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Influence of Boron Nitride and Carbon Additives on the Behaviour of Sintered AlN in a Steel-Making Environment

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Abstract

In an earlier work we showed that the corrosion of pure aluminium nitride by steels takes place via an attack on the grain boundary Al/O/N phases and through AlN decomposition, with oxidation of aluminium by the dissolved oxygen. To reduce this type of corrosion, we tried to remove alumina and Al/O/N phases from the grain boundary by adding to the initial powders a small quantity of BN or carbon. The quantity of added BN must be in strict accordance with the quantity necessary to clean the grain boundaries. Best results were obtained with 10 wt% of BN. Carbon addition, which helps to improve the thermal shock resistance as well, produces the same result, but through a different mechanism. Best results were obtained with quantities between 5 and 10 wt% of carbon.

1 Introduction

For economic reasons and to optimize their mechanical, thermal and thermochemical properties, the refractory parts and ceramic coatings used in the iron and steel industry are composed of a mixture of different materials. For example, carbon is added to improve the resistance to thermal shock of certain ceramic parts. In our earlier work[1] we have shown the importance of grain boundary phases in the behaviour of AlN against liquid steels. Here we have tried to improve the corrosion resistance of AlN by systematically adding BN or carbon, while verifying their influence on the properties of AlN each time.

2. Experimental

2.1 Preparation of sintered samples of AlN–BN and AlN–C ceramic materials

Initial powder mixtures were prepared by magnetic agitation in ethanol–acetone for 2–3 h in order to obtain homogeneous dispersions. These powders were kept in an oven at 100°C for 1 h and then milled once again before placing them in a graphite mould.

In the case of the AlN–BN mixture, only the 66% AlN–34% BN mixture could be densified to 88% of its theoretical density. We did not succeed in densifying the other compositions (50% AlN–50% BN and 34% AlN–66% BN) sufficiently to carry out experiments (Table 1). In the case of AlN–C a relatively low densification was obtained, compared to AlN–BN. The low density of AlN–BN and AlN–C substrates could be due to the reactivity of BN and C towards oxynitrides and oxides[2–5] which are present in the AlN powder: their influence has previously been proved in the sintering of AlN.[6]

The X-ray patterns of the AlN–BN and AlN–C substrates, obtained after the sintering process, show only the peaks corresponding to AlN, BN and C, which confirm the purity of the sintering products and the absence of any reaction between the materials.

2.2 Steels

We worked with three type of steel: A, extra mild low carbon; B, treated SiCa; and C, IFS ultra-low carbon steel. The chemical composition of these steels is given in Table 2.

3 Study of AlN–BN Behaviour with Respect to Steels

The study of the AlN reaction with steels A, B and C in the liquid state,[1] has shown that AlN presents weak corrosion resistance against these steels, and

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Table 1. Sintering conditions of AlN–BN and AlN–C mixtures

AlN rate (% mass)	66	50	34	95	90	80
BN rate (% mass)	34	50	66	0	0	0
Carbon rate	0	0	0	5	10	20
Temperature (°C)	1830	1850	1850	1820	1825	1830
Pressure (MPa)	23	23	23	28	29	30
Time (min)	30	35	40	60	60	60
d/d_{th} (%)	88	—	—	82	80	78

Table 2. Chemical composition of steels in p.p.m. by weight

Steels	*A*	*B*	*C*
C	430	1000	60
Si	120	3430	50
Al	450	250	440
Ti	0	110	670
N	46	36	26
Mn	1940	13 730	1850

that the steels A and B show a wetting character over AlN substrates.

This corrosion is the result of strong reactivity at the solid–liquid interface, during the wettability experiments, through a complex mechanism which can be divided into two stages:

(1) Thermal decomposition of aluminium nitride[7] and oxidation of the resulting aluminium by oxygen dissolved in steels:

$$2AlN_{(sol)} + 3[O]_{(steel)} \rightarrow Al_2O_{3(sol)} + N_{2(gas)}\uparrow \quad (1)$$

(2) Grain boundary attack through oxidation of AlON phases which are present at the grain boundaries:

$$2AlON_{(sol)} + [O]_{(steel)} \rightarrow Al_2O_{3(sol)} + N_{2(gas)}\uparrow \quad (2)$$

The boron nitride added to the AlN matrix reacts with Al_2O_3 and AlON phases during the sintering process[2,3] according to reactions (3) and (4), which helps in the removal of these parasite phases and in the cleaning of AlN grain boundaries:

$$Al_2O_{3(sol)} + 2BN_{(sol)} \rightarrow 2AlN_{(sol)} + B_2O_{3(gas)}\uparrow \quad (3)$$

$$2AlON_{(sol)} + 2BN_{(sol)} \rightarrow 2AlN_{(sol)} + B_2O_{3(gas)}\uparrow + N_{2(gas)}\uparrow \quad (4)$$

3.1 Wettability of AlN–BN substrates by steel

Experiments were performed using the sessile drop method, between 1520 and 1635°C, using the apparatus already described in Ref. 8. The metallic sample is kept under vacuum up to 1490°C (25–40°C before the melting point), at which point argon is introduced in the furnace with a little overpressure[1].

3.2 Contract angle

The contract angle between the steel drops and AlN–BN solid substrate remains constant and non-wetting, in the temperature range between drop formation and 1635°C (Fig. 1).

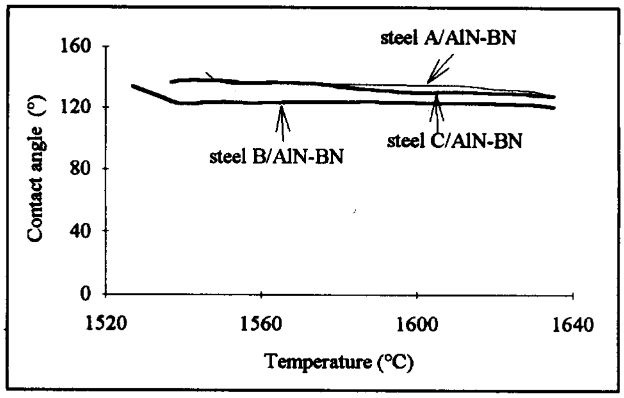

Fig. 1. Evolution of contract angle with temperature.

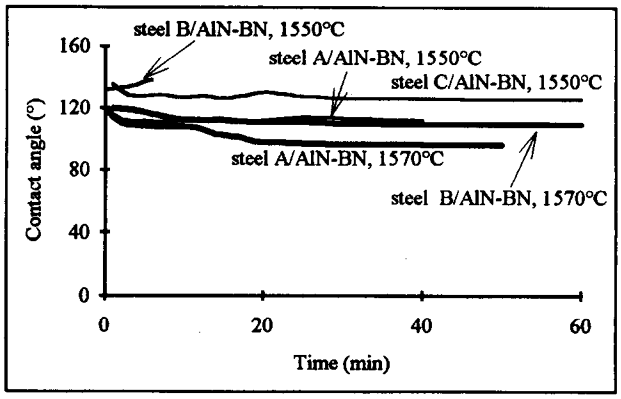

Fig. 2. Contract angle as a function of time.

The contract angle also remains constant as a function of time, at a given temperature, as shown in Fig. 2. For the system steel B/AlN–BN, a strong swelling of the liquid drop was observed at 1550°C, which made contact angle measurement almost impossible. The values for this system shown in Fig. 2, at 1570°C, are approximate because the measurement was made between two swellings.

3.3 Solid–liquid surface tension

Calculations for solid–liquid surface tension were obtained using Young's equation[1] while keeping σ_{sv} constant between the considered temperatures. We fixed σ_{sv} = 1000 mN m^{-1}, which is the value generally used by other authors.[9,10] This means that our observations only concern the variation of σ_{SL} and not its absolute value.

The solid–liquid surface tension for the systems of steels A and B over AlN–BN substrates, as a function of temperature, decreases immediately after liquid drop formation and stabilizes afterwards (Fig. 3); in the system steel C/AlN–BN, it slightly decreases between the temperature of drop formation and 1620°C.

At constant temperature, σ_{SL} for the system C/AlN–BN decreases rapidly during the first 10 min, which shows strong interaction between the

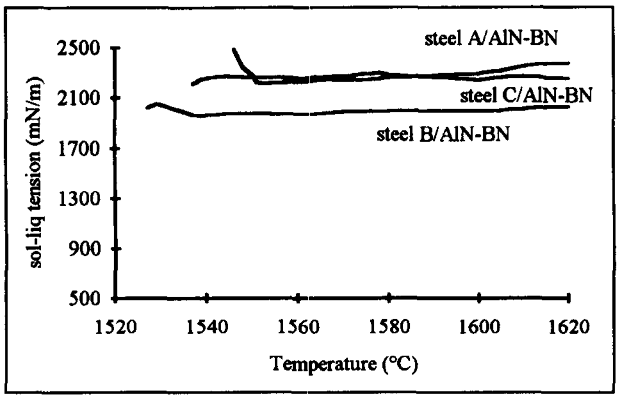

Fig. 3. Solid–liquid tension as a function of temperature.

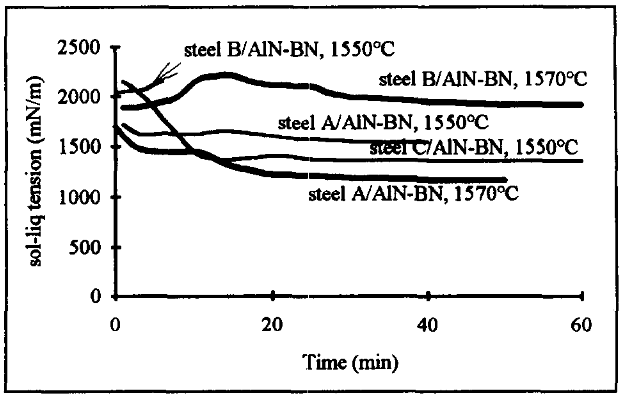

Fig. 4. Solid–liquid tension as a function of time.

steel and substrate at 1550°C (Fig. 4). At 1570°C the liquid drop started swelling, which made contact angle measurement impossible. The same type of behaviour was obtained in the case of A/AlN–BN, where stabilization was obtained after 20 min contract time. In all cases, this decrease in σ_{SL} value was more pronounced as the temperature was increased.

The results obtained by the dipping method (Table 3) have shown that the corrosion of AlN–BN is less than that of pure AlN, thus proving the effect of BN addition to the AlN matrix.

4 Discussion and Interpretation of Results

The addition of BN in the AlN matrix modifies considerably the wetting behaviour of steels A and B. We observe contact angles of 110 and 120° at 1550°C, respectively, with AlN–BN, whereas in the case of pure AlN (89% densified) these angles were 50° and 40°.[1] At a higher temperature, 1570°C, the same difference exists. The same effect is observed in the variation of solid–liquid surface tension, where the form of the curves in the two cases remains the same, while the value of $\Delta\sigma_{SL}$ varies (Table 4). These values can be assimilated approximatively as the free enthalpy of interaction at the solid–liquid interface per unit surface area ($\Delta G/S$).[11]

Table 3. Corroded thickness of AlN–BN and AlN small bars after contact with liquid steel for 1 h (in mm)

Substrate	*Pure AlN*[1] (d/d_{th} = 90%)		*66% AlN–34% BN* (d/d_{th} = 88%)		*90% AlN–10% BN* (d/d_{th} = 89%)
Steels	*1550°C*	*1650°C*	*1550°C*	*1650°C*	*1650°C*
A	0·06	>0·2	0·01	—	<0·01
B	0·048	0·2	0·026	—	<0·01
C	0·02	0·19	<0·01	0·1	<0·01

Table 4. Decrease in the solid–liquid tension of steels over AlN and AlN–BN substrates, at 1570°C, during the first 10 min

	$\Delta\sigma_{SL}$ *(mN m^{-1})*	
Steels	*AlN*[1]	*AlN–BN*
A	1000	300
B	2000	100
C	400	0

The fact that the contact angle of liquid steels over the AlN–BN substrates varied slightly (Figs 1 and 2) with temperature and time appears to be paradoxical, if we only consider the reactivity of AlN,[12,13] since in the AlN–steel systems the oxidation of the ceramic was the principal reason for the diminution of contact angle. To explain this behaviour we must consider the presence of BN and its reactivity with oxygen and alumina, which was certainly the origin of this non-wetting behaviour of steels. Compared to pure AlN, in the latter case, we have a competition between two chemical reactions:

- AlN oxidation through dissolved oxygen (1); and
- BN oxidation through alumina, the product of the AlN oxidation reaction (3).

$$2AlN_{(sol)} + 3[O]_{(steel)} \rightarrow Al_2O_{3(sol)} + N_{2(gas)}\uparrow \quad (1)$$

$$2BN_{(sol)} + Al_2O_{3(sol)} \rightarrow B_2O_{3(gas)}\uparrow + 2AlN_{(sol)} \quad (3)$$

$$2BN_{(sol)} + 3[O]_{(steel)} \rightarrow B_2O_{3(gas)}\uparrow + N_{2(gas)}\uparrow \quad (5)$$

Globally the reaction resulted in the oxidation of BN. Thus the intervention of BN takes place:

- during the sintering through reaction with Al_2O_3 and AlON, which gives AlN according to reaction (3), and cleans the grain boundaries;
- during contact with the liquid steel, where it consumes oxygen according to the global reaction (5) at the interface, and reduces the risk of AlN oxidation.

While eliminating the parasite secondary phases, boron nitride also eliminates the oxidation reaction at the interface and thus prevents the contact angle evolution.

We note also that the steels do not wet the AlN–BN ceramic and have relatively high values of σ_{LV} (1600 mN m^{-1}), which helps to avoid capillary penetration. Whereas, in the case of pure AlN, the steels have a wetting character which facilitates capillary penetration, while increasing the reactive surface. In all cases, these reactions give nitrogen and B_2O_3 at the given temperature. This phenomenon promotes the swelling of liquid drops, which is mentioned earlier. Another negative effect of these reactions is the appearance of porosity at the interface, which possibly helps the liquid to penetrate to new surfaces. Thus the quantity of BN should be sufficient to clean the grain boundaries, to consume the oxygen during sintering, but it should not be more than the required value, to avoid the formation of porosity as well as the liquid steel penetration. The results have helped us to determine an optimum value, which is 10% by weight.

AlN–BN samples prepared under these conditions show very little corrosion compared to pure AlN (Table 3). In the case of steel B at 1550°C, for example, we found through the dipping method, a corroded thickness of 60 μm for pure AlN and 10 μm for AlN–BN (34% BN) ceramic, whereas this value became almost zero for AlN–BN (10% BN).

5 Study of AlN–Carbon Mixture Behaviour Towards Steel B

5.1 Contract angle

The contract angle of steel B over AlN–C substrates depends upon the carbon content (expressed here in wt%). At 5% carbon, the contact angle remains constant and non-wetting ($120 < \theta < 140°$) between 1540 and 1630°C. With 10% carbon, the contact angle decreases rapidly with temperature, its values were 110° and 70° at 1550°C and 1570°C, respectively.

With 20% carbon, the wetting angle decrease is still more important than in the second case. We found that the wetting starts just after 1550°C. At constant temperature, the contact angle decreases rapidly during the first 10 min and then stabilizes at ~60° (Figs 5 and 6).

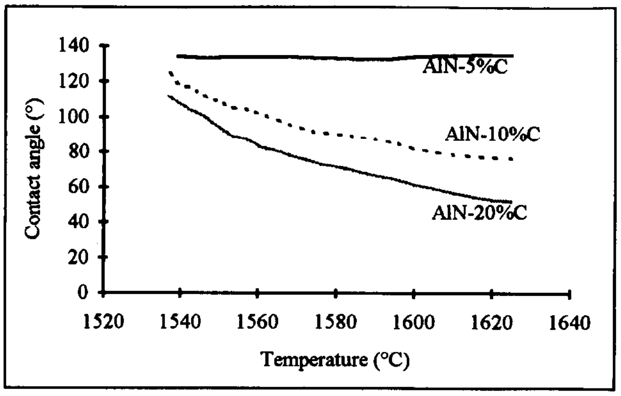

Fig. 5. Contract angle as a function of temperature.

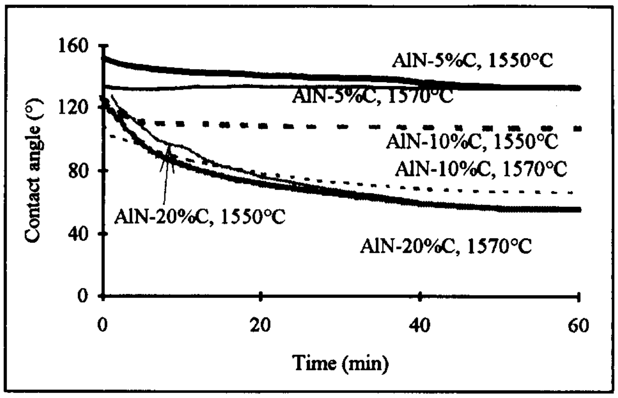

Fig. 6. Contract angle as a function of time.

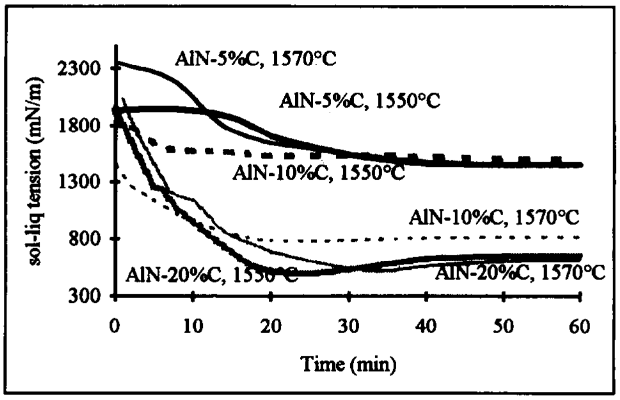

Fig. 7. Solid–liquid tension as a function of time.

5.2 Solid–liquid surface tension

With 5% carbon the solid–liquid surface tension decreases with time and becomes constant after 40 min. The σ_{SL} curve for the compositions with 10 and 20% carbon passes from a minimum value, with respect to the temperature. This minimum is more important for higher concentrations of carbon. This type of behaviour is characteristic of a chemical interaction at the solid–liquid interface,[11] and is particularly important at higher carbon concentrations.

6 Interpretation of Results

Overall, whatever the carbon concentration may be, the contact angle remains superior compared to pure AlN or carbon (Table 5). In the case of pure AlN or C, the angle is controlled through chemical reactions at the interface:

- In the case of pure AlN, these reactions start by the decomposition of AlN and oxidation of Al through oxygen present in the steel and by a grain boundary attack on the AlON phases.[1]
- In the case of pure carbon, the interaction takes

place by the dissolution of carbon in the steel, which promotes the formation of a low melting point liquid phase[14] around 1200°C (whereas the melting point of steel B is 1515°C). This interaction is probably the origin of the contact angle evolution and the corrosion of the substrate through liquid penetration.

The decrease in the melting point of steel due to the carbon dissolution was still more important for higher carbon concentrations (Table 5).

Thus for carbon concentrations between 5 and 20% the dissolution of carbon in the liquid steel seems to be the cause for the contact angle decrease.[11] This dissolution locally reduces the steel and decreases the oxygen content in the steel, which in turn reduces or slows down the oxidation of Al formed during the decomposition of AlN. The corrosion in this case takes place by AlN dissolution in the liquid steel. This mechanism explains the decrease in the corroded thickness of the substrates having higher carbon concentrations, whereas the effect of this phenomenon over the contact angle is an inverse one because the angle is controlled by the carbon dissolution (Table 5).

EDAX microanalysis confirms that the steel which penetrated into the substrate is rich in aluminium and Raman spectrometry detects the presence of carbon flakes in the corroded thickness. The presence of carbon in the AlN matrix greatly modifies the corrosion behaviour of the substrate towards steel B compared to the substrate with pure AlN:[1]

(1) During sintering, as in the case of BN addition, carbon reacts with AlON phases releasing CO, stable at high temperature,[15] which: (a) discourages densification during sintering, and thus a high porosity of 20% is obtained after sintering; and (b) eliminates the grain boundary attack when the substrate is in contact with liquid steel.
(2) The oxygen in the contact zone is eliminated by its reaction with dissolved carbon, and the resulting CO produces a small reducing atmosphere around the interface, which avoids direct oxidation of AlN through dissolved oxygen.[16]
(3) The only possible reaction is aluminium nitride decomposition, and dissolution of aluminium in steel. This dissolution takes place without alumina formation, due to the absence of oxygen at the interface, but the formation of alumina takes place on the liquid drop surface:

$$\mathrm{AlN} \rightarrow \mathrm{Al} + \frac{1}{2}\mathrm{N_2}$$

$$\mathrm{Al} \rightarrow \overline{\mathrm{Al}}$$

$$\overline{\mathrm{Al}} \rightarrow (\overline{\mathrm{Al}})_{\mathrm{liq-vap}}$$

$$(\overline{\mathrm{Al}})_{\mathrm{liq-vap}} + \mathrm{O_{2(gas)}} \rightarrow \mathrm{Al_2O_{3(sol)}}$$

The release of gas at the solid–liquid interface is due to the decomposition reaction (N_2) and also due to CO release, resulting from the reaction between dissolved oxygen and carbon. These gases promote swelling of the liquid drop and cavity formation at the interface, and result in the σ_{LV} values being superior to those pure iron.

Table 5. Influence of carbon content on corrosion of AlN matrix

wt% of C	*T_m (°C)*	*Corroded thickness (μm)*	*Θ(°)*
0	1515	300	40
5	1515	550	140
10	1500	450	110
20	1490	150	65
100	1200	1000	60

7 Conclusions

The addition of BN or carbon in an aluminium nitride matrix improves its corrosion resistance qualitatively and quantitatively, against different types of liquid steel and against type B steel in the case of AlN–C substrates.

The mixtures AlN–BN and AlN–C give comparable results but through different mechanisms. In the two cases we eliminates the AlON phase from the grain boundaries during sintering, through a reaction between BN and AlON with B_2O_3 release in the case of AlN–BN and through a reaction between carbon and AlON with CO release in the case of the AlN–C substrate.

In both cases the wetting angle increases compared to that obtained with pure AlN substrate (particularly in the case of 5 and 10% carbon) and the grain boundary attack is largely reduced.

Finally, in the two cases we reduces the presence of solid impurities in the liquid steel, because the identified reaction at a given temperature gives: 1, volatile B_2O_3 for BN addition; and 2, gaseous CO in the case of C addition. Only in the case of carbon dissolution at high temperatures can the initial carbon content in the steel be modified.

The rapid and preferential consumption of BN and C during the reaction, helps us to optimize their concentration in the mixtures:

- The quantity of BN should be just enough to clean the AlN grain boundaries and to participate in the consumption of dissolved oxygen. The optimum value was found to be 10% by weight (Table 3).

- The optimum carbon quantity should be calculated while keeping in mind the decrease in corrosion due to carbon presence and the reactivity of carbon with steels. Values of 5–10% were found to be optimum considering the corrosion and wettability results.

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