

COMBUSTION SYNTHESIS OF $(\alpha+\beta)$ -SiAlON COMPOSITES

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Introduction

Sialon is considered as a promising high-temperature structural material, due to its excellent mechanical properties and chemical stability [1-4]. There are two well-known sialons, α - and β -SiAlON, which are solid solutions based upon structural modifications of α - and β -Si₃N₄, respectively. α -SiAlON can be described by the formula $Me_{m/v}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ (Me stands for an interstitial metal ion of valence v) and β -SiAlON by Si_{6-z}Al_zO_zN_{8-z}. The α -SiAlON ceramics are in the form of equiaxed grains and feature high hardness, good wear and oxidation resistance, and excellent thermal shock resistance [3,4]. The β -SiAlON phase appears as elongated grains in the microstructure and is characterized by good fracture toughness [3,4].

The objective of this study is to investigate the effect of starting stoichiometry of the sample on the formation of α - and $(\alpha+\beta)$ -SiAlON through combustion synthesis in the SHS mode. The powder compacts were formulated with different molar ratios of Si/Si₃N₄ and various proportions of α/β -Si₃N₄. In addition, the effect of sample stoichiometry was explored on the combustion characteristics, including the propagation mode of self-sustaining combustion, flame-front velocity, and combustion temperature.

Experimental

The starting materials of this study included Yb₂O₃ (99.9%), Si ($\leq 45 \mu\text{m}$, 99%), α -Si₃N₄ ($\leq 45 \mu\text{m}$, 99%), β -Si₃N₄ ($\leq 45 \mu\text{m}$, 99%), SiO₂ ($\leq 45 \mu\text{m}$, 99.6%), Al (10 μm , 99.9%), and AlN (99%). Tables 1 and 2 list the starting compositions for the synthesis of α - and $(\alpha+\beta)$ -SiAlON, respectively. It should be noted that Si₃N₄ used in the samples of Table 2 can be the α or β phase, or a mixture of both. When green samples with mixed α - and β -Si₃N₄ powders were prepared, the proportion of α/β -Si₃N₄ ranged between 20/80 and 80/20. The reactant powders were dry mixed in a ball mill and pressed into cylindrical samples with a diameter of 7 mm, a height of 12 mm, and a compaction density of 40% relative to the theoretical maximum density (TMD). The SHS experiments were conducted in a combustion chamber under nitrogen of 2.17 MPa. A preheating temperature of 150 °C was required to assure self-sustaining combustion. Details of experimental setup and approach were reported elsewhere [5].

Table 1 Summary of starting compositions of samples for combustion synthesis of α -SiAlON

Samples	Compositions (mol%)			
	Yb ₂ O ₃	Si	α -Si ₃ N ₄	Al
SN01	2.73	59.77	12.89	24.61
SN02	2.80	57.61	14.39	25.20
SN03	2.86	55.51	15.85	25.78
SN04	2.95	52.95	17.64	26.46
SN05	3.04	49.73	19.88	27.35
SN06	3.16	45.58	22.78	28.48

Table 2 Summary of starting compositions of samples for combustion synthesis of $(\alpha+\beta)$ -SiAlON

Samples	Compositions (mol%)					
	Yb ₂ O ₃	Si	Si ₃ N ₄	SiO ₂	Al	AlN
SA1	3.00	47.58	19.02	1.13	20.91	8.36
SA2	2.91	50.74	16.90	1.09	20.26	8.10
SA3	2.83	53.26	15.20	1.06	19.76	7.89
SA4	2.77	55.27	13.80	1.04	19.36	7.76
SA5	2.72	57.00	12.65	1.02	19.01	7.60

Results and Discussion

The recorded sequence illustrating the SHS process on the formation of α -SiAlON from the sample SN05 is shown in Fig. 1, which features one or two localized reaction zones propagating spirally along the sample in a self-sustaining manner. The dilution of powder compacts with nitride phases of high concentrations could be responsible for the spinning combustion zone observed in this study.

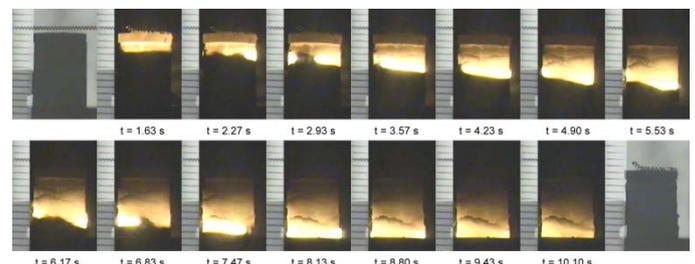


Fig. 1. A typical SHS sequence showing spiral propagation of combustion waves along the sample of SN05.

The reaction front velocity increases from 1.1 mm/s for the sample SN01 with increasing Si₃N₄ and approaches an asymptotic value of about 1.36 mm/s for the samples of SN05 and SN06. The increase of combustion velocity is due to an increase in the magnitude of reaction enthalpies liberated by enhanced nitridation of Si and Al. As Si₃N₄ is

further increased, the dilution effect of Si_3N_4 compensates the increase of reaction exothermicity.

The influence of the phase of Si_3N_4 on combustion velocity is presented in Fig. 2 for the samples of SA1 and SA2. An increase in the flame-front velocity with increasing ratio of $\alpha/\beta\text{-Si}_3\text{N}_4$ was observed. In Fig. 2, the lowest combustion wave velocity of 0.82 mm/s was detected in the sample SA2 containing 100% $\beta\text{-Si}_3\text{N}_4$. This is attributed to the fact that in addition to $\alpha\text{-SiAlON}$ the introduction of $\beta\text{-Si}_3\text{N}_4$ leads to the formation of $\beta\text{-SiAlON}$, which reduces the overall reaction exothermicity.

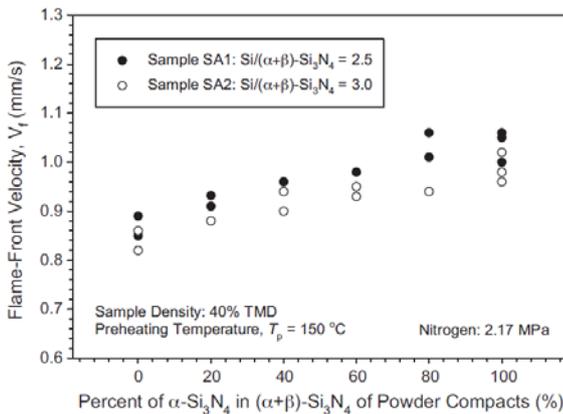


Fig. 2. Effect of molar proportion of α - to $\beta\text{-Si}_3\text{N}_4$ on flame-front velocity of powder compacts of SA1 and SA2.

XRD patterns of the products from samples of SN01-SN06 identify $\alpha\text{-SiAlON}$ as the dominant phase along with different amounts of Si. The presence of a large quantity of Si in the sample SN01 is caused by the significant sample melting that impedes the penetration of nitrogen. With the increase of the molar ratio of $\text{Si}_3\text{N}_4/\text{Si}$, the amount of Si left unreacted is considerably reduced. For the sample SN06, the residual Si is trivial in the final product.

For the green samples containing a mixture of α - and $\beta\text{-Si}_3\text{N}_4$, as indicated in Fig. 3(a)-(c), the products are $(\alpha+\beta)\text{-SiAlON}$ composites and the content of $\beta\text{-SiAlON}$ increases with decreasing ratio of $\alpha/\beta\text{-Si}_3\text{N}_4$. It is interesting to point out that even the sample with 100% $\beta\text{-Si}_3\text{N}_4$ also yields a composite of $(\alpha+\beta)\text{-SiAlON}$ and the corresponding XRD pattern is depicted in Fig. 3(d). For the samples of SA1 and SA2 with 100% $\beta\text{-Si}_3\text{N}_4$, comparable amounts of α - and $\beta\text{-SiAlON}$ about 46%-54% in the final composites. When a mixture of $(\alpha+\beta)\text{-Si}_3\text{N}_4$ was adopted, the increase of $\alpha\text{-Si}_3\text{N}_4$ enhanced the formation of $\alpha\text{-SiAlON}$. The content of $\alpha\text{-SiAlON}$ rises almost linearly to about 90% for the

sample with $\alpha/\beta\text{-Si}_3\text{N}_4 = 80/20$ and only $\alpha\text{-SiAlON}$ is present in the case of using 100% $\alpha\text{-Si}_3\text{N}_4$.

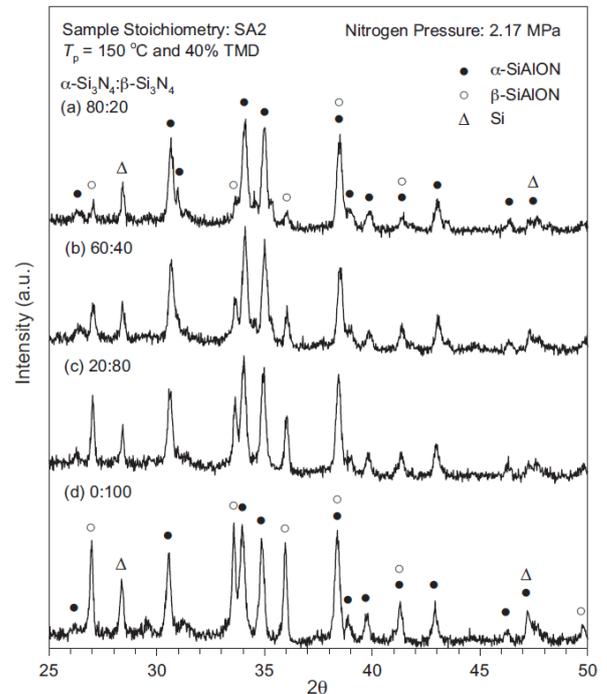


Fig. 3. XRD patterns of products from samples of SA2 with $\alpha\text{-Si}_3\text{N}_4$: $\beta\text{-Si}_3\text{N}_4 =$ (a) 80:20, (b) 60:40, (c) 20:80, and (d) 0:100.

Conclusions

For the sample containing pure $\alpha\text{-Si}_3\text{N}_4$, the SHS reaction yielded only $\alpha\text{-SiAlON}$. As a mixture of $(\alpha+\beta)\text{-Si}_3\text{N}_4$ was employed, the products were $(\alpha+\beta)\text{-SiAlON}$ composites, within which the content of $\beta\text{-SiAlON}$ increased with $\beta\text{-Si}_3\text{N}_4$. For the sample adopting 100% $\beta\text{-Si}_3\text{N}_4$, comparable amounts of α - and $\beta\text{-SiAlON}$ were produced.

References

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