# THE EFFECT OF ALN AS SINTERING AIDS ON MICROSTRUCTURE AND PROPERTIES OF $ZRB_2$ CERAMIC COMPOSITE

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***Abstract***

*The characteristics of advanced ultra-high temperature ceramics (UHTCs), such as strength at high temperature and oxidation resistance, allow them to be used in extreme environments including those associated with hypersonic flight, atmospheric re-entry and rocket propulsion. $ZrB_2$+εvol.%SiC ceramic composites were prepared by hot-pressing in a flowing argon atmosphere with AlN as a sintering aid in this paper. Compared with additive free $ZrB_2$, the doping of aluminium nitride as a sintering aid greatly improves the powder sinterability of zirconium diboride and nearly full dense composites were obtained by hot pressing. The mechanical properties were enhanced remarkably through these improvements in the sinterability and microstructure. The relation between sintering aid and sintering dynamics of $ZrB_2$ based UHTCs was investigated. The microstructures of the ceramic composites were investigated by SEM, EDS et.al. Mechanical and high temperature ablation resistant properties of the ceramic composites were tested using oxyacetylene facility.*

## 1 Introduction

The advanced ultra-high temperature ceramics (UHTCs) that allow them to be used in extreme environments possess high strength and oxidation resistance at high temperature. Transition metal borides such as $ZrB_2$ based composite have melting temperatures in excess of 3000℃ making it candidates for use as structural materials at temperatures above 1800℃[1-5]. $ZrB_2$ is reported to have excellent resistance to thermal shock and oxidation compared to other non-oxide structural ceramics. $ZrB_2$ is of interest for thermal protection materials because of favorable thermal stability, mechanical properties, and oxidation resistance.

Current research activities are still facing barriers to overcome their poor sinterability that limit a feasible dense components at affordable manufacturing conditions where temperature below 2000℃[6-7]. In order to improve the powder sinterability and mechanical properties of zirconium diboride, the aluminum nitride as a sintering aid was applied in fabricating ceramic composite by hot pressing. The role of additives for the sintering of covalent-bonded ceramics can be regarded as not only densification aids but also key elements for the microstructural development, since the kinds and amounts of additives influence the related properties of materials.

This study deals with the improvement in sinterability by hot pressed with the addition of AlN, The selection of sintering aid and sintering dynamics, microstructure and mechanical and high temperature ablation properties of $ZrB_2$ ceramic composite were studied.

## 2 Experimental procedure

Commercially available raw powders were used in this study. The $ZrB_2$ powders (Northest Institute For Non-ferrous Metal Research, China) had a purity of >99.5% and a particle size of 5 μm. The SiC powder (Xuzhou Hongwu Nanometer Materials, China) was predominantly α-SiC, and it had a reported purity of 98.5% and a particle size of 2 μm. Powders containing $ZrB_2$-SiC-AlN were mixed by wet ball-milling them for 8h in a polyethylene bottle, using WC balls and acetone as media. After mixing, the slurry was dried in a rotating evaporator. The usual ball-to-powder mass ratio employed was 3:1. The powder mixtures were fabricated by hot pressing in graphite dies which was lined boron nitride to

protect the dies from reacting with the powders. The powders were heated to a predetermined temperature at a heating rate of 15℃/min. At the same time, a pressure of 25~30MPa was applied. After holding for 60 min, the pressure was released and the sample was cooled to temperature below 200℃ in 4 hour. To be compared, $ZrB_2$ containing εvol.%SiC composite (ZS) was fabricated by hot-pressing at 2000℃ under 30MPa for 1 hour.

The final density of all $ZrB_2$ ceramic composites was measured using the Archimede's method, while the relative density was estimated by the rule of mixture. The microstructural features were analyzed by SEM on polished sections of the sintered samples. Flexural strength (σ) was in a three-point bending configuration tested at room temperature on 36.0×4.0×3.0mm$^3$ bar and a crosshead speed of 0.5 mm/min. Fracture toughness ($K_{Ic}$) was evaluated on 22.0×4.0×2.0mm$^3$ bars and the crosshead speed of 0.05 mm /min.Selected sample specifications and density of $ZrB_2$ based ceramics are listed in Table 1.

Table1 Selected sample specifications and density

| Sample | Content, vol.% | Abb | Density, % |
|---|---|---|---|
| 1 | $ZrB_2$+εSiC | ZS | 92 |
| 2 | $ZrB_2$+$\varepsilon_1$SiC+$\eta_1$AlN | ZSA1 | 97.2 |
| 3 | $ZrB_2$+$\varepsilon_2$SiC+$\eta_2$AlN | ZSA2 | 98.3 |
| 4 | $ZrB_2$+$\varepsilon_3$SiC+$\eta_3$AlN | GZSA | 100 |

## 3 Results and discussion

### 3.1Microstructure of $ZrB_2$-SiC-AlN Composite

#### *3.1.1 Sintering Dynamics*

The curve of sintering dynamics at different temperature was shown in Fig.1.

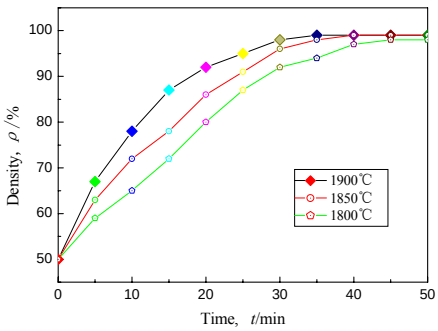


Fig.1 The curve of sintering dynamics at different temperature

The relatively density of $ZrB_2$ ceramic composite which improved with sintering temperature elevation can reach over 95% in 30 minutes.

The expression of instantaneous sintering speed according to Eq.(1):

$$\frac{d\rho}{dt} = A(\exp-\frac{Q/RT}{T})\left[f(\rho)/d^n\right] \quad (1)$$

where $A = C_\gamma V^{2/3}/R$ , $Q$ is sintering activation energy, $d$ is grain size, $n$ is a power exponent which depend on the relationship between $d$ and density rate, $A$ is material factor, $\gamma$ is surface energy, $V$ is molar volume, $C$ is constant, $f(\rho)$ is functions related to density. By getting the logarithm of Eq.(1):

$$\ln(Td\rho/dt) = Q/RT + \ln[f(\rho)] + \ln A - n\ln d \quad (2)$$

The relationship between density rate and time according to Eq.(2) was shown in Fig.2. The density rate reaches maximum value when sintering time is 20 minutes and then monotonically decreases trend during sintering process.

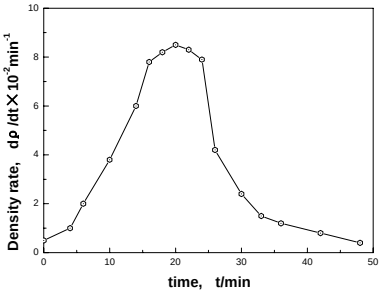


Fig.2 The relationship between density rate and time

#### *3.1.2 The Effect of AlN as Sintering Aids*

The boride oxide layer presenting on the surface of $ZrB_2$ powder played an adverse effect on its densification. To the $ZrB_2$ ceramic composites, some references have reported that AlN reacting with $B_2O_3$ which derives from the oxygen contamination upon the surface of the $ZrB_2$ particles, formed amorphous boron glass phase [8-9]. The addition of AlN can improve the sinterability of $ZrB_2$ by eliminating the oxide layers on the surface of $ZrB_2$ powder according to Eq.(3)[9]:

$$AlN + B_2O_3 \rightarrow BN + Al_2O_3 \quad (3)$$

It is therefore expected that effect of the AlN addition is to reduce the oxygen content of the $ZrB_2$ particles at relative low temperature during hot-pressing.

Compared with material ZS which relative density is 92%, the hot pressed ZSA specimens were at least 97% of theoretical density and were generally free of inherent defects. The relative density of GZSA is

definitely higher than ZS and ZSA can reach maximum value 100% (see Table 1).

*3.1.3 Microstructure of $ZrB_2$-SiC-AlN Composite*

The addition of AlN changed the sinterability and microstructure of the ZrB2 matrix composites remarkably, as shown in Fig.3. ZS had some residual porosity that scarcely dispersed on the boundary of $ZrB_2$ and SiC particles, as shown in Fig.1(a). Moreover, sintering temperature is 2000℃ and higher temperature can bring on the excessive growth of $ZrB_2$ particles which grain size is 5~8μm.

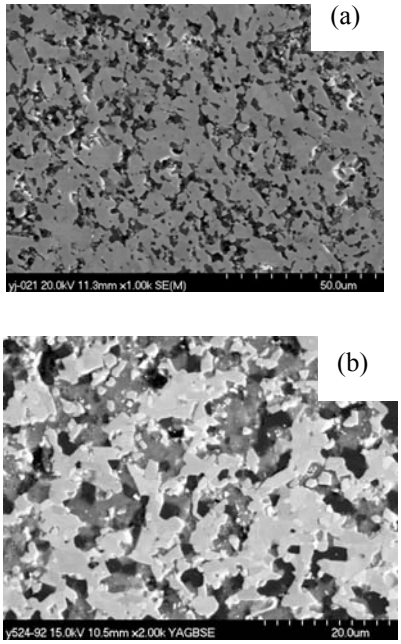


Fig.3 Microstructure of ZS and ZSA
(a)-ZS (b) –ZSA

The microstructure of ZSA is rather homogeneous, mean grain size is about 3μm and the residual porosity is very scarce (Fig. 3b). For one thing, that is because reaction process between AlN and boride oxide on the surface of $ZrB_2$ particles, which was envisioned to produce a ductile grain boundary phase at lower temperature to enhance densification. The other is due to the solid solution formed during hot pressing by reaction between aluminum nitride and silicon carbide.

It is obvious that the sintering aid plays a significant role during hot pressing. The mechanisms of sintering activation by doping can increase in volume diffusion and cause retardation of evaporation by the presence of a liquid phase[8]. The occurrence of a liquid phase not only favors $ZrB_2$ particle rearrangement but also enhances mass transfer kinetics. Without additives (as in the case of ZS), exaggerated grain growth is associated with rather slow densification due to surface oxide ($B_2O_3$) that retards diffusion mechanisms.

### 3.2 Mechanical Properties of $ZrB_2$ Ceramic Composite

The changes in the microstructure and the grain-boundary phase influenced the mechanical properties of $ZrB_2$ matrix composites significantly. To maintain fine grain sizes in $ZrB_2$ composite, processing temperatures must remain below 2000℃. The experimental values of mechanical properties were listed in Table 2. The 3-point flexural strength of material ZS at room temperature (RT) is 540~590 MPa and the fracture toughness is 3.20~3.50MPa·$m^{1/2}$. The maximum room temperature flexural strength and fracture toughness of ZSA and GZSA are higher than ZS, reaching 760MPa, 840MPa and 4.19 MPa·$m^{1/2}$, 5.73MPa·$m^{1/2}$ respectively.

Table2 Mechanical properties of hot pressed materials

| Material | $K_{IC}$, MPa·$m^{1/2}$ | σ, MPa |
|---|---|---|
| ZS | 3.20~3.50 | 540~590 |
| ZSA1 | 3.65~4.19 | 746~760 |
| ZSA2 | 3.72~4.17 | 501~634 |
| GZSA | 5.24~5.73 | 810~840 |

*3.2.1 Flexural Strength*

The flexural strength of material ZS, ZSA and GZSA is shown in Fig.4. The increase of the flexural strength of $ZrB_2$ composite is related to the optimal content of aluminum nitride as sintering aid. The flexural strength values of ZSA and GZSA can be all improved compared with materials ZS.

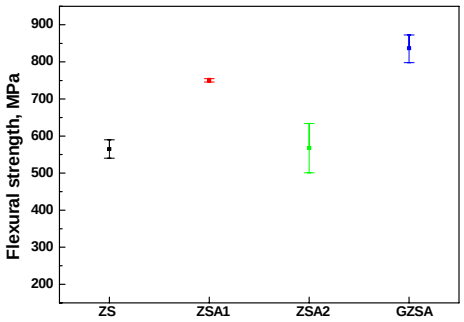


Fig.4 Flexural strength of ZS、ZSA and GZSA

The strengthen effect of ZSA1 and ZSA2 with different AlN content which indicates that the content of AlN exist an optimal range under hot-pressing condition. The flexural strength value by adding optimal sintering aid content can be

improved obviously, and the maximum RT flexural strength can reach or over 840MPa .

*3.2.2 Fracture Toughness*

The fracture toughness of material ZS, ZSA and GZSA is shown in Fig.5. Similarly, the increase of the fracture toughness of $ZrB_2$ composite is changed with the content of aluminum nitride. The fracture toughness values of ZSA and GZSA are higher than material ZS. The toughening effect of ZSA1 and ZSA2 is slightly different according to the different content of AlN. It indicates that the fracture toughness of $ZrB_2$ composite can be improved obviously by adding AlN as a sintering aid.

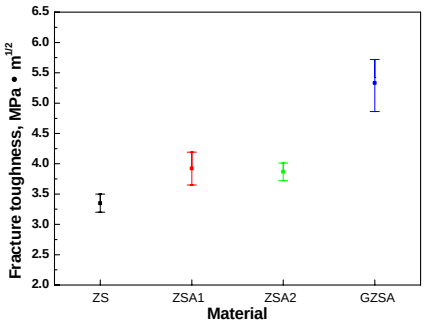


Fig.5 Fracture toughness of ZS、ZSA and GZSA

## 3.3 Ablation Properties

The ablation experiment of $ZrB_2$ ceramic composite is investigated by oxyacetylene blaze according to country standard. The ZSA composite was heated to 2340℃ for 300s and 2467℃ for 600s respectively. The relationship between ablative temperature and time was shown in Fig.6. The ablative set and material surface after ablation was shown in Fig.7.

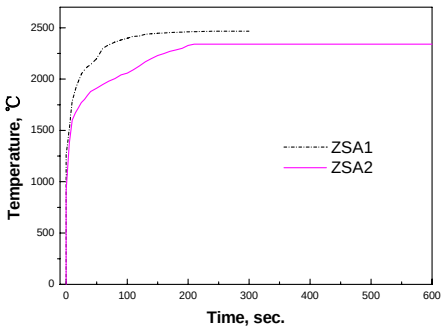


Fig.6 The relationship between ablative temperature and time

The profile of ZSA composite with a white oxidation film on the surface was intact. The result of diffraction patterns of surface after ablation was shown in Fig.8. XRD analysis was clearly confirmed the existence of crystalline $ZrO_2$ on the surface of material ZSA after ablation. The surface ablation is basically constituted by $ZrO_2$ particles, that is mainly caused by the oxidation of $ZrB_2$ within an oxidizing atmosphere. In addition to $ZrB_2$ composite, oxidation product on the surface was the C-O-Al-Zr systems (Fig.9 (a)) by EDS analyses detected.

Fig.7 Photo of ablative facility and material surface after ablation

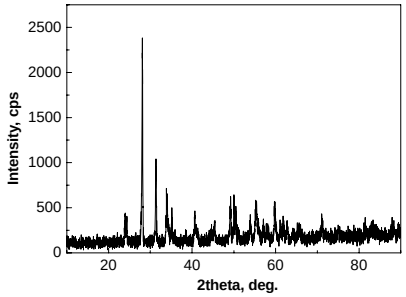


Fig.8 XRD patterns of ZSA after ablation

The microstructure of the surface oxidation area on the cross-sections of the bars ablated at high temperature under oxyacetylene ablation condition was detected by SEM-EDS analyses. The microstructural SEM investigation, shown in Fig.9, evidences the microstructure changes in materials ZSA, depending on temperature of blaze.

The microstructure of the transition layer in the sub-surface of the tested specimens contains the C-O-Al-Zr systems which could significantly depressed in the matrix material at high temperature in material ZSA (Fig.9(b)). The occurrence of loosen area by the SEM analyses confirm that the decrease of flexural strength at high temperature. It should be admitted that the sealing of gas formed during ablation by oxyacetylene blaze under oxidizing environment.

The systems containing C–O–Al–Si–Zr (Fig.9(c)) is the non-ablative area that indicated that the thickness of oxidation is very small in the material ZSA experienced under such an oxidizing condition.

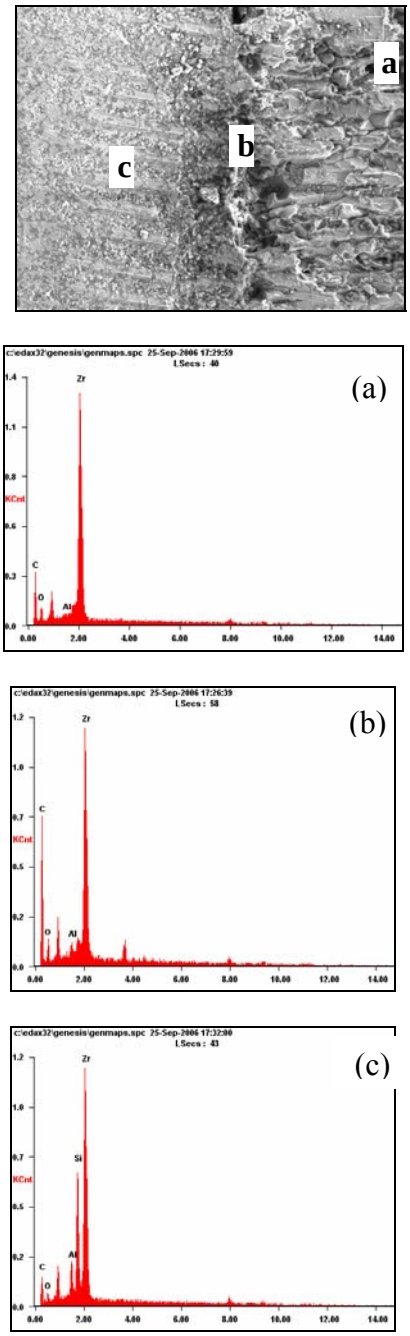


Fig.9 EDS patterns of ZSA after ablation

## 4 Conclusions

The effect of AlN as sintering aids on microstructure and properties of $ZrB_2$ ceramic composite was analyzed in detail. The major results of current analyses can be summarized as follows:

(1)The room temperature mechanical properties of ZSA ceramic composite were improved due to the introduction of the sintering aids. The fracture toughness and flexural strength at R.T was 5.73MPa·$m^{1/2}$ and 840 MPa respectively.

(2) The role of AlN as a sintering additive to the $ZrB_2$ ceramic composite was to reduce the sintering temperature and enhance the density. The effect of the optimal content for AlN as sintering aids on mechanical properties is notable.

(3) The microstructure of $ZrB_2$ ceramic composites after ablation by oxyacetylene blaze according to country standard is investigated. The surface oxidation area on the cross-sections of the bars after oxyacetylene ablation was detected by SEM-EDS analyses. The EDS results on surface regions are consistent with $ZrO_2$.

## Acknowledgements

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