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Ceramic nanolaminates—Processing and application

Jerzy Lis *, Leszek Chlubny, Michał Łopaciński,
Ludosław Stobierski, Mirosław M. Bućko

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-053 Krakow, Poland

Abstract

The self-propagating high-temperature synthesis (SHS) has been used in authors' works for preparation of ceramic nanolaminates, namely Ti_3SiC_2, Ti_3AlC_2 and Ti_2AlN. The possibility of obtaining near-single-phase materials, processing of SHS products into sinterable powders and densification of the powders by sintering and hot-pressing are discussed. Finally, polycrystalline nanolaminate materials with controlled phase composition and microstructure have been obtained. The materials have been investigated as structure materials by testing their mechanical properties. The possibility of using of prepared powders to obtain ceramic composites, ceramic bonds and FGM materials, as well as their potential application are discussed.

Keywords: Sintering; Composites; Mechanical properties; Nanolaminates

1. Introduction

Among many covalent materials such as carbides or nitrides there is a group of ternary compounds referred in literature as H-phases, Hägg-phases, Novotny-phases or thermodynamically stable nanolaminates. These compounds have an $M_{n+1}AX_n$ stoichiometry, where M is early transition metal, A is an element of A groups (mostly IIIA or IVA) and X is carbon and/or nitrogen. Heterodesmic structures of these phases are hexagonal, $P6_3/mmc$ and specifically layered. They consist of alternate near-close-packed layers of M_6X octahedrons with dominating covalent bonds and layer of A atoms located at the centre of trigonal prism. The M_6X octahedral, similar to those forming respective binary carbides, are connected one to another by shared edge. Variability of chemical composition of the nanolaminates is usually labelled by the symbol describing their stoichiometry, e.g. Ti_2AlN represents 211 type phase and Ti_3AlC_2–312 type one. Structurally, differences between the respective phases consist in the number of M-layers separating the A-layer: in the 211s there are two, whereas in the 321s three M-layers.[1–3]

This paper is focused on preparation of Ti_3SiC_2, Ti_3AlC_2 and Ti_2AlN by self-propagating high-temperature synthesis (SHS). SHS-derived powders were used as for obtaining fully dense polycrystals based on ceramic nanolaminates phases.

2. Experimental

Many methods were used to prepare the nanolaminate materials. Polycrystalline Ti_3SiC_2 was usually obtained in direct reaction of titanium, carbon and silicon for a long time at 1100 °C in graphite furnace in argon atmosphere.[4] The solid-state reaction was also performed by heating of TiH_2, Si and graphite mixture at 2000 °C[5] or TiC, $TiSi_2$ and TiSi mixture at 1400 °C.[6] In a single step reactive hot-pressing dense Ti_3SiC_2 materials were synthesized from Ti, SiC and graphite powders.[7] The other method was melting of Ti, Si and C powders in electric arc at 1200 °C.[8] Attempts to synthesize Ti_3SiC_2 in the polycrystalline form always resulted in materials containing TiC, mostly, and sometimes SiC, as a unwanted phase. Thin films of titanium–silicon carbide were crystallized by CVD method from gaseous titanium, silicon and carbon chlorides in hydrogen or by heating of titanium foil with SiC at 1500 °C in vacuum.[9]

Ti_3AlC_2 material was firstly prepared by sintering of cold-compacted powder mixtures of titanium, TiAl, Al_4C_3, and carbon under pure hydrogen for 20 h.[10] Tzenov and Barsoum synthesized bulk titanium–aluminium carbide, containing few amount of corundum, by reactive hot isostatic pressing of a mixture of titanium, aluminium carbide and graphite powders under 70 MPa at 1400 °C for 16 h.[11] Fully dense polycrystalline Ti_3AlC_2 was also fabricated by a solid–liquid reaction synthesis and simultaneous *in situ* hot-pressing of a mixture of Ti, Al and graphite powders at 1500 °C under 25 MPa for 5 min and subsequent annealing at 1200 °C for 20 min.[12]

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* Corresponding author. Tel.: +48 12 6172040.
E-mail address: lis@agh.edu.pl (J. Lis).

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Ti_2AlN has been less investigated due to difficulties in processing single-phase bulk material. Titanium–aluminium nitride thin films were formed by reactive magnetron sputtering from a Ti_2Al compound target in a mixed argon/nitrogen atmosphere.[13] Epitaxial growth[14] and glow discharge treatment[15] were also used for preparation of Ti_2AlN coatings on Ti alloys. It was stated that these coatings improved hardness, wear resistance and biocompatibility of the nitrided titanium alloys. Barsoum et al.[16] reported fabrication of bulk Ti_2AlN material using Ti and AlN powders as raw materials. The samples even hot-isostatic pressed at 1400 °C for 48 h still contained 10–15 vol.% of unwanted phases. Fully dense and single-phase Ti_2AlN material was successfully synthesized by a hot-pressing method using Ti, Al and TiN powders as starting materials.[17] The process was performed at 1400 °C for 1 h under pressure of 25 MPa.

The most successful preparation method of nanolaminate powders has been developed by the authors based on self-propagating high-temperature synthesis (SHS). Using powders of titanium, silicon and carbon black as reactants, a powder composed mainly of Ti_3SiC_2 and of minor amounts of TiC was synthesized.[18] Following ignition at 1050 °C, complete conversion of the reactants to the product was observed in a time of 2–5 s.

Ti_3AlC_2 synthesis was performed by SHS method using mixture of intermetallic compounds, namely TiAl and Ti_3Al, carbon powder and/or titanium powder in the respective molar ratios. The SHS reaction, initiated by local ignition, was performed in argon atmosphere. The products of the synthesis with use of TiAl were TiC as a dominating phase and Ti_3AlC_2 as a balance did not exceed 40 wt.%. The larger amounts of Ti_3AlC_2 were obtained when Ti_3Al was used as the precursor. In this case double titanium–aluminium carbide was a dominating phase, its amount exceeded 80 wt.%, and the balance was TiC.[19]

SHS synthesis of Ti_2AlN powder was performed in a similar way. The precursors were TiAl or Ti_3Al powders mixed with titanium or aluminium powders, respectively, and the reaction was conducted in nitrogen. Ti_2AlN accompanied by small amount of TiN, Ti_3AlN and Ti_3Al was a result of SHS reaction using TiAl as a precursor. Product obtained as a result of the SHS synthesis in Ti_3Al with metallic aluminium consists mostly of TiN and Ti_2AlN with some Ti_3Al and AlN. The reaction conducted in mixture of TiAl and Ti_3Al leads to creation of TiN as a dominating phase and small quantities of Ti_2AlN, Ti_3Al and AlN. In both titanium–aluminium materials the SHS reaction of the mixture of elements did not show positive results.[20]

The SHS-derived powders are good sinterable precursors for preparation of dense materials. Typical powders synthesized through SHS have a form of a porous sponge. Because of strong aggregation and agglomeration of the powders caused mainly by high temperature of SHS, reaction-grinding process is usually applied before densification. Pressureless sintering, hot-pressing and isostatic hot-pressing were successfully applied to obtain dense nanolaminate materials.[21–24] The applied temperatures differ from 1100 to 1600 °C depending on the process and the powder. It is worth to notice that during thermal treatment some structural changes accompanied with phase content changes can be observed. Sintering of Ti_3SiC_2 usually causes partially decomposition of this phase and small amounts of TiC and SiC are detected. Heat-treatment of Ti_3AlC_2 and Ti_2AlN also lead to formation of TiC and TiN type phases, respectively.[20,23,25]

3. Results and discussion

3.1. Mechanical properties

The specific structure of such compounds causes an extraordinary set of properties that are not observed in any typical metallic and ceramic material. The nanolaminate materials combine common ceramic properties like high stiffness, moderately low coefficient of thermal expansion and excellent thermal and chemical resistance with low hardness, good compressive strength, high fracture toughness, ductile behaviour as well as good electrical and thermal conductivity characteristic for metals.[3] The exceptional combination of such properties allows nanolaminate materials to be good machinable even by standard tools. The most interesting features of these materials are their very good mechanical properties. High fracture toughness and possibility of plastic deformation is result of complex fracture mechanism additionally depending on microstructure of the material, especially on grain sizes and their shapes. The mechanical properties of Ti_3SiC_2 materials are collected in Table 1. The values originate in the subject literature and our own experiments.[3,26]

Fig. 1 shows Young modulus of Ti_3AlC_2 materials prepared from different intermetallic precursors and hot-pressed at temperature range of 1300–1450 °C. It can be stated that elastic properties of such materials depend on phase composition changes due to the sintering conditions. Increase of the temperature of hot-pressing accompanied by increase of the TiC content makes materials much stiffer. The similar effect is observed in case of shear modulus changes (Fig. 2). Fig. 3 reveals that low hardness of the materials hot-pressed at lower temperatures, specific for the materials with high contents of Ti_3AlC_2, increase for the materials with the higher TiC content sintered at higher temperatures.

Increase of Young modulus caused by increase of the hot-pressing temperature is also observed in the Ti_2AlN materials. Fig. 4 shows changes of the Young and shear module for Ti_2AlN materials prepared from SHS-derived powder (TiAl and Ti mixture) and hot-pressed at different temperatures. The presence of

Table 1
Mechanical properties of Ti_3SiC_2 sintered polycrystals

Young modulus (GPa)	Shear modulus (GPa)	Poisson ratio	K_{Ic} (MPa m$^{0.5}$)	Fracture energy (J m^{-3})	Bending strength (MPa)	Hardness (GPa)
315–359	133–150	0.180–0.194	6.2 (bending) 9.4 (Vickers)	61	660	5.8 (Knopp) 2.8 (Vickers)

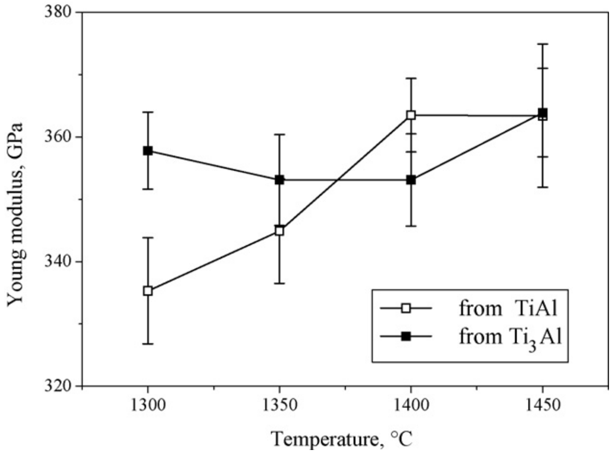

Fig. 1. Young's modulus of Ti_3AlC_2 materials prepared from different intermetallic precursors and hot-pressed at temperature range of 1300–1450 °C.

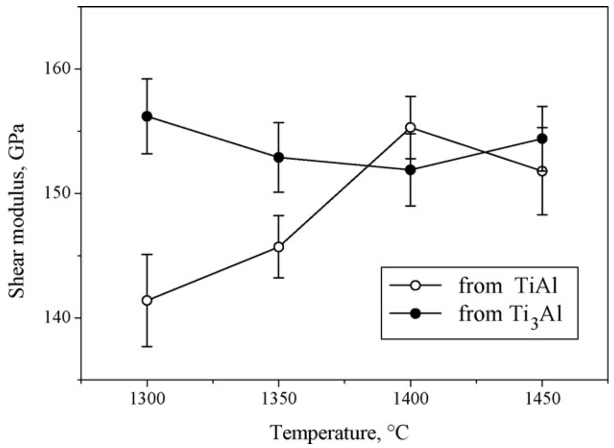

Fig. 2. Shear modulus of Ti_3AlC_2 materials prepared from different intermetallic precursors and hot-pressed at temperature range of 1300–1450 °C.

TiN-type phase in the dense materials leads to the improved of their elastic properties.

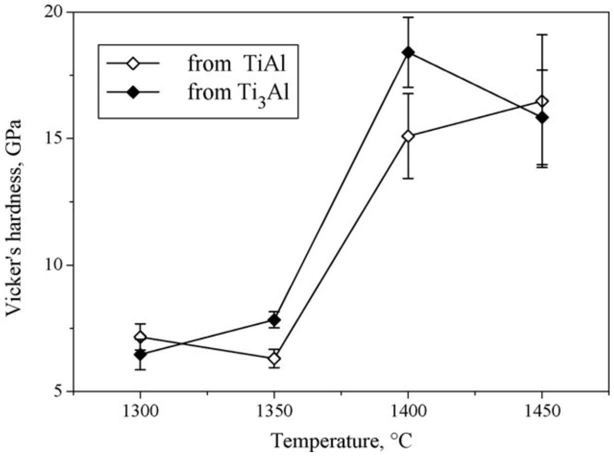

Fig. 3. Vicker's hardness of Ti_3AlC_2 materials prepared from different intermetallic precursors and hot-pressed at temperature range of 1300–1450 °C.

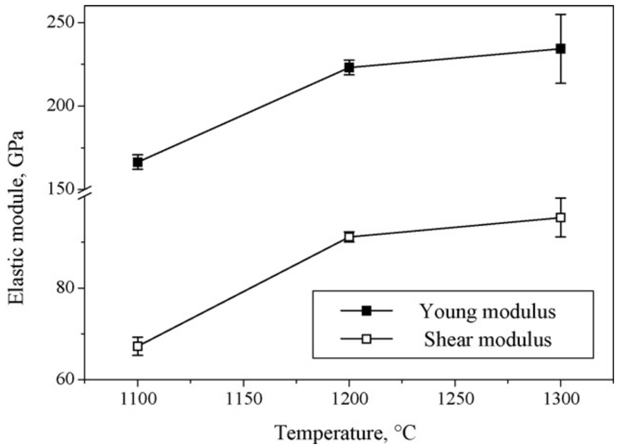

Fig. 4. Elastic module of Ti_2AlN materials hot-pressed at different temperatures.

Table 2
Fracture toughness of Ti_2AlN materials hot-pressed at different temperatures

Temperature (°C)	K_{Ic} (MPa m$^{0.5}$)
1100	7.00 ± 0.4
1200	8.2 ± 0.1
1300	Not measurable

Values of fracture toughness of these materials, measured by Vicker's indentation method, are presented in Table 2. The increase of amount of the much stiffer and much toughed TiN-type phase causes increase of the K_{Ic} value. It is worth to notice that the sample sintered at 1300 °C reveals pseudo-plastic properties similar as pure nanolaminate phases. Fig. 5 presents micrograph of the Vicker indentation made on the polished surface of Ti_2AlN material hot-pressed at 1300 °C.

4. Application of Ti_3SiC_2

Because of the most developed methods of preparation, Ti_3SiC_2 is the material that has been tested in different applications. Looking for an application as structure machinable ceramics, titanium–silicon carbide was successfully used as a matrix in CMC particulate composites with some other

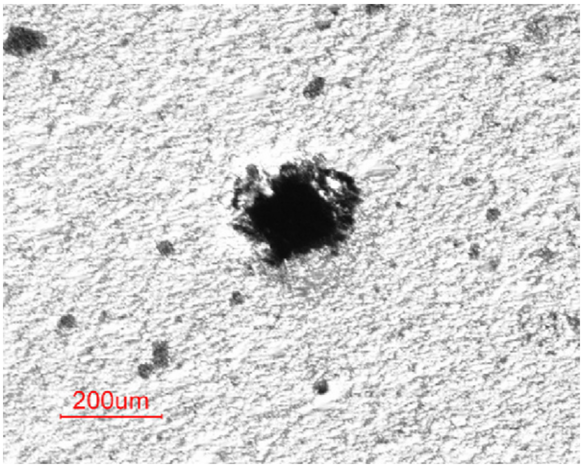

Fig. 5. Micrograph of the Vicker indentation made on the polished surface of Ti_2AlN material hot-pressed at 1300 °C.

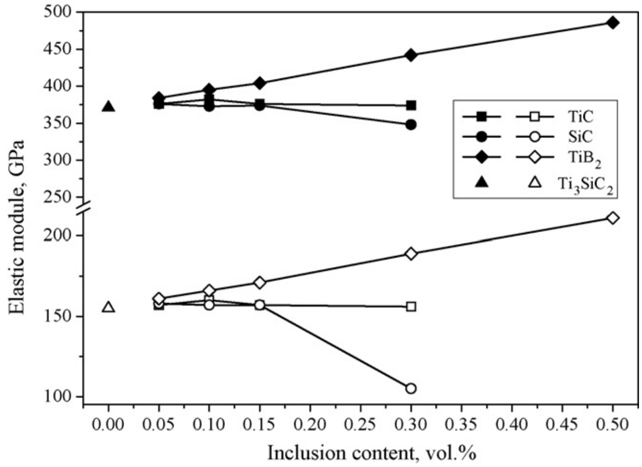

Fig. 6. Elastic properties of the Ti_3SiC_2-based composites.

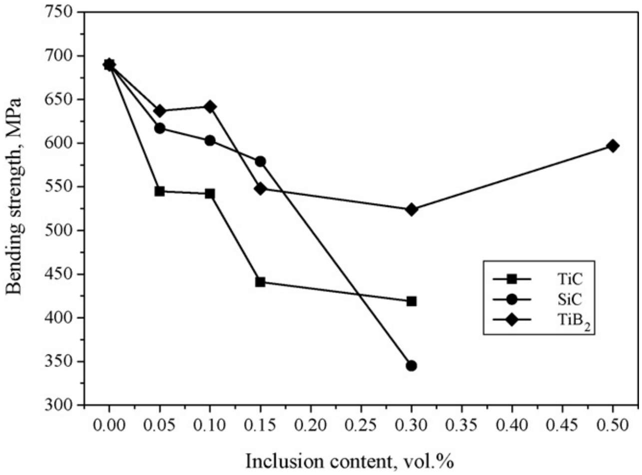

Fig. 8. Bending strength of the Ti_3SiC_2-based composites.

covalent phases as inclusions. The SHS-derived powder of titanium–silicon carbide was mixed with the respective amount of TiC, SiC or TiB_2 powders. The materials were hot-pressed at 1500 °C for 1 h under 25 MPa. It can be stated that addition of the stiff, covalent inclusions of TiB_2 significantly improved elastic properties of the composites (Fig. 6). In other cases, no changes or slightly decrease of the elastic module values can be observed.

Hardness of the composites depends mainly on the inclusion volume fraction (Fig. 7). Addition of the hard inclusions increases of the composite hardness. The larger amount of TiB_2 inclusions significantly improved of the composite hardness, whereas the SiC inclusions deteriorate it. All composites have worst bending strength than the pure Ti_3SiC_2 matrix but small amount of the inclusion increases their fracture toughness (Figs. 8 and 9). Such behaviour can be explained by complex fracture mechanism of the composites related to their microstructure. Fig. 10 shows examples of the crack path in the composites. Crack deflection, and crack branching can be observed in the micrographs.

The specific properties of the Ti_3SiC_2 allow using this compound as a bonding phase in diamond-based composites.[27] Composites were prepared from diamond powders of 3–6 μm and contained from 20 to 40 wt.% of Ti_3SiC_2. They were sintered using a high-pressure apparatus of Bridgman type at 1800 °C under 8 GPa load. Observations of microstructure showed that the relatively large blocky diamond grains of 5–10 μm were separated by thin channels of fine crystalline material. Hardness of the composites was comparable to the hardness of polycrystalline diamond materials with cobalt bonding phase. The wear tests revealed very good wear resistance of the composites especially the one having 20 wt.% of carbide additions.

Titanium–aluminium carbide can be also used to produce parts of add-on ceramic armour.[28,29] In this case, Ti_3SiC_2 acts as a laminar material combined with metal layer or as a functionally gradient material (FGM) with other ceramics. Such materials might replace currently used ceramic working elements adding the benefit of improved cracking resistance and fracture toughness. FGM of Ti_3SiC_2-Al_2O_3 has high damage energy and increased fracture toughness, especially. In order to effectively design functionally gradient materials all constituents need to be well defined in terms of elastic properties (Young's and shear module, Poisson's ratio) as well as thermal properties (thermal expansion coefficient, thermal conductiv-

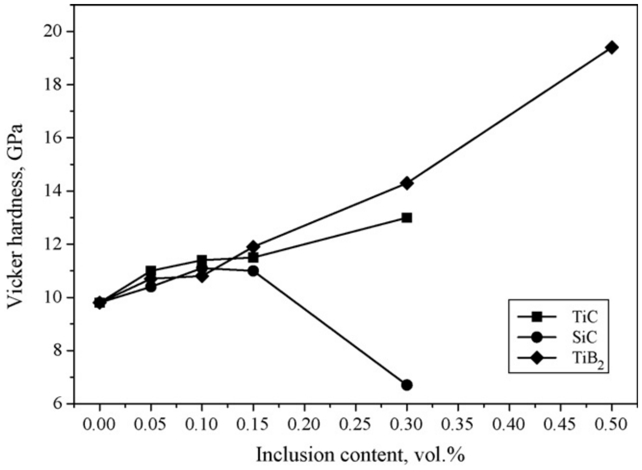

Fig. 7. Vicker's hardness of the Ti_3SiC_2-based composites.

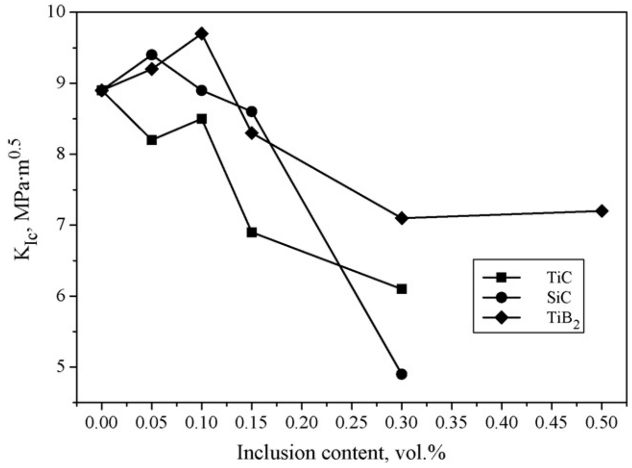

Fig. 9. Fracture toughness of the Ti_3SiC_2-based composites.

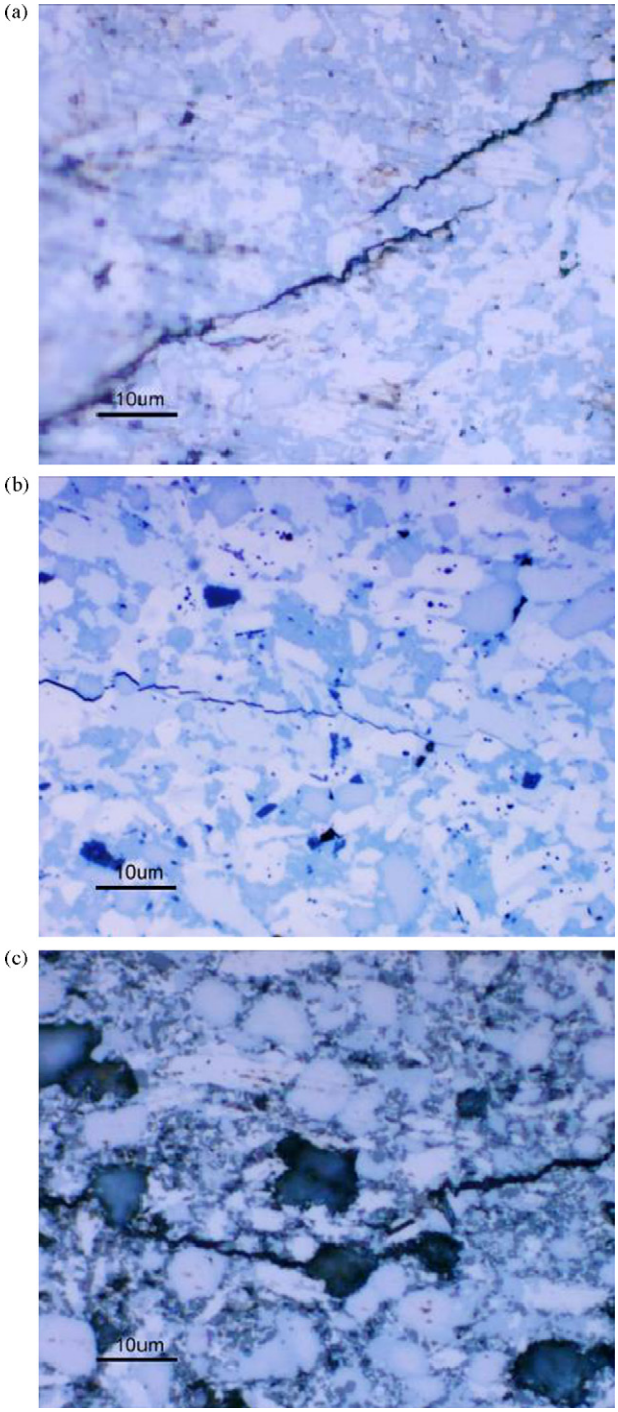

Fig. 10. Crack paths in the Ti_3SiC_2-based composites with: TiC (a), SiC (b) and TiB_2 (c) inclusions.

ity). These properties formed a basis for calculation of FGM lamina compositions and properties. Materials were sintered in hot-pressing regime under the pressure of 25 MPa in inert atmosphere of flowing argon at 500 °C for 1 h. A gradient in elastic moduli, Poisson ratio, hardness and fracture toughness can be observed in the FGM material. Increasing content of Ti_3SiC_2 in FGM laminate results in increasing pseudo-plastic deformation of material during indentation tests. This indicates it was possible to obtain a brittle-to-pseudo-plastic gradient ceramic material, which should have high stroke resistance and be able to work in armour applications.

5. Conclusions

Despite of many research works, the ceramic nanolaminates are the family of new materials that are still before their full recognition. The basic problems are related to obtaining of phase and property controlled polycrystals ready for testing their properties and potential applications. The SHS processing of powders and then their processing into sintered body seems to be one of the most promising techniques. It can be confirmed by, reported in the present paper, tests of applications of such prepared nanolaminates as ceramic machinable composites, bonded phases in diamond tools and compounds in FGM for ceramic armours.

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