

# MECHANICALLY ACTIVATED SYNTHESIS AND APPLICATION OF ULTRAFINE $\text{ZrSiO}_4$ POWDER<sup>①</sup>

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**ABSTRACT** Ultrafine highly-activated  $\text{ZrSiO}_4$  powder was synthesized at relatively lower temperature (1200 °C) using monoclinic  $\text{ZrO}_2$  powder and colloidal  $\text{SiO}_2$  through the mechanical activation in ball milling. The influence of milling time on the formation rate of  $\text{ZrSiO}_4$  was studied. When the mixed powder after milling for 120 h was calcined at 1200 °C for 2 h, the formation rate of  $\text{ZrSiO}_4$  reached above 95%. The influence of the synthesized  $\text{ZrSiO}_4$  as an additive to a bonding material for brazing ceramic to metal was also discussed.

**Key words** zircon( $\text{ZrSiO}_4$ ) mechanical activation solid synthesis brazing of ceramic to metal

## 1 INTRODUCTION

As an important raw material for ceramics and refractories,  $\text{ZrSiO}_4$  has very low thermal expansion coefficient and thermal conducting coefficient<sup>[1, 2]</sup>, therefore it is frequently used as additives to improve the properties of sintered bodies. The  $\text{ZrSiO}_4$ -based pigments have high dissolution resistance and chroma-luminance<sup>[3]</sup>, they are an important component for making high-quality emulsified ceramic fusion cakes and are very effective for improving the whiteness of the glazed surface and the quality of ceramic products. The synthesized high-purity ultrafine  $\text{ZrSiO}_4$  sintered body has good mechanical properties at high temperatures, it can be expected to be developed into a high-temperature structural material<sup>[5]</sup>. When developing a bonding material for brazing ceramics to metal, Cao *et al*<sup>[6]</sup> found that the synthesized  $\text{ZrSiO}_4$  was effective for adjusting and improving the thermal expansion coefficient of the bonding material and its wettability to metal.

The solid synthesis of  $\text{ZrSiO}_4$  is very difficult, it must be conducted at relatively higher temperatures, and the synthesized powders are

large in size and wide in distribution range, which is unfavourable for application. Subrt *et al*<sup>[7]</sup> and Zdujio *et al*<sup>[8]</sup> reported that the surface activation of the mixed powders caused by mechanical ball milling or grinding could promote the formation of compound oxides or even high-temperature phases. Under the actions of external forces, the macroscopic changes of the powders are the refinement of particles and the increase of the specific surface area, while the microscopic changes are the lattice distortion, the formation of lattice defects or even the occurrence of amorphousness, as a result, the powders are at high-energy metastable states. These mechanically activated powders have higher activity and stronger reaction abilities, thus can find wider applications in industries.

This paper reports the synthesis process of  $\text{ZrSiO}_4$  using mechanically activated mixed powders of  $\text{ZrO}_2$  and  $\text{SiO}_2$  and its application as an additive to a bonding material for brazing ceramics to metal.

## 2 EXPERIMENTAL

The raw materials for making the  $\text{ZrSiO}_4$

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powder were  $\text{ZrO}_2$  and colloidal  $\text{SiO}_2$  prepared by wet chemical method. X-ray diffraction analysis and size analysis of the raw materials show that  $\text{ZrO}_2$  is monoclinic (simplified as m- $\text{ZrO}_2$ ) with a grain size of 0.1~1  $\mu\text{m}$ , and  $\text{SiO}_2$  is amorphous (simplified as  $\alpha$ - $\text{SiO}_2$ ) with a grain size of about 0.5  $\mu\text{m}$ . After mixing m- $\text{ZrO}_2$  and  $\alpha$ - $\text{SiO}_2$  powders in equal mole fraction, the mixed powders were put in a steel attritor canister. The charge mass was 200 g; the ball diameters were 5 mm and 10 mm; the mass ratio of charge to ball was 1:3; the stirring ball crusher of a volume of 1.2 L was rotated at 250 r/min; the milling time was 40~120 h; no cooling system and protecting atmosphere were adopted. The as-milled powder was calcined at 700~1300  $^{\circ}\text{C}$  for 2 h.

The structural analyses were conducted with  $\text{CuK}\alpha$  radiation on SIMENS D/500 diffractometer by continuous scanning. The grain sizes were measured on small-angle Rigaku diffractometer with  $\text{CuK}\alpha$  radiation by step scanning at a rate of  $(1/32)^{\circ}/\text{step}$  (Kratky seam). The thermal analyses were performed on Dupont 9900 differential thermal analyzer at a rate of 10  $^{\circ}\text{C}/\text{min}$ . FT-IR spectra were measured on 740 FT-IR infrared spectrum analyzer.

The application of the synthesized  $\text{ZrSiO}_4$  to a bonding material for brazing ceramics to metal was also studied. The bonding material with additive of synthesized or natural  $\text{ZrSiO}_4$  was made into small balls of  $d=8\text{ mm}$ ; the balls were placed on surface-polished metallic plate and sintered at 700  $^{\circ}\text{C}$  for 30 min in muffle furnace. The wettability of the bonding material to the metal plate was evaluated by the spreading area; the larger the spreading area, the better the wettability. The thermal expansion coefficient of the bonding material was measured on DL-1500 dilatometer with bar samples.

### 3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of the mixed powder after milling for 120 h and calcination at different temperatures for 2 h. It can be seen that the particle sizes of  $\text{ZrO}_2$  and  $\text{SiO}_2$  are decreased but their crystal lattices remain un-

changed, i. e.  $\text{ZrO}_2$  is still monoclinic while  $\text{SiO}_2$  is still amorphous. After calcination at 1000  $^{\circ}\text{C}$ , there occur no new phases except that the diffraction peaks become a bit sharp. After calcination at 1100  $^{\circ}\text{C}$ , there forms a little  $\text{ZrSiO}_4$  phase and occurs a weak diffraction peak of tetragonal  $\text{ZrO}_2$  (simplified as t- $\text{ZrO}_2$ ). After calcination at 1200  $^{\circ}\text{C}$ , the powder is mainly composed of  $\text{ZrSiO}_4$  and a little m- $\text{ZrO}_2$ . Quantita-

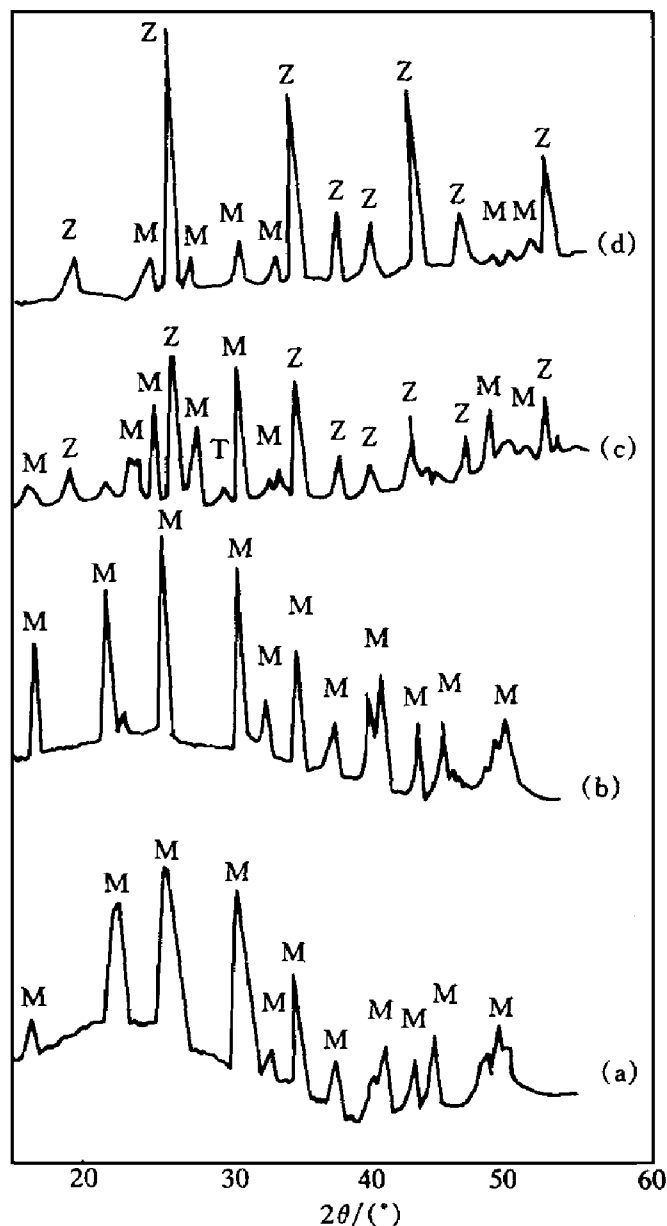
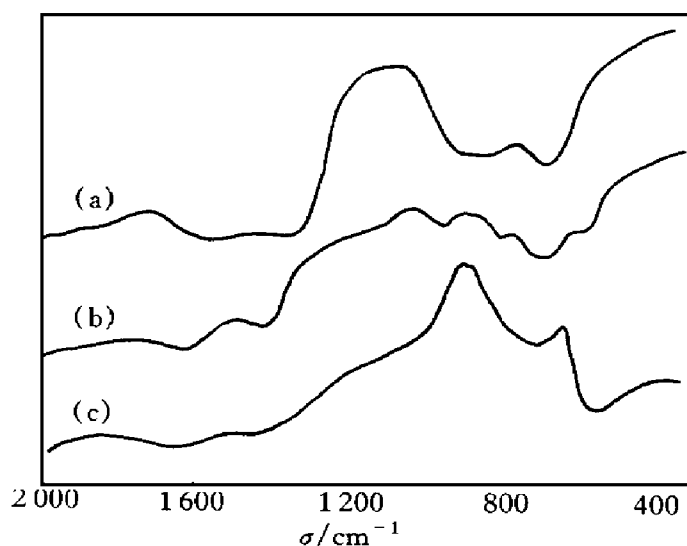


Fig. 1 XRD spectra of mixed power after milling and calcination at different temperatures

- (a) —As-milled;
- (b) —Milled+ calcined at 1000  $^{\circ}\text{C}$  for 2 h;
- (c) —Milled+ calcined at 1100  $^{\circ}\text{C}$  for 2 h;
- (c) —Milled+ calcined at 1200  $^{\circ}\text{C}$  for 2 h;
- Z— $\text{ZrSiO}_4$ ; M—m- $\text{ZrO}_2$ ; T—t- $\text{ZrO}_2$

tive analysis shows that the content of  $\text{ZrSiO}_4$  is over 95%. Calcination at higher temperatures does not affect the crystal lattices and phase constituents of the resultant powder. The content of  $\text{ZrSiO}_4$  cannot reach 100% even if the mixed powders are calcined at 1 300 °C. It can be seen from the FT-IR spectra in Fig. 2 that after calcination at 1 100 °C and 1 200 °C, there occur characteristic adsorption peaks of  $\text{ZrSiO}_4$  (vibrating adsorption peaks of  $\text{Zr-O-Si}$  bonds) at  $670\text{ cm}^{-1}$  and  $910\text{ cm}^{-1}$ , respectively. Both peaks enhance with increasing calcination temperature.

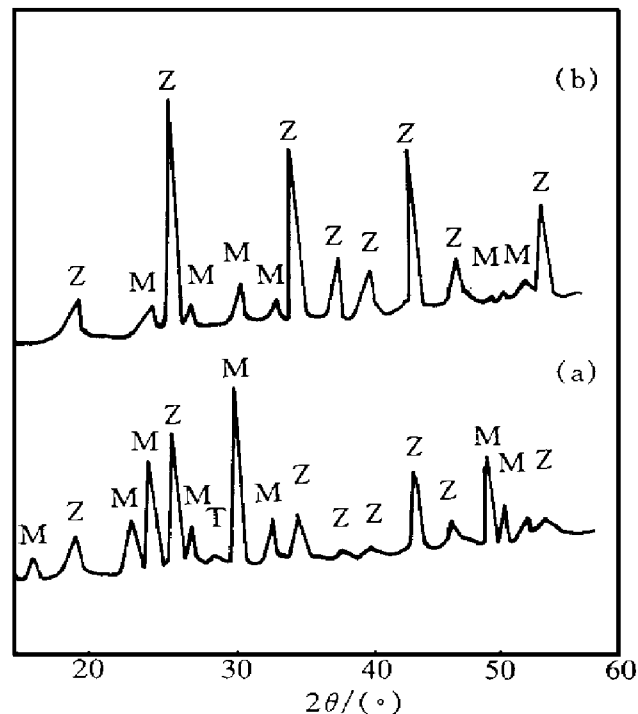


**Fig. 2** FT-IR spectra of mixed powder after milling for 120 h and calcination at 1 000 °C (a), 1 100 °C (b) and 1 200 °C (c)

The mechanical ball milling has a great effect on the formation rate of the  $\text{ZrSiO}_4$ . The mixed powders of  $\text{ZrO}_2$  and  $\text{SiO}_2$  without ball milling does not form  $\text{ZrSiO}_4$  after calcination at 1 300 °C for 3 h, while the mixed powders after milling for 120 h and calcination at 1 200 °C form more than 95% of  $\text{ZrSiO}_4$ . Fig. 3 shows the effect of ball milling on the formation rate of  $\text{ZrSiO}_4$ . After calcination at 1 200 °C for 40 h, the formation rate of  $\text{ZrSiO}_4$  in the mixed powders is about 40%.

Under the action of mechanical force, there will occur lattice distortion, local damage and various defects, or even form amorphous phases in the extreme cases in the solid materials, thus their free energies and reaction activities are improved. Li *et al.*<sup>[9]</sup> reported that after mechanical

activation for 20 min, the activation energy of pyrite was reduced to 52 kJ/mol from 69 kJ/mol, and after mechanical activation for 40 min, this value was further reduced to 48 kJ/mol. Our experiments also show that the mechanical activation makes the formation of the  $\text{ZrSiO}_4$  phase much easier. The grain size analysis by small angle X-ray scattering shows that the mean size of the synthesized  $\text{ZrSiO}_4$  is 0.6  $\mu\text{m}$  and the grain size ranges from 0.1  $\mu\text{m}$  to 2  $\mu\text{m}$ .



**Fig. 3** XRD spectra of mixed powder after milling for 40 h (a) and 120 h (b) and then calcination at 1 200 h

The pressure-tight brazing of ceramics to metal is necessary to be conducted in many industrial departments. The oxide brazing is a new but fast-developing brazing technology. A knotty problem in synthesizing bonding materials is how to improve the wettabilities of ceramics to metals, because only those bonding materials with good wettabilities can satisfy the pressure-tight requirements.  $\text{ZrSiO}_4$  is often used to adjust the thermal expansion coefficients of ceramics and other non-metallic materials; the natural  $\text{ZrSiO}_4$  can reduce the thermal expansion coefficients of the bonding materials, but simultaneously degrades the wettabilities of bonding materials to metals, while the mechanically activated

synthesized  $\text{ZrSiO}_4$  as an additive to the bonding materials not only reduces the thermal expansion coefficients of the bonding materials, but also has good wettability to copper and copper alloys. Fig. 4 shows the effects of bonding materials with additions of synthesized or natural  $\text{ZrSiO}_4$  on the wettabilities. It can be seen that the addition of the synthesized  $\text{ZrSiO}_4$  has no harmful effect on the wettability of the bonding material, while the addition of natural  $\text{ZrSiO}_4$  greatly degrades the wettability. Fig. 5 shows the effect of

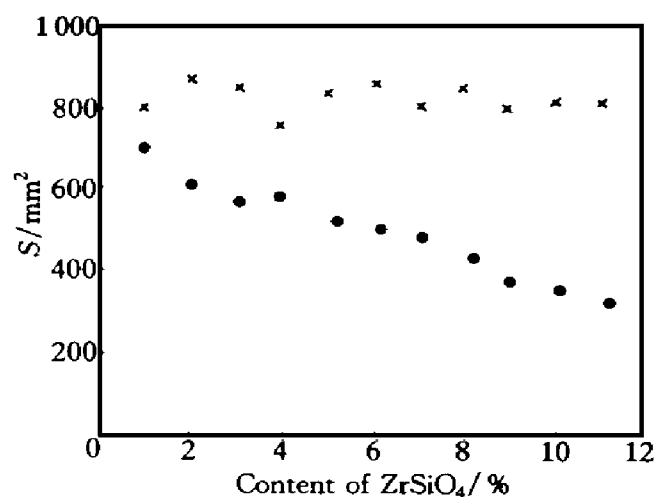


Fig. 4 Effects of addition of  $\text{ZrSiO}_4$  on wettability of bonding material

× —Synthesized  $\text{ZrSiO}_4$ ; ● —Natural  $\text{ZrSiO}_4$

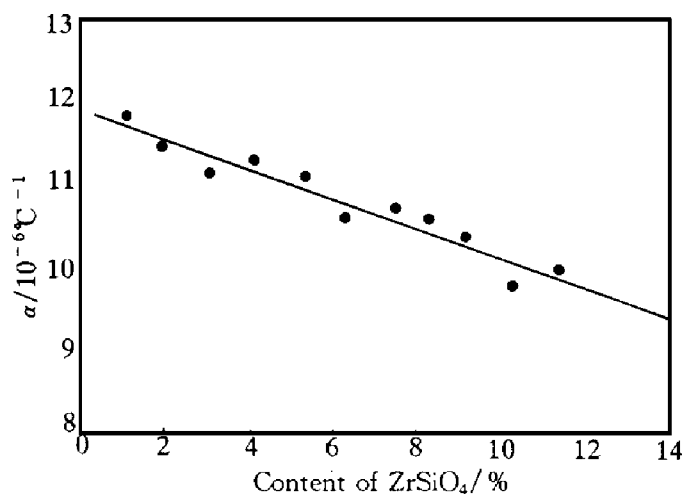


Fig. 5 Effect of addition of synthesized  $\text{ZrSiO}_4$  on thermal expansion coefficient of bonding material

adding synthesized  $\text{ZrSiO}_4$  on the thermal expansion coefficient of the bonding material. The results show that when the addition of the mechanically activated synthesized  $\text{ZrSiO}_4$  is 9%, the bonding material can be used to obtain high-quality pressure-tight brazing of  $\text{Al}_2\text{O}_3$  ceramics to copper or copper alloys.

## 4 CONCLUSIONS

(1) After milling the mixed powders of monoclinic  $\text{ZrO}_2$  and colloidal  $\text{SiO}_2$  for 120 h, ultrafine highly activated  $\text{ZrSiO}_4$  powder can be obtained by calcination at 1 200  $^\circ\text{C}$ , and its formation rate can be over 95%.

(2) The synthesized  $\text{ZrSiO}_4$  has high surface activity. When it is used as an additive to a bonding material, the bonding material can be used to obtain high-quality pressure-tight brazing of  $\text{Al}_2\text{O}_3$  ceramics to copper and copper alloys.

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