

The wettability of SiC ceramics by molten $E_2O_{3(ss)}/AlN$ ($E_2O_{3(ss)}$ = solid solution of rare earth oxides)

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Abstract

Wetting of SiC by molten $E_2O_{3(ss)}/AlN$ as a function of temperature up to 2000 °C was investigated under argon and nitrogen atmospheres. $E_2O_{3(ss)}$ is a solid solution of rare earth oxides produced from xenotime by hydrometallurgy. Wetting was evaluated from contact angle measurements using the sessile drop method. Contact angle was around zero under argon atmosphere, but could not be measured under nitrogen atmosphere, due to bubble formation. The interfaces between molten $E_2O_{3(ss)}/AlN$ and SiC were analysed by scanning electron microscope (SEM) and X-ray diffraction (XRD).

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1. Introduction

Silicon carbide (SiC) ceramics can be produced by liquid phase sintering, which allows obtaining a microstructure suitable for structural applications [1–6].

Metal oxides and aluminium nitride (AlN) mixes are used to produce the liquid phase during liquid phase sintering. The most common mixes are AlN/ Y_2O_3 , AlN/ $E_2O_{3(ss)}$, AlN/ La_2O_3 and AlN/ Er_2O_3 [1–6].

Wettability, one of the most important properties in liquid phase sintering, can be measured by contact angle (θ) using the sessile drop method. The main parameters affecting the contact angle are: atmosphere chemical composition, liquid and solid phases chemical compositions, viscosity of the liquid, temperature and time [7–20].

Wettability studies of ceramic systems using Y_2O_3/Al_2O_3 and $E_2O_{3(ss)}/Al_2O_3$ mixes have shown good results, with a contact angle near zero [21,22].

The aim of this work was to evaluate $E_2O_{3(ss)}/AlN$ wettability on SiC surface, to obtain data to optimise liquid phase sintering of SiC ceramics. $E_2O_{3(ss)}$ is a new material

obtained from xenotime by hydrometallurgy. This material, which behaves as a rare earth oxides solid solution, has great potential to be used as a producer of liquid phase in covalent ceramics sintering [23–25].

2. Experimental

Aluminium nitride, AlN (Hermann C. Starck, GRADE C (fine) – Germany), and $E_2O_{3(ss)}$, a solid solution of rare earth oxides, whose chemical composition is shown in Table 1, were used as starting powders. $E_2O_{3(ss)}$ was produced from xenotime by the hydrometallurgy process, in the Department of Materials Engineering – FAENQUIL.

The melting temperatures were measured for $E_2O_{3(ss)}/AlN$ mixes varying from 10 to 90 wt AlN, at 10% steps. All the mixes with more than 40 wt.% AlN had melting temperatures higher than 2000 °C. Therefore, NE1, NE2 and NE3 mixes (Table 2) were chosen to develop this work. The melting temperatures of the mixtures were measured according to DIN 51730 standard, by using three samples for each mix.

Mixes were prepared in an attrition mill for 1 h at 1000 rpm in isopropyl alcohol, then dried at 80 °C in a rotating drier, and pressed as spheres 4 mm in diameter at 90 MPa, in a semi-isostatic press (Monostatic 50 Powder Press – Simac).

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Table 1
Chemical composition of $E_2O_{3(ss)}$ determined by atomic emission spectrometry (ICP-AES)

Oxide	wt.%
Y_2O_3	43.90
Yb_2O_3	17.00
Er_2O_3	13.60
Dy_2O_3	11.00
Ho_2O_3	3.10
Tm_2O_3	2.50
Tb_2O_3	2.41
Lu_2O_3	2.00
Gd_2O_3	1.73
Sm_2O_3	0.41
Pr_2O_3	0.27
CeO_2	0.18
Nd_2O_3	0.18
Eu_2O_3	0.06
La_2O_3	0.04
ZrO_2	1.06
SiO_2	0.09
Insoluble	0.56

Table 2
Composition and melting temperatures of $AlN/E_2O_{3(ss)}$ mixes

Mixes code	Composition (wt.%)		Melting temperature ($^{\circ}C$)
	AlN	$E_2O_{3(ss)}$	
NE1	30	70	1830 ± 10
NE2	20	80	1820 ± 15
NE3	10	90	1830 ± 10

3. Results and discussion

Fig. 1 shows the evolution of the liquid NE3 mix on SiC plates under argon (a–d) and nitrogen (e–h) atmospheres. NE3 mix represents all the other compositions, because it produced the best contact angle results under argon atmosphere.

As can be observed, the liquid NE3 did not spread uniformly on the SiC plates under nitrogen atmosphere, because bubbles formed during the test, Fig. 1(e–h), possibly due to the increase in liquid viscosity caused by nitrogen dissolution into the liquid [17–22], hindering the measure of the contact angle. Fig. 1 represents the main events at random temperatures: sphere without deformation (a and e); sphere deformation at softening temperatures (b and f); nearly half sphere (c), spreading at melting temperature (d); bubble formation (g) and burst (h).

The behaviour of the $E_2O_{3(ss)}/AlN$ mixes under argon and nitrogen atmospheres was completely different, because under argon atmosphere their liquids spread out naturally on the SiC surface. Argon atmosphere did not interact with melting $E_2O_{3(ss)}/AlN$, while N_2 atmosphere influenced significantly the formation of bubbles.

Fig. 2 shows the temperature dependence of the contact angle (θ) of NE1, NE2 and NE3 mixes. Contact angle decreased when temperature and concentration of $E_2O_{3(ss)}$ mixes increased, confirming the thermodynamics theory and several experimental studies [7–16]. All mixes melted almost

In each wettability experiment, the spheres were placed on a 98.9% dense SiC plate (10.0 mm \times 10.0 mm \times 4.0 mm) manufactured by Wacker-Chemie GmbH, Germany, previously polished up to 1 μ m diamond suspension. The set was introduced into a graphite resistance furnace (ASTRO) and heated at 5 $^{\circ}C/min$, under 0.1 MPa argon or nitrogen atmosphere, up to the sphere melting temperature. The behaviour of the mixes on the SiC plate was observed using an imaging capture system consisting of a CCD COLOUR camera, a Matrox Meteor-2 board and an objective glass 4/50 mm. The contact angle was measured by a Leica – Qwin 2.3 standard software.

After cooling, the samples were cut perpendicularly to the interface and the microstructure were analysed by scanning electron microscopy (SEM). Phases were formed at high temperatures were analysed by X-ray diffraction (XRD).

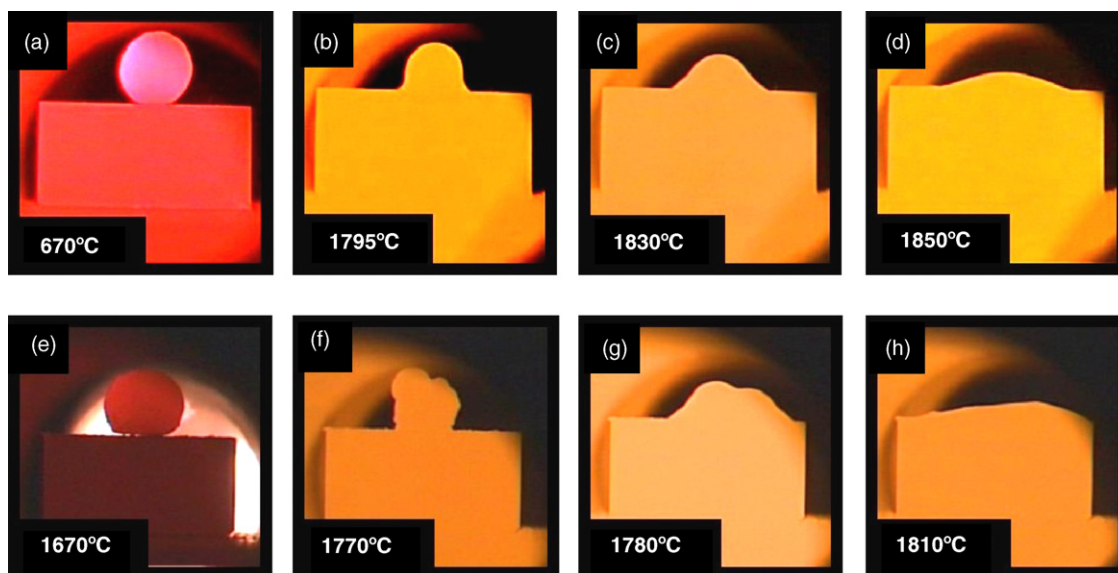


Fig. 1. Sequential images obtained by CCD camera of wettability tests employing NE3 mix on SiC under argon (a–d) and nitrogen (e–h) atmospheres.

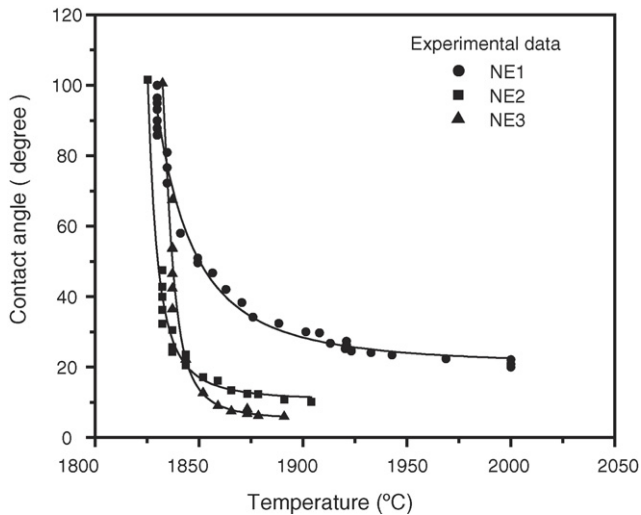


Fig. 2. Temperature dependence of contact angles (θ) of NE1, NE2 and NE3 mixes on SiC plates, under argon atmosphere.

at the same temperature and, after melting, the initial contact angle rapidly decreased. The behaviour of NE1, NE2 and NE3 curves suggests that their compositions are close to the eutectic composition in a hypothetical phase diagram of $E_2O_{3(ss)}/AlN$ system. It should be stressed that, even at temperatures near 2000 °C, NE1 did not wet the plate as much as the other mixes. Although the minimum contact angle of NE1 was 20°, in comparison with NE2 (10°) and NE3 (5°), its wettability was good. It can be observed that the contact angles increased with the increase in AlN content in the mixes. The low contact angles for mixes on SiC will probably result in better densification of SiC ceramics sintered by liquid phase sintering.

From the fitted curves shown in Fig. 2 Eq. (1) was deduced, considering $T \geq T_m$.

$$\theta_{NE1,NE2,NE3} = \theta_{\min} + \theta_P \exp[-\alpha_D(T - T_m)] \quad (1)$$

where θ_{\min} is the minimum contact angle, θ_P is the fitted curve parameter, T_m corresponds to the melting temperature and α_D is the exponential decay factor. Values for θ_{\min} , θ_P and α_D are shown in Table 3.

As a function of temperature, the contact angles of NE2 and NE3 mixes exhibited an exponential decay quite different from the decay observed for NE1 mix (Fig. 3). This difference can be attributed to the fact that viscosity increases when the AlN content increases in the mixes [18,20]. XRD of NE1, NE2 and NE3 mixes, after wetting tests, was similar to the XRD of Y_2O_3 and AlN system where appear Y_2O_3 and $Y_4Al_2O_9$ phases, possibly due to the similarity between the rare earth oxides. $E_4Al_2O_9$ phase formation is due to the chemical reaction of $E_2O_{3(ss)}$ with the Al_2O_3 originally present in the AlN surface [21,22].

Fig. 3 shows the interface between NE3 mix and SiC after wetting tests under (a) argon and (b) nitrogen atmospheres. A perfect bonding between mix and SiC can be seen in picture (a),

Table 3

Values of θ_{\min} , θ_P and α_D for NE1, NE2 and NE3 mixes

Mixes code	$\theta_{\min} (^{\circ})$	$\theta_P (^{\circ})$	$\alpha_D (^{\circ}C)^{-1}$
NE1	20	77.73	0.0278
NE2	10	56.80	0.0666
NE3	5	76.97	0.124

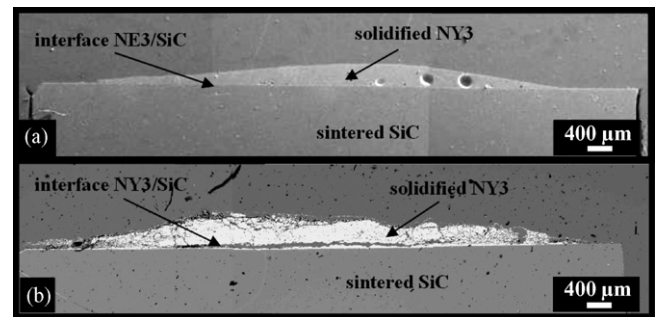


Fig. 3. SEM of interfaces between NE3 mix and SiC after wetting tests under argon (a) and nitrogen (b) atmospheres.

while a non-uniform bonding with many pores, resulting from bubble formation during the wetting tests, appears in picture (b).

4. Conclusions

The experiments revealed that the wettability of $E_2O_{3(ss)}/AlN$ mixes and SiC is excellent under argon atmosphere and that these materials are appropriate for use in liquid phase sintering of SiC. Under nitrogen atmosphere, however, the results were not promising. The increase in $E_2O_{3(ss)}$ quantities in the mixes promoted a better wettability on SiC, leading to the conclusion that NE3 is a better mix for sintering SiC by liquid phase, although the wettability of NE1 and NE2 was also excellent. These mixes are economically interesting, because they can be used with a large quantity of $E_2O_{3(ss)}$, whose cost is lower than the cost of separate rare earth oxides.

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