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# Functionally graded SiAlON ceramics

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## Abstract

Functionally graded SiAlON ceramics were developed by three different methods to improve the mechanical properties of SiAlONs; powder bed, rapid cooling and laminating. β-SiAlON compacts were embedded in two different homogeneously mixed powder bed compositions, α-SiAlON (100 wt.%) and AlN: BN (50:50 wt.%). The affect of powder bed composition and pressure on the formation of α-SiAlON on the compact surface was investigated. Rapid cooling to retain transformed α-SiAlON was also another method under investigation. Lamination is another method for production of functionally graded materials. For this purpose laminar type of functionally graded SiAlON ceramics with two layers, which have different compositions, were produced. Transition zone obtained in different methods were examined by phase characterization technique, microstructural investigations and hardness measurements. The results showed that laminar type is the most effective method for FGM SiAlON ceramics production.

*Keywords:* Functionally graded materials; Sialons; Sintering; Wear resistance

## 1. Introduction

Functionally graded materials have been investigated extensively since 1987. The aim of production of FGMs, is eliminating the macroscopic boundary in materials in which the material's mechanical, physical and chemical properties change continuously and which have no discontinuities within the material. Thus, these materials exhibit superior mechanical properties compared to monolithic and composite materials.[1]

Silicon nitride and its derivative SiAlON (solid solutions containing Al and O in addition to Si and N) ceramics constitute an important class of structural ceramics. They are suitable for many commercial applications requiring wear resistance, high toughness, chemical stability and heat resistance.[2] Due to these superior properties, SiAlON ceramics have many structural applications especially as wear components. It is well known that mechanical and chemical properties of SiAlON ceramics are affected by chemical composition and microstructure and crystal structure. In general, α-SiAlONs are in the form of equiaxed grains with high hardness and good wear resistance but low fracture toughness and thermal conductivity, whereas β-SiAlONs have elongated grains with high fracture toughness and good thermal conductivity but relatively low hardness. To combine the advantages of both SiAlONs, α/β-SiAlON composites have long been developed. These materials show intermediate values between those of α and β-SiAlONs.[3] However, α→β SiAlON transformation requires attention in compositional design and microstructure. There have been various studies in order to overcome α→β transformation problem with considerable success.[4] Microstructural improvements followed these studies which lead α/β SiAlON composites with much improved properties.[5] Further way to especially improve the mechanical properties for these materials is to functionally design in a gradient manner that their surfaces are rich in α-SiAlON. In this way, high hardness of α-SiAlON can be utilized at the surface and high toughness of β-SiAlON can be taken advantage of in the core.

Previously, Chen and co-workers developed graded insitu SiAlON ceramics by embedding β-SiAlON green compacts in an α-SiAlON powder.[6] Their results showed that compositions, microstructures and properties of the graded SiAlON ceramic change gradually from the hard α-SiAlON with spherical morphology on the surface to the tough and strong β-SiAlON with elongated grains in the core. Recently, Kang and Jiang developed a technique for insitu formation of α-SiAlON layer on β-SiAlON surface.[7] Their technique consists of

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packing a compact of β-SiAlON composition in α-SiAlON powder. They found that it is possible to control the thickness of the α-SiAlON rich layer by changing the pre-sintering conditions during heating to sintering temperature. In another study, Mandal and co-workers obtained a gradual change of α-SiAlON content from surface through core by rapid cooling method.[8] This gradual change is explained as a function of α→β SiAlON transformation. Pre-lamination of green compacts is another considerable technique for graded material production. Preliminary results for this technique were reported by Shen and Nygren.[9] However there has been no detailed information in this reference and also elsewhere.

In the present study, functionally graded SiAlON ceramics were developed by three different methods, namely powder bed, rapid cooling and lamination. Comparison of these methods especially with respect to graded layer thickness is discussed.

## 2. Experimental procedure

All SiAlON compositions were prepared by wet milling with isopropyl alcohol in a $Si_3N_4$ media. The slurries were dried into powders in a rotary evaporator, which then were sieved through 250 μm. After sieving, the powders were compacted into pellets at 25 MPa by uniaxial pressing followed by isostatic pressing at 300 MPa.

*For the powder bed method,* a composition rich in β-SiAlON (coded as B1) was selected as a compact composition to observe compact-powder bed interaction. Two different powder bed compositions, α-SiAlON (100 wt.%) and AlN:BN mixture (50:50 wt.%) were prepared. β-SiAlON rich pellets were embedded into the powder bed compositions, as schematically shown in Fig. 1. Both green and sintered pellets were embedded into the same powder bed composition in order to compare the effect of pre-sintering on the interaction. Sintering of the pellets was carried out under 22 bar nitrogen gas pressure at 1800 °C for 1 h. To understand the effect of pressure on the interaction zone, presureless sintering was also carried out for comparison.

*In the fast cooling method*, two different samples were heated and cooled very rapidly. The first one was B1 and the second one was B2, which is obtained from B1 by sintering in AlN/BN powder bed. The surface of B2 was ground until 70% β-SiAlON was obtained before fast cooling treatment. Then, the specimens were inserted in the same high speed cooling furnace. They were heated to 1600 °C at a rate of 15 °C /min and cooled rapidly by taking out of furnace.

*In the lamination method*, two different compositions, alpha rich (75% α, coded as A1) and two beta rich (80% β, and 75% β coded as B1 and B3, respectively), were prepared with Y, Sm and Ca dopants. The difference of B1 and B3 samples were the amount of liquid phases. B3 is containing the similar amount of liquid phase with A1 however B1 is containing higher amount of liquid phase. A1–B1 laminate and A1–B3 laminates were prepared by sequential filling of the die and pressing, as schematically shown in Fig. 2. The laminates were sintered in the condition as described in powder bed method.

The phase composition from the surface to the interior of the samples was determined by X-ray diffactometer (XRD) by successive grinding of the surface at 100 μm intervals.

The microstructural characterization of the sintered specimens was undertaken by scanning electron microscopy (SEM) in backscattered mode. The hardness change from the surface to the interior of the sample was measured by Vickers indentation method at 19,6 N load.

## 3. Results and discussions

### 3.1. Powder bed method

Change in the amount of β-SiAlON from the surface of the samples for green and pre-sintered compacts is shown in Figs. 3 and 4, respectively, after sintering in α-SiAlON and AlN:BN powder beds. Both figures clearly illustrate that AlN:BN powder bed is more effective for the formation of α-SiAlON at the surface than α-SiAlON powder bed. Formation of α-SiAlON rich layer on the component surface is due to transfer of α-SiAlON forming ions from the powder bed. This transfer could be in various ways: (1) Solid state reaction of powder bed with compact surface (2) formation of a liquid in the powder bed and its reaction with the surface (3) evaporation from powder bed and condensation on the compact. The first mechanism appears to be unlikely as the contact area of fine powder of the

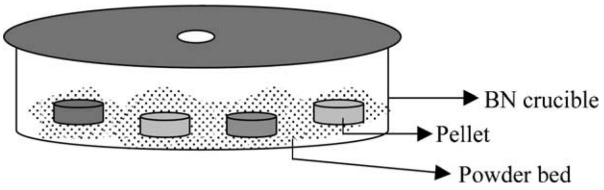


Fig. 1. Basic demonstration of powder bed method.

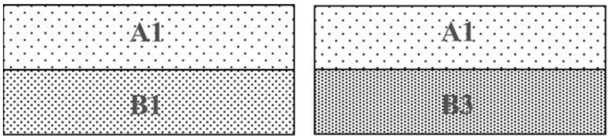


Fig. 2. Basic shape of designed FGMs.

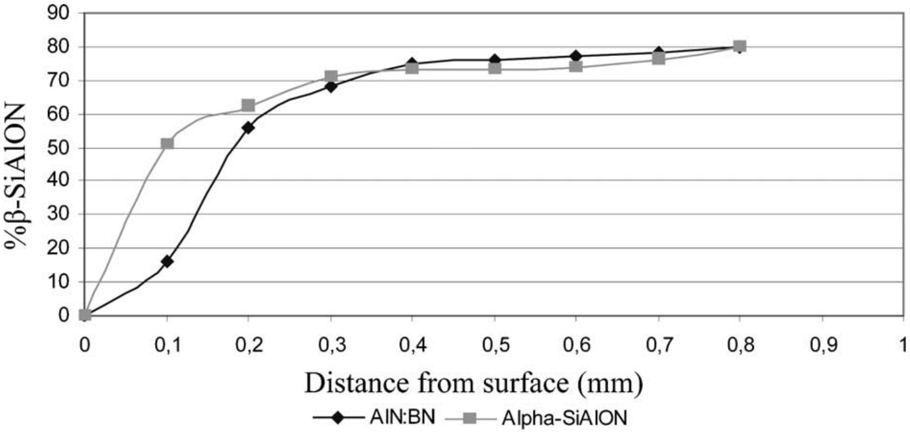


Fig. 3. Change in β-SiAlON ratio of green samples sintered in different powder bed.

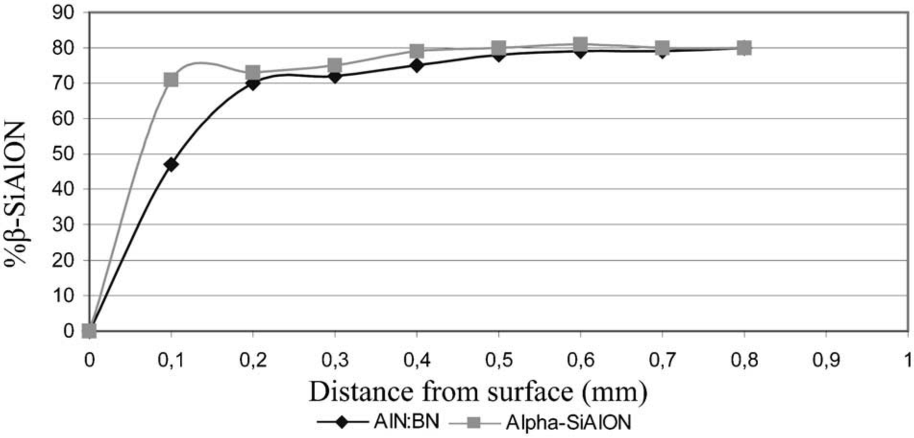


Fig. 4. Change in β-SiAlON ratio of pre-sintered samples sintered in different powder bed.

loose powder bed should be rather low for effective solid state reaction. The second mechanism is not applicable to AlN:BN powder bed as no liquid formation is expected. For α-SiAlON powder bed liquid formation should occur but not as much as one can expect due to loose powder bed. Therefore, it is likely that the material transfer occurs via vaporization of reactants from the powder bed and condensation on the surface of the compact for reaction. It is possible that AlN evaporates from the AlN:BN powder bed which then reacts with compact surface. By this way the surface composition becomes richer in AlN, causing α-SiAlON formation. Since less AlN is available from α-SiAlON powder bed, its effect on α-SiAlON formation at the compact surface is less.

Fig. 5 gives comparison of the amount of β-SiAlON change of the green and pre-sintered compacts in AlN:BN powder. The green compacts had more interaction with the powder bed than the pre-sintered compacts. This is presumably due to easy diffusion of condensed phases through less dense structure of β-SiAlON just before reaching full densification. The maximum thickness of the gradient zone is limited up to 400 μm.

The effect of nitrogen gas pressure during sintering on the thickness of the diffusion zone is determined in AlN:BN powder bed by using 1 and 22 bar gas pressure. The results indicated that, change in gas pressure during sintering has an influence on the thickness of the gradient zone (Fig. 6). The smaller gradient zone thickness at 1 bar can be attributed to sweeping of evaporating species away by flowing nitrogen gas which is used during sintering.

### 3.2. Fast cooling method

B1 sample was treated to investigate the effect of fast cooling method on the surface modification. There was no gradient layer after fast cooling on the surface of B1. This can be explained by the stability of β-SiAlON, not transforming to α-SiAlON on heating. When B2 sample is used in fast cooling experiments, about 300 μm the gradient zone was obtained at the surface (Fig. 7). This is probably due to its modified surface composition during sintering in AlN:BN powder bed, becoming more transformable.

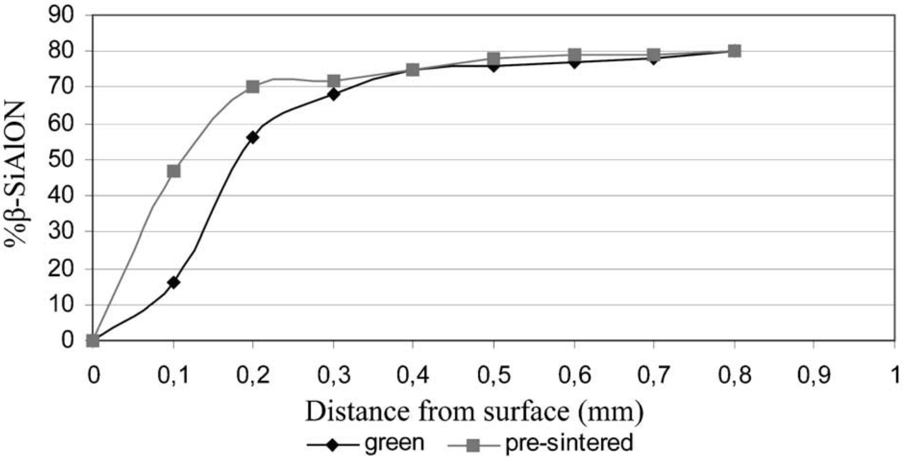


Fig. 5. Comparison of the amount of β-SiAlON on the surfaces of the green and pre-sintered compacts in AlN–BN powder bed.

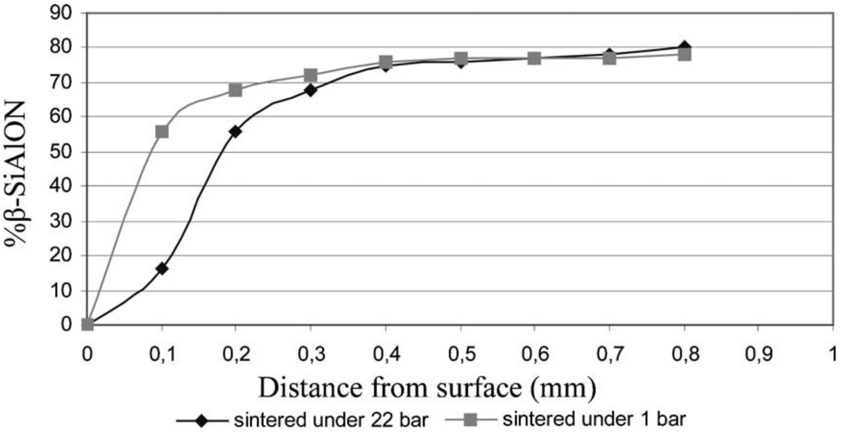


Fig. 6. Comparison of the amount of β-SiAlON on the surfaces of green compacts sintered under 22 and 1 bar in AlN–BN powder bed.

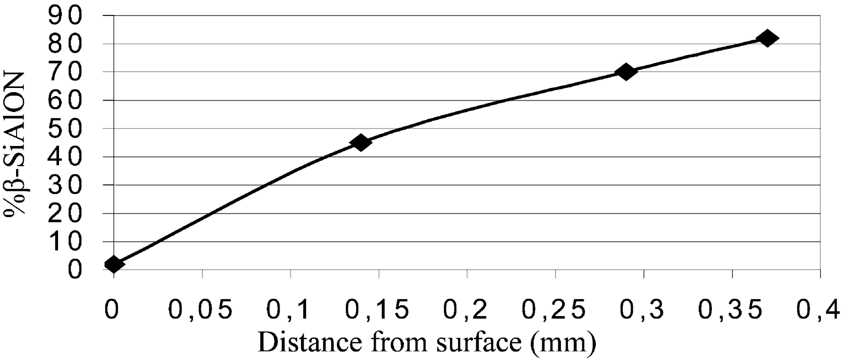


Fig. 7. Change in β-SiAlON ratio in B1 sample ground up in 70% β-SiAlON content as a function of fast cooling.

### 3.3. Lamination method

Visual examination showed that both A1 and B3 layers were intermixed showing that counter diffusion occurred. Phase composition change through the interface between A1–B3 laminate is given in Fig. 8. It is clear that there is a gradual transition from alpha rich region to beta rich region. The transitional zone is about 400 μm in thickness and the β-SiAlON amount in this zone changed from 20 to 70% as expected. The gradual change in the amount of the phases was also confirmed by SEM observations (Fig. 9). This confirms that counter diffusion of species has taken place between A1 and B3.

XRD measurements and microstructural observations coincided with the hardness measurements, as shown in Fig. 10. Hardness of the intermediate zone increases from 15 to 19GPa as going from β-SiAlON rich side to α-SiAlON rich side.

Another combination was prepared by using powders of A1 and B1. This laminate also showed a gradual transition zone similar to A1–B3 pair (Fig. 11). Hardness values increased gradually from 16 to about 19 GPa, going from β-SiAlON rich region to α-SiAlON rich region (Fig. 12). However, the gradient layer was longer in this sample, which may be due to easy diffusion of species in a larger amount of liquid phase in B1.

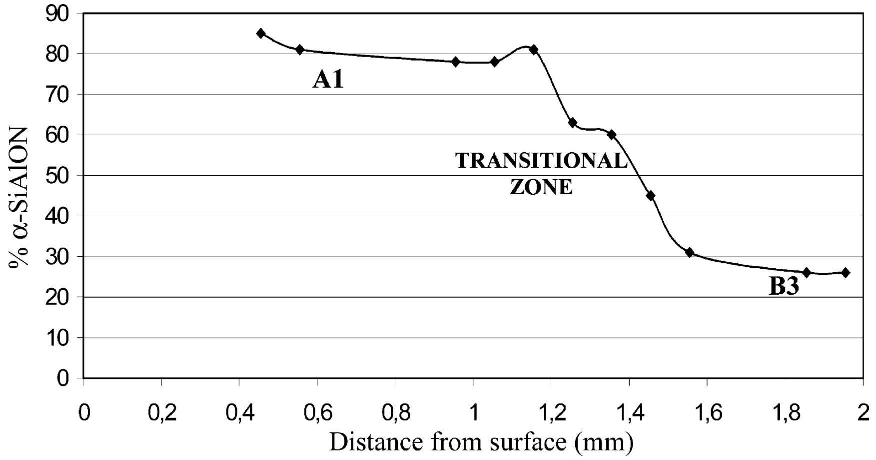
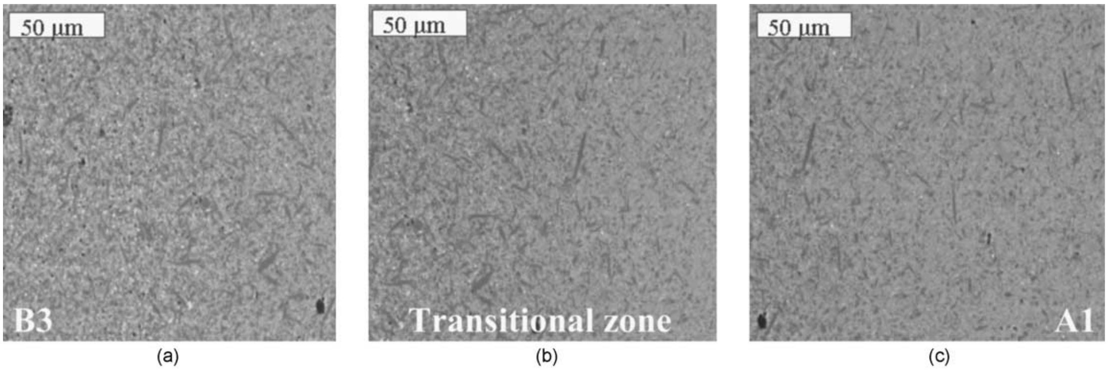


Fig. 8. Change in α-SiAlON ratio of A1–B3 laminate, ground up to 100 μm through the sample thickness.



(a) (b) (c)

Fig. 9. BEI–SEM images of A1–B3 laminate (a) transitional zone that is more close to beta rich region (b) medium of transitional zone, (c) transitional zone that is more close to alpha rich region.

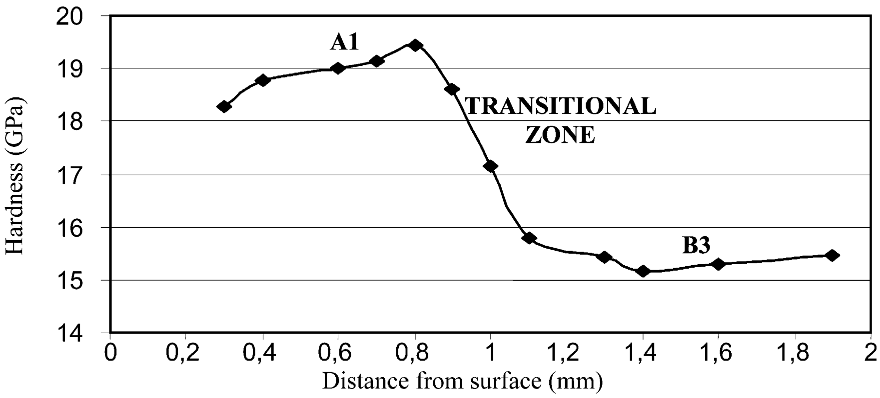


Fig. 10. Hardness measurements of designed A1–B3 laminate, through the thickness of the sample.

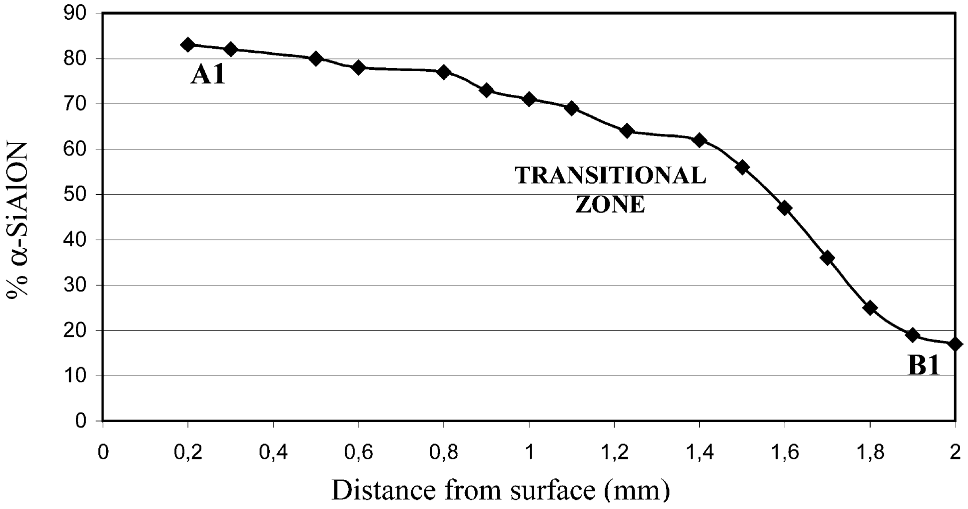


Fig. 11. Change in α-SiAlON ratio of A1–B1 laminate, ground up to 100 μm through the sample thickness.

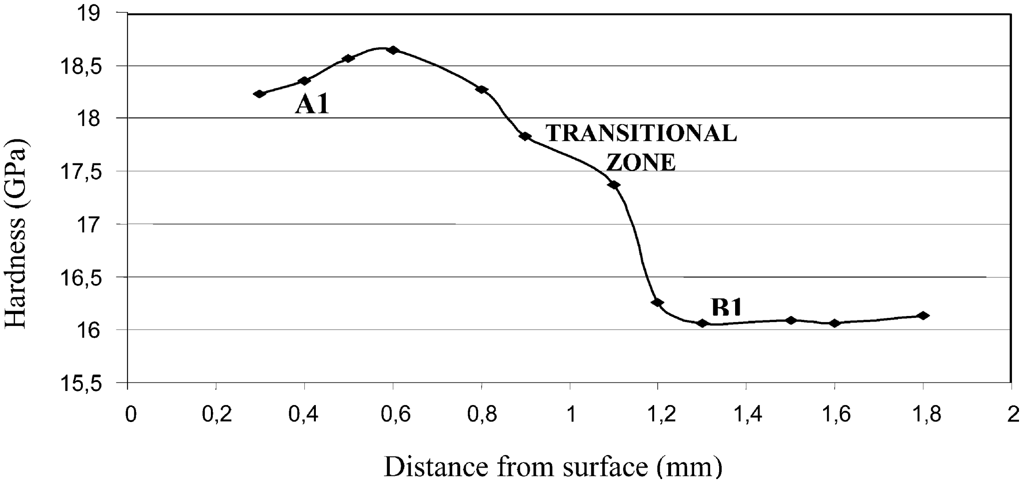


Fig. 12. Hardness measurements of designed A1–B1 laminate, through the thickness of the sample.

From the results given so far, it is evident that the gradient zone thickness on the surface varies between 200 and 400 μm, but limited to about 400 μm maximum in the powder bed and fast cooling methods. Considering that ceramic products usually need machining operation to bring them to the near net shape, and the amount of material removal during machining is about few hundred microns range depending on the application, both methods do not appear to be applicable. Furthermore, the methods are not practical in that the powder bed needs to be renewed at each sintering cycle and that specimen may crack during rapid cooling. Therefore the lamination method gives more promise for functionally gradient SiAlONs. This is because one can adjust physically the layer thickness as required, e.g. depending on machining allowance.

## 4. Conclusions

In this study, SiAlON ceramics enriched at the surface by α-SiAlON in order to improve surface hardness without loosing bulk toughness were attempted to be developed. Of the three different methods applied, physical lamination is the most effective one as its thickness can be controlled physically as required. Powder bed and rapid cooling is also effective to form an α-SiAlON rich surface layer but its thickness is limited to few hundred microns.

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