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Short communication

Protective coatings on RBSN

C.P. Hyndman, W.J. Tomlinson*

Department of N.E.S., Coventry University, Coventry CV1 5FB, UK

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Reaction bonded silicon nitride (RBSN) is formed by nitriding a porous silicon body. This gives the material two of its characteristic features. The shrinkage is virtually zero, and it has a porosity of about 10–20% [1]. In many cases, the porosity open to the surface is undesirable and some kind of glaze or coating may be applied. Glazes have been used for centuries to protect earthenware, and in a more technical application, alumino-silicate glazes have been found to strongly retard the oxidation of manganese ferrite in air at 1000°C [2]. However, the use of such protective coatings for RBSN is very limited [3], and the present work investigates the behaviour of a number of relatively thin coatings that have been used in service or are considered candidates for protection at high temperatures. The question of protection depends on the specific service conditions. The present technical evaluation is based on simple tests on the integrity of the coating, the oxidation in air without and with a deposit of sodium sulphate, and the effect of the coating in the unoxidised and oxidised conditions on the strength of the material.

Two RBSNs were used as substrates. One was of commercial purity (CP) with a porosity of 13.0%, and the other was high purity (HP) with a porosity of 16.6%. The main difference in the composition was the amount of iron impurity. This was 0.5% in the CP and 0.07% in the HP:. They were fabricated using standard commercial practice [4,5] to discs 30 mm diameter and 2.5 mm thick. Details of the substrates and two coatings are given in Table 1. The glaze (from ref. 3 and coded G in the Table) consisted of ball milling together 40 wt% MnO_2, 35 wt% SiO_2, and 25 wt% Al_2O_3 with isopropyl alcohol in a rubber ball mill for 16 h using sintered silicon nitride grinding media. The resulting slip was screened through a 38 micrometre sieve and dried. A glaze slurry suitable for spraying was then made by stirring the powder into ethoxyethanol containing 2 wt% ethyl cellulose as a binder. The coated substrates were then fired in static air and cooled to room temperature. Some other coatings not given in Table 1 but briefly examined and commented on later were prepared in a similar way. An exception was the silicon nitride bonded mullite coating (coded M in the Table). In this case, a milled slurry containing 80 wt% mullite and 20 wt% silicon was sprayed onto the commercial purity RBSN and reacted in flowing nitrogen to give a coating containing approximately 67% mullite and 33% RBSN. The highest purity oxides available were used in all the coatings.

Standard methods of sample preparation, microscopy, and X-ray diffraction were used. Methods of applying 1 mg cm^{-2} deposit of sodium sulphate on the surface, the oxidation procedure, and the mechanical testing using a disc flexure technique, have been described elsewhere [5,6].

The main results are summarised in Table 2. For convenience the strength of the coated material is also expressed as a ratio to that of either the CP or HP substrates in both the as-ground and oxidised in air conditions. Examination of polished sections showed no evidence that delamination or spalling of any coating occurred, and no noticeable pitting occurred in any of the specimens. It is also seen that in the CP/Mso material, all the mullite had reacted during firing.

Porosity dominates the oxidation and strength of the substrates. The high purity RBSN with a porosity of 16.6% has a lower strength (282 MPa) and a higher oxidation (7.74 mg cm^{-2}) than the commercially pure RBSN which has a porosity of 13.0%, a strength of 310 MPa, and an oxidation of 2.79 mg cm^{-2}. The presence of a salt deposit further decreases the strength but limits substantially the amount of oxidation. In these cases we may assume that the glassy reaction product which exists at high temperatures enlarges the pores by dissolving the edges, and at the same time blocking and preventing access of oxygen to the interior surface of the pores. The glaze reduces considerably the amount of

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* Corresponding author.

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Table 1
Materials and treatments

Material[a]		Coating treatment[b]			Coating characteristics		
Substrate	Surface condition	Temperature (°C)	Time (h)	Temperature of oxidation for 48 h (°C)	Av. thickness[c] (μm)	Bonding	Crystalline phases at room temperature[d]
CP	Ao	–	–	1300	–	–	Crist.
HP	Ao	–	–	1300	–	–	Crist.
CP	Aso	–	–	1300	18.1	Good	Crist., Trid.
HP	Aso	–	–	1300	25.0	Good	Crist., Trid
CP	G	1250	2	–	–	–	–
HP	G	1250	2	–	–	–	–
CP	Go	–	–	1250	13.3	Excellent	Crist., Trid., Braunite
HP	Go	–	–	1250	–	–	–
CP	Gso	1250	2	1250	23.6	Poor	Crist., Trid., Braunite
HP	Gso	1250	2	1250	–	–	–
CP	M	1445	4	1300	9.4	Excellent	SN, Mullite
CP	Mo	1445	4	1300	9.3	Excellent	SN, Si_2ON_2, Mullite, Crist.
CP	Mso	1445	4	1300	39.4	Excellent	SN, Crist.

[a] CP = commercial purity, HP = high purity, A = as ground, G = glazed, M = mullite/RBSN coating, o = oxidised in air, s = salt deposit. See text for details.

[b] all G in air, all M in nitrogen, all cooled to room temperature, except Go where the coating treatment was combined with the oxidation.

[c] Average of 10 readings along a 10 mm interface on a section.

[d] Crist. = cristobalite, Trid. = tridymite, SN = α and β Si_3N_4.

Table 2
Oxidation and strength

Material[a]			Oxidation			Strength		
Substrate	Surface condition	Number of specimens	Weight gain,w (mg cm^{-2})	Std. dev. (mg cm^{-2})	Ratio $\frac{W}{W_{Ao}}$	Mean,σ (MPa)	Std. dev. (MPa)	Ratio $\frac{\sigma}{\sigma_{Ao}}$
CP	A	10	–	–	–	310	21	–
HP	A	5	–	–	–	282	35	–
CP	Ao	8	2.79	0.74	1	255	14	1
HP	Ao	4	7.74	0.57	1	243	31	1
CP	Aso	8	1.48	0.19	0.53	242	29	0.95
HP	Aso	3	3.50	0.22	0.45	196	85	0.81
CP	G	1	(1.46)[b]	–	(0.52)[b]	(292)[b]	–	(1.15)[b]
HP	G	1	(1.64)[b]	–	(0.21)[b]	(303)[b]	–	(1.25)[b]
CP	GO	5	1.82	0.28	0.65	332	18	1.30
HP	GO	3	3.49	0.90	0.45	330	14	1.36
CP	Gso	5	-0.62	0.37	–	259	26	1.02
HP	Gso	3	0.85	1.22	–	256	23	1.05
CP	M	5	–	–	–	322	41	1.26
CP	Mo	5	1.69	0.61	0.61	270	42	1.06
CP	Mso	5	0.21	0.40	0.03	298	8	1.17

[a] See Table 1 and text for details.

[b] Parentheses indicate result from one specimen..

oxidation in air. In the presence of sodium sulphate, the reaction product is liquid at the oxidation temperature and part drips away giving a weight loss. In all cases, except the result for the single CP/G specimen, the glaze increased slightly the strength of the material. Two features of the mullite/RBSN coating are noteworthy. Firstly the amount of oxidation is reduced and this is very substantial when the coating has a salt deposit, and secondly, the strength is increased in all cases over that in the corresponding as-ground conditions. In particular, the strength of the hot salt corroded material (298 MPa) is barely reduced below the strength of the as ground uncoated material (310 MPa). A number of other coating materials have also been briefly evaluated.

These include alumina and an 8% ytteria-stabilised zirconia. All the coatings significantly degraded the strength of the RBSN substrate. In the case of alumina the strength was reduced by 40%.

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