Volume 54

2009

tions. The fabrication of SiAlON from pure raw material is expensive, and for this reason, SiAlON has been synthesized using clay minerals [4, 5, 6] and different solid

ciekłej. Termiczna analiza różnicowa przeprowadzona na próbce-parze dyfuzyjnej Cu-Ti nie ujawniła pików egzotermicznych mogących świadczyć, że reakcje tworzenia faz międzymetalicznych są typu SHS. Obserwacje mikroskopowe oraz mikroanaliza rentgenowska pozwoliły, w oparciu o układ równowagi fazowej miedź-tytan, rozpoznać szereg związków międzymetalicznych tworzących warstwę na granicy między miedzią a tytanem. Z pomiarów wynika, że gdy proces syntezy faz międzymetalicznych zachodzi z udziałem fazy ciekłej wzrost warstwy faz międzymetalicznych jest wielokrotnie szybszy niż w przypadku przemian strukturalnych zachodzących w wyniku dyfuzji reaktywnej. Pokazano, że z blachy miedzianej i folii tytanu ułożonych naprzemiennie w pakiet uzyskać można, na drodze wysokotemperaturowej syntezy faz międzymetalicznych z udziałem fazy ciekłej, kompozyt miedź-fazy międzymetaliczne. Utworzone w wyniku syntezy warstwy kompozytu zawierające fazy międzymetaliczne

Badano przemiany strukturalne związane z nową techniką uzyskiwania z blach miedzi i tytanu kompozytów warstwowych miedź-fazy międzymetaliczne. Analizowano wysokotemperaturowy proces formowania i wzrostu warstwy faz międzymetalicznych na granicy między miedzią a tytanem, który może przebiegać zarówno na drodze dyfuzji reaktywnej, jak i z udziałem fazy

# 1. Introduction

połączone są metalurgicznie z warstwami miedzi.

SiAlON ceramics are excellent materials for structural applications.  $\beta$ -SiAlON has a high fracture toughness and oxidation resistance at 1400°C [1]. These ceramics have a wide range of technically important applications, from cutting tools to specialized refractories. β-SiAlON is synthesized by different methods such as self-propagating at high-temperature (>1500 °C) [2] and carbothermal reduction by nitridation at 1450°C [3], where the SiAlON formation occurs by the vapor-liquid-solid mechanism [2]. Typically, to obtain such kind of ceramic, it is necessary to use high-purity powders in order to reach chemical equilibrium according to the formula  $Si_{6-z}Al_zO_zN_{8-z}$ , where the subscript z varies from 0.5 to 4.5 to obtain  $\beta$ -SiAlON solid solu-

waste materials such as aluminum dross [7]. β-SiAlON has been also obtained using fly ash [8]. One of the important characteristic of fly ash is its high content of spherical particles (cenospheres) with a high content of SiO<sub>2</sub> (50-60%), Al<sub>2</sub>O<sub>3</sub> (20-35%) and amorphous material [9]. Basically, the whisker formation depends on the impurities of the material, the morphology of the starting particles and the formation of an eutectic phase that acts as active site for nucleation. Taking into account that cenospheres have not been used for obtaining β-SiAlON, the main objective of this work is to inves-

Issue 2

## β-Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> SYNTHESIS BY CARBOTHERMAL NITRIDATION AT LOW TEMPERATURE USING CENOSPHERES

# NISKOTEMPERAUROWA SYNTEZA $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> DROGĄ KARBOTERMICZNEJ REDUKCJI I AZOTOWANIA PRZY UŻYCIU CENOSFER

 $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> was synthesized by carbothermal reduction of cenospheres at 1250°C for 5h under nitrogen atmosphere. The effect of AlN addition on β-SiAION formation was also studied. Mixtures of cenospheres, C and AlN (1.2, 2.4, 3.6 and 4.8wt%) were homogenized and disk pellets of 1.5 cm in diameter were conformed by uniaxial pressing at 20MPa. The amounts of AIN were determined by thermodynamic calculations using FactSage thermodynamic software. The samples were analyzed by X-ray diffraction and SEM. The formation of Si1.62 Alo.38 O1.38 N1.62 in samples containing less than 2.4 wt% of AlN was observed. The addition of AlN promotes the formation of  $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> fibers that were observed in samples containing 2.4 wt% of AlN. The experimental results were in a good agreement with thermodynamical predictions. The fibers formation occurred by vapor-liquid-solid mechanism.

*Keywords*: Fly ash, Cenospheres, β-Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub>

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tigate the synthesis of  $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> at low temperature using cenospheres.

## 2. Experimental

# Materials

Ultra high-purity  $\alpha$  – Al<sub>2</sub>O<sub>3</sub> powder (10 µm, 99.999%, Sasol), AlN powder (35 µm, cubic structure, 98.99%, Aldrich ) and C<sub>grahpite</sub> (35 µm) have been used. Cenospheres (35 µm) were obtained from fly ash by sieving through a 400 ASTM mesh. The chemical composition of the cenospheres was: 62.14 wt% SiO<sub>2</sub>, 25.32 wt% Al<sub>2</sub>O<sub>3</sub>, 5.00 wt% Fe<sub>2</sub>O<sub>3</sub>, 2.36 wt%. C, 0.44 wt% K<sub>2</sub>O, 0.91 wt% MgO, 0.97 wt% TiO<sub>2</sub>, 2.64 wt% CaO and 0.22 wt% Na<sub>2</sub>O, and others. Cenospheres contain mullite and quartz as a crystalline phases and a considerable amount of amorphous phase. Ultra high purity nitrogen was used as atmospheric gas.

#### FactSage equilibrium predictions

The possibility of  $\beta$ -SiAlON formation at low temperature was studied by using a thermodynamical software FactSage version 5.5. The initial amounts of species were based on the following reaction.

$$1.5Al_2O_3 + 3SiO_2 + 2.5N_2 + 7.5C \rightarrow Si_3Al_3O_3N_5 + 7.5CO$$
(1)

The stoichiometric amounts of  $Al_2O_3$  and  $SiO_2$  were introduced in the equilibrium mode of the software in mols. Nitrogen amount was determined based on the chamber volume of the experimental equipment (0.53 mol). The amount C was determined from thermodynamical calculations for the formation of  $\beta$ -SiAlON. The equilibrium conditions were 0.1MPa and 1250°C. The temperature was selected according to literature reports [8, 10] on the synthesis of SiAlON ceramics. Additionally, four compositions were introduced in the program in order to study the effect of AlN addition (0.2, 0.3, 0.4 and 0.5 mol) on the formation of  $\beta$ -SiAlON. The addition of AlN was selected based from previous reports that indicate that small additions of AlN enhance the formation of  $\beta$ -SiAlON [11].

## Experimental setup

Mixtures of cenospheres, C and AlN were homogenized in a plastic jar with alcohol and alumina balls for 10 h. Then the samples were dried for 12 h and disks of 1.5 cm in diameter were conformed by uniaxial pressing at 20MPa. The chemical composition of the mixture was adjusted by adding  $Al_2O_3$  in order to have a composition according to reaction (1). On the basis of the previous experiments, 40 wt% excess of C was added to the mixture. In order to confirm the equilibrium predictions, four samples containing AlN (1.2, 2.4, 3.6, 4.8wt%) were prepared following the procedure described above. The samples were heated for 5h at 1250°C under nitrogen flow rate of 1L/min in a tight closed tubular furnace. The surfaces of fracture of the samples after the test were analyzed by XRD and SEM.

# 3. Results and discussion

#### FactSage simulation

Table I shows the FactSage equilibrium calculations of  $\beta$ -SiAlON at 1250°C and 0.1MPa. The data confirm the effect of AlN additions on the kind of equilibrium phases. The results prove that the formation of SiAlON types without addition of AlN is not thermodynamically possible at 1250°C. The Si<sub>2</sub>N<sub>2</sub>O phase is present at equilibrium for the sample with no aluminum nitride addition. This compound has been reported [12] as an intermediate phase in the formation of O-SiAlON. As the AlN increased (1.2wt%) the Si<sub>3</sub>N<sub>4</sub> appears as an equilibrium phase, which during the synthesis of SiAlON is a key factor [11]. As the AlN content increases the  $\beta$ -SiAlON is present as the main phase at equilibrium.

TABLE 1

 $\beta$ -SiAlON solid solutions at equilibrium with others phases calculated by FactSage at 1250°C with 0.53 mol of N<sub>2</sub> gas

Variation of AlN	Solid Phases
(wt%)	1250°C
	C <sub>(graphite)</sub>
	$SiO_{2(cristobalite)}$
0.0	$Al_2O_{3(\textit{corundum})}$
	$Si_2N_2O$
	O-SiAlON
	$Al_2O_{3(\textit{corundum})}$
0.2	$Si_3N_4$
	β-SiAlON
	SiC
	β-SiAlON
0.3	X-SiAlON
	$Al_2O_{3(\textit{corundum})}$
0.4	β-SiAlON
	$Al_2O_{3(\textit{corundum})}$
0.5	β-SiAlON

According to these equilibrium calculations the

 $\beta$ -SiAlON formation is possible at 1250°C as the AlN content is increased.

#### X-Ray Difracction

Figure 1 shows diffraction patterns of samples synthesized at 1250°C for 5h under N<sub>2</sub> flow. As AlN increases,  $\beta$ -SiAlON was the main phase detected. These results are in agreement with those obtained by FactSage predictions as far as AlN effect is concerned. The addition of AlN up to 1.2wt% promotes the formation of  $Si_{1.62}Al_{0.38}O_{1.38}N_{1.62}$ , Figure 1a and b. This  $Si_{1.62}Al_{0.38}O_{1.38}N_{1.62}$  phase corresponds to the O-SiAlON type according to the following reaction [12]:

$$(2-x)Si_2N_2O_{(s)}+xAl_2O_{3(s)} \leftrightarrow 2[O - Si_{2-x}Al_xO_{1+x}N_{2-x}]_{(s)}$$
  
(2)  
where x is 0.38 in order to achieve Si\_{1.62}Al\_{0.38}O\_{1.38}N\_{1.62}

 $1 \beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub>  $2 \text{ O-Si}_{1.62} \text{Al}_{0.38} \text{O}_{1.38} \text{N}_{1.62}$  $3 \alpha - Al_2O_3$ 4 FeAl<sub>2</sub>O<sub>4</sub> 3 1 1 13 Intensity (A.U) 1 11111 d) 3 1 1 111 1 c) 111 b) 31 31 22 1 211 11 a) 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80  $2\theta$  (degrees)

Fig. 1. X-Ray Diffraction patterns of samples synthesized at  $1250^{\circ}$ C for 5 h under 1L/min of nitrogen; effect of AlN addition: **a**) 0 wt%; **b**) 1.2 wt%; **c**) 2.4 wt%; **d**) 3.6 wt% and **e**) 4.8 wt%

Previous studies [12] suggest that O-SiAlON is obtained by the formation of a liquid phase that is generated by high aluminum concentration levels. This liquid phase dissolves  $Si_3N_4$ . In this stage, Si, Al and N are precipitated from the liquid as O-SiAlON. As the amount of AlN was increased the formation of  $Si_3Al_3O_3N_5$  was achieved. As AlN increases there is more equivalent % of Al according to the  $Si_3N_4$ -AlN-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> quaternary system. The more stable phase corresponds to the  $\beta$ -SiAlON family instead of O-SiAlON as it can be seen in Figure 2 [13].





Fig. 2. Zone of stability to form  $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> in a quaternary system [13]

In the zone of stability of  $\beta$ -SiAlON solid solutions in the quaternary system Si<sub>3</sub>N<sub>4</sub>-AlN-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (Figure 2), the liquid could constantly be enriched with aluminum ions that are supplied by the decomposition of AlN to form Si<sub>3</sub>N<sub>4</sub> that reacts with Al<sub>2</sub>O<sub>3</sub> according to the reaction [14]:

$$3Si_{3}N_{4(s)} + 3Al_{2}O_{3(s)} \leftrightarrow 2 [Si_{3}Al_{3}O_{3}N_{5}]_{(s)} + 3SiO_{(g)} + N_{2(g)}$$
(3)

Alumina was present in all the samples as a final product, this compound was the source of AlN that act as nucleation sites for  $\beta$ -SiAlON formation during the carbothermal reduction process under a nitrogen atmosphere. However, Al<sub>2</sub>O<sub>3</sub> may require high temperatures to form AlN according to the reactions:

$$Al_2O_{3(s)} + 3C + N_{2(g)} \to 2AlN + 3CO_{(g)} \Delta G_{1250^\circ C} = +50.52kJ$$
(4)

$$Al_2O_{3(s)} + 3C + N_{2(g)} \to 2AlN + 3CO_{(g)}$$
  
$$\Delta G_{1400^\circ C} = -11.856kJ.$$
 (5)

The  $\text{FeAl}_2\text{O}_4$  spinel was also observed in all the samples after heat treatment and the peak intensity of this spinel was decreasing as the aluminum nitride content increased.

# Morphological characterization

Figure 3 shows the SEM micrographs of the heat-treated cenospheres-alumina-AlN samples at

1250°C for 5h under  $N_2$  atmosphere. Figure 3a corresponds to the sample without any AlN addition, the morphology was mainly composed by agglomerates with some elongated fibers. The addition of AlN (1.2 wt%) promoted the whiskers formation with fine fibers, (figure 3b). There was observed a drastic change in

morphology for the sample containing 2.4 wt% of AlN. The morphology was composed by some whiskers and a great amount of elongated fibers. As the AlN content increased above 2.4 wt%, the morphology consisted mainly of agglomerates (Figure 3d, e).



Fig. 3. Microstructures of samples synthesized at  $1250^{\circ}$ C for 5 h under nitrogen flow for different amounts of AlN, **a**) 0 wt%; **b**) 1.2 wt%; **c**) 2.4 wt%; **d**) 3.6 wt% and **e**) 4.8 wt%

Fibers formation (Figure 4a) was observed in the sample containing 2.4 wt% of AlN. EDS analysis showed that these fibers contain Mg and Ca, these elements were incorporated by self-diffusion into the  $\beta$ -SiAlON structure. The EDS analysis of the fibers showed that the amounts of Si, Al, O and N were close to those corresponding to the chemical composition of  $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub>. On the other hand, Figure 4b, showed the presence of Fe and Ti in the agglomerates formed in the samples

containing 4.8 wt% of AlN. All these elements were present in the cenospheres as oxides. In previous studies [15, 16, 17], it was observed that depending on the amount of elements such as Fe, Mg, Ca, the formation of  $\alpha$ -SiAlON and  $\beta$ -SiAlON phases is possible. This phenomenon was observed in the cenospheres-alumina-AlN samples synthesized in this work. The addition of AlN promoted the incorporation of iron into the SiAlON as the EDS spectra and the XRD patterns showed.



Fig. 4. SEM micrographs of synthesized  $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub>, **a**) fibers in sample with 2.4 wt% of AlN and **b**) agglomerates in sample with 4.8 wt% of AlN

Figure 5 shows a small spherical particle in the sample that contains 2.4 wt% of AlN. Droplets in the surface of the particle can be observed. These droplets indicat-

ed that there was a liquid formation during the synthesis, which acted as nucleation site for the formation of SiAlON fibers.



Fig. 5. EDS of the spherical particle with droplets

The formation of this liquid occurs as follows. Firstly

the iron oxide is reduced by carbon and reacts with the  $SiO_2$  according to the reaction:

$$1.5Fe_2O_{3(s)} + 7.5C_{(s)} + 2SiO_{2(s)} \to Fe_3Si_{(s)} + SiO_{(g)} + 7.5CO_{(g)}$$
  
$$\Delta G_{1250^\circ C} = -500.488kJ,$$
(6)

where s: solid and g: gas.

Secondly, the formation of alumina takes place according to the reaction:

$$2AlN_{(s)} + SiO_{(g)} + N_{2(g)} \leftrightarrow Si_3N_{4(s)} + Al_2O_{3(s)}$$
  
$$\Delta G_{1250^\circ C} = -454.968kJ.$$
(7)

As mentioned above the decomposition of AlN limits

$$3Fe_{3}Si_{(s)} + Al_{2}O_{3(s)} + 3N_{2(g)} + 2SiO_{(g)} \leftrightarrow Si_{3}N_{4(s)} + FeAl_{2}O_{4(s)} + Si_{2}N_{2}O + 8Fe_{(l)}$$

$$\Delta G_{1250^{\circ}C} = -165.834kJ.$$
(8)

The Si<sub>3</sub>N<sub>4</sub> formed in the reactions (7) and (8) acted as an intermediate phase for the formation of  $\beta$ -SiAlON solid solutions. The Si<sub>2</sub>N<sub>2</sub>O<sub>(*s*)</sub> are able to form O-SiAlON phases (see reaction (2)).

According to the reaction (8) there is the formation of a liquid that contains some amount of iron that activates the vapor-liquid-solid growth mechanism [3, 18, 19, 20]. Further, the reactions (7) and (8) suggest two sources of Si<sub>3</sub>N<sub>4</sub> formation in solids that activate the fibers nucleation and growth, mainly AlN. Nonetheless, an excess of Si<sub>3</sub>N<sub>4</sub> solids may avoid the fibers growth due to the increase of the nucleation rate for SiAlON formation while the fiber growth rate is limited. This effect was observed in the samples with AlN above 2.4wt%. Studies [19] confirm that increasing AlN additions enhanced the SiAlON whisker formation. In summary, the control of the amount of AlN in the chemical composition of the cenospheres promotes the synthesis of SiAlON with different morphologies. The formation of SiAlON fibers is important since these can be used as reinforcing materials for composites [19].

## 4. Conclusions

The feasibility to synthesize  $Si_3Al_3O_3N_5$  using cenospheres at low temperature (1250°C) under a nitrogen flow rate of 1L/min was demonstrated. These results are in agreement with those predicted by thermodynamic approach. The addition of 2.4 wt% of AlN promotes the  $Si_3Al_3O_3N_5$  fibers formation. The occurrence of a semi-molten phase activates the vapor-liquid-solid mechanism for fibers formation.

#### REFERENCES

- [1] T. Ekström, M. Nygren, J. Am. Ceram. Soc. 75
  (2) 259-76 (1992).
- [2] Y. Wu, H. Zhuang, F. Wu, J. Mater. Resear. 13, 1 166-72 (Jan. 1998).
- [3] Zuxiang Chen, J. Mater. Sci. 28 6021-25 (1993).

the formation of O-SiAlON types since AlN contributes to the formation of  $Si_3N_4$  that acts as a precursor for the formation of -SiAlON, as observed in the compatibility zone in the system  $Si_3N_4$ -AlN-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. The formation of alumina was confirmed by XRD analysis as a final product (Figure 1). Finally, Al<sub>2</sub>O<sub>3</sub> in the reaction (7) participates in the formation of liquid iron that promotes the  $\beta$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> growth according to the reaction:

- [5] J. Krest'an, P. Sajgalik, Z. Pánek, J. Eur. Ceram. Soc. 24 791-96 (2004).
- [6] M. D. Alcalá, J. M. Criado, F. J. Gotor, C. Real, J. Mater. Sci. 41 1933-38 (2006).
- [7] Y. Miyamoto, S. Kanehira, M. Radwan, Refractories Applications and News 9 1 14-17 (Jan/Feb 2004).
- [8] G. Shveikin, T. Timoshchuk, Inorg. Mater. 36 9 891-94 (Sep. 2000).
- [9] A. Jonker, J. H. Potgieter, J. Eur. Ceram. Soc. 25 3145-49 (2005).
- [10] M. Sopicka-Lizer, R. A. Terpstra, R. Metselaar, J. Mater. Sci. 30 6363-69 (1995).
- [11] L. J. Gauckler, H. L. Lukas, G. Petzow, J. Am. Ceram. Soc. 58 (1975) 7-8.
- [12] M. B. Trigg, K. H. Jack, J. Mater. Sci. 23 481-87 (1988).
- [13] G. Petzow, L. J. Gauckler, T. Y. Tien, S. Boskovic, In Factor in Densification and Sintering of Oxide and Non-Oxide Ceramics, 29-39 Tokyo (1979).
- [14] K. K. Strelov, Y. P. Gilev, I. L. Shabalin, F. A. Fekhretdinov, V. D. Snezhko, Ogneupory, 4 211-13 (April 1989).
- [15] J. D. Mackenzie, J. Temujin, M. E. Smith, K. Okada, Y. Kameshimo, J. Eur. Ceram. Soc. 23 1069-82 (2003).
- [16] Z. Yanping, Z. Hanrui, W. Shulin, J. Mater. Synth. and Processing 7, 1, 35-39 (1999).
- [17] J. Jiang, P. Wang, W. Chen, H. Zhuang, Y. Cheng, D. Yan, J. Eur. Ceram. Soc. 23 2343-49 (2003).
- [18] G. L e n g W a r d, J. Mater. Sci. 19 1726-36 (1984).

- [19] G. Liu, K. Chen, H. Zhou, et al., Materials Letters 59 3955-58 (2005).
- [20] H. L. Dickon, L. Y. Teresa, F. L. Kwong,

Received: 10 December 2008.

You - Fe Li, R. Yang, Materials Letters **62** 1349-52 (2008).