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Synthesis of a SiC-SiAlON Composite by Nitridation of a SiC-AlSi Mixture

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Abstract. SiC-SiAlON composite was produced from a mixture of SiC powders with wide particle size distribution and Al-34Si alloy powder by nitridation. The aluminum-silicon alloy was produced by the mechanical alloying method. The composition studied was 75 wt% SiC and 25 wt% (Al-34Si). The powder was compacted by uniaxial and cold isostatic pressing, forming tablets 25 mm in diameter and 10 mm thick. These tablets were then nitridized in a graphite resistance furnace. The heating rate up to 1000 ^{0}C was 20 ^{0}C/min, and 10 ^{0}C/min up to 1400 ^{0}C. Dwelltime at 1400^{0}C was 8 hours. Thermodynamic analysis of the system was accomplished. Powders of raw materials were characterized by sedimentation analysis, chemical analysis, scanning electron microscopy, and X-ray diffraction. The material obtained after nitridation was characterized by scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. The porosity and final density were determined by gas picnometry.

Introduction

SiC-SiAlON composites have attracted great technological interest because of their mechanical, chemical and thermal properties, which include excellent thermal shock resistance, high resistance to oxidation and corrosion, good resistance to molten alkaline metals, high thermal conductivity and low thermal expansion [1-3].

In recent years a variety of novel chemical synthesis routes has been used to prepare SiC-SiAlON composites. Among these, special attention was given to nitridation processes because they involve gas phase reactions with high reaction rates leading to β-SiAlON bonded silicon carbide (SiC) formation [6]. β-SiAlON is formed by simultaneous equivalent substitution of Al-O for Si-N and is commonly described by the formula $Si_{6-z}Al_zO_zN_{8-z}$. In this formula z can be varied continuously from zero to about 4.2 [4-6]. The homogeneity region of β-SiAlON extends along the line with constant metal: nonmetal ratio 3M:4X [4].

In the present work the thermodynamic analysis was important for the understanding of SiC-SiAlON composite formation including stability of constituent phases, since SiAlON solid solution would be formed in the mixture with SiC by reaction between Al-34Si (wt.) alloy and nitrogen during nitridation at high temperature (1400^{0}C).

From the thermodynamic point of view, the reaction between Al-34Si alloy and nitrogen can produce a β-SiAlON phase and can be described by the following reaction

$$2Si_{(s)} + 4Al_{(s)} + 2O_{2(g)} + 2N_{2(g)} \rightarrow Si_2Al_4O_4N_{4(s)} \quad (1)$$

We will further assume that the Al-34Si alloy nitridation results in β-SiAlON formation with z = 4. The Gibbs free energy variation of the reaction (1) was calculated according to the following equation

$$\Delta G_{Si2Al4O4N4} = \Delta G^0 + RT \ln [a_{Si2Al4O4N4}/(a_{Si})^2(a_{Al})^4(P_{N2,O2})^2 \quad (2)$$

Where

ΔG	=	Gibbs free energy
ΔG^0	=	Gibbs standard free energy of the $Si_2Al_4O_4N_4$ phase formation
R	=	gas constant
T	=	temperature of the $Si_2Al_4O_4N_4$ phase formation
a	=	activity of pure $Si_2Al_4O_4N_4$, Si and Al
P	=	nitridation normal pressure

The value of the standard Gibbs free energy of $Si_2Al_4O_4N_4$ formation in the mixture with SiC for the equation (2) was determined using thermodynamic data of thermo-calc databank system and found as ΔG^0 = - 282.365 kJ/mol at 1400^{0}C and normal pressure (0.1Mpa). The ΔG value calculated from equation (2) was –290.561 kJ/mol. The overall reaction between SiC and $Si_{6-z}Al_zOzN_{8-z}$ to form the composite can be described as

$$SiC_{(s)} + 2Si_{(s)} + 4Al_{(s)} + 2O_{2(g)} + 2N_{2(g)} \rightarrow SiC\text{-}Si_2Al_4O_4N_{4(s)} \quad (3)$$

In order to produce SiC-$Si_2Al_4O_4N_4$ composite in equilibrium condition, the overall Gibbs free energy of the system must be equal to the sum of the Gibbs free energies of the constituents, ΔG_{SiC} and $\Delta G_{Si2Al4O4N4}$. According to the literature, ΔG_{SiC} = -66.027 kJ/mol at 1400^{0}C [7]. Moreover, in order for the SiC-$Si_2Al_4O_4N_4$ composite to be formed, the stability and spontaneity condition must be satisfied [8] :

$$\Delta G < 0 \quad (4)$$

The overall Gibbs free energy of SiC-$Si_2Al_4O_4N_4$ system can be determined as

$$\Delta G_{SiC\text{-}Si2Al4O4N4} = \Sigma [\Delta G_{SiC} + \Delta G_{Si2Al4O4N4}] \quad (5)$$

which results in a value of

$$\Delta G_{SiC\text{-}Si2Al4O4N4} = -369.615 \text{ kJ/mol} \quad (6)$$

The purpose of the present investigation is to verify the stability of SiC-SiAlON composite and the viability of its production by means of nitridation, and to determine the stoichiometry of β-SiAlON formed in a SiAlON-bonded SiC.

Experimental Procedure

Al-34Si (wt%) alloy utilized in this study has been produced by mechanical alloying using high energy mill. The Al and Si commercial powders used were of BELGO BRASILEIRA S.A. and LiASA. Thus prepared alloy powder was analyzed for granulometry on Micromeritics 5100 laser sendimentograph. The powder of this alloy was then mixed with α-SiC powder (CASIL S/A) with wide particle size distribution (21-336 μm). The nominal composition of the mixture was 75%SiC and 25%Al-34Si in weight. The powder mixture was homogenized for 30 min in the alumina ball mill together with phenolic resin, which was used as a binder. The powder mixture was uniaxially and then cold isostatically pressed at 150 MPa and 200 MPa, respectively, into cylindrical samples of 25mm diameter and 12mm height. The average green density achieved was 2.36g/cm^3. Preliminary heat treatment was accomplished at 500^{0}C to remove the phenolic resin before the nitridation. For nitridation the samples were heated in graphite resistance furnace with the heating rate of 20^{0}C/min up to 1000^{0}C and 10^{0}C/min up to 1400^{0}C. Soaking time at 1400^{0}C was 8h. The final density was measured using gas picnometry techniques, the average value was determined to be 3.25 g/cm^3. Samples for microstructural observations were prepared using standard ceramographic procedure of multistep grinding and polishing. The microstructure of composites was investigated by scanning electron microscopy (SEM) on a Philips XL30 scanning electron microscope. Chemical composition was determined by energy dispersive spectroscopy (EDS) performed on EDAX DX-AUTO EDS analyzer attached to the microscope. The phases were identified by X-ray diffraction (XRD) on a Rigaku DMAX 2000 diffractometer (CuK_α radiation, 20 – 70^0 2θ).

Results and Discussion

Particle size distribution in the Al-34Si alloy is presented in Fig.1. It can be noted that mechanical alloying realized by high energy milling method for 15h produced powders with mean particle size of 3μm.

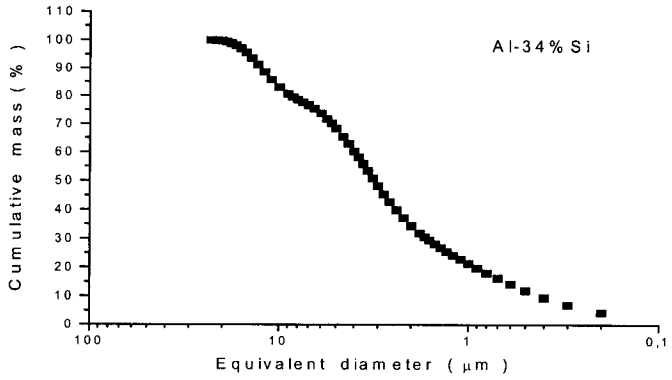

Fig.1 – Particle size distribution of Al-34Si alloy milled for 15h

Results of the chemical characterization of the raw materials used in the present investigation are presented in the Table 1.

Table 1 – Chemical analysis of aluminum, silicon and silicon carbide powders

Al		Si		SiC	
Impurities elements	(%)	Impurities elements	(%)	Impurities elements	(%)
Cd	0.0001	-	-	Cd	0.06
B	0.0003	B	0.0039	B	0.01
Fe	0.01	Fe	0.392	Fe	0.05
Cr	0.001	-	-	Cr	0.0045
Ni	0.003	Ni	0.0059	Ni	0.008
Zn	0.015	-	-	Zn	0.15
Si	0.02	-	-	P	0.15
Mn	0.004	Mn	0.049	Mn	0.03
Mg	0.001	Mg	0.0196	Mg	0.0045
Pb	0.005	P	0.0392	Pb	0.0045
Sn	0.0003	-	-	Sn	0.003
Bi	0.00005	-	-	Bi	0.0015
V	0.002	Ag	0.0045	V	0.003
Cu	0.006	Cu	0.0157	Cu	0.004
Na	0.008	-	-	-	-
Ga	0.004	-	-	Ga	0.0015
Ca	0.002	Ca	0.1568	Ca	0.05
Sb	0.0005	-	-	Co	0.004
Ti	0.002	Ti	0.1176	Ti	0.0015

The microstructure of SiC-SiAlON composite synthesized at 1400^0C is shown in Fig.2a. Microstructural analysis revealed that polished surface of the composite is characterized by three distinct regions, as can be seen in Fig.2a. The regions represented by larger and smaller grains in prominence, were identified as silicon carbide (SiC) grains. The fine-grained phase with high level of microporosity, in which the SiC grains are embedded, was identified as β-SiAlON. The inhomogeneous pores appear as darker areas. The phases presented in Fig.2a also were investigated by X ray image analysis as showed in Fig.2b-c, where the Al and Si distribution in the sample are shown. Results of the energy dispersive spectroscopy analysis (EDS) taken parallel with SEM micrography are shown in Fig.3. The presented EDS spectrum corresponds to the intergranular region of the sample. The results obtained reveal the presence of aluminum and silicon that are the constituent elements of β-SiAlON phase. Oxygen and nitrogen being too light elements for detection by the present analyzing techniques do not appear on the spectrum. However, the initial composition of the material together with the observed ratio of the Si and Al enable to conclude that the intergranular phase is a β-SiAlON.

(a) (b) (c)

Fig.2 – SEM micrography and energy dispersive X ray spectroscopy : a)SEM for SiC-SiAlON composite from 1400^{0}C; b) EDX from aluminum; c) EDX from silicon

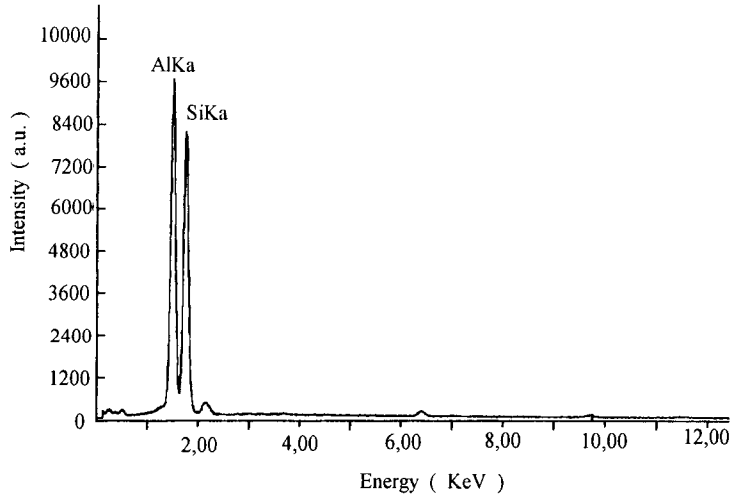

Fig.3 – EDS spectrum taken from intergranular region observed by SEM in Fig.1a

Results of the phase analysis of the SiC-SiAlON composite synthesized at 1400^{0}C are presented in Fig.4. The main crystalline phase present in the sample is 15R polytype of silicon carbide. The second crystalline phase that appears on the diffractogram was identified as a β–SiAlON. Lattice parameters of the β–SiAlON were refined to the values of a = 7.672 Å and c = 2.969Å using the least-square refinement program of Benoit [9]. The composition of the SiAlON phase, which was formed as a result of Al-34Si alloy nitridation, was determined according to a correlation between the lattice parameters and the value of coefficient z in the general formula $Si_{6-z}Al_zO_zN_{8-z}$ of β–SiAlON initially described by Jack [4] and recently refined by Loong et al [10]. The value of z was determined as 2.4 which enabled to tentatively describe the SiAlON formed in the investigated samples as $Si_{3.6}Al_{2.4}O_{2.4}N_{5.6}$.

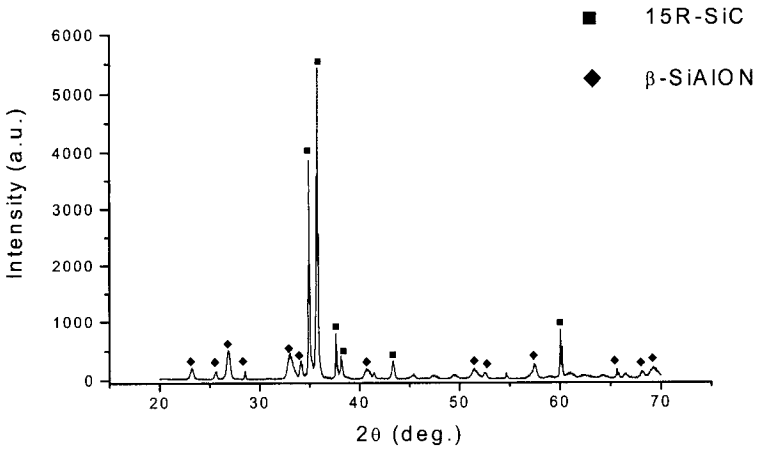

Fig.4 – X ray diffraction patterns of SiC-SiAlON composite synthesized at 1400^0C for 8h

Conclusion

The thermodynamic calculations accomplished for the SiC-SiAlON system indicated that the nitridation process may lead to formation of composite, where constituents of which are stable up to 1400^0C. Results of thermodynamic calculations were confirmed by experimental studies. Microstructural investigations and physical characterization confirmed the SiC-SiAlON composite formation. Both SiC and β-SiAlON phases were found to be present in the material directly after nitridation.

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