Materials, Mechanical Engineering and Manufacture

Edited by Huawu Liu, Yongxin Yang, Shijie Shen, Zhili Zhong, Laijiu Zheng and Peng Feng



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Selected, peer reviewed papers from the Second International Conference on Applied Mechanics, Materials and Manufacturing (ICAMMM 2012), November 17-18, 2012, Changsha, China

Edited by

Huawu Liu, Yongxin Yang, Shijie Shen, Zhili Zhong, Laijiu Zheng and Peng Feng



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Preface

This journal volume contains the accepted papers from the Second International Conference on Applied Mechanics, Materials and Manufacturing (ICAMMM 2012), held in Changsha, China, November 17-18, 2012. The scientific discipline behind this conference was theoretical and applied mechanics and its applications in materials and manufacturing fields. ICAMMM is concerned with the study of mechanical phenomena: the behavior of solids and fluids under the actions of forces. It has an enormous influence on the industrialized world, enabling technological developments in virtually every area that affects our lives, security, and well being. The aim of this conference was to put together individuals, institutes and countries, interested in cooperative actions for further development.

I would like to extend a warm welcome to all the authors and participants of this 2nd ICAMMM. We hope that this conference will be useful to the research and development in the field and all of you will have a wonderful experience with this fruitful conference, and at the same time enjoy the sights of Changsha in China.

The editors

The Second International Conference on

Applied Mechanics, Materials and Manufacturing

(ICAMMM 2012)

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CHAPTER 1:

Composites and Polymers

Finite Element Simulating of C/SiC Composite Bolt

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Keywords: C/SiC composite; bolt; elevated temperature; contact; finite element analysis.

Abstract. A numerical investigation was conducted to determine the mechanical behavior of C/SiC composites bolt under room temperature and elevated temperature. The influence of the contact friction coefficient on the stress and displacement was considered in the finite element analysis. The FEA results provided some valuable data for the engineering application of C/SiC composites bolt.

Introduction

With the maturity of manufacture technology, carbon fiber reinforced silicon carbide composite materials (C/SiC or CMC) have been widely used in hot structures such as spacecraft thermal protection system (TPS). The TPS needs to be mounted on the outer parts which are also made by CMC with fastenings. Therefore, CMC bolt is the best choice to connect two ceramic matrix composite (CMC) parts because of its consistent thermal expansion coefficient. In the elevate temperature over 1000 °C, only CMC has high specific stiffness, high specific strength and high damage toleration [1].

Hänsel D. and Hald H. [2] developed a rivet-type fastening bolt and tested and optimized it which combining the function of a screw and a rivet. They tested the bolt on tensile load under different temperatures and found that the static strength can be carried out up to 1600 °C. Their FEA work also confirms the thermal behaviors of the CMC bolt.

Dogigli M et al. [3] reported the application of the CMC bolt on X-38 body flap. The bolt was covered with a multilayer oxidation protection. Tensile and shear tests were carried out to get the deformation and strength properties of the bolt under typical loading condition. The wrench torque tests were also been conducted to describe the preloading capability of the bolt. It was found that the CMC bolt can work well on elevate temperature up to 1600 °C under tensile and shear load.

Böhrk H[4] presented the results of static and hot tests of ceramic matrix composite fasteners for heat shield attachment to a re-entry vehicle. He investigated the high temperature cycle effect occurring during atmospheric re-entry on the reduction of the tightening torque of the CMC fasteners. It was found that the Young's modulus of the material decreases with first-time loading. The hot testing results showed a significant improvement of the fastener is achieved with an anti-loosening device.

Hui M. et al. [5] conducted tensile test on 2D C/SiC bolts prepared by chemical vapor infiltration in a simulated re-entry environment. Their results showed that all the tensile strength of 2D C/SiC bolts at test temperatures of 1300°C, 1600°C and 1800°C decreased, respectively, retaining 85%, 92%, and 94% of the virgin properties at room temperature.

There have been considerable works to find out the basic properties of the CMC bolt, only a few studies were focused on finite element simulating which concern about all the geometric details of the bold and the contact problems between the screw bolt and the screw cap. In the present paper, a numerical study was carried out to investigate mechanical response with the influence of the contact friction coefficient for the 2D C/SiC bolt.

Finite Element Analysis

Geometric Model. SolidWorks was used to create the geometric model of the bolt. The bolt is 50 mm in length and 20 mm in diameter with a hexagon head. Fig. 1 illustrated the screw bolt with a hexagon screw nut.



Fig.1. Geometrical model of the screw bolt with a nut.

To increase the accuracy of contact simulation, the form of the screw thread was carefully created on the bolt and on the nut. Fig. 2 and Fig. 3 show the local details of the bolt and the nut.



Fig.2. Thread end on the screw bolt.



Fig.3. Thread inside the screw nut.

Finite Element Model. MSC PATRAN was used to generate the finite element meshing. The geometric model was imported into PATRAN and then a 0.1 mm global seeds was applied on the model. A ten nodal tetrahedral element was selected to mesh the screw bolt and the nut. Fig. 4 presents the meshed finite element model. The elastic properties for the analysis were listed in Table 1 [6]. Between the bolt and the nut, a surface to surface contact was defined with a friction coefficient which was set to 0 and 0.5 in two different analysis cases for comparing.





(a) Mesh of screw bolt.

(b) Mesh of screw nut.

Fig. 4. The finite element mesh of the screw bolt and the nut

rable 1 Weenanical properties of the 2D C/SIC								
E_1 [GPa]	$E_2[GPa]$	E_3 [GPa]	$G_{12}[\text{GPa}]$	$G_{23}[\text{GPa}]$	$G_{31}[\text{GPa}]$	Nu ₁₂	Nu ₂₃	Nu ₃₁
112.53	112.53	88.92	33.15	35.75	35.75	0.01	0.26	0.26

Table 1 Mechanical properties of the 2D C/S	C
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Boundary Conditions and Load. All three translation freedoms were set to 0 on the end surface of the screw head. As shown in Fig. 5, a linear progressive increasing10MPa surface pressure was applied on the surface of the screw nut within 10 seconds. Two loading case with room temperature and 1000 °C were created to simulate the response of the 2D C/SiC bolt in different environmental conditions.



Fig. 5. The loading condition of the screw bolt and the nut

Numerical Results. Fig. 6 shows the influence of the friction coefficient on the displacement and stress of the bolt. The results indicate that friction coefficient between screw bolt and screw nut will has a serious influence on the stress response and minor influence on the total displacement.





Fig. 7 presents the stress response of the bolt under room temperature mechanical loading comdition, 1000°C thermal loading, and 1000°C thermal plus mechanical loading, respectivily. It shows that the CMC has a very good thermal stability.



Fig. 7. Stress response in different loading conditions

Conclusions

From the data presented in this paper, the following results are concluded:

(1) Friction coefficient between screw bolt and screw nut has serious influence on the stress response and minor influence on the total displacement under pressure loading.

(2) The 2D C/SiC composite material has a very good thermal stability.

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The Preparation of CaZrO₃ Coating Ultra-fine Nickel Powders via Chemical Deposition

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Keywords :Nickel powders,surface modification,CaZrO₃,Composite nickel powders

Abstract: Aiming at flexible oxidation in the MLCC production, the surface modification of the ultrafine nickel powders has been carried out to coat Ni powders with CaZrO₃ by using chemical precipitation method. CaZrO₃-coated composite ultrafine nickel powders have been synthesized in methanol-water solvent by both precipitation agents solution and zirconium-calcium solution dripped into the Ni-particle-dispersed methanol solution at the meantime. Composite nickel powders obtained under the optimum conditions were characterized, It was approved that those composite nickel powders still possessed good dispersion, the resistance to oxidation and shrinkage were improved greatly.

Introduction

With the intense competition of MLCC market in the world, its price falls successively at over 10% per year. If enterprises of MLCC can't lower cost of production, they won't exist in the intense competition. The cost of inner electrode material takes up over 60% of all capacitor, while the cost of Ni electrode paste is about 60% of Pd electrode paste in the production of MLCC, and the cost of paste can fall 70% in the future. If enterprises of MLCC want to be the winner in the intense competition, the key was that low-priced metal replaced noble metal and was used as inner electrode material in MLCC^[1].

At present, two problems must be solved in the MLCC production in which low-priced metal is used to displace expensive metals^[2], (1)nickel powers are oxidized in the process of sintering, (2)the shrinkage rate between nickel powers and BaTiO₃ does not match. Scholars have conducted many trials^[3-8] in order to achieve the same sintering between low-priced metal of inner electrode and ceramic medium materials, which included that ultra-fine nickel powders were prepared, and ceramic medium material was doped to enhance anti-reduction, and surface of ultra-fine nickel powders were modified to enhance anti-oxidation and to lower the sintering temperature. The results showed that the surface modification of ultra-fine nickel powders was a effective method. For example, T.Hatano et al^[6] prepared composite material using BaTiO₃ coating nickel powders by Sol-gel method, the temperatures of outset-oxidation and outset-shrinkage increased respectively to about 200°C and 300°C.. The article introduced that the composite material was prepared using CaZrO₃ coating ultra-fine nickel powders and its properties were studied.

Experimental

Composite powder preparation. Distilled water and methanol were used for preparing methanol-water solvent, then nickel powders were put into the solvent and were dispersed for 60 minutes in ultrasound implement, then single dispersive system was formed. The dispersive system was stirred for 20 minutes, Two solutions, one mixed with $CaCl_2$ and $ZrOCl_2$ and another mixed

with $H_2C_2O_4 \cdot 2H_2O$ and $(NH_4)_2C_2O_4 \cdot H_2O$, were dripped simultaneously into the alcohol-water solution mixed with nickel powders and precipitated agent. After coating, the precipitate was separated from liquor by centrifugation, and was washed three to five times by using distilled water. The washed precipitate was dried at 70°C for 12h in a vacuum dry oven. The composite nickel powders spread in ceramic boat were put into tube-electricity furnace and were heated at setting temperature with argon of 99.99% purity as protecting gas. Before heating, argon was imported for 30 minutes to eliminate oxygen in stove, then composite nickel powders were heated at the speed of 5°C/min, after heating to setting temperature, the stove were kept warm for 30 minutes, then was cooled to room temperature, CaZrO₃-coated composite nickel powders were gained.

Composite powder characterization. Composite nickel powders coated and heated were weighed, and were spread in ceramic boat, then were put into tube-electric stove at 400°C and heated for 30 minutes in air atmosphere, then were taken out and cooled down, its oxidation rate was calculated according to the following formula.

 $N\% = \frac{\text{increasement of composite nickel powders/16}}{\text{the weight of sample/58.69}} \times 100\%$

Composite nickel powders morphology was characterized by SEM(JSM-6369LV Japan), its anti-oxidation was characterized by TG-DTA.

Result and Discussion

The principle of $CaZrO_3$ coating nickel powders. The process of $CaZrO_3$ coating nickel powders mainly included two phases, In the first phrase, nickel powders were uniformly dispersed in methanol-water solvent, the quantities of precursor particles were controlled by dripping speed of deposit cation(Zr,Ca solution) and deposit agents(oxalic acid), and existed between critical concentration of heterogeneous nucleation and critical concentration of homogeneous nucleation. The concentration of precursor particles met the condition of heterogeneous nucleation, then the precursor particles formed and grew prior with nickel powders acting as nuclei, the reaction equations were as the following.

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 \downarrow + 2NH_4Cl$$

 $ZrOCl_2 + (NH_4)_2C_2O_4 + H_2C_2O_4 \rightarrow Zr(C_2O_4)_2 \downarrow + 2NH_4Cl + H_2O$

In the second phrase, coated-powders heated in high temperature formed composite powders of CaZrO₃coating nickel powders, the reaction equation was as the following.

$$Zr(C_2O_4)_2 + CaC_2O_4 \rightarrow CaZrO_3 + 3CO_2\uparrow + 3CO\uparrow$$

Nickel powders coated by precursor(oxalic acid calcium, oxalic acid zirconium) presented loose state, the precursor could not defend nickel powders acting as core, loose package could become slowly dense layer after heat treatment, chemical reaction and change of phase, at this moment dense layer of CaZrO₃ could defend the core and composite powder of Ni/CaZrO₃ formed finally.

Morphology of composite nickel powders. Ultra-fine nickel powders used in inner electrode of MLCC not only were required for anti-oxidation and fine anti-shrinkage in high temperature, but also were required in diameter and shape. The SEM images of nickel powders and composite nickel powders heated were displayed in Fig1. Fig1 showed us that particle appearances of sample and composite nickel powders changed less and presented regular sphere. There were obvious differences between sample and composite nickel powders, the surface of sample was smooth and didn't have prick, while a rough layer of package could be observed obviously in the surface of composite nickel powders, the loose package which was heated became dense defend layer, the surface got coarse, aggregation between particles appeared slightly and diameter slightly magnified.





Fig1 SEM images of sample, composite nickel and composite nickel heated a, SEM of sample b, SEM of composite nickel powders heated

Anti-oxidation of composite nickel powders in high temperature. Ultra-fine nickel powders used in inner electrode of BME-MLCC must possess anti-oxidation in high temperature. The TG analysis of sample and composite nickel powders heated were proceeded, the results of TG-DTA were displayed in fig2. Fig2 showed us obviously that anti-oxidation of coated-nickel powders was improved well, the outset oxidation temperature, the peak of the most strongest releasing quantity of heat and complete oxidation temperature of the sample were respectively at 339.71°C, 497.70°C, 590.06°C, while the outset oxidation temperature, the peak of the most strongest releasing quantity of heat and complete oxidation temperature of composite nickel powders were respectively at 350.14° C, 683.93° C, 803.88° C.These temperature of composite nickel powders enhanced greatly compare with the sample's, especially the peak of the most strongest releasing quantity of heat and complete oxidation temperature of composite nickel powders enhanced greatly compare with the sample's, especially the peak of the most strongest releasing quantity of heat and complete oxidation temperature of composite nickel powders and complete oxidation temperature of composite nickel powders enhanced greatly compare with the sample's, especially the peak of the most strongest releasing quantity of heat and complete oxidation temperature of composite nickel powders and complete oxidation temperature





Anti-shrinkage of composite nickel powders in high temperature. There is a high demand for nickel powders used as inner electrode in MLCC, it is expected that shrinkage rate in high temperature is closed to medium layer. Anti-shrinkage rate of composite nickel powders was studied, the results showed in fig3. Fig3 told us that sintering shrinkage rates of the sample and coated-nickel powders enlarged with the increase of temperature, but the rates were different. The shrinkage rate of sample was up to 13.10% at 600°C,its shrinkage rate was almost up to 39.63% at 900°C, the range of enlargement was very great with the increase of temperature and the shrinkage extent was very serious, while anti-shrinkage of composite nickel powders coated by CaZrO₃ was

improved greatly, while the shrinkage rates didn't appear at 650°C and was only 5% at 900°C. The anti-shrinkage of coated-nickel powders was improved greatly and matched the shrinkage of BaTiO₃ ceramic medium layer. The problem of sintering matching between inner electrode using low-priced metal and BaTiO₃ ceramic medium layer was solved.



Fig3 The sintering shrinkage rates of the sample and composite nickel powders

Conclusion

The conclusion was as the followings according to the properties results of composite nickel powders prepared in optimized experiment condition, (1)The sample and the coated nickel powders were regular sphere, the surface of the coated nickel powders was slightly coarse, its diameter slightly enlarged and aggregation was more worse, (2)its anti-oxidation remarkably raised after coating, the temperature of initiating oxidation and complete oxidation greatly ascended, (3)anti-shrinkage rate of composite nickel powders in high temperature was well improved, (4)composite nickel powders possessed good dispersion, better conductivity, anti-oxidation in high temperature and fine shrinkage, and suited to act as inner-electrode material.

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Theoretical study of energy-level splitting of Cs₂NaPrCl₆ crystal

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Keywords: Complete energy matrix. Energy-level structure. Rare earth ion.

Abstract. The 91×91 complete energy matrix of $4f^2$ configuration ion Pr^{3+} in octahedral cubic crystal field has been constructed based upon the combination of Racah's group-theoretical consideration with Slater's wavefunctions. The energy levels of the neat hexachloride elpasolite crystals Cs₂NaPrCl₆ containing rare earth Pr^{3+} ion have been calculated. The results imply that the diagonalization to the complete energy matrix can be received as an effective method of performing a theoretical calculation to the rare earth compounds.

Introduction

Due to elpasolite systems $Cs_2NaLnCl_6$ contain a cubic crystal structure and the Ln^{3+} occupy the exact octahedral O_h symmetry, they are characteristic by relatively simple structure, well defined chromophoric and magnetic units, detailed optical spectra and so on [1-2]. Therefore, the elpasolite $Cs_2NaLnCl_6$ can provide model systems for the study of the energy levels and magnetic phenomena [3]. The unit cell group analysis of the elpasolite systems has been carried out utilizing a modified general valence fore field in order to provide a prerequisite for understanding the energy transfer phenomena by Ning et.al. [4]. On the other hand, as the typical and basic systems, $Cs_2NaLnCl_6$ crystals can provide the ideal cases for researching the interaction between RE ions and their surrounding environment and the basis for exploring the complex systems when they are doped with the RE ions. Besides, the Pr^{3+} ions have been proved to be a good candidate to high resolution laser spectroscopy, and the well characterized spectroscopic properties have simplified the experimental determination of energy levels [5]. In a word, the investigation of $Cs_2NaLnCl_6$ is beneficial to understand the physical origin of the crystal field effect and provide the valuable information for researching the optical and magnetic properties of the compounds.

The *f*-orbital delocalization has been derived using first-principles universal orbital-free embedding formalism as to investigate the effect on the ligand-field splitting energies in lanthanide-containing elpasolites [6]. As well as, the crystal field (CF) investigation to Ce^{3+} ion has been made by Chi et al. only considering the second- and fourth- order CF parameters [7]. However, we note that Stevens et.al. have reported that the effects of the sixth degree terms might well be much more important and in some cases actually dominating relative to the fourth degree term [8]. In this paper, based on a complete analysis to the single electron energy splitting, we will perform an analysis to the $4f^2$ configuration Pr^{3+} ion. Thus the dependence of electromagnetic structure of rare earth (RE) ions on crystal lattice structure and the interrelation between electromagnetic structure of RE ions and electrons lying in the compounds can be determined. Furthermore, it is helpful to get an insight into the macroscopic physical properties of compounds and promote the crossing development of atomic and molecular physics and condensed state physics. This work is performed as follows: firstly, the theory method has been established based on the combination of Racah's theoretical consideration with Slater's wavefunctions [9-11]. Secondly, the energy levels splittings of neat Cs₂NaPrCl₆ crystal will be calculated and discussed. The conclusions will be come to lastly.

Theory Model

A completely effective operator Hamiltonian of $4f^n$ configuration is [12]

$$\hat{H} = \hat{H}_0 + \hat{H}_{ee} + \hat{H}_{so} + \sum_{i=1}^4 \hat{H}_i(corr) + \hat{H}_{CF}$$
(1)

where, the first three parts are primarily responsible for a free ion. Their usual meanings have been explained by Newman [12]. The fourth part is

$$\sum_{i=1}^{4} \hat{H}_{i}(corr) = \delta(\psi, \psi')[\alpha L(L+1) + \beta G(G_{2}) + \gamma G(R_{7})] + \sum_{i} t_{i}T^{i} + \sum_{i=0,2,4} m_{i}M^{i} + \sum_{i=2,4,6} p_{i}P^{i}, \qquad (2)$$

and the first term are interaction between configurations of the same parity, introduced by three 'Trees' parameters α , β and γ , which are associated with the eigenvalues of Casimir operators for the Lie groups R_3 , G_2 and R_7 and used to specify the terms of $4f^n$ configuration (n \leq 4) [11, 13]. The usual meanings of the last three terms have been explained by Newman [12].

The fifth part of Eq (1) is CF effect, which can be expressed as:

$$\hat{H}_{CF} = \sum_{k,q,i} B_q^k C_q^{(k)}(i)$$
(3)

where, the rank k and projection q are limited by point group symmetry of the $4f^n$ ion lying in the crystal. Newman's superposition model (SM) connects the geometrical information with physical information containing in lanthanide crystal field parameters (CFPs) [12, 14], there exist the formulas

$$B_q^k = \sum_{\tau} \overline{B}_k(R_{\tau}) g_{k,q}(\theta_{\tau}, \phi_{\tau})$$
(4)

$$C_{q}^{(k)}(i) = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\theta_{i}, \phi_{i})$$
(5)

$$\overline{B}_{k}(R_{\tau}) = \frac{eq_{\tau}\langle r^{k}\rangle}{R_{\tau}^{k+1}},$$
(6)

where $\overline{B}_k(R_r)$ are the intrinsic CFPs, and the $g_{k,q}$ are related to the spherical harmonics functions [12]. According to the Hermiticity and time-reversal invariance of the CF Hamiltonian, there exists that k=0, 2, 4, 6 for *f* electron.

Thus, the complete energy matrix of $4f^n$ configuration ions can be established, we can calculate the energy levels splitting and perform the theoretical investigation by diagonalizing the complete energy matrix.

units of cm ⁻ .							
Parameters	F^2	F^4	F^{6}	α	β	γ	ζ
Cs ₂ NaPrCl ₆	67809	50375	32979	23.5	-636	1452	748

Table 1. The free ion parameters used in calculating the energy levels of $Cs_2NaPrCl_6$ crystal, all in

Table 2. Crys	stal field paramet	ers and strength qua	antities for Cs ₂ NaP	rCl ₆ crystal,	all in the unit of cm ⁻¹ .
		0		0 1 1	

Parameters	B_0^4	B_0^6	S_{cf}^4	S_{cf}^{6}	S_{cf}
Cs ₂ NaPrCl ₆	2178	263	726	73	421

Energy Levels Structure

For cubic hexachloride elpasolite Cs₂NaPrCl₆ crystal, the CF Hamiltonian equals to Eq (8) and their energy levels can be calculated using several free ion parameters and their respective CFPs. For $4f^2$ configuration, the parameters T^k are not allowed, and Tröster et al. believed that the influence of other parameters on the energy-level splitting can be neglected compared with parameters F^k and ζ in determination of the energy parameters [15]. Therefore, the complete Hamiltonians of a cubic symmetry has been established and we will adopt the parameters listed in Tables 1 and 2 in the calculation of the energy levels of $Cs_2NaPrCl_6$ crystal. Here we will study the energy levels of $4f^2$ configuration ion Pr^{3+} in O_h symmetry by diagonalizing the 91×91 complete energy matrixes.

The experimental energy-level data, together with the overall atomic parameters and CFPs, have been reported for neat Cs₂NaPrCl₆ crystal [16], as presented in Tables 1-3. The calculated 40 Stark levels for O_h point group symmetry have been obtained from 13 electronic multiplets of Pr³⁺ ion by diagonalizing the complete energy matrixes, as listed in Table 3, also shown are the energy assignments of O_h point group. Additionally, the differences Δ_1 between calculated and experimental CF splitting ($\Delta_1 = E(\text{expt.}) - E(\text{calc.})$) of the two systems also are tabulated in Table 3. We note that the relative error of our calculation results is nearly 0.1% less than the experimental values. Here the energy-level positions of the ³P and ¹I terms of 4f² configuration are higher than those of ¹D and ¹G terms and even occur to the admixture between them. This may be due to the same irreducible representations of ³P and ¹I terms, which produces large enough interaction to mix with each other or maybe result from the other interactions in compounds.

Additionally, we calculate the CF interaction strength quantities by introducing to S_{cf}^{k} and S_{cf} , they are defined as follows:

$$S_{cf}^{k} = \{\frac{1}{2k+1} [(B_{0}^{k})^{2} + 2\sum_{q>0} |B_{q}^{k}|^{2}]\}^{1/2},$$

$$S_{cf} = [\frac{1}{3} \sum_{k} (S_{cf}^{k})^{2}]^{1/2}.$$
(8)

The calculated values are presented in Table 2. We note that the value of S_{cf}^4 is nine times larger than that of S_{cf}^6 for Cs₂NaPrCl₆ crystal because of the bigger B_0^4 than B_0^6 . It may be attributed to that the Pr³⁺ ion sites at the cubic symmetry environment in Cs₂NaPrCl₆ crystal.

			<u>j ··· i</u>		 19				
T		C	Cs ₂ NaPrCl	l ₆		Е	_	7056	
Term	I^{*}	expt.	calc.	Δ_1		T_2	7281	7335	-54
$^{3}H_{4}$	Δ.	0	0	0	${}^{1}G_{4}$	A_1		9800	
114	Т.	236	244	8		T_1	9895	9884	11
		422	244 414	-0		Е		9929	
	E T	422	414	0		T_2		10541	
311	1 ₂	701	703	-2	$^{1}D_{2}$	T_2	16670	16687	-17
$^{\circ}H_{5}$	I_1	2295	2297	-2	2	Ē	17253	17242	11
	Γ_2	2400	2406	-6	$^{3}P_{0}$	A ₁	20622	20551	71
	Е	2643	2626	17	${}^{1}L$	A ₁	21161	21163	-2
2	T_1	2711	2737	-26	$({}^{3}P_{1})$	т.	21219	21105	34
$^{3}H_{6}$	E	4391	4398	-7	(1)	T	21217	21103	54
	T_2	4437	4455	-18		т Т		212/2	_
	A_2		4668			12		21401	_
	T_2	4807	4811	-4		A_2		21846	
	T_1	4877	4891	-14		I_2		22043	
	A_1	_	4919		2	Е		22101	
${}^{3}F_{2}$	Ē	5203	5194	9	$^{3}P_{2}$	T_2	22367	22405	-38
1 2	T.	5290	5262	28		Е	22492	22518	-26
^{3}F	T.	6615	6610	5	$^{1}S_{0}$	A_1		46558	
1'3	1 ₂ T	0015	6621	5					
	11	((70)	6660	10					
30	A_2	00/9	6669	10					
F_4	A_1	6965	6987	-22					

 T_1

7011

7033

-22

Table 3. Measured and calculated energy values of $Cs_2NaPrCl_6$ crystal, and their difference for each ${}^{2S+1}L_J$ multiplet is denoted with Δ_1 , all in units of cm⁻¹.

Conclusions

The complete energy matrix of $4f^2$ configuration has been constructed in octahedral cubic ligand field. As an application, we calculate the Stark energy-level of Cs₂NaPrCl₆ crystal by means of diagonalizing the complete energy matrixes. The results show that our complete energy matrix method is a recommentable method for calculating the energy levels splitting for $4f^2$ ions configuration in compounds. Thus, it will provide a good insight into the relative potential properties of the rare earth compounds. Furthermore, the sixth CFP is much smaller than the fourth CFP for Cs₂NaPrCl₆ crystal, which makes the fourth CF interaction playing an important role in the energy levels splitting.

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Preparation and characterization of Fe³⁺-doped TiO₂/diatomite composite

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Keywords: Diatomite; TiO₂; Iron ion doping; Photocatalyst;

Abstract. Fe^{3+} -doped TiO₂/diatomite composite photocatalyst were prepared by sol-gel method with titanium isopropoxide used as precursor material. The samples were characterized by SEM, XRD, XPS, BET surface area analysis and UV-Vis techniques. The results showed that the optimum concentration of Fe³⁺ in the composite catalyst was 0.2wt% when the quantity of TiO₂ loaded on the diatomite was 30.3wt%. Compared with the un-doped photocatalyst, the Fe³⁺-doped sample exhibited red shifts of absorption edge and significant enhancement of light absorption at 400~600 nm.

Introduction

 TiO_2 has been considered as one of the most promising photocatalysts ever since Honda and Fujishima [1] reported its photochemical properties. However, TiO_2 is not thermally stable and loses surface area readily when used as a high surface area powder. On the other hand, both the reaction mechanisms, under either UV or visible irradiation, indicated that preliminary adsorption of organic substrate on the TiO_2 surface exhibited an advantage for high efficient degradation. These have led to a number of attempts to anchor TiO_2 on high surface area supports, such as zeolites, activated carbon and clays, by a variety of chemical or physical methods, e. g., ionized cluster beam deposition, wet chemical methods, chemical vapor deposition and impregnation-desiccation [2]. Recently, one siliceous sedimentary rock, named diatomite, has received attention for its unique combination of physical and chemical properties. It was successfully used as adsorbent to remove various pollutants, and examined as perfect support for TiO₂ to prepare hierarchical structured catalysts [3].

The other disadvantage of TiO₂ is that it can only utilize a relative small part of the solar spectrum (UV light) for photocatalytic oxidation. Doping or combining of TiO₂ with various metal or non-metal ions was reported as a good tool to improve the photocatalytic properties and for enhancement of visible light response [4]. Amongst a variety of transitional metals, iron had been considered to be an appropriate candidate due to the fact that the radius of Fe³⁺ (0.79 A) is similar to that of Ti⁴⁺ (0.75 A), so that Fe³⁺ can be easily incorporated into the crystal lattice of TiO₂ [5].

Based on the above considerations, we prepared Fe^{3+} -doped TiO_2 /diatomite photocatalytic materials according to a sol-gel route in which diatomite particle was incorporated into the titanium isopropoxide sol during the course of the sol-gel process. The samples have been characterized by means of XRD, SEM, XPS, BET and UV-Vis technologies, and the optimum concentration of Fe³⁺ in the composite catalyst was studied.

Experimental

Materials and reagents. The following reagents were employed to prepare TiO_2 : titanium-(IV)-isopropoxide (97%) as TiO_2 source; hydrochloride acid (37%) as catalyst; Iron(III) nitrate (99%) as dopant source; ethyl alcohol (96%) as solvents. Diatomite was obtained from Sheng county in Zhejiang province of China. The sample was calcined at 500 °C to remove organic impurities before TiO_2 coated.

Preparation of Fe³⁺-doped TiO2/Diatomite. 10 mL of titanium isopropoxide was dissolved into 50 mL of anhydrous ethanol (solution A). Solution B consisted of 0.5 mL of HCl, 2 mL of distilled water and Fe(NO₃)₃· 9H₂O in the required stoichiometry. Then solution B was added drop-wise into solution A with stirring magnetically. After the drop, 5g of diatomite was added to the solution. The resultant mixture was stirred at room temperature for 30 min to hydrolysis until the transparent sol was obtained. The sol was then aged for 72 h until the formation of gel. Then dried and ground. At last, the powder was kept for 1 h under 500 °C in the oven.

Characterization. Surface morphologies of the samples were investigated using SEM (model SIRION-100, Fei Company, Holland). For the specific surface area and pore size evaluation, nitrogen gas adsorption method was used. N₂ gas adsorption–desorption isotherms were measured at -196 °C using a model Autosorb-1 nitrogen-adsorption apparatus (Quantachrome Corp., USA). The specific surface area, S_{BET} , was calculated based on the BET theory. Phases and crystallite sizes of the prepared samples were characterized by XRD technique. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK α radiation. The UV-Vis variations of the solution were analyzed by a Shimadzu UV-2550 spectrophotometer.

Results and discussion

SEM analysis. The diatomite used in this work was in the form of cylindraceous particle with bulk density of 616 g/L and median particle diameter of 10.25 μ m (Laser particle size). The oxide analysis in our previous study [6] showed that SiO₂ was the main component (67.3%) and the metal oxides (15.4% Al₂O₃, 7.07% Fe₂O₃, 3.97% K₂O, 3.87% ZnO, 1.36% TiO₂ and 1.05% CaO) were the minor constituents. Fig. 1 shows the SEM images of diatomite and Fe³⁺-TiO₂/diatomite. It clearly displayed the cylindrical figure and the special porous texture of diatomite, and the surface was completely modified after TiO₂ loaded. The quantity of TiO₂ loaded on the diatomite surface may mainly depend on the quantity of titanium isopropoxide used in the experiment and the nature of the surface. In this study, the loading on the surface of the diatomite was determined to be approximately 30.3% using the differential weight method.



Fig. 1 SEM images of (a) diatomite and (b) Fe^{3+} -TiO₂/diatomite.

Surface area study. Highly porous morphologies with improved surface area offer more adsorption sites for the dye molecules and enhance the reaction rate. Hence, determination of the specific surface area is often a prerequisite for studying and interpreting adsorption properties quantitatively [7]. In this work, the pore properties, i.e., S_{BET} , pore volume V, and average pore diameter R, of diatomite and Fe³⁺-doped TiO₂/diatomite powders were characterized by N₂ adsorption-desorption experiments. The results were listed in Table 1. It can be seen that the BET surface area and pore volume of Fe³⁺-doped TiO₂/diatomite were higher that that of the initial diatomite. This suggested that the prepared sample could show improved capability in adsorption and photocatalytic degradation. Jia et al [3] have prepared hierarchical porous TiO₂/diatomite materials by a layer-by-layer (LBL) assembly method, and also obtained a higher BET surface area and pore volume with diatomite.

I able 1	exture properties from	m nitrogen adsorption a	analysis
Sample	$S_{\rm BET}({ m m}^2/{ m g})$	$V(\text{cm}^3/\text{g})$	<i>R</i> (nm)
Diatomite	50.63	0.1296	10.24
Fe ³⁺ -TiO ₂ /diatomite	74.95	0.1540	8.221

XRD analysis. TiO₂ materials exist in three different crystalline phases: anatase, rutile and brookite. Fig. 2 shows XRD patterns of undoped and Fe³⁺-doped TiO₂/diatomite. It can be seen that both 0% and 0.2% Fe-doped samples had the anatase phase, and other crystalline phases were not detected. The reason may be that Fe³⁺ ions substituted Ti⁴⁺ ions and inserted into the crystal lattice of TiO₂ when the amount of Fe³⁺ ions was low, since the radii of Ti⁴⁺ and Fe³⁺ ions were similar. When the Fe³⁺ dopant percentage were 0.5% and 1.0%, the peaks of anatase phase decreased, while the peaks of rutile and iron oxide increased. Thus, the excess of Fe³⁺ dopant in the composite could lead to the phase transformation. It could be concluded from this experiment that almost all of Fe³⁺ in 0.2% Fe³⁺-TiO₂/diatomite were trapped in the crystal lattice of TiO₂, whereas 0.5% and 1.0% Fe³⁺-TiO₂/diatomite contained segregated iron oxide in addition to Fe³⁺ doped TiO₂.



Fig. 2 XRD patterns of Fe doped TiO₂/diatomite. Fig. 3 UV–Vis spectrum of Fe-doped sample.

UV-Vis analysis. Fig. 3 displays the UV–Vis absorption spectrum of undoped and Fe³⁺-doped TiO₂ powders. Pure TiO₂ exhibited an absorption edge rising steeply toward the UV region below 400 nm, which could be attributed to the band-gap excitation of anatase (3.2 eV), without absorption in visible region (>400 nm). Compared with the undoped photocatalysts, Fe³⁺-doped TiO₂ samples exhibited red shifts of absorption edge and significant enhancement of light absorption at 400~600 nm, and this enhancement increased as the doped Fe³⁺ percentage increased, accompanying with the change of powder color from white to primrose yellow. This result satisfies the aim of the study which was to increase the visible light absorption of Fe³⁺-doped TiO₂/diatomite powders.

XPS analysis. Fig. 4 shows the XPS spectra of Fe^{3+} -doped TiO₂/diatomite particles. Peaks of Ti 2p, Si 2p and O 1s were clearly observed for the sample in the wide spectra (Fig. 4a). Weak signals of Fe 2p could only be detected in the partial range of the XPS spectra, and the signals were fluctuant greatly, due to the low doping level, as shown in Fig. 4b. The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spin-orbital splitting photoelectrons for Fe^{3+} -TiO₂/diatomite were observed at 458 and 464 eV, respectively, which was consistent with the values of Ti⁴⁺ in the TiO₂ lattices. The comparison between the Ti 2p spectra of undoped TiO₂ and the doped TiO₂/diatomite (Fig. 4c and 4d) indicated that the latter had small binding energy shifts (the Ti $2p_{1/2}$ peak had a greater shift than the Ti $2p_{3/2}$ peak). It might infer that the doped Fe ions might diffuse into TiO₂ lattices to form the Fe-O-Ti bond.



Fig. 4 XPS spectra of synthesized Fe^{3+} -TiO₂/diatomite particles: (a) full range, (b) Fe, (c) Fe^{3+} -doped Ti and (d) undoped Ti in TiO₂

Conclusions

In this paper, Fe^{3+} -doped TiO₂/diatomite composite photocatalyst were successfully fabricated and characterized. It showed that the light absorption for the Fe-doped sample moved to a longer wavelength, and the doped Fe ions might diffuse into TiO₂ lattices to form the Fe-O-Ti bond.

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Research on VARTM Technology for fabricating Basalt fiber/vinyl ester composites

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Keywords: Basalt fiber/ vinyl ester composites, VARTM, injection strategy, air release additive.

Abstract. Basalt fiber has good sea water resistance, heat resistance and sound insulation. This shows that, basalt fiber is ideal material for ship manufacturing. Because of the bad fiber permeability, using VARTM process to produce large basalt fiber marine components still has deficiency. Taking basalt fiber/vinyl resin composite shell as object, research was taken to find the method of improving resin flow velocity and suitable resin injection strategy system in VARTM process. The results show that air release additive contributes to the resin's flow in preform body, and the tensile strength and flexural strength of components increase with the increase of air release additive's quantum when the quantum less than 0.5%. The resin flow's frontier of the components made by sequence injection strategy is always keeping the same and its velocity is uniform, which makes its quality is better than that made by embranchment injection strategy.

Introduction

VARTM (Vacuum Assisted Resin Transfer Molding) is a low cost composites molding technology, which has a sharp decline compared with RTM (Resin Transfer Molding) by using single rigid mold. And compared with hand lay-up molding technology, VARTM has advantages on environmental protection and high quality components, which makes it more and more application in preparation of ship shell, fan blade, and large composite components with added core and added reinforcing plate [1]. The basic processes of VARTM were: laid dry state fiber reinforced material on the molding surface of rigid mold to form preform body, covered the vacuum bag membrane upon preform body as upper mode, sealed the rigid mold and vacuum bag membrane into closed cavity with adhesive tape, vacuumed the cavity, while resin was injected into the cavity and infiltrated preform body under the vacuum action, cured preform body under room temperature and vacuum pressure completely, obtained composites component after demoulding [2].

Basalt fiber has better mechanical properties, better sea water resistance and sound insulation compared with glass fiber, which is ideal raw material for ship manufacturing [3][4]. But because of the bad permeability, using basalt fiber to produce large basalt fiber marine components with VARTM process is still a rare thing [5]. Focused on VARTM process, took basalt fiber/vinyl resin composites shell as object, researches were taken to find resin flow improving measures and resin injection strategy system with less dry spot defects, quick mold filling and good infiltrating effect.

Experiments

Raw materials and processes. The raw materials used in experiments were shown in Table 1. In which, basalt fiber fabric was $0^{\circ}/90^{\circ}$ and $\pm 45^{\circ}$ fabric, with density $400g/m^2$.

Experimental facility has been shown in Fig.1. Preform body was formed by layers according to the sequence of $0^{\circ}/90^{\circ}$, + 45° and -45°. Under the vacuum pressure drive, resin contained 1.2% curing agent and 0.2% accelerating agent resin came into cavity. After mold filling process, continued to keep room temperature and pressure to cure 24 hours.

Name	Basalt fiber	Vinyl ester	Curing	Accelerating	Air release
	fabric		agent	agent	additive
Specification	B400	AME6000	M50	DY7-3	BYK [®] -A560
Manufacturer	CPIC	Ashland	Akzo	Wuxi	BYK-Chemie
			Nobel N.V	DYHG	GmbH



Fig.1 Schematic view of vacuum assisted resin transfer molding process

Experimental methods. Enhance the resin fluidity. In order to enhance the resin flow velocity in basalt preform body, resin with 0.5% quantum of air release additive was compared with resin without air release additive. In order to assess the effect of air release additive on the composites property, 0.0, 0.2, 0.3, 0.4, 0.5 and 0.6% quantum of air release additive were distributed into resin separately, then tested the mechanical properties of component. Tensile strength and bending strength were separately taken on universal material testing machine WDW-200 according to GB/T1447-2005 and GB/T1449-2005 standards. Composites component were prepared as length, width and thickness 1000*700*40 mm.

Resin injection strategy system. Sequence injection strategy and embranchment injection strategy were tested in experiments. Schematic diagram of sequence injection strategy was shown in the left side of Fig.2 (a). Schematic diagram of embranchment injection strategy was shown in the right side. The implementation of sequence injection strategy was shown in Fig.2 (b). The pipes in sequence injection strategy test were set parallel along with the length direction. When the resin flew a little ahead of the second pipe, then closed the first pipe while opened the second pipe. While in embranchment injection strategy a competent pipe was set along the length direction, branch pipes were connected to the competent pipe and paralleled to each other. Resin flew in the competent pipe and numbers of branch pipes at the same time.



Fig.2 Schematic diagram of sequence and embranchment injection strategy

Results and discussion

The resin flow distance-time curve of the component's bottom layer has been shown in Fig.3. The flow velocity of resin with air release additive is 9% or so faster than that of resin without air release additive. It shows that adding air release additive can decrease the operation time, in favor of infiltrating the preform body before solidification, which can guarantee the quality of large components molding. The effect of air release additive's quantum on component's tensile and flexural strength has been shown in Fig.4. Adding air release additive can enhance resin's tensile and flexural strength, whose reason is that: air release additive can effectively eliminate the volatilized air in resin and resident air in preform body, increasing the components' density and the fiber content to enhance components' mechanical properties [6]. With the increase of air release additive's quantum, tensile and flexural strength also improve. When quantum of air release additive achieves 0.4% and 0.5%, flexural strength and tensile strength reaches apex respectively. Too much air release additive adverse to the combination surface between resin and fiber, so as to decrease the flexural strength and tensile strength and tensile strength.



Fig.3 Resin flow velocity contrast figure Fig.4 Air release additive's effect on mechanical properties

Table 2 Statistics of dry spots and void contents							
Name of	Dry spots	Coefficient	Resin	Coefficient	Void	Coefficient	
defects	[%]	of Variance	enrichment	of Variance	contents	of Variance	
		[%]	[%]	[%]	[%]	[%]	
Sequence	3.2	8.8	2.5	7.5	1.6	9.2	
injection							
Embranchment	3.6	10.2	3.1	9.7	1.7	8.9	
injection							

The experimental conditions of the resin injection strategy system test were: vacuum pressure 95kpa, environment humidity 60%, environment temperature 15°C, resin temperature 20°C. Composites component was prepared as length, width and thickness 1000*700*40 mm. Sample areas were uniformly distributed in the whole component. Each sample was 200*200 mm. Defect assessment items were dry spot, resin enrichment and micro pore. The diameter of the micro defects was defined as 1 mm or less. The percentage of defect areas in total areas was tested. Image processing technology was used to analysis and do statistics on micro pore defects based on image obtained from optical microscope. The average results of defects assessment has been shown in Table 2. The results show that defects by sequence injection strategy are less than those by embranchment injection strategy. The reason is that: during sequence injection strategy, the frontier of resin flow is always keeping the same and its velocity is uniform, which can inhibit defect formation. During embranchment injection strategy, the resin flow frontiers will appear butt state, which is easy to form the air package, and easy to make macro and micro flow mismatching [7]. Dry spot is shown in Fig.5 (a) and micro pore is shown in Fig.5 (b).

(h)



Fig.5 Dry spots and void contents in composites

Summary

VARTM process has obviously influence on composite components. Through experiments, some conclusions have been researched:

For large basalt composite components, those made by sequence injection strategy have better quality than those made by embranchment injection strategy. The resin flow's frontier of sequence injection strategy is always keeping the same and its velocity is uniform. During embranchment injection strategy, the resin flow frontiers will appear butt state, which is easy to form the air package, and hard to match macro and micro flow.

Resin with air release additive has a faster flow velocity than that without air release additive in preform body.

Quantum of air release additive has influence on component's tensile strength and flexural strength. The tensile strength and flexural strength of components increase with the increase of air release additive quantum when the quantum less than 0.5%. But tensile strength and flexural strength will decrease when the quantum more than 0.5%.

Acknowledgements

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Design, Synthesis and Photophysical Properties of Novel Tetrahedral Carbazole-Bridged Silanes with Benzimidazole Groups

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Keywords: Luminescence; Organosilicon Compounds; Carbazole; Benzimidazole; OLEDs

Abstract. Two novel luminescent molecules based on tetrahedral silicon core with the carbazole and benzimidazole groups, bis(6-(1*H*-benzo[d]imidazol-1-yl)-9-ethyl-9*H*-carbazol-3-yl)dimethylsilane (1) and bis(6-(1*H*-benzo[d]imidazol-1-yl)-9-ethyl-9*H*-carbazol-3-yl)diphenylsilane (2), were designed, synthesized and fully characterized by IR, ¹H NMR, ¹³C NMR and elemental analysis. Thermal results show that these compounds have high thermal stability and glass-transition temperature (T_g). The results based on the photophysical properties and molecular calculations reveal that they are fluorescent with emission in the region of violet to blue and own large HOMO-LUMO band gaps, making them potentials as blue emitters, host materials or charge blocking materials in organic light-emitting diodes (OLEDs) display.

Introduction

In the past decades, many efforts have been devoted to the developments of luminescent materials to meet the demand for the fabrication of organic light-emitting diodes (OLEDs) [1-3]. It is demonstrated that the OLEDs performances depend not only on the emission materials but also on the hosts and charge transporting materials. Based on previous reports, the luminescent materials can be designed through proper structure modify and chemical methods and thus numerous luminescent materials have been designed and utilized in OLEDs [4-5]. Among various materials, small tetrahedral silicon-based molecules have been attracted much attention due to their many advantages, such as well-defined structures, high thermal stability and high color purify. Because of the facile modify on silicon-cored molecules, a large number of silicon-centered compounds have been designed, synthesized and utilized as emitter, host materials as well as charge-transporting materials for OLEDs [6-10]. Additionally, they could be used as interesting tetrahedral ligands to construct functional metal-organic frameworks (MOFs) with intriguing topologies and extensive applications, such as molecular recognition, gas storage, catalysts, *etc* [11-12].

Enlightened by these attributions on OLEDs and MOFs of organosilicon compounds, we have designed and synthesized a series of phenyl-bridged silanes with imidazole, pyrazole and benzimidazole as functional groups in our previous reports [13-15]. The optical properties reveal that they could be potentially used as blue emitters or charge blocking materials for OLEDs. In this article, we introduce carbazole as the bridge instead of phenyl since carbazole possesses well-established hole-transporting ability, wide-band energy, applications as phosphorescent host materials, and facility of tuning the HOMO levels by changing the N-substituent [16-20]. Previously He et al presented two carbazole-bridged silanes with fluorine groups emitting blue light efficiently in the condensed state with high quantum efficiencies [6]. However, due to the steric effect, the synthesis is difficult and the yield is low. Thus herein we synthesized two novel tetrahedral carbazole-bridged silanes with benzimidazole groups, bis(6-(1H-benzo[d]imidazol-1-yl)-9-ethyl-9H-carbazol-3-yl)dimethylsilane (1)and bis(6-(1H-benzo[d]imidazol-1-yl)-9-ethyl-9H-carbazol-3-yl)diphenylsilane (2) with high yields. Then a comprehensive investigation including thermal stability, photophyscial properties as well as theoretical calculations were presented.

Experimental

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone. FTIR were recorded on a Bruker Tensor27 spectrophotometer. ¹H NMR and ¹³C NMR spectra were measured on a Bruker AVANCE-300 or 400 NMR Spectrometer. TGA was performed with a MettlerToledo SDTA-854 TGA system in N₂ at a heating rate of 10°C/min. DSC measurements were carried out in MettlerToledo DSC822 series. The fluorescence spectra were determined with F-7000 spectrophotometer. Luminescence quantum yields were measured using quinine sulfate in 0.1N H₂SO₄ ($\Phi = 54.6\%$) as reference [21].

Synthesis of bis(6-bromo-9-ethyl-9*H*-carbazol-3-yl)dimethylsilane (3). In a three-necked flask, *n*-BuLi (4 mL, 10 mmol,2.5 M in hexanes) was added into N-ethyl-3,6-dibromocarbozole (2.36 g, 10 mmol) in freshly dried THF (100 mL) dropwise at -78°C under argon. The reaction solution was stirred for another 2h at -78°C, and then dichlorodimethylsilane (0.64 g, 5 mmol) was added at -78°C. After the end of the addition, the mixture was allowed to warm to room temperature and stirred overnight. After that, the reaction mixture was refluxed for another 1h. Then the reaction mixture was quenched by 30 mL H₂O and the organic layer was separated. The organic layers was washed by brine, dried over anhydrous MgSO₄ and filtered. Removal of the solvents under vacuum gave the crude product, which was subjected to column chromatography to obtain a white solid, **3**. Yield: 75%. IR (KBr pellet cm⁻¹): 3030, 2970, 2922, 1593, 1477, 1450, 1375, 1254, 1150, 1065, 835, 723, 650. ¹H NMR (300 MHz, CDCl₃) δ 0.55 (s, 6H), 1.38 (t, 6H), 4.35 (q, 4H), 7.32 (d, 2H), 7.49 (d, 2H), 7.53 (dd, 2H), 7.88 (d, 2H), 8.13 (d, 2H), 8.41 (s, 2H).

Synthesis of bis(6-bromo-9-ethyl-9*H*-carbazol-3-yl)diphenylsilane (4). The synthetic procedure of **4** is similar to that of compound **3** except dichlorodiphenylsilane instead of dichlorodimethylsilane and a white solid was obtained. Yield: 62%. IR (KBr pellet cm⁻¹): 3033, 2971, 2920, 1695, 1591, 1476, 1450, 1375, 1249, 1149, 1063, 834, 725, 651. ¹H NMR (300 MHz, CDCl₃) δ 1.37 (t, 6H), 4.33 (q, 4H), 7.24~7.89 (m, 18H), 8.15 (d, 2H), 8.42 (s, 2H).

Synthesis of bis(6-(1*H***-benzo[d]imidazol-1-yl)-9-ethyl-9***H***-carbazol-3-yl)dimethylsilane (1). A mixture of compound 3** (2 mmol, 1.28 g), benzimidazole (0.54 g, 8 mmol), CuI (0.077 g, 0.4 mmol), 18-crown-6 (0.14 g, 0.55 mmol) and K₂CO₃ (1.73 g, 12.5 mmol) was heated in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (6 mL) at 180°C for 64 h under argon. After cooling to ambient temperature, the mixture was dissolved in 100 mL CH₂Cl₂-H₂O mixture. The water layer was separated and extracted with CH₂Cl₂ (3x30 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL). Then the solution was dried over anhydrous MgSO₄ and filtration by evaporation of solvent under reduced pressure gave a brown solid. A yellow solid was obtained by column chromatography (CH₂Cl₂/MeOH as eluent). Yield: 45%. IR (KBr pellet cm⁻¹): 3052, 3020, 2973, 2925, 1654, 1595, 1521, 1450, 1382, 1302, 1290, 1254, 1223, 1103, 1063, 1008, 812, 740, 671, 577, 528. ¹H NMR (400 MHz, DMSO, ppm) δ 0.63 (s, 6H), 1.37 (t, 6H), 4.34 (q, 4H), 7.12~ 7.45 (m, 12H), 7.65~7.72 (m, 4H), 8.13 (s, 2H), 8.57 (d, 2H). ¹³C NMR (100 MHz, DMSO, ppm): δ -2.4, 14.5, 39.2, 108.9, 110.3, 112.3, 113.2, 124.4, 125.6, 129.8, 130.2, 131.5, 134.2, 138.5, 143.7. Anal. Calcd for C₄₄H₃₈N₆Si: C, 77.84; H, 5.64; N, 12.38. Found: C, 77.65; H, 5.43; N, 12.55.

Synthesis of bis(6-(1*H*-benzo[d]imidazol-1-yl)-9-ethyl-9*H*-carbazol-3-yl)diphenylsilane (2). The synthetic procedure of **2** is similar to that of **1** except using **4** as the starting material instead of **3** and a yellow solid was afforded. Yield: 38%. IR (KBr pellet cm⁻¹): 3052, 3020, 2973, 2925, 1654, 1595, 1521, 1450, 1382, 1302, 1290, 1254, 1223, 1103, 1063, 1008, 812, 740, 671, 577, 528. ¹H NMR (400 MHz, DMSO, ppm) δ 1.35 (t, 6H), 4.35 (q, 4H), 7.03~ 7.47 (m, 22H), 7.62~7.73 (m, 4H), 8.15 (s, 2H), 8.60 (d, 2H). ¹³C NMR (100 MHz, DMSO, ppm): δ 15.3, 42.1, 107.5, 109.3, 112.0, 112.2, 113.4, 113.5, 118.7, 119.3, 123.9, 124.3, 125.1, 125.7, 127.6, 128.6, 129.9, 130.1, 131.5, 134.5, 138.6, 143.8. Anal. Calcd for C₅₄H₄₂N₆Si: C, 80.76; H, 5.27; N, 10.46. Found: C, 80.12; H, 5.30; N, 10.66.

Results and Discussions

The carbazole-bridged silanes with benzimidazole groups, 1 and 2, were prepared following the modified literature methods [6,22]. As shown in Scheme 1, a mono-lithiated reaction firstly happened between N-ethyl-3,6-dibromocarbozole and *n*-BuLi. Then the product reacted with R_2SiCl_2 (R=Me, Ph) and dibromo- derivatives, **3** and **4** were afforded. Compounds 1 and 2 were successfully synthesized *via* between dibromo- derivatives and benzimidazole according to Ullmann condensation reaction in 45% and 38% yields, which are higher than those of the products from tetrabromo-derivatives [6]. It is worthy to note that **3** and **4** are useful intermediates for introduction of many different structural features by using various coupling reactions, such as Suzuki, Sonogashira and Heck reaction, *et al.*



Scheme 1. Synthesis of compounds 1 and 2. (i) (a) *n*-BuLi/THF, -78°C, 2h; (b) R₂SiCl₂ (R=Me, Ph), -78°C, rt, overnight, refluxing for 1h; (ii) CuI, 18-crown-6, K₂CO₃, DMPU, 210°C, 64h.

The thermal properties of **1** and **2** were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results show that both of them have a high thermal stability over 350 °C. Their glass-transition temperatures (T_g) are 95 and 110°C, which are substantially than those of tetraarylsilanes (26-53°C) [23].



Fig. 1 (a) UV-vis absorption of 1 and 2; (b) PL spectra of 1 and 2 in CH₂Cl₂ solution; (c) PL spectra of 1 and 2 in the solid state

Fig. 1 shows the electronic absorption and fluorescence spectrum of the compounds 1 and 2 in CH₂Cl₂ solution and in the solid state. Compounds 1 and 2 show a similar intense absorption with λ_{max} at ~315 nm, which can be attributed to the π - π * transitions involving the carbazole and benzimidazole groups. Moreover, compounds 1 and 2 are all luminescent in solution and in the solid state. In solution, the λ_{max} of emission in solution for them is similar at ~365 nm. Compounds 1 and 2 are both fairly efficient emitters in solution, as indicated by their quantum efficiency with 16% and 20%, respectively. In the solid state, the emission spectra for 1 and 2 are considerably red shifted

compared with those in solution, which may be due to the various intermolecular interactions, such as π - π stacking interactions. These results indicate that both of them can be potentially applied as blue emitters for OLEDs.

To gain a deeper insight into the electronic and luminescent properties, molecular orbital calculation have been performed at the level of B3LYP/6-31G(d) using the Gaussian 03 suite of programs. As shown in Fig. 2 (compound **1** as the representative), the HOMO and LUMO orbitals are similar, with dominating contributions from entire molecules, indicating that the HOMO and LUMO levels are π and π^* orbitals involving the carbazole and benzimidazole groups. And the results prove that the electronic absorption and luminescence for these compounds can be assigned to π - π^* transitions. It is noted that large HOMO-LUMO band gaps of 4.38 eV and 4.33 eV for **1** and **2** are observed, making them potentially useful candidates as either host materials or charge-blocking layers in OLEDs.



Fig. 2 Emission spectra of compounds 1 and 2 in the solid state

Summary

In conclusion, we have successfully synthesized two novel tetrahedral carbazole-bridged silanes with benzimidazole groups. For both of them, the combination of their high thermal stability, luminescence, and large HOMO-LOMU gaps makes them promising candidates as blue emitters, host materials or charge-blocking materials in OLEDs. The further investigation will focus on the fabrication of electroluminescent devices as well as functional MOFs based on these compounds.

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Load-Carrying Capacity of Cantilevers of Anti-Flood Barriers Made of FRP Composite Structural Profiles

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Keywords: Anti-flood barrier, cantilever, FRP composite, structural profile, experimental verification, loading test, actual behaviour, failure mechanism, load-carrying capacity, statistical evaluation.

Abstract. After the devastating floods in the Europe and Czech Republic especially, in 1997, 2002 and 2007 years, the need of the anti-flood protection was very actual and delicate. One of the ways, how to solve this problem in the case of usual or lower water level, is the usage of anti-flood barriers. The paper is focused on the experimental verification of the actual behaviour, load-carrying capacity and failure mechanisms of the cantilevers made of FRP composite profiles "PREFEN", which are in reality used as columns of anti-flood barriers. The investigated water-proof profile of H-cross-section is composed of epoxy resin and glass fibres.

Introduction

During the period of last two decades the extensive development of advanced structural systems for civil engineering works can be characterized by application of wider spectra of basic materials used for load-carrying structural components. Thus beyond traditional materials such as reinforced concrete, masonry, steel and timber also the fibre-reinforced polymers become a basic generating substance of structural parts and systems.

Over the past period, there have been significant developments in composite processing methods such as pultrusion, filament winding and resin transfer molding and resin infusion molding. These methods use different fiber reinforcement for different applications. Higher quality FRP materials are now available in shapes and forms more attractive for civil engineering. The contemporary challenge is to make them more cost effective for various structural components. Mechanical properties of FRP make them convenient for widespread applications. Fiber-reinforced polymer composites have desirable properties for extreme environments because they are noncorrosive, nonconductive, and lightweight. They are also noted for sufferable souse in drinking water-stations or sewage disposal plants. Three broad divisions, into which utilization of FRP in civil engineering can be classified, are usually indicated: application for new construction, repair and rehabilitation, and architectural implementation.

One of the examples of FRP composite structural members is the profile of "PREFEN" developed and produced by the company of "PREFA KOMPOZITY", Inc. at Brno city (see e.g. [1], [2]). The PREFEN profiles are thermoset members composed of two dominant physical substances with a composition "binding – reinforcement" = "resin – fibres" produced by the pultrusion technology. Binding can be polyester, vinylester or epoxy resin, for example; glass, carbon or basalt fibres are used mostly for the reinforcement. The "PREFEN" profiles are produced in a wide assortment of cross-section types and dimensions (I-sections, U-sections, tubes, rods, slabs, cable boxes, etc.).

These profiles have been, among others, used as the main load-carrying member of the anti-flood barrier construction. The profiles PREFEN represent the columns of the vertical anti-flood wall, which are constructed as the cantilevers fixed to the ground bases through the steel base foot. Based on the company requirements the loading tests have been performed to verify the load-carrying capacity of the test specimens subjected to the bending and shear loading actions aimed to obtain information about the resistance and stiffness as the supporting documents for the structural design.

Experimental Verification of Cantilevers

The object of loading tests were the columns for the anti-flood wall made of the composite profile of "PREFEN H 152 x 152 x 9.5". Test specimens and steel base foot simulating the column fixing to the support have been supplied by the client (PREFA KOMPOZITY, Inc.). It was required to verify the load-carrying capacity of specimens under bending and shear loading actions. The arrangement and methodology of loading tests have been discussed with the client during the preparation and realization of experiments, to ensure the real conditions corresponding with the actual operating loading actions and supporting tested component.

Test specimens. For the loading tests total of $2 \ge 3 = 6$ test specimens: specimens "TD" – "long" specimens, and specimens "TK" – "short" specimens. The schemes of test specimens are drawn in Fig. 1 – "long" and "short" cantilevers. Thus, always three specimens of the same length have been tested. Fig. 1 also illustrates the overall test arrangement for the verification of their capacity and strain in the loading progress. The deformation (deflection) of the column during loading actions caused by the concentrated loading represented by the force has been measured just in the place of its position. From the static viewpoint the test specimen is the fixed cantilever placed horizontally in the testing device (unlike the actual position in the anti-flood wall structure), with regards to the more suitable position of the hydraulic jack.



Figure 1: Test arrangement and test specimens - short cantilever "TK", long cantilever "TD"

Test Arrangement. The aim of the tests of long cantilevers was to verify the actual behaviour (deformation in loading progress), failure mechanism at the reaching ultimate loads, and in particular, the stiffness including the influence of bending and shear together, if the one-sidedly fixed structural member is subjected to transverse force. The aim of the short cantilever tests was to verify the shear resistance of the column section and the mechanism of the failure caused by predominant shear.

Test Realization. The specimens have been loaded using hydraulic jack; the concentrated force has been introduced by steel hinge bearing with the cutting edge perpendicular to the longitudinal axis of the specimen. The column has been loaded by the steps; on each loading step the values of the deflection in the place of the force have been measured. The shots of experiment realization, loading test arrangement and measurement apparatus installation are shown in Figs. 2 and 3. The results of the deflection monitoring during the loading process have been elaborated graphically in the form of the relationships "transverse force F - deflection w", drawn in Fig. 4.



Figure 2: Test arrangement and test realization - short cantilever "TK"



Figure 3: Test arrangement and test realization - long cantilever "TD"

Test Results. Summarized test results for both groups of specimens have been elaborated using regression analysis. The resulting dependences are illustrated in Fig. 4. While, as it is evident from graphic drawing, the parts of the activation and compensation of the testing device in the initial loading phase, which is clearly seen in the lower part of relationships of the particular specimens (see Fig. 4 left), have been excluded.



Figure 4: Relationships "force F – deflection w" – short cantilever "TK", long cantilever "TD"; regression analysis substitution – short cantilever "TK", long cantilever "TD"

Table 1. Test fesuits – utimate foad-carrying capacities						
Test specimen	TD 1	TD 2	TD 3	TK 1	TK 2	TK 3
Ultimate capacity [kN]	12.5	13.0	13.6	53.0	46.0	50.0

Γable 1: Test results – ult	imate load-carr	ying ca	pacities
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Test specimens failure mechanism corresponding with the load-carrying capacity is evident from the shots in Fig. 5. The ultimate load is connected to the failure in the cantilever fixing characterized by the buckling of the compressed flange in the place of timber wedge and adjacent web part of H-profile. In all cases the triangular deformation of the compressed flange occurred; this effect caused the breakage of timber wedge in fixing.



Figure 5: Test results - illustration of failure mechanisms

Summary

Based on the aims defined by experimental programme, the following conclusions can be formulated:

- For long test specimens "TD" the "modulus of elasticity" comprising the influence of shear in bending can be derived as EM-Q = 11055 MPa. This relationship can be taken as the base for the definition of deflection of the column of mentioned section, caused by transverse force.
- For short specimens "TK" the actual shear resistance is given by the values in Table 1.

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Tribological behavior of Si₃N₄-hBN Ceramic Materials sliding against Fe-B alloy without lubrication

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Abstract. The tribological behavior of Si_3N_4 -hBN composites sliding on Fe-B alloy without lubrication was investigated by using a pin-on-disc wear tester. The results showed that, the addition of hBN to Si_3N_4 could not effectively improve the tribological characteristics of Si_3N_4 -hBN when it slid against Fe-B alloy. Without lubrication, the wear of Si_3N_4 -hBN composites was resulted from cracking and fracture, while the hard phase Fe₂B in Fe-B alloy spalled off during the friction test. So, high friction coefficients (>0.9) and high wear coefficients (>1×10⁻⁵mm³/Nm) were obtained.

Introduction

From the aforementioned works[1-3], it can be found that the friction coefficients of Si_3N_4 /metal under unlubricated condition between 0.4 and 0.9 and wear coefficient higher than 1×10^{-5} mm³·N⁻¹m⁻¹. This result cannot come up to the engineering application criteria proposed by Czichos [4]. The incorporation of hBN is a goal to further enhance the tribological performance of Si_3N_4 .

The earlier research work of this paper's authors [5] found that the friction coefficient of Si_3N_4 -hBN/stainless steel pairs under the unlubricated condition rapidly decreases to 0.03 with the increase in sliding distance. In the meantime, the wear coefficients of Si_3N_4 -hBN ceramic and stainless steel are lower than $1 \times 10^{-6} \text{ mm}^3 \cdot \text{N}^{-1}\text{m}^{-1}$. Such excellent tribological characteristics are new finding in ceramic-metal pairs and quite attractive in engineering application. However, it is noteworthy that only few studies have been concerned the tribological characteristics of Si_3N_4 -hBN ceramic sliding against other metals.

Recently, Fe-B cast alloy as a novel anti-abrasive material has attracts the attentions of scholars, just because of their low production cost, simple melting, low alloy consumption and excellent casting properties and wear resistance [6]. At present, the investigations of Fe-B alloy were mainly concerned in the microstructure, mechanical properties and wear performance. However, the tribological characteristics of Fe-B alloy have not investigated. In particular, the influence of the hard phase borides on the tribological characteristics would be needed to deeply study.

Therefore, to enrich tribology theory and expand the engineering application of Si_3N_4 -based ceramic and Fe-B alloy, the tribological behavior of Si_3N_4 -hBN ceramic (the addition of hBN is 30 Vol.% or less) against Fe-B alloy without lubrication is investigated in this paper. The influence of hBN and hard phase borides on the tribological mechanism are further discussed through measuring friction coefficient and wear coefficient, observing wear morphology and analyzing the components of the tribological surface.

Experiment

Test rig and materials

Friction and wear experiments were carried out on a pin-on-disc device in which an upper disc contacts a bottom pin under unlubrication condition. The pin specimen was fixed, and the disc specimen rotated at different speeds. A normal load was applied on the stationary pin, and the friction force was continuously measured by using a strain gauge.

The specimens of Si₃N₄-hBN composed of 0, 5, 10, 20, 30 vol.% hBN (SN0-SN30) were sintered by hot-pressing under 30MPa pressure at 1800°C for 30min of dwell time. The microstructure of Si₃N₄-20% hBN composite was composed of elongated β -Si₃N₄ and layered hBN. Table 1 shows the related physical and mechanical properties of the Si₃N₄-hBN specimens.

Table 1 Physical and mechanical properties of Si ₃ N ₄ -hBN specimens								
Specimens	SN0	SN5	SN10	SN20	SN30			
hBN amount(Vol.%)	0	5	10	20	30			
Density (gcm ⁻³)	3.31	3.17	3.10	2.97	2.94			
Porosity (%)	0.84	0.90	0.91	1.04	1.05			
Bending strength (MPa)	812	758	613	541	465			
Vickers hardness (GPa)	19.9	19.6	15.3	9.3	6.7			
Fracture toughness (MPa \cdot m ^{1/2})	8.01	7.80	7.14	5.97	5.50			

The specimens of Fe-B were melted in a 10 kg medium frequency induction furnace, and low carbon steel bar, ferromanganese, ferrosilicon, ferroboron and pig iron were used as furnace charge for controlling the chemical content. Considering the size requirement of disc specimen, the molten metal was poured into chemically bonded sand molds to produce $\Phi45$ mm×60mm test bar. Then, the disc specimens were machined from the bar. The XRD analysis result of Fe-B alloy shows the borides in Fe-B alloy are Fe₂B in Fig.1.



Fig.1 X-ray diffraction pattern of Fe-B alloy

The pin (SN0-SN30) in the size of $5 \times 5 \times 10$ mm with a filleted end were used to form flat contacts, so that the contact surface area is about 20mm²; the disc, as the friction pairs, was machined from Fe-B alloy (HBS), in the size of 44 mm in diameter and 6mm in thickness. They were finished by grinding to achieve a surface roughness (Ra) of 0.8 μ m or less.

Procedure

At room temperature the specimens were tested in laboratory air (T=22-25°C, RH=30-40%) at a constant sliding speed (v=1.31ms⁻¹) and normal load (w=10N). The sliding distance was 850m. The friction coefficient f is directly determined by the tester. The wear coefficient k is given by $k = \frac{\Delta m}{(\rho wx)}$, where Δm represents the mass wear volume assessed by weight loss using a microbalance (accuracy = 0.1 mg), w is the normal load, x is the sliding distance, and ρ is the density. In addition, when the wear coefficients were lower than 10⁻⁶ mm³N⁻¹m⁻¹ magnitude, the

measurable values would be equal to zero. The initial running-in period was not accounted for the calculation of f and k. Wear coefficients and friction coefficients were obtained from the average of the values taken from 3 runs.

The morphologies of the wear debris and worn surfaces were examined by scanning electron microscope (SEM). The wear debris phase constitution was determined with X-ray diffraction (XRD). In addition, the chemical characterization of the worn surfaces was analyzed by using energy-dispersive X-ray spectroscopy (EDS).

Result and discussion

Fig.2 (a) presents the friction coefficients of the specimens in stable state without lubrication. Fig.2 (b) shows the complete set of wear coefficients for the same experiments. From Fig 2, it could be easily found that, without lubrication, the addition of hBN to Si_3N_4 was not benefit to the friction and wear behavior of Si_3N_4 -hBN/HBS pairs. Fig.2 (a) shows that, the friction coefficients were all higher than 0.8. When hBN content was 30 vol.%, the friction coefficient is up to about 1.38. Fig.2 (b) presents that, the wear coefficients of pin an disc specimens were all higher than $10^{-5} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$ magnitude. With the increase of hBN content, the wear coefficients of Si_3N_4 -hBN pins increased, and the wear coefficients of HBS discs sliding against Si_3N_4 -hBN pins decreased.



Fig.2 Friction coefficient (a) and wear coefficient (b) of Si₃N₄-hBN/HBS pairs without lubrication

Fig.3 gives the morphologies of SN30/HBS pairs. From Fig.3 (a), it can be seen that some transfer layers are distributed on the SN30 pin surface. The high magnification image of local area indicated by an arrow is shown in the top left corner of Fig.3 (a). This SEM observation manifests brittle fractures appear on the transfer layers and a lot of wear debris are distributed around the transfer layers. EDS analysis results of the transfer layer area on the SN30 pin surface are shown in Table 2. From the table it can be found that the transfer layers are mainly composed of Fe element, oxygen element and a spot of silicon element. So, as discussed above, the transfer layer should be metals and metal oxides coming from HBS disc. The morphology of the worn surface of HBS disc sliding against SN30 pin is shown in Fig.3 (b). It can be seen from the figure that some outstanding areas and the large particles appear on the worn surface.

The SEM observation and XRD analysis of the wear debris collected during the wear test of SN30/HBS pair are shown in Fig.4. It can be seen from Fig.4 (a) that the wear debris is composed of fine and loose particles, which is similar to the wear debris morphology shown in Fig.7. Moreover, the XRD results of the wear debris reveal that, as shown in Fig.4 (b), besides Fe and iron oxides coming from HBS disc, the wear debris contains Si_3N_4 coming from SN30 pin.



Fig.3 SEM images of the worn surface of SN30/HBS pair: (a) SN30 pin and (b) HBS disc Table 2 EDS analysis of the worn surface of SN30 pin sliding against Fe-B alloy

Area	Atomic concentration (%)			
	0	Si	Fe	
Transfer layer	41.57	6.24	52.18	
15kU* X1.000 100m 17-87	180 160 140 120 120 100 60 40 20 10 20		9₃ ● 9₄ ○ 1₄ □ 70	



Fig.5 shows the morphology of the cross-section of the HBS disc after sliding against SN30 pin. It can be found from the figure that some fine cracks distribute on the cross-section, and cracks growth leads to the brittle fracture and spalling. The morphology also indicates the cracks distribute on the hard phase Fe₂B. As discussed above, the hard phase Fe₂B in HBS disc is easy to break, resulting in a lot of wear debris.



Fig.5 The subsurface of Fe-B alloy disc sliding against SN30 pin without lubrication

It can be concluded from the discussion above that, for the SN30/HBS sliding pairs, at the first stage of friction process, the micro-bulges on the wear surface of SN30 pin ploughed the wear surface of HBS disc. Because the hardness of Fe₂B phase is much higher than that of matrix [7], Fe₂B phase was outstanding during the friction process. With the increase of friction, the impact of the micro-bulges on the wear surface of SN30 pin against the Fe₂B bulges leaded to the brittle fracture

and spalling. As a result, a large amount of were debris was forming. Under upper disc-on-bottom pin mode, most of the wear debris was carried away from the wear surface due to the effect of gravity, but some wear debris was still left in the wear interface leading to abrasive wear. The wear debris in the wear interface was oxidized and ground, and so that then the wear debris layer, which was similar to metal transfer layer, was forming on the wear surface of SN30 pin. This wear debris layer exhibited fracture during the wear process, and became wear debris again, which dynamically aggravated the degree of abrasive wear.

Fig.6 shows the morphology of the worn surface of SN0 pin sliding against HBS disc. It can be seen that the worn surface is smoother than that of SN30 pin, and only a little wear debris adhere on the wear surface. The research work above manifests that, when Fe-B alloy discs slide against Si₃N₄-hBN pins, the wear mechanism is dominated by abrasive wear, so the friction coefficients and wear coefficients are all high. With the increase of hBN content, on the one hand, the mechanical property of Si₃N₄-hBN ceramic decrease, which results in the formation of more wear debris with the increase of hBN content and aggravates the abrasive wear. Hence, the friction coefficients and wear coefficients of Si₃N₄-hBN pins increase with the increase of hBN content. On the other hand, the decrease of mechanical properties of Si₃N₄-hBN pins weakens the plough ability, and so that then the wear coefficients of Fe-B alloy discs decrease with the increase of hBN content.



Fig.6 SEM image of the worn surface of SN0 pin sliding against Fe-B disc without lubrication

Conclusions

(1) When Si_3N_4 -hBN pins sliding against Fe-B alloy discs, the addition of hBN can't effectively reduce friction.

(2) Without lubrication, when Si_3N_4 -hBN pins sliding against Fe-B alloy discs, the impact of the micro-bulges on the wear surface of Si_3N_4 -hB pins against the Fe₂B bulges leaded to the brittle fracture and spalling, and the wear mechanism was dominated by abrasive wear. In this case, the friction coefficients were all higher than 0.9 and the wear coefficients were all higher than 10^{-5} mm³/Nm magnitude.

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Isothermal Crystallization Behavior of Poly (L-lactic acid)/

Surface-grafted Silica Nanocomposites

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Key words: Poly(L-lactic acid); Silica; Isothermal crystallization; Composities

Abstract: The Poly(L-lactic acid)(PLLA)/surface-grafting silica(g-SiO₂) nanocomposites were prepared by melt blending. The isothermal crystallization behavior of PLLA/g-SiO₂ nanocomposites with different content of g-SiO₂ was investigated by optical depolarizer. In isothermal crystallization from melt, the induction periods and half times for overall PLLA crystallization ($95^{\circ}C \le T_c \le 120^{\circ}C$) were affected by the crystallization temperature and the content of g-SiO₂ in nanocomposites. The results showed that g-SiO₂ as a kind of heterogeneous nucleating agent can reduce induction periods and half times for overall PLLA crystallization. The thermal properties of PLLA/g-SiO₂ samples were also investigated by differential scanning calorimetry (DSC), The results showed that the crystalline degree of PLLA was improved as the presence of g-SiO₂.

1. Introduction

Poly(L-lactic acid)(PLLA), as a kind of biodegradable polymer that get rid of the dependence of petroleum recourses, has gained considerable momentum in recent years [1-5] due to its properties such as biodegradability, non-toxic to the environment, etc [6]. However, the application of PLLA was limited because of its brittleness and especially low crystallization [7]. Thus, it is necessary to improve PLLA to make it fully competitive with commercial thermoplastics. To improve crystallization and blending have been used to modify PLLA. Inorganic fillers are often introduced into PLLA as nucleating agents to increase crystallization rate, some works have given us many helpful references [8-10]. For example, Pluta et al. [8] studied the crystallization behavior and the morphology of neat PLA and PLA/OMMT nanocomposites. His work has shown that clay particles act as nucleating agent for the crystallization of the matrix PLA, but he didn't report the overall crystallization rate and spherulite growth rate of PLA before and after nanocomposites preparation. Nam et al. [9] have described the detailed crystallization behavior and morphology of pure PLA and PLA/C₁₈-MMT nanocomposite, including overall crystallization rate, crystallization kinetics and spherulitic texture of PLA. Krikorian and Pochan [10] amply investigated the crystallization behavior of organoclay reinforced PLLA nanocomposites. Their research was base on two types of organoclay with different extent of compatibility with PLLA. The bulk kinetics studies and radial spherulite growth rates indicated that when a high degree of filler-polymer matrix compatibility is present, nucleation properties of the organoclay are low relative to the less compatible organoclay. Their works are convincing and worth reference, but further investigation should be carried out because it is well known that 10% or 15% of nano-filler is too high to nanocomposites.

PLLA nanocomposites with SiO₂ have been reported[12-16], Linbo Wu et al[12-13] reported PLLA/SiO₂ nanocomposites were prepared via in situ melt polycondensation of L--lactic acid in the presence of acidic silica sol. The SiO₂ nanoparticles acted as nucleation agents in the PLLA matrix and enhanced its nucleation rate and overall crystallization rate, especially at high crystallization temperatures. However, their research ignored the effect of SiO₂ content to crystallization. Thus, in this paper, in order to improve the compatibility and adhesion between SiO₂ and PLLA matrix, the SiO₂ were surface-grafted with *L*-lactic acid oligomer. And the isothermal crystallization behavior of PLLA/surface-grafting silica(g-SiO₂) nanocomposites with different content of g-SiO₂ has been investigated in detail. Furthermore, the influence of the content of g-SiO₂ nano-composites was investigated.

2. Experimental Section

2.1 Materials

Poly(L-lactic acid) (PLLA) ($M_w=1.95\times10^5$) was purchased from Zhejiang Hisun Group. (China). g-SiO₂ were supplied by Shanghai university.

2.2 Preparation of PLLA/g-SiO₂ nanocomposites

PLLA and g-SiO₂ were dried over night at 45°C under vacuum respectively to remove residual water. Blending of PLLA and g-SiO₂ was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 4min, then at 64 rpm for 4 min. The processing temperature was set at 180°C. The composites with various amounts (1, 3, 9%) of g-SiO₂ nanoparticles were prepared. Products were hot pressed at 180°C under 10 MPa for 3 min to prepare sheets. The sheets were then cooled down by being compressed at room temperature under 10 MPa for 15 min.

2.3 Characterization

Depolarized-light intensity measurement: The overall isothermal crystallization behavior of PLLA was investigated by GJY-IIIoptical depolarizer in the region from 100° to 120° . The electronic signals transformed from the measured optical depolarizer were amplified and then recorded on the Recording and Data Acquisition for further analyzing.

Differential scanning calorimeter: DSC 200 PC (Netzsch, Germany) was used to measure the

equilibrium melting temperature (T_m^0) . The sample was heated to 190°C and maintained at that

temperature for 5 min to make sure that the polymer crystals were melted completely. Then the sample was quenched to the crystallization temperature T_c (110°C) by liquid nitrogen, held at that temperature for at least 30 min to ensure complete crystallization. At last, the sample was heated at the heating rate of 20°C/min.

3. Results and discussion

3.1 Overall isothermal crystallization behavior

Traditionally, isothermal crystallization behavior can be investigated by using depolarized-light intensity [15, 16] technique as the transmitted light intensity (I) increases with the increasing of crystallinity and finally levels off when crystallization completes. In our research, we used the relative light intensity (I_r) defined by the following equation as an index of crystallinity:

$$I_r(\%) = 100 \times \frac{(I_t - I_0)}{(I_\infty - I_0)}$$
(1)

where I_t and I_0 are the *I* values at $t_c = t$ and 0, respectively, I_{∞} is the *I* value when crystallization

completes. Fig.1 shows the effect of the g-SiO₂ content and the crystallization temperature (T_c) against the induction period t_i and the crystallization rate ($1/t_{1/2}$). With the increasing of crystallization temperature, t_i become shorter due to the enhancement of the macromolecule segment active ability, and t_i has the maximum value when crystallization temperature is 105 °C, However, t_i become longer with further increasing of crystallization temperature, which result from the formation of spherulite restricted by excessive macromolecule segment activity. The t_i peak of PLLA/g-SiO₂ shift toward lower T_c , which indicate that g-SiO₂ can serve as a good heterogeneous nucleating agent for the crystallization of PLLA in the composites. At same time, the content of g-SiO₂ has great impact of induction period. The t_i decrease by adding more content of g-SiO₂, which confirm again that g-SiO₂ has good heterogeneous nucleation effect. Figure.1 also shows the trend of crystallization rate ($1/t_{1/2}$) with different T_c and g-SiO₂ content. The crystallization rate increase with the increasing content of g-SiO₂ which also can attribute to the heterogeneous nucleation effect of g-SiO₂. However, the crystallization rate of PLLA/g-SiO₂ composites with above 3%g-SiO₂ has the maximum value when crystallization temperature is 110°C, which is different from the induction period.



Fig.1 Induction periods (t_i) and crystallization rate ($1/t_{1/2}$) for PLLA/ g-SiO₂ composites with different g-SiO₂ content and crystallization temperature

3.2 Crystallization thermodynamics

The crystallization thermodynamics parameters of neat PLLA and PLLA/g-SiO₂ nanocomposites are listed in Table 1. These samples were measured by DSC after 30min isothermal crystallization at 110°C. By considering ΔH_m^* , melting enthalpy of 100% crystalline PLLA, as 93.7J/g [17], we have estimated the value of crystalline degree χ_c of PLLA in different systems. χ_c of composites should based on the equation:

$$\chi_c = \frac{\Delta H_m}{(1-\phi)\Delta H_m^*} \times 100\%$$
⁽²⁾

where ϕ is the weight fraction of filler in nanocomposite and ΔH_m is the heat of fusion.

According to the data listed in Table 1, It is clear that $g-SiO_2$ nanoparticles can serve as a nucleating agent for the crystallization of PLLA in the composites. Compared to the neat PLLA, the crystalline degree χ_c of PLLA matrix increases above 3% $g-SiO_2$ content. The crystallization temperature (T_c) and the melting temperature (T_m) seem to be independent of loading of $g-SiO_2$ particles.

Sample		T_{c} (°C)	T_m (°C)		χ _c (%)	
PLLA		119.57	155.37	16.79	18.05	
PLLA/g-SiO ₂	1wt%	127.05	152.16	9.963	10.71	
	3wt%	127.37	153.13	18.95	20.38	
	9wt%	119.39	152.44	22.19	23.86	

Table 1 Thermal parameters of PLLA and PLLA/ g-SiO₂ nanocomposites

4. Conclusions

Investigations on the isothermal crystallization behavior were carried out on the intercalated PLLA nanocomposites prepared by melting blend. The results showed that the g-SiO₂ as a kind of heterogeneous nucleation agent can reduce t_i and $t_{1/2}$. And the crystalline degree of PLLA matrix increases above 3% g-SiO₂ content.

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Synthesis of high solid content acrylic-polyurethane hybrid emulsions with low viscosity

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Key words: acrylic-polyurethane, emulsion, high solid content, PSD, viscosity.

Abstract. The emulsion polymerization of methyl methacrylate (MMA) with butyl acrylate (BA) using aqueous polyurethane dispersion as seed was undertaken to prepare acrylic-polyurethane (PUA) hybrid emulsions with high solid content. The concentrations of the anionic groups were varied by adding different amount of dimethylolpropionic acid (DMPA). The emulsions with a similar bimodal particle size distribution (PSD) were obtained. The viscosity of the emulsions is about 350 mPa's while the solid content is about 55%.

Introduction

Polyurethane (PU) resins, due to their high performance, especially in abrasion resistance, chemical resistance and mechanical flexibility, are widely used in different areas such as coatings and adhesives for wood, textiles and automobiles^[1,2]. As the requirements of environmental protection, there is an increasing need to optimize the performance of water-borne polymer systems to replace the solvent-based systems to reduce VOCs^[3-5]. Therefore, aqueous polyurethane emulsions with high solid content, facilitating fast drying and easy transportation, have attracted increasing attention during recent years^[6].

However, the performances of aqueous polyurethane are usually inferior to the solvent-borne polyurethane, such as less dispersion stability and water resistance of the cast film, due to the introduced hydrophilic groups or surfactants^[7]. In addition, the higher cost of polyurethane dispersions also limits their commercial use. Thus, many new approaches have been explored to solve the problem, such as acrylic or epoxy modifications of PU^[8,9]. PUA is a kind of excellent polymer materials, especially for coating and adhesive, due to their superior properties such as decorativity, protectiveness, and corrosion resistance. Although some PUA emulsions with solid content as high as 50% have been obtained^[10], the viscosity was always not investigated systematically.

In this paper, we prepare the PUA hybrid emulsions by seeded emulsion polymerization. And how the PSD makes an effect on the viscosity of the emulsions with high solid content is investigated systematically.

Materials and methods

Materials. Poly-1,4-butylene adipate (PBA, M_n =2000, Qingdao Xinyutian Chemical Co., Ltd.,China) were dried and degassed at 100 °C under a vacuum for 2 h before use. Isophorone diisocyanate (IPDI, supplied by Skshu Paint Co., Ltd., China), and hydroxyethyl methacrylate (HEMA, Mitsubishi Chemical Co., Ltd, Japan) as an end capping agent, were used as received. Dimethylolpropionic acid (DMPA, supplied by Skshu Paint Co., Ltd., China) was dried at 50 °C for 48 h in a vacuum oven. Triethylamine (TEA, 99 wt% purity) as neutralization agent was dried over 4A molecular sieves before use. Methyl methacrylate (MMA) and butyl acrylate (BA) were used as acrylic monomers.

Synthesis of the water-borne polyurethane dispersions. PBA were charged into a dry vessel fitted with a reflux condenser and a mechanical stirrer. The content was heated up, followed by the addition of IPDI. Then DMPA was charged into the mixture. The polyaddition reaction was continued with continuous stirring. After the NCO terminated prepolymers were obtained, a known amount of HEMA was introduced into the reactor and the NCO-HEMA coupling reaction was allowed to take place. The HEMA terminated prepolymers were cooled down to a lower temperature, and TEA was added and mixed for a certain of time. Finally, distilled water was fed to the reactor and the phase inversion took place with a vigorous stirring. The resulting products were stable dispersions with a solid content of about 30%.

Preparation of PUA hybrid emulsions. The acrylic monomer (MMA and BA) was added into the reactor at a constant feed rate under stirring. After the complete addition of monomers, a part of the initiator was then added. About 0.5 h later, the remained initiator was added into the reactor and the reaction took place for a certain of time. Finally, after removing residual VOCs under reduced pressure, a acrylic-polyurethane hybrid emulsion was obtained.

Measurement. The particle size distribution of emulsion was measured by dynamic light scattering method using Zetasizer 3000 (Malvern Instruments). And the viscosity of the emulsion was measured using a rotational viscometer (NDJ-9S, Shanghai Precision Scientific Instrument Co., Ltd.) at a rate of 60 r/min.

Results and discussion

Effect of added amount of DMPA. During the preparation of the PU prepolymers, DMPA is used not only as the chain extender, but also as the medium of introducing hydrophilic group. Therefore the added amount of DMPA will affect the length of PU chain, and also determine the content of the ionic group. Thus the particle morphology, particle size distribution, particle hydrophilicity and the viscosity of emulsion will be varied by adding different amount of DMPA. In this paper, the added amount of DMPA was varied from 3.5% to 8%, and the characteristics of the resulted latexes are summarized in Table 1.

Table 1 The FSD and viscosity of FOA emuisions												
PU samples	D35	D40	D45	D50	D55	D60	D65	D70				
DMPA[%]	3.5	4	4.5	5	5.5	6	6.5	7				
Solid content [%]	55.6	53.8	53.9	51.4	52.8	55.0	50.2	55.2				
Number of peaks	1	2	2	2	2	2	2	2				
ø _s [%]	100	74.8	83.9	87.4	97.1	67.6	67.8	29.0				
ø _L [%]	0	25.2	16.1	12.6	2.9	31.8	32.2	70.8				
d _s [nm]	165	194	144	122	111	76	72	100				
d_L [nm]		396	397	398	407	504	537	483				
w _s [nm]	91.4	193	145	125	102	128	119	125				
w_L [nm]	0	129	125	133	107	338	343	232				
d _{Vm} [nm]	165	245	185	157	119	212	221	371				
d _{Nm} [nm]	140	148	88	68	67	22	20	37				
η [mPaˈs]	359	81	55	51	93	354	98	314				

Table 1 The PSD and viscosity of PUA emulsions

DMPA, the added amount of DMPA is with respect to the total amount of PBA, IPDI and DMPA; $ø_s$ and $ø_L$, the volume fraction of small and large particles; d_s and d_L , the mean diameter of small and large particles by volume; w_s and w_L , the peak width of small and large particles, d_{Vm} and d_{Nm} , the mean diameter of total particles by volume and number.

The particles were suggested as rigid balls. Thus the volume of small and large particles could be calculated by the following equations, respectively:

$$V_s = \frac{\pi d_s}{6}$$

(1)

$$V_L = \frac{\pi d_L^3}{6} \tag{2}$$

And then the approximate calculations of the number ratio of large particles to small particles (N_L/N_S) were taken as the following equation:

$$\frac{N_L}{N_S} = \frac{\phi_L V_S}{\phi_S V_L} \tag{3}$$

And the results are shown in Table 2.

With the increase of the added amount of DMPA from 40% to 55%, the d_s and d_{Nm} of PUA emulsions decrease gradually and the PSD of small particles become narrower, while the volume fraction of small particles increases. This behavior is due to the increase of the content of carboxylic acid introduced by DMPA. It is likely that with the increase of the content of hydrophilic carboxyl group in PU chain segment, the surface activity of PU prepolymer becomes stronger, which leads to a decrease of the particle size. However, the mean diameter of large particles of PUA emulsions keeps 400 nm with the increase addition of DMPA from 4% to 5.5%. It may be due to the different composition between large and small particles: most of the PU segments with the hydrophilic carboxyl group are in the small particles while the large particles mainly consist of acrylic segment. When the added amount of DMPA is above 6%, the PSD does not vary regularly as the former. It is likely that the competition takes place between interfacial tension and ionic strength of the particles with a high addition of DMPA.

Table 2 The N_L/N_S and d_L/d_S of PUA emulsions **PUA** D35 D40 D45 D50 D55 D60 D65 D70 samples $N_{\rm L}/N_{\rm S}$ [%] 0 3.96 0.92 0.42 0.06 0.16 0.11 2.17 2.04 2.76 3.26 3.67 6.63 7.46 4.83 d_I/d_S --

Particle size distribution. Table 1 shows that the PUA emulsions with various particle size distribution were obtained. The PSDs of PUA emulsions of D35 and D40 are shown in Figure.1. All the PUA emulsions except D35 have bimodal particle size distribution, but the PSD width, the volume fraction and the mean particle size of small and large particles are obviously varied. Even though D35 has a monomodal PSD, while both D60 and D70 have bimodal PSD and D60 has smaller particle size and more small particles than D70, the viscosity of the three dispersions is similar and much higher than the others.



Figure. 1 PSD of PUA emulsions



Figure. 2 Variation of the viscosity of PUA emulsion with the solid content

Effect of solid content on viscosity. In order to determine the maximum attainable solid content, a study was undertaken by preparing a PUA emulsion, which has the similar recipe as D60 but less amount of water, with a solid content as high as 64%. Then the emulsion was diluted in steps. The results were shown in Figure 2. When the solid content is lower than 50%, the viscosity of the PUA emulsion is very low. The viscosity increases slowly with the content of solid varying from 50% to 58%, and increases sharply when the solid content is above 58%. Therefore, in order to prepare PUA emulsions with low viscosity, the solid content of the emulsion should be lower than 58%.

Summary

The viscosity of high solid content emulsions is sensitive to many factors. In this work, the effect of the added amount of DMPA and the PSD are mainly investigated. A series of high solid content PUA emulsions were obtained successfully and the viscosity is lower than 360 mPa⁻S. In addition, in order to prepare PUA emulsions with low viscosity, the designed solid content of the emulsion should be lower than 58% in the present work.

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Electrochemical Polymerization and Electrochromic Properties of Poly(3-methoxythiophene)/NiO Composite Films

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Keywords: poly(3-methoxythiophene); NiO; electrochromic

Abstract. Poly(3-methoxythiophene)/NiO (PMOT/NiO) composite films were electrochemically synthesized on a ITO surface in the ionic liquid 1-butyl-3-metyllimidazolium hexafluorophosphate ([BMIM]PF₆) by a potentiodynamic polymerization method. The PMOT/NiO composite films were characterized by energy-dispersive X-ray analysis(EDS) and scanning electron microscopy (SEM). Electrochemistry properties of the prepared film was characterized by cyclic voltammetry. Spectroelectrochemistry and electrochromic properties of the PMOT/NiO composite were characterized using various experiment techniques in [BMIM]PF₆.

Introduction

In recent years, polythiophenes, a very versatile class of conjugated polymers, are still of growing interest due to their potential applications in the development of new materials such as in the field of electrochromic devices, light emitting diodes and energy storage[1,2]. Among conducting polymers, poly(3-methoxythiophene) (PMOT) has been received a significant share of attention. PMOT, as an important derivative of polythiophene, has led to numerous applications in the fields of microelectronics and optoelectronics to its high conductivity and high tensile strength and flexibility. For example, Nano-poly(3-methoxythiophene) (NPMOT) was electrochemically synthesized on an ITO surface in the ionic liquid 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM]BF₄) by a potentiodynamic polymerization method. The NPMOT films showed a good optical contrast and the ability of switching under atmospheric pressure[3].

Conducting polymer/metal oxide composite films have gained extensive attention. Because of their unique molecular structure and apparent synergistic effect, these composite films can display an improved electrochromic effect and specific capacities[4]. Poly(3-bromothiophene) (PBrT) was electrochemically synthesised on nano-WO₃ surface in the ionic liquid 1-butyl-3-metyllimidazolium hexafluorophosphate ([BMIM]PF₆) by potentiodynamic method. Experimental results show that the electrochemical activity of the PBrT/WO₃ nanocomposite films was significantly improved due to the contribution of unique structure and interactions between PBrT andWO₃[5]. Organic/inorganic nanocomposite films based on poly(3-methoxythiophene) (PMOT) andWO₃ were prepared by a consecutive two-step electrochemical method. The obtained PMOT/WO₃ nanocomposite films were also characterized by cyclic voltammetry to investigate their electrochemistry properties which display significant enhancement of electrochemical activity than that of pure PMOT and WO₃ films[6]. In this work, PMOT/NiO composite films were prepared using electrochemical method. The morphology, structural and electrochromic properties were investigated on the film.

Sample preparation

All the chemicals were analytic grade reagents without further purification. The PMOT/NiO composite film on an indium tin oxide (ITO) $(1 \times 1 \text{ cm}^2)$ conducting glass substrate was prepared by two consecutive steps in a conventional three-electrode cell system. An ITO conducting glass $(1 \times 1 \text{ cm}^2)$ had been pretreated with ultrasonic cleaning with acetone, anhydrous ethanol and distilled water for 5 min, respectively and dried in air at 80 °C. Deposition electrolytes consisted of 0.1M nickel nitrate, sodium acetate and potassium nitrate at room temperature. The electrochemical

experiments were performed on a CHI660C electrochemical working station (CHI, Chenhua, Shanghai, China) using a saturated Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. The electrodeposition of NiO films were performed under a voltage of +1.5V for 300s. After deposition, sample was washed with deionized water and dried in air at 80 °C. A SEM image of the surface of NiO film is presented in Figure 1. Relatively uniform nanoparticles were formed in the range of 10 to 20 nm. PMOT was then deposited on this NiO film as a second step by a potentiodynamic polymerization method involving scanning the potential repeatedly between -1.0V and +2.0V versus a Ag/Ag⁺ reference electrode at a scan rate of 100 mV/s for 3 cycles in 2M 3-methoxythiophene in 5ml [BMIM]PF₆. After electrochemical polymerization, the PMOT/NiO composite film was washed with acetone for several times to remove unreacted monomer and dried in air.



Fig. 1 SEM image of NiO film deposited on ITO glass substrate.

Characterization

The morphologies were characterized using scanning electron microscopy (SEM, Hitachi S-4700, 15kV). The composition of the products was analyzed by energy dispersive X-ray detector (EDS, Thermo Noran VANTAG-ESI). Spectroelectrochemical studies were carried out on a UV-Vis spectrophotometer (UV-759s, Shanghai, China) in the wavelength range of 350-750 nm.

Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode electrochemical cell with PMOT/NiO film as the working electrode, Ag/Ag^+ reference electrode and Pt counter electrode. [BMIM]PF₆ was employed as electrolyte. The cyclic voltammetry (CV) measurements were performed at room temperature.

Results and discussion

The morphology of the PMOT/NiO film were examined by SEM microscopy. Figure 2 shows the surface morphology of the PMOT/NiO film. It can be seen that PMOT are nanoparticles with size of 30-50 nm. The energy dispersive spectrometry (EDS) analysis was employed to determine the composition of the PCIT/WO₃ film. The EDS patterns of the PMOT/NiO film are shown in Figure 3. It reveals that the main elements in samples are S, C from PMOT and Ni from NiO.


Figure 4 shows the cyclic voltammograms of the PMOT/NiO composite film in [BMIM]PF₆ electrolyte at a scan rate of 20 mV/s. The anodic part of the voltammogram consists of two peaks at 0.11V and 0.76V. On the reverse scan two reduction peaks are observed. The PMOT/NiO film exhibited different color during the potential scanning sweep: at the oxidized state (E= +1.2 V) the coloration of the film is blue, and at the reduced state (E= -1.0 V) it is red. Fig. 5 shows the in absorption spectra of the polymer recorded at various applied potentials in [BMIM]BF₄. PMOT/NiO composite films were easily switched between the fully reduced (red) and fully oxidized (blue) states.





Figure 5 Spectroelectrochemistry of PMOT/NiO films at the following potentials: -0.4 and 0.6 V.

Switching times and optical contrast in PMOT/NiO films are determined with a change in transmittance at 660 nm where the maximum transmittance difference between redox states were observed in the visible region. For this aim, square wave potential step method was coupled with optical spectroscopy to investigate the switching ability of PMOT/NiO films between its neutral state and doped state (Fig. 6). The time required to attain 80% of the total transmittance difference was found to be 5.6 s.



Fig. 6 Optical and electrical current responses as a function of experimental time of the PMOT/NiO film under continuous double potential step measurement between -0.2 and 1.6 V.

Conclusions

In this paper, In this paper, the PMOT/NiO composite films were prepared by two consecutive electrochemical steps. At first the NiO film was grown by a potentiostatic method in nickel nitrate electrolytes, and then PMOT was deposited on the NiO film by a potentiodynamic polymerization method in 2M solutions of 3- methoxythiophene in [BMIM]PF₆. The PMOT/NiO composite films showed good electrochromic properties.

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Preparation of fly ash hollow glass bead /titanium dioxide composites by

chemical precipitation

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Keywords: fly ash glass hollow bead; titanyl sulfate; hydrolysis precipitation; composite particles; hydrolysis rate; activation

Abstract. To obtain a kind of composite particles material which has the property of both fly ash glass beads (FA) and titanium dioxide (TD), chemical hydrolysis precipitation method was adopted. Each process condition was investigated and the results were characterized by titanyl sulfate hydrolysis rate and the effect of FA coated TD. Composite structure and properties were characterized by means of X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and testing physical properties of FA/TD. The results show that the surface of FA has been coated with TD uniformly and compactly after titanyl sulfate hydrolysis and cladding content roasted. The optimal preparation conditions are hydrolysis cladding temperature 100°C, time 180min, matrix slurry concentration 0.5%, titanyl sulfate solution dosage 0.5g/g and titanyl sulfate solution drop way for the graded way. The hiding power and whiteness of the composite powder are respectively 35.47 g/m² and 54.43. The results also show that the composite powder has similar pigment performances with TD and it is much whiter than material.

Introduction

Fly ash is a kind of residue and byproduct to thermal power plant after pulverized coal combusted. Due to the large accumulation of fly ash, it has caused serious environment pollution. It has great practical significance to carry out comprehensive utilization of fly ash. FA, which presents spherical hollow structure observed by electron microscope is selected and separated from fly ash, and its weight accounts for 50% - 70% of the total fly ash ^[1]. The hollow bead has excellent performances, such as light body, non-toxic, high activity, small particle size, high compressive strength, wear resistance, good dispersion liquidity, low thermal conductivity, low price and so on. It has been widely used as functional additive in the fields of building materials, rubber, plastic, paint, chemical, marine, aerospace and other industries.

On one hand, the floating beads with the interface of the organic matrix may become the weak link of the composite owing to the smooth surface of FA and poor compatibility with the polymer; on the other hand, the whiteness of flash ash is low, only about 40%, which can not meet the requirements of the light-colored filler. TD, as a kind of white pigment, is thought to be the world's best pigment. Its property is stable, insoluble in water, alcohol, almost no reaction with the acid-base, but also has excellent weather resistance, opacity and gloss. The composite particles were prepared with FA as core and TD as shell, which can significantly improve the performance of fly ash, and achieve both functions. Lu Hongbin^[2] studied a kind of thermal insulation coating

technology about FA/TD, whose heat-reflective ratio up to 97.76%, with a significant effect of reflective insulation. Zhang Yun ^[3] studied the effect of fly ash activated to the coated beads and explored the coating process conditions. However, the studies above were not related to composite pigments function, and the study in preparation process and structural characterization was not detailed enough. In this paper, enhancement to the physical performance of fly ash glass beads and pigment performance of composite particles was our goal. FA/TD composite was prepared by chemical precipitation method, and the preparation process conditions, structure and properties of composite particles were also studied.

Experiment

Raw Materials and Reagents. FA(600 mesh) were provided by Shanghai Gerunya Nanometer Material Co., Ltd. TiOSO₄ solution, concentration of 152g/1000mL, was provided by Jiaozuo Chemical Plant. Sodium dodecyl benzene sulfonate (DBS) and ammonia, which were analytical grade, were both provided by Beijing Jingwen Huabo Commerce Center.

The chemical composition of FA depends on the chemical composition of raw coal and pulverized coal combustion degree. It is different greatly in chemical composition between different coal sources and different countries ^[4, 5]. The main chemical analysis results were listed in Table 1.

rable i the chemical analysis results of my ash glass beaus									
Composition	SiO ₂	Al_2O_3	K ₂ O	CaO	Fe ₂ O ₃	Na ₂ O	MgO	TiO ₂	Loss
Content/%	52.38	36.61	2.12	1.73	1.41	1.16	1.06	0.54	2.57

	Table 1	The Chemica	l analysis	results	of fly	ash	glass	bead	ds
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Chemical Precipitation Coating Process. Preparation of FA/TD composite particles by chemical precipitation included two parts. One was FA with alkali activated, and the other part was hydrolysis precipitation of titanyl sulfate and roast of hydrolyzate.

It had two purposes for FA to be activated: Firstly, to remove dirt on the surface of FA; Secondly, to make floating beads surface roughened by the use of micro dissolution of NaOH, thereby enhancing the binding force between beads and coatings ^[6]. Weigh a certain amount of activated FA, then place it in a three-necked flask with deionized water, and then add 1% of the total beads of SDBS as dispersant, stirring so that microspherical particles fully dispersed, and then heat it in water bath to the designed hydrolysis temperature. TiOSO₄ solution is then added in a manner. Start timing when thermostat hydrolysis begins, meanwhile the pH value is kept constant at about 2.5 with ammonia. Stop to stir when hydrolysis time reaches. Remove the three-necked flask and cool it for a period of time, then wash it until neutral with deionized water at about 70°C. After filtration, it is dried at 80°C until calcination treatment.

Evaluation Tools. The amount of TD generated in reaction of titanyl sulfate hydrolysis is measured by hydrolysis rate. The larger the hydrolysis rate is, the more TiO_2 is. The hydrolysis rate of titanium saline solution is defined as the ratio of TD-quality contained in calcined composite product and TD-quality contained in the added titanyl sulfate solution.

Hiding power refers to the ability of pigment coating into a homogeneous coating film so that the background color of the coated surface is no longer appeared. The test method of hiding power is in accordance with GB1709-79.

D/MAX 2000 X-ray powder diffractometer is used to analysis the crystalline phase of the powder, and field emission scanning electron microscope, model JSM-7001F is used to observe the morphology of raw materials and coating particles. The whiteness of samples are measured by WSB-3 type whiteness meter and the infrared spectra of powder is measured by SPECTRUM100 type infrared spectroscopy.

Results and discussion

Orthogonal experiments to the better experimental conditions. The process of FA coated with hydrolyzate of $TiOSO_4$ included two processes, one was hydrolysis of $TiOSO_4$ and the other was hydrolyzate adsorption of $TiO_2 \cdot nH_2O$ on FA surface. Therefore, it was necessary to do investigation and optimization by orthogonal experiment.

Orthogonal experiments were conducted with 5 factors and 4 levels of [L16 (45)] on conditions of TiOSO₄ dosage and other factors. The factors and levels (Correlational studies about TiOSO₄ separate hydrolysis were referred to ^[7-9]) and the results were listed in Table 2. The composite performance was characterized by titanyl sulfate hydrolysis rate and hiding power ^[10]. FA which were activated by alkali were as matrix core, and the hydrolysis coatings in various conditions needed roasted at 700°C, and then the roasted product needed to be tested.

In Table 2, K (1 (2), i, j) represented the average of $TiOSO_4$ hydrolysis rate (the hiding power of composite particle material) in column j factor corresponding to i level. The range indicated the maximum difference of average number which was corresponded to four levels of each factor. It reflected the impact degree of various factors on $TiOSO_4$ hydrolysis rate and hiding power of composite particles. The greater the range was, the more the hydrolysis rate of $TiOSO_4$ and hiding power of composite particle materials were affected.

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Project	TiOSO ₄ solution dosage (g/g using TiO ₂)	Temperature (℃)	Time (min)	Matrix slurry concentration (%)	Drop way	Hydrolysis rate (%)	Hiding power (g/m ²)
1	0.5	70	60	0.5	Added all at once	65.84	0
2	0.5	80	90	1.0	3 drops/s	76.1	60.82
3	0.5	90	120	1.5	1 drop/s	42	59.72
4	0.5	100	180	2.0	Added in graded way	64	0
5	1.0	70	90	1.5	Added in graded way	76.98	50.26
6	1.0	80	60	2.0	1 drop/s	45.19	62.3
7	1.0	90	180	0.5	3 drops/s	43.74	38.28
8	1.0	100	120	1.0	Added all at once	81.48	39.28
9	1.5	70	120	2.0	3 drops/s	72.16	41.35
10	1.5	80	180	1.5	Added all at once	48.13	46.26
11	1.5	90	60	1.0	Added in graded way	84.72	31.04
12	1.5	100	90	0.5	1 drop/s	69.53	32.42
13	2.0	70	180	1.0	1 drop/s	77.64	45.08
14	2.0	80	120	0.5	Added in graded way	76.54	31.47
15	2.0	90	90	2.0	Added all at once	70.38	52.06
16	2.0	100	60	1.5	3 drops/s	81.7	36.34

Table 2 Orthogonal experimental table of preparation of fly ash floating bead-TiO₂

K (1, 1, j)	61.985	73.155	69.362	63.913	66.457	
K (1, 2, j)	61.847	61.490	73.248	79.985	68.425	
K (1, 3, j)	68.635	60.210	68.045	62.203	58.590	
K (1, 4, j)	76.565	74.178	58.377	62.932	75.560	
Range	14.718	13.968	14.871	17.782	16.970	
K (2, 1, j)	30.135	34.172	32.420	25.543	34.400	
K (2, 2, j)	47.530	50.212	48.890	44.055	44.197	
K (2, 3, j)	37.767	45.275	42.955	48.145	49.880	
K (2, 4, j)	41.238	27.010	32.405	38.928	28.192	
Range	17.395	23.202	16.485	22.602	21.688	

As was shown in Table 2, it was different in range between hydrolysis rate and hiding power. Other factors for the evaluation of primary and secondary indicators were as follows. For hydrolysis rate, it was matrix slurry concentration> TiOSO₄ solution drop way> hydrolysis time> TiOSO₄ dosage> hydrolysis temperature, and for hiding power, it was hydrolysis temperature> matrix slurry concentration> TiOSO₄ dosage> hydrolysis temperature> matrix slurry concentration> TiOSO₄ dosage> hydrolysis temperature.

Pigment property of the final product was reflected in hiding power. Composite particle materials could not eventually put into use until the hiding power and other indicators data were good. So when the two indicators were affected quite by various factors and the hydrolysis rate was not low, the conditions of good hiding power data was optimum. Therefore, the hydrolysis temperature of 100°C was chosen. Other optimum factors were as follows: matrix slurry concentration 0.5%, titanyl sulfate solution drop way for the graded way, titanyl sulfate solution dosage 0.5g/g and hydrolysis temperature 100°C. The combination of conditions did not appear in the orthogonal table, so the results of new sample in these conditions were as follows: hydrolysis rate was 82.52%, hiding power was 30.47 g/m² and the whiteness was 54.43%. As a result of this set of data was better than all the data in orthogonal table, this combination of conditions was the optimal conditions for this test.

X-ray Diffraction Analysis. The XRD patterns of FA and hydrolysis coatings roasted and not roasted were shown in Fig. 1. As Fig. 1*A* was shown, most of the raw materials were glass phase, a small amount of crystalline phase was quartz and others were mullite diffraction peaks. As indicated in Fig. 1*B*, the majority of diffraction peak remained the coated substrate, and also presented a low and broad diffraction peak of anatase TiO₂. It was shown that TiO₂ • H₂O was a kind of poor crystalline anatase-type microcrystalline. As was shown in Fig.1*C*, the peak of the anatase type titanium dioxide were sharp and significant after roasted at 700°C, indicating that the matrix were basically covered by TiO₂.

Scanning Electron Microscope Analysis. Using SEM to observe the morphology of FA which were activated and not, coated and not. SEM images of the samples were shown in Fig.2. As Fig.2*a* showed, the shape of FA raw material was regular spherical and its surface was quite smooth. Also,





Fig.2. SEM images of samples: a. raw material of FA; b. unactivatied and coated of FA; c. activatied of FA; d. activatied and coated of FA

its ability of reflecting light was good. After activation treatment, the floating bead surface had become rough, which were a lot of small particles. It could be inferred that the fly ash surface was corrosion not in the form of pitting corrosion, but in the form of surface corrosion. Because of the interaction among FA, the thin layer had been rolled into a cylindrical surface attached to the floating bead to increase the roughness of the surface of beads. By comparing FA that were shown in Fig.2*a*~2*d*, most of titanium dioxide on surface of FA which were unactivatied and coated were lost, and only a small amount attached to the particle surface. It was also obvious that titanium dioxide were blocky stocked, and the coating was not uniform. However, the coatings of FA which were activated and coated were uniform and compact, which greatly increased the hiding power of the composite particles.



Fig.3 IR Spectrum of samples: A-the IR spectrogram of FA/T; B- the IR spectrogram of FA; C- the IR spectrogram of TiO₂

IR Spectrum Analysis. By comparing Fig. 3*A*, *B*, *C* curve, it was shown that complexes of FA/T kept the original vibration peak of TiO₂ at 2338cm⁻¹, but a new small peak appeared at 2268cm⁻¹. It could be inferred that the surrounding chemical environment of the original bond changed, which might due to the Si-O bond breaking or Al-O bond breaking that presented on the surface of fly ash floating beads. In addition, the vibration absorption at 1113cm⁻¹ was stronger than the fly ash glass beads and TiO₂. The reason might be the presence of Ti-O bond to strengthen the Si-O-Si bond, or forming a new chemical Si-O-Ti bond. Therefore, TiO₂ and FA were integrated closely.

Conclusions

(1) The surface of fly ash hollow glass bead turned rough when it was activated by alkali, and it was easier for titanium dioxide to be deposited on it. Also, it made cladding layer uniform, density and better hiding power performance.

(2) For the fly ash hollow glass beads which were activated, the optimal preparation conditions for: hydrolysis cladding temperature 100°C, time 180min, matrix slurry concentration 0.5%, titanyl sulfate solution dosage 0.5g/g and titanyl sulfate solution drop way for the graded way.

(3) As was shown in XRD analysis, the peak of the anatase type titanium dioxide were significant after roasted at 700°C, indicating that the matrix were basically covered by TiO₂. The pictures of SEM indicated that in the composite particle materials of FA/TD, TiO₂ has coated on the surface of fly ash floating beads with uniform and dense film. According to IR spectrum analysis, it has formed a new chemical Si-O-Ti bond on the surface of TiO₂ and FA by use of their hydroxies, respectively. Therefore, TiO₂ were integrated closely with fly ash glass beads.

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Preparation of Aluminum Composite Ceramic Membrane by Inorganic Precursor Sol-gel Method

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Abstract. Al_2O_3 - SiO_2 - ZrO_2 composite sol was prepared with aluminum nitrate, zirconium oxy-chloride, etc as precursors, by which Al_2O_3 - SiO_2 - ZrO_2 composite ceramic microfiltration membrane was achieved. Stable boehmite sol can be obtained by adding $Al(NO_3)_3$ into ammonia but not the reverse. The stability of the composite sol depends on the ratio of Si/Zr. The aperture of the composite membrane can be micron level. It has good effect on sewage treatment.

Introduction

As an important kind of structural and functional material, inorganic ceramic membrane draws more and more attention, and is well applied in water treatment. Composite membrane can separate the system which is difficult to be dealt with by conventional ceramic membrane, and it has been used for the separation of aqueous medium liquid, such as drinking water desalination, softening, wastewater treatment, etc. The surface morphology and surface modification characteristics of composite membrane are conducive to exploring application prospects in liquid separation, such as water treatment [1-3].

Since it is featured by simple process equipment, low cost, controllable chemical composition and acceptable applications in the preparation of highly pure and small-aperture ceramic membrane at relatively low temperatures, the sol-gel method is generally considered as one of the most effective methods to prepare composite ceramic membrane [4]. Depending on the difference of initial raw material, the sol-gel process can be divided into two ways: organic way and inorganic way [5]. The precursors are generally organic metal compound or inorganic salts. Due to the limitations and high-cost of Alkoxide, the sol-gel method with inorganic salt as a precursor has drawn more and more attention in recent years by virtue of its price advantage.

Experiment Process

Experimental Drugs

Reagents used in experiment are shown in table 1, all reagens are analytical reagents.

Reagent Name	Molecular Formula	Reagent Name	Molecular Formula
Aluminum Nitrate	Al(NO ₃) ₃ ·9H ₂ O	Anhydrous Ethanol	CH ₃ CH ₂ OH
Zirconium Oxychloride	ZrOCl ₂ ·8H ₂ O	Ammonia	$NH_3 \cdot H_2O$
Tetraethyl Orthosilicate	$(C_2H_5)_4SiO_4$	Nitric Acid	HNO ₃

Preparation of Alumina Sol with Inorganic Salt Precursor

With Al(NO₃)₃ as the raw material to provide alumina and ammonia as a catalyst, 1 mol / L aqueous ammonia is heated to 80°C to 90 °C in water bath, and then an appropriate amount of 1 mol/L of Al(NO₃)₃ is added to hydrolyze, and after a certain time of reaction add nitric acid to precipitate the peptization. Then clear AlOOH sol will be got after a period of aging.

The device for the preparation of aluminum sol is shown in Fig. 1.



Fig. 1, Experimental equipment of AlOOH sol

Preparation of SiO₂-ZrO₂ Sol

Dissolve $ZrOCl_2 \cdot 8H_2O$ into anhydrous ethanol, add TEOS of a certain percentage after magnetic heating and stirring dissolution, and then conduct water bath for certain time after stirring for a period of time, thus getting a kind of colorless transparent solution. In addition, a light blue transparent sol will be obtained after aging for a period of time.

Preparation of Inorganic Membrane and Structural Characterization

Add the prepared SiO_2 -Zr O_2 sol into the AlOOH sol, and stir for 2 to 3 hours to obtain the composite sol. Coat the composite sol on the surface of porous ceramic tube, and after drying and calcinations, an inorganic membrane will be obtained.

Observe the morphology of the membrane with a scanning electron microscope (SEM).

Results and Analysis

The Effect of Feeding Sequence on Al (NO₃)₃ Hydrolysis Reaction

With Al $(NO_3)_3$ as aluminum source, prepare AlOOH (boehmite) sol by peptization method. Use ammonia as the hydrolysis-promoting agent or precipitating agent to study the impact of different feeding sequence and manner on hydrolysis reaction.

According to the experiment, it can be found that the solution will have precipitate upon the ammonia when it is added into the $Al(NO_3)_3$ solution; the precipitate will quickly disappear after being stirred and the solution will become clear and transparent again. Until the amount of the added ammonia is twice of the volume of the $Al(NO_3)_3$ solution of the same concentration, the precipitation will not continue dissolving. It can be seen from the reaction in Eq.1.

$$Al(NO_3)_3 + 3NH_3 \cdot H_2O \to Al(OH)_3 \downarrow + 3NH_4NO_3.$$
⁽¹⁾

Since $Al(OH)_3$ is amphoteric, it will not continue undergoing hydrolysis and the above reaction will reverse when the solution is acidic; but when $Al(OH)_3$ is added into the aqueous ammonia, the reaction process at this time is conducted under alkaline conditions and $Al(OH)_3$ will undergo the following hydrolysis reaction in Eq.2 and produce stable AlOOH precipitation; this reaction is not reversible.

$$Al(OH)_3 \xrightarrow{alkali} AlOOH \downarrow +H_2O$$
. (2)

Therefore, only drop $Al(NO_3)_3$ into the ammonia can obtain stable boehmite precipitation, and prepare boehmite sol by further adding appropriate peptizer.

The Effect of Sol Ingredients on the Colloidal Stability

The stability of composite sol has an important effect on membrane-forming properties. Data on the gelling time of the three-components composite sols are arranged by two methods: fix Si/Zr ratio and use Al/Zr ratio-gelling time to make Fig. 2 (a); fix Al/Zr ratio and use Si/Zr ratio- gelling time to make Fig. 2 (b).



Fig. 2, Effect of composition on stability of the composite sol

As shown in Fig.2 (a), in the same Si/Zr, the gelling time of the system remains substantially unchanged, but the gelling time becomes shorter as Si/Zr increases; It can be also seen from Fig.2 (b) that all the gelling time of the system tends to decrease as Si/Zr increases when Al/Zr is fixed, and when Si/Zr is larger, the trend will slow down. Thus, it is thought that Si/Zr is a main factor to determine the stability of the system and Al/Zr plays a secondary role.

This is because step-by-step hydrolysis is adopted in the experimental process. The hydrolysis processes of separate $Al(NO_3)_3$ hydrolysis will not be affected; but the hydrolysis processes of zirconium and silicon have interaction on each other. In addition, the literature [6, 7] shows that pH=7 at the isoelectric point of AlOOH, pH=2 at the isoelectric point of SiO₂ and pH=4.9 at the isoelectric point of ZrO₂. In Si-Zr sol, pH=2, and the sol is uncharged at that time while zirconia sol is positively charged. Under the PH value (about 3.6) in the composite sol, the AlOOH particles and the zirconia sol have positive charge while the organic silica sol has a negative charge. The isoelectric point of ZrO₂ is closer to the pH value of the system than that of AlOOH, so it can reunify with the sol more easily. Thus, it can be concluded that the reunion among the respective components of the sol results in gelling and the stability of the sol depends on Si/Zr.

Preparation of Composite Membrane

Use Al₂O₃ ceramic tube as a coating carrier and conduct certain pretreatment. Prepare the composite membrane by repeated dipping-drying-firing method. The scanning electron micrograph of the base body and the three-time coating surface is shown in Fig. 3.

It can be seen from the SEM photograph that the surface of the prepared composite membrane is connected by flake particles, the pore distribution is very even and the number of pores in unit size is large, as shown in Fig. 3 (b), which can have a better filtration effect on water treatment, as shown in Table 2.

	Chroma	Turbidity (NTU)	Fluoride (mg/L)	Coliform (piece)
Before treatment	40	9	1.5	29
After treatment	13	2	0.9	1

Table 2, Several Indices of Water Before and After Filtration by Composite Membrane



(a) Supporter (b) Composite membrane Fig.3, Supporter and Composite membrane

Conclusion

With inorganic salt Al (NO₃)₃ as a precursor to prepare alumina sol, feeding sequence and manner affect the hydrolysis of Al (NO₃)₃ significantly. Only after adding Al(NO₃)₃ into NH₃•H₂O, undergoing hydrolysis under alkaline conditions and then adding peptizer, can AlOOH sol with clear appearance and stable performance be obtained. And further prepare Al₂O₃-SiO₂-ZrO₂ composite sol and the sol stability depends on the Si/Zr ratio.

With Al_2O_3 ceramic tube as the coating carrier, use the composite sol for several coating, and prepare Al_2O_3 -SiO₂-ZrO₂ composite ceramic membrane whose average pore size is in the micron level with even pore distribution. Composite membrane has a good filtering effect on sewage and can improve the water chroma, turbidity, fluoride and colliform counts to great extent.

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Tribological characteristics of different components on C/C-SiC composites fabricated by warm compacted in-situ reaction

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Keywords: C/C-SiC, tribology, carbon, brake materials.

Abstract. C/C-SiC brake composites, based on reinforcement of carbon fiber and dual matrix of carbon and silicon carbide, were fabricated by warm compacted-in situ reacted process. Rules about the influence of different components on the friction and wear characteristics of the C/C-SiC composites are ascertained. As hard particle, the SiC has the function to the formation of friction film, which is in favor of increasing the coefficient of friction (COF) and decreasing the wear rate. The resin carbon plays the role of enhancing the COF, but they are easy to be cut and increase the wear rate. The graphite plays the lubrication function, and right volume content of graphite is helpful to forming friction film to reduce the wear rate. The C/C-SiC composite fabricated by the warm compacted-in situ reaction can with best tribological performance when the components volume fraction of carbon fibre, SiC, graphite and resin carbon are 15.5%, 37.0%, 22.1% and 20.8%, respectively, which the COF and the wear rate can reach the maximum and the minimun value of 0.44 and 1.1 μ m/cycle respectively.

Introduction

C/C-SiC have been developed for their use as brake materials since the end of 20 century. It is reported that they are promising candidates for advanced brake system [1-3]. In comparison to grey cast iron or carbon/carbon, C/C–SiC brake composites exhibit high COF, extremely low wear rates, and high thermal shock resistance, especially strong environmental adaptability. Some countries, such as Germany, America, China and France have launched their theoretic and applied research gradually [1, 4-6]. For example, C/C-SiC brake composites fabricated by Central South University for engineering machine and high-speed train have succeed tested in laboratory, and the ceramic brake disk is mounted on a metallic mat and can resist a maximum application temperature of about 800°C.

Nowadays, the main preparation methods of C/C-SiC composites include: (1) a gas phase route, also refer to as chemical vapor infiltration (CVI), (2) a liquid phase route including the polymer impregnation/pyrolysis (PIP), and liquid silicon infiltration (LSI) also called (reactive) melt infiltration (RMI or MI) processes, as well as (3) a ceramic route, i.e. a technique combining the impregnation of the reinforcement with a slurry and a sintering step at high temperature and pressure, also refer to high pressure-sinter process (HP-Sinter). Each of the formed routes displays advantages and drawbacks. In order to promote the application of C/C-SiC brake composites, the authors invented warm compacted-in situ reacted process (WCISR) for the first time at home and abroad. In comparison to the former routes, the WCISR exhibit many advantages, such as simple technology, large range of raw material choice and low preparation cost. C/C-SiC brake composites fabricated by WCISR have succeeded applied on magnetic levitation vehicle, high-speed train, advanced car and so on.

The friction and wear of ceramic materials is a complicated topic and involves several variables. Since the components volume affect the mechanical properties of the composite, they certainly influence its tribological properties. Although some researchers investigated the friction and wear of C/C-SiC brake composites, most of their studies were performed with the composites fabricated by CVI and RMI. In this study, C/C-SiC brake composites fabricated with WCISR were tested against steel disk in order to investigate their wear mechanisms and the effect of different components on the friction and wear.

Experimental

Fabrication. The diameters and lengths of the T700 carbon fiber used in this study were 7 μ m and 3-10 mm, respectively, according to information supplied from the Toray Corp.of Japan. Matrix were originated from graphite powders (grain size 40-50 μ m), phenolic resin and Si powders (grain size 10-20 μ m) containing 99.3 mass% Si. Table 1 shows the compositions of samples used for this study. The content of SiC was obtained by supposed all the Si powders reacted with carbon, and the content of resin carbon was obtained by supposed all the phenolic resin was pyrolysed to resin carbon and the yield was about 60 wt%. WCISR was based on four steps[3]. The density of the resulting C/C–SiC was about 2.0g/cm³, and open porosity was about 10%.

Testing methods. Tribological behavior was studied by using a MM-1 000 friction testing machine with C/C-SiC composites as static plate and corresponding steel disk as moving plate. The sizes of test samples and corresponding steel disk were $\varphi 75 \times \varphi 53 \times 16$ mm. The experimental conditions were: the brake linear speed was 20m/s, the rotary inertia was 1kg·cm·s² and the brake pressure was 50N/cm². Each wear test was repeated three times and the average values of the measurements were expressed in the results.

The wear rate of the test samples were measured with the help of the micrometer. The open porosity and bulk density of samples were measured by Archimedes' method. The phase identification was performed by means of X-ray diffraction (XRD) (model Rigaku D/max 2550PC, Japan). The microstructure and fracture morphology were measured with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) (model JSM-6360LV, Japan) and three-dimensional digital video microscope (model KH-7700, Questar, America).

Results and discussion

Friction and wear properties. Fig.1 shows the values of the average friction and wear properties of the test samples. The samples of F1, F2 and F3 show different tribological performance depending on the carbon fiber volume. It can be seen that the COF increases at first but decreases at last with the increasing of the carbon fiber volume, while the wear rate has contrary current. In comparison to the S2, S1 and F2 samples, the COF enhancing slightly but the wear rate reducing sharply with increasing SiC volume. However, with the same volume fraction of carbon fiber and graphite, the COF of the samples of G2, R1 and R2 doesn't reduce as the resin carbon reduces but the SiC increases, which means the resin carbon has the function of enhancing COF. But the resin carbon has litter effect on the wear rate. Although the SiC volume fraction of the samples of G1 and G2 is the same, and the gross volume fraction of the graphite and the resin carbon is also basic homology, the COF and the wear rate of the two samples are different, which indicates although both graphite and resin carbon are carbon matrics, they have different function to the tribological characteristices of C/C-SiC brake composites for their different crystal structure.

It can be seen from the Table 1 as well that the highest COF (0.44) and the lowest wear rate 1.1 μ m/cycle are obtained for F2. However, the G1with the lowest SiC volume fraction while the highest graphite has the lowest COF (0.20), and its wear rate is the highest that reaches as high as 5.7 μ m/cycle.

SEM micrographs of the worn surface. Under the same brake condition, different samples has different worn surface appearances (as shown in Fig. 2). The sample of F2 with lowest graphite volume have formed complete friction film, and the F1 and F3 samples have similar worn surface micrographs. The S1 and S2 samples formed friction film as well, but a small mount of carbon fiber reveal in the worn surface. The friction film of G1 which has the highest graphite volume is uneven, and the worn debris accumulate together on the worn surface. Many plow furrow and much carbon fiber on the G2 worn surface. As the R1 and R3 samples, certain friction films on the R1, but the friction films are incomplete and there are flaking phenomenon in the middle of the worn surface, and the friction films of R2 are not continuous.

Influence of components. Some researchers have pointed out the fiber can not strengthen the matrix unless the space between each fiber is less than 0.8 mm. At the same time, the larger fiber volume is, the more uniform distribution in the matrix and the reinforced effect is, for brake composites the wear rate is more lower. However, when the fiber volume surpasses certain limit, the bonding strength between the fiber and the matrix will decrease, then the fiber will be easier to be stripped and drawn, which leads to the wear rate increasing. In this study, it is shown that when the carbon fibre content is 15.5% the C/C-SiC composite with best tribological performance.

The XRD results show that all the SiC in the samples are face-centered cubic β -SiC. β -SiC has high hardness, good wear-resisting, good corrosion-resisting and high heat conduction. The SiC exists in the C/C-SiC composites as hard particle, which has the function of increasing COF and fixing the worn debris during the brake process. The graphite and carbon fiber which have lower hardness and strength are tending to be cut to worn debris. Some parts of the worn debris accumulate in the worn surface, as the SEM micrographs of S1 worn surfaces shown in Fig. 3. These worn debris forms the friction film and play the role of lubrication, then the composites have better tribological performance.

The higher of the SiC volume is, the smaller interspace between hard particle is. Then the worn debris are easier to form friction film on the worn surface, so the tribological performance of S1 is better than the S2. However, it not means that the more SiC volume bring the better tribological characteristics. The former researches of the authors show the best SiC volume fraction of C/C-SiC brake composites is about 36%-38%.

In contrast of the COF change curves between the G1 and the G2 (as shown in the Fig.4). The curve of the G1 is steady and without obvious vibration. However, the curve of the G2 has great vibration correspondingly, and its average COF is higher than the G1's obviously. This indicates that the graphite, which with layer structure and is easy to slip, has the lubrication function and prevents vibrating during the brake process.

The graphite is added in the form of powers during the composites preparation process, and it felt the other components depends upon the Si-C reaction, so the felted strength is decided by the volume of SiC. The volume fraction of graphite in G1 is as high as 52.5% while SiC is only 10%. Although the graphite worn debris is easy to form friction film, they can not form complete friction film under the condition of the SiC volume is not enough. Then the felted intensity is low and the graphite is easy to fall off during brake, so the tribological performance of G2 is better than G1.

The resin carbon is amorphous carbon and its crystal structure is not complete [7]. Its degree of hardness and strength are higher than that of the graphite. The main function of resin carbon in C/C-SiC composites is integrating the other components during the composites preparation process and adjusting the COF.

In compare to the tribological properties and the worn surface SEM pictures of the samples G2, R1 and R2, there has not obvious changes of the COF when the SiC volume changes much, which indicates that the resin carbon has the function of increasing COF. But the G2 has the largest wear rate, while the R1 has the smallest. Under the condition of lower SiC volume fraction, the harder resin carbon grain enhances the friction force in the form of attrition, then the COF does not decrease obviously because of the reducing of SiC.

Summary and conclusions

(1) The COF and the wear rate of the C/C-SiC brake composites fabricated by the WCISR can arrive the maximizing value of 0.44 and the minimum value $1.1 \mu m/cycle$ respectively.

(2) The C/C-SiC composite with best tribological performance when the components volume fraction of carbon fibre, SiC, graphite and resin carbon are 15.5%, 37.0%, 22.1% and 20.8%, respectively.

(3) The SiC as hard particle has the function to the formation of friction film, which is in favor of increasing the COF and decreasing the wear rate. The resin carbon plays the role of integrating the other components and enhancing the COF, but they are easy to be cut and increase the wear rate. The graphite plays the lubrication function, and a right volume content of graphite is helpful to form friction film to reduce the wear rate.

Acknowledgements

Table 1 Formulation of C/C-SiC brake

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Specimens

Fig.2. SEM of worn surfaces of C/C-SiC for (a) sample F2, (b) sample S2, (c) sample G1, (d) sample R1 and (e) sample R2.



 $\frac{1}{100}$ Fig.4. Friction coefficient curves of C/C-SiC for (a) Sample G1, (b) of worn surfaces Sample G2. sample S1.

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Magnetoelectric effect of the Ba_{0.8}Sr_{0.2}TiO₃-CoFe₂O₄ ceramic composites by molten-salt synthesis method

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Keywords: Ba_{0.8}Sr_{0.2}TiO₃-CoFe₂O₄; molten-salt synthesis method; Magnetoelectric effect.

Abstract. This paper presents the structural, ferroelectric, ferromagnetic, resonance and magnetoelectric (ME) properties of multilayered ME composites fabricated using molten-salt synthesis method. The compositions corresponding to $CoFe_2O_4$ (CFO) with particle size of ~ 150 nm and $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) with particle size of ~ 100 nm were chosen as ferromagnetic and ferroelectric phases. The largest direct magnetoelectric (DME) and converse magnetoelectric (CME) coefficients of the multilayered ME composite were, respectively, 36 μ V/cm·Oe at a bias magnetic field of 2800 Oe and 1.16×10^{-3} G/V at a frequency of 30 kHz. In addition, the corresponding interfacial coupling coefficient was calculated to be 3.2×10^{-5} . For the multilayered ME composite, the resonance frequency of 4.97 MHz and bandwidth of 30 kHz were obtained using capacitance-frequency spectrum method.

Introduction

Magnetoelectric (ME) materials, due to their intrinsic ME effect, have been focused increasingly for their potential applications in inductors, sensors and filters [1-3]. The ME effect is defined as an electric polarization response to an applied external magnetic field, also called direct magnetoelectric (DME) effect, or an induced magnetization response to an applied external electric field, also called converse magnetoelectric (CME) effect [4,5]. In general, the effect is quantitatively characterized by ME coefficient [5]. The DME coefficient α_E and CME coefficient α_B could be described by the following expressions [5,6]: $\alpha_E = \delta E / (\delta H_{ac})$ and $\alpha_B = \delta B / (\delta V)$, where δE is the electric field, δH_{ac} is the amplitude of ac magnetic field, δV is the applied voltage, and δB is the magnetic induction. Up to date, the coefficients for various ME materials have been reported [7]. Among the ME materials, layered composites have become a central issue, since they possess stronger ME properties in comparison with the single-phase materials or particulate composites [3,4]. Most recently, the layered ME materials are mainly fabricated by epoxy-bonding method [8] and deposition method [2,6]. Alternatively, molten-salt synthesis technique has been used to obtain multilayered ME composites such as CoFe₂O₄ (CFO)/ BaTiO₃ (BTO) [1]. Of the multilayers, however, little literature has been published about the resonance frequency and CME property of the multilayered ME composite. In this paper, we chose BST and CFO as piezoelectric and ferromagnetic phases, respectively. Multilayered BST/CFO composite was fabricated using molten-salt synthesis method. The structural, ferroelectric, ferromagnetic, resonance, DME and CME properties of the composite were investigated in detail.

Experiment

The molten-salt synthesis process was employed as follows to prepare stoichiometric (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ -xCoFe₂O₄ (x=0, 0.1,0.2,0.3,0.4 and 1 respectively) powder. Thestarting materials were of reagent grade BaCO₃ (>99%), TiO₂ (>99.2%), Co₂O₃ (>99.5%) and Fe₃O₄ (>99.7%). In a typical synthesis (x = 0.4): Co₂O₃, Fe₃O₄, BaCO₃, SrCO₃, TiO₂, NaCl and NP-10 (nonylphenyl ether) were mixed in a stoichiometric molar ratio 10:20:12:3:15:15, ground for 20min, and then sonicated for 10 min. The mixture was transferred to a crucible, pretreated at 400°C for 2 h, and then loaded into

a furnace, where the temperaturewas maintained at 800 $^{\circ}$ C for 20 min, then cooled to room temperature in air. Pure Ba_{0.8}Sr_{0.2}TiO₃ and CoFe₂O₄ productswere obtained afterwashing the quenched material several times with deionized water to remove the NaCl salts.

The phase structures of the composites were characterized by X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V.). To study the morphology of the composites, Scanning Electron Microscope (SEM, Quanta 200) was used to observed the composites. Magnetic measurements were studied using a vibrating sample magnetometer (VSM, LakeShore 7404). Ferroelectric properties were carried out by using ferroelectric tester (PremierII, Radiant Technologies).

Results and analysis

Fig.1 shows the XRD patterns of the (1-x) $Ba_{0.8}Sr_{0.2}TiO_3$ -xCoFe₂O₄ ceramic composites with x=0, 0.1,0.2,0.3,0.4 and 1. It can be seen that pure CoFe₂O₄ ceramic has single-phase cubic spinel structure, pure $Ba_{0.8}Sr_{0.2}TiO_3$ ceramic has single-phase Tetragonal perovskite structure, and other composites with x=0.1,0.2,0.3,0.4 are respectively composed of tetragonal perovskite $Ba_{0.8}Sr_{0.2}TiO_3$ phase and cubic spinel CoFe₂O₄ phase ,without any intermediate phase or impurity phase .The intensity of BST peaks decreases with the decrease of BST concentration in the composites. The lattice constant for ferrite phase in composite with 20% ferrite concentration is a=8.366Å ,and the ones for ferroelectric phase are a=3.982Å and c =3.990Å (c/a=1.002).



Fig.1 XRD patterns of the (1-x) BST-xCFO ceramic composites.

The backscattered SEM micrographs of the (1-x) Ba_{0.8}Sr_{0.2}TiO₃-xCoFe₂O₄ ceramic composites with x=0.2,0.3 and 0.4 are shown in fig.2. It indicates all the composites show dense microstructure, less pores and no cracks, as well as BST phase and CFO phase grains coexist in the composites, which the BST phase appears as white area and CFO phase appears as black area. The dark area increases with increasing the CFO concentration. At x=0.2,the spinel CFO grains are comparatively well dispersed in the perovskite BST matrix . With x increasing to 0.3 and 0.4,the some isolated spinel CFO grains begin to aggregate .



Fig.2 Backscattered SEM micrographs of the (1-x)BST-xCFO ceramic composites with x=0.2(a), x=0.3 (b) and x=0.4 (c)

Fig.3 displays the leakage current density-electric field (*J-E*) behavior of the (1-x)BST-xCFO ceramic composites with x=0.1,0.2,0.3 and 0.4. With increasing the CFO concentration, the leakage current densities of composites increase. At an applied electric field of 10kv/cm, the leakage current densities of composites with x=0.1,0.2,0.3 and 0.4 are 4.4×10^{-5} A/cm², 1.0×10^{-4} A/cm², 1.7×10^{-4} A/cm², and 2.6×10^{-4} A/cm², respectively. Due to the comparatively low resistivity of CFO phase, as the concentration of CFO phase in the composites increases , the aggregation of CFO phase, which is demonstrated in the above SEM micrographs, leads to the decrease of composites resistivity.

The polarization-electric field (*P*-*E*) hysteresis loop of the composite measured at room temperature is shown in Fig.4. The loop demonstrates typical ferroelectric characteristic for the ME composite, in which the coercive field (E_c) of 4.2 kV/cm is obtained. The remnant polarization (P_r) of the loop is 1.0 μ C/cm², which is equal to that of the CFO/BTO core-shell composite synthesized by a sol-gel technique, but smaller than that of bulk BTO [9]. It should be noted that the loop is not saturated, which could be attributed to the influence of space charge [9] and/or the leaky characteristic [2].



corresponding induced voltage is $30 \,\mu V$.



Fig.3 The leakage current density-electric fieldFig.4 The ferromagnetic hysteresis loops(J-E) behavior of the (1-x) BST-XCFO ceramicof the (1-x)BST-xCFO ceramic compositescomposites.at room temperature.



Fig.5 The ferroelectric hysteresis loops of the (1-x)BST-xCFO ceramic composites with x=0, 0.1, 0.2 ,0.3 and 0.4 [(a) x=0 ;(b) x=0.1 ; (c) x=0.2 ; (d) x=0.3 and (e)x=0.4].

The variation of magnetization as a function of magnetic field at room temperature is shown in fig.5 for the $(1-x)Ba_{0.8}Sr_{0.2}TiO_3-xCoFe_2O_4$ ceramic composites with x=0.1, 0.2, 0.3, 0.4 and 1 at the maximum applied magnetic field of 15kOe. The hysteresis loops show all the composites display ferromagnetic characteristics. The saturation magnetization (M_s) values of the composites with x=0.1,0.2,0.3,0.4 and 1 are 7.02, 18.54, 32.14, 43.53 and 113.17 emu/g,respectively. The remnant magnetization (M_r) values of the composites with x=0.1, 0.2, 0.3, 0.4 and 1 are 1.62, 4.14, 7.82, 10.68 and 10.53 emu/g, respectively. The M_s value of the composites shows in fig.6. It displays the ferromagnetic properties of composites are diluted with increasing ferroelectric phase concentration. The coercive field (H_c) values of the composites with x=0.1,0.2,0.3,0.4 and 1 are 279.18, 320.97, 400.59, 481.55 and 256.17 Oe, respectively. The H_c values of composites are all larger than that of pure CoFe₂O₄ bulk ceramic. One is the change in the total magnetocrystalline anisotropy energy related to the ME coupling due to the compressive stress in the CFO phase caused by the lattice mismatch between the CFO and BST phases. The other is that the CFO particle size and particle distribution in composites compared to that of pure CFO bulk can affect the coercive field [10]. Fig. 6 shows the DME coefficient α_E for the BST/CFO composite. It is noteworthy that α_E shows a strong dependence on bias magnetic field H_{dc} varying from 27 to 7200 Oe. In the range of 27 to 400 Oe, α_E decreases with the increasing bias magnetic field. For $H_{dc} > 400$ Oe, α_E first increases to a peak value under bias field of 2800Oe, then decreases with the increasing bias magnetic field. Evidently the shape of α_E curve is similar to that of piezomagnetic coefficient of the BST/CFO substrates as reported previously, since the H_{dc} dependence of ME coefficient α_E tracks the H_{dc} dependence of the piezomagnetic coefficient. Furthermore, the maximal α_E (Fig. 6) is 36 μ V/cm·Oe, and its

The frequency dependence of CME coefficient α_B was measured as shown in Fig. 7. The frequency is in the range of 30 to 200 kHz because of the limitation of the instruments. The figure shows that, in general, α_B decreases with increasing frequency, thus it is expected that α_B will be enhanced if the



magnetic field H_{dc} for the multilayered BST/ CFO composite.



frequency is less than 30 kHz. The maximal value of α_B here, 1.16×10^{-3} G/V at 30 kHz, is about two orders of magnitude bigger than that of the BST /CFO core-shell composite [11]. This could be attributed to the percolation and imperfect polarization in the core-shell structure [11]. Furthermore, the largest α_B for the multilayered BST /CFO composite is comparable to that for the three-phase composite prepared by bonding piezoceramic, metal cap and magnet [10]. Additionally, the phasic difference of the multilayered composite is larger than that of BTO /CFO composite [11].

Conclusions

We have successfully fabricated multilayered BST /CFO composites by using molten-salt synthesis method. XRD pattern shows that no impurity other than BST and CFO phases exists. The SEM images illustrate that the BST and CFO layers are alternately arranged but with delamination at the interface. The coexistence of ferroelectric and ferromagnetic properties indicates that the multilayered composite is magnetoelectric. The DME, CME and interfacial coupling coefficients are found to be $36 \,\mu\text{V/cm}$ ·Oe under the bias magnetic field of 2800 Oe, 1.16×10^{-3} G/V at a frequency of 30 kHz and 3.2×10^{-5} . Consequently, it is concluded that the ME effect will be enhanced if the interfacial property is optimized. Besides, the electromechanical resonance frequency of the multilayered composite is measured to be 4.97 MHz, which may provide the possibility of designing high frequency ME devices.

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An experimental investigation of the dynamic mechanical behaviors of hollow spheres filled syntactic foam

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Keywords: Syntactic foam; Dynamic behavior; Strain rate sensitivity; compressive properties; Tensile properties; Split Hopkinson bar;

Abstract: Dynamic mechanical behaviors are critical to the engineering applications of hollow spheres filled syntactic foams. The potential of such composites cannot be fully realized unless the effects of strain rate on their mechanical properties are fully understood. In this study, both the compressive and the tensile behaviors of an epoxy syntactic foam filled by ceramic microspheres were experimentally investigated over the strain rate range from 0.001 to 2000 s⁻¹. The compressive and tensile tests at high strain rates were carried out by means of split Hopkinson pressure bar (SHPB) and split Hopkinson tensile bar (SHTB), respectively. The stress-strain responses and failure mechanisms were examined quantitatively and qualitatively. The experimental results indicate that both the compressive and the tensile behaviors of syntactic foam are highly sensitive to strain rate. Moreover, a comparison of the stress-strain curves suggests that the compressive and tensile behaviors are dominated by different failure mechanisms, which consequently lead to distinct effects of strain rate on the compressive and tensile behaviors of syntactic foam.

Introduction

Syntactic foams are manufactured by filling a polymeric matrix with hollow spheres called microspheres or microspheres. In general, epoxy resins, polyesters, silicones, polyurethanes, and several other polymers are used as binders, while the fillers have been made of glass, carbon, ceramics, polymers, and even metals. Compared with standard foams (containing blown gas bubbles only), syntactic foams are preferred when high specific mechanical properties are required, rather than just low density [1]. As a class of advanced lightweight composites, syntactic foams have been widely employed in more and more engineering applications, e.g., marine equipments for deep sea operations [2], core materials of sandwiches [3, 4], structural components in aerospace industry [5].

Such wide applications of syntactic foams call for the determination and understanding of their mechanical properties. Large numbers of experimental studies on the mechanical properties of syntactic foams have been reported [6-10]. These reports characterize the tensile, compressive, flexural properties, and the associated failure features, and extensively explore the property-structure relations, which provide a fundamental understanding of the dependence of the bulk properties on the intrinsic properties of constituent phases, e.g., matrix properties [11], size and wall thickness of microspheres [12, 13], and interface strength [14], and volume fraction of filler phase [15]. However, most of the aforementioned research activities are focused on the quasi-static conditions, e.g., at a strain rate of 0.001 s⁻¹. The investigations on the dynamic properties of syntactic foams, especially dynamic tensile properties, are limited, even though these foams are frequently used in many applications at high loading rates.

The aim of the present work is to experimentally measure and characterize the strain rate effects on the mechanical properties of an epoxy-ceramic microspheres syntactic foam including compressive and tensile properties. Dynamic compressive and tensile tests of the prepared syntactic foam have been carried out by means of split-Hopkinson pressure bar (SHPB) and split-Hopkinson tensile bar (SHTB), respectively. Quasi-static experiments were also performed to study the foam behaviors over a wider strain rate range from 0.001 to 2000 s⁻¹.

Experimental Procedure

Material and Specimen. Epoxy resin E51 hardened by DDM and PA651 was used as matrix material. Resin and hardeners were mixed with the ratio 100: 25: 7 (E51: DDM: PA651) by weight. Hollow ceramic microspheres with commercial grade SLG supplied by Envirospheres Pty Ltd were selected as fillers. The micrograph of these microspheres is shown in Fig. 1 and the physical properties are presented in Table 1. Syntactic foam containing microspheres with volume fraction $V_f = 20\%$ was fabricated for the experimental tests in this study.



Fig. 1. Micrograph of the ceramic microspheres.

Technical Specifications	Value
Particle Size Range [µm]	20-300
Mean diameter [µm]	130
Average shell thickness [µm]	13
Relative density [gcm ⁻³]	0.6-0.8

Table 1 Physical properties of the ceramic microspheres.

Dumbbell shape specimen recommended by ASTM D1708 standard as shown in Fig. 2(a) was used for measuring the tensile properties. For compressive test, cylindrical specimen with the thickness-diameter ratio L/D=1 as shown in Fig. 2(b) was adopted. Epoxy resin with microspheres was injected into the molder of the same shape as the test specimen. Rough samples were firstly prepared by this molding procedure, and then machined to eliminate the skin effect, ensuring that all surfaces of the test specimens were free of large visible flaws and imperfections.



Fig. 2. Shape and dimensions of test specimens (mm): (a) tensile specimen; (b) compressive specimen.

Experimental Test Setup. Quasi-static uniaxial tensile and compressive experiments were performed on a SUNS universal testing machine at room temperature. Longitudinal strain was measured by EIR LE-05 laser extensometer whose measurement resolution is up to 0.001 mm;

therefore it has sufficient accuracy to measure the tiny deformation of syntactic foam in the stretching process. By adjusting the crosshead speed, the tensile and compressive specimens were loaded at strain rate of 0.001 s^{-1} .

The split Hopkinson bar (SHB) system was employed to investigate the dynamic behaviors of the syntactic foam at high strain rates. The split Hopkinson bar (SHB) system including split Hopkinson pressure bar (SHPB) and split Hopkinson tensile bar (SHTB) was originally developed by Kolsky [16]. As an efficient device for characterizing dynamic material behavior, it has been widely used to obtain stress-strain curves for engineering materials at high strain rates between 10^2-10^4 s⁻¹ compared to the quasi-static test, where the strain rate is maintained in the range of $10^{-3}-10^{-1}$ s⁻¹. A schematic of the SHB system is shown in Fig. 3.



Fig. 3. The schematic diagram of the SHB apparatus: (a) SHPB; (b) SHTB.

The specimen is placed between two long slender bars, called incident and transmission bar. A striker bar is launched at high speed using a gas gun to impact with the incident bar and generate an elastic wave, which travels along the bar length and interacts with the specimen. The incident wave undergoes reflection and transmission at the incident bar-specimen and specimen-transmitter bar interfaces depending on the relative impedance of the bar and specimen materials. Strain gages, one each at the centre of the incident and the transmitter bars, are placed to record the strain response as the wave propagates. An oscilloscope records the two strain gage signals obtained through a strain gage conditioner and transfers data to the computer for analysis. According to Hopkinson's original one-dimensional stress wave theory and the signals of the strain gages that were recorded, the stress, the strain, and the strain rate with respect to time (t) can be calculated as follows:

$$\sigma(t) = \frac{A_0}{A_s} E_0 \varepsilon_t(t) \tag{1}$$

$$\varepsilon(t) = -\frac{2C_0}{L_s} \int_0^t \varepsilon_r(t) dt$$
⁽²⁾

$$\dot{\varepsilon}(t) = -\frac{2C_0}{L_s} \varepsilon_r(t) \tag{3}$$

where A_0 and A_s are the cross-section area of the bar and the specimen, respectively; and E_0 is the Young's modulus of the bar material. C_0 is elastic wave speed in the bar material. L_s is the length of specimen; $\varepsilon_r(t)$ and $\varepsilon_t(t)$ correspond to the time dependent strain signal of the reflected and transmitted wave, respectively. Eq. 1 and Eq. 2 can be used to develop stress-strain graphs, from which the dynamic mechanical properties of the tested material, e.g., elastic modulus, strength, can be determined.

Regarding the dynamic tensile test of brittle materials, a common solution for clamping of the specimen has not been reported. In this study, according to the SHTB apparatus, the joints of the tensile specimen were proposed as shown in Fig. 4(a). The joints were first threaded connected to the incident and transmission bars of the SHTB. The tensile specimen was then adhesively bonded to the joints using Cyanoacrylate 7144. After curing for 4 hours at room temperature, the dynamic tensile test would be conducted. To validate the results obtained from the SHTB signals, a sample specimen was fitted with a strain gage and tested as shown in Fig. 4(b).



Fig. 4. Additional devices for dynamic tensile test: (a) joints; (b) strain gage on specimen for calibration.

Fig. 5 shows a comparison of the strain results calculated from the bar signals by Eq. 2 and directly read from the strain gage, corresponding to a tensile test at strain rate of 1000 s^{-1} . It can be observed that the strain results from both measurements are close to each other, indicating that the joints and adhesive bonding method utilized in this study have a minimal effect on the strain readings.



Fig. 5. Comparison of strains calculated from bar signals and directly read from the strain gage.

Results and Discussion

Following the experimental procedure described above, the quasi-static tests were performed at strain rate of 0.001 s^{-1} , the dynamic tests were performed at three levels of strain rate: 200 s^{-1} , 1000 s^{-1} , 2000 s^{-1} . At least five specimens were tested at each strain rate level to account for variations in specimen density and microstructure. The resultant compressive and tensile stress-strain curves are shown in Fig. 6. For dynamic tests, the strain rate of each test cannot keep constant, but fluctuate around the target level. Thus, the stress-strain curves presented in Fig. 6 are averages of the five valid data at each strain rate. A comparison of the stress-strain curves in Fig. 6 yields the following observations.

The stress-strain curves in Fig. 6 indicate that the failure mechanisms of syntactic foam under compressive loading and tensile loading are different. As shown in Fig. 6(a), the compressive stress-strain curve of syntactic foam can be divided into two distinct regions: an elastic region followed by a plateau region. The elastic region showing linear trend corresponds to the elastic behavior of the foam. At the end of the elastic region, the microspheres get fractured and the hollow space exposed by the fracture of microspheres is consumed by the materials while getting further compressed. The plateau region thus corresponds to the energy absorption in the process of crushing of microspheres. From the tensile stress-strain curves in Fig. 6(b), a sudden load drop instead of a plateau region is observed when the failure strength is reached, indicating that the failure mechanism of syntactic foam under tensile loading is dominated by brittle fracture.



Fig. 6. Stress-strain responses of syntactic foam at different strain rates: (a) under compressive loading; (b) under tensile loading.

The experimental results as shown in Fig. 6 indicate that both the compressive and the tensile behaviors of syntactic foam are highly sensitive to strain rate over the range covered in this study. Notably, the strain rate effects on the mechanical behaviors of syntactic foam under compressive loading and tensile loading are also different. Taking the data points in the elastic region of the stress-strain curves for linear fitting, the slope of the fitting line is obtained as the modulus of elasticity. The compressive modulus of syntactic foam gradually increases as the strain rate increases. In contrast, an increase in the strain rate results in a decrease in the tensile modulus. At the strain rate of 2000 s⁻¹, increase in the compressive modulus and reduction in the tensile modulus relative to the quasi-static condition (0.001s⁻¹) are approximately 87.1% (from 2.02 to 3.78 GPa) and 47.5% (from 2.55 to 1.34 GPa), respectively. Furthermore, the compressive strength of syntactic foam monotonically increases from 73.5 to 128.8 MPa when the strain rate is increased from 0.001 to 2000 s^{-1} as shown in Fig. 6(a). For the tensile strength, the rate dependence over the strain range covered in this study is more complicated. It is noted, from Fig. 6(b), that the tensile strength increases from 26.8 to 40.2 MPa, corresponding to the strain rate increasing from 0.001 to 1000 s^{-1} . However, this trend of increasing tensile strength reverses thereafter. The tensile strength drops from 40.2 to 35.8 MPa as the strain rate is further increased from 1000 to 2000 s⁻¹. To give more details about the variation of the strength of syntactic foam with strain rate, the tested data at each level of strain rate are taken for linear fitting. Linear fits for the compressive strength in Fig. 7(a) yield:

$$\sigma_{c}(\text{MPa}) = \begin{cases} 73.72 + 0.1588\dot{\varepsilon} & 0.001 \le \dot{\varepsilon} \le 240 \text{ s}^{-1} \\ 109.48 + 0.0097\dot{\varepsilon} & 240 \le \dot{\varepsilon} \le 2103 \text{ s}^{-1} \end{cases}$$
(4)

Linear fits for the tensile strength in Fig. 7(b) yield:

$$\sigma_{t}(\text{MPa}) = \begin{cases} 27.41 + 0.0148\dot{\varepsilon} & 0.001 \le \dot{\varepsilon} \le 1004 \text{ s}^{-1} \\ 47.79 - 0.0055\dot{\varepsilon} & 1004 \le \dot{\varepsilon} \le 2082 \text{ s}^{-1} \end{cases}$$
(5)



Fig. 7. Variation of the syntactic foam strength with strain rate: (a) compressive strength; (b) tensile strength.

The strain rate-dependent mechanical behaviors of syntactic foam may be attributed to two reasons. On one hand, mechanical properties of the matrix material are critical to the bulk properties of syntactic foam. Consequently, the rate dependency of the foam is significantly determined by the rate sensitivity of the matrix material. Viscoelasticity of the epoxy resin is likely to cause the strain rate dependency of the matrix and therefore of the foam. On the other hand, the distinct effects of strain rate on the compressive and tensile behaviors of syntactic foam can be attributed to the different failure mechanisms. Under compressive loading, as reported by Li et al. [17], the micro-crack propagates through microspheres at dynamic loading rates instead of bypassing or debonding them as happens in quasi-static deformation. Such a rate dependent damage mechanism will result in a stronger failure resistance (peak stress) and better energy dissipation capacity (plateau stress) of the foam at high strain rates. Under tensile loading, the syntactic foam behaves in a brittle manner. This brittle fracture mechanism heavily depends on the properties of the interface between microspheres and epoxy resin, which determines the load transfer between the components. Thus, different interface properties, e.g., stiffness, strength, and damage evolution, at different strain rates are considered to contribute to the strain rate-dependent tensile behavior of syntactic foam.

Conclusions

In this work, both quasi-static and dynamic mechanical responses of an epoxy syntactic foam filled by ceramic microspheres were experimentally investigated over the strain rate range from 0.001 to 2000 s^{-1} . The resultant stress-strain curves at various strain rates indicate that both the compressive and the tensile mechanical behaviors of syntactic foam are highly strain-rate sensitive. A comparison of the stress-strain curves suggests different failure mechanisms of syntactic foam under compressive and tensile loading, which consequently lead to the distinct effects of strain rate on the compressive and tensile behaviors of syntactic foam.

Under compressive loading, the syntactic foam undergoes strain-rate hardening over the range covered in this study. Both compressive modulus and compressive strength monotonically increase as the strain rate increases. Under tensile loading, an increase in the strain rate results in a decrease in the tensile modulus. The trend in rate sensitivity of tensile strength experiences a transition when the strain rate rises up to a critical level of approximately 1000 s^{-1} . The syntactic foam undergoes strain-rate hardening when the strain rates are below this level, but softened beyond this level. These experimental findings provide a fundamental understanding of the dynamic mechanical behaviors of syntactic foam, which could be helpful for the design and engineering applications of this foam at high strain rates.

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Experimental Research on failure of filament wound composite pipe

under axial tension

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Key words: filament wound, composite, winding pattern

Abstract: Experimental investigations were performed on strain characteristic of filament wound composite pipes. Pipes were wound with S-1 glass fiber and epoxy resin, and then subjected to axial tension. Three kind of winding pattern were adopted. The displacement-Load data were recorded. The process of failure was analyzed and functional failure was defined. Based on experimental result of three kind of winding pattern, the effect of winding pattern on axial limited load was presented. There is apparently influence on pipes axial limited load caused by winding pattern.

Introduction

For their high strength-to-weight ratio and good corrosion resistance, filament wound composites are becoming an important class of engineering materials for a wide range application in aerospace industry, chemical plant and nuclear industries.

For particularity of winding process, the product of filament wound composite often is revolution, pipes or tanks for example. It is important that failure of filament wound composite pipes under different loading conditions, such as axial tension, internal pressure and torque. Mechanical behavior, damage and failure of $\pm 55^{\circ}$ filament wound composite was investigated in Jian Bobai[1]. Carroll[2] performed mechanical tests on filament wound composite cylinders under different loading type and loading rate. Relation between failure and loading rate of filament wound composite was figured out. Effect of winding angle on failure was presented in Mertiny and F. Ellyin[3] and biaxial monotonic behaviors of a multidirectional glass fiber epoxy pipes were shown in Martens M, Ellyin F[4]

There are several winding techniques and the wet helical winding is utilized frequently. When the winding process completes, the surface of mandrel is covered by diamond shaped repeated unit cell (RUC) as shown in Fig. 1.



Fig.1 Diamond shaped repeated unit cell

Fiber arrangement in filament wound composite wound can be called winding pattern and it is determined by winding parameters. If the winding parameters were changed, different winding pattern could be obtained

In this paper, axial tension test would be performed. The specimens of different winding patterns were prepared. Displacement-load behavior was recorded and analyzed. The influence of winding pattern on failure and limited load was investigated.

Material and Experiment

The cylindrical specimens are wound with S-1 glass fiber and epoxy resin, manufactured by wet helical winding technology. Winding angle, the angle between direction of fiber band and axis of cylinder, is 45° and winding layers are 7. Inner diameter is 30mm and length of specimen is 300mm. Tabs of glass fiber/epoxy composite are placed at each end of cylinders. Some Specimens for test are shown in Fig.2.



(a)Some specimens prepared for test (b) Geometrical of specimens Fig.2 Cylindrical specimen of filament wound composite for axial tension

Three kinds of winding patterns were adopted. In the first situation, there was only one repeated unit along hoop direction and three units for the second and five units for the third one.

Outer diameters of cylinder are measured at three different positions (dash line in Fig.2) before test. All tests were performed in WDW-2000 mechanics test machine; loading rate was 1mm/min. Two short steel round sticks were inserted into cylinder at each end for preventing crash by hydraulic grips.

Experimental result and discussion

The experimental results are given in Table.1, Table.2 and Table.3. In Table.1, Table.2 and Table.3, 'Max Load' is max load sustained by specimens during the test. 'Strength' is max engineering axial stress calculated with 'Max Load', inner diameter and outer diameter of specimens. 'Average' is arithmetic average value of 'Strength'. 'Cv' is coefficient of variance. The dash '--' means invalid result.

Index	Max Load (KN)	Strength (Mpa)	Averag (Mpa)	Cv(%)
01	43.08	208.8		
02	46.23	216.4	2011	- -
03	39.16	189.8	206.6	6.5
04	43.18	209.3		

Table 1 Axial Strength of winding pattern I

Index	Max Load (KN)	Strength (Mpa)	Average (Mpa)	Cv(%)			
01	44. 0	216.4					
02	40.434	196.6					
03			199.05	6.5			
04	40.149	196.6					
05	39.537	191.6					

Table 2 Axial Strength of winding pattern II

Table 3 Axial Strength of winding pattern III

Index	Max Load (KN)	Strength (Mpa)	Average (Mpa)	Cv(%)
01	16.121			
02	16.981			
03	36.255	176.7	176.83	0.7
04	36.326	176.1		
05	36.874	178.7		

As shown in Table.1, Table.2 and Table.3, limit axial load decrease from first winding pattern to third. For the winding pattern I, limit axial load is 206.6Mpa and 176.83Mpa for winding pattern III. Axial strength descends 14.4% from winding pattern I to winding pattern III. These results prove that winding pattern has significant effect on strength of filament wound composite pipe.

The influence of winding pattern is resulted from fiber arrangement in filament wound composite. During the process of winding, fiber band cross each other and make up diamond figure like Fig.1. As introduced in section "Material and Experiment, number of repeat unit in winding

pattern III is less than that in winding pattern I. It means more fiber crossing point exiting in winding patter III and more possibility of damage under loading. Because of more possibility of damage caused by more repeat units, strengths of filament wound composites reduce.

Conclusion

The effect of winding pattern on strength of filament wound composite pipes was investigated in this paper with axial tension experiments. The experimental results showed that winding pattern has obvious influence on characteristic of strength of filament wound composite pipes. More repeat unit concluded in pipes less strength they have. Such decreasing of strength of filament wound composites pipes caused by winding pattern should be considered in structure design and analysis.

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Influence of Si₃N₄ Addition on the Mechanical Properties and Microstructure of Unfired A1₂O₃-C Slide Plate

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Keywords: A1₂O₃-C, slide plate, Sialon, Microstructure

Abstract. The effects of Si_3N_4 addition on the room temperature physical properties and hot modulus of rupture(HMOR) of unfired $A1_2O_3$ -C slide plate were investigated by using tabular corundum and reactive alumina as starting materials, aluminium powder and silicon powder as antioxidation agents, phenolic resin as binder. The phase composition and microstructure was characterized by X-Ray diffraction (XRD), scanning electron microscope (SEM), and EDAX. The results showed that with addition of Si_3N_4 , the compactness of $A1_2O_3$ -C slide plate decreased, the room temperature strength deduced. Due to formed cylindrical sialon as a binder phase, the hot modulus of rupture increased.

Introduction

In recent years, with the increase in ladle capacity and the change of steel type, traditional unfired $A1_2O_3$ -C slide exhibits poor performance during casting, such as low hot strength, poor thermal shock property, poor oxidation resistance and short service life, which limit its application. In order to improve the performance and service life of unfired slide plate, the effects of zirconia-corundum, Mg-Al alloy and other additives on the performance and microstructure were investigated by drawing lessons from references[1-4]. In this work, the influences of Si₃N₄ on unfired bricks were discussed.

Experimental

The main starting materials were tabular corundum of various particle size and reactive alumina. The chemical composition was tabulated in table 1. Other starting materials were -196 graphite flake, aluminium powder (particle size: <74µm; chemical composition: Al: 98.44%; Al₂O₃: 1.08%); silicon powder (particle size: <74µm, chemical composition: Si: 97.24%; Fe₂O₃: 0.47%; SiO₂: 1.28%; CaO: 0.56%); β -Si₃N₄(particle size: <36µm; chemical composition: Si \geq 55.0%; N \geq 35.0%; Fe \leq 3.0%; O \leq 3.0%; bulk density \geq 3.2g/cm³; main mineral: \geq 90% β -Si₃N₄).

	Tuble I Cheim	eur compositio	ii oi tiie iiiaii se	arting materials	
	Al_2O_3	SiO_2	Fe ₂ O ₃	Na ₂ O	CaO
Tabular corundum	99.7	0.02	0.13	0.14	0.05
Reactive alumina	99.8	0.03	0.02	0.08	0.02

 Table 1
 Chemical composition of the main starting materials

The starting materials were weighed according to the predetermined formulation in table 2, drymixed, and then intimately wet-mixed with addition of 4% phenolic resin. The mixtures were first formed into cylindrical specimens of $25mm \times 25mm \times 25mm$ and specimens of $\varphi 36mm \times 40mm$. The shaped samples were cured at 200° C for 12h. The cold strength was tested according to relevant national standard. The thickness of oxidation layer was measured. The hot modulus of rupture was determined at 1400°C for 0.5h. SEM was conducted to observe the microstructure of the fracture surface of the samples. XRD was conducted to analyze the phase.

	Table 2	2 The composition of the samples (wt. %)					
Sample code	0#	1#	2#	3#	4#		
Tabular corundum	86	81.5	81.5	81.5	80.5		
Reactive alumina	4	4	4	4	4		
Silicon powder	1.5	1.5	1.5	1.5	1.5		
Aluminium	7	7	7	7	7		
Graphite flake	1.5	1.0	0.5	0.0	0.0		
β -Si ₃ N ₄	0.0	5.0	5.5	6.0	7.0		

Results and Discussion

The effect of Si_3N_4 addition on room temperature physical properties. Table 3 shows the physical properties of the samples at room temperature. With the increase of Si_3N_4 additions, the bulk density of the samples decreases, apparent porosity increases, and cold strength decreases. The cold strength of unfired $A1_2O_3$ -C slide plate was determined by the amount of phenolic resin and particle size distribution. The bulk density of Si_3N_4 is far less than that of tabular corundum. Hence, when corundum fines were substituted with Si_3N_4 fines, the bulk density of sample decreased, apparent porosity increased and strength increased.

 Table 3
 Room temperature physical properties of the samples

	1	1 2 1	1	1	
Sample code	0#	1#	2#	3#	4#
Cold crushing strength/MPa	151.2	117.0	114.2	110.6	100.7
Cold modulus of rupture/MPa	19.5	18.5	18.0	17.8	17.0
Bulk density /g/cm ³	3.09	3.02	3.00	2.99	2.96
Apparent porosity/%	5.3	8.46	8.63	9.88	10.33

The effect of Si_3N_4 addition on the hot modulus of rupture and microstructure. Table 4 shows the hot modulus of rupture of the samples. With the increase of Si_3N_4 additions and decrease of graphite flake amount, the HMOR at 1400°C first decreased and then increased. XRD in figure 1 shows Al_3C_4 and Al_2OC were generated except C and Al_2O_3 in sample 0#. XRD in figure 2 shows sialon was generated in sample 4#.

	Table 4	Table 4 Hot modulus of rupture of the samples						
Sample code	0#	1#	2#	3#	4#			
HMOR/MPa	41.75	34.2	44.1	45.8	48.7			



Fig.1 XRD of the matrix of sample 1# after HMOR Fig. 2 XRD of the matrix of sample 4# after test

HMOR test



4800 20.0kV 15.0mm x1.00k SE(M) 1mm x1.00k SE(M) 20.0kV 14

(c) Sample 0#

(d) Sample 4#





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Fig. 3a and b reveal that sample 0# and 4# both show intergranular fracture and transgranular fracture. Visible cracks were observed in sample 0# in Fig. 3c, which suggests the bonding between grains and matrix isn't very tight. It can be seen from Fig. 3e that some fibrous substances are formed between grains and matrix in sample 0#. EDAX analysis (not displayed) showed the fibrous substances are composed of three kinds of elements of Al, O and C. With the help with XRD, it might be deduced that the substances are Al₃C₄ and Al₂OC. According their morphology, it could be deduced that they were produced by gas phase formation mechanism. Al first reacts with CO in the pore to form gaseous Al₂O, which further reacts with CO to form Al₃C₄ on the surface of liquid or solid, and finally form fibrous shape by epitaxial growth. Fibrous Al₃C₄ strengthened the modulus of rupture of slide plate.

It could be seen from Fig. 3d that sample 4# has a homogeneous structure and tight bonding between grains and matrix. Well-developed cylindrical crystals were formed in the gaps of sample 4# in Fig. 3f. EDAX analysis (not displayed) showed the cylindrical substances are composed of four kinds of elements of Si, Al, O and N. It might be deduced that the substances are SIALON, which plays a bridge-like role and strengthens the bonding between grains and the matrix. According their morphology, it could be deduced that they were produced by the solid solution of Al_2O_3 in Si_3N_4 . So the HMOR of the material is improved.

Conclusions

With the increase of Si_3N_4 additions, the bulk density of the unfired $A1_2O_3$ -C samples decreased, apparent porosity increased, and cold strength decreased. The HMOR at 1400°C for 0.5h first decreased and then increased. The reason is that with addition of Si_3N_4 , the densification of materials decreased and the room temperature properties decreased. However, cylindrical sialon were formed at elevated temperature, which could improve the hot modulus of rupture of $A1_2O_3$ -C slide plate.

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