

Reaction Sintering of Biocompatible Al₂O₃–hBN Ceramics

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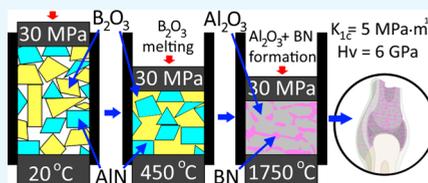
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ABSTRACT: Biocompatible Al₂O₃–hBN ceramic was sintered from AlN and B₂O₃ precursors by reaction hot pressing at 1750 °C and 30 MPa for 8 min. The ceramic was compared to nonreactive (NR) one sintered from Al₂O₃ and BN under the same sintering conditions. The NR ceramic possesses 9% porosity as opposed to only 2% porosity for the reaction sintered Al₂O₃–hBN. The reaction sintered ceramic has crack resistance in the region of 5.0 ± 0.1 MPa·m^{1/2}, which is approximately 20% higher than previously reported pure Al₂O₃ or Al₂O₃–hBN sintered without reaction support. The higher amount of hBN in the developed Al₂O₃–hBN material (27 vol %) facilitates hardness lowering to the region of 6 GPa, which is closer to the bone hardness and makes the ceramic machinable. Reaction sintering of the Al₂O₃–hBN composite opens a new area of creation and formation of load-bearing Al₂O₃–hBN ceramic bioimplants.



1. INTRODUCTION

The use of biomedical implants is well established in clinical procedures, which relieve patient's pain and increase quality of life. The implantation procedures offer enormous clinical advantages, but deleterious foreign body responses (FBRs) are well-acknowledged phenomena in in vitro applications. Coatings are more flexible in material choices, and Morais et al. concluded that selecting appropriate biocompatible coating materials for implantable devices can minimize the body's negative response without compromising implant functionality.¹

Metal alloys are historically the preferred choice for orthopedic implants, displaying the optimal mechanical properties in terms of load bearing and tribology. However, recent recalls of implantable devices such as metal-on-metal total hip replacements have highlighted the problem of hypertoxicity of a significant number of patients to the presence of metal ions.²

The generation of particulate debris is well demonstrated in a study by Hesketh et al. through simulated wear of high-carbon CoCr hip replacement heads and cups. Surface damage and the formation of subsurface cracks are observed, and short periods of severe wear due to corrosion occurring during the running-in period are noted.³ Ceramics in general are more biostable and have shown excellent properties in orthopedic applications and have a good track record of use in sliding surface applications.^{4–6}

Ceramics are very hard and when finished to a smooth surface provide to survive comparatively well in load-bearing tribo-pairs. The weak point for the application of ceramics in biosystems is low crack resistance, which is usually referred to as low toughness.

The high chemical stability of pure alumina ceramics makes them key candidates for a range of biomedical devices.⁷

However, low fracture toughness (~4 MPa·m^{1/2}) and poor machinability again significantly limit their application fields. The most popular method of alumina toughening is an addition of partially stabilized tetragonal zirconia crystals to the Al₂O₃ matrix.^{8,9} Alumina–zirconia composites are the most popular ceramics in use and are manufactured under the trade name BIOLOX Delta. BIOLOX Delta is an alumina matrix composite, which combines the excellent tribological behavior of alumina with the good mechanical/toughness properties of yttria-stabilized zirconia.¹⁰ There are however difficulties in controlling phase stability in such materials.¹¹ Instability results in gradual material strength degradation (so-called aging) caused by the spontaneous transformation of metastable tetragonal ZrO₂ particles into a monoclinic crystalline form.^{12,13} The transformation manifests itself macroscopically in a 4% volume gain. Generally, the transformation begins from the material surface, which leads to surface roughening and significantly reduces load-bearing capabilities of the material. Both processes present an essential disadvantage for the devices, where minimizing interfacial friction is optimal and load bearing is paramount (e.g., in joints).

An addition of hBN (hexagonal boron nitride) is an established approach to alumina toughening while also maintaining material biocompatibility.^{14–16} Low modulus and soft graphite-like boron nitride inclusions prevent crack development by means of the crack tip blunting.¹⁷ Al₂O₃ toughness rises with the hBN content of up to 30 vol %.¹⁵ The

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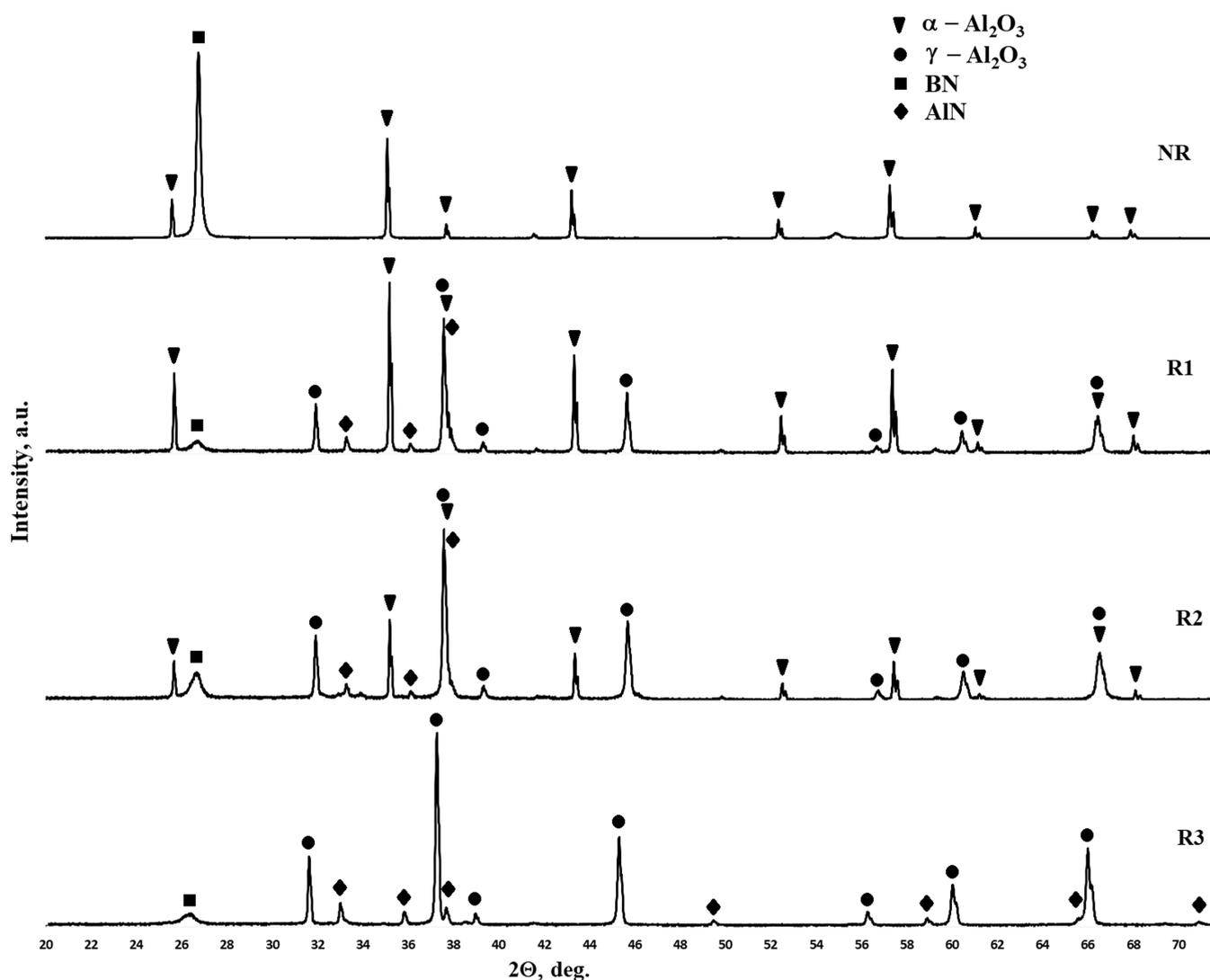


Figure 1. X-ray diffractometry of the hot-pressed samples.

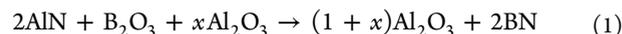
presence of a soft phase demonstrates an additional advantage as the ceramic becomes machinable with conventional CNC machining approaches. It should be, however, noted that the presence of the hBN refractory soft phase hinders the material sinterability.^{18,19} The developed Al_2O_3 –hBN composite sintering routes are energy- and time-consuming. For instance, Kusunose et al.¹⁶ produced the ceramic via a complex procedure consisting of (i) 24 h mixing of Al_2O_3 powder with boric acid and urea, (ii) several hours of annealing in H_2 at 1000 °C and in N_2 at 1600 °C to produce Al_2O_3 –BN nanocomposite powder, (iii) 72 h ball milling of the produced powder, and (iv) 1 h hot pressing of the milled powder in N_2 at 1700 °C and 30 MPa. This demonstrates that novel sintering approaches are needed to fully utilize the Al_2O_3 –hBN ceramic potential in biomedical applications.

During the last decade, the authors of the present work developed the reactive hot pressing approach to manufacturing of graphite-contained heteromodulus ceramics.^{20–22} The approach is based on a single-stage fast (several minutes) hot pressing procedure of the milled precursor powder mixture. The ceramic composite phases are formed during the material consolidation. The consolidation was shown to be essentially intensified with the reaction-induced atom mobility

and an additional heat, which was released during the in situ exothermic reactions. A graphite phase, produced during reactions, was shown to nucleate in the form of nanostructured platelets.²¹ The platelets have been shown to efficiently increase ceramics fracture resistance.¹⁷ The present work is an extension of the developed approach to Al_2O_3 –hBN composite manufacturing by simplifying green body (the powder mixture before sintering) preparation and the sintering process itself.

2. RESULTS AND DISCUSSION

X-ray analysis of the sintered samples (Figure 1) demonstrates the completion of the following reaction:



where $x = 1, 1.5, 3$. It is possible to see that BN is in hexagonal form. The X-ray diffractio (XRD) peak of hBN reactively formed in R1–R3 samples is essentially lower and broader than that of the NR sample. It could be caused by fine and defected grains of the in situ obtained boron nitride. Some occurrences of unreacted AlN crystals in the sintered samples can be explained considering the properties of B_2O_3 . Boron oxide, being a low melting point ($T_m = 440$ °C) phase, could

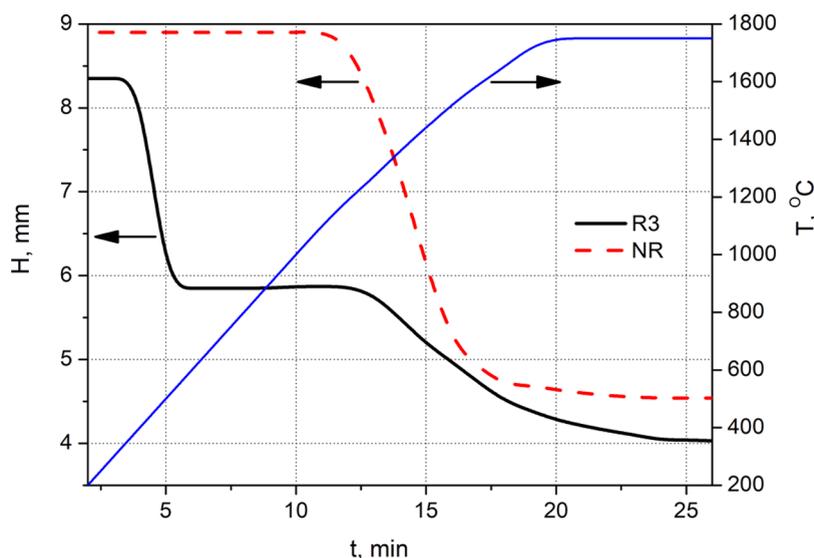


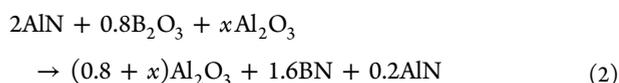
Figure 2. Densification (H , the sample height) kinetics for reactive (R3) and nonreactive (NR) samples alongside the process temperature (blue line).

Table 1. Composition^a, Density (ρ), Porosity (P), Hardness, and Indentation Toughness (Crack Resistance K_{IC}) of the Composites

#	Al ₂ O ₃ (wt %/vol %)	BN (wt %/vol %)	AlN (wt %/vol %)	ρ (g/cm ³)	ρ_{th}^a (g/cm ³)	P (%)	H_V (GPa)	K_{IC} (MPa·m ^{1/2})
R1	87.4/80.2	8.9/15.6	3.7/4.2	3.58	3.66	2	12.5	4.8
R2	80.7/70.1	13.7/22.8	5.6/6.1	3.44	3.51	2	10.6	5.1
R3	76.6/65.8	16.6/27	6.8/7.2	3.35	3.43	2	6.7	4.9
NR	86/76.5	14/23.5	0	3.21	3.55	9	2.6	

^aEstimated according to the right-hand side of eq 2.

be partially evaporated and thus avoid the sintering process before the completion of reaction 1. It is also possible that highly hygroscopic B₂O₃ could accumulate some amount of water from air before the weighting of initial powder. Both mentioned properties would shift the reaction 1 stoichiometry into B₂O₃ depletion. This will create a slight excess of AlN. Taking this into the account and presuming 20% B₂O₃ depletion, the actual reaction taken place can be described using the following equation



Reaction 2 does not alter the obtained results considerably but should be considered in the future for the material composition improvement. The initial R1–R3 powders consisted of α -alumina, boron oxide, and aluminum nitride. However, the sintered materials contained γ -Al₂O₃, evidently emerging as a result of the reaction.

It should be emphasized that a processed specimen of zero porosity would, in theory, give a sample height of 4 mm (see Figure 2). The height excess therefore indicates the void fraction in the sample volume. Comparison of sample R3 and nonreactive (NR) sample shrinkage presented in Figure 2 shows the essential influence of the chemical reaction on the kinetics of material consolidation. The initially pressed NR powder occupied a larger volume, which can be explained by the loose structure of hBN particles. R3 shrinkage between 400 and 500 °C is considered to be connected to boron oxide melting at 440 °C. By filling the pores between AlN and Al₂O₃ particles, B₂O₃ thus facilitated an essential consolidation of the

green body. Intense densification of the NR powder started at 1100 °C, indicating the plastic deformation of alumina grains. However, the sample shrinkage decelerated substantially even before the highest temperature (1750 °C) was reached and the sample failed to achieve a nonporous state. The latter correlated with the results presented in refs 16, 23, where boron nitride was shown to impede alumina consolidation, evidently interfering with the Al₂O₃ grain contacts. On the contrary, the second consolidation stage of the R3 charge, while starting at a slightly higher temperature (~1200 °C), continued for approximately 6 min, constituted isothermal dwelling, and facilitated the reaction allowing the sample height to decrease to the expected 4 mm.

The measured density values corresponding to the shrinkage dependencies are shown in Table 1. The NR sample had more than four times the pore volume as compared to the reactively sintered. The NR had low hardness, and indentation cracks could not be measured due to the poor surface quality (even after polishing). The hardness of the reactively sintered ceramics (R1–R3 samples) decreased with the hBN content, while fracture toughness did not vary considerably, being approximately 20% higher than that of alumina¹⁶ and corresponding to the values for Al₂O₃–BN composites presented by Li et al.¹⁵

3. CONCLUSIONS

Biocompatible Al₂O₃–hBN ceramic was sintered from AlN and B₂O₃ precursors by a one-stage energy-efficient reaction sintering approach. The sintering reaction was carried out at 1750 °C and 30 MPa uniaxial pressure with a holding time of 8

min. The ceramic has a low porosity of 2% and is relatively soft with Vickers hardness at just above 6 GPa and fracture toughness of approximately 4.9 MPa·m^{1/2}. Further investigations on the B₂O₃–AlN high-temperature reaction kinetics and mechanisms, as well as the Al₂O₃–hBN structure and biocompatibility, are required to further enhance the properties of the developed ceramic composite. This novel reaction sintering route for Al₂O₃–hBN ceramics opens a new area of manufacturing load-bearing Al₂O₃–hBN ceramic bioimplants.

4. EXPERIMENTAL PROCEDURE

All commercially available powders of B₂O₃ (2–10 μm), α-Al₂O₃ (~30 μm), hBN (~10 μm), and AlN (~50 μm) produced by Donetsk Reactive Factory, Ukraine, were used as starting materials. The material purity as stated by the manufacturer was around 99.00 atom %. The comparatively large (millimeter-sized) boron oxide crystals were handground to approximately 100 μm particle size before mixing with other components.

The starting green body compositions were chosen to correspond to the stoichiometry of reaction 1 (see Table 2). Additionally, to compare the reaction-led and nonreaction hot pressing routes, the product phase powders were also mixed in the molar ratio of Al₂O₃/BN as 3:2.

Table 2. Green Body Compositions

sample #	x	AlN (wt %)	B ₂ O ₃ (wt %)	Al ₂ O ₃ (wt %)	BN (wt %)
R1	1.5	17.9	15.2	66.9	
R2	2	26.9	22.8	50.2	
R3	1	32.3	27.4	40.2	
NR				86.05	13.95

The weighed powders were mixed and milled in a high-energy planetary mill (1500 rpm) in a zirconia jar with 10 mm zirconia balls (ball-to-powder ration 10:1) for 30 min. Zirconia contamination during the milling was at around 1 wt %. The milled powder was loaded into a cylindrical graphite die (internal diameter, 10 mm) in an amount which produced, postsintering, a 4 mm high ceramic disc accounting for 100% density. The die was heated with AC (50Hz) current in the hot-pressing machine DCS-0 produced by SRC Synthesis (Kiev, Ukraine). The heating rate was approximately 100 °C/min. The samples were produced at 1750 °C and 30 MPa with an 8 min hold at the highest temperature. The process was carried out without any protective atmosphere.

The bulk sample density was measured using the Archimedes' method and the theoretical densities (ρ_{th}) were estimated according to the rule of mixtures. The crystalline phases were determined by X-ray diffraction (XRD). Vickers hardness measurements were performed with the load of 147 N for 20s on polished surfaces. The fracture toughness was estimated by measuring the crack lengths generated by the Vickers indentations. The toughness (crack resistance) was calculated according to the formula of Evans and Charles.²⁴

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Notes

The authors declare no competing financial interest.

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