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Effect of Y_2O_3 Addition on Alumina–Hex Boron Nitride Composites

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Abstract

Hot-pressing is the only process to densify alumina–hexagonal boron nitride composites. It must be applied at 1750°C — 40 MPa, under nitrogen, but it does not reduce the porosity lower than 8% for composites with alumina contents lower than 70 vol%, and leads to anisotropic composites due to the orientation of the boron nitride platelets perpendicular to the pressing axis. Furthermore, the composites' behaviour during their use in the continuous steel casting is mainly due to the porosity and anisotropy.

To increase their resistance to oxidation by oxygen and corrosion by molten steel, and to change the effect of their microstructure, some yttrium oxide additions have been used. Yttrium oxide, by helping the alumina sintering, increases the composite's densification and so its mechanical strength, and by increasing the grains cohesion, it allows us to change the hot-pressing programme to obtain a more isotropic composite. Also, by reaction with alumina, it forms yttrogarnet (YAG) which protects the composite from oxidation by forming a protective liquid phase at the surface, following the reaction with boron oxide formed by the boron nitride oxidation. However, this liquid phase is eroded by the molten steel and so, cannot increase the corrosion resistance, but it is possible to stop this corrosion by an addition of neodymium oxide.

1 Introduction

The alumina–hexagonal boron nitride composites have interesting properties used in the continuous casting of low carbon steel, substituting to alumina–graphite. Indeed, boron nitride brings to the composites its good thermal shock resistance and its low wettability by the molten metals.

But it resists poorly to the oxidation and acts as a sintering inhibitor. So, the composite's densification, that needs hot-pressing shaping, does not exceed 92% of the theoretical density for alumina contents lower than 80 wt% (70 vol%). So a considerable porosity is maintained into composites that allows the gas exchanges and so, enhances the oxidation too. For that reason, some yttria additions have been tested to increase the densification of these composites and their oxidation resistance.

This oxide addition was chosen because yttria is a sintering help for alumina by the aluminum vacancies formation, characteristic of an electron donor.[1-5] This effect is attributed to its ionic radius which is larger than the aluminum radius (r Y^{3+} = 0·093 nm, r Al^{3+} = 0·05 nm) and the phenomenon follows the mechanism:

$$\frac{3}{4}O_2 + 3\,Y^{x}_{Al} \leftrightarrows \frac{3}{2}O^{x}_{0} + 3\,Y^{\circ}_{Al} + V'''_{Al}$$

Moreover, these vacancies increase the alumina plasticity and so, can help the BN flakes orientation when the pressure is applied during hot-pressing, and limit the vaults formation between these platelets that creates a considerable porosity in the composites.

Also, the Y_2O_3 addition can lead to the appearance of yttrogarnet $Y_3Al_5O_{12}$ (YAG) by *in situ* reaction with Al_2O_3: yttrogarnet whose corrosion resistance in molten steels was shown to be better than BN, W. Sinclair and M B. Trigg.[6-8]

2 Experimental Procedure

Commercial grade powders, 772 SB PECHINEY Alumina and GREPSI Hexagonal Boron Nitride flakes were used to prepare the composites. Starting from a 4 μm homogeneous BN powder after attrition, two slurries were prepared in the 66 vol% methyl ethyl ketone-34 vol% ethanol azeotrope, with specific dispersants, 0·8 wt% phosphate ester for alumina and yttria, and 2 wt% Polyvinyl Pyrrolidone for BN. After 10 min of ultrasonic disintegration, necessary to crumble these powders, both slurries were mixed together for 42 h by ball-milling and 5 h by a slow attrition before to be dried and sieved.

The powder was hot-pressed at 1750°C and 40 MPa for 30 min in nitrogen atmosphere with a heating rate of 30°C/min.[9–10] All these parameters are controlled by a computer which allows us to obtain the shrinkage rate during sintering.

The properties of Y_2O_3 doped alumina–BN composites were determined: density, flexural strength, SEM observations and XRD analysis. For flexural strength measurements, the crack propagation is parallel to the pressing axis of hot-pressing.

The composites, whose behaviour were studied at high temperatures, were chosen with 60 wt% alumina and 0, 0·5 and 2·5 wt% Y_2O_3 in reference to Al_2O_3 content.

These composites were tested for resistance to thermal shocks. After having been cut into bars of 20 × 3 × 4 mm^3, they were heated in a vertical tube furnace at a chosen temperature and then dropped into agitated oil at room temperature. Then, the samples were broken by the 3 point bending test; the variation of the flexural strength versus the temperature difference ΔT, between the initial hot temperature and the quenching medium, allows to determine the critical value ΔT_c.

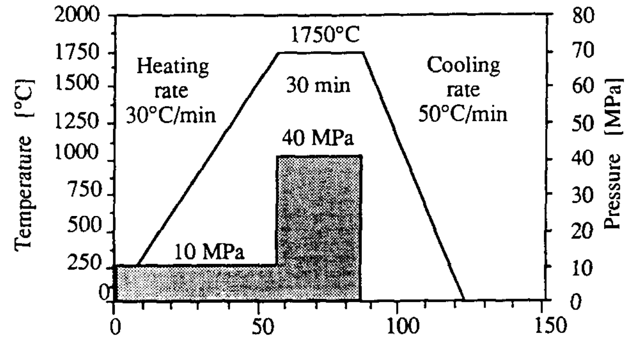

Fig. 1. Hot pressing cycle.

The oxidation resistance was studied on cubic samples of 10 × 10 × 10 mm^3 treated in oxygen at 1300°C, by measurements of the oxidized layers depths versus soaking time, for the two main directions, parallel and perpendicular to the pressing axis.

Also, the corrosion resistance was obtained by studying the corroded layers on fingers with dimensions 45 × 10 × 10 mm^3 immersed into liquid steel at 1580°C ± 10°C for 30 min (Fig. 2).[10–11] The steel oxidation is limited by the addition of a slag whose composition is given in Table 1. An erosive condition is maintained by the forced movement of steel due to the furnace induction and the rotation of the samples at the speed of 2 rpm.

The oxidized and corroded samples were studied by SEM observations and XRD analysis.

Table 1. Chemical composition of the slag

Components	*Contents*
SiO_2	34·3 ± 2·0
CaO	33·0 ± 2·0
MgO	1·3 ± 0·5
Na_2O	5·8 ± 1·0
F_2	8·6 ± 1·5
Fe_2O_3	0·4 ± 0·5
Al_2O_3	10·0 ± 1·0
MnO	1·3 ± 0·5
C	6·1 ± 1·5

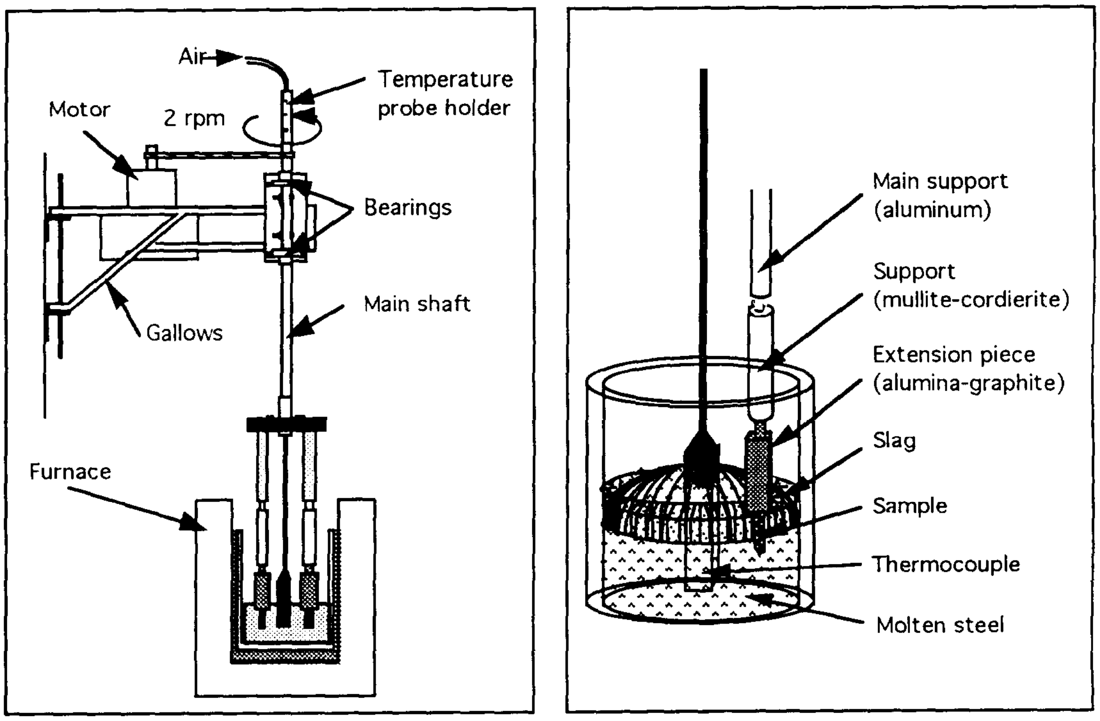

Fig. 2. Corrosion test set-up.

3 Results and Discussion

3.1 Densification and flexural strength

3.1.1 Undoped composites

Without Y_2O_3, the composite densification is limited to 92% of the theoretical density, for alumina contents lower than 70 wt%, due to vault formations between the BN platelets during hot-pressing[5] (Fig. 3). To reduce this drawback and densify composites, a pressure of 40 MPa must be applied at the soaking temperature which must be at least 1750°C, to achieve a sufficient plasticity of the alumina grains and so to allow orientations of the BN flakes. So, the material has an anisotropic microstructure with BN flakes orientated perpendicularly to the pressing axis and separated by strata of alumina grains between these platelets.

The reference hot-pressing cycle, presented in Fig. 1 and optimized by D. Goeuriot,[9] allows us to minimize the unfavourable orientations of BN platelets. It is divided into three successive segments:

Fig. 3. Fracture faces of an undoped composite with an important porosity due to a bad BN platelets orientation.

- Heating in N_2 atmosphere at 30°C/min rate under a pressure of 10 MPa to limit the chemical reaction between Al_2O_3 and BN to form AlN and B_2O_3.
- Temperature soaking at 1750°C under a pressure of 40 MPa for 30 min, to allow the BN flakes to orient perpendicular to the pressing axis.
- Cooling to room temperature at 50°C/min rate without applied pressure.

3.1.2 Yttria doped-composites

3.1.2.1 Sintering shrinkage of doped-composites. The sintering shrinkage curves, presented in Fig. 4, show differences between the composites' behaviour depending on their boron nitride and yttria contents:

- For composites with alumina content lower than 70 wt%, the curves for Y_2O_3 additions indicate that the beginning of densification and the temperature of the maximum of densification rate are shifted back by about 150°C.[12] Furthermore, these composites are particularly sensitive to the alumina plasticity for the BN platelets orientation. So, with yttria, the vacancies formation in alumina grains increases their plasticity and so allows the BN platelets orientation at lower temperatures.
- For composites containing 80 wt% Al_2O_3, the shrinkage beginning temperature is also decreased by the yttria presence, but the maximum shrinkage rate temperature and that of the end of the 'rapid' step of densification at 1400°C are not changed by yttria additions. For these composites which contain only 30 vol% of BN, the BN flakes dispersion is already sufficient to limit the contacts between them, and the vaults formation is so limited. The flakes orientation is so easy under a pressure of 40 MPa at 1750°C, that the yttria effect does not appear.

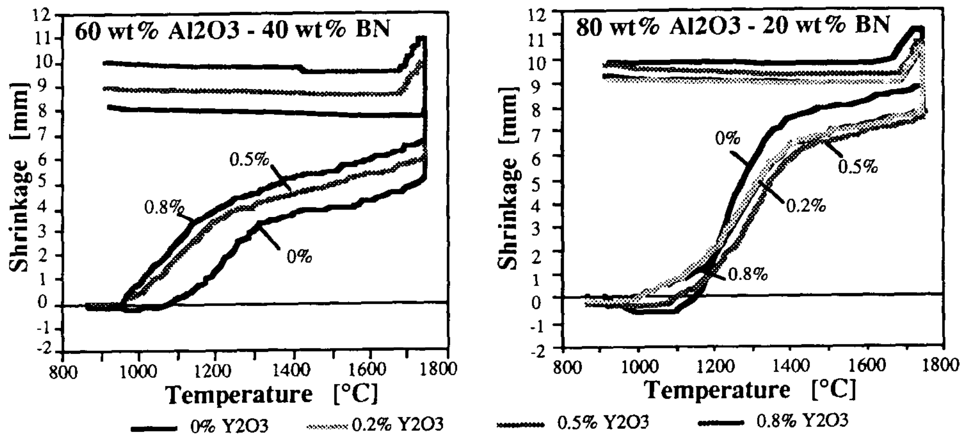

Fig. 4. Shrinkage of the Y_2O_3 doped composites during hot-pressing.

Fig. 5. Fracture faces of 0·5 wt% yttria doped composites (30 wt% BN–70 wt% Al_2O_3). Presence of strata of alumina and BN.

3.1.2.2 Doped composites microstructures. Due to the favourable effect of yttria on alumina sintering, the composites hot-pressed at 1750°C under 40 MPa following the reference cycle of Fig. 1 present a very nice orientation of the BN flakes. The microstructure is so composed by successive strata of BN platelets and alumina grains (Fig. 5).

3.1.2.3 Optimal addition of yttria. Despite the effect of yttria on composite shrinkage (mentioned before), it has a low influence on the final densification at 1750°C. For all alumina contents, the densities of doped composites and hot-pressed composites with the reference cycle, show a maximum increase of their densification of about 1% in comparison with undoped samples (Fig. 6). This increase obtained for additions of 0·5 wt% yttria considering Al_2O_3.

3.2 Hot pressing cycles influence (Fig. 7)

As the shrinkage temperature could be decreased by 150–200°C, different hot-pressing cycles were tested, with soaking temperature reduced to 1550°C and two different moments of pressure rise, at soaking temperature to obtain a favourable orientation of BN platelets, and at 1050°C below the alumina sintering temperature.

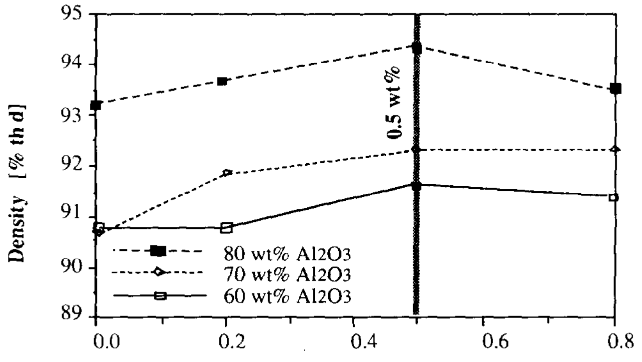

Fig. 6. Y_2O_3 additions effects on the composite densities after hot-pressing at 1750°C–40 MPa for 30 min.

So, four hot-pressing cycles were tested to densify the alumina–BN composites.

- 1750: the reference cycle presented in Fig. 1, with a soaking temperature of 1750°C and a pressure of 40 MPa applied during this temperature soaking.
- 1750–40: 40 MPa pressure is applied at 1050°C, below the soaking temperature at 1750°C.
- 1550: is the same cycle as 1750 with a soaking temperature reduced by 200°C, at 1550°C.
- 1550–40: is the same cycle as 1750–40 with a soaking temperature reduced to 1550°C.

The densification rates and flexural strengths were determined for two Y_2O_3 contents: 0·1 wt% and 0·5 wt% Y_2O_3 in reference to alumina and two alumina contents: 70 wt% and 80 wt%. The results are presented in Fig. 7.

3.2.1 Composites doped with 0·1 wt% Y_2O_3

There is not enough Y_2O_3 to densify the composites with 70 wt% alumina and only the reference cycle, 1750, allows us to obtain the most densified composites with the highest flexural strength.

For this temperature, applying high pressure (40 MPa) before the alumina shrinkage, which happens above 1100°C, leads to a poor orientation of BN flakes. This disorientation remains when the temperature rises and so impedes the densification, so that, the porosity of the sintered composite that follows the 1750–40 cycle is higher and it shows a lower flexural strength.

Samples sintered at 1550°C are less dense and so present lower flexural strengths too.

For the 80 wt% Al_2O_3 composite, there exists no important difference between the cycles in regard to their densification. For this composition, the low content of BN has little effect on the densification, as has been explained in Section 3.1.2.1.

But the flexural strengths are significantly higher if the soaking temperature is 1750°C. This difference is not only due to the porosity, but also certainly to a higher anisotropy of the material at 1750°C owing to a sufficient plasticity of alumina that allows the BN orientation during the pressure application. This plasticity which only occurs above 1100°C, does not allow us to obtain anisotropic composites at 1550°C and corresponding to these composites possess lower strengths.

For this composition also, applying 40 MPa at 1100°C is unfavourable to the BN orientation and so to the flexural strength.

3.2.2 Composites doped with 0·5 wt% Y_2O_3

Hot-pressing with 0·5 wt% Y_2O_3/Al_2O_3, allows us to densify the alumina–boron nitride composites

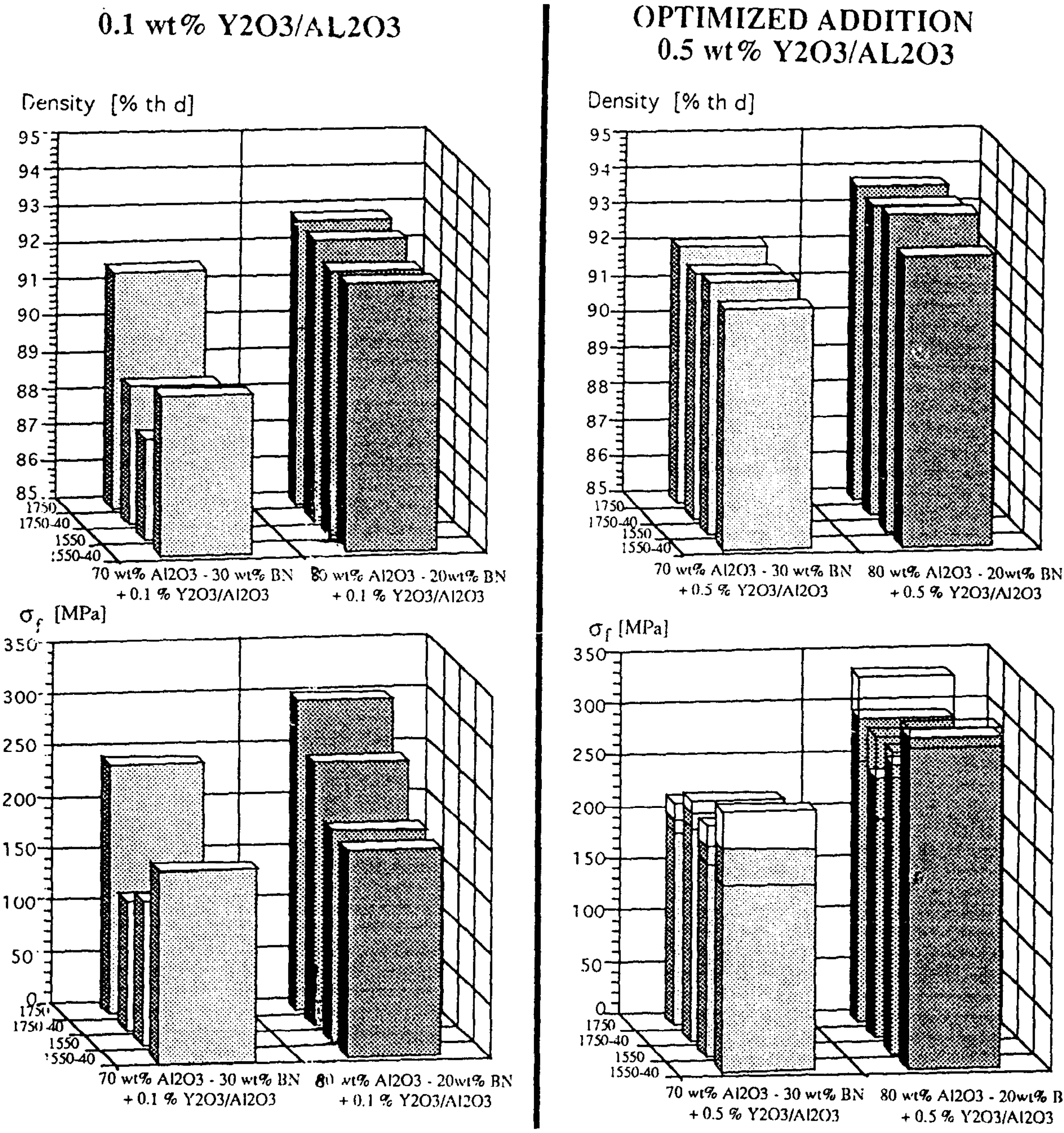

Fig. 7. Densities and flexural strengths of composites with 0·1 and 0·5 wt%/Y_2O_3 considering Al_2O_3.

and even the 70 wt% Al_2O_3 composites. Also, flexural strength is considerably increased by the addition of 0·5 wt% Y_2O_3 for all the applied cycles.

Part of these increments can be due to higher densification. But we can show that the highest strengths are measured for composites for which the pressure was applied at low temperatures, (1750–40 and 1550–40 cycles), even though the densities are a little lower than for the 1750 and 1550 cycles. The yttria addition has a significant favourable effect on the flexural strength of the alumina– boron nitride composites.

3.2.3 Discussion

3.2.3.1 Undoped composites. In the case of a high anisotropic composite formed by strata of alumina between the BN platelets, the fracture is propagating during flexural bending tests perpendicularly to the orientation of the platelets through the alumina boundaries or grains. When the crack meets a BN platelet, it by-passes along the Al_2O_3–BN boundary. This case corresponds to the 'pull-out' phenomenon of reinforcement.

But if the platelets are not perpendicularly orientated to the pressing axis, the fracture can follow it and propagate through this platelet between the 001 crystallographic planes.

So, less energy is spent to limit the fracture propagation, and the flexural strength of the composite is significantly decreased.

So, to reach the highest flexural strengths for undoped composites, BN platelets must be oriented. This needs the reference cycle to be used, with a soak at 1750°C under 40 MPa.

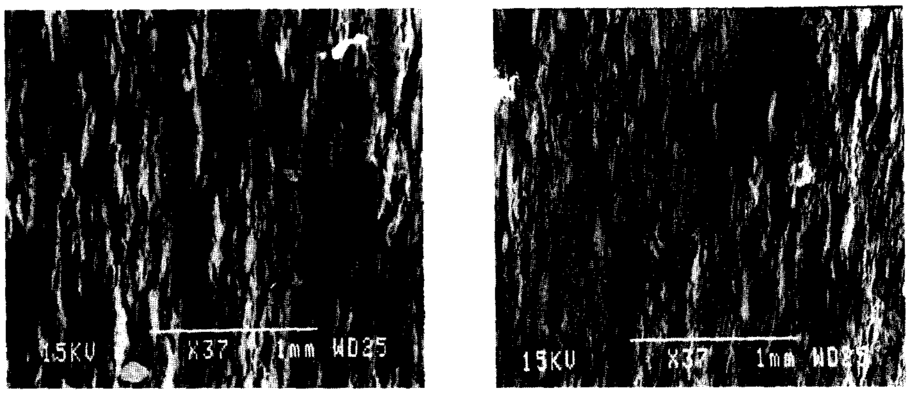

Fig. 8. Fracture faces of hot-pressed (1800°C — 40 MPa) boron nitride: (a) pure boron nitride; (b) BN with 2·3 vol% of Y_2O_3.

3.2.3.2 Doped composites. Samples that have been hot-pressed with a pressure rise at 1050°C (cycles 1750–40 and 1550–40) are considerably more porous due to the formation of vaults between the BN platelets. However, they have higher flexural strength due to the presence of yttrium at the boundaries, increasing the adhesion between alumina grains and BN platelets and cohesion between the BN platelets themselves, as shown on the fracture faces of Fig. 8. The fracture is more transgranular into the doped samples. In fact, the energy, spent to propagate the fracture through the BN flakes is more significant than that of by-passing. A. G. Evans[13] presented his theory (Fig. 9) on the reinforcement of boundaries in composites and the fiber or platelets debonding. There is a critical value of the ratio between the fracture energies of the interface and the platelet, for that, the fracture propagates either along the boundary or through the platelet.

The mechanism of crack deflection also occurs for these high energy boundaries and can thereby increase the flexural strength too (Fig. 10).

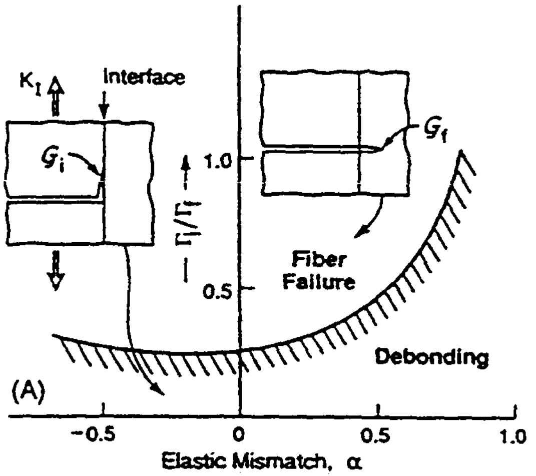

Fig. 9. Conditions of debonding of a fiber, perpendicular to the fracture (Ref. 13).

3.2.4 Conclusions

Without yttria, the alumina–boron nitride composites need to be hot-pressed at least at 1750°C under 40 MPa under nitrogen with a pressure rise during temperature soaking, to reach the highest flexural strengths. So the composites have an anisotropic microstructure constituted by strata of alumina between the BN platelets.

With yttria, composites can also be shaped without orientation of the BN platelets, also having a good flexural strength, and by the reinforcement of boundaries due to the presence of yttrium. So, we can suppose that it is easier to sinter these composites, perhaps by hot isostatic pressing.

3.3 Other properties

With yttria, property studies were performed to find out the composition that seems to be the best compromise on the different properties that composites need for the molten-steel casting, like good resistance to thermal shocks, oxidation and corrosion by the molten metals. This composition is 40 wt% BN and 60 wt% Al_2O_3.

3.3.1 Thermal shock resistance (Fig. 11)

Without yttria, the thermal shock resistance was

Fig. 10. Deflection of cracks into doped composites (30 wt% BN–70 wt% Al_2O_3) hot-pressed following the 1750–40 cycle.

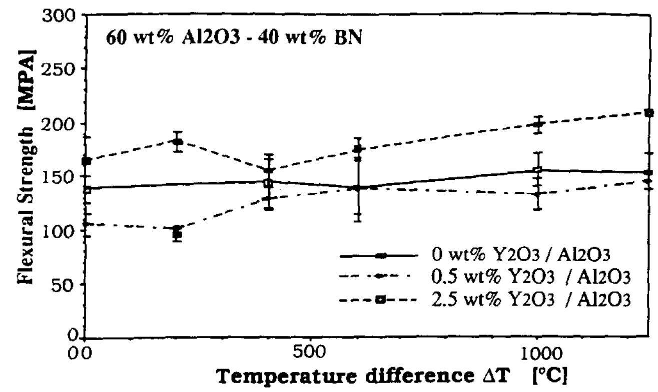

Fig. 11. Thermal shock resistance of yttria doped composites after oil quenching at 25°C.

studied for all the compositions between 50 and 90 wt% alumina contents. No drop of flexural strength in plotting it against temperature difference ΔT was observed, except perhaps for the highest alumina content.

With yttria, in spite of the temperature difference that exceeds 1200°C for some tests, the flexural strength curves of Fig. 11 show no fall, a slight increase can even be noticed for the highest yttria content.

In fact, all these composites have about 8 vol% of porosity, that is favourable to the thermal shock resistance. Moreover, microcracks appear during hot-pressing due to the significant thermal expansion coefficients mismatch between alumina (7–10 × 10^{-6} K) and boron nitride (0·7 × 10^{-6} K in the direction perpendicular to the pressing axis). The initial low flexural strengths prove that the microcrack length and density are high. So, it could be expected that the thermal shocks cause only quasi-static crack propagations. That does not affect the composites' flexural strengths.

So, the alumina–boron nitride composites' properties make them highly resistant to thermal shocks and no deterioration of the mechanical properties could be observed.

3.3.2 Oxidation

3.3.2.1 Undoped composites. Without yttria, composites are readily oxidized above 1100°C, according to the following mechanism, divided into two successive steps:[10,14]

$$2\,BN + 3/2\,O_2\,(g) \rightleftarrows B_2O_3(l) + N_2\,(g)$$

$$9\,Al_2O_3 + 2\,B_2O_3(g)(l) \rightleftarrows 9\,Al_2O_3 \cdot 2\,B_2O_3\ (A9B2)$$

The plotting of the oxidation depth versus time at 1300°C under O_2 (Figs 12 and 13) shows the oxidation kinetics in the two directions, perpendicular and parallel to the pressing axis for anisotropic materials.

3.3.2.2 Perpendicular to the pressing axis. Without yttria, and perpendicular to the pressing axis, the oxygen can migrate between the debonding 001 planes of the hexagonal boron nitride and oxidizes their platelets very quickly and forms significant quantities of B_2O_3. A part of this boron oxide is unable to react with alumina and so migrates to the surface along with the nitrogen formed. There, it forms a protective liquid layer that closes the pores and thereby stops the gas exchange (Fig. 14). So, the oxidation protection is assumed to be that of boron oxide alone and, in this direction, the effect of yttria on the oxidation rate could not be observed.

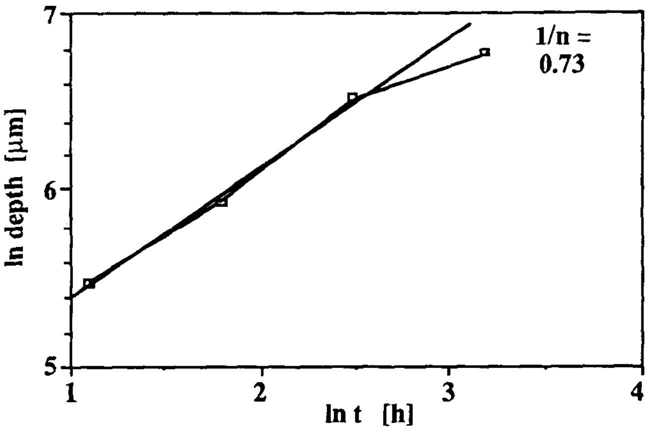

Fig. 13. Evolution of the oxidized layer depth with 0·5 wt% Y_2O_3/Al_2O_3 (parallel to the pressing axis).

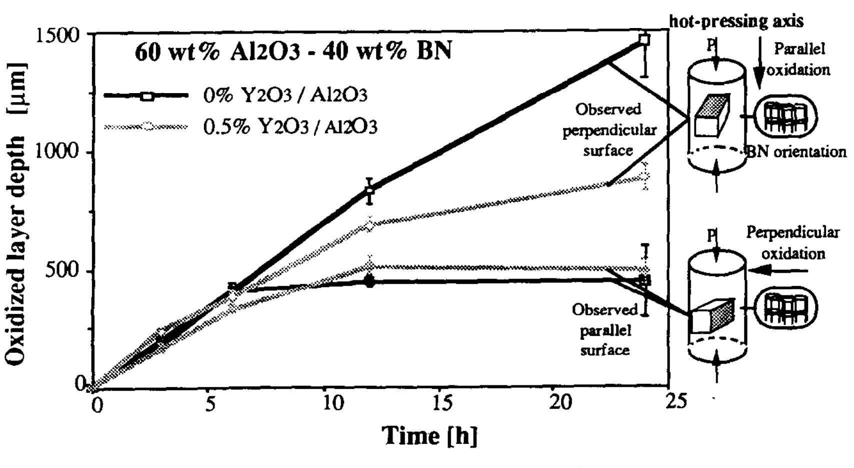

Fig. 12. Evaluation of the oxidized layer depths versus time with and without yttria additions.

Fig. 14. Cross-section of the oxidized scale in the case of oxidation perpendicular to the pressing axis. Presence of a dense liquid layer.

Also, at the surface, above this protective layer, the boron oxide's evaporation leads to enrichment in alumina and A9B2 chimneys can form. This chimney shape is caused by the exhaustion of volatile boron oxides and nitrogen (Fig. 14).

3.3.2.3 Parallel to the pressing axis. Without yttria, the oxidation follows a linear kinetic, that means there is a reaction limiting step:

$$\text{Depth} = kt$$

Following this oxidation direction, oxygen meets the BN flakes oriented perpendicularly and only oxidizes some first 001 planes. So, there is little boron oxide, B_2O_3, formed by oxidation of the boron nitride, that dissolves the alumina grains. Then, there is a crystallization of A9B2 in the form of bars of about $10 \times 0{\cdot}8 \times 0{\cdot}8\ \mu m^3$ in dimension, following the remaining nonoxidized BN planes. So this crystallization occurs perpendicularly to the pressing axis as shown in Fig. 15. Then there is a penetration of the oxygen between these A9B2 bars, and the mechanism happens again.

With Y_2O_3, the mechanism is more complex. The composite is, before oxidation, composed of Al_2O_3, BN and yttrogarnet, $Y_3Al_2(AlO_4)_3$, formed *in situ* by the reaction between Al_2O_3 and Y_2O_3 during hot-pressing. EDS analysis showed the yttrium migration to the surface during oxidation. Then, this material forms at the surface as a protective amorphous layer constituted of Al, B, Y, O, N, present around and under the A9B2 crystals. That allows part of the open pores to close due to the A9B2 crystallization, so limiting the gas exchange and thereby the oxidation rate. But the kinetic law does not follow a parabolic curve as for an O_2 diffusion-controlled mechanism, but this law follows:

$$\text{Depth}^{1{\cdot}4} = k't$$

So the oxidation mechanism with yttria is dual, consists of kinetics of O_2 diffusion mechanism due to the protective layer and of reaction-controlled mechanism.[10,14]

3.4 Corrosion by molten steel

The same samples tested for oxidation were dropped into molten steel covered with a slag containing $34{\cdot}3 \pm 2{\cdot}0$ wt% SiO_2 and $33{\cdot}0 \pm 2{\cdot}0$ wt% CaO, as presented in Table 1. This test combines two corrosive mechanisms.[10–11]

— oxidation of boron nitride by the dissolved oxygen in iron and by FeO

— alumina dissolution by the slag which is particularly reactive with Al_2O_3, forming mullite or calcium aluminates with SiO_2 and CaO respectively.

In iron, the yttria-doped composites are oxidized by a mechanism similar to the one in oxygen with the A9B2 crystallization. But there is an erosion of the protective layer observed after the tests of oxidation by the movement of the molten steel. So, although the corroded layer depths with yttria (Table 2) are smaller, the attack is significant as can be observed in Fig. 16, because this liquid layer at the surface is eroded and the alumina grains are carried off along with it.

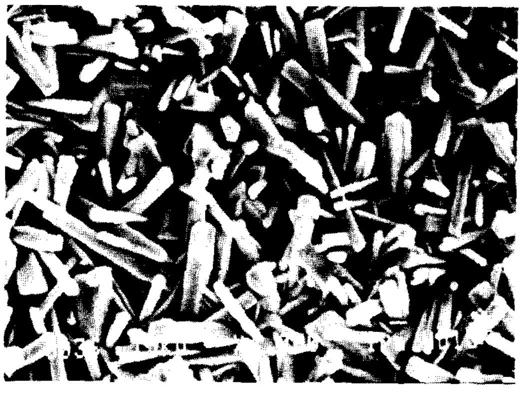

Fig. 15. Oxidized scale for oxidation parallel to the pressing axis: A9B2 crystals and open porosity.

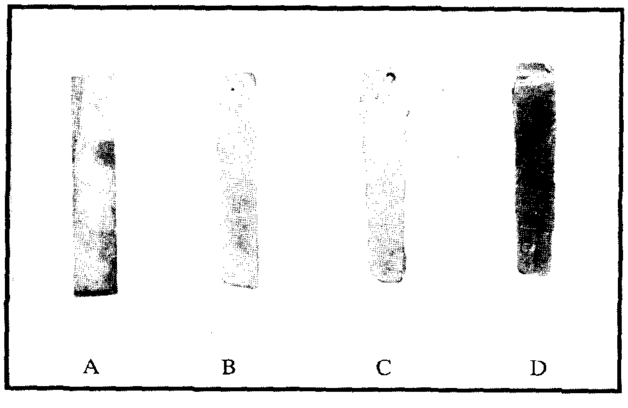

Fig. 16. Corroded samples cross-section: (A) uncorroded sample (reference); (B) 0 wt% Y_2O_3; (C) 0·5 wt% Y_2O_3; (D) 2·5 wt% Y_2O_3.

Table 2. Corroded layer depthes depending on the yttria contents

Sample (60 wt% Al_2O_3–40 wt% BN)	*Corroded layer depth in slag (μm)*	*Corroded layer depth in iron (μm)*
0 wt% Y_2O_3/Al_2O_3	10–20	500–600
0·5 wt% Y_2O_3/Al_2O_3	100	300
2·5 wt% Y_2O_3/Al_2O_3	30	150

In the slag, the corrosive attack is slightly more significant with yttria too. The reaction between yttria and alumina to give YAG, consumes a part of the alumina grains that are smaller and so more reactive to react with the slag.

Moreover, the 2·5 wt% yttria content composite has cracks, mostly longitudinal and 'V' shaped. They indicate that this composite did not withstand the thermal shock induced by immersion in liquid steel. That was not detected in its behaviour during thermal shock at 1250°C. So, either the yttria content must be limited in order to avoid considerable deterioration of the mechanical properties of the composite in contact with iron, or it should be necessary to pre-heat the composite specimen prior to this contact.

Although, yttria addition offers much resistance to oxidation by O_2 resistance, but does not protect the alumina–boron nitride composites from the corrosion by slag and molten steel. But other studies allow us to increase this corrosion resistance by neodymium oxide additions to lead to very inert composites.[10–12]

4 Conclusions

Without Y_2O_3 additions, the improvement of mechanical properties of the Al_2O_3–BN composites is maximum; if the BN platelets are oriented perpendicularly to the pressing axis during hot-pressing. This microstructure is attained by hot-pressing at 1750°C with a pressure rise from 10 to 40 MPa at this soaking temperature.

With 0·5 wt% Y_2O_3/Al_2O_3, it is possible to modify the microstructure by changing the hot-pressing cycle to obtain a more isotropic material by a pressure rise at only 1050°C. This yttria addition allows us to reduce the soaking temperature by 200°C, from 1750 to 1550°C, leading to more densified composites with increased mechanical strengths, due to the more stronger cohesion caused by Y_2O_3.

This 0·5 wt% Y_2O_3 addition increases the oxidation resistance of the composite too, by reaction at the surface between YAG, alumina and B_2O_3, forming a liquid phase that protects the material by closing the pores created by the A9B2 crystallization.

But Y_2O_3 decreases the corrosion resistance to molten steel, because this liquid phase is easily eroded and unable to protect the material. Moreover its concentration should not exceed 0·5 wt%/Al_2O_3, in order to limit the damage caused by the thermal shock during the immersion in liquid steel.

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