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Preparation of aluminium boride by powder technology

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Abstract

The problem with using boron in a sintering process is the formation of a surface layer of oxide [Combust., Explosion Shockwaves 10 (1974) 539] which hampers the process. The incorporation of reducing elements into the amorphous boron is done by powder technology. Suitable working conditions were designed to provide sintered boride free of oxide. The reducing elements served the double purpose of forming borides and of avoiding the formation of boric oxide in the first stage of sintering. Hermetically sealed crucibles were designed for the sintering by thermal shock. The source materials were amorphous boron and atomized aluminium.

Keywords: A. Sintering; A. Powders: solid state reaction; D. Borides; D. Glass ceramics

1. Introduction

The reducing elements were incorporated into the amorphous boron by powder technology. The elements were chosen from the Ellingham diagram [1] and the thermo-dynamic data shown in Table 1.

Compaction was by cold isostatic pressing (CIP) which gives great uniformity to the pressure distribution in the sample [2] and density close to the theorical [3]. Low compacting pressures between 200 and 350 MPa [4] are normally used for materials showing ceramic behaviour during the process as is the case with boron. We raised this pressure to 700 MPa since aluminium is the minor element; this raised its surface energy and facilitated the sintering.

Industrial atmospheres in sintering contain nitrogen or dissociated ammonia [5] so they are not appropriate to our materials as they would produce boric nitrates and hydrides. For this reason, the green compact sintering was done with crucibles specially designed for the process, able to withstand thermal shock in noncontrolled atmosphere and all nonequilibrium conditions.

Sintering requires that material transference and phase transformations occur in all conditions [6]. The aluminium particles were irregular shape [7], with a thin layer of oxide produced during atomization which would hinder particle contact and retard the sintering process [8].

Small particles were used, greatly improving the diffusion and heating rate [9]. The exothermic oxidation of the aluminium samples raises the crucible temperature. The aluminium oxide generated was reduced over the whole temperature range by 1–2% magnesium content in a raw boron. The method of manufacturing borides is by aluminium excess [10–13].

The heat generated by the formation of aluminium oxide raises the temperature in the crucible and facilitates the formation of aluminium borides which require high temperatures (Fig. 1) [14].

Of the two majority borides—AlB_{10} and AlB_{12}—was found to be thermodynamically superior is the αAlB_{12} (AlB_{10} is only stable between 1933 and 2123 K) [15] as was confirmed by our diffractograms.

2. Experimental procedure

An alternative way of sintering (cheaper) in order to obtain aluminium boride was done using B_2O_3 and BO_3H_3 (both high purity) as boron contributers and atomized aluminium. Both these products were milled

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to increase surface contact and reduce porosity for better sintering. Boric oxide was prepared from boric acid by heating at 670 K. Small particles (20 μm) were used, so the volumetric difussion and the heating rate are high. The oxidation of the aluminium samples is exothermic and the crucible temperature raises.

Amorphous boron as a raw material produce oxides reduction in the whole temperature scale by the magnesium content on the boron raw (0.5–1%).

The samples were compacted by cold isostatic pressing (at pressures up to 375 MPa) with multiple cycles of compaction-milling-compaction. We used the simplest method know as "dry bag" cold pressing [16]. Fig. 2 lists the operations carried out.

The procedure of manufacturing (in particular the mixing and homogenization) is difficulted by the amorphous boron (it was obtained for deposition in steam phase) [17,18], since the it has the possibility of becoming agglomerated before the sintering process. This implies the utilization of organic solves and ultrasound techniques.

Sucessive cycles of compactión-sintering-milling and thermal shock were suitable procedures for preparing aluminiun borides. These procedures supply to aluminum high activation energy. To minimize the heating time and to prevent the formation of Al_2O_3 and B_2O_3, a thermal shock was applied at 1373 K. This technique requiered a modification of the previusly designed air-tight crucibles (hermetically sealed) to make them resistant to the thermal shocks and using of vitreous coatings for the green compact. This techniques promote the formation of aluminium borides free of oxides using air atmosphere (1 atm).

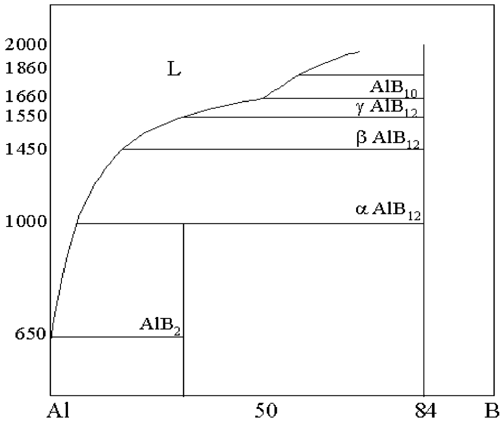

Fig. 1. Phase diagram of Al–B system [15].

3. Results and discussion

Ordinary crucibles and preheating promote oxides and borides during the sintering process (Figs. 3 and 4), so we designed special crucibles sealed to oxigen for this work, to produce aluminium borides free of oxides, as shown in Figs. 5–8.

The oxides $Al_{18}B_4O_{33}$ and $Mg_3B_2O_3$ (magnesium appearing as a contaminant of the amorphous boron used) were formed in the preheating stage [20] of sintering.

$$2Al_2O_3 + 2B_2O_3 \rightarrow 2Al_2O_3B_2O_3$$

$$9(2Al_2O_3.B_2O_3) \rightarrow 2Al_{18}B_4O_{33} + 5B_2O_3$$

Fig. 3 illustrates round skeins of aluminium oxide (white circle) and others lengthened (white) rectangle. Small mixed oxides (white ellipse) are scattered throughout the matrix.

Fig. 4 shows aluminium oxides (white circle) and mixed oxides of various shapes and sizes (white rect-

Table 1
Formation heat of inorganic oxides [19]

Reaction	cal/mol	kJ/mol
2 Al (s) + 3/2 O_2 (g) = Al_2O_3 (s)	−404.080	−1691.5
Mg (s) + 1/2 O_2 (g) = Mg O (s)	−144.090	−603.0
Ti (s) + O_2 (g) = Ti O_2 (s)	−288.360	−955.9
Zr (s) + O_2 (g) = Zr O_2 (s)	−262.980	−1100.9
C (graphite) + O_2 (g) = CO_2 (g)	−93.690	−392.0

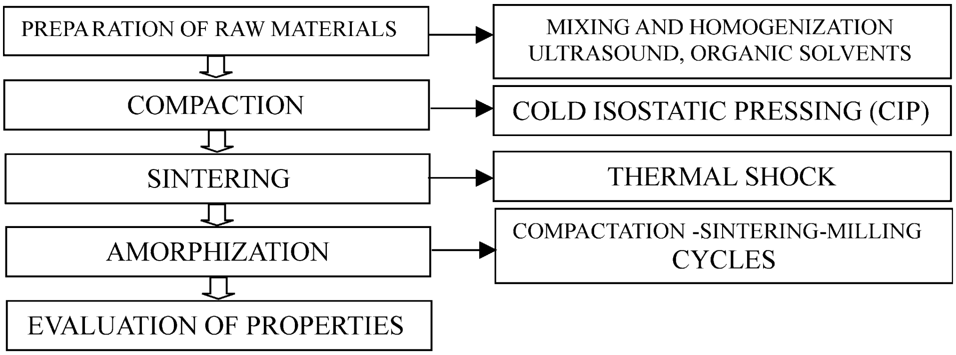

Fig. 2. List of operations carried out.

angle). All these were formed in oxidizing conditions of sintering when the sealing of the crucibles was deficient. The starting material of both samples was amorphous boron and atomized aluminium.

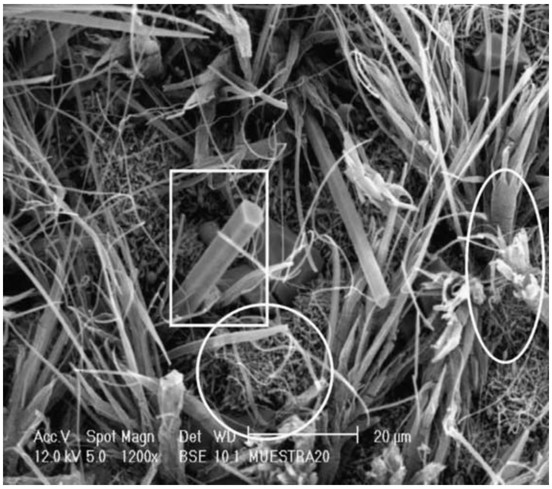

Fig. 3. Aluminium, boron and mix oxides. Sintering 1373 K, 30 min.

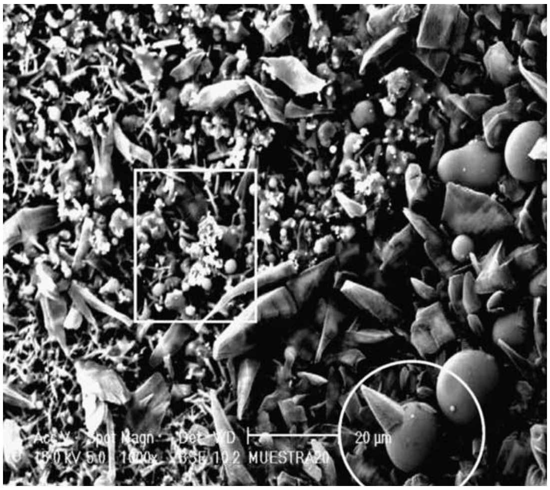

Fig. 4. Aluminium oxides. Sintering 1373 K, 30 min.

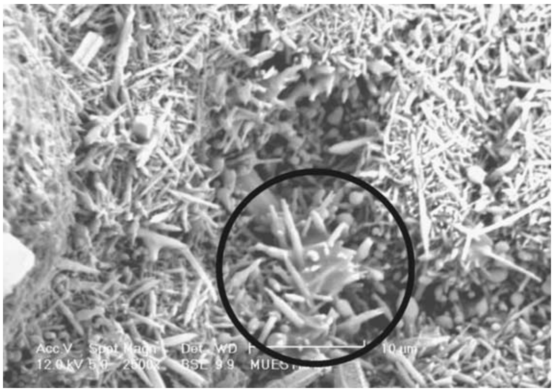

Fig. 5. Aluminium borides in formation. Sintering at 1373 K, 30 min.

The borides were prepared by sintermetallothermal techniques from boron, boric acid and boron oxide [21,22]. Compaction was by CIP to avoid interconnected porosity [23] since pores nucleate oxides. The temperatures were between 1073 and 1273 K, a range that favours the formation of $Al_4B_2O_9$ [24]. This mixed oxide is descomposed at 1373 K, liberating B_2O_3 [24] which reacts with aluminium at any temperature above its melting point and forms $Al_{18}B_4O_{33}$ [25,26]. The only way to avoid the formation of $Al_4B_2O_9$ is by controlling the initial temperature [27,28].

Fig. 6. Aluminium borides already formed. Sintering at 1373 K, 30 min.

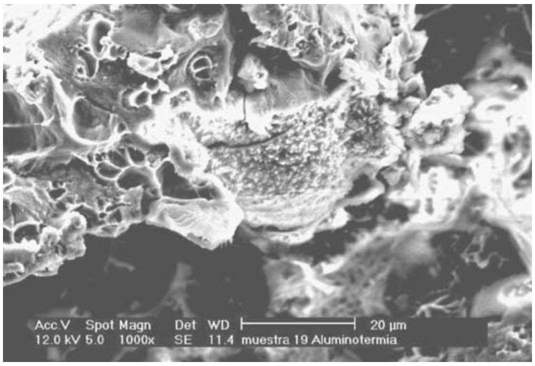

Fig. 7. Aluminium borides. Sintering at 1373 K, 30 min.

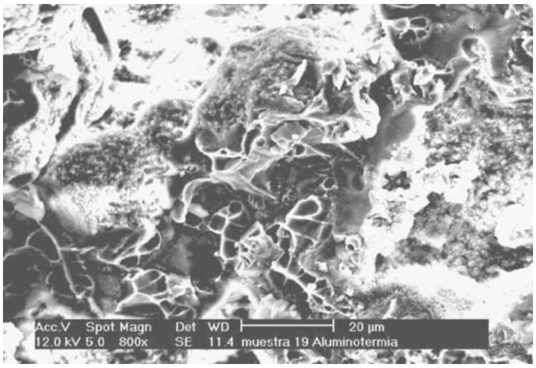

Fig. 8. Aluminium borides. Sintering at 1373 K, 15 min.

We bypassed this problem by using thermal shocks which raise the temperature to 1673 K in a matter of seconds without any preheating phase. This method called for a re-designed of the airtight crucibles to make them resistant to the thermal shock.

We used this method for the samples shown in Figs. 5–8. All the samples were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and micro-analysis by energy dispersive spectroscopy (EDS).

The samples were prepared in series of ten which were subjected to different processes of compaction and to sintering in different atmospheres and at different temperatures.

Figs. 5 and 6 illustrate the initial and the final stages of the formation of aluminium borides. Fig. 5 shows a treatment of boric oxide and atomized aluminium, the initial stage of the formation of AlB_{10} indicated by the black circle. The white needles observed in the matrix are those of aluminium oxide.

Fig. 6 shows the final stage of the formation of aluminium boride (large black circle). Little trace of oxide remain; the black rectangle outlines a small sphere of aluminium oxide and the small circle indicates a mixed oxide.

Figs. 7 and 8 illustrate the formation of aluminium borides, both samples prepared from boric acid and atomized aluminium. No oxide is observed in the matrix which is formed of aluminium borides AlB_{10} and AlB_{12} mainly the former.

Fig. 9 gives diffractographs of the samples denominated series 1, 2 and 3, whose composition was of B–25% Al by weight. Series 1 was prepared by CIP and

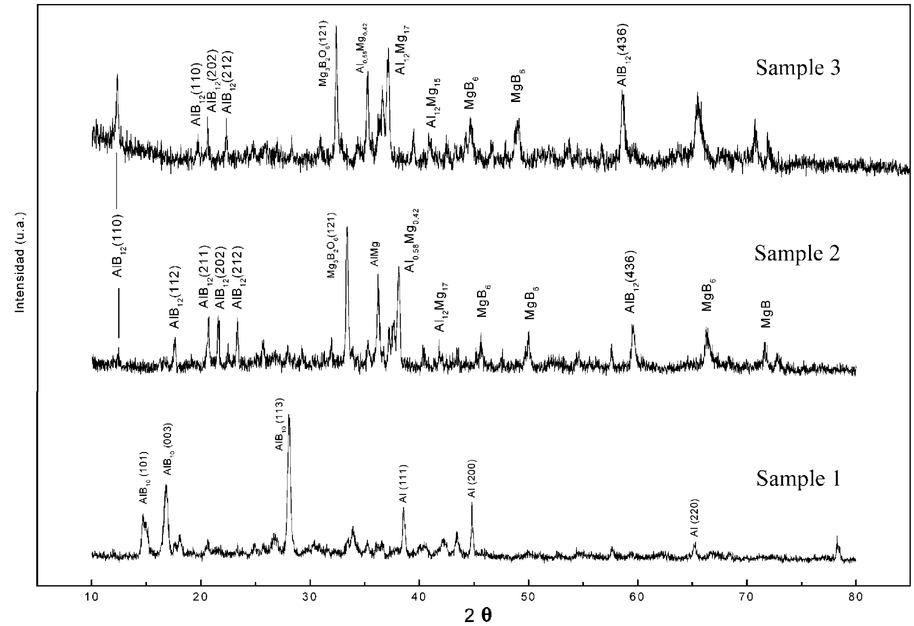

Fig. 9. Difraction patterns of the samples of series 1–3. B–25Al%.

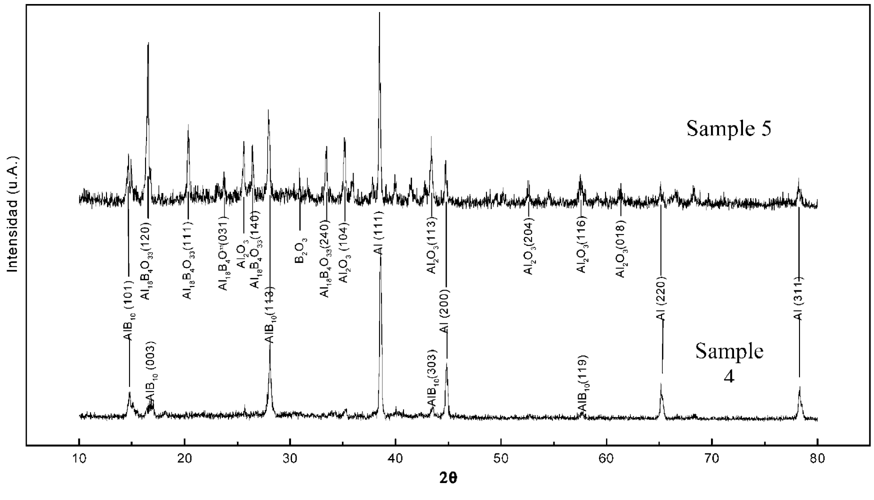

Fig. 10. Difractograms to the samples 4 and 5. Sintermetallothermics from (B_2O_3–Al). 45 min, 1373 K.

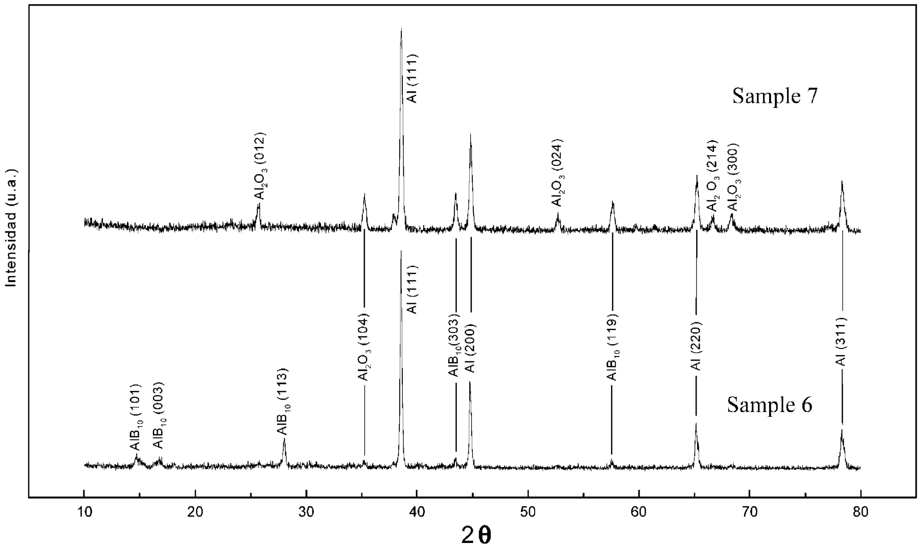

Fig. 11. Difractograms to the samples of the series 6 and 7. Sintermetallothermics from (BO_3H_3–Al). 45 min, 1373 K.

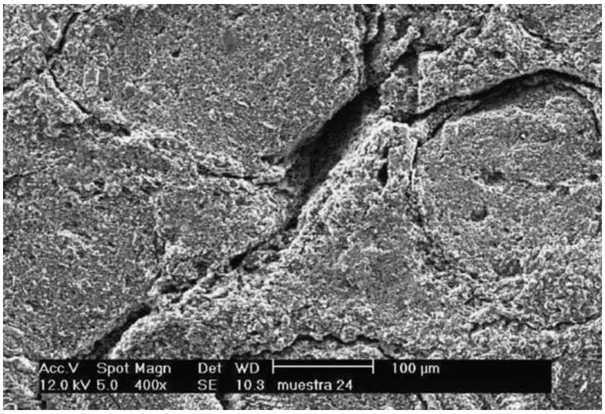

Fig. 12. Vitreous B–Al.

successive cycles of compaction-sintering-milling in oxidizing atmosphere and at low temperature (1373 K) with only slight oxidation. Series 2 and 3 were prepared by CIP and a single cycle of compaction-sintering-grinding. Series 2 was sintered at 1693 K and Series 3 at 1713 K, both in non-oxidizing atmosphere, producing many borides and mixed oxides.

The magnesium borides in samples 2 and 3 are from the traces of magnesium in the initial amorphous boron.

The procedure using B_2O_3 and Al as the starting material, compacted by CIP, (sample 5) at 1373 K for 45 min., promoted the formation of oxide and vitreous B-Al, whereas sintering with gravity compaction at 1373 K for 30 min (series 4) formed aluminium borides (Fig. 10).

Sintering in non-oxidizing atmosphere with energic CIP (sample 6) at 1373 K promoted abundant oxides (Fig. 11), while sintering in nonoxidizing atmosphere with gravity compactation (sample 7) at the same temperature, formed aluminium borides (Fig. 11).

The heat generated by sintermetallothermic process raises the temperature in the crucible from 1373–673 to 2073 K. Fig. 12 illustrates the effect produced in the matrix by thermal shock used. No oxide is observed in a vitreous sintered matrix with a great crack.

4. Conclusions

1. A procedure for making borides and vitrous compounds was developed from boron plus a chemical reductant.
2. The incorporation of the reducing elements into amorphous boron was achieved by powder technology. Suitable working conditions were designed to give a sintering aluminium boride free of oxide.
3. Successive cycles of compacting-sintering-milling and thermal shock were found suitable for boride sintering.
4. Preheating was avoided by the use of special crucibles, comply with all non.equilibrium conditions, which we develop for this work.
5. Isostatic cold compacting was found to be the best way to obtain oxide-free borides.
6. Sintermetallothermics and reactive sintering were the procedures for preparing oxide-free borides, with the advantage that they avoided intermediate steps.
7. Green sintering was made possible by the use of thermal shock and the special flux.
8. The exothermal reactions of the oxidizing of the aluminium raised the temperature in the crucible from the 1373 up to 2070 K, temperature at which AlB_{10} was obtained.

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