal energy storage ability of the paste. Xu and Li [5] prepared form-stable PCM composites by incorporating paraffin into diatomite particles, then mixing it with cement paste to form a PCM-based cement composite. When mechanical and heat storage properties were tested, the results showed that compressive strength decreased with the increase of PCM replacement level. Félix and Aguiar [16] also studied the mechanical properties of cement mortar with incorporated PCM microcapsules. They found that compressive strength and flexural strength decreased significantly with the increase of PCM dosage. Li and Wu [7] studied heat transfer and heat storage properties of cement–mortar board with PCM composite. Cheng et al. [17] studied the

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Table 1
Properties of PX25.

Material	Melting temp. (°C)	Paraffin content (%)	Heat storage capacity (kJ/kg)	Bulk density (kg/L)
PX25	22–25	60	96	0.65

thermophysical properties of PCM–concrete brick. Li et al. [18] investigated paraffin leakage and minimization in thermal energy storage composites with different water/cement ratio. Their results revealed that the amount of exuded paraffin increased with the water content in the mixture. However, they did not give details of the prevention mechanism. It has also been found that a large number of form-stable PCM composites are normally fabricated by incorporating PCM into porous particles without any protective layer on the surface of form-stable PCM. These ‘unprotected’ form-stable PCMs are used to prepare thermal energy storage composites [3,5,18]. If the ambient temperature is higher than the PCM melting temperature of, PCM will leak from porous materials and the heat storage property will decrease. Previous research has mainly focused on the preparation of form-stable PCM or on the thermal and mechanical properties of PCM and cement composite. For these ‘unprotected’ form-stable PCMs, leakage of PCM during the fabrication of thermal energy storage composites has not been discussed in the literature. However, it should be noted that any possible leakage of PCM reduces the heat storage property of the composite and decreases the workability of the PCM particles and cement mixture.

PX25 is a commercial ‘unprotected’ form-stable PCM from Rubitherm, containing paraffin in a secondary supporting structure (hydrophilic fumed silica). It has similar characteristics to those of other ‘unprotected’ form-stable PCMs. For that reason, PX25 was selected as an example in this paper. It was incorporated into cement paste to fabricate thermal energy storage composites. The problem of PCM leakage during fabrication of thermal energy storage composites was investigated. The support material of PX25 is hydrophilic fumed silica, which is far smaller than support materials commonly used in other literature [5–9], such as perlite, diatomite, expanded graphite, and silica fume. To reduce the risk of leakage, three types of nano-silica powder (hydrophilic fumed silica, hydrophobic fumed silica, and precipitated silica) were utilized as potential modifiers to investigate the possibility of preventing leakage of PCM during the fabrication process. Hydrophilic fumed silica was chosen to investigate whether an extra amount of supporting material was helpful for leakage. Hydrophobic materials are commonly used for absorbing oil. The particle size of hydrophobic fumed silica is the same as that of the supporting material hydrophilic fumed silica, so hydrophobic fumed silica was selected to study the influence of the surface property of modifiers. Hydrophobic precipitated silica was selected to study the influence of a modifier with a larger particle size. The modifier prevention mechanism and the mechanical properties of thermal energy storage composites were also investigated.

2. Experiments

2.1. Materials

The basic properties of form-stable PX25 from Rubitherm Technologies GmbH are shown in Table 1. The microstructure and particle size distribution of PX25 were analyzed using scanning electron microscopy (SEM) and laser particle size analyzer (LPSA), respectively. The results are given in Figs. 1 and 2. Particle size ranged mainly between 200 and 400 μm . However, some broken PX25 particles were observed from the SEM image. The 0–50 μm section of the particle size distribution curve can also explain this phenom-

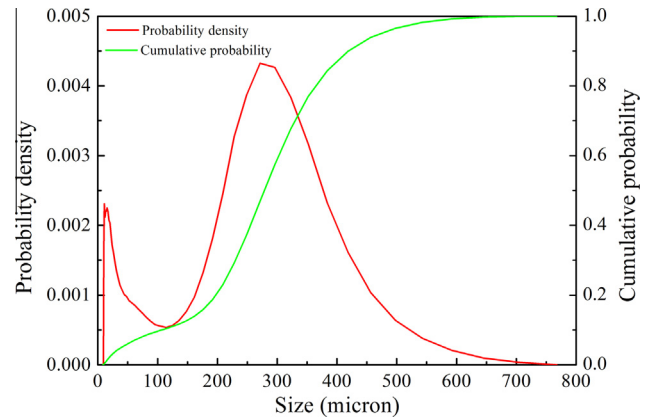


Fig. 1. Particle size distribution of PX25.

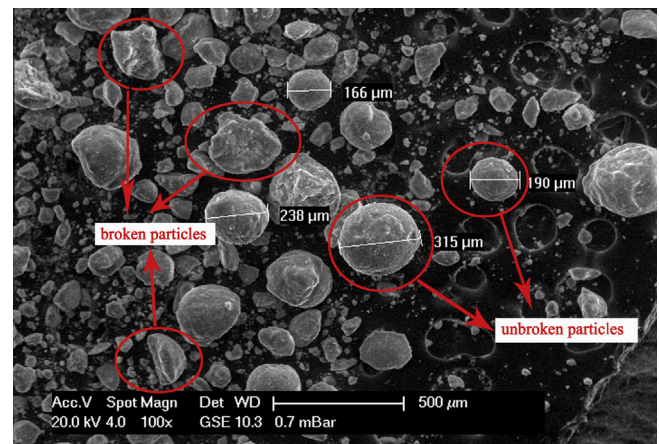


Fig. 2. SEM image of PX25.

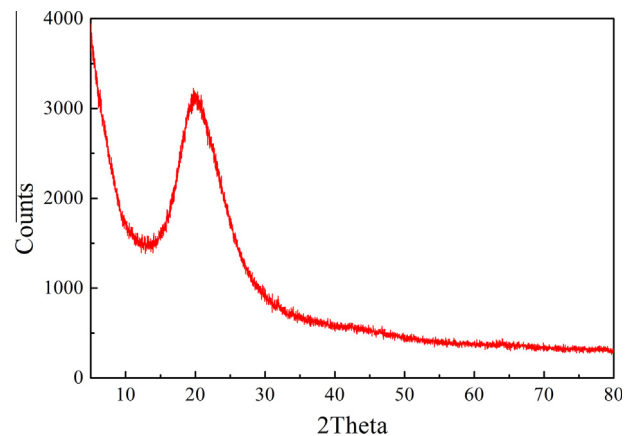


Fig. 3. XRD spectral of PX25.

enon. Fig. 3 shows the X-ray diffraction (XRD) spectrum of PX25. No characteristic peaks appear in the XRD spectrum revealing that the supporting material is amorphous silica. Three different types of nano-SiO₂ were used as modifiers to investigate their efficiency in preventing leakage of paraffin from the PX25. Hydrophilic fumed silica (fs1) was supplied by Chengqixin (Shenzhen) Co., Ltd. Hydrophobic fumed silica (fs2) and precipitated silica (ps2) were purchased from Evonik Degussa (China) Co., Ltd. The details of these three modifiers are shown in Table 2. Their SEM images (see Fig. 4) show that the particle sizes of the two fumed silicas and the precip-

Table 2
Details of three modifiers.

Modifiers	Type	Specific surface area (m ² /g)	pH value	Loss on drying 105 °C (%)	Loss on ignition 1000 °C (%)	SiO ₂ content (%)	Bulk density (kg/m ³)
fs1	CYA-200	200 ± 25	3.6–4.5	≤1.5	≤2.5	≤99.8	50 ± 20
fs2	R972	110 ± 20	3.6–5.5	≤0.5	≤2.0	≥99.8	50 ± 20
ps2	D10	90	10.3	≤3	≤7	≥98	100

itated silica were approximately 80–100 nm and around 3–10 μm, respectively. Portland composite cement (PC 32.5) was used for fabrication of the thermal energy storage composite.

2.2. Preparation of thermal energy storage composite and mechanical property test

Thermal energy storage composites were fabricated by mixing PX25 particles with cement and water. The water/cement ratio and PX25/cement (P/C) ratio were chosen to be 1.0 and 0.43, respectively. The P/C ratio was determined by considering the paraffin content in fabricated products. In this case, the paraffin content was about 3 kg/m² when the composites were used to produce a panel 20 mm in thickness, which is optimal for real applications [18]. The water/cement ratio was determined by the workability of the composites. PCM melts when the operational temperature is higher than its melting point. The mass fraction of melted PCM increases with an increase of operational temperature. The temperature of construction site environments is generally below 35 °C, even in summer. Therefore, to obtain the highest leakage ratio, all experiments in this study were carried out in a room where the temperature varied between 30 °C and 35 °C (which is above the melting point of PX25). If the modifier could improve the paraffin leakage under this condition, it would also be effective when used at other temperatures.

To prevent paraffin leakage, PX25 was surface-modified by mixing it with the three different nano-silicas separately. Because of the very high surface energy of the nano-silicas, they can easily deposit on the surfaces of PX25 particles. The dosages of fs1 (mass of fs1/mass of PX25) were designed as 3%, 6%, 7.5%, 9%, and 10.5%, respectively. The dosages of fs2 (mass of fs/mass of PX25) were designed as 0.7%, 1.4%, 2.0%, 2.3%, and 2.6%, respectively. The mass fraction of ps2 was the same as that of fs1.

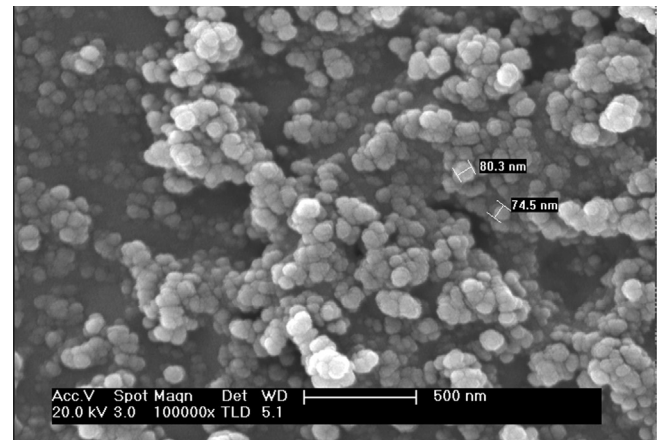
The fabrication process was as follows. PX25 and modifier were first dry mixed at the low speed of 60 r/min for 1 min in a mixer, after which the cement was added. After the substances were uniformly mixed, water was finally added and the mixture obtained was mixed for another 2 min at 60 r/min. The mixer was then stopped and material on the surface of the mixer was scraped down. Finally, a 3 min mixing phase at 60 r/min rotation speed ended the mixing procedure. The fresh PX25–cement mixture was cast in 40 * 40 * 40 mm³ steel molds for compressive strength testing. After 24 h curing, samples were demolded and cured in water until the day of testing (7 and 28 days). The mechanical properties were tested and the influence of the three modifiers on paraffin leakage was also investigated.

3. Results and discussion

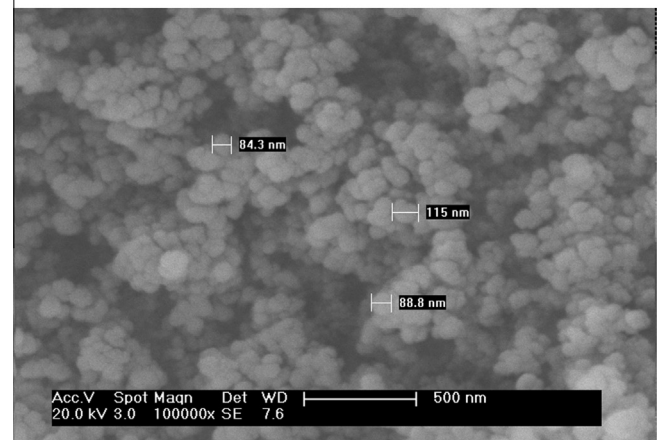
3.1. Leakage of PCM

The nonmodified PX25–cement mixture after mixing is shown in Fig. 5. The exuded liquid from the nonmodified PX25 was found

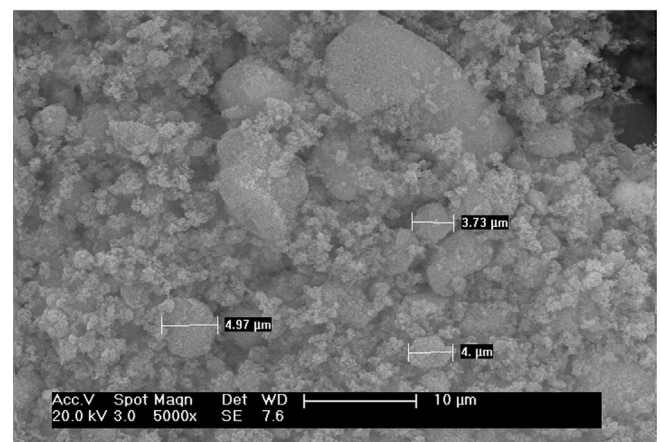
to segregate on top of the mixture. After initial hardening of the mixture, the paraffin was poured out and placed in a room at 20 °C (which was lower than the melting point of PX25) for 24 h. The liquid mixture solidified completely and no extra liquid was found in the mixture after 24 h cooling. Thus we concluded that the exuded liquid mixture was 100% paraffin. The leakage ratios (defined as the mass fraction of the exuded paraffin to the total paraffin contained in the PX25) were calculated and are given in Table 3.



(a)



(b)



(c)

Fig. 4. SEM images of three modifiers (a) fs1, (b) fs2 and (c) ps2.



Fig. 5. Leakage of paraffin in the thermal energy storage composite.

Table 3
Leakage details of thermal energy storage composites during fabrication.

Cement (%)	PX25 (%)	Water/cement ratio	Leakage ratio (%)
70	30	1	57.3

As shown in Table 3 the leakage ratio was 57.3%, which could significantly decrease the heat storage capacity of thermal energy storage composites. PX25 is a composite of paraffin and hydrophilic fumed silica. When water comes into contact with PX25, water molecules quickly combine with fumed silica particles. This causes the paraffin to separate from the supporting material, and then leakage of paraffin occurs. The leakage ratios of paraffin given in Table 3 indicate that phase change material composites based on hydrophilic supporting material must not be directly applied in cementitious mixtures because of serious loss of paraffin.

3.2. Minimization of paraffin leakage

3.2.1. Methodology and thermal properties of thermal energy storage composites

To prevent paraffin leakage during the mixing process, hydrophilic fumed silica, hydrophobic fumed silica, and hydrophobic precipitated silica were used to modify PX25 before mixing it with cement and water. The SEM images of these modifiers are displayed in Fig. 4. Different dosages of these three modifiers were mixed with the PX25 as a surface-coating material. The incorporated dosage of modifier candidates was defined as the mass fraction of modifier to PX25. The leakage-preventing efficiency of these modifiers was evaluated in terms of the method used in Section 3.1, and the results are displayed in Table 4. It can be seen from Table 4 that the mass of paraffin leakage decreased with the increase of the mass fraction of ps2 and fs2. When the dosages of fs2 and ps2 increased to 2.3% and 9.0%, respectively, no visible leakage could be found. Thus 2.3% for fs2 and 9.0% for ps2, respectively,

are regarded as the optimum dosage for preventing leakage of paraffin during the fabrication of thermal energy storage composites. However, the morphology of fresh mixtures with these two modifiers in Fig. 6 revealed that lump-like pieces formed in the fresh mixture system with the ps2 modifier, whereas no such heterogeneity occurred in the PX25–cement mixture with the fs2 modifier. This inhomogeneity phenomenon may be caused by the surface property or the larger particle size of ps2. The fs2 was modified by dimethyldichlorosilane and methyl radicals condensed on the particle surface. However, ps2 was modified by dimethicone and ring structures formed on its surface. The difference of surface modification may result in the difference in paraffin adsorption capacity of these particles. Moreover, the number of hydroxyl groups of ps2 is greater than that of fs2, but the particle size of fs2 is much smaller than that of ps2. Torró-Palau et al. [19] also studied the rheological characterization of polyurethanes by the addition of these two hydrophobic silica powders. Their results showed that the addition of silica to the polyurethane produced an increase in viscosity that was more important for the fumed than for the precipitated silica due to the differences in particle size. As shown in the first row of Table 4, even when the incorporated dosage of hydrophilic fumed silica was as high as 10.5%, liquid paraffin still appeared on the surface of the mixture during the mixing process, as shown in Fig. 7(a). Fig. 7(b) shows the PX25–cement mixture after the addition of fs2, and no visible leakage can be found. It can be concluded that hydrophilic fumed silica is not a suitable leakage-modifier, whereas fs2 is the most suitable modifier.

To determine the influence of fs2 on the latent heat of prepared thermal energy storage composites, differential scanning calorimetry (DSC) experiments were performed. The DSC measurement was performed in the temperature range -20 – 40 °C at 5 °C/min constant heating/cooling rate and under a nitrogen gas atmosphere environment. Fig. 8 presents the DSC curves of the exuded paraffin, PX25, PX25–cement composites (PC), and PX25–cement–fs2 composites (PCF). The details of onset melting temperature (T_{Onset}), peak melting temperature (T_{Peak}), and latent heat of samples, obtained from the DSC curves in Fig. 8, are presented in Table 5. It can be seen that in comparison with the exuded paraffin, the phase change temperatures of PX25 were shifted slightly. This is probably attributable to the physical interactions between paraffin and supporting materials [5]. The T_{Onset} and T_{Peak} of the PCF were close to those of PX25. However, the phase change temperatures of PC were largely shifted to lower temperatures compared with the pure PX25. The possible reason is that some paraffin may remain in the smaller pores of PX25 particles, resulting in a freezing point depression of paraffin according to the Gibbs–Thompson equation (Eq. (1)) [20]. The melting temperature decreases with the decrease of pore size, as shown in Eq. (1). Li et al. [18] also studied the phase change behavior of paraffin absorbed by diatomite with different pore sizes. Their results revealed a decrease in the melting point with the decrease of the pore size. Further research is needed to validate these findings.

$$\Delta T = \frac{2\gamma_{CL}}{\Delta S_{fv} \cdot r} \quad (1)$$

Table 4
Optimizing test of paraffin leakage with three modifiers.

	Modifier	Ratio of modifiers to PX25 (%)									
		0.7	1.4	2.0	2.3	2.6	3.0	6.0	7.5	9.0	10.5
Leakage ratio (%)	fs1	–	–	–	–	–	56.3	57.4	56.7	53.2	55.4
	fs2	41.3	17.7	Little	0	0	–	–	–	–	–
	ps2	–	–	–	–	–	45.4	21.8	Little	0	0

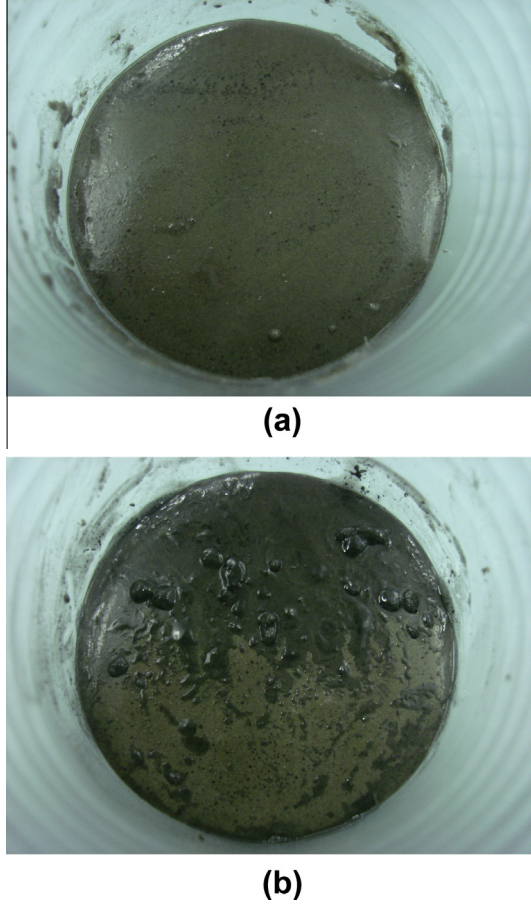


Fig. 6. PX25–cement mixture with fs2 and ps2 (a) PX25–cement mixture with 2.3% fs2 and (b) PX25–cement mixture with 9.0% ps2.

where ΔT is the undercooling with respect to the normal melting point, °C; γ_{CL} the crystal/liquid interracial energy, J/m²; ΔS_{fv} the entropy of fusion of the crystal per unit volume, J/m³ °C; r the pore radius, m.

From Fig. 8 and Table 5 it can be seen that the latent heats of PC and PCF were much lower than that of pure PX25, and the latent heat of PCF was higher than that of PC. The latent heats of the exuded paraffin in the melting (H_m) and freezing (H_f) processes were 142.3 kJ/kg and 154.1 kJ/kg, respectively. For PX25, H_m and H_f are 78.11 kJ/kg and 79.61 kJ/kg, respectively, which is close to the theoretical values (H_m : $142.3 \times 60\% = 85.38$ kJ/kg, H_f : $154.1 \times 60\% = 92.46$ kJ/kg). For PCF and PC, the latent heats of melting and freezing were measured to be 13.44 kJ/kg, 14.20 kJ/kg, 4.48 kJ/kg, and 5.24 kJ/kg, respectively. Taking into account the measured leakage ratio of $L_m = 57.3\%$, the theoretical value of the latent heat can be described by the following relation:

$$H_{theory} = H_{PX25} \cdot \varphi_{PX25} \cdot (1 - L_m) \quad (2)$$

where H_{theory} is the theoretical value of the latent heat of composites with PCM, kJ/kg; it can be the latent heat in the melting (H_m) or freezing (H_f) process; H_{PX25} the measured value of the latent heat of PX25, kJ/kg; φ_{PX25} the mass fraction of PX25 in the mixture, %; L_m the measured leakage ratio, %.

Since the mass fraction of PX25 in PC was 30%, the theoretical values of H_m and H_f should be 10.01 kJ/kg and 10.20 kJ/kg respectively, based on Eq. (2). However, their measured values were 4.48 kJ/kg and 5.24 kJ/kg respectively. This difference is attributed to the inevitable loss of paraffin during fabrication, such as residue left on the surface of the container and evaporation of paraffin.

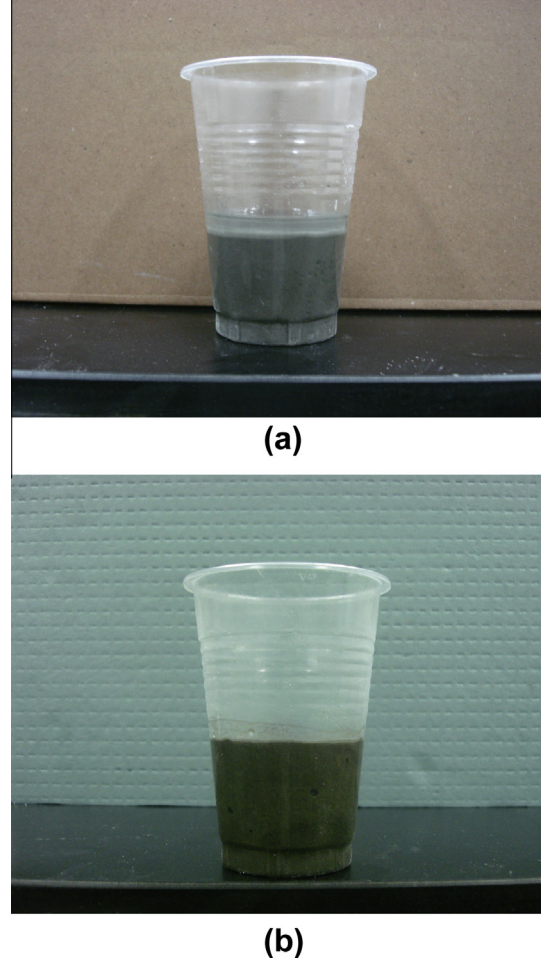


Fig. 7. Comparison of PX25–cement mixture after the addition of fs1 and fs2 (a) after the addition of 9.0% fs1 and (b) after the addition of 2.3% fs2.

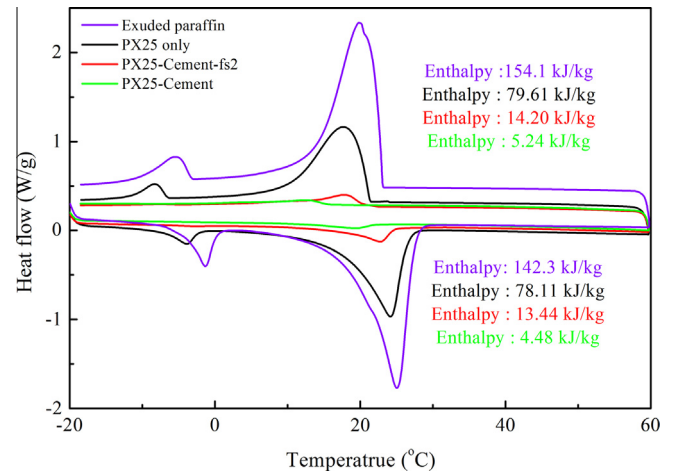


Fig. 8. DSC curves of PX25 and different PX25–cement composites.

Such paraffin loss cannot be measured accurately. In this paper, the inevitable loss ratio of paraffin is defined as follows:

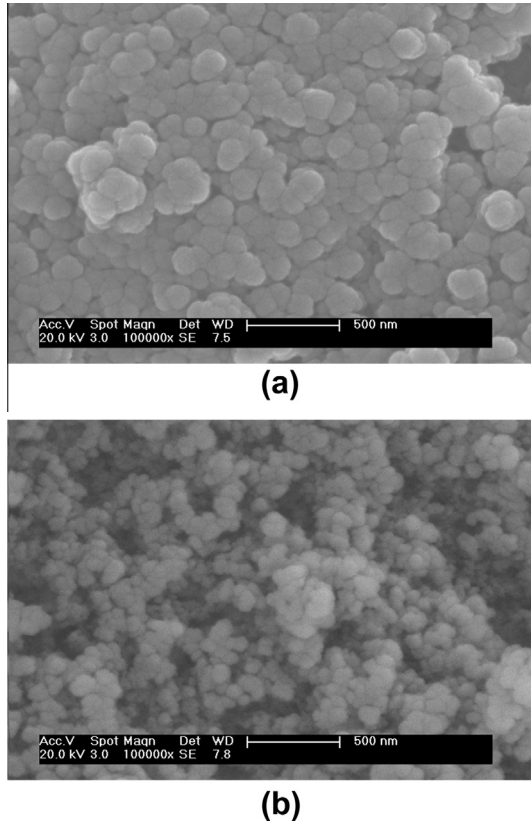
$$L_i = 1 - \frac{H_{measure}}{H_{theory}} \quad (3)$$

where L_i is the inevitable loss ratio of paraffin, %; $H_{measure}$ the measured value of latent heat, kJ/kg.

Table 5

Thermal parameters of PX25 and different PX25–cement composites.

Samples	Melting process			Freezing process		
	T_{Onset} (°C)	T_{Peak} (°C)	H_m (kJ/kg)	T_{Onset} (°C)	T_{Peak} (°C)	H_f (kJ/kg)
Leaked paraffin	19.58	25.05	142.3	23.07	19.83	154.1
PX25	17.42	24.13	78.11	21.32	17.66	79.61
PX25–cement (PC)	11.45	19.40	4.48	15.58	12.37	5.24
PX25–cement–fs2 (PCF)	17.16	22.77	13.44	20.62	17.80	14.20

**Fig. 9.** Comparisons of SEM images of PX25 particle and PX25–fs2 mixture surface (a) SEM images of PX25 surface and (b) SEM images of PX25 surface after being mixed with fs2.

According to Eq. (3) and latent heat values of PC, the inevitable loss ratios of H_m and H_f are 55.24% and 48.63%, respectively.

Although no liquid paraffin separated from the mixture after the addition of fs2, the inevitable loss of paraffin certainly occurred in the PCF system because of the identical fabrication conditions in

PCF and PC systems. Supposing that the value of the inevitable loss ratio in the PCF system is exactly the same as that in PC system, i.e. $L_i = 55.24\%$ for H_m and 48.63% for H_f , then the expected latent heat of PCF can be expressed as:

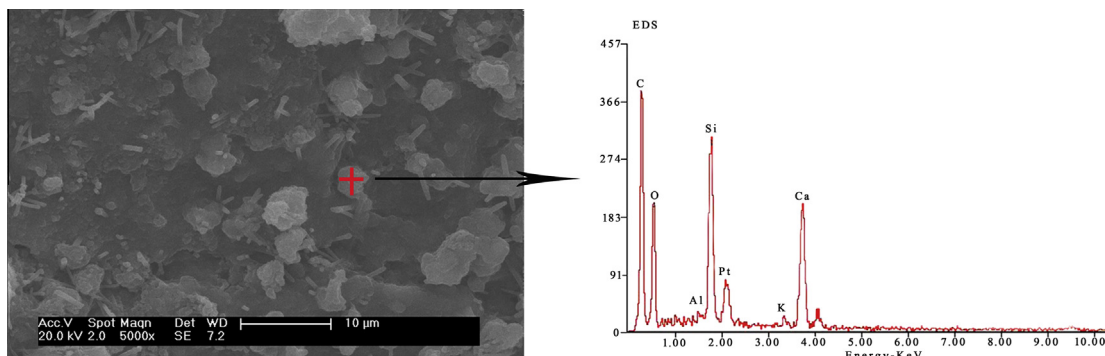
$$H_{E-PCF} = H_{PX25} \cdot \varphi_{PX25} \cdot (1 - L_i) \quad (4)$$

where H_{E-PCF} is the expected latent heat of PCF, kJ/kg.

According to Eq. (4), the expected values of H_m and H_f for PCF should be 10.42 kJ/kg and 12.27 kJ/kg, respectively. The measured values of H_m and H_f for PCF were in fact 13.44 kJ/kg, 14.20 kJ/kg, which is little higher than the expected values. In other words, the exuded paraffin was partially absorbed by the fs2. It can be concluded, therefore, that the addition of fs2 effectively reduced the paraffin loss during fabrication and increased the latent heat of the composites.

3.2.2. Investigation of mechanism

PX25 modified with hydrophobic fumed silica powders showed no leakage of paraffin during mixing with cement and water to produce thermal energy storage composites. Two possible reasons may contribute to the minimization of paraffin leakage. One is that the hydrophobic powder distributed uniformly on the surface of PX25 particles and then prevented the leakage of paraffin. The other is that the hydrophobic powder could not prevent the paraffin leakage and just absorbed the exuded paraffin. To verify these two assumptions and determine the mechanism for prevention of hydrophobic nano-silica powders, three experiments were performed. Firstly, PX25 particles and fs2 were uniformly mixed. SEM images showing the differences before and after the mixing are shown in Fig. 9. From comparison of Figs. 9(a) and (b), and 4(b), it can be observed that the fs2 was uniformly distributed on the surface of PX25 particles. Secondly, modifications after hardening of the PX25–cement–fs2 mixture were evaluated by means of SEM and energy-dispersive spectroscopy (EDS), as shown in Fig. 10. It can be seen from Fig. 10 that quantities of small particles were distributed on the substrate. The results show that these particles were rich in silica from EDS. It is difficult, however, to verify whether these particles are small PX25 or fs2-coated paraffin composite, because the PX25 is a type of silica-encapsulated composite

**Fig. 10.** SEM images and EDS analysis of hardening samples.

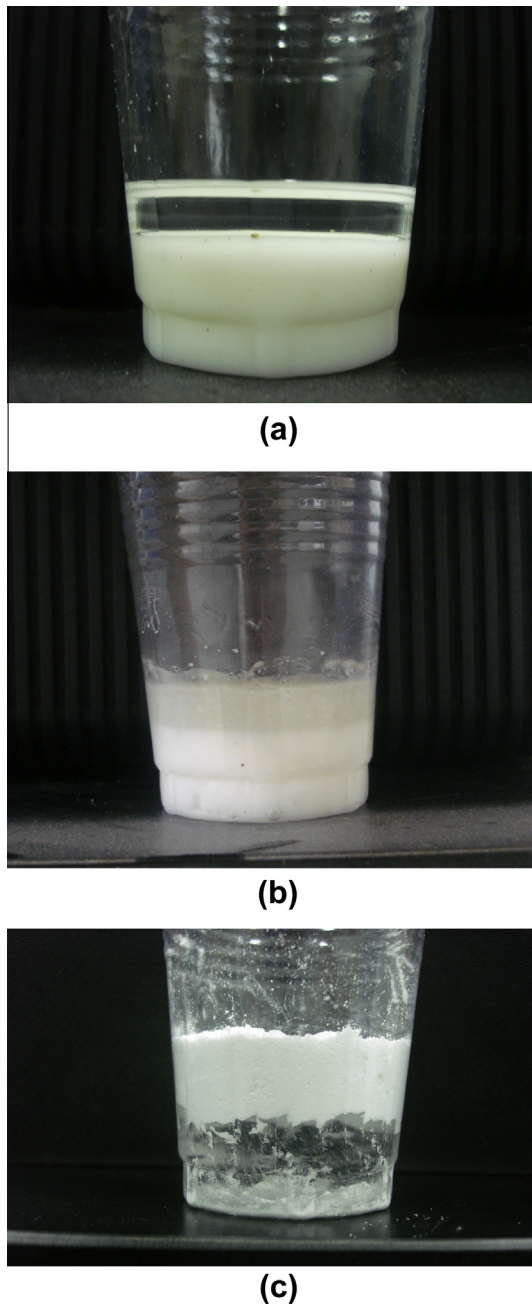


Fig. 11. Mixtures of water and PX25, PX25–fs2 and fs2 (a) mixture of water and PX25, (b) mixture of water and PX25–fs2 and (c) mixture of water and fs2.

PCM. Further work is needed to investigate the modification mechanism.

Finally, water was added into the PX25 and PX25–fs2 mixtures. Fig. 11 shows the mixtures after mixing uniformly. Fig. 11(a) shows the mixture of water and PX25. It is obvious that transparent paraffin has separated from the PX25 and floats on top of the mixture. The leakage ratio was 76%. However, transparent mucus as shown in Fig. 11(b) appears on top of the PX25–fs2 mixture during the mixing process. This mucus is mixture of paraffin and fs2. The amount of exuded paraffin was calculated from the amount difference between mucus and fs2. The calculated leakage ratio was 65%. It can be observed in Fig. 11(c) that the fs2 floated on the surface of the water when it was mixed with water. If fs2 can definitely change the surface state of PX25, PX25–fs2 powders could float on the water surface and no paraffin would separate to the top of the mixture. Obviously, paraffin leakage still occurred in

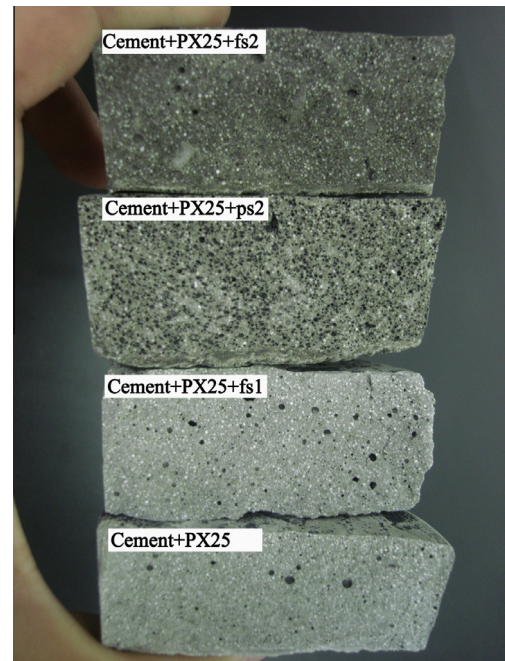


Fig. 12. Cross section of four samples.

Table 6

Mix proportion of different powders for compressive strength test.

Groups	Modifier (%)	PX25 (%)	Cement (%)	W/C	P/C
Non-modifier	0	30.0	70.0	1	0.43
fs1	3.0	29.0	68.0	1	0.43
fs2	0.7	29.8	69.5	1	0.43
ps2	3.0	29.0	68.0	1	0.43

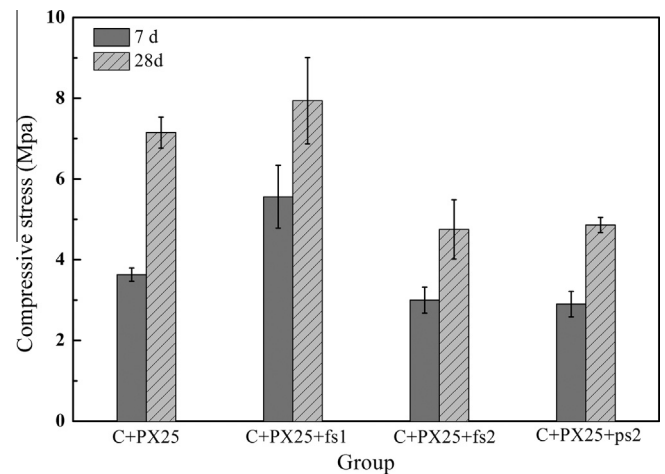


Fig. 13. Compressive strength of thermal energy storage composites at 7 and 28 days.

the PX25–fs2 mixture. As discussed above, it can be concluded that the addition of hydrophobic fumed silica could prevent the leakage of paraffin to a certain extent, but the major role of hydrophobic powder such as fumed silica was to absorb the paraffin after it had separated from PX25 particles.

3.3. Mechanical property testing of thermal energy storage composite

After the prevention testing of paraffin leakage, we broke the hardened samples shown in Figs. 5 and 7. The color difference on

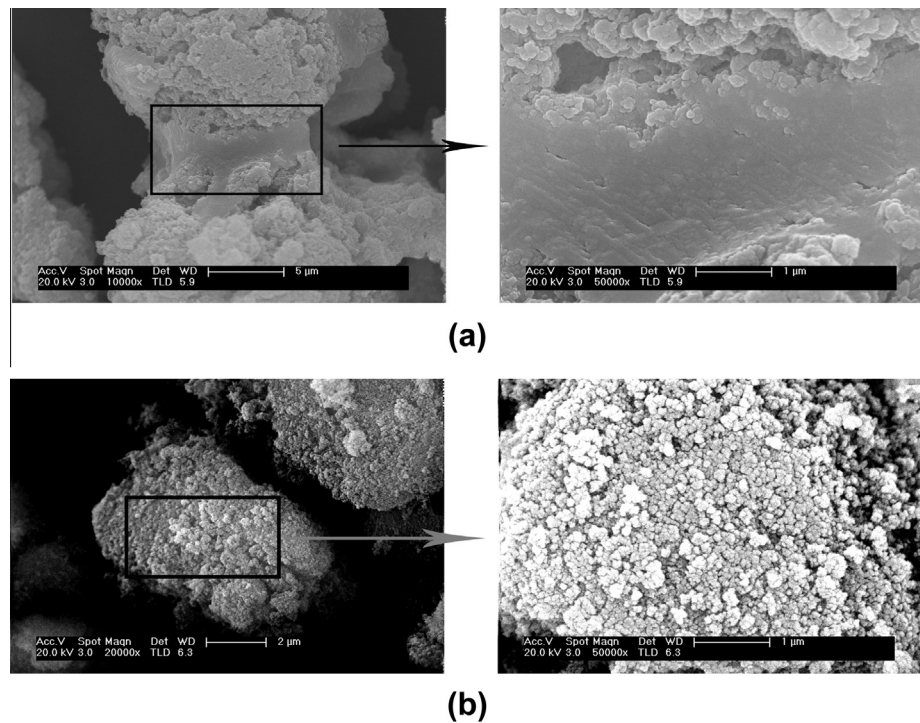


Fig. 14. SEM images of hydrophilic fumed silica immersed in different solutions for 7 days at 20 °C (a) SEM images of fs1 submerged in saturated Ca(OH)_2 solution for 7 days and (b) SEM images of fs1 submerged in distilled water for 7 days.

the cross-section of different samples can be observed easily, as shown in Fig. 12. The color of the samples was darkened by the addition of fs2 and ps2. This darkening could be attributed to a decrease in the degree of hydration of the cement caused by the addition of these two modifiers. To verify the above hypothesis, compressive strength testing was performed. The mix proportions of different powders are given in Table 6. As shown in Table 6, fs1, fs2, and ps2 were used as modifiers, and the replacement levels were 9.0%, 2.3%, and 9.0%, respectively, by weight of PX25–cement mixture. The water/cement (W/C) ratio and PX25/cement (P/C) ratios were 1 and 0.43, respectively. Fig. 13 presents the compressive strength of four groups at 7 and 28 days. As shown in Fig. 13, compressive strength reduced with the addition of fs2 or ps2, whereas it increased with the addition of fs1. When fs2 or ps2 were added, the strength reduction percentages at 7 days were 17.4% and 20.1%, respectively. The corresponding strength reduction percentages at 28 days were 33.6% and 32%, respectively. However, with the addition of fs1, the compressive strength increases were 53.2% at 7 days and 11% at 28 days.

The typical particle size of the modifier used in this experiment was much smaller than that of cement particles. The decreased compressive strength can be explained by the observation that the hydrophobic powders (fs2, ps2) and the absorbed paraffin were distributed on the surface of cement particles and slowed down the hydration process of the cement. In contrast, the hydration process of the cement could not be decelerated by the addition of hydrophilic particles. Meanwhile, these nano-silica particles might act as a potential reactive supplementary binder uniformly dispersed in the thermal energy storage composite. To verify the potential alkali-reactivity of these nano-particles, hydrophilic fumed silica was submerged in a saturated Ca(OH)_2 solution and distilled water for 7 days at 20 °C. Then its SEM images were analyzed as shown in Fig. 14. It can be seen in Fig. 14(a) that an amorphous substance formed on some regions of the nano-silica clusters in the sample submerged in saturated Ca(OH)_2 solution.

However, no change occurred in the fs1 after being submerged in distilled water, as shown in Fig. 13(b). As Ca(OH)_2 would be formed during the hydration process of cement, CSH gel might be formed by the chemical reaction of these nano-silica clusters with Ca(OH)_2 . As a consequence, the compressive strength would be increased by the addition of hydrophilic fumed silica.

4. Conclusions

Leakage of paraffin was prevented by mixing hydrophobic nano-powder modified PX25, cement, and water to produce thermal energy storage composites. The hydrophobic fumed silica functioned perfectly in preventing leakage of paraffin compared with precipitated silica. The mechanism of preventing PCM leakage is that hydrophobic nano-powders absorb most exuded paraffin rather than preventing PX25 contact with water during mixing. Because of the hydrophobization of hydrophobic materials, the compressive strength of thermal energy storage composites decreases with their addition. However, the addition of hydrophilic fumed silica could increase the compressive strength of thermal energy storage composites due to its potential chemical reaction activity when met calcium hydroxide released by hydration of Portland cement.

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低纤维掺量纤维混凝土的抗弯性能研究

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摘要: 采用四点弯曲试验对低纤维掺量的纤维混凝土进行测试时, 在软化段试验容易失稳, 因此, 寻求其他测试方法来解决这一问题显得十分必要。本文采用缺口梁试件的三点弯曲试验对两种低纤维掺量的混凝土的抗弯性能进行了研究。结果表明, 钢纤维混凝土的抗弯性能优于聚烯烃纤维混凝土, 但前者的抗弯性能离散度较高。此外, 对 midpoint 挠度和裂缝口张开位移关系的分析表明, 二者呈现较好的三线性关系。

关键词: 纤维混凝土, 韧性, 三点弯曲, 挠度, 裂缝口张开位移

Flexural Properties of Fiber Reinforced Concrete with Low Fiber Content

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Abstract: Conducting four point bending test on fiber reinforced concrete (FRC) beams with low fiber content has been observed to be unstable at the softening branch, so it is necessary to find other methods to solve this problem. This study investigated the flexural properties of two different FRCs with low fiber contents through three point bending test on notched beams. The results show that steel fiber reinforced concrete had higher flexural properties than polyolefin fiber reinforced concrete while the former exhibited much larger divergence in flexural properties over the latter. In addition, the relation between mid-span deflection and crack mouth opening displacement was discussed and a trilinear relationship was established.

Key Words: Fiber reinforced concrete, toughness, three point bending, deflection, crack mouth opening displacement

1 引言

混凝土材料的脆性和其强度密切相关。近年来, 随着高性能和高强混凝土的大力发展, 混凝土材料的脆性大幅增加。为解决这一问题, 在混凝土中加入一定量的纤维, 可以有效提高材料的阻裂能力及韧性。韧性作为评价纤维混凝土(FRC)的一个重要指标, 其主要的试验测试方法有单轴抗拉试验和弯曲试验。单轴抗拉试验操作起来较为困难, 对试验机和试件尺寸要求较高, 且试验的稳定性饱受争议。因此, 弯曲试验在表征 FRC 性能方面应用最为广泛, 且被很多标准所采用。ASTM C1018^[1]之前一直被广泛应用于 FRC 抗弯性能的评定, 然而由于该标准自身的许多缺点诸如难以准确判断初裂点的挠度值, 韧性指数对纤维种类和掺量不敏感等等, 于 2006 年被废除使用并由 ASTM C1609^[2]所取代。ASTM C1609 和 ASTM C1018 在试验方法上大致相同, 均为采用中点挠度进行控制的四点弯曲试验, 其主要区别在于不同的性能评价体系。采用挠度来进行试验控制的一个缺点是, 由于挠度和裂缝扩展方向相同, 因此对于纤维掺量较低的材料, 试验在软化段容易发生失稳^[3]。Banthia^[4]最近也指出, ASTM C1609 中规定的加载速度对于低纤维掺量的混凝土而言过高从而影响了试验的稳定性, 只有当初始加载速度大幅降低时(由 0.025–0.075 mm/min 降到 0.001–0.015 mm/min), 才能得到完整的软化段曲线。然而, 较低的加载速率使得整个试验耗时 60 到 75 分钟, 试验测试显得十分低效。

除了标准的试验方法外, 很多研究者^[5-7]采用缺口试件的三点弯曲试验来表征 FRC 的抗弯性能, 这一方法来源于对混凝土断裂性能的研究^[8]。该方法通常采用裂缝口张开位移(CMOD)来控制实验, 并同时记录试件在弯曲过程中的挠度变化, 通过荷载-挠度($P-\delta$)曲线下的面积来计算断裂能从而表征材料的韧性。由于 CMOD 与裂缝扩展方向相垂直, 且

其大小在测试过程中单调增加，因此该试验有很高的稳定性，即便对于普通混凝土，也可以获得完整的软化段曲线。据此，本文采用缺口试件的三点弯曲试验研究了低纤维掺量条件下 FRC 的力学行为，并讨论了试验过程中 *CMOD* 和挠度的关系。

2 试验概述

2.1 原材料及配合比

试验用水泥为 I 型硅酸盐水泥，粗集料为最大粒径 25 mm 的石灰石，细集料为天然河砂。粗集料和细集料的吸水率分别为 2% 和 1.85%，饱和面干状态下的比重分别为 2.59 和 2.67。试验采用了两种化学外加剂，分别为聚羧酸系高效减水剂（SP）以及引气剂（AEA）。试验选用了两种纤维，分别为波纹状钢纤维和聚烯烃纤维，其性能见表 1。

表 1 试验用纤维的性能
Table 1 Properties of fibers

	比重	长度 /mm	横截面	长径比	抗拉强度/ MPa	弹性模 量/GPa	纤维数 (根/kg)
波纹钢纤维	7.8	50	圆形，d=1.3 mm	38	1000	180	1,600
聚烯烃纤维	0.92	40	矩形，1.4×0.105 mm	90	620	9.5	185,000

本试验选取了五个配合比进行研究，分别为基准配比，纤维体积率（ V_f ）为 0.35% 的钢纤维混凝土，以及 V_f 为 0.2%，0.35% 以及 0.5% 的三组聚烯烃纤维混凝土，详细配比如表 2 所示。配比中控制水灰比在 0.3 左右，调整 SP 掺量使得新拌混凝土的坍落度在 150mm 左右，掺入适量 AEA 使得材料的含气量在 6% 左右。

表 2 配合比
Table 2 Mix proportions

	水泥 (kg/m ³)	集灰比		水灰比	化学外加剂与水泥 质量比 (%)		纤维体积率 (%)
		石灰石	砂		SP	AEA	
R	415	2.52	1.68	0.3	0.7	0.02	--
SF035	415	2.52	1.68	0.31	0.7	0.02	0.35
PF02	415	2.52	1.68	0.31	0.7	0.02	0.2
PF035	415	2.52	1.68	0.31	0.7	0.02	0.35
PF05	415	2.52	1.68	0.31	0.7	0.02	0.5

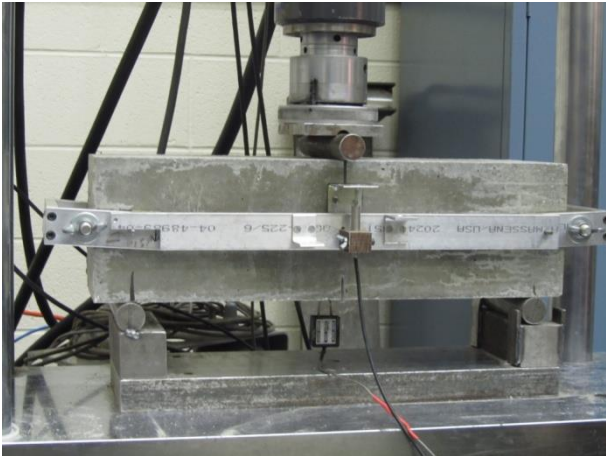


图 1 三点弯曲试验装置图
Figure1 Test setup for the three point bending test

2.2 成型及养护

材料的成型及养护按照 ASTM C192^[9]进行。每个配比成型三个直径 100 mm，高为 200

mm 的圆柱体试件测试抗压强度，三个 $150\text{ mm}\times 150\text{ mm}\times 525\text{ mm}$ 的小梁试件进行三点弯曲试验。所有的试件成型 1 天后拆模，然后标准养护至 28 天。

2.3 三点弯曲试验

在三点弯曲试验之前，采用手持式石材切割机在小梁试件底部中央预制一个深度为 25 mm，宽度为 3 mm 的缺口。试验采用吨位为 89 kN 的 MTS 试验机进行测试，支撑点之间的跨距为试件高度的 3 倍即 450mm，整个试验的装置如图 1 所示。图中夹式引伸计悬挂于预先粘结在试件底部的两个刀片上面，用于测量 *CMOD*。LVDT（Linear Variable Differential Transformer）安装在固定于试件中高处的一个铝制框架上，用于准确量取试件挠度。夹式引伸计的测量范围为 4 mm，标距为 10 mm，LVDT 的测量范围为 5 mm。

整个测试采用 *CMOD* 控制试验，在 *CMOD* 达到 0.2 mm 之前，测试速率为 0.025 mm/min，之后每隔 30 s 测试速率翻倍直至测试速率达到 0.8 mm/min。试验过程中由于操作失误，配比 PF05 的一个试件发生破坏，因此只有两个有效数据。

3 试验结果和分析

3.1 抗压性能

材料的抗压强度见表 3。基准配比的强度高于 FRC，这可能是由于纤维的加入在材料内部引入了一定的缺陷，比如纤维和基体之间的过渡区。钢纤维混凝土的强度和基准相比降低了 17%，且和相同 V_f 的聚烯烃混凝土的强度相当。聚烯烃混凝土的强度随着 V_f 的增加而降低。

表 3 各配比的 28 天抗压强度值
Table 3 Compressive strength results at 28 days

28 天抗压强度 (MPa)	
R	62.8±0.68
SF035	52±1.10
PF02	58.4±1.63
PF035	53.4±1.16
PF05	48.3±1.35

3.2 抗弯性能

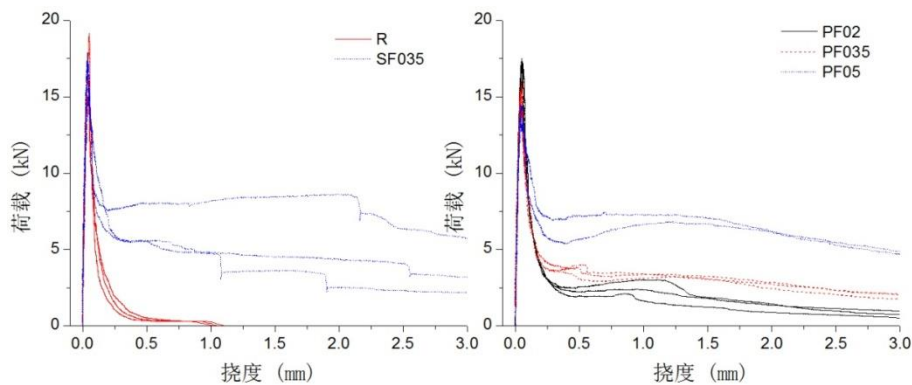


图 2 各配比的荷载 - 挠度曲线
Figure2 Load-deflection diagrams for all the mixes

各配比 28 天龄期时的 $P-\delta$ 曲线如图 2 所示。基准混凝土在 $\delta=1\text{ mm}$ 左右荷载趋近于 0，而 FRC 具有较长的软化段，在较大挠度处依然能够承受一定的荷载。基准混凝土不同试件的软化曲线较为接近，而 FRC 的软化曲线和纤维种类有关。对于钢纤维混凝土，不同试件的软化曲线差异较大，而聚烯烃混凝土在相同 V_f 下软化曲线十分接近。由于各配比的混凝土基体相同，因此这种差异可能和纤维在混凝土内部的分布状况有关。图 3 给出了试件断裂后断裂面的纤维分布情况，从图中可以看出，钢纤维混凝土试件断裂面上纤维分布十分不均匀，且不同试件断裂面的纤维总数存在较大差异，而聚烯烃混凝土试件断裂面上纤维分布相

对较为均匀。表 1 中根据单根纤维尺寸特征, 给出了单位质量下两种纤维的根数, 可以看出聚烯烃纤维的数目高出钢纤维两个数量级, 考虑到两种纤维的密度差异, 相同 V_f 下聚烯烃纤维的数目依然是钢纤维数目的十多倍。因此可以看出, 足够的纤维数目是保证纤维在基体内部均匀分散从而获得稳定力学性能的重要前提。

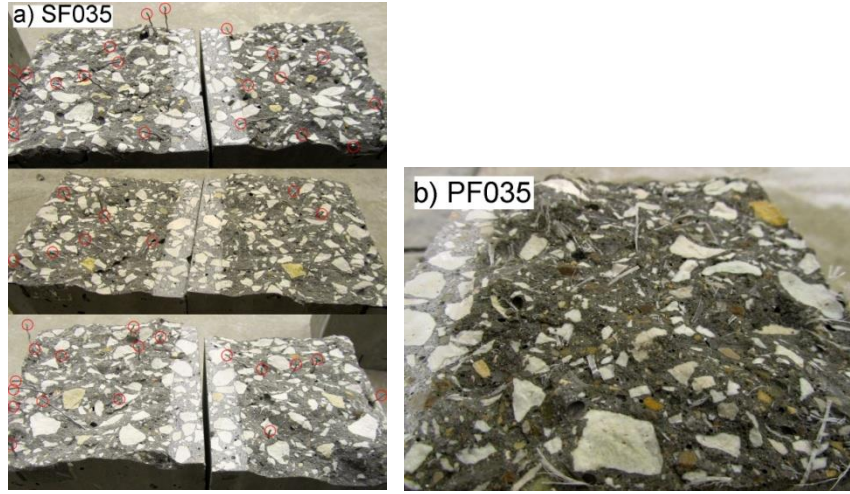


图 3 断裂面纤维分布: a) SF035 (钢纤维由红圈标出), b) PF035
Figure3 Fiber distributions on fracture surfaces of SF035 (a) and PF035 (b)

表 4 给出了各配比混凝土的抗弯性能。断裂能依据 RILEM TC 50-FMC^[10]进行计算, 即 $P-\delta$ 曲线下的面积与初始韧带面积的比值。从结构设计的角度来讲, $\delta \leq 3 \text{ mm}$ 时的断裂能较为重要^[7], 因此本文只给出了 $\delta=3 \text{ mm}$ 时的断裂能 $G_{F,3\text{mm}}$ 以及残余荷载 $P_{R,3\text{mm}}$ 。从表中可以看出, 掺加 0.35% 的钢纤维以及 0.2% 的聚烯烃纤维并未降低试件的峰值荷载, 这和之前纤维对材料抗压强度的影响有所不同。对聚烯烃纤维混凝土而言, 试件的峰值荷载随着 V_f 的增加而降低。由于钢纤维混凝土软化段曲线较为离散, 而聚烯烃纤维混凝土软化段曲线较为接近, 因此前者的断裂能和残余荷载的离散程度远大于后者。例如, SF035 的残余荷载和断裂能的变异系数分别为 50% 和 35%, 而 PF035 在这方面只有 8.3% 和 4.4%。SF035 的残余荷载高于 PF035, 主要是由于钢纤维具有较高的强度和弹模。此外, 在材料破坏过程中钢纤维主要是拔出破坏, 消耗较多能量, 而聚烯烃纤维主要为断裂破坏, 能量耗散较少, 因此 SF035 的断裂能亦高于 PF035。当聚烯烃纤维掺量从 0.2% 增加到 0.35% 时, 材料的性能增幅不大, 然而当继续增加至 0.5% 时, 残余荷载和断裂能分别大幅增加了 148% 和 92%。

表 4 各配合的抗弯性能
Table 4 Results of Flexural properties

	R	SF035	PF02	PF035	PF05
$P_{\max}$, kN	16.85 (2.07)	16.91 (1.19)	17.14 (0.12)	15.67 (0.33)	14.17 (0.56)
$P_{R,3\text{mm}}$, kN	--	3.71 (1.84)	0.75 (0.22)	1.93 (0.16)	4.78 (0.14)
$G_{F,3\text{mm}}$, N/m	111.6 (11.93)	902.1 (313.95)	367 (45.96)	540.4 (23.88)	1036.6 (58.48)

注: 括号中所列数值为标准差

3.3 中点挠度和裂缝口张开位移的关系

各配比 28 天时的 $P-CMOD$ 曲线如图 4 所示。对比图 2 和图 4, 发现二者十分相似, 这表明 δ 和 $CMOD$ 之间存在着一定联系。为了研究二者之间的关系, 图 5 给出了配比 R 和 PF02 的 $\delta-CMOD$ 关系图, 并同时给出了相应的 $P-CMOD$ 曲线。从软化段曲线可以看出, 荷载首先急剧下降, 到一定值后稳定缓慢地继续降低, 这一过程可以通过一个双线性软化模型进行简化, 模型中的斜率变化点称之为断裂点。在断裂点处, 裂缝扩展至试件上表面, 基体丧失大部分承载能力, 而对于 FRC, 纤维开始承受荷载。基于此, 我们可以把 $\delta-CMOD$ 关系图进行以下划分。在加载的线弹性阶段, δ 和 $CMOD$ 之间呈现线性关系, 之后随着微裂纹的

生成和扩展, δ - $CMOD$ 曲线的斜率逐渐降低, 在峰值荷载处, 宏观裂纹在缺口处形成并开始向试件上表面扩展。由于 δ 与 $CMOD$ 的比值与裂纹长度有关^[11], 因此在断裂点前后, δ 与 $CMOD$ 的比值应当有所差异。断裂点后 δ - $CMOD$ 存在明显的线性关系, 而在断裂点前, 从图中可以看出, 二者也近乎线性关系。因此, 不考虑峰值荷载前的一小段非线性过渡区, 可以近似的用三线性模型来描述 δ 和 $CMOD$ 之间的关系, 如图 5 中的 k_1 , k_2 和 k_3 所示。

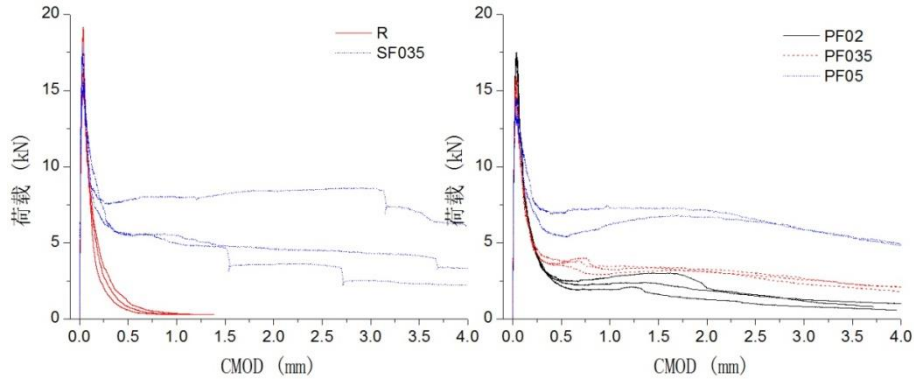


图 4 各配比的荷载- $CMOD$ 曲线
Figure4 Load- $CMOD$ diagrams for all the mixes

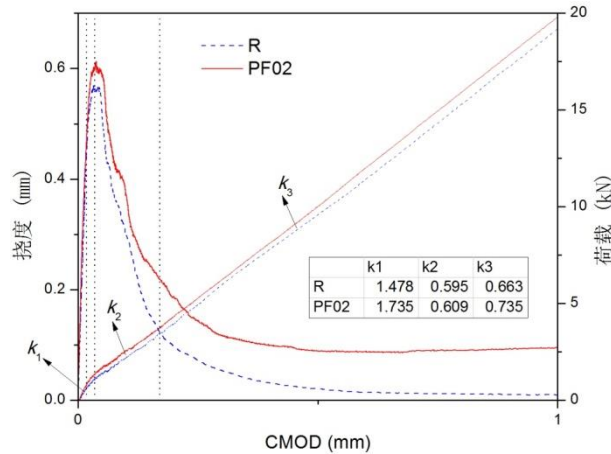


图 5 配比 R 和 PF02 的荷载- $CMOD$ 曲线及挠度- $CMOD$ 曲线
Figure5 Load- $CMOD$ and deflection- $CMOD$ diagrams for R and PF02

基于 δ 和 $CMOD$ 之间的三线性模型, 表 5 给出了各配比的拟合结果。可以看出, k_1 远大于 k_2 和 k_3 , k_1 值分布在 1.5 和 1.9 之间, k_2 和 k_3 分别为 0.6 和 0.7 左右。基准配比在各个阶段的斜率值均小于 FRC, 这种差异在线弹性阶段难以解释, 然而在试件开裂后, 纤维的阻裂作用可能使得相同挠度下 FRC 的 $CMOD$ 值小于基准, 从而提高了 δ 与 $CMOD$ 的比值。纤维种类以及纤维掺量对各阶段的斜率值没有明显影响。

表 5 基于挠度和 $CMOD$ 之间三段线性关系的拟合结果

Table 5 Fitted results based on the trilinear relationship between deflection and $CMOD$

	R	SF035	PF02	PF035	PF05
k_1	1.643 (0.182)	1.811 (0.156)	1.796 (0.121)	1.761 (0.121)	1.795 (0.084)
k_2	0.574 (0.019)	0.585 (0.016)	0.611 (0.003)	0.657 (0.003)	0.605 (0.025)
k_3	0.668 (0.006)	0.710 (0.015)	0.726 (0.008)	0.720 (0.011)	0.720 (0.017)

注: 括号中所列数值为标准差

4 结论

本文采用缺口梁试件的三点弯曲试验, 研究了在纤维掺量较低的前提下, 钢纤维和聚烯

纤维混凝土的抗弯性能。试验证明了该测试方法相比挠度控制的四点弯曲试验,具有较高的稳定性。钢纤维混凝土相比聚烯烃纤维混凝土具有更优异的抗弯性能,然而由于纤维掺量较低,钢纤维在混凝土中的分布较不均匀,从而造成不同试件的抗弯性能差异较大,这不利于其在工程中的应用。此外,本文分析得出三点弯曲试验中挠度和 *CMOD* 存在简单的三段线性关系,这有助于简化试验装置,采用 *P-CMOD* 曲线直接对材料的抗弯性能进行研究。

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Effect of reserved texture on mechanical properties of cold drawn pearlitic steel wire

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Keywords: pearlitic wire, texture, cold drawn

Abstract: In this paper, pearlitic steel wire with/without reserved texture were investigated with the help of mechanical test system, scanning electron microscope (SEM) and XRD. Experimental result shows that: Tensile strength of two wire are almost same. After cold drawn tensile strength of wire with reserved texture are higher than tensile strength of the without one. Before cold drawn, two wires have same microstructure of isometric pearlite and after drawing the wire with reserved texture has less shear deformed pearlitic colony. Intensity of $\langle 110 \rangle$ fiber texture in the wire with reserved texture are stronger than the without one at all strains. The stronger $\langle 110 \rangle$ texture mean the orientation of α -ferrite lamella were more closely and improve working hardening rate of pearlitic wire.

1.Introduction

High strength steel wire was widely used in many fields, such as wire rope, tire cord, springs and suspension bridge cable[1]. Relative research[2-5] on deformation pearlitic wire focused on controlling microstructure to improve the tensile strength of steel wire have achieved a great deal of success that it have reported the tensile strength of cold drawn pearlitic steel wire have achieved 6.3GPa. Evolution of texture during drawing was also widely investigated[6,7] but there were no research on how the texture affect mechanical properties of steel wire. Recent studies[8,9], texture of α -ferrite in cold drawn steel should be reserved after austenite heat treatment. How is the effect of reserved texture on the cold drawing process should be focus on.

In this paper, deformed pearlitic steel wires with/without reserved texture was investigated. Effect of reserved texture on mechanical properties of cold drawn wire was discussed.

2.Experimental procedure

Pearlitic steel wires used were produced by Sha-steel Group Company, PR China. The chemical composition of the wires were shown in Table1.

Table 1 Composition analysis of experimental steels (wt%)

C	Si	Mn	Cr	V	S	Fe
0.83	0.3	0.71	0.19	0.07	0.003	Bal.

After pickling and phosphating[10], hot-rolled wire rods (12mm and 5.5mm diameter) were successively drawn to a diameter of 5.1 mm with a total reduction of 82% and 14% (ie., $\epsilon=1.7$ and 0.15).

Heat treatment of deformed wires were carried out in salt bath of 950°C for 5 min, Wires were put into salt bath of 550°C for 5 min at once. After in salt bath wires were cold in air to room temperature. After treatment, the wire drawn from 12mm have reserved texture and wire from 5.5mm have no reserved texture.

Tensile strength of this wires were tested by using a universal testing machine. This test were operating at a constant speed of 2 mm/min. Evolution of microstructure of cold drawn wires was examined using a FEI Siron-400 scanning electron microscope (SEM). Texture tested were used D-Max 2000 to test three pole figures calculated to integral pole figure. Using integral pole figure to calculate the intensity of $\langle 110 \rangle$ fiber texture.

3. Results and discussion

3.1 Mechanical properties The tensile strength of wires as a function of true strain was presented in figure 1.

Tensile strength of wires increase with the increase of true strain from 0 to 3. Before drawing, this two steel wires with/without different reserved texture have almost same tensile strength. After cold drawing, tensile strength of steel wire with reserved texture are higher than the without one. Reserved texture improve working hardening rate of pearlitic wire.

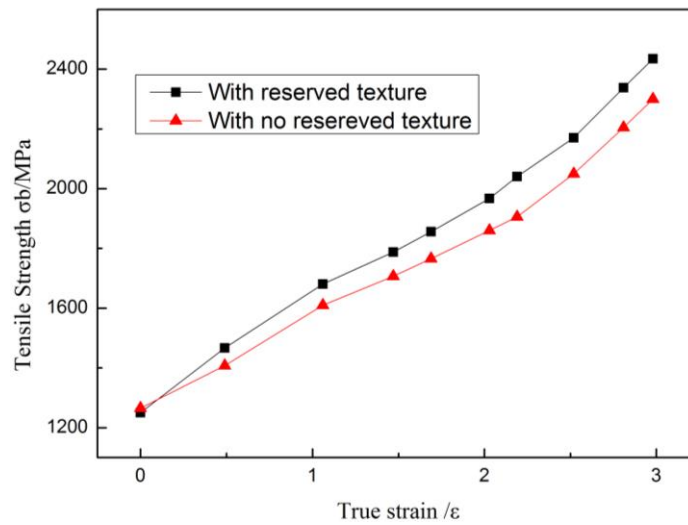
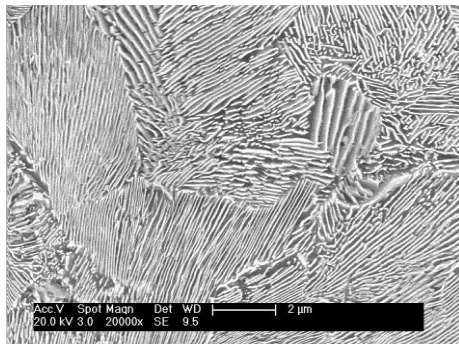


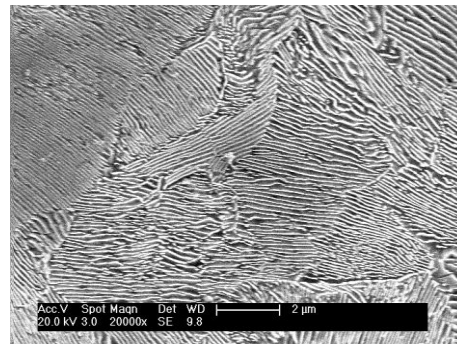
Fig.1. Relationship between tensile strength and true strain of two wires

3.2 Microstructure evolution Wires were observed from the longitudinal section as figure 2. Figure 2a,2b show before drawing, both of the two pearlitic wires' microstructure are same isometric pearlite. Lamellae of ferrite and cementite is complete and parallel to each other in one colony.

After drawing pearlitic lamella of wires thinned and rotated to be parallel to drawing direction. Pearlite have turned into fibrous microstructure after heavily drawing. Comparing microstructure of wires with and without reserved texture, as figure 2c and 2d show there were no visible different when at $\epsilon=0.5$. There were more cementite lamella bent or fractured in wire without reserved texture than with one as figure 2e, 2f, 2g and 2h.



(a) $\epsilon=0$



(b) $\epsilon=0$

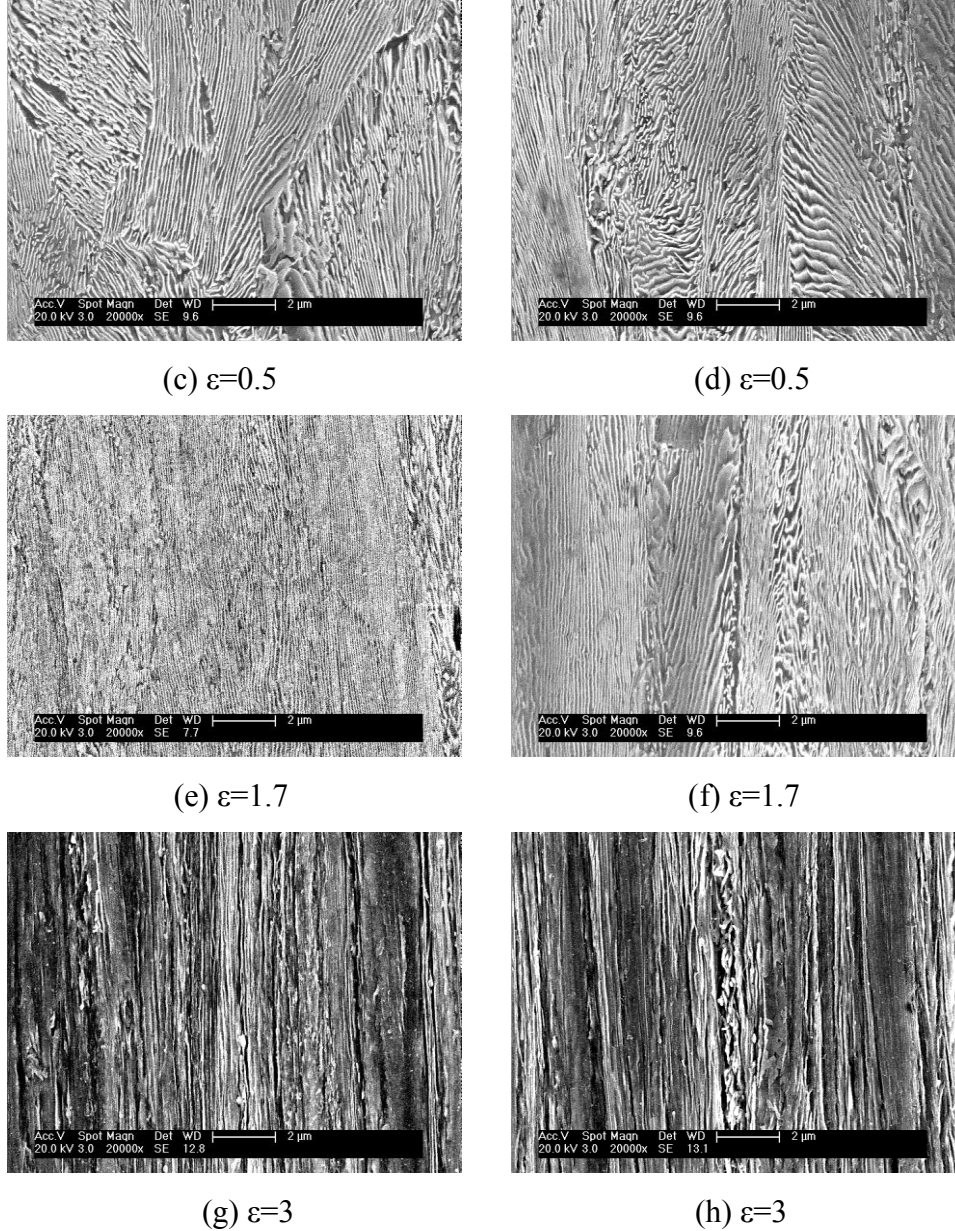


Fig.2 Microstructure of steel wires after cold drawing 1st column: with reserved texture 2nd column: without reserved texture

3.3 Texture analysis Change of intensity of $\langle 110 \rangle$ texture in two wires were shown in figure 3. Figure 3 shows that intensity of $\langle 110 \rangle$ texture of wires increase with the increase of true strain from 0 to 1.69. Intensity of $\langle 110 \rangle$ texture of wire with reserved texture is higher than the without one. The evolution of α -ferrite's texture in the two wires drawn to different strains was measured by using inverse pole figure measured in the drawn direction corresponding to the true strain of 0,0.49,0.93,1.69 as shown in figure 4. Comparing inverse pole figure of two wires, the α -ferrite's orientation in wire with reserved texture turn into $\langle 110 \rangle$ pole more quickly.

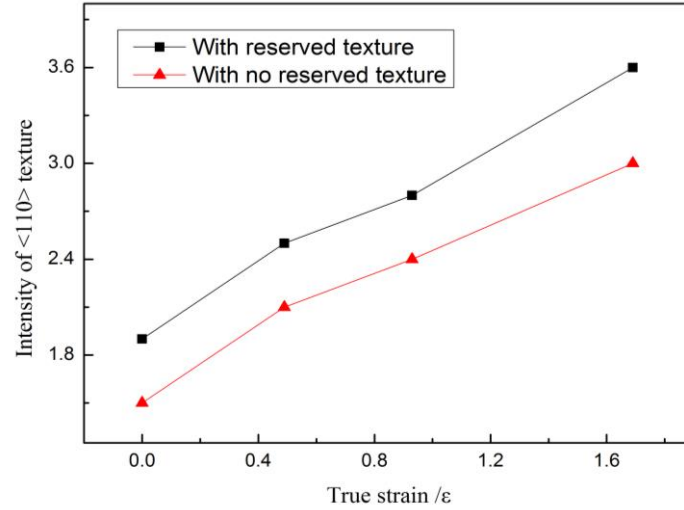


Fig.3. Relationship between textural intensity and true strain of two wires

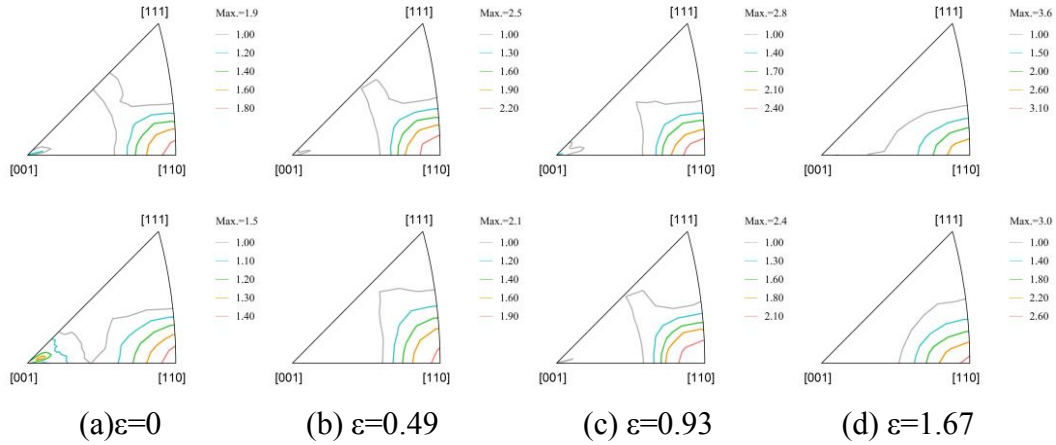


Fig.4 Inverse pole figure of two wires in different strains. The first line is the wire with reserved texture and second line is the wire with no reserved texture

3.4 Discussion Reserved texture improve working hardening rate of pearlitic wire. Intensity of $\langle 110 \rangle$ texture in wire with reserved texture are stronger than the without one at all strain. Studies[3,6,11-12] have demonstrated that closely orientation of pearlite improve the mechanical properties. Microstructure of pearlite is composite structures of two phase: α -fe and cementite. Deformation of this two phase are more closely to composite materials of laminate structure. α -fe(soft phase) deform more than cementite(hard phase) when deformation was not heavily. If α -fe's $\langle 110 \rangle$ orientation were not in or near to the drawing direction the pearlitic colony must rotate to the direction. When α -fe's $\langle 110 \rangle$ orientation were nearly perpendicular to the drawing direction rotation will be difficulty, pearlitic colony were subjected high shear stresses. Cementite lamellae may bent or fracture. Fractured cementite cause stress concentration and become micro-crack resource when wire was subjected stresses.

Reserved texture make intensity of $\langle 110 \rangle$ fiber texture higher during drawing. Higher $\langle 110 \rangle$ textural intensity means there are more pearlitic α -fe's $\langle 110 \rangle$ orientation are closely to drawing direction. Less pearlite need rotate to deform, less cementite lamellae may bent or fracture and more pearlite may get thinning. It reduce shear deformation and improve the hard working rate of pearlitic wire.

4.Conclusion

1) Reserved $\langle 110 \rangle$ texture improve working hardening rate of pearlitic wire. After drawing, tensile strength of wire with reserved texture are higher than the without one at all strains.

2) Intensity of $\langle 110 \rangle$ texture of wire with reserved texture is higher than wire without reserved texture at all strains. It indicated orientation of pearlite near to drawing direction and reduce shear deformation of pearlite.

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奥氏体化热处理后珠光体钢丝织构再分布

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摘要: 采用电子背散射衍射技术 (EBSD) 对冷拔钢丝的组织及奥氏体化热处理后钢丝的组织状况进行了测试, 并结合扫描电镜研究组织形貌变化, 探讨冷拔钢丝奥氏体化后的组织状况。结果表明: 拉拔形变钢丝中珠光体片层转向平行于拉拔轴向, 形成<110>丝织构, 并随应变量的上升织构强度上升。拉拔钢丝奥氏体化热处理后得到等轴状珠光体组织有一定的<110>丝织构, 织构强度随原应变变量增大而上升。

关键词: 珠光体钢丝; 组织; EBSD; 奥氏体化热处理

Effect of austenitizing on texture redistribution of cold drawn pearlitic steel wire

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Abstract: To investigate the effect of austenitizing on texture redistribution of cold drawn pearlitic steel wire. SEM(scanning electron microscopy) and EBSD(electron backscatter diffraction) were used to research the microstructure and texture of as-drawn and annealed steel wires. The result showed that the lamellar of as-drawn pearlite steel wire steered to the drawing axis, forming <110> fiber texture, and the intensity of texture rose with the strain. After heat treatment, the wire had a microstructure of equiaxed pearlite which contains <110> fiber texture in the ferrite. And the intensity of the texture rose with the rising of the original strain.

Key words: pearlitic steel wire; texture; EBSD; austenitizing heat treatment

冷拔珠光体钢丝因具有高强度而广泛应用于汽车轮胎用钢帘线, 晶圆切割丝等领域^[1-2], 此类钢丝在冷拔达到一定尺寸时, 因为加工硬化程度深, 塑性变形困难, 需要进行完全奥氏体化热处理恢复等轴状珠光体组织, 恢复钢丝塑形, 以继续冷拉拔变形。珠光体钢丝随着冷拉拔的进行, 应变变量不断增大, 强度不断升高, 组织形貌由等轴状珠光体团变成纤维状组织, 同时, 钢丝中铁素体产生明显的<110>丝织构^[3-5]。对于钢丝中组织形貌的研究广泛, 织构对于钢丝力学性能的影响也已经受到广泛关注^[6-7]。现有的研究集中在冷拉拔过程中铁素体产生的<110>丝织构, 而对于钢丝奥氏体化热处理后恢复等轴状的珠光体钢丝中铁素体的组织状况研究尚未涉足。本文以形变珠光体钢丝奥氏体化热处理过程

中织构变化为研究对象, 探究了奥氏体化热处理后珠光体钢丝的组织状况。

1 实验材料与方法

实验材料为江苏省沙钢集团生产的 SWRS82B 盘条, 冷拉拔成不同应变量的钢丝。其主要添加合金元素成分如表 1 所示, 不同试样规格如表 2 所示。

表 1 实验材料的主要化学成分 (wt%)

C	Si	Mn	S	P	Cu	Fe
0.83	0.22	0.73	0.005	0.015	0.01	余量

表 2 钢丝试样信息

试样编号	直径/mm	累计应变变量	形变量%
1	7.15	1.04	64.5
2	5.5	1.56	79.0
3	4.5	1.96	85.9
4	4.0	2.20	88.9

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钢丝试样的热处理过程均为先在 850 °C 保温 10 min 奥氏体化处理, 后于 550 °C 盐浴等温淬火 5 min 后空冷。热处理完成后截取纵截面样品机械抛光后用 4% 硝酸酒精溶液腐蚀, 以进行 SEM 组织观察。电子背散射衍射 (EBSD) 样品用 5% 高氯酸酒精溶液电解抛光 (电压 40 V, 电流 0.8 A, 时间为 20 s)。试验数据采集使用 Sirion 场发射扫描电镜及 EDAX-TSL 公司的电子背散射衍射系统。EBSD 信息采集时取钢丝纵截面直径中心处, 区域大小约为 200 μm × 250 μm , 步长约 0.2 μm , 试验数据分析采用 TSL 公司的 OIM-Analysis 软件。

2 实验结果与分析

2.1 冷拔钢丝组织形貌与组织

图 1 是冷拔钢丝纵截面组织图片与织构信息图, 由图 1 (a) (b) 可知, 未经拉拔的盘条组织为等轴状的珠光体, 随着应变量的增加, 珠光体组织沿轴向拉长, 在大应变下呈纤维状。由图 1 (c) (d) 可知, 随着钢丝不断拉拔变形, 钢丝中铁素体取向向 $\langle 110 \rangle$ 集中, $\langle 110 \rangle$ 织构强度由盘条时的 1.3 上升到应变量为 2.2 时的 7.6。由图 1 (e) (f) 可知在大应变下, 铁素体取向集中在 $\langle 110 \rangle$ 方向, $\{001\}\langle 110 \rangle$ 、 $\{110\}\langle 110 \rangle$ 及 $\{111\}\langle 110 \rangle$ 丝织构明显。

体心立方金属的拉伸变形, 开动的滑移系主要是 $\{110\}\langle 111 \rangle$, 钢丝的拉拔过程中, 晶体的 $\langle 110 \rangle$ 方向转到力轴方向。因此拉拔变形钢丝产生 $\langle 110 \rangle$ 丝织构。

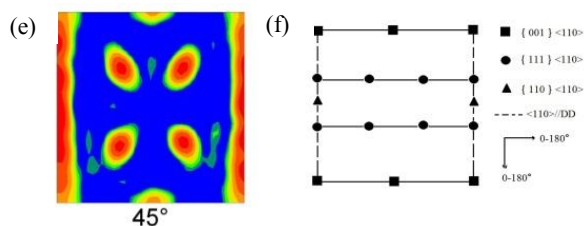
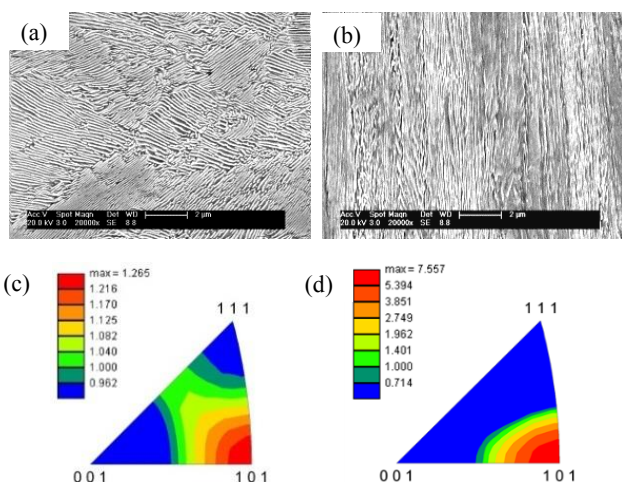


图 1 不同应变钢丝组织 SEM 及织构图片

(a) (b) 分别为应变量为 0 及 2.2 样品纵截面 SEM 组织图片; (c) (d) 分别为应变量为 0 及 2.2 样品织构反极图; (e) (f) 为应变量 2.2 钢丝样品 45° ODF 图及其解析图

2.2 热处理后钢丝的组织形貌

图 2 为不同应变钢丝样品热处理后得到的组织图片, 从图中可以看到, 经过热处理后, 钢丝组织均为等轴状珠光体。经统计, 各样品的珠光体片层间距相近。

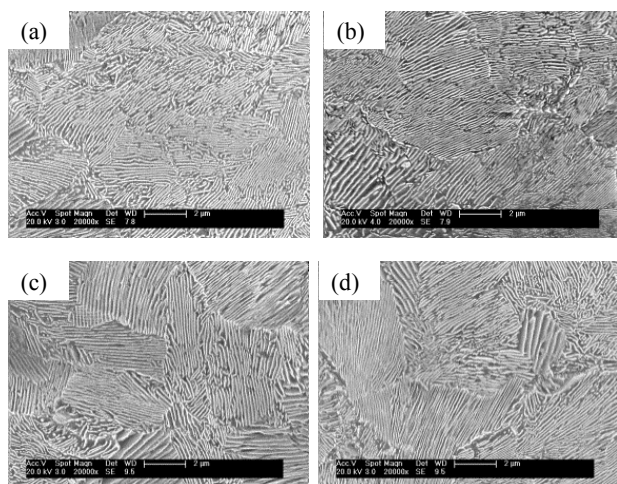


图 2 不同钢丝样品热处理后纵截面组织 SEM 图片

(a) $\epsilon=1.04$; (b) $\epsilon=1.56$; (c) $\epsilon=1.96$; (d) $\epsilon=2.2$

2.3 热处理后织构的再分布

图 3 为经热处理后, 不同应变钢丝试样的铁素体织构图。从图 (a) 可以看到, 热处理后得到的珠光体组织中铁素体 $\langle 110 \rangle$ 织构强度明显下降, 钢丝原始应变量越大, 热处理后, $\langle 110 \rangle$ 织构强度越大。从图 (b) (c) 可以看到, 热处理后, 铁素体中 $\{001\}\langle 110 \rangle$ 、 $\{110\}\langle 110 \rangle$ 及 $\{111\}\langle 110 \rangle$ 织构均有部分保留。

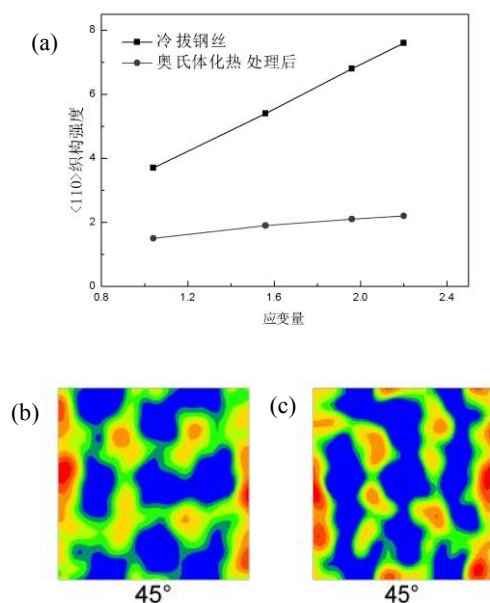


图3 不同应变钢丝热处理后织构图
(a) 织构强度-应变趋势图; (b) (c) 应变1.04及2.2
钢丝样品热处理后45°ODF图

2.4 热处理后织构分析

对形变钢丝进行奥氏体化热处理, 铁素体经 $\alpha \rightarrow \gamma \rightarrow \alpha$ 的固态相变之后, 冷拔形变产生的铁素体<110>丝织构强度明显下降, 但没有完全消失, 在热处理后的珠光体中得以部分保留。现有的理论研究^[8-13]表明: 在珠光体 $\rightarrow$ 奥氏体的相变过程中: 为了降低新相形核的表面能, 奥氏体与铁素体之间的取向关系服从K-S关系: $\{011\}\alpha // \{111\}\gamma$; $\langle 111 \rangle \alpha // \langle 101 \rangle \gamma$, 故在珠光体 $\rightarrow$ 奥氏体转变后, 珠光体中的织构部分保留到奥氏体中。在奥氏体-珠光体相变时, 新相珠光体中渗碳体与奥氏体间, 渗碳体与铁素体间也存在特定的位相关系^[14], 故在珠光体 $\rightarrow$ 奥氏体 $\rightarrow$ 珠光体的相变过程中, 原珠光体中的织构以特定的位相关系部分保留到新的珠光体中。

G. Gottstein^[10-12], T. Tomida 等人^[13]在研究低碳钢的轧制织构时, 通过理论分析与计算板织构经过相同的相变过程, 同样会出现织构部分保留的情况, T. Tomida 提出当新相产生在两个取向相近的母相晶界上时, 织构会有较多的保留。本实验中, 原应变更大的冷拔钢丝织构更强, 取向更接近, 因此在热处理保留的织构更多, 即原应变越大, 在热处理后, <110>织构强度越大。

3 结论

1)冷拔珠光体钢丝中珠光体片层转向平行于拉拔轴向, 形成<110>丝织构, 并随应变量的上升织构强度上升。

2)经奥氏体化热处理后, 钢丝样品组织为等轴状珠光体, 形变钢丝的<110>织构部分保留。钢丝原应变越大, 热处理后样品<110>织构强度越高。

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石墨烯晶畴的常压化学气相沉积法制备及其生长机理研究

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摘要: 常压下, 尺寸为 10 μm 的六边形高质量石墨烯晶畴制备了出来, 并系统研究了生长混气比、生长时间以及铜箔表面质量对石墨烯晶畴形貌和尺寸的影响。实验发现石墨烯晶畴的形貌受 CH_4/H_2 混气比影响最大, 混气比在 1:75 到 1:100 范围内可以制备出六边形石墨烯晶畴。随着生长时间的增加, 六边形石墨烯晶畴尺寸逐渐增大, 且厚度也在增加。铜箔表面粗糙度越小, 石墨烯晶畴的尺寸越大, 形貌越规整, 分布也越均匀。六边形石墨烯晶畴的生长遵循边缘扩散机制。大尺寸石墨烯晶畴的制备需要较低的甲烷浓度、较高的温度以及较长的生长时间。

关键词: 石墨烯晶畴; 生长机理; 常压化学气相沉积法

Study of preparation and growth mechanism of graphene domains at atmospheric chemical vapor deposition method

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Abstract: High-quality hexagonal graphene domains with the lateral size around 10 μm were successfully prepared by an atmospheric pressure chemical vapor deposition. The effects of hydrogen flux rate, growth time and quality of copper foil on the morphology, size and quality of graphene domains were systematically investigated. We found that the formation and growth of hexagonal graphene domains was very sensitive to the hydrogen flux rate, and hexagonal domains were obtained when the ratio of methane to hydrogen changed from 1:75 to 1:100. With the increase of growth time, the lateral size and thickness of hexagonal graphene domains are increased. In terms of the purity and crystallinity of the graphene, the high surface smoothness of the copper foil showed an appreciable improvement in the quality of the graphene domains. The growth mechanism of single layer hexagonal graphene domains could be attributed to the edge diffusion mechanism. Preparation of large scale graphene domains needs low methane concentration, high temperature and long growth time.

Key words: graphene domains; growth mechanism; atmospheric chemical vapor deposition

1 引言:

石墨烯具有优异的物理性能^[1-5], 包括纳米级别的厚度、超高的室温电子迁移率、良好的透光性能, 使其在电子器件、触摸屏^[6-8]等领域有着巨大的潜在应用价值。自从 2004 年 Geim^[9]课题组通过微机械剥离法制备出石墨烯以来, 引起了学术界和工业界的

广泛关注。初期，石墨烯是通过微机械剥离法制备出来的，尺寸只有几十微米，产量小，只能用于理论研究。为了实现石墨烯的大规模工业化生产，各种各样的制备方法逐步发展起来，其中化学气相沉积法是最具有希望实现石墨烯薄膜产业化生产的方法。2009年，Li^[10]等通过化学气相沉积法第一次在铜箔基底上制备了单层大尺寸石墨烯薄膜，由于铜箔基底较低的碳溶解度和便宜的价格，使得铜箔成为了最受关注的催化基底。自此以后，石墨烯制备领域发展迅速。石墨烯薄膜是由大量的晶畴组成的，导电性受晶界数量的影响严重。晶畴尺寸越小，晶界数量越多，石墨烯载流子的散射就越严重，因此提高晶畴尺寸可以减少晶界数量，进而提高石墨烯薄膜的导电性。

石墨烯晶畴的尺寸、形貌等受铜箔基底表面形貌、生长温度、生长时间、生长混气比等影响较大，深入研究这几种因素的作用对于制备高质量石墨烯薄膜具有重要意义。本文深入研究了常压下铜箔表面形貌、混气比、生长时间对石墨烯晶畴的形貌、尺寸的影响。进一步制备了六边形的石墨烯晶畴，研究了其生长的机理。在深入理解以上因素之后，我们制备了尺寸达到百微米级别的大尺寸石墨烯晶畴，并对其进行了微结构表征。

2 实验

2.1 石墨烯晶畴的制备

石墨烯制备采用的是常压化学气相沉积法（APCVD）。生长基底为 25 μm 厚铜箔（alfa, 99.8%），气源为高纯 CH_4 （99.99%），高纯 H_2 （99.999%）和载气高纯 Ar（99.999%），设备为石墨烯制备化学气相沉积系统。

开始阶段首先将铜箔剪成 1.5 cm^2 的方片，放入丙酮、乙醇、去离子水中各超声 10min，然后 N_2 吹干。接着将铜箔放在石英板上，石英板置于石英管中间部位。随后通入 300sccmAr 20min 用于排除石英管中的空气。为了将空气排除干净，使用真空泵进行抽压至 5pa 左右，进而 Ar 回填。然后开启加热装置，至 1000 $^\circ\text{C}$ ，Ar 气氛下退火 0.5h。进入生长阶段后，保持 Ar300sccm， CH_4 0.8sccm， H_2 流量随实验参数而定，生长时间为 6min。生长完成后关闭 H_2 ， CH_4 气源，在 Ar 气氛下降至室温，拿出样品。石墨烯制备过程结束。

2.2 石墨烯晶畴的转移

石墨烯的转移是按传统的湿法转移进行的。首先，将长有石墨烯的铜箔置于匀浆机上，在 3000rpm，60s 条件下，涂覆一层 PMMA。然后置于加热板上 130 $^\circ\text{C}$ 烘烤 5min，进行固化。接着将铜箔放置于 1M 的过硫酸铵溶液中进行腐蚀，待铜箔完全腐蚀干净后，将漂浮的 graphene/PMMA 薄膜转移至干净的去离子水中漂洗 2h，重复漂洗三次，直至完全干净为止。接着将薄膜转移至目标基底上，放置于热板上 60 $^\circ\text{C}$ 下烘干，随后在 150 $^\circ\text{C}$ 下加热 30min，使石墨烯与目标基板紧密贴合。去除 PMMA 是在 55 $^\circ\text{C}$ 的热丙酮溶液下进行的，时间为 2h，重复三遍，直至 PMMA 完全去除。

2.3 石墨烯晶畴的表征

石墨烯晶畴表征所使用的仪器分别是：Novel MV-6100 光学显微镜；FEI Serion Field Emission 扫描电子显微镜，加速电压为 15KV；LabRAM HR UV-Visible 拉曼光谱，激光波长是 514nm；Veeco Nanoscope 原子力显微镜，轻巧模式。

3 结果讨论

3.1 铜箔基底对石墨烯晶畴的影响

铜箔基底表面粗糙度对石墨烯晶畴的形貌与尺寸影响显著。这里我们通过对未经抛光处理与经过抛光处理铜箔制备的石墨烯晶畴之间的差异研究铜箔基底表面粗糙度对石墨烯生长的影响。图 1 (a) 是未经抛光的铜箔光学显微镜图，可以看到铜箔表面存在大量的冷轧痕迹，这是与铜箔的加工方式有关。图 1 (b) 是经过机械抛光与电化学抛光的铜箔光学显微镜图，可以看到铜箔表面形貌非常平滑，冷轧痕迹去除完全。

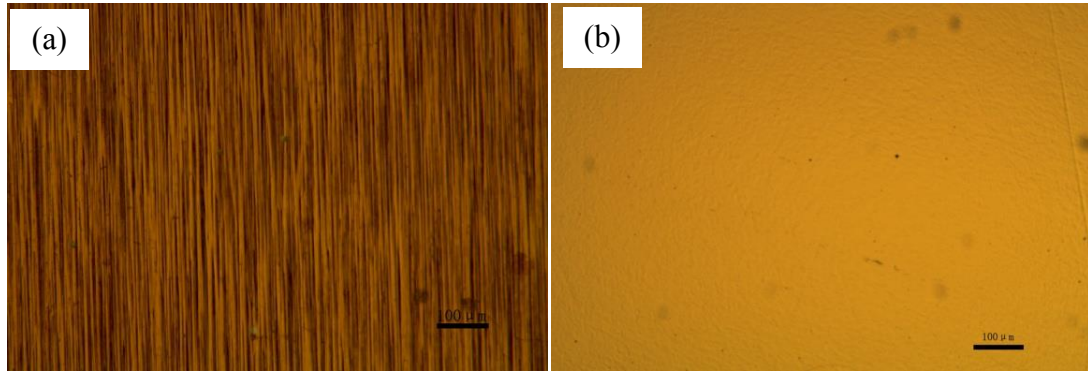


图 1 (a) 未经抛光处理的铜箔光学显微镜图；(b) 经过机械抛光与电化学抛光处理的铜箔光学显微镜图

分别在此两种铜箔表面生长石墨烯晶畴，生长参数为 $\text{Ar}:\text{H}_2:\text{CH}_4=300\text{sccm}:100\text{sccm}:1.5\text{sccm}$ ，生长时间 6min。生长完毕后，将铜箔放在双氧水中浸泡 30 秒，然后进行光学显微镜观察。图 2 (a) 是铜箔表面石墨烯晶畴的光学显微镜图，可以看到大量六边形石墨烯晶畴，这些晶畴基本呈现单向排列。除了六边形晶畴之外，还有无规则的石墨烯生成，这些石墨烯成核生长的位置基本都是在轧痕上，而且在铜箔氧化后这些石墨烯呈现出明显的黑色，说明这些石墨烯厚度比较厚。图 2 (b) 是扫描电子显微镜图，可以更加清晰的看到，压延痕迹处的石墨烯形貌非常不规则，表面形貌也不均匀。在两条不规则石墨烯带的中间有部分规整的六边形石墨烯晶畴出现，见于图 2 (b) 中的插图，可以看到石墨烯晶畴的六边形非常规整，角度约为 120° 。图 2 (c) 是将此样品转移到 $300\text{nm SiO}_2/\text{Si}$ 基底上的光学图片。从颜色上看，不规则形貌的石墨烯颜色非常深，而六边形石墨烯晶畴颜色很浅，进一步说明在轧痕上形核生长的石墨烯较厚。分别对六边形石墨烯晶畴（红色圆圈所示）与不规则石墨烯（黑色十字架所示）进行拉曼光谱表征，结果见于图 2 (d)：六边形石墨烯晶畴的 2D 峰与 G 峰的强度比 $I_{2D}/I_G \approx 3.5$ ，半高全宽 (FWHM) 约为 32.4cm^{-1} ，表明六边形石墨烯晶畴是单层结构，D 峰的缺失说明石墨烯晶畴质量非常高，缺陷较少。不规则石墨烯的 2D 峰与 G 峰强度比 $I_{2D}/I_G \approx 0.48$ ，半高全宽 (FWHM) 约为 63cm^{-1} ，说明石墨烯是多层结构，除此之外 D 峰强度较高，说明缺陷较多，石墨烯质量较差。造成这样情况的原因是压延痕迹处

的铜晶粒含有较多的杂质和缺陷，表面能量较高吸引的甲烷分子较多，因此石墨烯生长为非平衡生长，导致形貌不规则，层数较厚，质量较差。

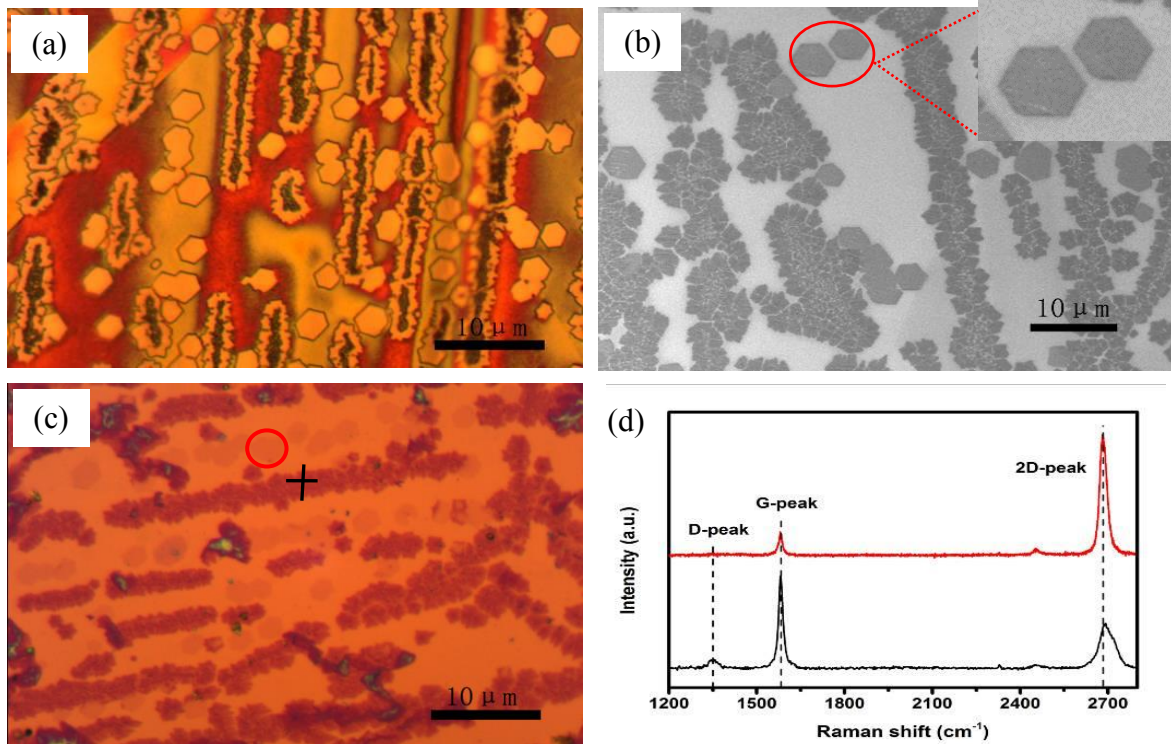


图 2 (a) 未抛光铜箔表面石墨烯晶畴光学显微镜图；(b) 石墨烯晶畴 SEM 图；(c) 转移至 300nmSiO₂/Si 基本上的石墨烯晶畴光学显微镜图；(d) 六边形石墨烯晶畴与不规则石墨烯晶畴的拉曼光谱图（红线数据为六边形晶畴，黑线数据为不规则晶畴）

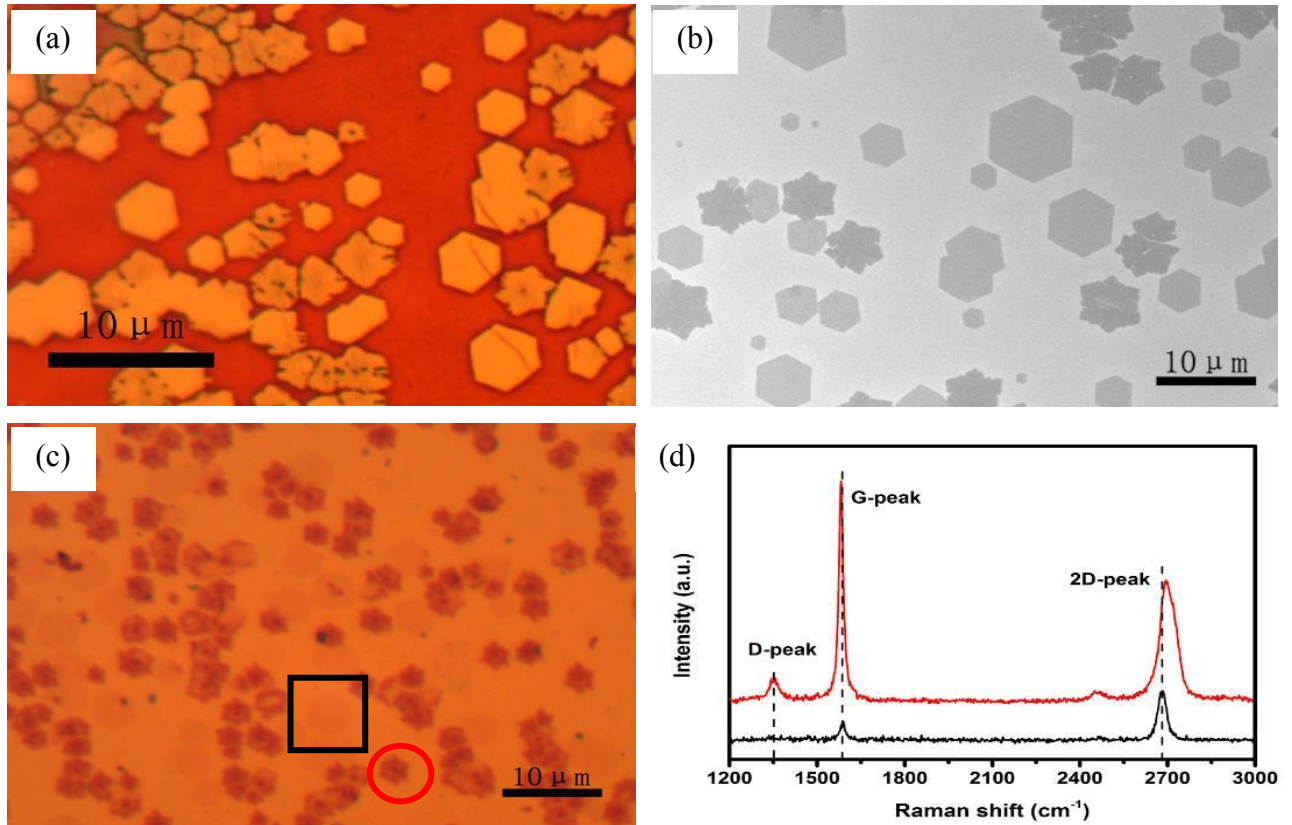


图 3 (a) 抛光铜箔表面石墨烯晶畴的光学显微镜图；(b) 抛光铜箔表面石墨烯晶畴的 SEM 图；(c) 转移至 300nm SiO₂/Si 基板上的石墨烯晶畴光学显微镜图；(d) 六边形石墨烯晶畴与雪花状石墨烯晶畴拉曼光谱图

图 3 是经过抛光处理的铜箔生长的石墨烯晶畴光学显微镜图；由图 3 (a) 可知，铜箔抛光后制备的石墨烯晶畴分布比较均匀，不会沿着压延痕迹生长。图 3 (b) 是相应的扫描电镜图片。将石墨烯晶畴转移到 300nm SiO₂/Si 基底上，如图 3 (c) 所示，可以明显的展示出晶畴之间的颜色差异，表明了不同晶畴之间厚度不同。拉曼光谱进一步支持了这种观点，对图 3 (c) 中黑色方框与红色圆圈的六边形晶畴进行拉曼光谱表征，结果示于图 3 (d)，其中黑色线和红色线代表的的数据分别与黑色方框、红色圆圈所框的六边形晶畴相对应。拉曼结果表明，颜色较浅的六边形晶畴的 $I_{2D}/I_G=2.63$ ，2D 峰半高全宽 (FWHM) 为 34cm^{-1} ，说明此类晶畴为单层，D 峰的缺失进一步表明晶畴结构完整，缺陷数量较少。颜色较深的晶畴 $I_{2D}/I_G=0.55$ ，2D 峰的半高全宽 (FWHM) 为 58cm^{-1} ，表明此类晶畴为多层结构，在 1350cm^{-1} 处出现了明显的 D 峰，即缺陷峰，表明此类晶畴中缺陷较多，质量较差。

由以上结果可以知道，经过处理的铜箔制备的石墨烯晶畴质量较好，因此有必要在制备石墨烯之前对铜箔进行抛光处理。

3.2 铜箔基底与石墨烯晶畴的相互作用

不同于其他过渡族金属，如 Ni 等，对碳原子有比较大的溶解度。金属 Cu 的碳溶解度非常小，这与 Cu 的电子结构相关。Cu 的最外层电子结构为 $3d^{10}4s^1$ ，其 d 层电子已经被填满了，只有 4s 轨道有一个电子，这个电子会与石墨烯平面外的 π 电子相互配对，使得 Cu 与石墨烯之间产生较弱的相互作用^[11]。这种弱相互作用可以起到催化的作用，但无法控制石墨烯的形貌，尺寸。图 4 (a) 是六边形石墨烯晶畴的 SEM 图，图片中包含两个铜晶粒，铜晶粒之间的晶界线非常明显，如黑色箭头所指。在晶界线的两边，有石墨烯晶畴形成。六边形石墨烯晶畴可以跨越晶界线生长（红箭头所指是铜晶界），同时保持了较完好的六边形形貌，这证明了石墨烯与铜基底之间的弱相互作用。图 4 (b) 展示了在同一个铜晶畴上面取向不同的六边形石墨烯晶畴的分布图，红色线与蓝色线所指的石墨烯晶畴的取向不同。在同一个铜晶粒处既有取向相同的石墨烯晶畴，又有取向不同的石墨烯晶畴，这表明了铜箔与石墨烯之间的弱相互作用。而在 Ru (0001) 上由于石墨烯与其之间存在较强的相互作用，晶畴只有一个相对取向^[12]。

虽然石墨烯与铜箔基底之间存在弱相互作用，但是石墨烯的存在会使石墨烯与铜箔基底之间产生应力，进而产生表面重构^[13]。图 4 (a)、(c) 清晰的展示出了铜箔表面的重构。铜箔晶粒表面存在着大量的条纹，见于图 4 (a) 中的红色箭头，条纹之间的间距较小，而且排列较为平行。在 1000°C 以上的高温下，铜箔上面的原子运动比较剧烈，导致晶粒表面的条纹会不断的向前运动。当这些条纹遇到石墨烯晶粒时由于石墨烯的阻碍作用，条纹运动速度降低，导致条纹在石墨烯晶粒边缘处发生扭转，如图 4 (a)、(c) 蓝色方框区域。随着石墨烯晶畴的生长，会覆盖边缘处的条纹，致使条纹完全覆盖在石墨烯晶畴之下。由于石墨烯晶畴对条纹产生较大的应力作用，条纹运动速度会更加缓慢，因而内部条纹间距会有所扩大，并大于裸露铜箔处的条纹间距，如 4 (a) 橙色箭头与紫色箭头所示。石墨烯晶畴内部不同区域处产生的应力大小也会有所不同，因此内部的条纹在运动过程中速度不一致，最终导致弯折的出现，如图 4 (c) 黑色箭头所指。基于以上分析，我们认为石墨烯与铜箔基底之间的相互作用是比较复杂的，虽然相互作用力较弱，但是影响却非常深刻，内在原理仍旧需要更为深入的研究。

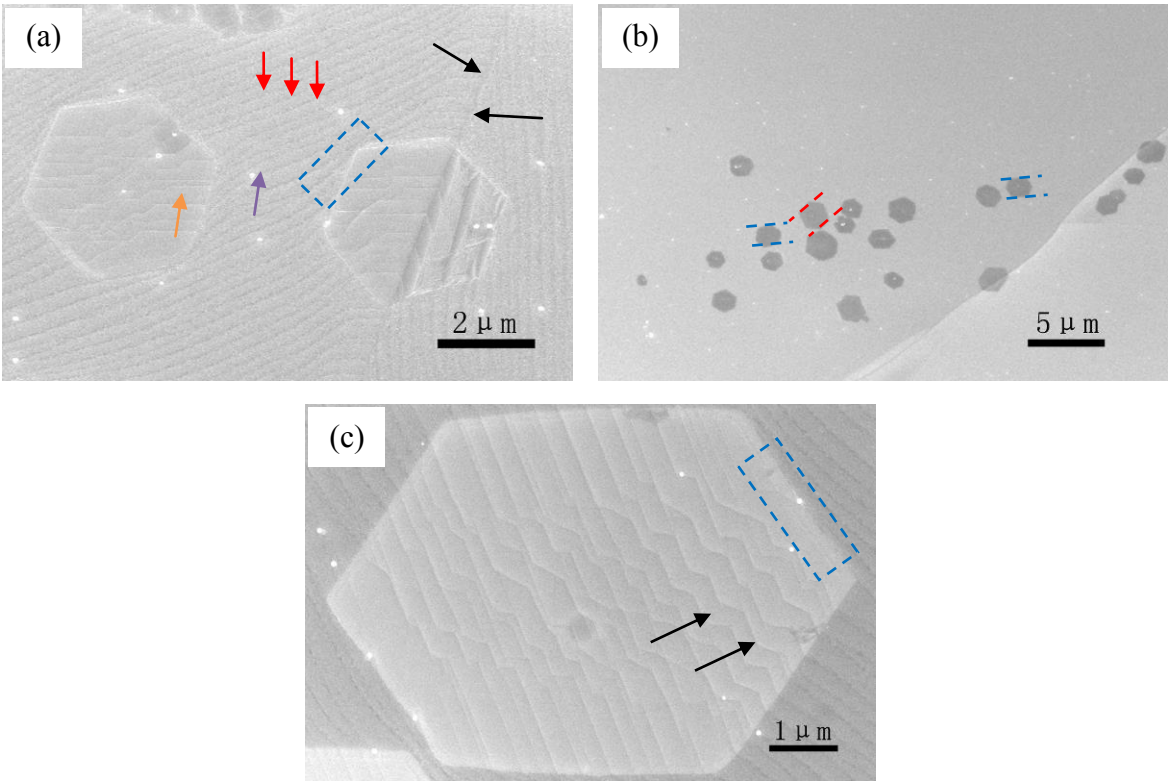


图 4 （a）跨越铜箔晶界的六边形石墨烯晶畴 SEM 图；（b）同一个铜晶粒上，不同取向的六边形石墨烯晶畴 SEM 图；（c）六边形石墨烯晶畴 SEM 图

3.3 不同混气比对石墨烯晶畴的影响

为了研究不同混气比对石墨烯晶畴的影响，这里我们设置了六组不同的 CH₄，H₂ 混气比进行研究。具体的生长参数如表 1 所示：

表 3.1 不同 H₂ 流量下石墨烯晶畴制备工艺参数

生长温度 (℃)	Ar 流量 (sccm)	CH ₄ 流量 (sccm)	H ₂ 流量 (sccm)	生长压力 (torr)	生长时间 (min)	降温速率 (℃/min ⁻¹)
1030	300	0.8	20	常压	8	20
			40			
			60			
			80			
			120			
			160			

图 5 是生长完成后的石墨烯晶畴光学显微图片。图 5（a）是 CH₄/H₂=1:25 下的图片，可以看到，石墨烯晶畴基本都连接在了一起，石墨烯的覆盖率超过了 90%，而且有非常明显的多层结构出现。当 CH₄/H₂ 比值变成 1:50 后，如图 5（b）所示，石墨烯

的覆盖率降低，有单个分离的晶畴出现，但是大部分晶畴仍然相互连接在了一起，晶畴的尺寸约 $15\mu\text{m}$ 左右，形状不规则，边缘不光滑。除了不规则晶畴外，还出现了部分六边形晶畴，如黑色方框所示，六边形晶畴的尺寸小于不规则晶畴，而且大部分与圆形晶畴连接在了一起。进一步提高氢气含量至 CH_4/H_2 比值为 1: 75，如图 5 (c)，出现了大量六边形石墨烯晶畴，平均尺寸约为 $7.5\mu\text{m}$ ，较图 5 (a) 要更小，表明氢气含量提高后刻蚀作用增强，对石墨烯晶畴的生长起到阻碍作用。 CH_4/H_2 比值变为 1:100 后六边形石墨烯晶畴的数量更多，不规则晶畴数量进一步减少，同时六边形晶畴的尺寸较之前更小。氢气含量提高至 120sccm 后，如图 5 (e)，在石墨烯晶畴尺寸变小的同时，六边形石墨烯晶畴的边缘发生钝化，有些晶畴甚至变成了类圆形。当氢气流量进一步提高至 160sccm 时，如图 5 (f)，石墨烯晶畴的平均尺寸降低至 $2.1\mu\text{m}$ ，边缘形貌更加圆滑。通过此对比试验我们得出结论，氢气流量增加，石墨烯晶畴的尺寸逐渐降低，石墨烯晶畴的形貌从无规则变化至规则六边形最后变成类圆形，说明氢气的刻蚀作用不断的提高。为了制备规则的六边形晶畴， CH_4/H_2 比值范围在 1:75 至 1:100 比较合适。

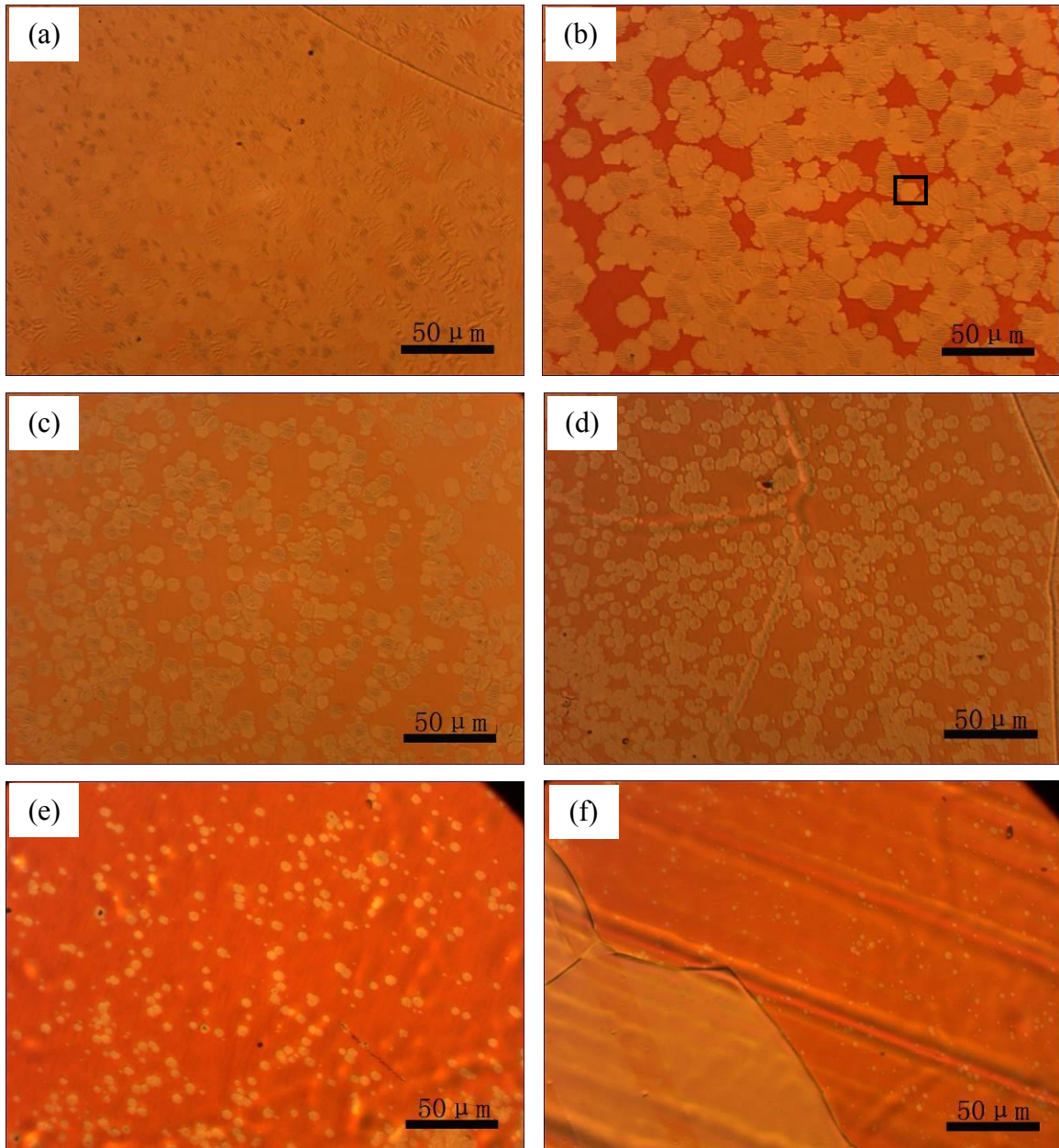


图 5 不同氢气含量下石墨烯晶畴的光学显微镜图片：（a）-（f）分别为 $\text{CH}_4/\text{H}_2=1:25$ ；1:50；1:75；1:100；1:150；1:200

3.4 生长时间对石墨烯晶畴的影响

在生长温度为 1030°C ， CH_4 0.8sccm， H_2 80sccm 下，我们分别将生长时间设定为 3min，8min 和 11min，研究生长时间对石墨烯晶畴的影响。生长完毕后，石墨烯形貌如图 6（a）-(c)所示。图 6(a)是生长 3min 的石墨烯晶畴 SEM 图，晶畴尺寸约为 $2\mu\text{m}$ ，形核密度比较小，形貌为六边形。图 6（b）是生长时间延长为 8min 的石墨烯晶畴 SEM 图，图中六边形晶畴的尺寸长大至约为 $8\mu\text{m}$ ，石墨烯晶畴的数量较图 6（a）有所提高，六边形石墨烯晶畴数量较多，除此之外有不规则形状的石墨烯晶畴开始出现。而且六边形晶畴的尺寸有大有小，这说明晶畴的成核时间不同。生长时间延长至 11min，石墨烯形貌如图 6（c）所示，六边形石墨烯晶畴的尺寸大约 $10\mu\text{m}$ ，面积不断增大，开始有一些石墨烯晶畴相互连接。除此之外，不规则形貌的石墨烯晶畴数量也不断提高，在某些区域甚至出现了类似于雪花状的石墨烯晶畴。

因此总结到：随着时间的延长，石墨烯生长过程中接触到的甲烷越来越多，在某些区域由于甲烷分子聚集过多，分解产生了大量的碳原子，以至于无法充分扩散从而聚集在一起，形成了不规则形貌的石墨烯晶畴。而在某些区域，例如铜表面光滑，缺陷较少的区域，甲烷分子聚集数量正合适，分解形成的碳原子充分扩散，从而使得石墨烯晶畴成长处于一种平衡稳定的状态中，从而形成了形貌规整的六边形石墨烯晶畴

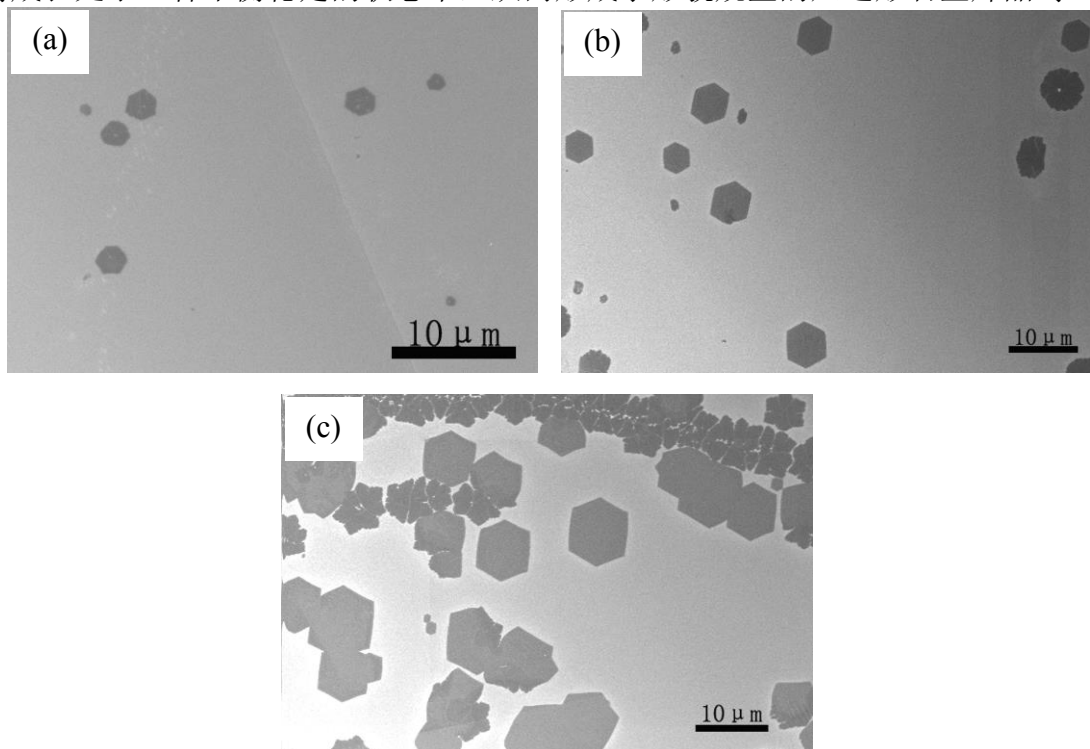


图 6 不同生长时间下石墨烯晶畴的 SEM 图：（a）生长时间 3min 时石墨烯晶畴的 SEM 图；（b）生长时间 8min 时石墨烯晶畴的 SEM 图；（c）生长时间 11min 时石墨烯晶畴的 SEM 图

3.5 石墨烯晶畴生长机理

首先，在大面积铜箔某些局部区域铜箔表面冷轧痕迹较少，铜箔表面较为平整，缺陷数量较少，表面能较低；同时，这些区域的边界层厚度较为适中，活性甲烷分子

从边界层扩散至表面层数量适中，完全裂解形成活性碳原子。之后进入成核阶段，Gao^[14]等通过第一性原理计算表明，成核时碳原子之间相互接触形成碳原子链，进而形成具有五元环与六元环相互结合的早期石墨烯晶核，这些晶核最终成为适宜石墨烯生长的晶核。晶核形成之后开始长大过程，由于铜箔表面缺陷较少较为平整，因此表面能较低，吸附的甲烷分子数量较少，分解后形成的活性碳原子数量也少，生长阶段接近平衡生长，碳原子有足够的弛豫时间找到晶核边界处能量最低的位置，并在此与晶核相连接，如图 7（a）所示，生长过程遵循边界扩散机制（edge diffusion mechanism）。由传统的 wulff 结构动力学理论^[15]可知，晶体形貌是由生长速度最慢的面或者边决定的，第一性原理计算已经证实，石墨烯的 zigzag 边缘生长速度最慢^[16]，因此最终形成的晶畴是具有 zigzag 边缘的晶畴，即为六边形晶畴。

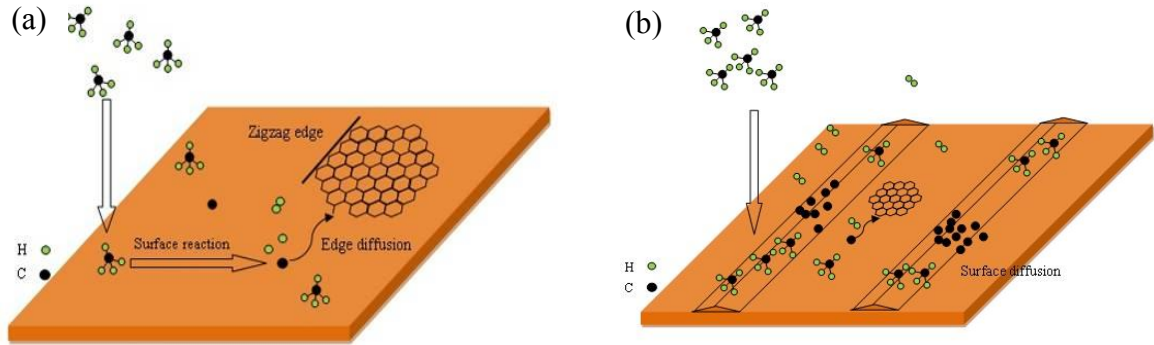


图 7（a）单层六边形石墨烯晶畴生长示意图；（b）压痕处不规则石墨烯晶畴生长示意图

在未抛光的铜箔表面，如图 7（b）所示，由于存在较多的压延痕迹，压延痕迹处铜箔缺陷较多，表面能较大，同时由于压延痕迹较高，导致边界层的厚度较厚，活性甲烷分子吸附在压痕上面的数量就越多，进一步裂解产生的碳原子就越多，碳原子弛豫时间就越短，因此石墨烯的生长不再遵循边界扩散机制（edge diffusion mechanism），而是遵循传质输运（mass transport）的表面扩散机制（surface diffusion mechanism），是一种非平衡生长机制，因而其形貌发生变化，具体的形貌与碳原子的数量相关。而在两条压痕之间的平滑区域，石墨烯晶畴的生长条件与图 7（a）中的一致，因此生长的晶畴多为六边形晶畴。

3.6 大尺寸石墨烯晶畴的制备与表征

3.6.1 大尺寸石墨烯晶畴的制备

为了制备大尺寸石墨烯晶畴，我们前期做了大量的实验，分别探讨了不同 CH_4/H_2 比值、生长时间，生长温度，生长基底等对石墨烯晶畴的影响。在掌握并深入了解了影响石墨烯生长的因素后，我们开始尝试制备大尺寸石墨烯晶畴。我们设定的目标是制备百微米级别的石墨烯晶畴。在前期的实验基础上，我们认识到，影响石墨烯晶畴尺寸最大的因素是 CH_4/H_2 ， CH_4 的浓度越小，越有利于制备大尺寸石墨烯晶畴。由于实验室设备所限，在使用纯 CH_4 的情况下，我们的设备能达到的 CH_4/H_2 极限值为 0.8sccm: 200sccm，即 1:250，在这个比值下，我们通过实验发现无法实现制备百微米级别大晶畴的目标。因而，我们更换了气源，即 CH_4 浓度为 500ppm 的 $\text{CH}_4\text{-Ar}$ 混合气作为碳源。在制备大尺寸石墨烯晶畴的时，我们设定的具体生长参数表 3.3 所示：

表 3.3 大尺寸石墨烯晶畴制备工艺参数

生长温度 ($^{\circ}\text{C}$)	Ar 流量 (sccm)	CH ₄ 流量 (sccm)	H ₂ 流量 (sccm)	生长压力 (torr)	生长时间 (min)	降温速率 ($^{\circ}\text{C}.\text{min}^{-1}$)
1030	300	40	20	常压	60	20

3.6.2 大尺寸石墨烯晶畴的表征

1. 光学显微镜表征

生长完成后，剪去部分长有石墨烯后的铜箔，放在双氧水中浸泡 30s，然后在光学显微镜下观察。图 8（a）是制备完成后的石墨烯晶畴光学显微镜图片，六边形晶畴的尺寸约为 140 μm ，而且此大晶畴可以跨越三个不同的铜箔晶粒生长，说明了石墨烯与铜箔之间的弱相互作用。图 8（b）是 SEM 图，图中标尺是 3mm，可以看到石墨烯晶畴的尺寸比较大，另外，图中石墨烯晶畴的尺寸由下向上逐渐减小，这是由于在生长过程中气流方向是沿着图中铜箔的下方向上方流动的，因此下方的铜箔最先接触到甲烷分子，而且接触的甲烷分子含量最多，时间最长，因而生长的最大。

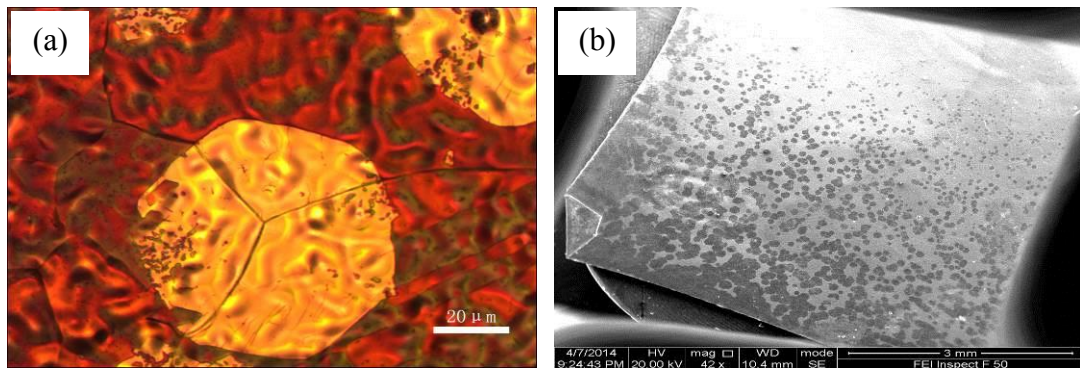


图 8（a）石墨烯大晶畴光学显微镜图；（b）石墨烯大晶畴 SEM 图

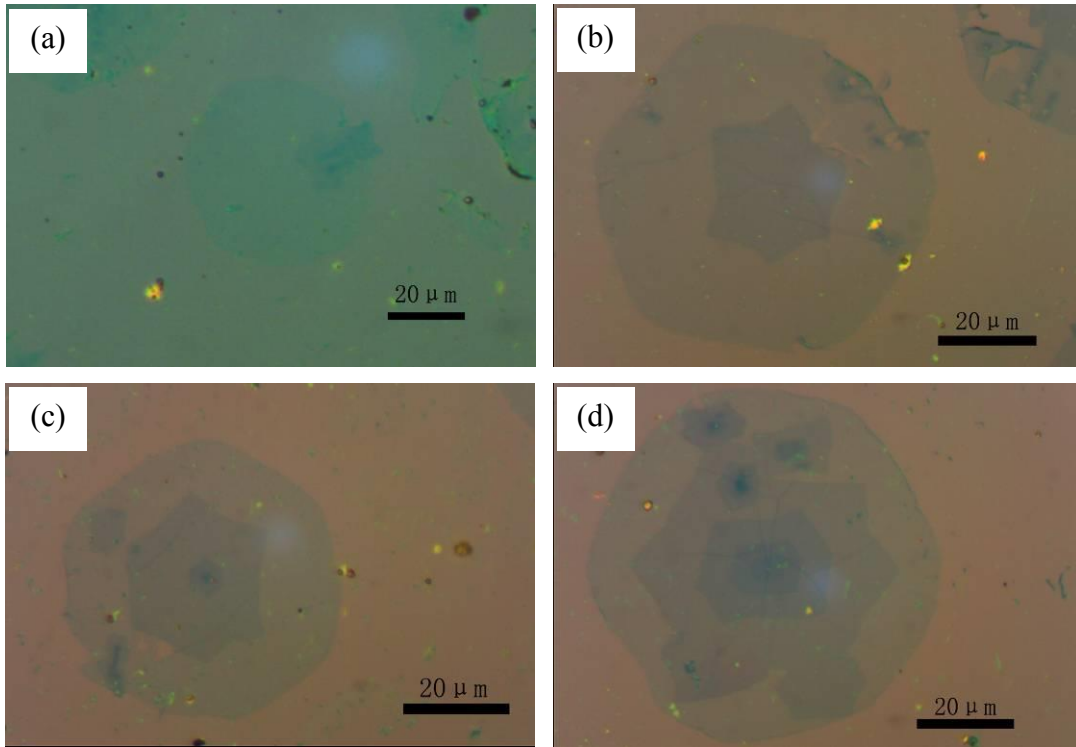


图 9 转移到 300nm SiO₂/Si 基板上的石墨烯晶畴光学显微镜图 (a) - (d) 分别是单层、双层、四层、五层石墨烯晶畴

将生长完成后的石墨烯晶畴转移到 300nm 的 SiO₂/Si 基板上，观察光学显微镜。图 9 展示了石墨烯晶畴的光学显微图片。图 9 (a) - (d) 分别展示了单层石墨烯晶畴，双层石墨烯晶畴，四层石墨烯晶畴与五层石墨烯晶畴的光学显微镜图片。石墨烯晶畴的成核生长机理已经分析过，多层石墨烯是在第一层的下面形成的。最上一层的晶畴基本都是圆形，这可能是由于氢气过量导致刻蚀作用过大，将石墨烯晶畴刻蚀成了圆形。而第一层下面的第二层石墨烯形貌类似于雪花状，图 9 (c) 中的第三层，图 9 (d) 中第四、五层形貌呈现六边形，这可能是与接触到的氢气甲烷量不同有关，越底层的石墨烯接触到的甲烷，氢气量越少，生长过程中越接近平衡生长的条件，因而形成了六边形的晶畴。

2. 大尺寸石墨烯晶畴的拉曼光谱表征

拉曼光谱可以快速且无损的检测出石墨烯的层数，并且能通过 D 峰的情况进一步判断石墨烯的质量，因而是迄今为止，表征石墨烯最为常用的技术。对于不同层数的石墨烯其拉曼光谱的特征峰强度与形貌不同，基于此，我们可以利用拉曼光谱快速的对石墨烯的厚度进行判断。石墨烯的拉曼光谱特征峰有三个：D 峰，缺陷峰，可以用来判断石墨烯的质量；G 峰，平面内 sp² 碳原子的振动峰；2D 峰，起源于石墨烯内的双声子共振过程，是石墨烯拉曼特征峰里面最重要的峰，也是判别石墨烯与其他碳材料的依据。对于单层石墨烯而言，它的 2D 峰可以用一个尖锐且对称的洛伦兹峰拟合，而随着石墨烯层数的提高，2D 峰逐渐变宽，且需要多个洛伦兹峰进行拟合，这是由于随着石墨烯层数的增加，其电子能带结构发生了劈裂。除了用 2D 峰判断石墨烯层数，G 峰也可以用于快速判别石墨烯层数，由于 G 峰起源于碳原子 sp² 的平面内振动，石墨烯层数越多，则碳原子 sp² 的平面内振动越强，G 峰强度越高。Ni Z H^[17]等证实 G 峰强度几乎是随着石墨烯层数的增加呈现线性增加。

在这里我们对制备的多层大尺寸石墨烯晶畴进行了拉曼光谱表征，图 10 (a) - (d) 是测试的不同层数的石墨烯晶畴的光学显微图片，10 (e) 是 1-4 层石墨烯的拉曼光谱图，10 (f) 是相应的 2D 峰以及相应的拟合洛伦兹峰。如图 10 (a) 所示，我们测试的大尺寸晶畴是四层结构，最上层的单层石墨烯形貌呈现圆形，第二层类似雪花状，第三层呈现六边形，第四层位于成核中心处，尺寸较小，光学显微镜下无法看清其形貌。红色的十字标记是我们的拉曼测试点，分别是位于第一、二、三、四层处。拉曼光谱如图 10 (e) 所示，可以观察到，D 峰强度较小，说明石墨烯晶畴质量较好，存在的缺陷主要来自于边界处的无序；随着层数的增加，石墨烯的 2D 峰强度逐渐变小，宽度变大而且发生了一定程度上的蓝移，这是由于层数增加，石墨烯的电子结构发生变化，从而导致了这种现象^[57]。除此之外，随着石墨烯层数的增加，石墨烯拉曼 2D 峰可以用不同个数的洛伦兹峰拟合。根据 Graf^[18]等的研究，单层石墨烯可以用一个尖锐且对称的洛伦兹峰拟合，双层石墨烯可用四个不同的洛伦兹峰拟合，三层、四层石墨烯可用两个不同的洛伦兹峰拟合，我们的实验结果证实了这种理论，如图 10 (f) 所示。除了这种方法判断石墨烯层数外，Ni Z H^[17]等的研究表明通过 G 峰强度的变化也可以快速判断石墨烯的层数，他们认为，随着石墨烯层数的增加（1-4 层），G 峰强度几乎是成线性变化的，我们的实验结果也证实了这一点，如图 11 (a) 所示，G 峰强度的变化随着石墨烯层数的变化呈现直线变化。除此之外，2D 峰的半高全宽（FWHM）也随着石墨烯层数的增加而逐渐增大，11 (b) 呈现了半高全宽的变化规律。

拉曼光谱的结果证实了我们制备的大尺寸石墨烯晶畴具有较高的质量，而且多层石墨烯的拉曼光谱结果证实了文献中的有关结论。

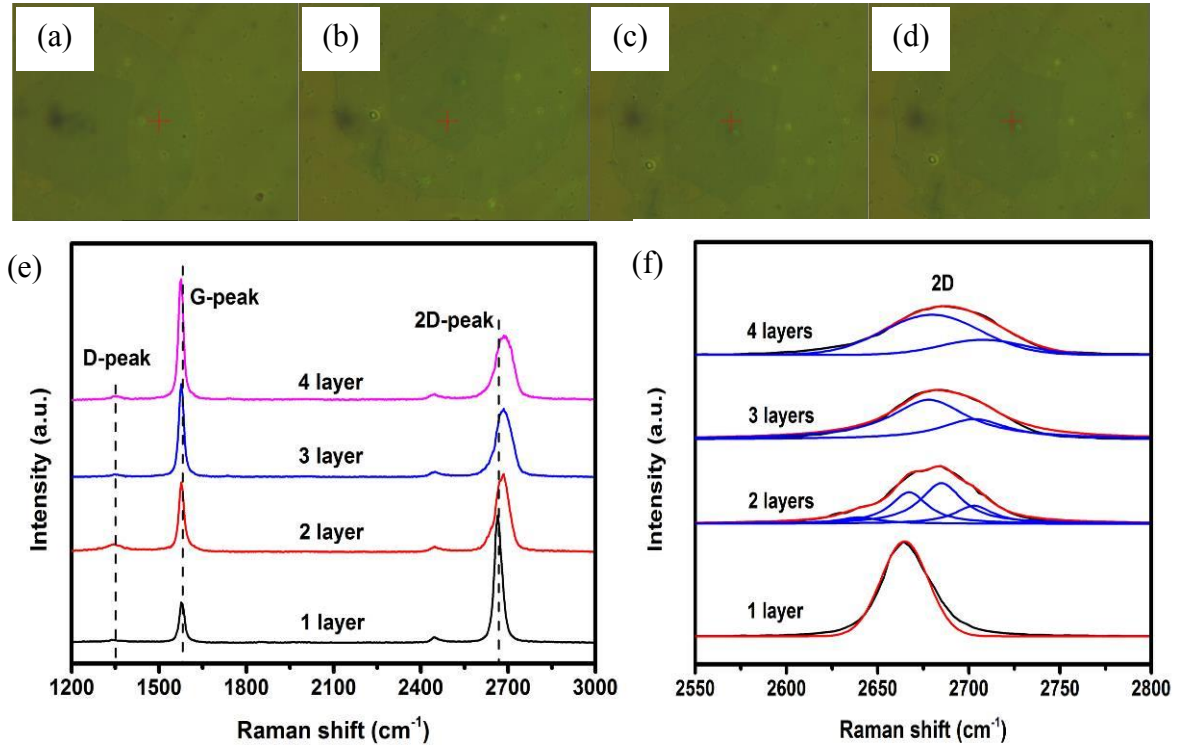


图 10 四层大尺寸石墨烯晶畴的拉曼光谱图：(a) - (d) 单层至四层石墨烯拉曼光谱测试位置（红色十字架是测试位置）；(e) 不同层数拉曼光谱图；(f) 不同层数石墨烯晶畴 2D 峰拟合峰

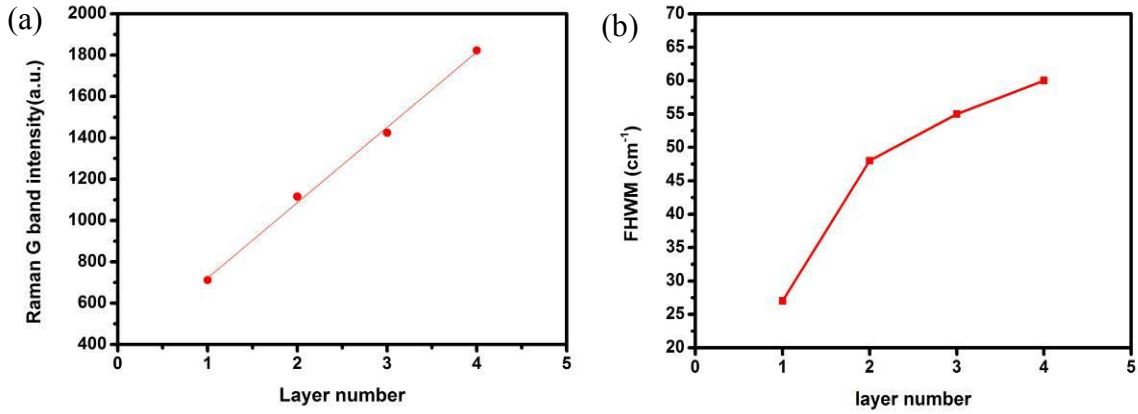


图 11 (a) 石墨烯 G 峰强度随层数变化图; (b) 石墨烯 2D 峰半高全宽 (FWHM) 随层数变化图

3. 大尺寸石墨烯晶畴的原子力显微镜表征

原子力显微镜是测量石墨烯厚度最直接的方法,虽然这种方法效率比较低,同时由于石墨烯与基底之间存在相互作用力,例如范德华力等等,导致测量的结果有 0.5-1nm 的误差存在,但是原子力显微镜仍旧有其优势,通过原子力显微镜我们可以清楚的看到石墨烯晶畴的外观形貌,也可以得到宏观层面上的石墨烯厚度。

图 12 (a) 是我们制备的大尺寸石墨烯晶畴的原子力显微镜图片,图 12 (b) 是相应的振幅图,图 12 (c) 是石墨烯边缘的高度变化图。从图 12 (a) 中可以看到石墨烯晶畴的形貌类似于圆形,石墨烯晶畴上面存在一些白色的杂质,这可能是残留的 PMMA 或者腐蚀铜箔后残留的杂质;图 12 (b) 是相应的振幅图,石墨烯晶畴在振幅图中表现的更加清晰,杂质等颗粒也更加清楚。图 12 (c) 表示的是 (a) 中白色线条区域的高度变化图,其中两个蓝色十字架处的高度差是 0.848nm,由于石墨烯与基底之间存在相互作用,所以有一定的误差,因此可以认为石墨烯晶畴边缘处为单层。

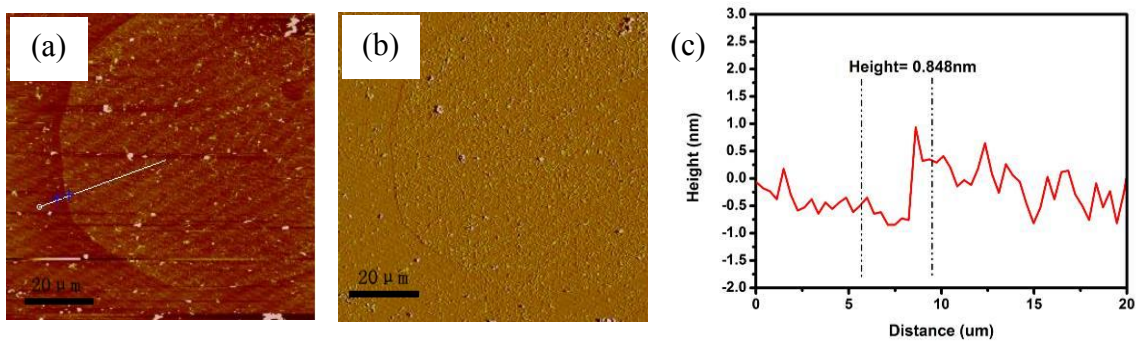


图 12 (a) 大尺寸石墨烯晶畴 AFM 图; (b) 相应的振幅图; (c) 大尺寸石墨烯晶畴边缘高度图

4 结论

本文通过常压化学气相沉积法制备了石墨烯晶畴,并研究了不同影响因素对晶畴生长的影响。实验发现铜箔基底对石墨烯晶畴的形貌以及层数影响非常大,经过抛光处理后的铜箔制备的石墨烯晶畴分布比较均匀,形貌为规整的六边形。铜箔与石墨烯之间是一种弱相互作用,并且石墨烯晶畴的存在会造成铜箔晶面的重构。 CH_4/H_2 比值范围在 1:75 至 1:100 时,可以制备得到大量规则的六边形石墨烯晶畴。生长时间越长,

石墨烯晶畴的尺寸越大，而且石墨烯晶畴的形核时间也有先后顺序。单层六边形石墨烯的形成遵循的是边缘扩散机制，而不规则石墨烯的形成则遵循表面扩散机制。大尺寸石墨烯晶畴的制备需要较低的甲烷浓度、较长的生长时间。单层、双层、三层和四层石墨烯的拉曼图谱中其 2D 峰可以分别用一个、四个、两个和两个洛伦兹峰进行拟合。

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碳酸酐酶微生物诱导矿化修复混凝土裂缝可行性探究

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摘要: 本文选用一类嗜碱芽孢杆菌, 其代谢产物碳酸酐酶可促进 CO_2 可逆水合反应, 通过试验证明, 在提供充足 Ca^{2+} 的条件下, 此菌具有修复混凝土裂缝的能力。试验中通过对纯化菌株的生长曲线测定, 确定其最佳培养时间为 24-28h, 最适 pH 为 8, 随着 pH 升高, 碳酸酐酶菌生长能力和酶化活力下降, 但 pH 为 12-13 时仍存在活菌, 并且能够维持一定酶化活力, 其对混凝土环境具有一定的耐受性。在溶液环境中, 通过试验证明了碳酸酐酶菌具有加速碳酸钙沉积的能力, 进一步在混凝土裂缝自修复试验中, 验证了提供充足 Ca^{2+} 条件下, 碳酸酐酶微生物诱导矿化修复混凝土裂缝具有可行性。

0 引言

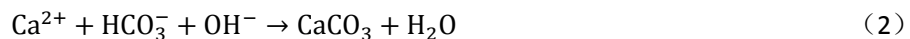
混凝土材料是当今世界上用途最广、用量最大的建筑材料之一。但是混凝土材料脆性大, 易开裂, 在其服役的过程中容易遭受外界介质侵蚀, 致使混凝土材料的性能不断降低。混凝土裂缝修复技术引起研究界广泛关注, 并取得了一系列研究成果。

研究发现, 自然界中某些微生物可以依靠自身产酶与外部环境相互作用, 逐渐诱导方解石形成。方解石作为天然石材具有很好的稳定性, 其与水泥石材料良好的相容性和环境友好性, 相比于传统的裂缝修复技术如: 表面处理法, 灌浆法, 环氧树脂或聚合物砂浆填充法^[1], 具有不可比拟的优势。

美国 Ramachandran^[2]等人最早在 2001 年发表文章叙述了微生物矿化可用于混凝土裂缝修补。一类嗜碱菌能够抵抗混凝土内部高碱性环境, 当混凝土开裂发生后, 随着水和氧气的进入, 细菌激活后诱导产矿填充裂缝, 尤其对混凝土开裂早期裂缝修复作用显著。荷兰代尔夫特理工大学 Jonkers 等人^[3]直接将一种嗜碱芽孢杆菌加入混凝土, 能够在开裂表面区域沉积碳酸钙。Van Tittelboom 等人^[4]利用硅胶固载脲酶菌, 在混凝土高碱环境下利用脲酶菌酶化作用诱导 CaCO_3 沉积修复裂缝, 达到优秀的修复效果; 比利时根特大学 Wang 和 De Belie 等人^[5]为提高细菌在混凝土高碱环境下存活率, 采用硅胶和聚氨酯作为保护剂固载细菌修复裂缝, 能够有效填充裂缝并获得一定的强度恢复, Wang 等人^[6]还在试验中利用微胶囊固载细菌作为修复剂, 采用不同配比在不同环境介质中进行自修复, 最大修复裂缝宽度可达 970 μm 。

综上所述研究成果发现, 寻找合适的微生物, 要求其不仅具有优异的耐高碱能力, 并且微生物组分的加入并不影响混凝土自身性能, 成为微生物诱导矿化修复混凝土裂缝研究的关键。

本实验选用一类嗜碱菌, 其能够代谢产生碳酸酐酶 (Carbonic Anhydrase, CA), 碳酸酐酶能显著提高 CO_2 可逆水合反应, 加快 HCO_3^- 生成, 反应如 (1)、(2) 式^[7]。基于此反应, 本文对碳酸酐酶微生物诱导矿化修复混凝土裂缝进行可行性探究。



1、实验

1.1 菌种及培养

实验选用一种能够产生碳酸酐酶的菌种。菌株发酵培养基见表1, 调节发酵培养基pH=7, 置于三角瓶中, 于121℃高温灭菌25 min。取出灭菌后三角瓶置于烘箱烘干, 待用。接种碳

酸酐酶纯化菌株于无菌培养基，在30℃振荡培养箱中培养，振荡频率为170r/min。

表1 菌株的纯化培养基

Sucrose	Na ₂ HPO ₄ · 12H ₂ O	MgSO ₄	CaCO ₃	KCl	(NH ₄) ₂ SO ₄	Yeast Extract
10.0	2.507	0.2561	1.0	0.1	0.5	0.2

为掌握本实验选用菌种生长情况，确定最佳培养时间，了解其完整的生长曲线，调节培养基初始 pH 为 7，从接种到液体培养基开始算起，应用多功能酶标仪每隔 2h 测量培养菌液的光密度（optical density， OD）以反映细菌数量，波长选用 400nm，根据测量结果绘制细菌生长曲线。

1.2 碳酸酐酶微生物与混凝土高碱环境相容性

1.2.1 不同初始 pH 下碳酸酐酶微生物生长特性

试验采用液体培养基，分别将培养基初始 pH 调节为 6、8、10、12、13，然后接种碳酸酐酶纯化菌株，在 37℃，170r/min 振荡培养箱中培养，监测培养过程中 OD 值随时间变化情况。

1.2.2 不同 pH 下碳酸酐酶微生物酶化活力测定

试验采用液体培养基接种胶质芽孢杆菌，在 37℃，170r/min 振荡培养箱中培养 24h 得到新鲜的胶质芽孢杆菌菌液，其中含有丰富的碳酸酐酶。取出后直接调节菌液 pH 为 6、8、10、12，静置半小时后依次取各 pH 值下菌液，测量其 OD 值和碳酸酐酶活性。

酶活测定方法参照Pocker Y 和Stone JT [8]的方法，略有改进。称量0.0018 g 乙酸对硝基苯酯pNPA，先用0.5 mL 无水酒精溶解，另将0.0156 g 二乙基丙二酸用10 mL 磷酸缓冲液溶解，两者混合后作为工作液。分别吸取1 mL 培养液，稀释5 倍，吸取1 mL 稀释液与1 mL 工作液混合，35℃ 反应30 min，迅速置于冰浴中冷却。400 nm 处测定吸光度，对照标准曲线求出生成对硝基苯酚的量，计算比较胶质芽孢杆菌在两种不同培养液中的CA 酶活性。

标准曲线的绘制，分别吸取1 mmol /L 对硝基苯酚（称量0.0139 g 对硝基苯酚溶于100 mL，0.2 mol /L， pH 6.8 的磷酸缓冲液中）标准溶液1.5、1.35、1.2、1.05、0.9、0.75、0.6、0.45、0.3、0.15 和0 mL，分别加水至15 mL，在波长400 nm 处测定吸光度，绘制标准曲线，并得出直线方程见图1。

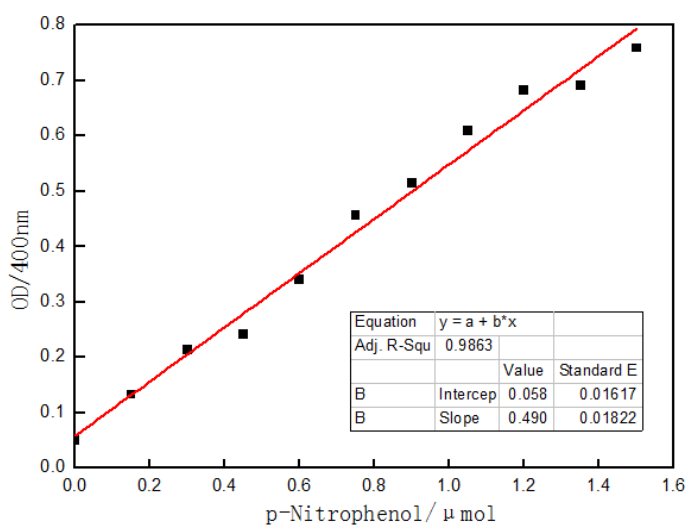


图1 对硝基苯酚物质的量与吸光度的关系

1.3 碳酸酐酶微生物加速诱导碳酸钙沉积

菌株培养 24 h 后，在 4℃、8000 r/min 下高速离心 10 min，去掉上层清液。加去离子水洗涤 1 次后重复离心过程，得到高浓度菌株湿细胞，浓度为 2.3×10^9 cells/mL，冷藏待用。

采用玻璃干燥器作为反应容器如图 2 所示，上层放若干个 50ml 塑料烧杯，按高浓度菌液与 $\text{Ca}(\text{NO}_3)_2$ 按一定质量配比配置反应溶液，测试初始钙离子浓度后分置于塑料烧杯中。下层装有足量的潮湿的 NH_4HCO_3 颗粒，为反应体系提供 CO_2 和适合矿化的碱性环境。设置相等初始 Ca^{2+} 浓度的硝酸钙溶液对照组，不同时间后取烧杯中溶液，采用 EDTA 滴定方法监测 1h、3h、6h、12h、24h、48h 和 72h 溶液中 Ca^{2+} 浓度。收集溶液中沉淀产物，对其进行物质成分和微观形貌分析。



图 2 碳酸酐酶菌加速诱导碳酸钙沉积试验装置图

1.4 混凝土裂缝自修复效果及表征

1.4.1 试件成型与裂缝制作

根据不同需要，成型圆柱形试件和棱柱状试件。圆柱状试件成型采用 PVC 塑料模具，试件尺寸 $\phi 110\text{mm} \times \text{H}45\text{mm}$ ，棱柱状试件采用三联试模，试件尺寸 $40\text{mm} \times 40\text{mm} \times 160\text{mm}$ 。

将培养所得的高浓度菌液与硝酸钙作为自修复剂组分，在试件成型过程中，按不同组别配比要求直接加入，具体配比见表 1。成型后在室温条件下养护 1d，之后放入标准养户室养护 28d，待用。

表 2 水泥基材料试件配合比/g

组分 组别				
	水泥	水	水胶比	自修复剂
A	1300	520	0.4	无
B	1300	520	0.4	硝酸钙
C	1300	520	0.4	细菌
D	1300	520	0.4	细菌+硝酸钙

取养护 28d 的水泥净浆试件人工制作裂缝，裂缝宽度控制在 $200 \sim 300 \mu\text{m}$ 之间,将开裂后试件放入自来水中，并通入空气养护修复。

1.4.2 渗透系数法表征混凝土裂缝自修复效果

圆柱形试件裂缝自修复效果用渗水试验表征,将整个过水断面近似为孔隙分布均匀的结构,假设水压通过开裂圆柱形试件符合达西定律,并在修复开始前测试开裂圆柱形试件初始渗透系数,由达西定律计算渗透系数。试验过程中保持水头恒定,即常水头测量渗透系数。

$$k = \frac{Q \cdot L}{A \cdot \Delta h}$$

其中:

k为渗透系数, m/s

Q为水流量, m³/s

L为试件高度, m

A为试件横截面积, m²

Δh为水头差, m

渗水试验采用的实验装置示意图和实物图见图 3。

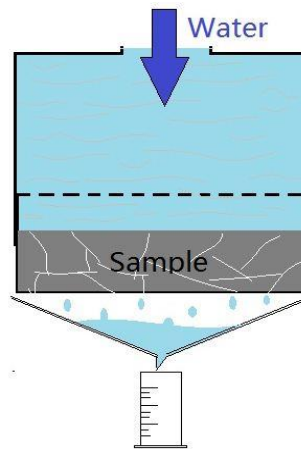


图 3 渗水试验装置示意图

1.4.3 裂缝面积修复率表征混凝土裂缝自修复效果

将开裂试件浸没在水中养护修复,不同时间后对裂缝区域拍照,运用 Image J 软件对照片进行二值化处理。以裂缝区域灰度值上限设定灰度阈值,只显示灰度值在阈值以下的像素图像,获取不同修复时间下裂缝区域二值化图像,通过计算不同修复时间已修复裂缝区像素占初始裂缝像素比例,确定裂缝面积修复率,面积修复率计算公式如式:

$$\text{修复率}\% = \left(1 - \frac{\text{相应龄期下裂缝区像素值}}{\text{初始裂缝区像素值}} \right) \times 100\%$$

2、结果与讨论

2.1 碳酸酐酶微生物生长曲线

按照上述培养基组分配置液体培养基,调节培养基初始 pH 为 7,测定不同培养时间下菌液 OD 值和 pH 值,绘制胶质芽孢杆菌生长曲线见图 3。

由图 4 中 OD₄₀₀ 值曲线变化规律看出,碳酸酐酶微生物生长曲线呈现出典型的四个时期。在 0-8h 内,胶质芽孢杆菌生长处于调整期,由于胶质芽孢杆菌刚刚接种到培养基上,

其代谢系统需要适应新的环境，此时期 OD_{400} 无太大变化；进入 10h 后， OD_{400} 快速增长并达到较高程度，在 10-22h 内，胶质芽孢杆菌生长处于对数期，此时期胶质芽孢杆菌生长最快，代谢旺盛；在 24-28h 期间，此时期由于营养消耗，营养物比例失调，有害代谢产物累积等因素，胶质芽孢杆菌数目保持相对稳定，生长进入稳定期，此时期总细菌数达到最高水平，细胞代谢产物积累达到最高峰；28h 以后， OD_{400} 开始缓慢下降，胶质芽孢杆菌生长进入衰退期，细菌死亡速度大于新生速度，细菌数目呈现负增长。

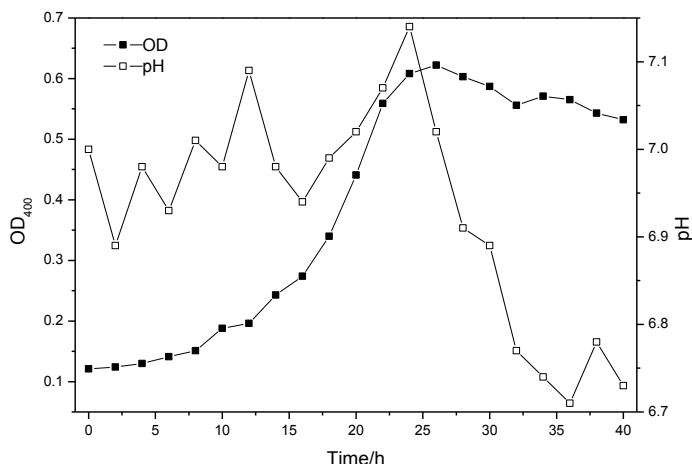


图 4 胶质芽孢杆菌生长曲线

pH 变化总体呈下降趋势，但下降幅度不大，最低 pH 值为 6.71。分析其原因，培养基 pH 变化主要受两方面影响：(1) CO_2 的吸收溶解，(2) 培养基中 $CaCO_3$ 的溶蚀。在前 16h，由于细菌生长主要出于调整期和对数前期，菌体数目和 CA 酶量增长较慢，pH 呈无规律的上下波动；随着培养时间的进行，细菌生长进入对数期后期和稳定期，期间菌液中菌体数量逐渐增大，CA 酶量也积累增多并达到最高峰，CA 酶活性很强，对培养基溶液中 $CaCO_3$ 产生溶蚀现象，即 $CaCO_3$ 结合溶液中 H^+ 形成 $CaHCO_3$ ，导致培养基溶液 pH 逐渐升高；但当培养基中 $CaCO_3$ 量减少后， CO_2 的吸收溶解超过 $CaCO_3$ 的溶蚀，培养基溶液酸化，pH 降低。

由以上试验表明：培养胶质芽孢杆菌最佳时间应为 24-28h，此时期胶质芽孢杆菌生长处于稳定期，细菌总数和代谢产物积累达到最大。

2.2 不同碱性环境下碳酸酐酶微生物生长特性和酶化活力

2.2.1 不同初始 pH 对碳酸酐酶微生物生长特性的影响

试验中分别将培养基初始 pH 调节为 6、8、10、12、13，然后接种胶质芽孢杆菌，在 $37^\circ C$ ，170r/min 振荡培养箱中培养，培养过程中菌液 OD 值随时间变化情况见图 5。

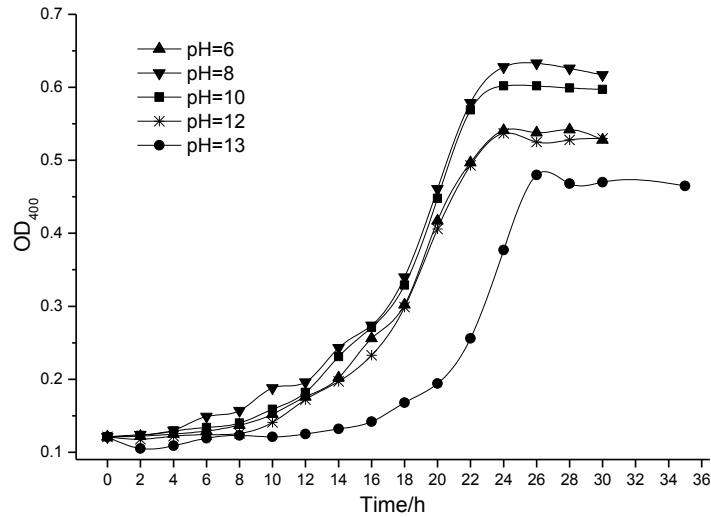


图 5 不同初始 pH 下菌液 OD 值随培养时间的变化

从图 5 曲线中可看出，在初始 pH=6 下，菌液 OD 值上升不快，说明酸性培养基并不适合嗜碱菌生长。试验中选用一类能够代谢产生碳酸酐酶的嗜碱芽孢杆菌，从图 4 中可看出，其生长情况仍会受到溶液碱度的影响，当 pH 为 8 时，最适合碳酸酐酶微生物生长，随着培养基初始 pH 值的增大，对数期出现时间有不同程度延迟，细菌的生长能力降低。pH 值为 12 时，稳定期细菌数目明显减少，当 pH 高达 13 时，对数期出现时间明显延迟，在起初的 16h 内，细菌的生长几乎处于停滞状态，达到稳定期时浓度峰值明显降低。

2.2.2 不同碱性环境下碳酸酐酶微生物酶化活力

分别取 pH=6、8、10、12 下菌液 1 mL，稀释 5 倍，吸取 1 mL 稀释液与 1 mL 工作液混合，35℃ 反应 30 min，迅速置于冰浴中冷却。400 nm 处测定吸光度，对照标准曲线求出生成对硝基苯酚的量，计算比较胶质芽孢杆菌在不同 pH 培养液中的 CA 酶活性见表 3。

表 3 不同 pH 下生成对硝基苯酚的量及 CA 酶活性

pH	A ₄₀₀	p-nitrophenol / μmol	Enzyme activity/U
6	0.571	0.72	0.024
8	0.597	1.10	0.037
10	0.469	0.84	0.028
12	0.337	0.45	0.015

图 6 为在 pH=6、8、10、12 时碳酸酐酶酶活性情况，并以 pH=8 时最大酶活性为 1，计算其他 pH 下的相对酶活性。分析其中可知：在 pH=8 时 CA 酶活性最高，在酸性条件下 CA 酶活性降低，下降幅度为 35%，pH 增大到 10，CA 酶活性降低 24%，当增大到 12 时，CA 酶活性降低幅度达到 60%。

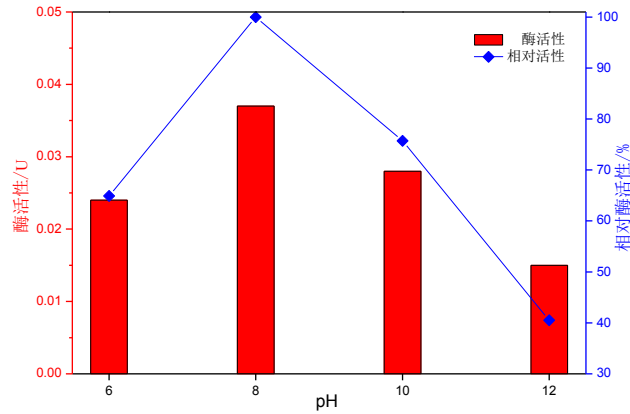


图 6 不同 pH 下酶活性及相对酶活性

综合不同初始 pH 对碳酸酐酶微生物生长特性和不同碱性环境对碳酸酐酶微生物酶化活力的影响规律可发现，酸性环境不利于碳酸酐酶微生物生长代谢，在 pH 为 8 时的碱性环境下，最适宜碳酸酐酶微生物生长代谢，单位时间内能产生更多的碳酸酐酶，且酶活性高，随着碱度的提高，碳酸酐酶微生物生长特性和酶化活力都有不同程度降低，表现在生长特性方面，细菌繁殖生长对数期延迟出现，稳定期细菌 OD₄₀₀ 峰值下降；在酶化活力方面，稳定期碳酸酐酶活性降低。在混凝土孔隙环境中，pH 值在 12-13 之间，碳酸酐酶菌生长和酶化活力将受到较大程度的影响，但从试验结果来看，仍存在活菌，并能够维持一定的酶化活力。当混凝土开裂发生时，水进入裂缝使得裂缝水环境 pH 下降到 9-10 之间，在此碱性环境中，碳酸酐酶菌能够正常生长代谢并进行酶化反应。

2.3 碳酸酐酶微生物加速诱导碳酸钙沉积

2.3.1 溶液环境下微生物诱导加速 Ca²⁺沉积

对两组别烧杯中溶液，采用 EDTA 滴定方法监测 1h、3h、6h、12h、24h、48h 和 72h 溶液中 Ca²⁺浓度。Ca²⁺浓度随时间变化曲线见图。

试验过程中，两组别都观察到有白色沉淀物质产生，由图 7 可以看出，Ca²⁺浓度在水和菌液中浓度随时间都呈下降趋势，两组别第一天 Ca²⁺浓度下降最快，随时间的进行 Ca²⁺浓度下降速度减慢，溶液中 Ca²⁺浓度趋于稳定。两曲线相比较，菌液中 Ca²⁺浓度下降更快，72h 菌液中 Ca²⁺浓度更低，证明了本试验选用的碳酸酐酶菌具有加速钙离子沉积的作用。

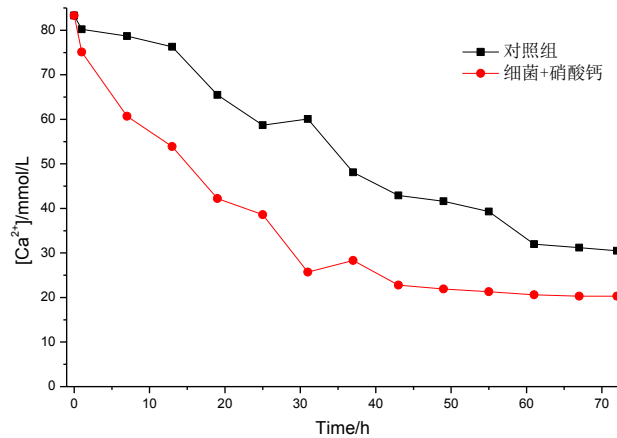


图 7 不同组别 Ca²⁺浓度随反应时间的变化

2.3.2 沉积产物 XRD 分析

收集两组别沉淀产物，用酒精洗净后过滤烘干磨细。对两组别白色沉积物质做 XRD 分析，采用 MDI JADE 5.0 对 XRD 图谱进行物相检索，发现两者都为方解石晶型，见图 8，从图可看出，两组别沉积方解石晶型主特征峰位置一致，但峰强度有一定差异。微生物诱导矿化形成的方解石晶体主特征峰峰强度较低，而对照组所得方解石主特征峰峰强较高。这是因为方解石晶体在微生物产生的有机大分子调控下，会产生多级生长和相互聚集，当晶体生长基元生长到一定尺寸后，不同生长单元由于受到大分子基团的静电排斥和空间位阻等一系列作用，抑制了晶体正常的动力学、热力学生长，导致晶体不能正常发育。因此，微生物诱导矿化形成的方解石晶体结晶程度较差[9]。

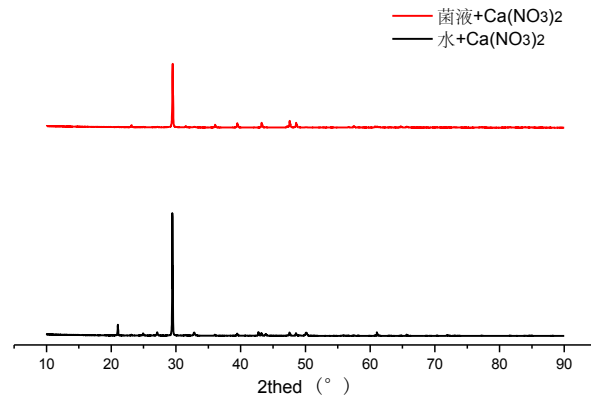
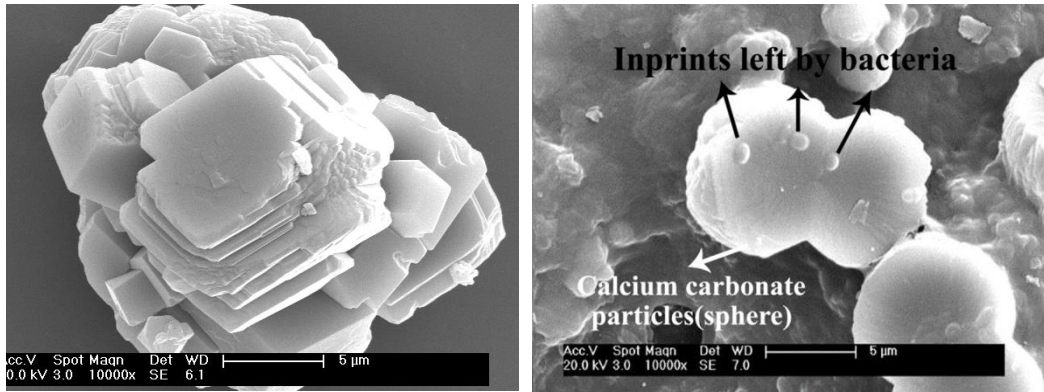


图 8 对照组和碳酸酐酶微生物诱导沉积碳酸钙 XRD 图谱

2.3.3 方解石 SEM 图

用扫描电镜（Scanning electron microscope, SEM）观察两组别沉积方解石形貌如图9，虽然两组别获得的沉淀物质同为方解石类型，但两者表现出来的形貌却完全不同。对照组形成的方解石晶体以斜六方晶格结构发育，晶体粒径大小分布不均且较大，出现片状或斜方六面体单晶、孪晶和其聚集体，见图（a）；微生物组形成的方解石晶体形貌是大小不一的花生状型，尺寸在 $10\mu\text{m}$ 左右，表面光滑，图9（b）还显示在沉淀颗粒上可见 $1\mu\text{m}$ 左右大小的印痕，暗示微生物在矿化中的成核作用。



(a)

(b)

图 9 化学法和微生物法沉积碳酸钙形貌

2.3 碳酸酐酶微生物诱导碳酸钙沉积修复混凝土裂缝效果

分别利用渗透系数法和裂缝面积修复率法表征碳酸酐酶微生物诱导碳酸钙沉积修复混凝土裂缝效果。

采用渗透系数法，按要求保持试件端部水压恒定，即以常水头法测量试件开裂后修复 5d、10d、20d、30d 后的渗水量，由达西定律计算渗透系数，不同组别试件渗透系数随修复时间变化曲线见图 10。

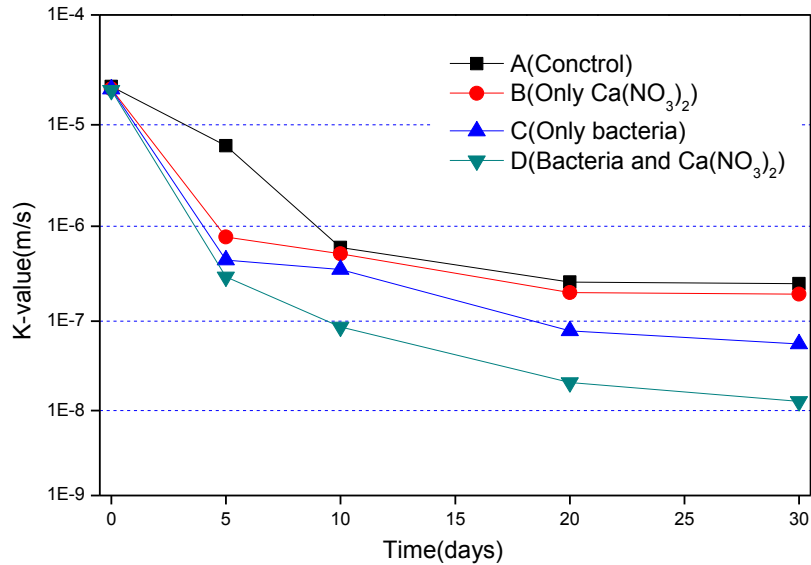


图 10 各组别试件渗透系数随修复时间的变化

分析图 10，比较三组试件渗透系数变化趋势，A、B、C、D 四组别渗透系数均随修复时间呈下降趋势，修复前期下降迅速（10d 前），修复后期（10d 后）下降速度减缓，最后渗透系数趋于稳定。其中 A 组别（水泥净浆无自修复剂）渗透系数随修复时间下降最慢；B 组别（添加自修复剂单一组分—硝酸钙）渗透系数随时间下降较 A 组别稍快，但总体下降速度在较低水平；C 组别（添加细菌）渗透系数下降较 B 组别快，说明当细菌存在时，可加速 CO_2 水合可逆反应，可依靠混凝土内部 $\text{Ca}(\text{OH})_2$ 提供 Ca^{2+} ，从而达到自修复效果；D 组别同时添加细菌和硝酸钙，硝酸钙能够为矿化提供额外的 Ca^{2+} ，裂缝自修复效果最佳，在修复 5d 后渗透系数与 A、B 组修复 30d 渗透系数相近，修复 30d 无渗水现象发生。

采用面积修复率法，将开裂的棱柱形试件置于水中浸没，并持续通入空气养护，观察不同修复时间后不同组别裂缝表面区域修复状况并拍照，图 11 为 A 组别修复 10d 和 30d 后裂缝表面区域碳酸钙填充状况，图 12 为 D 组别修复 10d 和 30d 后裂缝表面区域碳酸钙填充状况。利用 Image J 软件对裂缝照片进行二值化处理，图 13 展示了利用 Image J 软件对照组 A 裂缝二值化处理图像。根据定义计算各组别裂缝面积修复率，各组别裂缝自修复率随修复时间的变化曲线见图 14。

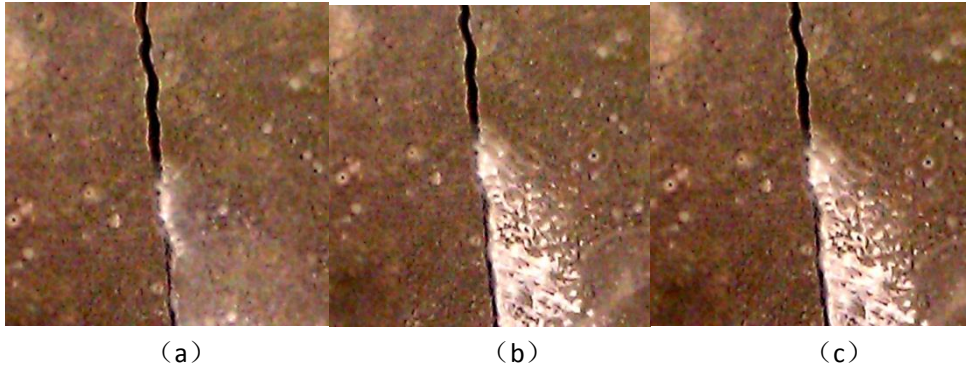


图 11 A 组别试件不同修复时间下裂缝表面区域碳酸钙填充状况，其中 (a) 为裂缝初始状态，(b) 为修复 10d 后裂缝表面区域碳酸钙填充状况，(c) 为修复 30d 后裂缝表面区域碳酸钙填充状况。

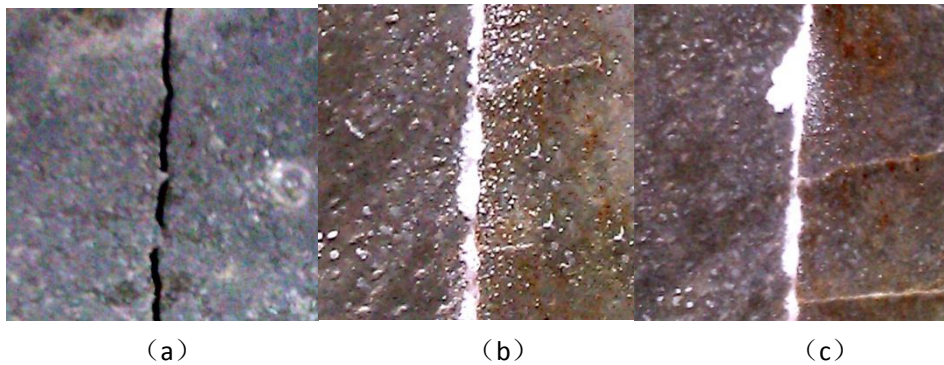


图 12 D 组别试件不同修复时间下裂缝表面区域碳酸钙填充状况，其中 (a) 为裂缝初始状态，(b) 为修复 10d 后裂缝表面区域碳酸钙填充状况，(c) 为修复 30d 后裂缝表面区域碳酸钙填充状况。

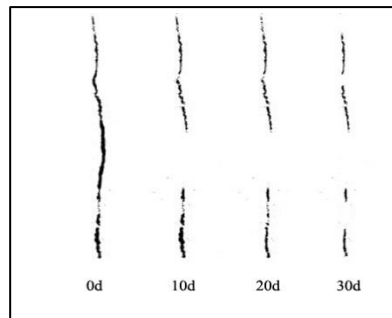


图 13 A 组别试件裂缝随修复时间二值图的变化

由图 14 可知，添加自修复剂 D 组别修复 5d 裂缝自修复率达到 90%以上，修复 30d 后平均自修复率为 99.2%，相比于未添自修复剂 A 组别高出了 150%，修复效果明显，修复 30d 后添加自修复剂单一组分硝酸钙的 B 组别自修复率为 43.7%，说明硝酸钙也能提高裂缝自修复率，但修复作用相比于对照组并不明显，分析其原因为更多的游离钙离子加速了碳酸钙在裂缝区的沉积；而 C 组别只添加细菌而不提供额外 Ca^{2+} 的情况下，依靠混凝土自身内部 $\text{Ca}(\text{OH})_2$ 仍可实现自修复，且效果较明显，5d 自修复率达到 70.9%，30d 自修复率可达到 81.3%。

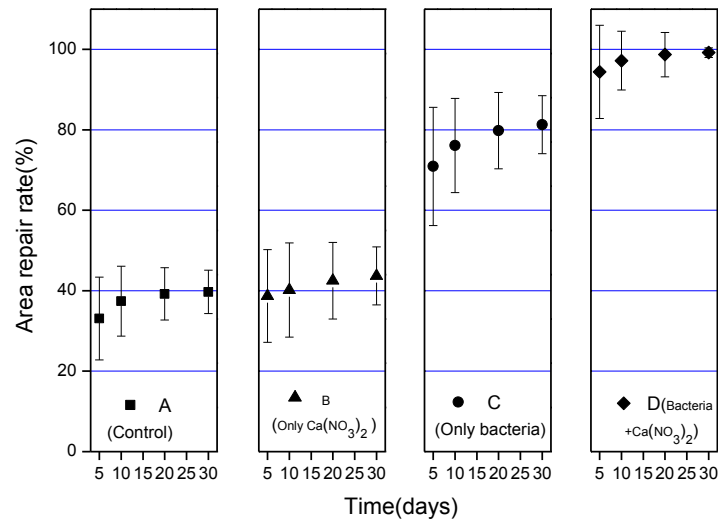


图 14 不同组别裂缝自修复率随修复时间的变化

3、结论

本文选用一类嗜碱芽孢杆菌，其能够代谢产生碳酸酐酶，通过对纯化菌株的培养试验，探明了此菌种生长曲线，确定了其最佳培养时间为 24-28h。对不同初始 pH 条件碳酸酐酶菌生长特性以及不同 pH 对碳酸酐酶化活力影响规律试验得出，酸性条件不适合碳酸酐酶菌生长代谢和酶化反应，碱性环境下最适 pH 为 8，随着碱度的提高，碳酸酐酶菌生长能力和酶化活力将下降，但 pH 为 12-13 时仍存在活菌，并且能够维持一定酶化活力，说明本试验采用的嗜碱芽孢杆菌对混凝土环境具有一定的耐受性，混凝土裂缝水环境中 pH 更利于碳酸酐酶菌酶化反应。在溶液环境中，通过试验证明了碳酸酐酶菌具有加速碳酸钙沉积的能力，并通过混凝土裂缝自修复试验，验证了在提供充足 Ca^{2+} 条件下，依靠碳酸酐酶促进 CO_2 水合反应的原理，碳酸酐酶微生物诱导矿化修复混凝土裂缝具有可行性。

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MoS₂/C 复合材料的制备与电化学性能研究

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摘要: 以钼酸钠、硫脲及不同的有机碳源(无水葡萄糖、蔗糖和可溶性淀粉)为原料, 用简单易操作的水热法合成了纳米花状类石墨烯 MoS₂/a-C 复合材料, 并在还原气氛中 800℃下热处理 2h 后得到最终产物。用 X-射线衍射(XRD)、场发射扫描电镜(FE-SEM)、高分辨透射电镜(HR-TEM)和拉曼光谱等对样品进行了表征。由 XRD 和 HR-TEM 的结果显示有部分无定形碳插入了 MoS₂ 层间。讨论了纳米花状类石墨烯 MoS₂/a-C 复合材料可能的生长机理, 并对其作为锂离子电池负极材料的电化学性能做了研究, 探讨了不同碳源对其电化学性能的影响机理。

关键词: MoS₂/C 复合材料; 锂离子电池; 负极材料

锂离子电池是目前使用最广泛的可充电移动电源, 至今为止, 它已被广泛应用于手机、笔记本电脑、数码相机、电子翻译器等方面, 此外, 它还在医学器件、电动汽车、航空航天、国防军事等领域有着广泛的应用前景和发展空间^[1]。锂离子电池电极材料是目前锂离子电池研究的核心, 其中对于负极材料的研究主要集中于以下几个方面: 较低的电极电位、较高的比容量及良好的循环稳定性、与电解质和粘合剂等电池组成部分的良好兼容性、较低的生产成本以及安全无污染的环境友好性。目前石墨由于循环稳定性好, 工作电压较高, 材料来源广, 生产成本低廉而被广泛用为锂离子电池负极材料, 且已商业化。但是, 石墨电极的比容量却相对较低(~375 mAh/g), 这也限制了锂离子电池的进一步发展。因此, 如何制备出性能更好的负极材料成了近年来锂离子电池研究的热点。

具有典型层状结构的二硫化钼(MoS₂)拥有与石墨相似的结构: 层内 S-Mo-S 原子之间由较强的共价键结合, 而层与层之间则由较弱的范德华力结合^[2]。正是由于 MoS₂ 层间较弱的键合, 使得其可以通过插层的方法在其层间引入外来的分子、原子或离子而不改变其层内的结构, 形成复合材料。作为锂离子电池负极材料, MoS₂ 有着很高的初始容量(~670 mAh/g), 其特殊的层状结构利于 Li⁺ 的嵌入与脱出。然而, 由于其本身低的电子/离子电导率及在脱嵌锂过程中严重的体积膨胀使得其循环稳定性极低^[3]。此外, 在电池反应过程中, MoS₂ 与 Li⁺ 发生反应生成了难溶的 Li₂S, Li₂S 又催化了电解液的分解从而形成了厚的聚合物层导致了不可逆的容量损失, 这也是其循环稳定性差的原因^{[4],[5]}。因此如何提高 MoS₂ 的循环稳定性, 成了 MoS₂ 作为锂离子电池负极材料研究的关键。

如果将 MoS₂ 与碳材料结合起来形成复合材料, 可能会获得高容量和良好循环稳定性的电极材料。Wang 等用水热法合成了用二硫化钼包覆的碳纳米管复合材料, 并研究了其电化学性能, 发现该复合材料有较高的比容量(400 mAh/g)和良好的循环稳定性^[6]。Zhang 等制备出了 MoS₂-C 纳米管, 在 100 次充放电循环后仍然具有 776 mAh/g 的储锂容量^[3]。Chang 等用水热法合成了类石墨烯 MoS₂/C 复合材料, 初始储锂容量高达 962 mAh/g, 在 100 次循环之后仍然有 912 mAh/g^[7]。对于将 MoS₂ 与碳材料结合起来的复合材料的研究已经不少, 然而对于不同碳源对该种复合材料的电化学性能的研究却鲜有报导。

本文通过以钼酸钠、硫脲及不同的有机碳源(无水葡萄糖、蔗糖和可溶性淀粉)为原料, 用温和的水热法合成了纳米花状类石墨烯 MoS₂/a-C 复合材料, 并在氩气和氢气混合气氛中 800℃下热处理 2 h 后得到最终产物。本文还讨论了纳米花状类石墨烯 MoS₂/a-C 复合材料可能的生长机理, 并对其作为锂离子电池负极材料的电化学性能做了研究, 探讨了不同碳源对其电化学性能的影响机理。

将一定质量的钼酸钠 (Na₂MoO₄·2H₂O) 和硫脲 (NH₂CSNH₂) 溶于去离子水中, 搅拌的同时加入一定质量的无水葡萄糖。搅拌数分钟后, 将溶液转移到 100 ml 的聚四氟乙烯和不锈钢制成的反应釜中并密封, 在烘箱中 200℃下加热 24 h。自然冷却到室温后, 通过过滤、并用去离子水和酒精分别冲洗数次获得产物, 在 80℃下真空烘干 12 h。其他条件相同的情况下, 将无水葡萄糖改为蔗糖和可溶性淀粉(保证碳原子的摩尔质量与无水葡萄糖相同), 合成其他碳源的 MoS₂/a-C 复合材料。为了清晰描述, 将样品标记为 MoS₂/a-C-1、MoS₂/a-C-2、MoS₂/a-C-3, 分别对应于无水葡萄糖、蔗糖、可溶性淀粉作为碳源的

复合材料。为了更好的对比,在相同的条件下,不加入任何碳源,制备了 MoS_2 。

将烘干后的产物放入石英舟中,置于有氩气和氢气混合气体的管式炉中 $800\text{ }^\circ\text{C}$ 下退火 2 h ,然后冷却至室温。

采用德国 Bruker 公司生产的 D8-Discover 型 X 射线衍射仪对样品进行 XRD 分析,以 Cu 靶 $\text{K}\alpha$ 为辐射源 ($\lambda=1.5406\text{ \AA}$),扫描速度 $0.15^\circ/\text{s}$,扫描范围 $10^\circ\sim 80^\circ$ 。将样品取少量于导电碳胶上,采用荷兰 FEI 公司的 Sirion-200 场发射扫描电镜(FE-SEM)观察样品形貌。将样品取少量超声分散在无水乙醇中,然后滴 $1\sim 2$ 滴到铜网上,采用荷兰 FEI 公司的 G2 20 透射电镜(TEM)观察样品形貌。取少量样品于载玻片上,采用 LabRAM HR UV-Visible 共聚焦拉曼光谱仪对样品进行 Raman 光谱表征,采用背散射集合配置,激发波长 514.5 nm ,波数范围 $200\sim 2000\text{ cm}^{-1}$ 。

采用双电极模拟电池对样品进行电化学测试。以锂片为对电极和参比电极,聚丙烯膜为隔膜,电解液为 1.0 M 的 $\text{LiPF}_6\text{ EC/DMC}$ (体积比 $1:1$) 溶液。将 80% 质量比的活性材料, 10% 的乙炔黑, 10% 粘结剂聚偏氟乙烯(PVDF)充分混合,并均匀涂覆在作为集电器的铝箔上,然后在 $110\text{ }^\circ\text{C}$ 下真空干燥 12 h 后得到工作电极。在充满氩气的手套箱中进行电池的组装。

我们提出了 $\text{MoS}_2/\text{a-C}$ 复合材料的生长机制。在水热过程中主要有两个反应: (1), 碳源的碳化与聚合, 形成碳纳米球; (2), 由 $\text{CS}(\text{NH}_2)_2$ 分解得到的 H_2S 与 Na_2MoO_4 反应生成 MoS_2 晶须。^[8]这两个反应同时发生。在初始阶段, 碳源团聚、碳化形成碳胶体, 与 MoS_2 相互交织在一起。随后, 在 MoS_2 片层堆积的过程中, 有部分碳留在了 MoS_2 层间, 在 $800\text{ }^\circ\text{C}$ 下退火后, 形成了新的复合材料。同时, 由于碳胶体的存在, 抑制了 MoS_2 片层的堆积。但是对于不同的碳源, 在反应的过程中仍然存在不同之处。葡萄糖分子很小, 蔗糖分子稍大且有网状结构, 而淀粉分子则是链状的大分子, 所以其反应过程不尽相同。对于葡萄糖, 在溶液中, 有一些 MoO_4^{2-} 离子围绕在葡萄糖分子周围, 同时溶液中也存在着 HS^- 离子, 在水热反应过程中, 葡萄糖分子聚合、碳化形成碳胶体, 同时边上围绕着 MoO_4^{2-} 离子与 HS^- 离子反应生成了 MoS_2 , 最终形成了如图 2(a)所示的纳米花结构。对于蔗糖, 有更多的 MoO_4^{2-} 离子围绕在蔗糖分子周围, 从而更多的 MoS_2 晶须分散在碳球中, 形成了花状的纳米球结构, 如图 2(b)所示。然而, 对于淀粉, 只有少量的 MoO_4^{2-} 离子围绕在其分子周围, 它们可以直接聚合、碳化形成碳纳米球而没有 MoS_2 分散在其中, 从而 $\text{MoS}_2/\text{a-C}$ 有两种形态, 如图 2(c)所示。这一过程同时也会抑制 MoS_2 的生长, 有更多的无定型碳没有插入到 MoS_2 的层间, 而只是包裹在了其表面。总而言之, 不同的生长机制导致了不同的电化学性能。蔗糖拥有适合的分子大小, 有利于锂离子的插入与脱出, 从而具有最好的电化学性能。

综上所述, 我们简单的水热法合成了 $\text{MoS}_2/\text{a-C}$ 复合材料。其 XRD 和 TEM 结果显示有部分无定型碳插入了 MoS_2 层间。对样品的电化学性能研究显示了 $\text{MoS}_2/\text{a-C}$ 复合材料拥有更高的比容量和跟稳定的循环性。其中 $\text{MoS}_2/\text{a-C-2}$ 表现出最高的比容量和最好的循环稳定性。 $\text{MoS}_2/\text{a-C-2}$ 的电化学性能有如此显著的提高, 主要是由于其拥有适合的分子大小, 有利于锂离子的插入与脱出, 从而具有最好的电化学性能。同时我们讨论了纳米花状类石墨烯 $\text{MoS}_2/\text{a-C}$ 复合材料可能的生长机理, 并探讨了不同碳源对其电化学性能的影响机理。

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An Investigation of the Nanomechanical Properties of $0.5\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ – $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ Thin Films

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For practical application, the functional piezoelectric film in microelectromechanical systems should meet the requirement of physical properties, as well as the mechanical properties. In this article, $0.5\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ – $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (0.5BZT–0.5BCT) thin films with varied properties were prepared on (100) Si substrates via a sol–gel technique at different annealing temperatures. The effects of the annealing temperature on the morphology, piezoelectricity, hardness, and elastic modulus were studied. Particular attention was paid to the surface frictional behavior of films, and the changes in the friction force can be radically explained in terms of differences in the hardness/elastic modulus ratio and the residual stress of films. And, it reveals that the higher ratio of hardness to elastic modulus and tensile residual stress can contribute to a lower friction force for 0.5BZT–0.5BCT film during sliding friction.

I. Introduction

PIEZOELECTRIC thin films are an essential component in MEMS (microelectromechanical systems) actuators, which can convert mechanical energy into electrical energy, and vice versa, have been extensively used in aviation, optoelectronics, biotechnology, and other fields.^{1,2} With the increasing interest in this area, many problems in MEMS actuators have been encountered in the past decades. One of the troubling questions is the failures induced by mechanical weakness and friction of the rubbing surfaces. Compared with the macroscopic engineering world, the size of piezoelectric film in MEMS actuators is always down to micro/nanometers, resulting in very different mechanical properties and high surface forces such as frictional and adhesive forces, which seriously undermine the lifetime, reliability, and performance of MEMS devices.³ Nowadays, the nanoindentation tester, atomic force microscopy (AFM) have been proved to be useful techniques to study mechanical and frictional behavior on the nanoscopic scale.^{4,5} Many research institutions such as UC Berkeley, Sandia National Laboratory have carried out investigations on this field.⁶

So far the best investigated piezoelectric films for MEMS applications are based on lead zirconate titanate (PZT), with piezoelectric constant of $d_{33} = 100$ – 120 pm/V.⁷ As a

commercial piezoelectric thin film in MEMS, the mechanical properties of PZT thin films including interfacial adhesion, elastic modulus and hardness, tribological characteristic have been deeply studied.^{8,9} However, the usage of PZT will be seriously restricted due to Pb toxicity. Thus, there exists an urgent need for researchers to develop lead-free piezoelectric materials with high performance to replace PZT. As many non-Pb piezoelectric systems have been developed such as BaTiO_3 -based, $(\text{Bi},\text{Na})\text{TiO}_3$ -based, $(\text{Na},\text{K})\text{NbO}_3$ -based, however, all of which show piezoelectric property lower than PZT.¹⁰ Recently, $(1-x)\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ – $x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ Pb-free solid solution [abbreviated as $(1-x)\text{BZT}$ – $x\text{BCT}$] has attracted great attention for its high piezoelectric coefficient about 560–620 pC/N when $x = 50$.¹¹ This is because the 0.5BZT–0.5BCT is located around the morphotropic phase boundary area that the energy barrier for polarization rotation is lower than other compositions,¹⁰ which is the same case for PZT. As then, immense investigations have been conducted on the $(1-x)\text{BZT}$ – $x\text{BCT}$ system and among them, many achievements have been made on $(1-x)\text{BZT}$ – $x\text{BCT}$ thin films. Piorra¹² reported the piezoelectric response of approximately 80 pm/V and a dielectric coefficient of about $\epsilon_r = 1010$ for 0.5BZT–0.5BCT thin film deposited by pulsed laser deposition, these obtained values are close to PZT thin film.⁷ Very recently, Jalalian¹³ showed that large piezoelectric coefficient in 0.5BZT–0.5BCT thin films can reach up to 140 pm/V, which is higher than that of PZT thin films. Therefore, 0.5BZT–0.5BCT thin film is found to be a potential candidate to replace PZT in MEMS devices. There has been little research, however, on the nanomechanical properties of 0.5BZT–0.5BCT films, including their hardness (H), elastic modulus (E), and tribological behavior, and an understanding of the underlying factors affecting tribological properties is still lacking.

In this article, sol–gel method was adopted to fabricate 0.5BZT–0.5BCT thin films for its advantages in terms of compositional homogeneity, the possibility of covering a larger substrate area, cost-effectiveness, and compatibility with integrated circuit when compared with other methodologies. Considering the annealing temperature largely affect the microstructure and properties of samples during the sol–gel process, four different annealing temperatures were adopted and its effect on the microstructure as well as their piezoelectric and nanomechanical properties was investigated. Particular attention was paid to the evolution of the tribological properties with sintering temperature in the 0.5BZT–0.5BCT films. The goal of this work was to fabricate the high piezoelectric 0.5BZT–0.5BCT thin film and make the first move to study its nanomechanical and tribological properties for potential MEMS applications.

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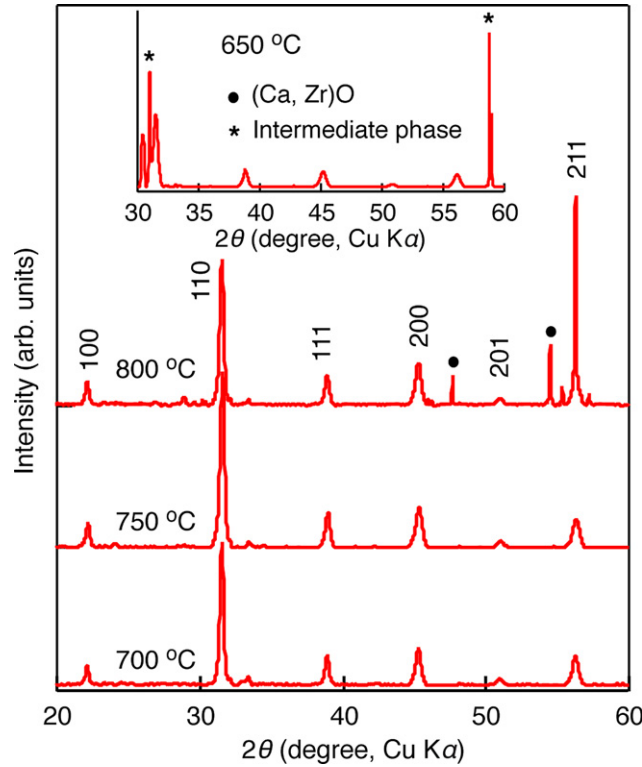


Fig. 1. XRD patterns of 0.5BZT-0.5BCT films annealed at different temperatures. (Inset: 650°C-annealed film with strong impurity phase peak).

II. Experimental Procedure

Analytical graded barium acetate $[\text{Ba}(\text{CH}_3\text{COO})_2]$, calcium acetate monohydrate $[\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$, tetrabutyl titanate $[\text{Ti}(\text{OC}_4\text{H}_9)_4]$, and zirconium oxynitrate $[\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}]$ were used as starting materials. Glacial acetic acid and 2-methoxyethanol (2-MOE) were used as the chelating agent and solvent, respectively. The details of solution preparation procedure is almost same as in Ref. [14], and the only difference is the substitute of absolute alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) by 2-MOE for the 2-MOE was found to be an effective solvent to improve the electric properties of films in the sol-gel technique according to our work and Ref. [15]. The 0.5BZT-0.5BCT solution was finally deposited on (100)-oriented single crystalline Si substrate by multiple cycles of spin-coating, drying, and pyrolysis, and then followed by annealing under four different temperatures: 650°C, 700°C, 750°C, and 800°C. The thickness of these studied films is ~800 nm, as measured by field-emission scanning electron microscopy (not shown).

The phase structure of all the samples was determined by X-ray diffraction (XRD) using a Rigaku Rint 2200 V powder diffractometer (Rigaku, Tokyo, Japan) with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$), at a scanning rate of $1^\circ/\text{min}$. The surface morphology of the crystallized microstructure of the 0.5 BZT-0.5BCT films was observed by AFM (SII Nano Technology Inc., Tokyo, Japan). The measurements of local piezoelectric displacement were carried out by keeping the scanning probe microscope tip fixed on the grain of interest with a DC voltage from -40 to 40 V to record the piezoresponse signal. The nanomechanical properties, including elastic modulus (E) and hardness (H), were measured via a Micro Materials NanoTest instrument with a Berkovich diamond indenter. To avoid surface and substrate effects, the maximum penetration depths were controlled

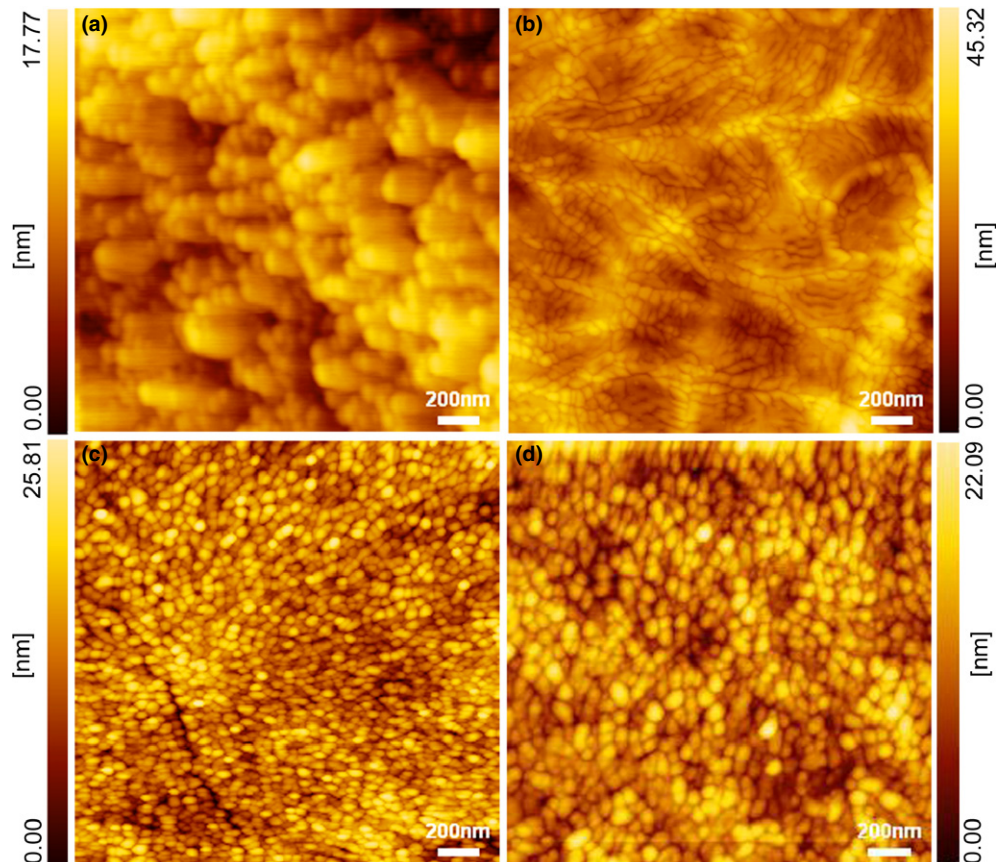


Fig. 2. Atomic force microscopy images for 0.5BZT-0.5BCT piezoelectric thin films annealed under different temperatures. (a): 650°C, (b): 700°C, (c): 750°C, (d): 800°C.

within 100 nm in the nanoindentation tests, and every sample was measured in a 5×5 matrix to minimize the error. As for tribological characteristics, the frictional behavior of 0.5BZT–0.5BCT thin films were measured through force–distance curves in the backward and forward directions using the friction mode of the AFM in contact mode. The vertical and lateral resolutions of the AFM are about 0.01 and 0.2 nm, respectively. In this measurement, the aluminum-coated silicon cantilever with curvature radius of 10 nm was used so that the superficial nanometric corrugation of films would be detected. The sliding speed was 2 $\mu\text{m/s}$ and the applied force was in the range of 0–20 nN.

III. Results and Discussions

(1) Microstructure and Morphology of 0.5BZT–0.5BCT Thin Films

The XRD patterns for 0.5BZT–0.5BCT films annealed at different temperatures are shown in Fig. 1. Compared with the films annealed at temperatures of 650°C and 800°C, the 0.5BZT–0.5BCT films annealed at 700°C and 750°C consist of single perovskite phase and have better crystallinity than the other samples, as evidenced by a sharpening of the diffraction peaks. At 650°C, crystallization is not complete, with pyrochlore phase and perovskite phase coexisting in the film. When the postannealing temperature was raised to 800°C, very small amounts of impurities appeared in the film. This is mainly because the higher annealing temperature (800°C) could provide enough energy for Ca and Zr to diffuse from the perovskite structure to react with oxygen.

Figure 2 shows the AFM morphology images for films annealed under different temperatures and as can be seen, with the increased annealing temperature the film surface becomes more homogeneous and denser. It is obvious that the film annealed under 650°C has various grain shapes and sizes comparing with others, which is caused by coexisting intermediate phase and perovskite phase according to XRD results and the larger grains may be core-shell structured BaCO_3 (CaCO_3) @ TiO_2 (ZrO_2) depending on our previous work.¹⁴ As the annealing temperature improved, the grain became larger and more homogeneous. The root mean square (RMS) surface roughness value and averaged grain size were obtained by Nano Navi II Analysis Software (SII Nano Technology Inc.), and their dependency of annealing temperature was summarized in Fig. 3(a). It is observed from Fig. 3(a) that with the postannealing temperature increases from 700°C to 800°C, the average grain size increases from 38 to 59 nm, whereas the RMS value decreases from 7.10 to 3.31 nm. Usually, the grain size obtained from AFM image is statistical average value,¹⁶ here, the measurement error is about 6–11 nm. In the 0.5BZT–0.5BCT film sintering process, diffusion is the main means of mass transfer and is controlled by the vacancy concentration gradient. Kuczynski¹⁷ proposed the neck stress model, as shown in Fig. 3(b). When two spherical particles come into contact with each other, the stress in the neck surface, σ_p , is tensile, whereas the stress in the center of contact for the particles, σ_2 , is compressive. It has been calculated that¹⁸ the formation energy for a vacancy in the tensile stress areas is lower than in the compressive ones, resulting in a higher vacancy density in the neck surface than at the contact center. Therefore, the vacancy diffusion would run from the neck surface to the contact center, whereas the atoms diffuse along the opposite direction. The main sources for the atoms include the surface, and intracell and grain boundaries, and the corresponding diffusion paths are shown in Fig. 3(b). With the filling in of the neck and migration of structural units in contact areas, the pore shrinks, and the particles approach each other. As a result, the porosity decreases, and grains are developed at elevated temperatures. The higher the temperature is, the higher the self-diffusion coefficient will be. Hence, the grain

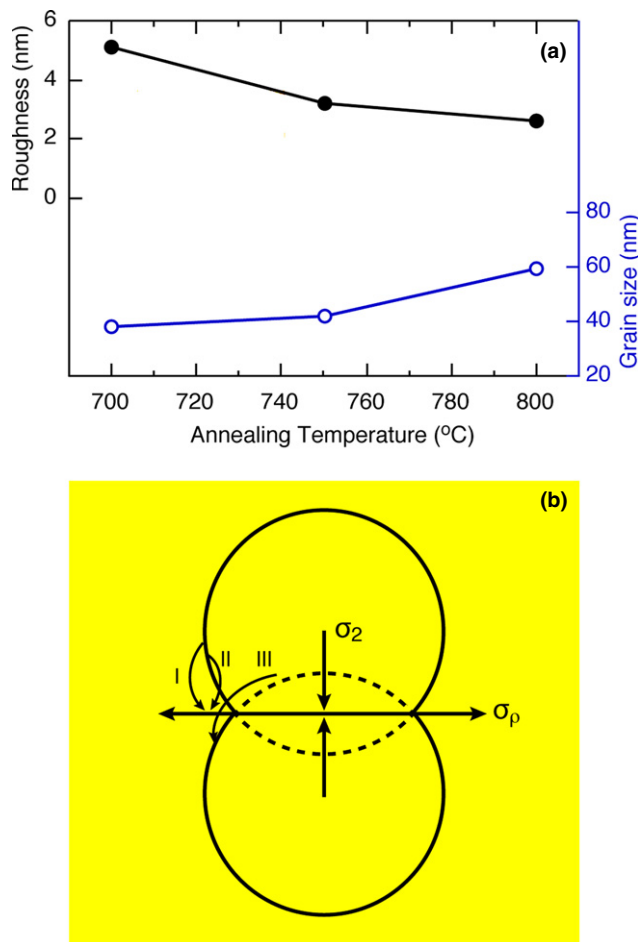


Fig. 3. (a) Roughness and average grain size dependence of annealing temperature. (b) The neck stress model and different diffusion paths for atoms during the annealing process. I: from surface to neck, II: from grain interior to neck, III: from grain boundary to neck.

size increases, and the film becomes smoother and denser with increasing annealing temperature, which is consistent with the AFM results.

(2) Piezoelectric Properties of 0.5BZT–0.5BCT Thin Films

Figure 4(a) presents the typical piezoelectric response dependence of the applied voltage for the 0.5BZT–0.5BCT film annealed at 800°C. As can be seen, a well-shaped displacement–voltage (D – V) “butterfly” loop is obtained and the piezoelectric hysteresis loop (d_{33} – V) is determined from the D – V curve by Eq. (1):

$$d_{33} = (D - D_0)/(V - V_0) \quad (1)$$

where D_0 and V_0 are the piezoelectric deformation and voltage at the intersection, respectively. Because the piezoelectric response obtained from AFM is a local signal, to achieve a relatively representative piezoelectric coefficient for different films, at least 20 “butterfly loops” like in Fig. 4(a) were obtained for all samples. The d_{33} dependence on the annealing temperature is given in Fig. 4(b), and it can be seen that the d_{33} increases as the postannealing temperature increases. The piezoelectricity for the 650°C film is poor because of the presence of a nonferroelectric pyrochlore phase, whereas for nanocrystalline films, the trend in d_{33} with annealing temperature can be ascribed to the grain-boundary (GB) effect and film densification. It is well-known that¹⁹ GBs are nonferroelectric and could provide possible sites for space-charge

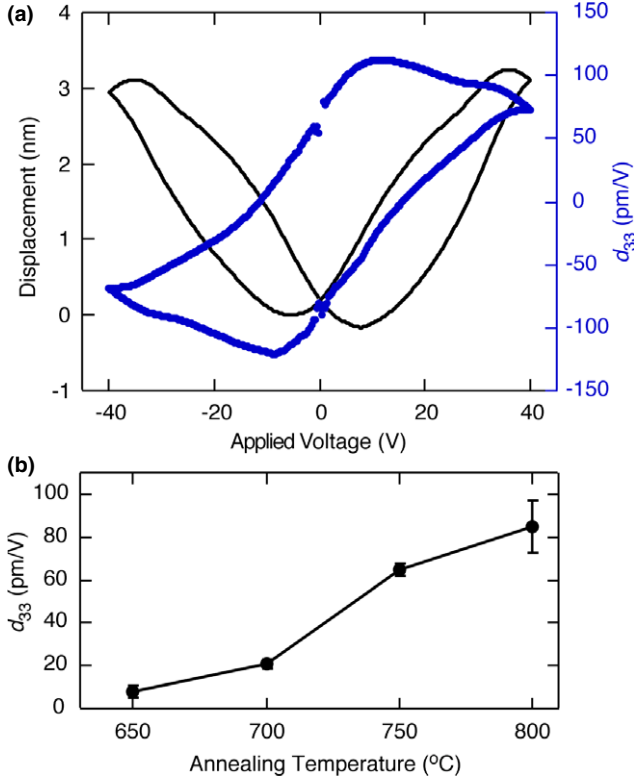


Fig. 4. (a) Typical local piezoelectric response versus applied voltage for the 0.5BZT–0.5BCT film annealed at 800°C. (b) d_{33} value of the films as a function of annealing temperature.

“pinning”, the thus-formed space-charge layer would hinder polarization in the film by its space-charge field, in other words, reduce the piezoelectricity of the film. Meantime, denser microstructure with less porosity would reduce the possibility of domain “pinning” at pore areas, thus, be helpful for domain reversal and good piezoelectricity.²⁰ Combine with AFM images, it is reasonable to observe a larger piezoelectric coefficient in the film annealed at high temperature even though there is a bit of secondary phase existing in 800°C 0.5BZT–0.5BCT thin film, whose effective piezoelectric coefficient d_{33} is estimated to be ~85 pm/V, which is close to values obtained for PZT films.⁷

(3) Mechanical Characterization of 0.5BZT–0.5BCT Thin Films

The variations of E and H with annealing temperature are summarized in Fig. 5(a). It is clear that E and H improve with higher annealing temperature, but then drop a little in the film annealed at 800°C. For the ionic 0.5BZT–0.5BCT material, the bonding is delocalized, and the mechanical properties are greatly influenced by extrinsic factors such as impurities, precipitates, grain boundaries, etc.²¹ And the stiffness will be reduced because stress becomes concentrated at the intersection between two boundaries.²² Belova *et al.*²³ have derived that the effective diffusivity for atoms increases with increased volume fraction of grain boundaries for nanocrystalline materials. Therefore, less grain boundaries in films annealed at higher temperature will lead to fewer stress concentrations and less plastic deformation, which will result in improvement of the elastic modulus and hardness. Also, the slight drop in both H and E for the film annealed at 800°C can be attributed to the formation of small amounts of impurities, as indicated by XRD (shown in Fig. 1), which can accelerate the plastic deformation process because of the high-energy around impurities.

The frictional behavior of the 0.5BZT–0.5BCT films annealed at different temperatures is summarized in

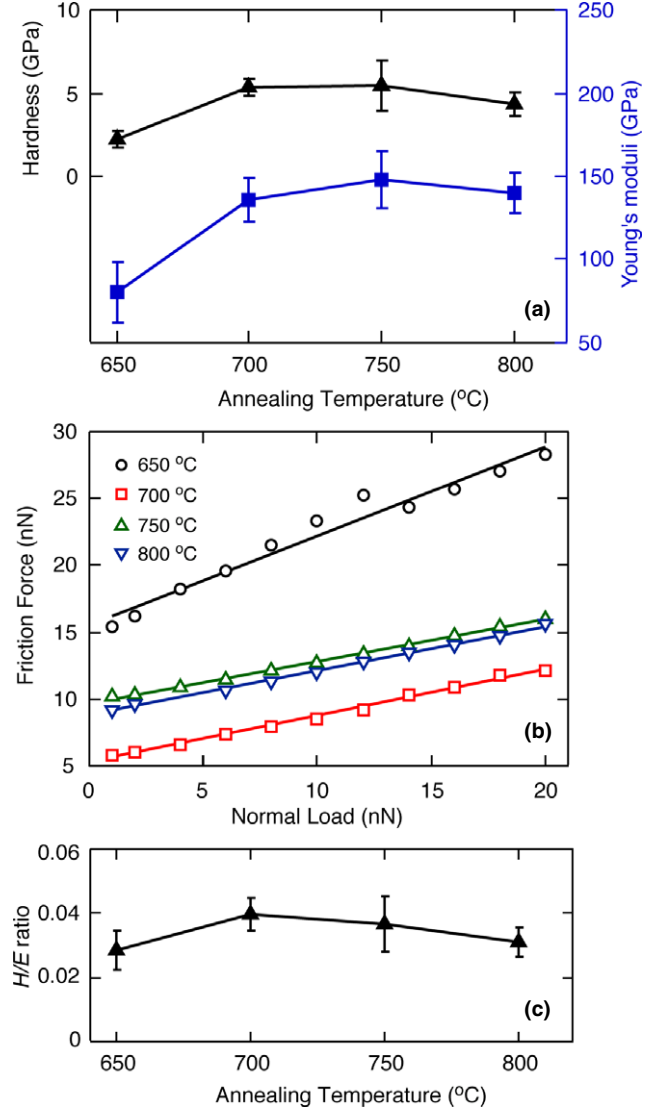


Fig. 5. (a) Dependences of the hardness and Young's modulus on the postannealing temperature of different samples. (b) Friction versus normal load curve. (c) Ratio of the hardness to the elastic modulus of the 0.5BZT–0.5BCT films.

Fig. 5(b). In general, the relationship between the friction force and the normal load for nanocrystalline films can be expressed as follows:

$$F = F_0 + fF_n^\beta \quad (2)$$

F is the measured friction force between the film and probe; F_n is the applied normal load; F_0 is the friction force when the applied load is zero; f is the friction coefficient; and β is a fitting exponent. When the fitting exponent β is set to 1, the degree of fitting is optimal. That is, F presents a linear relationship with F_n , as can be seen in Fig. 4(b). Obviously, although the 700°C film has highest RMS value as seen in Fig. 3(a), its friction force is the lowest. Tribological interactions are known to be extremely complex, depending on roughness, tribochemical reactions, and structural rearrangement, all of which have great effects on the tribological

Table I. Residual Stress in Films Annealed at Different Temperatures

Annealing Temperature (°C)	650	700	750	800
Residual Stress (GPa)	−0.313	0.515	1.459	2.275

The negative sign “−” indicates that the residual stress is compressive.

properties.²⁴ In this experiment, all of the samples were measured under constant surrounding temperature and humidity, using a certain AFM tip; therefore, no structural rearrangement was expected to occur, and the tribochemical reactions were supposed to be similar for all the films, as the amounts of atoms which compose the films are very much the same. Friction is a typical non-equilibrium process, which is energy-dissipative by converting the mechanical energy into thermal energy. That is, the mechanical properties of a sample have a great effect on its frictional behavior. Researchers^{25,26} have discovered that nanostructured materials with a high ratio of hardness to elastic modulus (H/E) can exhibit improved wear properties. Therefore, it is acceptable to take the ratio of H/E to evaluate the friction behavior of the 0.5BZT–0.5BCT thin films. The H/E values for the different films are summarized in Fig. 5(c). It is clearly observed that the 650°C film has the lowest ratio, whereas the 700°C film has the highest ratio, corresponding to the highest and lowest friction force, respectively, as seen in Fig. 5(b). The results suggest that a low ratio of H/E can lead to a high friction force and, to some extent, poor wear properties, which is in accordance with Ref. [25]. Detailed observations showed that the 800°C film is abnormal compared with others, because its ratio of H/E is smaller than for the 750°C film, but it is accompanied by a lower friction force than 750°C film. Another mechanical factor that can influence the tribological behavior of films certainly exists. Reports have shown that the residual tensile stress retained in the film can reduce the adhesion force.²⁷ To have a better understanding of the influence of the residual stress on the tribological behavior, small-angle XRD, as described elsewhere,²⁸ was used to measure the residual stress in the films, and the results are summarized in Table I. These results show that the residual stress is tensile and increases with annealing temperature for the 700°C, 750°C, and 800°C films, but for the film annealed at 650°C, the stress is compressive and about 313 MPa. This may be attributed to the interaction between the thermal stress and the lattice stress, resulting in the conversion from tensile to compressive stress.²⁹ Comparing the different residual stresses in the films, it is easy to identify that the tensile stress could reduce the friction force and that higher tensile stress reduces it more, which may be related to the stress relaxation, however, the underlying mechanism is still under investigation.

IV. Conclusions

In this work, 0.5BZT–0.5BCT thin films were prepared via the sol–gel process and annealed under different temperatures. For nanocrystalline films, the piezoelectricity and nanomechanical properties are mainly related to the microstructure such as grain size, density, and second phase, and the tribological behavior is largely affected by the residual stress and the ratio of the hardness to the elastic modulus, that is, greater tensile stress and a higher H/E ratio can result in a lower friction force. Among the investigated 0.5BZT–0.5BCT thin films, the 800°C-annealed film showed potential application in MEMS devices with a high piezoelectric constant up to 85 pm/V, elastic modulus and hardness about 140.09 and 4.35 GPa, respectively, and relatively low friction force during sliding friction. However, there is still many investigations to be done in this field to make the 0.5BZT–0.5BCT thin film real practice.

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Cellular Automaton Modeling of Ferrite-austenite Transformation

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A two-dimensional cellular automaton (CA) model is adopted to simulate ferrite (α)-austenite (γ) transformation in a low-carbon steel. The kinetics of phase transformation is determined by interface mobility and carbon diffusion. The model simulates the evolution of microstructure and carbon distribution during α - γ transformation. The heat treatment processes, including isothermal heating at 760°C, subsequent cooling to room temperature and then tempering at different temperatures for different times, are simulated. The results show that after isothermal heating at 760°C for 5 min and cooling down to room temperature at 5°C/s, the carbon concentration field is non-uniform. The uniformity of carbon distribution increases gradually during tempering at 400°C for 20 min, while the carbon distribution becomes uniform within 5 min when tempered at 500°C or 600°C.

Key words: modeling, cellular automaton, ferrite-austenite transformation, low-carbon steel

1. Introduction

With the development of numerical models, such as the phase field (PF), Monte Carlo (MC), and cellular automaton (CA) models, a number of simulations have been carried out to study the microstructure evolution during ferrite-austenite transformation [1-4]. Nevertheless, limited work associates the microstructure simulation with the processing and properties in practice. The present authors proposed a two-dimensional (2D) CA model for the simulation of the ferrite (α)-austenite (γ) transformation to understand the processing-microstructure-property relationships of low-carbon enameling steels [5]. In this paper, the previously developed CA model is applied to simulate α - γ transformation and the carbon distribution during a series of heat treatment processes. The simulation results are applied to understand the mechanisms of some experimental phenomena of a low-carbon enameling steel.

2. Experimental phenomena and cellular automaton model

A cold-rolled enameling steel, containing 0.07 wt.% C, 0.51 wt.% Si, 1.23 wt.% Mn, 0.05 wt.% P and 0.004 wt.% S, exhibits a short yield platform and a low yield strength (322 MPa) after isothermal heating at 760°C for 5 min and subsequent air cooling ($\sim$ 5°C/s), which is lower than the as-rolled yield strength (354 MPa). After tempering at 400°C for 5 min, 10 min, and 20 min, the yield strength increases to 387 MPa, 394 MPa and 401 MPa, respectively. When tempered at 500°C or 600°C for 5-20 min, the yield strength remains nearly unchanged at about 393 MPa. The CA simulations are performed to understand the mechanism of the experimental phenomena.

In the present CA model, the computational domain is divided into a lattice of 236×348 square cells with cell size of $0.3 \mu\text{m}$, corresponding to a real domain of $72 \mu\text{m} \times 105 \mu\text{m}$. Each cell is characterized by the variables of grain orientation, α phase fraction, interface indicator symbol, and mean carbon concentration. A pseudo-binary Fe-C alloy with initial concentration $u_0 = 0.2962 \text{ mol.\% C}$ (corresponding to 0.116 equilibrium γ phase fraction at 760°C) is adopted for simplicity. The phase transformations of both $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ are simulated, while the coarsening of ferrite grains is not considered. The heat treatment processes used in the simulations are identical with those used in the experiment that consists of isothermal heating at 760°C for 5 min, subsequent cooling to room temperature at 5°C/s , and tempering at 400°C - 600°C for different times.

The migration velocity of the α/γ interface, v_n , is calculated by [6]

$$v_n = M_{eff} \cdot \left\{ -RT_M (k_e - 1) [u^\alpha(T) - u_e^\alpha(T)] / V_m \right\} \quad (1)$$

where M_{eff} is the interface mobility, R is the gas constant, T_M is the allotropic transformation temperature, V_m is the molar volume. $u^\alpha(T)$ is the actual carbon concentration in ferrite at T , and k_e is the equilibrium partition coefficient, defined as $k_e = u_e^\gamma(T) / u_e^\alpha(T)$, where $u_e^\gamma(T)$ and $u_e^\alpha(T)$ are the equilibrium concentrations in ferrite and austenite at T , respectively. The values of $u_e^\gamma(T)$ and $u_e^\alpha(T)$ are obtained from the phase diagram calculated by Pandat software [7]. Eq. (1) indicates that the interface velocity v_n is determined by M_{eff} , taken as $4.2 \times 10^{-7} \exp(-14700/RT) \text{ m}^4/\text{J}\cdot\text{s}$ [8], and the local concentration difference $u^\alpha(T) - u_e^\alpha(T)$, while $u^\alpha(T)$ is controlled by carbon diffusion. Defining the mean carbon concentration as $u = \phi u^\alpha + (1-\phi)u^\gamma$, where ϕ is the α phase fraction, carbon diffusion in 2D is calculated by

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial x} \cdot \left[D(\phi) \frac{\partial u^\alpha}{\partial x} \right] + \frac{\partial}{\partial y} \cdot \left[D(\phi) \frac{\partial u^\alpha}{\partial y} \right] \quad (2)$$

where $D(\phi)$ is the diffusion coefficient associated with the α phase fraction ϕ , determined by $D(\phi) = \phi D^\alpha + k_e(1-\phi)D^\gamma$. The carbon diffusivities in the α and γ phases, D^α and D^γ , are taken as $2.2 \times 10^{-4} \exp(-122500/RT)$ and $1.5 \times 10^{-5} \exp(-142100/RT) \text{ m}^2/\text{s}$, respectively [1].

3. Results and discussion

During the isothermal heating process, $\alpha \rightarrow \gamma$ phase transformation accompanied with carbon redistribution takes place. According to the experimental observations, the nucleation sites of austenite are preferentially distributed at the ferrite grain boundaries. The number of ferrite grains and austenite nuclei are also obtained from metallography.

The simulated evolution of the carbon concentration field of an Fe-0.2962 mol.% C alloy during isothermal heating at 760°C is shown in Figure 1. The lower 8 levels and the upper 6 levels of the color legends in Figure 1 show the carbon distributions in the α phase and γ phase, respectively. As $\alpha \rightarrow \gamma$ phase transformation proceeds, austenite grains grow until the γ phase fraction reaches the equilibrium value (about 0.116), and the carbon distribution becomes uniform gradually. The carbon concentrations in both phases reach the equilibrium values after isothermal heating at 760°C for around 150 s.

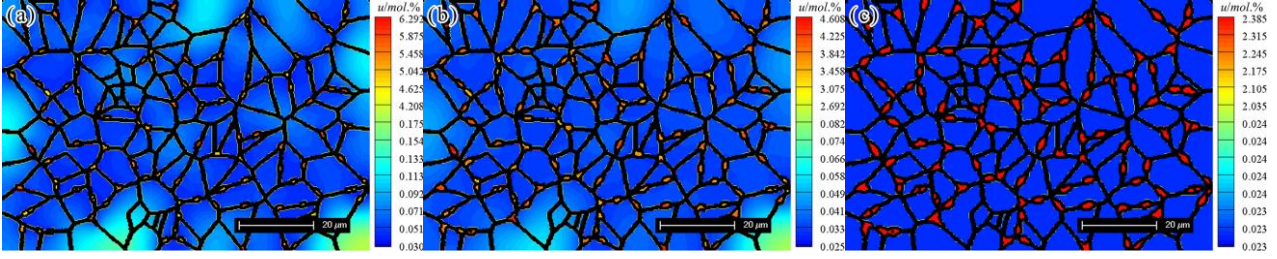


Figure 1 Simulated evolution of the carbon concentration field of an Fe-0.2962 mol.% C alloy during heating at 760°C for: (a) 0.5 s; (b) 1 s; (c) 300 s.

Figure 2 shows a comparison of the simulated and experimental microstructures after isothermal holding at 760°C for 300 s. The black and white colors in Figure 2 (a) indicate the ferrite and austenite phases, respectively, while the grain boundaries are represented by the gray color. It is noted that the simulated microstructure agrees well with the experimental observation.

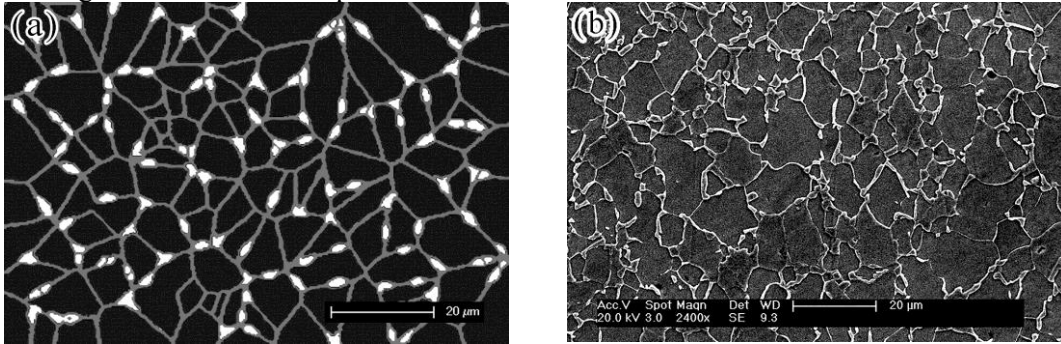


Figure 2 Comparison of microstructures after heating at 760°C for 300 s: (a) simulation; (b) SEM image.

Figure 3 shows the simulated carbon distribution after isothermal heating at 760°C for 5 min, cooling down to room temperature at 5°C/s and then tempering at 400°C-600°C for different times. During cooling, $\gamma \rightarrow \alpha$ transformation and carbon diffusion take place. When the temperature is below 600°C, $\gamma \rightarrow \alpha$ transformation ends and the retained austenite transforms to supersaturated ferrite, while carbon diffusion continues according to the model assumptions. It is evident that the carbon distribution is quite non-uniform when cooling down to room temperature (Figure 3 (a)). This is due to the fact that the high cooling rate leads to insufficient diffusion of carbon atoms from the retained austenite to the ferrite phase. For the tempering process, only carbon diffusion takes place. During tempering at 400°C for 20 min, the uniformity of carbon distribution increases gradually (Figure 3 (b) and (c)). When tempered at 500°C or 600°C for 5 min, the carbon distribution becomes uniform (Figure 3 (d)) due to the relatively high carbon diffusivity. It is obvious that sufficient carbon diffusion is beneficial to forming high concentration Cottrell atmospheres, which contributes to a high yield strength. Accordingly, based on the simulation results shown in Figure 3, it is understandable that when tempering at 400°C, the yield strength increases with tempering time, while tempering at 500°C or 600°C, the tempering time has less effect on the yield strength.

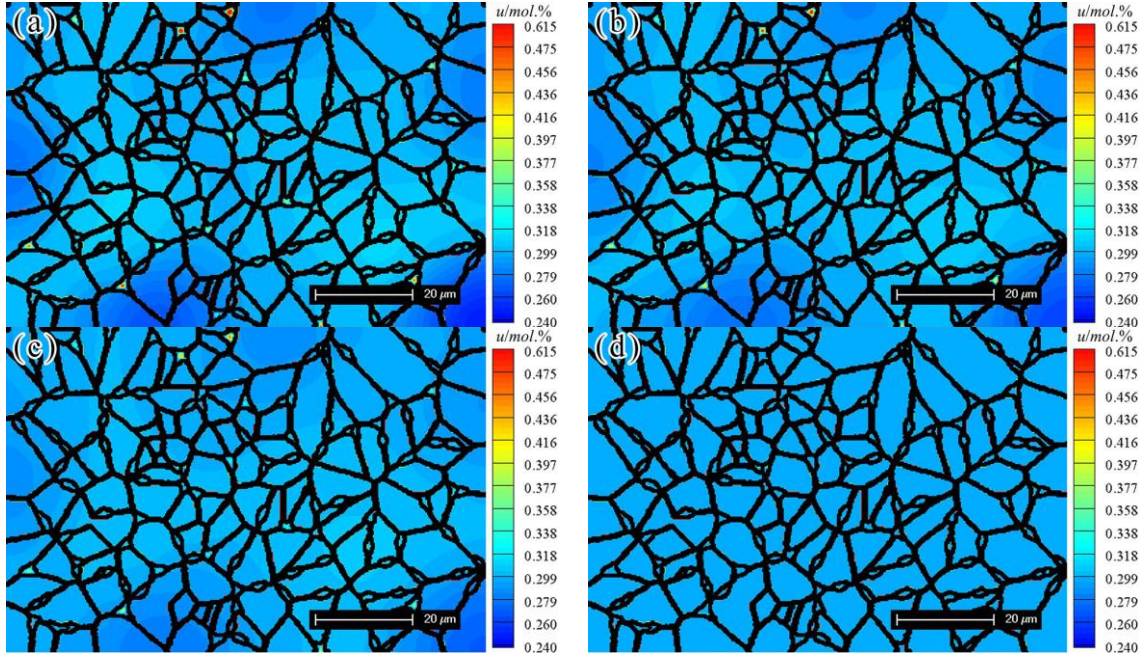


Figure 3 Simulated carbon distribution of an Fe-0.2962 mol.% C alloy after heating at 760°C for 5 min and cooling down to room temperature at 5°C/s (a) without tempering; and tempering at: (b) 400°C for 5 min; (c) 400°C for 20 min; (d) 500°C or 600°C for 5 min.

4. Conclusions

A two-dimensional cellular automaton model is applied to simulate the ferrite (α)-austenite (γ) transformation in a low-carbon steel. The heat treatment processes consisted of isothermal heating at 760°C for 5 min, subsequent cooling to room temperature at 5°C/s, and tempering at 400°C-600°C for 5-20 min are simulated. During the isothermal heating, $\alpha \rightarrow \gamma$ phase transformation accompanied with carbon redistribution takes place. The carbon distribution becomes uniform gradually with holding time in both the α and γ phases. The simulated microstructure agrees well with that obtained experimentally. When cooling to room temperature at a rate of 5°C/s, the carbon concentration field is non-uniform. It becomes gradually uniform during 400°C tempering for 20 min. While tempering at 500°C or 600°C, the carbon distribution becomes uniform within 5 min. The simulation results are used to understand the experimental phenomena that the yield strength increases gradually with increasing tempering time when tempering at 400°C, and the yield strength remains a nearly unchanged during tempering at 500°C or 600°C for 5-20 min.

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