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Preparation and Property of Black Pottery for Bioactivity

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Abstract: The black pottery with bioactive multifunction (BPBM) was prepared by introducing rare earths, magnetic materials and other additives. The preparation method and bioactivity property were studied respectively. The results showed that, through optimizing the chemical composition and processing parameters, the bioactivity pottery with far infrared emission and antibacterial ability could be prepared, by common roller hearth kiln.

Key words: functional ceramic; bioactivity; black pottery; rare earth; preparation method
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Black pottery was an excellent page in history of Chinese ceramics[1~3]. Due to its complicated preparation and sintering process, it had been lost for over 3000 years. Luckily, it was settled and endowed with new process and performance in 1989, under the hard work of many archaeologists and ceramic technicians. It is well known that black pottery is famous for its black like carbon, bright like mirror, hard like porcelain and sound like music. And its exquisite preparation process and elegant sculpt have attracted more and more people. At present, most pottery products have been classified into medium and high grade[4~6], mainly prepared by hand-made processing, such as wheel-made method, and carbon penetration by sealing kiln and smoking craft, consequently leading to its difficult manufacture in bulk. Especially, most black pottery is fit to view not to use, can not meeting the needs of modern people.

With the development of science and technology, more and more attention has been paid to the function and quality, especially to special ceramics, which should meet not only the items of good antibacterial property, far infrared irradiation and magnetic property, but bulk manufacture with automatization, good quality under control and good performance in consistency. Now, there are many functional ceramics such as far infrared ceramic, magnetic ceramic and antibacterial ceramic[7~9]. Moreover, the functional ceramics[10] with far infrared irradiation, biological magnetic field and negative ions have attracted great attention for its improvement in organism metabolism, by reducing the cluster volume of water molecules[11] and the surface tension of water[12].

Combined with the preparation process of traditional ceramic, the composite materials with bioactivities including far infrared irradiation and antibacterial property, were prepared by using cheap raw materials, such as rare earth, magnetic materials and other additives. Moreover, the exquisite black pottery was manufactured by common roller hearth kiln successfully.

1 Experimental

1.1 BPBM preparation

Combined with the preparation process of traditional ceramic, the BPBM was prepared by blending ferric tourmaline, magnetic materials, additives and water in fixed proportion. The composition and preparation process are shown in Table 1 and Fig. 1, respectively.

Table 1　Composition of raw materials used for preparation of black pottery (%, mass fraction)

FT	MM	Kaoline	SiO_2	Al_2O_3	CaO	$Ce(NO_3)_3$	Others
10	27	10	10	15	15	3	10

* FT-Ferric tourmaline; MM-Magnetic materials

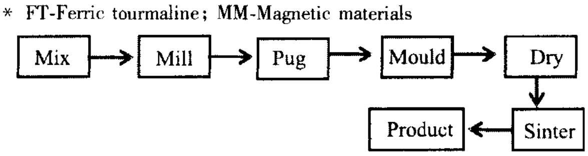

Fig. 1　Preparation process of BPBM

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The detailed preparation process is as follows. The selected materials were mixed together according to the composition in Table 1. Before blending, the raw materials were milled to the requested average sizes such as tourmaline 8 μm, magnetic materials 2.5 μm, kaoline 4 μm, silicon dioxide 2 μm, alumina 9 μm, and calcium oxide 4 μm. Then the above materials were mixed with 3% neodymium nitrate, 20% water and other additives and milled for another 24 h. Thereafter, the agitation was carried out using the vacuum Pug Mill with extrusion ratio of 1∶1, feeding shaft 11 $r \cdot min^{-1}$ and extruding shaft 9 $r \cdot min^{-1}$. The body was molded by wet pressing and dried in air to have a water percentage of 1.8%. The last sintering procedure was run for 3.5 h, at a reductive atmosphere by a common roller hearth kiln with 25 m in length.

1.2 BPBM characterization

Microstructures of PBPM were characterized by SEM (Philips XL30-TMP). High temperature physical property was tested by the CRY-2 differential thermal analysis (DTA).

1.3 BPBM performance

The antibacterial property was evaluated by JC/T897-2002 standard of Antibacterial Property of Antibacterial Ceramic. The activating water property was tested by DCAT21 Auto Surface Tension-Meter. FTIR spectrum was obtained by a VECTOR22 made in Germany. Then the BPBM was magnetized by an MCG-GB4.5/3.0 magnetizing apparatus whose magnetic field strength was tested by an HT20-Agauss meter.

2 Results and Discussion

2.1 Microstructures of BPBM

The microstructures of as-prepared BPBM at different temperatures are shown in Fig.2.

From Fig.2, it can be seen that the microstructures of BPBM become more and more densified with the increase of sintering temperature, and there are almost no pores at 950 ℃ with an average size below 4 μm, as shown in Fig.2(b). With further increase in temperature, some huge granules are formed quickly, resulting in many pores between them and other small ones, as shown in Fig.2(c).

It is thought that with the increase of temperature, granules develop under sintering innervation, resulting in the gradual increase of average size and the transfer and elimination of some pores on the surface, which leads to the achievement of densified body with good performance. At a lower sintering temperature, there is an incomplete growth, accompanying the appearance of many pores and other defects, as shown in Fig.2(a). While at a higher sintering temperature, the huge granules grow in an abnormal way. At the same time, the pores between huge ones and small ones are difficult to remove, resulting in a worsening performance.

2.2 Effects of sintering atmosphere on magnetic property of BPBM

The existence of Fe in the ceramic body is greatly responsible for the magnetic property and color of BPBM. For example, when Fe exits in the form of Fe_2O_3, the ceramic shows a red color and bad magnetic property, but when in Fe_3O_4, it shows a black color and good magnetic property. In particular, the color of ceramic doped with Fe depends on the sintering atmosphere.

For the reductive atmosphere during sintering, the continuous CO gas is input, that is, the existence form of Fe is transformed from Fe_2O_3 to Fe_3O_4. In present work, the black pottery was prepared successfully at 950 ℃, under the action of SiO_2, CaO and Al_2O_3, suggesting the transformation from Fe_2O_3 to Fe_3O_4.

2.3 Effects of heating velocity on high-temperature physical property of BPBM

Fig.3 shows the DTA curve of the BPBM materials.

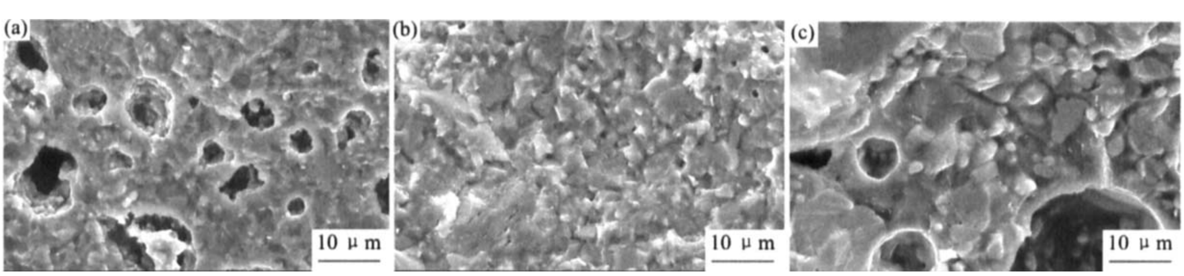

Fig.2 Microstructures of BPBM at different temperatures
(a) 940 ℃; (b) 950 ℃; (c) 1050 ℃

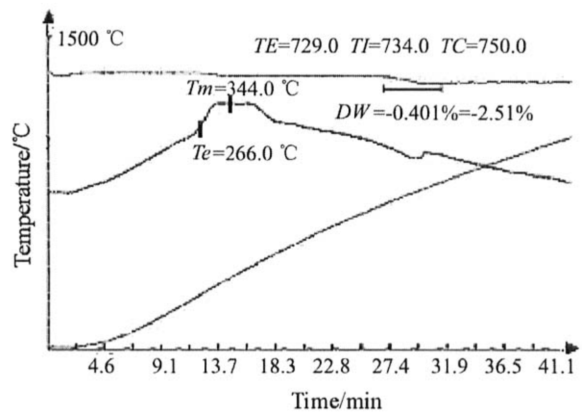

Fig.3 DTA curve of BPBM materials

TE: Extrapolated onset temperature; *TC*: Termination temperature of weight changing; *TI*: Starting temperature; *TM*: Peak value

In general, there are four kinds of water in ceramics. The first is free water, completely on the outside of mineral granules, expelled at 120 ~ 150 ℃. The second is layer water, layers of clays, expelled at 300 ~ 500 ℃. The third is crystal water, incompletely inside of crystal lattice, expelled at 200 ~ 800 ℃. The fourth is structure water, one of components of minerals and combined tightly with other components instead of existing in water form, expelled at 500 ~ 900 ℃. It is requested that the effects of water should be taken into account. If the sintering has a fast heating speed at the stage of expelling water, it is apt to having different temperatures such as at the top and bottom of the kiln and body, thus leading to the breakup of the pottery. Whereas at a slow heating-speed, the sintering cost will be higher. From Fig. 3, it can be seen that the TG curve begins at 266 ℃ and ends at 750 ℃, with a peak value at 344 ℃. It is very important to have an optimal heating speed according to the above situation.

2.4 BPBM property

2.4.1 Far infrared irradiation The far infrared irradiation spectra of the BPBM was evaluated with the testing temperature of 100 ℃. It is found that the BPBM has a normal-direction emissivity of 0.86 in the range of 800 ~ 1500 nm.

2.4.2 Antibacterial property Table 2 lists the antibacterial property of BPBM.

From Table 2, it can be clearly seen that the BPBM has excellent antibacterial performance. Under the coordinating action of rare earth and Fe ions from tourmaline and magnetic materials, the Fenton reaction takes place in the system[13], resulting in the production of ·OH, thus leading to an excellent antibacterial property. However, the relative mechanism is being studied in our laboratory.

Table 2 Antibacterial property of BPBM

Subject	Percentage/%
Escherichia coli ATCC25922	97.7
Staphylococcus aureus ATCC6538	96.18

2.4.3 Magnetic property In order to keep the magnetic performance, it is important for BPBM to be magnetized. The BPBM are slowly put through the magnetizing apparatus, for only 1 s, with magnetic field strength being 800 ~ 1400 gauss, suitable for health protection.

2.4.4 Effects on surface tension of water Fig.4 shows the effects of BPBM on the surface tension of water.

From Fig.4, it can be seen that when compared with black sample, the surface tension decreases significantly due to the action of BPBM. It is suggested that, due to the cooperation of rare earth, far-infrared materials and magnetic materials, the cluster volume of water molecules is reduced, that is, the BPBM can activate water molecules and reduce the water cluster.

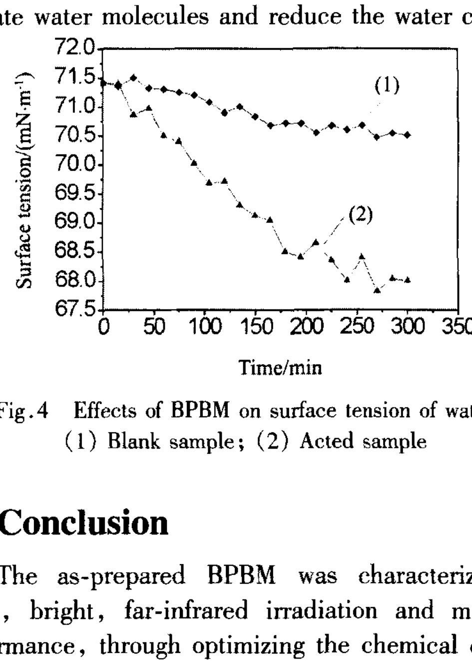

Fig.4 Effects of BPBM on surface tension of water
(1) Blank sample; (2) Acted sample

3 Conclusion

The as-prepared BPBM was characterized by black, bright, far-infrared irradiation and magnetic performance, through optimizing the chemical composition and preparation parameters. The qualified products were achieved just by a common molding instrument and a common roller hearth kiln.

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