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# Mechanical Properties and Performance

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R & D OF ADVANCED CERAMICS ACTIVITIES IN CHINA AND SHANGHAI  
INSTITUTE OF CERAMICS CHINESE ACADEMY OF SCIENCES (SICCAS)

Dongliang Jiang

The State Key Lab. of High Performance Ceramics and Superfine Microstructure  
Shanghai Institute of Ceramics, Chinese Academy of Sciences  
1295 Ding-Xi Rd, Shanghai 200050, China

ABSTRACT

There has been a long term and sustained research and development effort in advanced ceramics in China over last few decades. In this presentation, an overview of recent research and development in the area of advanced ceramics and ceramic matrix composites will be presented. Some key results from national projects funded by Ministry of Science and Technology and National Nature Scientific Foundation of China will be provided. In addition, recent results of R & D activities in Shanghai Institute of Ceramics (SICCAS) especially in ceramic matrix composites, transparent ceramics, bio-ceramics, and mesoporous materials will also be presented.

CMC development is one of the most active research areas in SICCAS including the preparation and characterization of C/SiC and SiC/SiC composites. Various techniques such as chemical vapour infiltration (CVI), hot pressing, and liquid/vapour silicon infiltration (L/VSI) were used to fabricate high performance CMCs, depending on the different application requirements. A modified chemical vapor infiltration (CVI) process, which had been defined as temperature-pulsing CVI was successfully used to deposit SiC matrix into carbon fiber preforms. The final properties of CMCs were strongly dependent on the processing conditions and the nano-SiC particle size. Nano-SiC particulate phases impregnated into the fiber bundles show the reduced interaction between fibers and matrix. Active fillers in polymer impregnation and pyrolysis (PIP) aid to form new phases in the matrix to lower the volume shrinkage and provide improved performances for the composites. In the area of transparent ceramics,  $\text{Al}_2\text{O}_3$ , Nd-YAG, Ce-YAG, La-Y $_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$  and AlON systems are being studied extensively. Among them, the in line transmittance of transparent  $\text{Al}_2\text{O}_3$  has reached 70%; the average output power of 1at% Nd-YAG laser transparent ceramic with size  $22 \times 39 \times 4.5 \text{ mm}^3$ , at 500Hz is around 100W; The transmittance of Ce-YAG scintillation transparent ceramic at 550nm was 80%. The development of high quality transparent ceramics is mainly associated with the understanding of the fundamental principles underlying the advanced processing technologies and nanopowder synthesis and dispersion technology. An overview will be presented on the research and development efforts in biomaterials especially in hard implant materials such as

teeth, knee, bone repair, and biocompatible coatings. In addition, some examples of recent development in mesoporous materials developed for drug delivery will also be provided. Finally, the colloidal processing processes for developing high performance ceramics were also referred.

## 1. BRIEF OVERVIEW OF THE RECENT RESEARCH ACTIVITY IN CHINA

Most of China's research program is funded by the Ministry of Science and Technology, including the Basic Sciences (973 Program) and High Technology Research and Development Programs (863 program). In accordance with the government's guiding principles for the national development of science and technology, the National Natural Scientific Foundation of China also provide financially supports for basic research and applied basic research, the funding is usually smaller except for the key and major ones. Some basic and application programs can also be funded by other Department, local government and companies.

In the field of materials science especially in advanced ceramics, the already funded 973 programs include nano-materials & technology; information functional ceramics, thermo-electric materials, bio-ceramics, new energy materials, C/C composites etc. In consideration of the environmental, energy and human health issues, the funded 863 program include solid oxide fuel cell (SOFC), bio-ceramics, advanced ceramics, composites etc. In recent years, the NNSFC, Chinese Academy of Sciences and local government of Shanghai put a lot of money for research on transparent ceramics, ultrahigh temperature ceramics (UHTC) and composites etc.

## 2. MAIN RESEARCH ACTIVITIES IN SICCAS

In this part, the major research activities of advanced ceramics in SICCAS including the CMC, transparent ceramics, and biomaterials will be addressed. The low cost, eco-friendly processing technologies for developing high performance ceramics were also referred.

### 1. CMC processing

Continuous fiber reinforced ceramic matrix composites, such as C<sub>f</sub>/SiC, SiC<sub>f</sub>/SiC composites have been widely recognized as the most promising candidates for brake disks, heat exchangers, advanced aero-engines, fusion power reactors and space usage for their outstanding characteristics including high toughness, low density, thermal and chemical stability, radiation tolerance and so on<sup>[1,2]</sup>. Especially, the C<sub>f</sub>/SiC composites, for their relatively lower cost, larger-scale production and better thermal stability at elevated temperature, have been extensively investigated. Conventionally, continuous fiber reinforced SiC composites can be prepared by chemical vapor infiltration (CVI)<sup>[3,4]</sup>, hot pressing (HP)<sup>[5,6]</sup>, reaction sintering (RS)

[7], and polymer impregnation and pyrolysis (PIP)<sup>[8]</sup> etc techniques.

### 1.1 Temperature pulsing chemical vapor infiltration <sup>[9,10,11,12]</sup>

A novel route of temperature pulsing chemical vapor infiltration (T-pulsing CVI) was developed to prepare interfacial coatings. In the T-pulsing CVI process, thermal pulses were created by combining induction heating with water cooling, in which the power from the frequency generator was modulated by an artificial intelligence industrial controller.

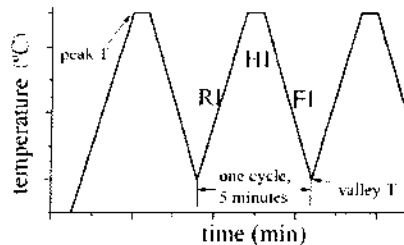


Fig.1 The temperature pulse rate curve

Fig.1 shows the temperature-time set curve from the artificial intelligence industrial controller. One cycle contained in the curve includes three steps: (i) linear temperature rising (RI), (ii) temperature holding (HI), and (iii) linear temperature falling (FI). Methane and MTS were employed as precursors of PyC and SiC, respectively. The hydrogen to MTS mole ratio was maintained at 10, and the flux of  $\text{CH}_4$  was  $10 \text{ cm}^3 \cdot \text{min}^{-1}$ . Argon was used as dilute gas.

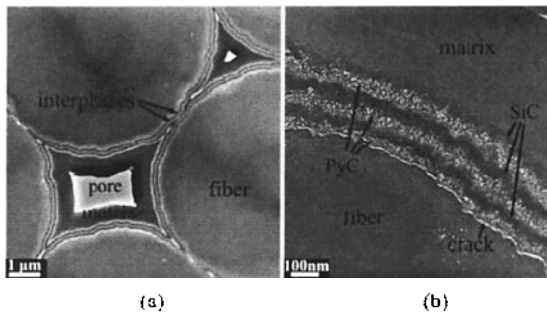


Fig.2 TEM micrographs: (a) inter-fiber configuration; (b) multilayered interfacial coatings

Typical microstructures of the interfacial layers fabricated by T-pulsing CVI were characterized by transmission electron microscopy (TEM), Fig.2. Fig.2a shows the inter-fiber configuration of the composites, in which multilayered interphases can be observed clearly. Fig.2b shows the TEM micrograph of the interfacial region, indicating that the homogeneous nano-scale PyC and SiC alternating layers were formed. The temperature-pulsing CVI can be successfully applied to design and precisely adjust the composition and thickness of the

interfacial coatings in CMCs.

As shown in Fig.3, the interfacial debonding can be clearly observed. This fracture behavior will be more effective for improving the mechanical properties of the composites through the stress transfer and crack deflection mechanism. Load-displacement curve from bending test of the as prepared 3D C/SiC composite shows the typically linear and nonlinear parts.

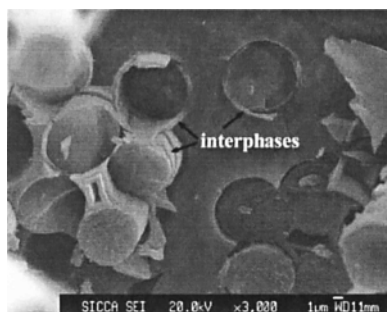


Fig.3 Fractography of the composite showing the interfacial debonding

The flexural strength is about  $474.0 \pm 36.9$  MPa, indicating that T-pulsing CVI may provide another way to design and fabricate CMCs with well controlled interfacial layers and improved properties.

### 1.2 C/SiC composite prepared by HP<sup>[6,13,14,15]</sup>

High performance C/SiC composites were prepared through hot pressing (HP) by using SiC nanopowder as the matrix. The strength and fracture toughness of C/SiC composites would increase with the decrease in SiC particle size and the increase in the modulus of carbon fiber at a proper sintering temperature and pressure. Fig.4 shows the fracture behaviors of the composite with SiC particle size as 50nm, the highest bending strength (500.1MPa) and fracture toughness ( $16.9 \text{ MPa} \cdot \text{m}^{1/2}$ ) were obtained at 1850°C under 20MPa, using M40JB fiber as the reinforcement. Fiber pull-out was clearly observed (Fig.4a). The strong interaction between the SiC matrix and the fiber might lead to the potential damage of the fiber during fabrication, as shown in Fig. 4b.

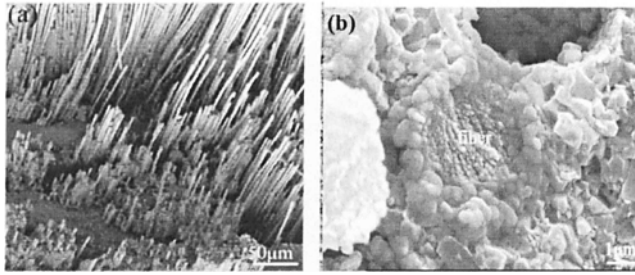


Fig.4 Fracture behaviors of the composite with different SiC particle inclusion: (a) SiC particle size is 50nm, (b) Fracture surface showing the strong fiber/matrix interaction when use sub-micrometer SiC particle (500nm)

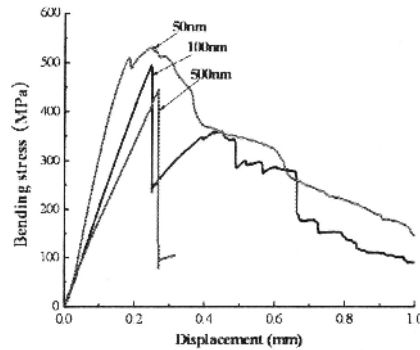


Fig.5 Stress-displacement curves of C/SiC composites using different SiC particle for matrix formation

Fig.5 indicates that using nano-SiC as the matrix, the prepared C/SiC composite demonstrates the typically non-catastrophic fracture behavior. With the increase in the particle size of SiC, the fracture toughness decreases correspondingly. As using 500nm SiC powder, the fracture toughness is down to  $7.5 \text{ MPa}\cdot\text{m}^{1/2}$ , similar to that of brittle ceramics.

### 1.3 Vapor silicon infiltration (VSI) process<sup>[16,17]</sup>

The bulk density and the open porosity of C/SiC composites prepared by VSI are shown in Fig.6 as a function of infiltration temperature. The sintered density reached  $2.25 \text{ g/cm}^3$  with the porosity as 6% at  $1700^\circ\text{C}$ . The fracture surface (Fig. 7 a) showed the dense matrix after VSI at  $1700^\circ\text{C}$ . An obvious fiber pull-out (Fig. 7 b) was observed after fracture although the silicon content is quite high (14.5 vol %).

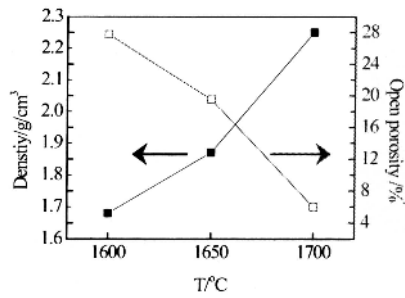


Fig.6 Density and porosity of the VSI C<sub>p</sub>/SiC

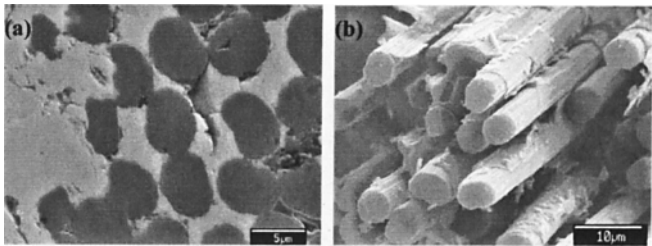


Fig.7 Cross section (a) and fracture surface of the VSI composites (b)

Stress-displacement curves (Fig.8) showed the non-catastrophic fracture behavior of VSI composites. It shows that the work of fracture (WOF) decreased after the composite was densified. WOF decreased from 12.13 to 9.54 kJ·m<sup>-2</sup> with the increase in density, when temperature increased from 1650°C to 1700°C. However, the strength kept almost the same (239.5±35.6MPa at 1650°C and 238.9±41.2MPa at 1700°C).

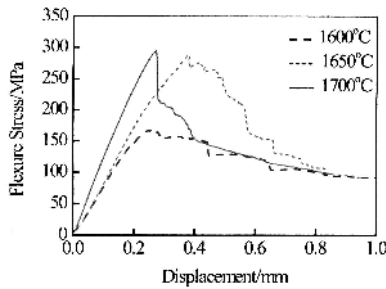


Fig.8 Stress-displacement curves of the VSI composites

#### 1.4 Active filler enhanced PIP process (R-PIP)<sup>[18,19,20,21,22]</sup>

The incorporation of active fillers to the matrix during polymer impregnation can enhance the PIP process by reducing the volume shrinkage of the matrix. Usually, active filler will react with the reactive atmosphere and the decomposed species of the preceramic polymer. These reactions usually lead to the volume expansion and could be used to compensate the polymer shrinkage during the pyrolysis process. Aluminum (Al) is the well recognized active filler. Fig.9 shows the variation of density as the PIP cycles, using the 2.5D preforms. It is clear that the bulk density increases quickly for the initial several cycles with Al-loading. Stress/displacement curves of the composites are shown in Fig.10. With Al loading, the composite shows higher flexural strength due to the strong bonding caused by reactions between the matrix and fibers.

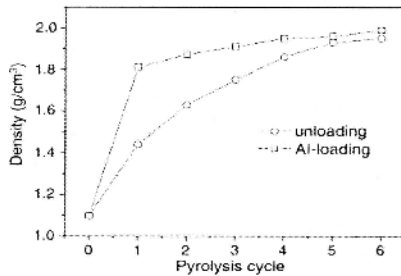


Fig.9 Relationship between the density and the pyrolysis cycle of the composites with and without active filler loading

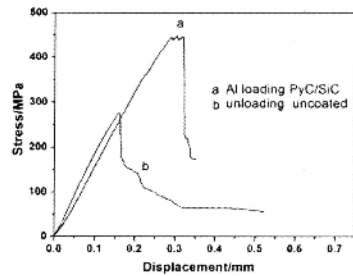


Fig.10 Stress/displacement curves of the 2.5D composites with and without active filler loading

Another role for active filler is to increase the anti-oxidation behavior of CMC composites. The lifetime of CMCs which are partly made of carbon is strongly depended on the efficiency of the anti-oxidation systems used to reduce the oxygen permeability. Extensive studies have been undertaken to improve the oxidation resistance of carbon fiber reinforced CMCs, and most are related to the application of boron-bearing species.

Dong et al proposed a facile route to fabricate carbon fiber reinforced ceramic matrix composites (C/SiC-BN) by an active-filler-controlled polymer pyrolysis (AFCOP) process. In the proposed process, boron was introduced into the carbon fibers as active filler to form some boron-bearing species by in-situ reactions during the subsequent heat-treatment process. The composites were prepared by PIP using PCS as the polymer precursor. XRD patterns of the obtained composites confirmed the presence of H-BN. With the presence of BN, the oxidation of the composites was greatly improved. The weight losses of C/SiC and C/SiC-BN after being oxidized at 800°C for 10h were ~36% and ~16% respectively and most of the carbon fibers in

C/SiC-BN composites were well retained while those in C/SiC composites were oxidized, Fig.11.

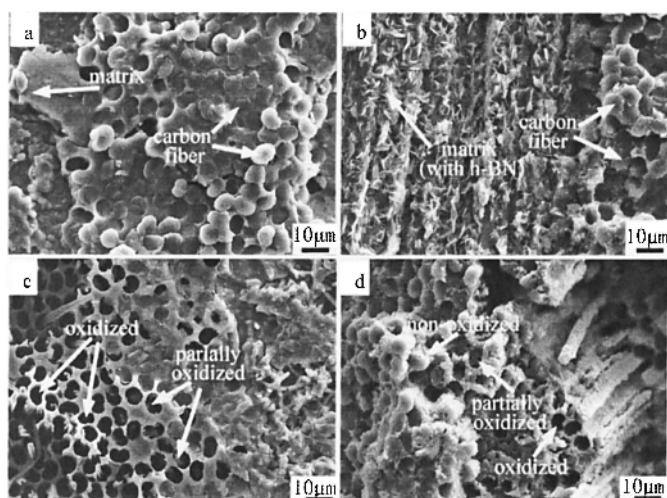


Fig.11. SEM observation on the fracture surface of the composites: (a) without filler before oxidation, (b) with B filler before oxidation, (c) without filler after oxidation at 800°C for 10h, (d) with B filler after oxidation at 800°C for 10h.

The above mentioned techniques (T-pulsing CVI, HP, L/VSI and R-PIP) can be used successfully for microstructure design and properties optimization. Deposition of multilayered coating and matrix can be controlled easily by T-pulsing CVI. Combined with nano-SiC infiltration, HP shows its superiority on fabrication of high performance C/SiC composites. L/VSI is the facile and economic way to prepare CMCs, and microstructure control was proved to be effective for improving the final properties of the composite. R-PIP can improve the efficiency of regular PIP process, and the flexural strength is shown to be highly dependent on the surface coating properties of the fibers. However, precise microstructure control and process optimization is still an important issue for the future study.

## 2. TRANSPARENT CERAMICS

Compared with single crystals, transparent ceramics offer several advantages, for example, lower cost, easy fabrication of materials of large size, and especially those with high melting points. Currently, transparent ceramics have found a wide range of application in lighting, solid state lasers, scintillators, windows and battle field etc.

Nanotechnology and vacuum or atmosphere sintering approaches make the fabrication of highly transparent ceramic materials possible. To prepare transparent ceramics, a strict control

of the characteristics of initial powder was required. Nano particles with narrow size distribution, mono-dispersion and high chemical purity is recommended for the subsequent densification process. The nanopowder is commonly prepared by sol-gel technology, co-precipitation, thermal decomposition of salts, solid-phase synthesis, combustion, freezing, and hydrothermal methods etc. The sample can be fully densified by hot pressing, hot isostatic pressing or pressureless sintering in vacuum or atmosphere. To reduce the grain growth during the densification process, usually a long holding time at relatively low temperature are recommended.

## 2.1 Transparent ceramics for lighting - $\text{Al}_2\text{O}_3$

Since the first translucent polycrystalline alumina was developed by Coble in the 1960s, continued efforts are made to improve the optical qualities of alumina ceramics because they are a potential alternative to corundum single crystal. It was believed that the optical qualities of  $\text{Al}_2\text{O}_3$  ceramics could be improved by increasing the purity and density and by controlling the microstructures. However, the needed degree of optical transparency has not yet been achieved after half a century's effort. In fact,  $\alpha\text{-Al}_2\text{O}_3$  (corundum) with hexagonal crystal structure is optically uniaxial and birefringent. Therefore, it is impossible to prepare transparent alumina ceramics with randomly oriented grains due to the existence of the numerous interference of optical axis.

In a recent study, Wang et.al.<sup>[23]</sup> proposed a simple route to prepare transparent polycrystalline alumina ceramics with well controlled orientation of individual grains. They used slip casting process to prepare the green bodies and simultaneously applied a strong magnetic field to the slurries. It was found that the grains have been successfully orientated in the alumina ceramics after sintering, Fig.12. The in-line optical transmission is much higher than that of the randomly orientated  $\text{Al}_2\text{O}_3$  because the optical axes of the individual grains are parallel to each other. Samples that were slip cast in a strong magnetic field exhibited higher optical transparency than those prepared without using a magnetic field, Fig.13. To prepare transparent alumina, Wang's group also investigated the gelcasting process based on epoxy system<sup>[24,25]</sup>.

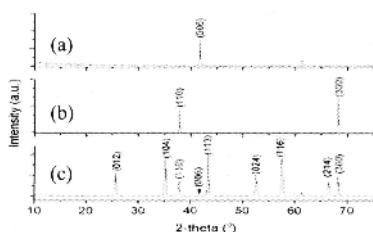


Fig.12. X-ray diffraction patterns of alumina slices cut, (a) perpendicular to and (b) parallel to the magnetic field, and (c) slip cast without a magnetic field.

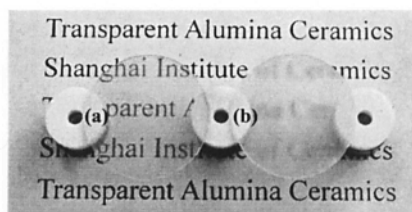


Fig.13. Polycrystalline alumina ceramics from slip casting (a) with and (b) without a magnetic field. The samples are placed 8 mm above the paper.

2.2 Transparent ceramic for laser (Nd:YAG)

In 1995, Ikesue et al.<sup>[26,27]</sup> first demonstrated the possibility of fabricating transparent Nd:YAG ceramics of sufficient quality for solid-state lasers with reasonable efficiency. Since then, Nd:YAG laser ceramics have attracted considerable attention because the optical quality has been improved greatly and highly efficient laser oscillations could be obtained with comparable efficiency to YAG single crystals.<sup>[28]</sup> Compared with YAG single crystal laser materials, YAG ceramics have several prominent advantages: (1) easy fabrication; (2) scalability in size; (3) high doping concentration; (4) better homogeneity of the doping ions; (5) ease of achieving composite structure and so on. Ceramic technology also makes it easier to incorporate several dopant ions into the YAG material compared with single crystals grown from a melt, thus the lattice deformation leading to optical birefringence and wave front distortion can be circumvented.

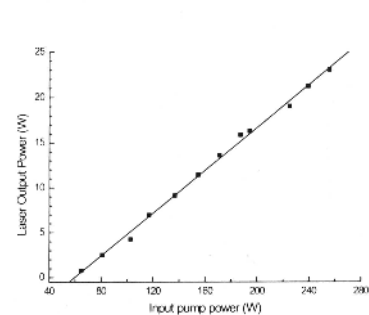


Fig.14 Laser power input-output curve with pump frequency of 1000Hz, obtained 23W continuum laser output

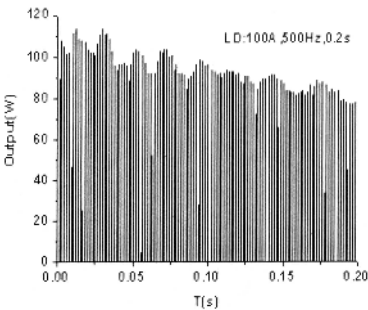


Fig.15 Nd:YAG transparent ceramics heat capacity, average output power reached 100W

In SICCAS, Pan et al have successfully developed the transparent Nd: YAG ceramics for laser [29,30,31,32,33,34]. A continuum laser output of 23W has been reported, Fig.14. For Nd:YAG transparent ceramics heat capacity, the average output power is now 100W, Fig.15. They also tried a laminar-structured of YAG/1.0 at. % Nd: YAG/YAG transparent ceramic to improve the laser performance<sup>[35]</sup>. Other laser ceramics (such as Yb:YAG<sup>[36]</sup>, YAG:Tb<sup>[37]</sup>, YAG:Eu<sup>[38]</sup> etc.) in SICCAS were also well studied.

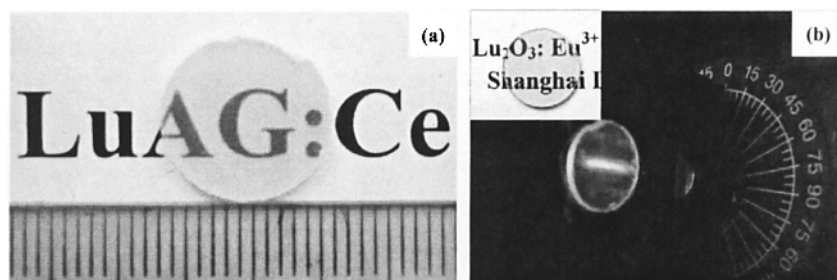
2.3 Transparent ceramics for scintillator

The development of scintillator and phosphor materials started at the end of 19th century. The CaWO<sub>4</sub> and ZnS-based phosphor powders were introduced in practice very soon after. In the

late forties the first single crystal scintillators NaI:TI and CsI:TI appeared and has been widely used till today. The latest class of materials scintillation optical ceramics came into use relatively recent when appropriate technology was developed to obtain competitive material properties mainly for materials where single crystals cannot be prepared or their production is extremely expensive<sup>[39]</sup>.

An interest in new scintillator materials is pushed by increasing number of medical, industrial or scientific applications, requiring higher material performance. The main transparent ceramic systems include (Y,Gd)<sub>2</sub>O<sub>3</sub>:Eu,Pr(YGO), Gd<sub>2</sub>O<sub>2</sub>S:Pr,Ce,F(GOS), and Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>:Cr,Ce (GGG). In recent years, new systems (Ce doped BaHfO<sub>3</sub> and Eu<sup>3+</sup> or Tb<sup>3+</sup>-doped Lu<sub>2</sub>O<sub>3</sub>) were also under study.

The studied transparent ceramics system in SICCAS including Eu<sup>3+</sup>, Pr<sup>3+</sup> doped Lu<sub>2</sub>WO<sub>6</sub><sup>[40,41]</sup>, Ce doped YAG<sup>[42]</sup>, LuBa<sub>3</sub>B<sub>9</sub>O<sub>18</sub><sup>[43]</sup>, LuAG:Ce<sup>[44,45]</sup>, BaBPO<sub>5</sub><sup>[46,47]</sup>, Eu:Gd<sub>2</sub>O<sub>3</sub>-HfO<sub>2</sub><sup>[48]</sup>, Ce:SrHfO<sub>3</sub><sup>[49]</sup> and La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:Ti<sup>[50]</sup> etc. A series of transparent ceramics were successfully prepared with well improved properties. Recently, Shi et al<sup>[51]</sup> prepared Ce:YAG with near complete absorption for lights at wavelengths below 480nm. The transparent ceramics show remarkably enhanced light emission intensity and much suppressed concentration quenching effect than those of Ce:YAG ceramics at the same Ce doping levels. Liu et al reported the LuAG:Ce transparent ceramics fabricated by the solid-state reaction method. The relative density reaches 99.5%. The transmittance in the visible light region reaches 70%<sup>[52]</sup>. Shi et al reported the Eu doped Lu<sub>2</sub>O<sub>3</sub> from a novel co-precipitation process. The optical in-line transmittance in the visible wavelength region reached 80%<sup>[53]</sup>. The Ce doped LuAG and the Eu doped Lu<sub>2</sub>O<sub>3</sub> ceramics are shown in Fig 16.



**Fig.16** Optical images of (a) Ce doped LuAG and (b) the Eu doped Lu<sub>2</sub>O<sub>3</sub> transparent ceramics

## 2.4 Transparent ceramics for lens

The first transparent ceramic lens for the digital camera was developed successfully by CASIO. The material (LUMICERA) has the same light transmitting qualities as optical glass commonly used in today's conventional camera lenses, however, it has two very important properties: high

refractive index (2.08) and superior strength. This will make it possible to create zoom lenses for cameras with greatly reduced profiles.

In recent years, the development of transparent ceramics lens is also in active. A complex system  $\text{Ba}(\text{MgTa})\text{O}_3$ , with cubic lattice structure, has been studied. The material showed excellent properties with high refractive index (2.05-2.10) at 580nm and the light transmission rate can reach 76%. The material preparation process is still under refining for further improving the performance.

In addition to the above mentioned transparent ceramic systems, there are other systems studied in SICCAS including the infrared ceramics for windows, domes and armors such as  $\text{SiAlON}$ ,  $\text{AlON}$ ,  $\text{Y}_2\text{O}_3$ <sup>[54,55]</sup> etc.

Transparent ceramics with excellent physical, mechanical and other properties have been a key material for commercial (high-tech industry) and defense applications. The present results showed that the development of high quality transparent ceramics is mainly associated with the understanding of the fundamental principles underlying the advanced processing technologies.

### 3. BIOMATERIALS

Having existed for around half a century, the development of biomaterials is not a new area of science. But the demand for implants and prostheses made from biomaterials is constantly growing. The materials need to be very robust and active for promoting tissue regeneration. Scientists have developed bone implants from metal alloys and ceramics. The most promising substances are made of Ti,  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$ . Because they do not interact with biological processes in the body, they are not usually rejected. In addition, interaction between biomaterials and natural tissues is an important subject for biomaterial science. Such information is essential to aid the design of new biocompatible biomaterials.

The research activities of biomaterials in SICCAS cover a wide range including bioactive materials and tissue engineering scaffolds, nano-biomaterials for controlled drug release, bio-labeling and diagnostic, biomaterials surface engineering for medical implants, optical fiber materials for medical device etc. In this paper, two research areas will be introduced.

#### 3.1 Biomaterials surface coating

The research of biomaterials surface coating started from 1959 using Plasma spraying technique on the surface of Ti alloys for bone replacement. With almost 50 years of scientific research and technical buildup, the technologies for biological coating have been well developed and found orthopedic applications<sup>[56, 57, 58]</sup>. In order to improve the cytocompatibility and antibacterial properties, different techniques have been developed including loading drugs, nano silver powders, surface treatment etc<sup>[59,60,61,62]</sup>. In recent years, novel bioactive coatings have also been developed, including wollastonite, dicalcium silicate, nano- $\text{TiO}_2$  and nano- $\text{ZrO}_2$

coatings, which possess excellent bioactivity and biocompatibility as well as high bonding strength to Ti-6Al-4V substrate<sup>[63,64,65]</sup>. In order to improve the bioactivity, biocompatibility and antibacterial property of titanium and its alloys, Si-, Ag-, Ca-, P- and Na-ion was also incorporated into the coating through ion implantation technique<sup>[66,67]</sup>. Fig.17 showed the plasma spraying system and the coated parts for hip replacement etc. applications.

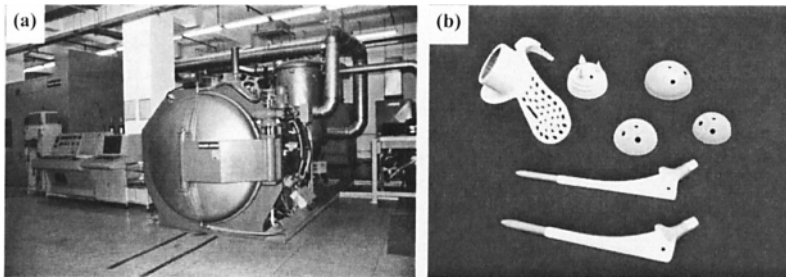


Fig.17 Optical images of (a) Vacuum-atmospheric plasma spraying system and (b) biocompatible coatings

### 3.2 Nano-biomaterials for controlled drug release

Amorphous mesoporous silica materials with a non-toxic nature, tunable pore diameter, and very high specific surface area with abundant Si-OH bonds on the pore surface are promising candidates for use as carriers in drug delivery systems<sup>[68]</sup>. Conventional mesoporous silica materials (such as MCM-41 and SBA-15) exhibit sustained-release properties, but their drug storage capacity is relatively low, and also the irregular bulk morphology is not perfect for drug delivery. In this report, two advances in SICCAS will be addressed.

**Stimuli-responsive controlled drug release.** Recently, Shi's group has successfully synthesized HMS spheres with a 3D pore-network shell<sup>[69,70]</sup>. The drug storage capacity of this system is three times higher than that of the reported MCM-41 system<sup>[71]</sup>. Subsequently, a novel stimuli-responsive controlled drug-release system was developed by using PAH/PSS multilayers as a coating to cap the mesopore openings of drug-loaded hollow mesoporous silica spheres. In this way, the drug release rate from the new system can be well-controlled by changing the pH value (or the salt concentration) of the release medium. This system, which combines the advantages of both high drug storage capacity and the property of stimuli-responsive controlled release, has potential applications in drug delivery<sup>[72]</sup>, Fig.18.

**Drug targeted delivery.** For drug delivery system, the efficiency of drugs to the targeted delivery has always a hot research area and has attracted considerable attention in recent years. Shi's group reported a new kind of uniform magnetic nanocomposite sphere (MCMS) with a

magnetic core/mesoporous silica shell structure.<sup>[73,74]</sup> Based on this advance, a novel kind of rattle-type hollow magnetic mesoporous sphere (HMMS) with  $\text{Fe}_3\text{O}_4$  particles encapsulated in the cores of mesoporous silica microspheres were successfully fabricated by Sol-gel reactions on hematite particles<sup>[75,76]</sup>. The ring-shaped cavity between the magnetic core and the mesoporous silica shell has been generated by a simple hydrothermal treatment and  $\text{H}_2$  reduction process. Using IBU as a model drug, hollow magnetic mesoporous spheres can realize a significantly higher storage capacity of drug because of the rattle-type structure than the corresponding magnetic/mesoporous spheres without the cavities. The release experiments identify a sustained-release behavior of IBU from the present drug storage system and the release process follows a Fick's law. This hollow magnetic mesoporous spheres are a promising candidate material as drug targeted delivery carriers. Fig.19 shows the possible mechanism for the formation and the relevant microstructure of mesospheres.

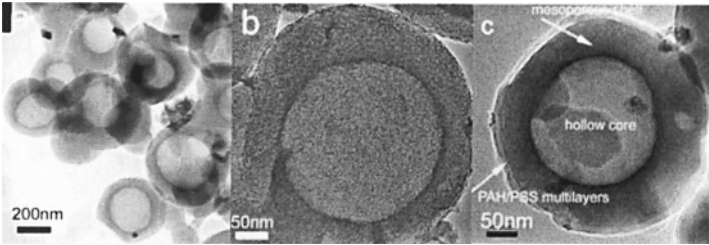


Fig.18 TEM images (a, b) of hollow mesoporous silica sphere (HMS) with a 3D pore network, core-shell structure, (c) with polyelectrolyte multilayer coating as a stimuli-responsive controlled drug-delivery system.

In addition, for the drug delivery system, there are also extensive works in SICCAS using mesoporous bioactive glass<sup>[77]</sup>, porous HA<sup>[78,79]</sup>, and  $\text{Fe}_2\text{O}_3$  hollow spheres<sup>[80,81]</sup> etc composites.

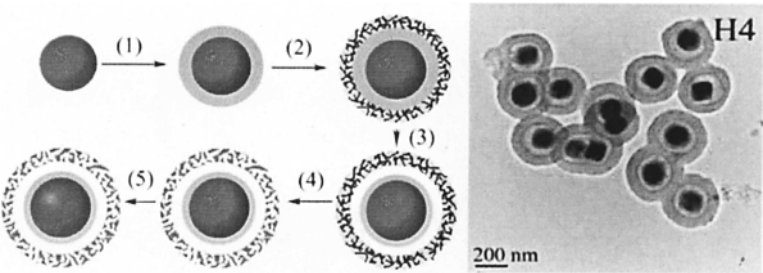


Fig.19 Schematic illustration of the synthesis and the TEM image of MFeCMS nanospheres.

From dental repairs to controlled drug release or total organ/joint replacement, almost every human being on earth will be exposed to one biomaterial or another during their lifetime. Artificial organs are necessary to support part or all of their essential functions thereby improving quality of life. In biomaterial science, interaction between biomaterials and natural tissues is still an important subject. The informations are essential to aid the design of new biocompatible materials.

#### 4. ADVANCED PROCESSING

Colloidal processing, which has the potential for eliminating detrimental heterogeneities and avoiding their reintroduction during the successive processing steps, has long been reported as the most potential cost effective and eco-friendly route to prepare ceramic composites with improved stability at low cost. In colloidal processing, particle dispersion is often the limiting factor, affecting both the rheology and the homogeneity of suspensions and the properties of samples before and after sintering. There are several colloidal processing techniques, including tape casting, gel casting, direct coagulation casting etc. In this report, the study on aqueous tape casting and gelcasting process in SICCAS will be addressed briefly.

##### 4.1 Tape casting

Tape casting is a prominent process to produce thin and flat green sheets for the fabrication of ceramic substrates and multilayered structures. Organic solvents are commonly used as the liquid vehicle, but the volatility and toxicity of these solvents has lead to increasing interest in research on the aqueous tape casting process.

A lot of ceramic tapes have been prepared in SICCAS, including silicon carbide<sup>[82]</sup>, silicon nitride<sup>[83]</sup>, titanium carbide<sup>[84]</sup>, titanium nitride<sup>[85]</sup>, hydroxyapatite<sup>[86]</sup>, alumina<sup>[87]</sup>, zirconia<sup>[88]</sup>.

The design of laminated structure was guided by finite element method (FEM) to optimize the mechanical and other properties. A series of laminated composites with well improved properties were developed, including SiC/C<sup>[89]</sup>, SiC/TiC<sup>[90]</sup>, Al<sub>2</sub>O<sub>3</sub>/TiC<sup>[91]</sup>, Al<sub>2</sub>O<sub>3</sub>/HA<sup>[92]</sup>, Al<sub>2</sub>O<sub>3</sub>/Ni<sup>[93]</sup>, TiN/Al<sub>2</sub>O<sub>3</sub><sup>[94]</sup> etc. Fig. 20 showed the FEM simulation of a symmetrical layered SiC/SiO<sub>2</sub> ceramic with gradual thermal residual stress distribution. The initial results were shown in Table 1. Compared with pure SiC and 90%SiC-10%TiC (SiO<sub>2</sub>) ceramics fabricated by the same process, the designed composites showed excellent mechanical properties. The tested strength was close to the theoretical value. The strengthening and toughening mechanisms of the ceramic were ascribed to surface compressive residual stress<sup>[90]</sup>.

Table 1 Comparison of tested strength of SiC/SiOT layered ceramic with theoretical

| Calculated residual stress (MPa) | Tested residual stress (MPa) | Theoretical strength(MPa) | Tested strength (MPa) |
|----------------------------------|------------------------------|---------------------------|-----------------------|
| -126                             | -129                         | 840                       | 834                   |

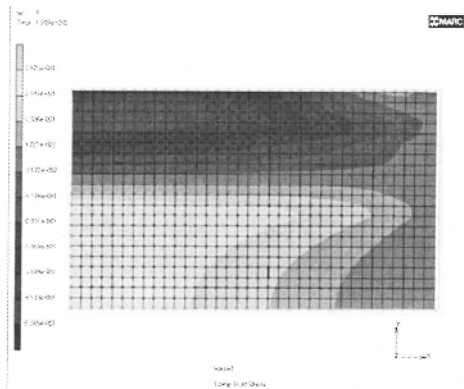


Fig.20 FEM analysis of SiC/ SiOT system

4.2 Gelcasting

Gelcasting is an attractive highly versatile fabrication process to prepare ceramic green body with high-quality and complex shape<sup>[95]</sup>. The process is based on the polymerization of organic monomers and solidification of slurry to green body. In gelcasting, slurry made from ceramic powder and a water-based monomer solution is prepared and poured into a mold, followed by the polymerization *in-situ* to immobilize the particles in a gelled part. The samples were removed from the mold when it was still wet, then dried and fired. In recent years, gelcasting has been widely studied to produce ceramic materials. Jiang's group studied the gelcasting of SiC<sup>[96]</sup>, TiC<sup>[97]</sup>, Al<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C<sup>[98]</sup>, HA<sup>[99]</sup>, HA/ZrO<sub>2</sub>, ZrB<sub>2</sub><sup>[100]</sup> etc. For SiC system, after gelcasting and drying, the relative density and the bending strength of the green body was 57% and 40MPa, respectively. After sintering at 2200°C, SiC samples can be densified to a relative density of 98%. The mechanical properties of the obtained pieces are satisfying, with the flexural strength, toughness and the hardness as 539±89MPa, 3.46±0.31 MPa·s<sup>1/2</sup> and 26.2±0.97 GPa, respectively. Further study on this system is still under way.

Colloidal processing is proved to be a facile, environmental conscious route to obtain ceramic composites with large size, complex shape and high quality at low cost. However, the in depth research on the surface chemistry, rheology, polymer science etc. is still needed for understanding its principal mechanism especially for nano powder processing.

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