

© 2020

Qi Rong Yang

ALL RIGHTS RESERVED

DESIGNING TOUGHER AND AMORPHIZATION-RESISTANT BORON CARBIDE

CERAMICS

By

QI RONG YANG

A dissertation submitted to the

School of Graduate Studies

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

Graduate Program in Materials Science and Engineering

Written under the direction of

Richard A Haber

Approved by

New Brunswick, New Jersey

October, 2020

ABSTRACT OF THE DISSERTATION

Designing Tougher and Amorphization-Resistant Boron Carbide Ceramics

By Qi Rong Yang

Dissertation Director:

Richard A. Haber

Boron carbide is a superhard ceramic that has attracted considerable research attention for decades. However, hard ceramics are generally considered brittle due to the lack of energy dissipation mechanisms, such as dislocation slip, deformation twinning, and micro-cracking, to accommodate irreversible deformation. The highly covalent nature of boron carbide and the low symmetry in its crystal structure imply that localized dislocation movement is difficult. In fact, despite numerous transmission electron microscopy (TEM) studies, localized dislocation movement has never been identified. The lack of plasticity hinders the widespread use of boron carbide in common engineering applications that demand a level of compliance in materials. Boron carbide also suffers from stress-induced amorphization that has a deleterious effect on its mechanical properties. Amorphization occurs when the consolidated boron carbide experiences pressure exceeding its strength, leading to the formation of nano-scale amorphous bands inside the crystalline matrix. The network of amorphous bands acts as a “path of least resistance” for crack growth leading

to catastrophic failure. This thesis focuses on resolving the two prevailing issues of boron carbide (brittleness and susceptibility to stress-induced amorphization) and proposes a design strategy for fabricating the next-generation boron carbide with enhanced toughness and resistance to amorphization.

In this thesis, dislocation mediated plasticity was enabled in boron carbide by tuning its bond characteristics by adding Al to its crystal structure. The addition of Al-B and Al-C bonds increased the propensity of ionic bonds and allowed inter-icosahedra (planar) glide to occur. The toughness of boron carbide could be further increased by making eutectic composite with ZrB_2 and particulate composite with TiB_2 . The tougher diborides provided a means to blunt crack tips and accumulated residual stress at the phase boundaries. The presence of residual stress deflected the crack path and preferentially guided the crack to travel between the phase boundaries.

Stress-induced amorphization was resolved through Si/B co-doping. Si/B co-doped boron carbide was synthesized in various ways (arc melting, diffusion couple, and reaction hot-pressing) and characterized to understand the role of Si in reducing amorphization. We found that as little as 1 at.% addition of Si substantially suppressed amorphization when compared to B-doping alone. Our TEM study comparing the single crystal undoped and Si/B co-doped boron carbide revealed a dramatic change in deformation behavior. Instead of forming long distinct parallel amorphous shear bands, Si/B co-doped boron carbide manifested short and diffusion micro cracks. The mechanism implies that the involvement of Si facilitates local fragmentation as opposed to large-scale amorphization and microcracks.

Lastly, a composite comprised of Si/B co-doping and 10 wt% TiB₂ reinforcement was synthesized. Compared to Si/B co-doped boron carbide, the composite showed an improvement in toughness (10%), hardness (6%), strength (21%), and smaller grain size while minimizing a density increase (4%). Our composite has similar overall mechanical properties to a commercial boron carbide tiles while having 6% higher in elastic modulus and 44% higher in amorphization resistance.

ACKNOWLEDGMENTS

“If I have seen further it is by standing on the shoulders of giants” – Sir Isaac Newton 1675

Sir Isaac Newton’s quote from 1675 eloquently summarizes my gratitude for those who have helped me during my graduate studies. The second half of the quote, in particular, “...by standing on the shoulders of Giants” resonates deeply. It is a constant reminder that advancement in science, no matter how small or large, is predicated on the support of those around us and the wealth of knowledge garnered by those before us.

First and foremost, Prof. Richard A. Haber, my Ph.D. advisor. Thank you for your invaluable support throughout my graduate studies. Your support comes in many forms. Thank you for entrusting me to exercise my intellectual freedom to the fullest extent in a lab that seemingly has an infinite resource. I never once worried about running out of equipment time, replenishing supplies, or needing new equipment because we have them all! Your advice on presentation skills, life lessons, or simple conversation echo deeply and I will take them with me wherever I go. I cannot be more thankful for the super team you assembled. I didn’t think going to work could become my passion. Without a shred of doubt, this lab been the most fun and rewarding professional environment I’ve ever experienced.

Behind every super team, there is an unsung hero. Your body of knowledge, perseverance, and patience inspire me to be more like you. This paragraph is to acknowledge Dr. Chawon Hwang. I’m grateful that you took me under your wing when all

hope seemed gone. You taught me everything from performing basic laboratory tasks to designing research plans, to writing and publishing journal articles, and eventually becoming an independent researcher. Every step of the way, you challenged my thinking and pushed me for perfection, although at times frustrating, but in the end extremely rewarding. Every bit of my academic accomplishment can be attributed to you. Your mentorship may be temporary but my gratitude is forever.

Mentorship comes in many forms and to my surprise, a mentor can also be a life-long friend. Prof. Kelvin Y. Xie, thank you for always finding the time to answer my pesky questions. No matter if the phone call was 11 AM during a weekday or 11 PM over the weekend, you always managed to find time between classes and proposal writing to teach me something new. You always motivate me to achieve greatness.

Every high-performing team requires a great facilitator. Special thanks to Michelle M. Sole for making this lab functional! Without you, I don't think we'll have gloves to wear or paychecks to take home. Without a doubt, you are an integral part of this team.

I'm grateful for the funding and support from funding agencies: Defense Advanced Research Projects Agency (DARPA) and Materials for Extreme Dynamic Environments (MEDE).

Last but not least, to all former and present Haber group members: Vladislav Domnich, Atta Khan, Berra Beyoglu, Jun Du, Sukanya Murali, Azmi Mert Celik, Kent Christian, Metin Ornek, Kanak Kuwelkar, Eoin McAleer, Mark Schaefer, Mustafa Alazzawi, Sweta Kondapalli, Ian Maher, Vince Delucca, Tyler Munhollon, Anthony Etzold, Zeynep Ayguzer, Mike Gagnepain, and Joe Prati. Thank you for the friendship that

made work feel like family. I will always cherish the time we explored local restaurants, playing PUBG and Fun Run tournaments. I had a blast working with you guys. To Kanak and Azmi: we spent countless times exploring new restaurants in my early graduate career. Thank you for those awesome memories. To the special Swol Team 3+ and the Hot Press Crew: You know who you are. The long hours in the hot press room made work fun. I cannot ask for a better team.

DEDICATION

To the angels in my life:

I'm grateful to have you watching over me. I cherish every moment we spent together. Sometimes I miss you dearly and I wish you could be here. It comforts me to know that when I look up to the clouds you are always there.

TABLE OF CONTENTS

ABSTRACT OF THE DISSERTATION	ii
ACKNOWLEDGMENTS	v
DEDICATION	viii
TABLE OF CONTENTS.....	ix
PREFACE	xvi
CHAPTER 1	1
Introduction	1
Goal and objectives	5
Summary of contents.....	6
CHAPTER 2	10
Abstract	11
Introduction	12
Materials and methods	12
Materials processing.....	14
Bulk microstructure characterization.....	15
Indentation and assessment of deformation behavior.....	15
Amorphization analysis using Raman spectroscopy	16
Computational analysis.....	16

Results and discussion.....	18
Confirmation of Al-doping.....	18
Experimental observation of deformation behavior	20
Explanation of dislocation movement	23
Deformation mechanisms in boron carbide solid-solution systems	26
Conclusion.....	27
Acknowledgment	28
References	29
Figures	34
Supporting information	40
Fig. S1: SEM and EDS map	41
Fig. S2: ζ -factor analysis.....	42
Fig. S3: Corresponding HADDF and BF images of Fig. 3A and 3C	43
Fig. S4: Corresponding HAADF and BF images of Fig. 3B and 3D	44
Fig. S5: Additional supporting HRTEM images of deformation behaviors	45
Fig. S6: Amorphous shear bands in undoped boron carbide	46
Fig. S8-S10: Examination of possible Al-doped structure	48
Table S1: Formation energy and chemistry of all stable Al-doped boron carbide structures	51
Fig. S11: Detailed deformation and failure process of (B ₁₂) C-Al-C	52

Fig. S12: Detailed deformation and failure process of (B_{12}) B-Al-C	54
Fig. S13: Detailed deformation and failure process of ($B_{11}C$) C-Al-C.....	56
References.....	58
CHAPTER 3	58
Abstract	59
Introduction	59
Material and Methods.....	61
Results and Discussion.....	63
Microstructure	63
Hardness anisotropy due to microstructure texturing.....	64
Crystallographic orientation and its effect on the hardness anisotropy	65
Toughness anisotropy and crack propagating behaviors	66
Residual stress calculation.....	68
Raman stress mapping	69
Conclusions	72
Acknowledgment	73
References	74
Tables	77
Figures.....	78
Supplementary Figures.....	89

Supplementary Information.....	91
Area fraction calculation	91
Model assumptions and deformed volume equivalent	92
Volume fraction calculation	94
CHAPTER 4	96
Abstract	97
Introduction	98
Materials and Methods	100
Sputter deposition and sintering processes	100
Characterizations and mechanical properties evaluation.....	101
Results and Discussion.....	103
TiB ₂ sputter-deposited B ₄ C powder	103
The sintered body of sputter-deposited B ₄ C powder and comparison to the conventional particulate mixing method	103
Effect of small amount TiB ₂ addition.....	104
Challenges in obtaining dense bodies of TiB ₂ sputter-deposited B ₄ C.....	105
Summary	107
Acknowledgments	108
References	109
Figures	111

Supplementary Figures.....	115
Supplementary Information.....	119
Calculation of the residual stress	119
CHAPTER 5	121
Abstract	122
Introduction	123
Materials and Methods	127
Processing.....	127
X-ray diffraction	127
Microstructural imaging and composition semi-quantification.....	127
Chemical quantification.....	128
Raman spectroscopy and amorphization analysis	128
Results and Discussion.....	130
Bulk phase identification	130
Microstructural characterization.....	130
Phase identification using Raman spectroscopy.....	131
Structural modification due to Si/B co-doping.....	132
Correlation between 210/240 cm ⁻¹ Raman peak intensities and Si content	134
Implication for lattice defects due to Si-doping	135
Absolute elemental quantification of B ₁₂ (B,C,Si) ₃	136

Suggested amorphization mitigation by Si/B co-doping	137
Conclusions	140
Acknowledgment	141
References	142
Figures	147
Supplementary Figures.....	157
CHAPTER 6	159
Abstract	160
Introduction	161
Materials and Methods	163
Results and Discussion.....	166
Summary	172
Acknowledgments.....	173
References	174
Figures	177
Supplementary Figures.....	181
CHAPTER 7	186
Introduction	186
Establishing confidence in comparison:.....	188
Amorphization vs chemistry on the surface	190

Amorphization vs chemistry at depth.....	191
Conclusion.....	192
References	193
CHAPTER 8	194
Abstract	194
Introduction	196
Materials and Methods	198
Results and Discussion.....	199
Conclusions	202
Acknowledgment	203
References	204
Tables	205
Figures.....	206
CHAPTER 9	209
Conclusions	209
Perspective	212
CHAPTER 10	216
Future work	216

PREFACE

In meeting the requirement of a thesis by publication, the author has to complete at least 3 first-author and 2 co-author publications. This dissertation comprises a collection of publications, an unpublished manuscript, as well as unpublished results that represent major accomplishments of the author. These papers serve as individual chapters of this thesis. Chapters 3, 4, 5, 6, and 8 were published in peer-reviewed journals where Chapter 2 contains a complete manuscript to be submitted to a peer-review journal. Chapter 7 contains results for a future publication.

Published work as part of this thesis:

1. Yang, Qirong, Christopher J Marvel, Yidi Shen, Chawon Hwang, Jun Du, Eric D. Gronske, Kelvin Y. Xie, Steven R. Mecurio, Qi An, Martin P. Harmer, and Richard A. Haber. "Dislocation mediated plasticity in boron carbide (B₄C) via Al-doping." (To be submitted)
2. Yang, Qirong, Chawon Hwang, Atta U. Khan, Vladislav Domnich, Eric D. Gronske, and Richard A. Haber. "Anisotropy and residual stress in B₄C-ZrB₂ eutectic." *Materials Characterization* 155 (2019): 109797.
3. Hwang, Chawon, Stephen DiPietro, Kelvin Y. Xie, Qirong Yang, Azmi M. Celik, Atta U. Khan, Vladislav Domnich, Scott Walck, Kevin J. Hemker, and Richard A. Haber. "Small amount TiB₂ addition into B₄C through sputter deposition and hot pressing." *Journal of the American Ceramic Society* 102, no. 8 (2019): 4421-4426.
4. Yang, Qirong, Chawon Hwang, Christopher J. Marvel, Ankur Chauhan, Vladislav Domnich, Atta U. Khan, Jerry C. LaSalvia, Martin P. Harmer, Kevin J. Hemker, and Richard A. Haber. "Fabrication and characterization of arc melted Si/B co-doped boron carbide." *Journal of the European Ceramic Society* 39, no. 16 (2019): 5156-5166.

5. Xiang, Sisi, Luoning Ma, Qirong Yang, Yvonne Dieudonne, George M. Pharr, Jing Lu, Digvijay Yadav et al. "Tuning the deformation mechanisms of boron carbide via silicon doping." *Science advances* 5, no. 10 (2019): eaay0352.
6. Yang, Qirong, Azmi Mert Çelik, Jun Du, Jerry C. LaSalvia, Chawon Hwang, and Richard A. Haber. "Advancing the mechanical properties of Si/B co-doped boron carbide through TiB₂ reinforcement." *Materials Letters* 266 (2020): 127480.

CHAPTER 1

Introduction

From the first weapons carved from stones and bones to the colorful sculptures and pottery handcrafted from clays, ceramics has been an integral part of our society. Today, much of the research in ceramics has shifted its focus to advanced ceramics, a term used to describe ceramics with exceptional electrical, thermal, physical, and mechanical properties. Boron carbide (B_4C), in particular, has been the subject of intense studies due to its excellent chemical resistance, high Seebeck coefficient, high neutron absorption, and superior physical and mechanical properties [1, 2]. For these reasons, boron carbide is widely used in engineering applications such as grinding tools, water jet nozzles, radiation shields, thermoelectric generators, and most notably protection armor plates [3, 4].

Like all ceramics, boron carbide suffers from brittleness due to a lack of large-scale plasticity. Ceramics can often experience localized dislocation movements under small contact loading, such as nano-indentation, but dislocation movements across a large area do not occur at room temperature [5-8]. It is a mystery why boron carbide, in particular, does not display any sign of dislocation movement even at a small scale [9-11], even though other boron rich icosahedral materials do, i.e. boron suboxide [12] and boron phosphide [13]. The treatments to improve the toughness of boron carbide largely involve in reinforcing the microstructure with tougher ceramics or metals [14-20]. While the composites improve the toughness and change the crack propagating behaviors of boron

carbide, it also diminishes the hardness and adds weight. Strategies that directly address the lack of dislocation and dislocation movement have not been considered.

Boron carbide is also known to experience a sudden loss of strength and toughness due to an anomalous event also known as stress-induced amorphization when subjected to high-pressure events [10, 11, 21]. Amorphization has been described as the inhomogeneous loss of crystalline order in localized zones scattered within a crystalline volume, forming nano-scale bands with large aspect ratios. Experimentally, amorphization has been observed plate-impact tests, uniaxial diamond anvil cell compression, mechanical scratching, and indentation experiments [11, 22-25]. Although foreign atom doping (B and Si) has been proposed as a strategy to suppress amorphization, the extent of amorphization reduction, mechanical properties, and the deformation behaviors of doped boron carbide have not been studied [25].

Intrinsic brittleness and susceptibility to stress-induced amorphization have hindered the widespread use of boron carbide. Resolving both issues has become a priority in the research communities in designing the next-generation boron carbide. This thesis focuses on tackling the brittleness of boron carbide directly by enabling room temperature dislocation movement and secondary phase reinforcement. The thesis also delivers a comprehensive understanding of mitigation of amorphization via Si/B co-doping. Finally, the thesis proposes a design strategy for fabricating next-generation boron carbide with enhanced toughness and amorphization mitigation.

- [1] V. Domnich, S. Reynaud, R.A. Haber, M. Chhowalla, Boron Carbide: Structure, Properties, and Stability under Stress, *J. Am. Ceram. Soc.* 94(11) (2011) 3605-3628. 10.1111/j.1551-2916.2011.04865.x.
- [2] F. Thevenot, Boron carbide—a comprehensive review, *J. Eur. Ceram. Soc.* 6(4) (1990) 205-225. 10.1016/0955-2219(90)90048-K.
- [3] M. Bouchacourt, F. Thevenot, The Properties and Structure of the Boron-Carbide Phase, *J Less-Common Met* 82(1-2) (1981) 227-235. Doi 10.1016/0022-5088(81)90223-X.
- [4] A.K. Suri, C. Subramanian, J.K. Sonber, T.S.R.C. Murthy, Synthesis and consolidation of boron carbide: a review, *International Materials Reviews* 55(1) (2010) 4-40. 10.1179/095066009x12506721665211.
- [5] T. Page, L. Riester, S. Hainsworth, The plasticity response of 6H-SiC and related isostructural materials to nanoindentation: slip vs densification, *MRS Online Proceedings Library Archive* 522 (1998).
- [6] T.F. Page, W.C. Oliver, C.J. McHargue, The deformation behavior of ceramic crystals subjected to very low load (nano) indentations, *J. Mater. Res.* 7(2) (1992) 450-473.
- [7] M. Matsumoto, H. Huang, H. Harada, K. Kakimoto, J. Yan, On the phase transformation of single-crystal 4H-SiC during nanoindentation, *J. Phys. G: Nucl. Part. Phys.* 50(26) (2017) 265303.
- [8] D. Ghosh, G. Subhash, G.R. Bourne, Room-temperature dislocation activity during mechanical deformation of polycrystalline ultra-high-temperature ceramics, *Scripta Materialia* 61(11) (2009) 1075-1078.
- [9] D. Ge, V. Domnich, T. Juliano, E.A. Stach, Y. Gogotsi, Structural damage in boron carbide under contact loading, *Acta Mater.* 52(13) (2004) 3921-3927. 10.1016/j.actamat.2004.05.007.
- [10] S. Xiang, L. Ma, B. Yang, Y. Dieudonne, G.M. Pharr, J. Lu, D. Yadav, C. Hwang, J.C. LaSalvia, R.A. Haber, Tuning the deformation mechanisms of boron carbide via silicon doping, *Sci. Adv.* 5(10) (2019) eaay0352.
- [11] M. Chen, J.W. McCauley, K.J. Hemker, Shock-induced localized amorphization in boron carbide, *Science* 299(5612) (2003) 1563-6. 10.1126/science.1080819.
- [12] C. Kunka, Q. An, N. Rudawski, G. Subhash, J. Zheng, V. Halls, J. Singh, Nanotwinning and amorphization of boron suboxide, *Acta Mater.* 147 (2018) 195-202.
- [13] Q. An, W.A. Goddard III, Ductility in crystalline boron subphosphide (B₁₂P₂) for large strain indentation, *The Journal of Physical Chemistry C* 121(30) (2017) 16644-16649.

- [14] D.C. Halverson, A.J. Pyzik, I.A. Aksay, W.E. Snowden, Processing of boron carbide-aluminum composites, *J. Am. Ceram. Soc.* 72(5) (1989) 775-780.
- [15] S. Tariolle, F. Thevenot, M. Aizenstein, M. Dariel, N. Frumin, N. Frage, Boron carbide–copper infiltrated cermets, *Journal of solid state chemistry* 177(2) (2004) 400-406.
- [16] C. Hwang, S. DiPietro, K.Y. Xie, Q. Yang, A.M. Celik, A.U. Khan, V. Domnich, S. Walck, K.J. Hemker, R.A. Haber, Small amount TiB₂ addition into B₄C through sputter deposition and hot pressing, *J. Am. Ceram. Soc.* (2019) 4421-4426. 10.1111/jace.16457.
- [17] C. Hwang, Q. Yang, S. Xiang, V. Domnich, A.U. Khan, K.Y. Xie, K.J. Hemker, R.A. Haber, Fabrication of dense B₄C-preceramic polymer derived SiC composite, *J. Eur. Ceram. Soc.* 39(4) (2019) 718-725. 10.1016/j.jeurceramsoc.2018.12.029.
- [18] Q. Yang, A.M. Çelik, J. Du, J.C. LaSalvia, C. Hwang, R.A. Haber, Advancing the mechanical properties of Si/B co-doped boron carbide through TiB₂ reinforcement, *Materials Letters* (2020) 127480.
- [19] Q. Yang, C. Hwang, A.U. Khan, V. Domnich, E.D. Gronske, R.A. Haber, Anisotropy and residual stress in B₄C-ZrB₂ eutectic, *Mater. Charact.* (2019) 109797. 10.1016/j.jeurceramsoc.2019.08.024.
- [20] K. Sairam, J. Sonber, T.C. Murthy, C. Subramanian, R. Hubli, A. Suri, Development of B₄C–HfB₂ composites by reaction hot pressing, *Int. J. Refract. Met. H.* 35 (2012) 32-40.
- [21] D.E. Grady, Shock-Wave Strength Properties of Boron-Carbide and Silicon-Carbide, *J. Phys. IV* 4(C8) (1994) 385-391. 10.1051/jp4:1994859.
- [22] X.Q. Yan, Z. Tang, L. Zhang, J.J. Guo, C.Q. Jin, Y. Zhang, T. Goto, J.W. McCauley, M.W. Chen, Depressurization amorphization of single-crystal boron carbide, *Phys. Rev. Lett.* 102(7) (2009) 075505. 10.1103/PhysRevLett.102.075505.
- [23] M.W. Chen, J.W. McCauley, Mechanical scratching induced phase transitions and reactions of boron carbide, *J. Appl. Phys.* 100(12) (2006) 123517. 10.1063/1.2405742.
- [24] S. Zhao, B. Kad, B.A. Remington, J.C. LaSalvia, C.E. Wehrenberg, K.D. Behler, M.A. Meyers, Directional amorphization of boron carbide subjected to laser shock compression, *Pro. Nat. Acad. Sci.* 113(43) (2016) 12088-12093.
- [25] Q. Yang, C. Hwang, C.J. Marvel, A. Chauhan, V. Domnich, A.U. Khan, J.C. LaSalvia, M.P. Harmer, K.J. Hemker, R.A. Haber, Fabrication and characterization of arc melted Si/B co-doped boron carbide, *J. Eur. Ceram. Soc.* 39(16) (2019) 5156-5166. 10.1016/j.jeurceramsoc.2019.08.024.

Goal and objectives

Boron carbide is limited by its intrinsic brittleness and susceptibility to stress-induced amorphization. The goal of this thesis is to address both limitations and propose a path for designing boron carbide ceramics with enhanced toughness and resistance to stress-induced amorphization. In doing so, 6 objectives are established:

1. Promote room temperature dislocation movement in boron carbide
2. Increase the toughness of boron carbide by secondary reinforcement (ZrB_2 and TiB_2)
3. Mitigate pressure-induced amorphization in boron carbide by foreign atom doping (B and Si)
4. Understand the deformation behaviors of undoped and Si/B co-doped boron carbide
5. Investigate and isolate the effect of Si-doping from B-doping
6. Propose a materials design strategy for next-generation boron carbide with enhanced toughness and resistance to stress-induced amorphization

Summary of contents

In this thesis, chapters 3, 4, 5, 6, and 8 are represented by 5 published articles. Chapter 2 contains a manuscript that is ready to be submitted to a peer-reviewed journal. Chapter 7 encompasses unpublished data that will be prepared into a manuscript for future submission.

Chapters 2, 3, and 4 focus on addressing the brittleness of boron carbide, while chapters 5, 6, and 7 cover the mitigation and understating of stress-induced amorphization via foreign atom doping. Chapter 8 proposes a design strategy for next-generation boron carbide ceramic with enhanced toughness and resistance to amorphization. Chapter 9 summarizes major findings and provides perspectives gained from the thesis. Lastly, chapter 10 paves the way for possible future work that arises from the limitation of this work. A summary of each chapter is as follows:

Addressing the brittleness of boron carbide (objective 1 and 2):

Chapter 2: It has been a long-standing mystery that boron carbide (B_4C) does not appear to experience any sign of localized plasticity at room temperature despite numerous transmission electron microscopy (TEM) studies that have been conducted on its deformation behaviors. The lack of dislocation movement is a result of strong covalent bonds between B and C atom. For the first time, we found that the dislocation movement can be enabled when Al was introduced to the crystal structure of boron carbide. The presence of Al-C bonds increases the overall ionic bond characteristic which in term lowers

the lattice friction. This profound result indicates that deformation behaviors of ceramics can be tuned through atomic doping.

Chapter 3: Eutectic composites possess highly textured microstructure and mechanical properties that often surpass their constituents. Here, B_4C - ZrB_2 eutectic composite was prepared through arc melting; and its hardness and toughness were characterized and related to the microstructure. We found that the tougher ZrB_2 and the residual stress at the phase boundaries guided the crack propagation direction. As a result, the B_4C - ZrB_2 eutectic composite showed a substantial increase in indentation toughness compared to monolithic boron carbide ceramic.

Chapter 4: B_4C - TiB_2 composite was prepared through magnetron sputtering and reaction hot pressing. This processing method showed more uniformly dispersed fine TiB_2 grains compared to conventional (powder mixed) prepared composite. As low as 2.3 wt% TiB_2 addition resulted in a 15% improvement in indentation toughness while resulting in less than 2% increase in density. The improvement can be attributed to the combination of crack impeding by TiB_2 grains and crack deflection at the B_4C - TiB_2 interfaces.

Enhancing and understanding amorphization resistance of boron carbide (objective 3, 4, and 5):

Chapter 5: Boron carbide undergoes stress-induced amorphization when subjected to large non-hydrostatic stresses that exceed its elastic limit. This has been proposed as the source for the abrupt loss of shear strength in boron carbide which limits its engineering applications. Si/B co-doping was suggested as one of the means to suppress stress-induced

amorphization but this has not been experimentally verified. By utilizing arc melting, we prepared Si/B co-doped boron carbide with increased Si content as compared to conventional methods. Through Raman analysis in conjunction with an indentation and elemental analyses based on SEM and STEM (ζ -factor microanalysis), it is suggested that Si/B co-doping is a promising avenue for suppressing stress-induced amorphization.

Chapter 6: Although Si/B co-doping has been shown to suppress stress-induced amorphization, its deformation behavior is not well understood. In this chapter, a well-controlled study was carried out to directly compare the deformation behaviors of Si/B co-doped boron carbide. Here, we report that a small amount of Si doping (~ 1 atomic %) leads to a substantial decrease in stress-induced amorphization due to a noticeable change of the deformation mechanisms in boron carbide. In the undoped boron carbide, the Berkovich indentation-induced quasi-plasticity is dominated by amorphization and microcracking along the amorphous shear bands. This mechanism resulted in long, distinct, and single-variant shear faults. In contrast, substantial fragmentation with limited amorphization was activated in the Si/B co-doped boron carbide, and manifested by the short, diffuse, and multivariant shear faults. Microcracking via fragmentation competed with and subsequently mitigated amorphization. This work highlights the important roles that solute atoms play on the structural stability of boron carbide and opens up new avenues to tune deformation mechanisms of ceramics via doping.

Chapter 7: Recently, B-doped boron carbide has also demonstrated an impressive resistance to amorphization. The B-C-Si solid solution complicates an accurate assignment of reduction of amorphization to purely Si-doping. To investigate and isolate the effect of B-doping from Si-doping, a B-B₄C and a SiB₆-B₄C diffusion couples were prepared. B and Si/B diffused into the B₄C side to form a chemistry gradient. Amorphization information across both diffusion zones was compared to boron carbide with an identical B/C ratio, but different in Si content. We found that an increase in B content correlated with an increase in the reduction of amorphization. More importantly, the involvement of Si, at the same B/C ratio, substantially suppressed amorphization. This study decoupled the effectiveness of the amorphization reduction of B from Si.

Boron carbide with enhanced toughness and amorphization resistance (objective 6):

Chapter 8: The overall mechanical properties of Si/B co-doped boron carbide is unknown. A preliminary assessment indicates that a reduction in hardness and strength is likely to occur due to weakening in the atomic bond strength by atomic doping. Here, we delivered a comprehensive report on the mechanical properties of Si/B co-doped boron carbide; and proposed an effective strategy to improve the mechanical properties through TiB₂ reinforcement. Vickers hardness of 25.0 GPa, an indentation toughness of 2.1 MPa·m^{0.5}, Young's modulus of 430 GPa, and flexural strength of 338 MPa were measured for Si/B co-doped boron carbide. The reinforcement with TiB₂ increased the overall mechanical properties to 26.6 GPa for hardness, 2.3 MPa·m^{0.5} for indentation toughness, and 410 MPa and flexural strength.

CHAPTER 2

Note: Chapter 2 contains an unpublished manuscript that will be submitted

Enabling dislocation mediated plasticity in boron carbide (B₄C) via Al-doping

Qirong Yang¹, Christopher J. Marvel², Yidi Shen³, Jun Du¹, Chawon Hwang¹, Eric D. Gronske¹, Kelvin Y. Xie⁴, Steven R. Mercurio⁵, Qi An³, Martin P. Harmer², and Richard A. Haber^{1,†}

¹*Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA*

²*Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA*

³*Department of Chemical and Materials Engineering, University of Nevada, Reno, NV 89557, USA*

⁴*Department of Materials Science and Engineering, Texas A & M University, College Station, Texas 77843, USA.*

⁵*H&M Analytical, Cream Ridge, NJ 08514, USA*

[†]Corresponding author's email: Rich.haber@rutgers.edu & address: [607 Taylor Road, Piscataway, NJ 08854, USA. Tel: +1](#) (848) 445-5924, FAX: +1 (732) 445-5926

Abstract

Dislocation slip, deformation twinning, phase transformation, and cracking are the energy dissipation mechanisms to accommodate irreversible deformation in materials. The absence of dislocation movement has been attributed to the ease of cracking and the low damage tolerance observed in boron carbide. Here, we demonstrated that dislocation slip was enabled in boron carbide by Al doping. The activation of dislocation slip is explained by quantum mechanics simulation, which suggests strain energy is released through icosahedral slip facilitated by inter-icosahedral and chain bond breaking and reconfiguring. The new insight obtained from this work indicates atomic doping could be an effective strategy to tune deformation mechanisms in boron carbide, which provides a significant potential for limiting amorphization and crack propagation in boron carbide and opens a new way to engineer enhanced damage tolerance in brittle ceramics.

Keyword: Boron carbide; Dislocation; Doping; Transmission electron microscopy; Molecular dynamic simulation

Introduction

Superhard crystalline solids such as boron carbide, boron suboxide, cubic boron nitride, and diamond are characterized by remarkable hardness (>40 GPa) owing to their strong covalent bonding [1-4]. Among all superhard materials, boron carbide is most widely used in structural engineering applications (e.g. grinding tools, wear-resistance parts, neutron-absorbing shields, thermal electric components, ceramic armor [5-10]) for its commercial availability and low density (2.52 g/cm^3). Boron carbide is composed of buckyball-like 12-atom icosahedra located at the vertices of a rhombohedral structure [11-13]. The structure is complete by a 3-atom linear chain across the longest body diagonal in the $[111]_r$ direction. For example, boron carbide can have either $B_{11}C$ (11 B and 1 C atoms for C-rich B_4C) or B_{12} (12 B atoms for B-rich $B_{13}C_2$) icosahedra, and a C-B-C 3-atom linear chain [5].

The supreme hardness comes at a price, however, as the covalent bonding limits the relaxation of the crystal lattice upon straining, which leads to brittle fracture rather than deforming plastically. The strong covalent bonding between B-B and B-C atoms in boron carbide implies that plastic deformation is difficult at room temperature. The assertion is confirmed by transmission electron (TEM) studies where no evidence of dislocation or deformation twinning has been observed in boron carbide ceramics mechanically deformed at room temperature [14-18]. Under the typical loading regime, boron carbide fails through brittle fracture initiated when the applied stress exceeds the accumulative stress at the crack tip. At non-hydrostatic loading pressures with a high shear stress component (i.e. ballistic impacts above 850-900 m/s, diamond anvil compression tests, and indentation experiments), carbide notoriously fails through stress-induced amorphization [1, 15, 19,

20]. The high shear stresses trigger the collapse of icosahedra, leading to the formation of a network of nano-scale amorphous bands. The deleterious loss in shear strength of boron carbide subjected to pressures above its elastic limit (18-20 GPa) is attributed to the prevalence in crack nucleation and propagation inside the amorphous bands [21-23].

Substantial effort has been devoted to overcoming the susceptibility to fracture by making ceramic composites with reinforcement particles (e.g. SiC, TiB₂, ZrB₂, or HfB₂ [24-27]). The toughening strategy relies on slowing the crack traveling speed and altering the crack propagating behavior by introducing tougher components in the microstructure. However, the intrinsic brittleness of boron carbide due to the lack of energy dissipating mechanisms limits the composite toughening approach. Recently, B-enrichment and Si-doping have shown to mitigate stress-induced amorphization by as much as 30-31% when compared to undoped boron carbide [16, 28]. A combined strategy consists of particulate reinforcement and atomic doping has also been proposed [29]. We hypothesize that if an additional deformation mechanism exists, such as dislocation slip, then it could competing with the progression of brittle fracture and amorphization by consuming part of the deformation energy.

In this study, we report that doping boron carbide with Al could lead to dislocation activities. The dislocation movement competed with the other deformation mechanisms of boron carbide (brittle fracture and amorphization), resulted in localized micro-cracking and less amorphization. The rationale based on density functional theory (DFT) simulations suggested that the Al-doped structure can withstand large shear strain without the destruction of icosahedra and part of the strain energy is dissipated through icosahedral slip.

Materials and methods

Materials processing

A total of 10 g of boron carbide (Grade HD20, H.C. Starck), amorphous boron (Grade I, H.C. Starck), and aluminum (Alfa Aesar) powders were mixed according to B:C:Al atomic ratio of 82.33:12.67:5. The powder mixture was cold-pressed without a binder additive using a 25 mm $\varnothing$ steel die sets. The pellet was placed on a water-cooled Cu hearth inside an arc melting furnace (Arc 200, Arcast). The chamber was purged several times with 99.999% purity argon gas before melting using an electric arc discharged from a W electrode at 500 Amp. The melt was cooled to room temperature, flipped, and remelted for a total of 5 times to ensure homogenous mixing. The ingot was manually crushed into fine powders using a steel mortar and pestle set and subsequently washed with HCl then rinsed with methanol to remove the Fe contamination. The powders were dried in Ar flow at 120 °C for 12 hours. Subsequently, 4 g of the dried powders were loaded into a 20 mm $\varnothing$ graphite die with BN covered interior and consolidated using Spark Plasma Sintering (SPS, 10-3, Thermal Technology LLC) apparatus to 1950 °C for 5 mins at 50 MPa. The heating rates were 150 °C/min from room temperature to 600 °C and 300 °C/min to sintering temperature. The sintered specimens were sandblasted and surface ground to remove graphite contamination on the surfaces, and finally, sectioned using a diamond wheel and polished down to 0.25 μm using diamond suspensions for further characterization. Undoped boron carbide was prepared following the identical melting, crushing, sintering, and polishing procedures.

Bulk microstructure characterization

Polished specimens were characterized using a field emission scanning electron microscope (FE-SEM; SIGMA Zeiss) equipped with an energy-dispersive X-ray spectroscopy detector (EDS; Oxford Instruments). Elemental distribution was revealed using SEM-based EDS spectral imaging. Phase identification and lattice parameters of the consolidated specimens were determined using X-ray diffraction upon crushing the sintered specimens into fine powders using a steel mortar and treated with HCl to remove Fe contamination. Powder diffraction was conducted using an X'Pert Pro diffractometer (PANalytical) with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The peak positions were corrected using a silicon standard (SRM 640e, NIST). Phase identification and lattice parameter determination via Rietveld refinement were carried out using JADE software (Jade 9, Materials Data). Raman spectroscopy was used to detect the chemical change as a result of Al-doping. Raman analysis was carried out using an Invia Reflex (Renishaw) microscope equipped with a 532 nm (2.33 eV) laser.

Indentation and assessment of deformation behavior

Small-scale contact loading via Berkovich indentation (100 mN, NanoTest Vantage, Micro Materials Ltd.) was used to deform Al-doped and undoped boron carbide at room temperature. Thin foils for scanning transmission electron microscopy (STEM) were prepared by cross-sectioning the Berkovich indents in order to capture the deformation zone beneath the surface using the in-situ lift-out method with a focused ion beam (FIB, FEI SCIOS). High-resolution STEM imaging and EDS were completed on an aberration-corrected instrument (JEOL ARM-200CF). Chemical analysis was conducted by applying ζ -factor microanalysis which is a TEM-based EDS approach that simultaneously

determined specimen thickness and composition, thus enabling X-ray absorption corrections [30]. ζ -factor microanalysis has been successfully utilized to obtain elemental composition accurately for boron carbide solid solutions [28, 31, 32].

Amorphization analysis using Raman spectroscopy

Vickers indentation was conducted to activate stress-induced amorphization. The indents were placed using an automatic hardness tester (VH3300, Wilson) at 4.9 N load with a hold time of 10 s. Raman spectroscopy is an established technique to evaluate amorphization in boron carbide as a result of mechanical stress [18, 28, 33-35]. Raman mapping (532 nm, 2.33 eV) was carried out around the indents with a step size of 0.5 μm . A total of 5 indents were completed for each bulk sample and the intensity of the 1810 cm^{-1} amorphous peak amongst an array of 2D Raman spectra was integrated and visualized to create amorphization color maps.

Computational analysis

All density functional theory (DFT) calculations were performed based on the plane-wave basis set and the generalized gradient approximation (GGA) type Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional implemented in Vienna ab initio simulation package (VASP) [36-39]. The pseudopotentials of B, C, and Al were generated using the projector augmented wave (PAW) method with $2s^22p^1$, $2s^22p^2$, and $3s^23p^1$ treated as valence electrons, respectively [39]. The plane wave cutoff, the energy convergence for the electronic self-consistent field (SCF), and the force convergent criterion were set to 450 eV, 10^{-5} eV, and 10^{-2} eV/Å, respectively, in all simulations. A Γ -centered k-point mesh method was used for Brillouin zone integration with a fine mesh density above $2\pi \times 1/40 \text{ \AA}^{-1}$.

For the shear deformation of Al-doped B-C systems, $2 \times 2 \times 2$ supercells were constructed with ~ 120 atoms for three plausible configurations and then shear them in the (001)[100] slip system which is the most plausible slip system for boron carbide within 11 possible slip systems [22]. A 3-index rhombohedral plane and direction were used to represent the plausible slip system. The ideal shear deformation was applied by constraining shear strain along (001)[100] slip while relaxing the stress in the other five strain components [40]. A less dense $2 \times 2 \times 2$ K-point grid mesh in the Brillouin zone was employed in the shear deformation. The residual stresses were less than 0.5 GPa in the constrained structure relaxation.

Results and discussion

Confirmation of Al-doping

The doping of Al into the boron carbide lattice (solid-solution) is confirmed using three independent techniques, X-ray diffraction (XRD), Raman spectroscopy, and Energy-dispersive spectroscopy (EDS) (Fig. 1). XRD shows that both Al-doped and undoped samples exhibit the characteristic rhombohedral structure of boron carbide (Fig. 1A). A closer look at the (021) reflection reveals a downshift in the peak position for the Al-doped sample, suggesting a large lattice due to Al-doping [41, 42]. We obtained hexagonal lattice constant of $a = 5.64 \text{ \AA}$ and $c = 12.33 \text{ \AA}$ for Al-doped boron carbide compared to $a = 5.60$ and $c = 12.07$ for the undoped material. The anisotropic expansion in the c parameter suggests modification occurred in the 3-atom chain, which also lies in the c -axis. Small amounts of C and WB_2 were found in both samples and the sources can be attributed to the free C in the as-received powders and W from the electrode, respectively.

A typical Raman spectrum (shown in Fig. 1B) of the undoped boron carbide has a series of features from 530 to 1090 cm^{-1} originating from inter- and intra-icosahedra bonds and a sharp peak at 478 cm^{-1} attributing to the vibration modes from the 3-atom chain [14, 43]. The Al-doped boron carbide also shares similar characteristics from 478 - 1090 cm^{-1} suggesting the overall structural symmetry is unchanged, i.e. the structure remains rhombohedral. A closer inspection reveals subtle modifications have been made due to Al-doping. A noticeable downshift in the high wavenumber regime (729 - 1090 cm^{-1}) in the Al-doped boron carbide indicates icosahedra are enlarged due to B-enrichment [44-46]. A slight reduction in the 478 peak intensity with respect to the 1090 cm^{-1} peak suggests Al-doping weakens the chain structure. Moreover, the $265/322 \text{ cm}^{-1}$ doublet, associated with

disorder-induced phonon [5], is absent in the Al-doped boron carbide. Instead, a new 189 cm^{-1} peak was identified. To the best of our knowledge, this peak is reported for the first time for Al-doped boron carbide. Because of the similarity in the peak position with disorder-induced phonon peaks in Si-doped boron carbide [28], we conjecture that the 189 cm^{-1} peak is also related to lattice defects created by the 3-atom chain modification. Taking into account the XRD and Raman results, we propose that Al-doping primarily modifies the 3-atom chain while the overall structure symmetry remains unchanged.

The distribution of Al in the overall microstructure was determined using scanning electron microscopy (SEM) based energy-dispersive spectroscopy (EDS), shown in Fig. 1C. Overall, Al is reasonably homogenous with a sparse secondary phase of WB_2 was detected. (A complete EDS data is presented in Fig. S1). A more accurate chemical analysis was carried out using ζ -factor microanalysis through STEM-EDS. It was determined that the compositions of the Al-doped and undoped boron carbides are Al = 0.6, B = 84.8, C = 14.6 at.% and B = 80.5, C = 19.5 at.%, respectively. The STEM-EDS spectrum for the Al-doped sample depicts an Al peak (1.49 KeV), shown in Fig. 1D. As a means to validate the STEM-EDS based analysis, the elemental concentrations versus sample thickness is shown in Fig. S2. Here the atomic concentrations are independent of sample thickness, thereby indicating that the measurements are properly calibrated and accurate. Particularly of note, the measured Al content in the Al-doped sample is substantially lower than the nominal values of 5 at.% which was the initial doping concentration. It's plausible that the intense heat ($>3000\text{ }^\circ\text{C}$) from the arc evaporated Al during arc melting.

Experimental observation of deformation behavior

The preliminary deformation behavior assessment is conducted using Raman spectroscopy inside of Vickers indentation. The sharp tip from the indenter imposes large stresses that can trigger stress-induced amorphization in boron carbide ceramics [14, 18, 28, 35]. A typical Raman spectrum acquired from the pristine surface and inside the residual indent for undoped and Al-doped boron carbide is displayed in Fig. 2A and 2B, respectively. Three new Raman features associated with amorphous boron carbide at 1320, 1520, and 1810 cm^{-1} are identified inside the residual indent, superimposing the low wavenumber Raman bands attributed to the crystalline phase [1, 34]. Raman point analysis reveals that the intensity of amorphous peaks is smaller for Al-doped boron carbide.

To further understand the extent of amorphization inside the entire residual indent, 2D Raman mapping was performed. Only the 1810 cm^{-1} peak intensity was used to construct the amorphization intensity heat map to avoid competing Raman signals from C, which exists in our samples. An averaged amorphization heat map for undoped and Al-doped boron carbide overlaying the optical image of the Vickers indentation is illustrated in Fig. 2C and 2D. A quick inspection reveals amorphization is contained entirely inside the residual indent. The highest amorphization intensity is located at the center of the residual indent where it experiences the highest pressure. By integrating the number of pixels containing amorphization intensity, we obtained 501 versus 399 pixels for undoped and Al-doped boron carbide, respectively, or a reduction of ~20% in the amorphous area. The difference in the amorphous area can be better understood by comparing their amorphization intensity population in a histogram, as shown in Fig. 2E. The intensity population of Al-doped boron carbide skews highly towards the lower amorphization

intensity compared to the undoped counterpart, suggesting Al-doping is effective at suppressing highly amorphized regions. We further quantify the total amorphization intensity by summing the normalized intensity of each pixel and obtained a reduction of 44% in the Al-doped boron carbide. This suggests at the same stress level, other energy dissipating mechanisms (dislocation slip, deformation twinning, and micro-cracking) may occur during deformation, competing with the process of stress-induced amorphization.

To investigate if other energy dissipating mechanisms are activated during indentation, the cross-sectional TEM foil of undoped and Al-doped boron carbide were extracted from the Berkovich nanoindentation. Fig 2A and 2C depict low angle annular dark-field (LAADF) micrographs of deformed zones directly under Berkovich indents. The imprint of the indenter is marked by a grey dashed triangle. The difference in the size of the imprint is caused by the sectioning the indents slightly off-center, therefore the size of the deformation zones cannot be compared directly. Here, we compare the difference in the deformation features. The diffused and increased diffraction intensity presented in the LAADF micrographs directly under the indent is caused by indentation-induced strain and therefore represents the damaged materials surrounded by the pristine material in the relatively smooth, grey regions. Long and distinct line features (marked by arrows in Figs. 3A and 3B) can be readily observed in the undoped boron carbide. Amorphous shear bands or cracks evolved from the shear bands have been reported to exist in specific crystallographic planes, which manifest in long and near parallel lines [15, 16]. High-resolution STEM confirms numerous amorphous bands and amorphization-driven cracks were inside the near-parallel line features in undoped boron carbide, shown in Fig. S6 of SI. On the other hand, the deformed features in the Al-doped boron carbide are difficult to

discern (Fig. 3C). A closer inspection of the deformed regions reveals that Al-doped material exhibits localized, multi-directional micro-cracking (marked by arrows in Fig. 2D). These fractures are unlikely related to amorphization because they do not follow specific crystallographic planes. Furthermore, High-resolution STEM did not find evidence of amorphous shear bands inside the micro-cracks. These observations suggest Al-doping activates a new energy dissipation mechanism, such as micro-cracking, similar to what is found in the B-rich and Si-doped boron carbide [16, 18]. (The corresponding bright-field (BF) and high angle annular dark-field (HAADF) images of Fig. 3 can be found in Fig. S3 and S4. Additional supporting high-resolution TEM images of deformation behavior and amorphous shear bands can be found in Fig. S5)

The most significant discovery regarding plastic deformation in the Al-doped boron carbide was made in the vicinity of cracks. Fig. 4 displays LAADS images showing multiple dislocations emanating from cracks for two different TEM specimens of indented Al-doped boron carbide. (The corresponding BF and HAADF images of Fig. 4 can be found in Fig. S7). It is interesting to note many dislocations within the same group are approximately parallel to each other (e.g. dislocation labeled 1-3 in Fig. 4B and 1-5 in Fig. 2D). This observation suggests that they are from the same dislocation source and glide in the same plane. The stress concentration (likely caused by cracking) triggers the operation of a dislocation source, from which the dislocations are able to multiply. Groups of near-parallel dislocation also suggest that the dislocations are mobile, which the motion could dissipate deformation energy during the room temperature indentation. The dislocation activities are not observed in the deformed undoped boron carbide in the study, which is consistent with the previous reports [14-18]. In fact, to the best of our knowledge,

dislocation movement has not been reported for undoped, B-rich, or Si-doped boron carbide mechanically deformed at room temperature. On the contrary, in this study, we found Al-doping (as little as 0.6 at.% Al) dramatically altered the deformation behavior of boron carbide by activating dislocation movement in addition to amorphization and micro-cracking.

Explanation of dislocation movement

To uncover possible mechanisms of dislocation movement, we constructed the stable configurations of Al-doped boron carbide and applied shear deformation to the structures. We used DFT simulations to down select all the possible proposed Al-doped boron carbide structures (Fig. S8-S10 in SI). We found that only three configurations, namely (B₁₂) C-Al-C, (B₁₂) B-Al-C, and (B₁₁C) C-Al-C kinked chains, are plausible because of their negative formation energies, which are -1.28, -0.816, and -0.236 eV, respectively. (Formation energies for other stable structures are listed in Table S1 in SI). Because of its lowest formation energy, the experimentally observed Al-doped system likely contains mostly (B₁₂) C-Al-C kinked chain while other stable structures could coexist.

The most possible slip system of boron carbide structure is (001)_r/[001]_r according to a previous theoretical study [22]. We applied the ideal shear deformation on Al-doped structures to this slip system and compare the findings to both undoped ((B₁₁C) C-B-C) [47] and B-rich ((B₁₂) C-B-C) [48] boron carbide, as shown in Fig. 5A. The ideal shear strengths of (B₁₂) C-Al-C, (B₁₂) B-Al-C, and (B₁₁C) C-Al-C are 25.3, 24.9, and 28.7 GPa, respectively, which are lower than that of undoped (39.0 GPa) and B-rich boron carbide (45.8 GPa). A decrease in ideal shear strength suggests that it is easier to shear the Al-doped structures than undoped or B-rich boron carbide. Complementary indentation

analysis also measured a lower Vickers hardness of 28.1 ± 1.2 GPa for Al-doped boron carbide compared to 30.0 ± 0.7 GPa for undoped boron carbide.

To elucidate the atomistic details responsible for the dislocation movement, we investigated the deformation failure mechanism of the most probable Al-doped configuration, i.e. (B₁₂) C-Al-C kinked chain. Fig. 5B displays the intact (B₁₂) C-Al-C kinked chain structure under no strain. As shear strain increases to 0.136 (Fig. 5C), the bonds connecting two adjacent icosahedra from different shear planes are broken (black circle) creating an opening. The Al atom in the chain is pushed and kinked towards the opening (black arrow). The destruction of the inter-icosahedra bonds slightly decreases the shear stress, from 21.9 GPa to 21.2 GPa. As the strain increases to 0.263 (Fig. 5D), the Al atom is free from the original C-Al-C chain and enters the opening created by the missing inter-icosahedra bonds. The breaking of the C-Al-C chain significantly releases the shear stress from the maximum of 25.3 GPa to 2.1 GPa. After the structure relaxes, the further increase in strain is accompanied by an increase in shear stress to 11.4 GPa. At 0.364 strain (Fig. 5E), a new C-Al-C chain in the opening and inter-icosahedra bonds are restored, resulting in a plane of misplaced icosahedra. (Step by step atomistic details of the failure process can found in Fig. S11 in SI). This is in contrast with the ideal deformation behaviors of undoped and B-rich boron carbide, which show structural (icosahedra) failure leading to the formation of an amorphous shear band [22, 48]. We further investigated the ideal shear deformation of (B₁₂) B-Al-C; and it also demonstrates the ability to withstand large strain by icosahedral planar slip (Fig. S12). Oppositely, (B₁₁C) C-Al-C did not show structural recovery during the shear deformation suggesting B₁₁C is more susceptible to disintegration than B₁₂ icosahedra, as shown in Fig. S13. Considering that (B₁₁C) C-Al-C

is the least probable configuration of the three stable Al-doped structure, its deformation behavior does not undermine the overall deformation behavior (icosahedral slip) of Al-doped boron carbide. The deformation mechanism proposed by DFT simulation suggests the modification of the chain chemistry and structure allows boron carbide to enable dislocation slip through icosahedral glide without the destruction of the icosahedra.

The changes in the bond length, strength, and characteristics due to Al-doping could explain its ability to promote icosahedral slip. The DFT simulation suggests that the breaking of inter-icosahedra bond and the migration of the free Al atom are the main mechanisms leading to the icosahedral slip. Al-doped boron carbide has the longest inter-icosahedra B-B bond when compared to other boron carbide systems. (The bonding information regarding B-rich and Si-doped boron carbide are obtained from where else [41, 49, 50], shown in Fig. 6). The elongated inter-icosahedra bond weakens the bond strength and triggers the failure process as shown in Fig. 5B. This is in contrast with theoretical and experimental observations of undoped boron carbide where the intra-icosahedra bonds break first [22, 23]. Perhaps the biggest difference among the boron carbide systems is in the intra-chain bonding strength. Al-doped boron carbide has a significantly longer, thus weaker, chain bond when compared to other boron carbide systems. Since the migration of the free Al atom is necessary to promote icosahedral glide, it is reasonable to assume the weakening of the 3-atom chain due to Al doping contributes significantly to the dislocation movement. Lastly, the change in the bond characteristics in the chain structure also plays a role in facilitating the icosahedral slip. The replacement of B-C bonds with Al-C bonds in the chain structure increases the ionic bonding characteristic which can lower the Peierls stress (lattice fracture), making dislocation movement more favorable. Ceramic systems

posse ionic bonding, such as SiC, MgO, and Al₂O₃ [51, 52], have been reported to accommodate permanent deformation through dislocation slip. The combined effects of weakening in the inter-icosahedra and intra-chain bonds and decrease in the lattice friction due to Al-doping contribute to the dislocation movement in boron carbide.

Deformation mechanisms in boron carbide solid-solution systems

Using our experimental observation, computational results, and literature data, we constructed a schematic that depicts the energy dissipation mechanisms as a function of inter-icosahedral and intra-chain bonds (Fig. 6). The undoped boron carbide deforms through brittle fracture under normal conditions and experiences accelerated fragmentation through stress-induced amorphization when subjected to high energy deformations [15]. Recent reports found that B-enriched and Si-doped boron carbide can exhibit micro-cracking to dissipate strain energy, leading to a reduction in amorphization by 30-31% [16, 28]. In the current work, we discovered Al-doping mitigates amorphization by 44%, and the enhanced reduction is attributed to a combination of energy dissipation mechanism, notably dislocation movement and micro-cracking. This is in contrast with metal systems (e.g. Mg [53]) where the presence of solute atoms strengthens the materials by hindering the movement of dislocations. The effect of solute in ceramic systems is complicated and not well understood, and would require more research attention. In this specific case, the presence of solute atom (Al in boron carbide) promotes dislocation. Our results suggest doping in ceramics systems can promote dislocation activities and the design strategy can be applied to other brittle ceramic systems.

Conclusion

We discovered the modification of the chain structure of boron carbide through Al-doping promotes mobile dislocations that emanate from the crack tips during room temperature indentation. The mechanisms provided by the DFT simulations suggest large strain is released through icosahedral slip, which is facilitated by inter-icosahedral and chain bond breaking and Al atom migration. High-resolution TEM revealed Al-doped boron carbide exhibits localized, multi-directional micro-cracking compared to the long, near-parallel shear bands in the undoped boron carbide. The energy released during the icosahedral slip and micro-cracking consume strain energy and compete with the progression of amorphization. Complementary Raman analysis confirmed a 44% reduction in amorphization in the Al-doped boron carbide. These findings suggest the deformation behaviors of boron carbide can be controlled through structural modification via atomic doping. The insight gained from this work paves a roadway for engineering damage-tolerant brittle ceramics.

Acknowledgment

This work was supported by the Army Research Laboratory under Cooperative Agreement [W911NF-12-2-0022]; YD and QA were supported by the National Science Foundation (CMMI-1727428).

References

- [1] V. Domnich, Y. Gogotsi, M. Trenary, T. Tanaka, Nanoindentation and Raman spectroscopy studies of boron carbide single crystals, *Appl. Phys. Lett.* 81(20) (2002) 3783-3785. 10.1063/1.1521580.
- [2] D. He, Y. Zhao, L. Daemen, J. Qian, T. Shen, T. Zerda, Boron suboxide: As hard as cubic boron nitride, *Appl. Phys. Lett.* 81(4) (2002) 643-645.
- [3] Q. Huang, D. Yu, B. Xu, W. Hu, Y. Ma, Y. Wang, Z. Zhao, B. Wen, J. He, Z. Liu, Nanotwinned diamond with unprecedented hardness and stability, *Nature* 510(7504) (2014) 250-253.
- [4] Y. Tian, B. Xu, D. Yu, Y. Ma, Y. Wang, Y. Jiang, W. Hu, C. Tang, Y. Gao, K. Luo, Z. Zhao, L.M. Wang, B. Wen, J. He, Z. Liu, Ultrahard nanotwinned cubic boron nitride, *Nature* 493(7432) (2013) 385-8. 10.1038/nature11728.
- [5] V. Domnich, S. Reynaud, R.A. Haber, M. Chhowalla, Boron Carbide: Structure, Properties, and Stability under Stress, *J. Am. Ceram. Soc.* 94(11) (2011) 3605-3628. 10.1111/j.1551-2916.2011.04865.x.
- [6] F. Thevenot, Boron carbide—a comprehensive review, *J. Eur. Ceram. Soc.* 6(4) (1990) 205-225. 10.1016/0955-2219(90)90048-K.
- [7] A.U. Khan, V. Domnich, R.A. Haber, Boron carbide-based armors: Problems and possible solutions, *Am. Ceram. Soc. Bull.* 96(6) (2017) 30-35.
- [8] A.K. Suri, C. Subramanian, J.K. Sonber, T.S.R.C. Murthy, Synthesis and consolidation of boron carbide: a review, *International Materials Reviews* 55(1) (2010) 4-40. 10.1179/095066009x12506721665211.
- [9] J.-L. Innocent, D. Portehault, G. Gouget, S. Maruyama, I. Ohkubo, T. Mori, Thermoelectric properties of boron carbide/HfB₂ composites, *Materials for Renewable and Sustainable Energy* 6(2) (2017) 6.
- [10] T. Maruyama, S. Onose, Fabrication and thermal conductivity of boron carbide/copper cermet, *Journal of nuclear science and technology* 36(4) (1999) 380-385.
- [11] R. Lazzari, N. Vast, J. Besson, S. Baroni, A. Dal Corso, Atomic structure and vibrational properties of icosahedral B₄C boron carbide, *Phys. Rev. Lett.* 83(16) (1999) 3230. 10.1016/S0927-0256(00)00009-4.
- [12] H. Hubert, B. Devouard, L.A. Garvie, M. O'Keeffe, P.R. Buseck, W.T. Petuskey, P.F. McMillan, Icosahedral packing of B₁₂ icosahedra in boron suboxide (B₆O), *Nature* 391(6665) (1998) 376-378.

- [13] H. Clark, J. Hoard, The crystal structure of boron carbide, *J. Am. Chem. Soc.* 65(11) (1943) 2115-2119. 10.1021/ja01251a026.
- [14] D. Ge, V. Domnich, T. Juliano, E.A. Stach, Y. Gogotsi, Structural damage in boron carbide under contact loading, *Acta Mater.* 52(13) (2004) 3921-3927. 10.1016/j.actamat.2004.05.007.
- [15] M. Chen, J.W. McCauley, K.J. Hemker, Shock-induced localized amorphization in boron carbide, *Science* 299(5612) (2003) 1563-6. 10.1126/science.1080819.
- [16] A. Chauhan, M.C. Schaefer, R.A. Haber, K.J. Hemker, Observed Mitigation of Local Amorphization in Boron-Rich Boron Carbide, Available at SSRN 3414007 (2019).
- [17] S. Zhao, B. Kad, B.A. Remington, J.C. LaSalvia, C.E. Wehrenberg, K.D. Behler, M.A. Meyers, Directional amorphization of boron carbide subjected to laser shock compression, *Pro. Nat. Acad. Sci.* 113(43) (2016) 12088-12093.
- [18] S. Xiang, L. Ma, B. Yang, Y. Dieudonne, G.M. Pharr, J. Lu, D. Yadav, C. Hwang, J.C. LaSalvia, R.A. Haber, Tuning the deformation mechanisms of boron carbide via silicon doping, *Sci. Adv.* 5(10) (2019) eaay0352. <https://doi.org/10.1126/sciadv.aay0352>.
- [19] D.E. Grady, Shock-Wave Strength Properties of Boron-Carbide and Silicon-Carbide, *J. Phys. IV* 4(C8) (1994) 385-391. 10.1051/jp4:1994859.
- [20] X.Q. Yan, Z. Tang, L. Zhang, J.J. Guo, C.Q. Jin, Y. Zhang, T. Goto, J.W. McCauley, M.W. Chen, Depressurization amorphization of single-crystal boron carbide, *Phys. Rev. Lett.* 102(7) (2009) 075505. 10.1103/PhysRevLett.102.075505.
- [21] Q. An, W.A. Goddard III, Atomistic origin of brittle failure of boron carbide from large-scale reactive dynamics simulations: suggestions toward improved ductility, *Phys. Rev. Lett.* 115(10) (2015) 105501. 10.1103/PhysRevLett.115.105501.
- [22] Q. An, W.A. Goddard, 3rd, T. Cheng, Atomistic explanation of shear-induced amorphous band formation in boron carbide, *Phys. Rev. Lett.* 113(9) (2014) 095501. 10.1103/PhysRevLett.113.095501.
- [23] K.Y. Xie, Q. An, T. Sato, A.J. Breen, S.P. Ringer, W.A. Goddard, 3rd, J.M. Cairney, K.J. Hemker, Breaking the icosahedra in boron carbide, *Proc Natl Acad Sci U S A* 113(43) (2016) 12012-12016. 10.1073/pnas.1607980113.
- [24] C. Hwang, S. DiPietro, K.Y. Xie, Q. Yang, A.M. Celik, A.U. Khan, V. Domnich, S. Walck, K.J. Hemker, R.A. Haber, Small amount TiB₂ addition into B₄C through sputter deposition and hot pressing, *J. Am. Ceram. Soc.* (2019) 4421-4426. 10.1111/jace.16457.
- [25] C. Hwang, Q. Yang, S. Xiang, V. Domnich, A.U. Khan, K.Y. Xie, K.J. Hemker, R.A. Haber, Fabrication of dense B₄C-preceramic polymer derived SiC composite, *J. Eur. Ceram. Soc.* 39(4) (2019) 718-725. 10.1016/j.jeurceramsoc.2018.12.029.

- [26] K. Sairam, J. Sonber, T.C. Murthy, C. Subramanian, R. Hubli, A. Suri, Development of B₄C–HfB₂ composites by reaction hot pressing, *Int. J. Refract. Met. H.* 35 (2012) 32-40.
- [27] Q. Yang, C. Hwang, A.U. Khan, V. Domnich, E.D. Gronske, R.A. Haber, Anisotropy and residual stress in B₄C–ZrB₂ eutectic, *Mater. Charact.* (2019) 109797. 10.1016/j.jeurceramsoc.2019.08.024.
- [28] Q. Yang, C. Hwang, C.J. Marvel, A. Chauhan, V. Domnich, A.U. Khan, J.C. LaSalvia, M.P. Harmer, K.J. Hemker, R.A. Haber, Fabrication and characterization of arc melted Si/B co-doped boron carbide, *J. Eur. Ceram. Soc.* 39(16) (2019) 5156-5166. 10.1016/j.jeurceramsoc.2019.08.024.
- [29] Q. Yang, A.M. Çelik, J. Du, J.C. LaSalvia, C. Hwang, R.A. Haber, Advancing the mechanical properties of Si/B co-doped boron carbide through TiB₂ reinforcement, *Materials Letters* (2020) 127480.
- [30] M. Watanabe, D.B. Williams, The quantitative analysis of thin specimens: a review of progress from the Cliff-Lorimer to the new zeta-factor methods, *J Microsc* 221(Pt 2) (2006) 89-109. 10.1111/j.1365-2818.2006.01549.x.
- [31] C. Marvel, A. Etzold, V. Domnich, K. Behler, J. LaSalvia, R. Haber, M. Watanabe, M. Harmer, ζ -Factor Development and Quantification of a Boron Carbide and Silicon Hexaboride Diffusion Couple, *Microscopy and Microanalysis* 24(S1) (2018) 742-743.
- [32] C. Marvel, K. Behler, J. LaSalvia, V. Domnich, R. Haber, M. Watanabe, M. Harmer, Extending ζ -factor microanalysis to boron-rich ceramics: Quantification of bulk stoichiometry and grain boundary composition, *Ultramicroscopy* (2019). 10.1016/j.ultramic.2019.04.008.
- [33] A. Chauhan, X. Sun, K.T. Ramesh, K.J. Hemker, Dynamic failure mechanisms of granular boron carbide under multi-axial high-strain-rate loading, *Scripta Materialia* 173 (2019) 125-128.
- [34] V. Domnich, Y. Gogotsi, M. Trenary, Identification of pressure-induced phase transformations using nanoindentation, *MRS Online Proceedings Library Archive* 649 (2000).
- [35] G. Subhash, D. Ghosh, J. Blaber, J.Q. Zheng, V. Halls, K. Masters, Characterization of the 3-D amorphized zone beneath a Vickers indentation in boron carbide using Raman spectroscopy, *Acta Mater.* 61(10) (2013) 3888-3896. 10.1016/j.actamat.2013.03.028.
- [36] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational materials science* 6(1) (1996) 15-50.
- [37] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54(16) (1996) 11169.

- [38] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B* 47(1) (1993) 558.
- [39] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59(3) (1999) 1758.
- [40] D. Roundy, C. Krenn, M.L. Cohen, J. Morris Jr, Ideal shear strengths of fcc aluminum and copper, *Phys. Rev. Lett.* 82(13) (1999) 2713.
- [41] B. Morosin, A. Mullendore, D. Emin, G. Slack, Rhombohedral crystal structure of compounds containing boron-rich icosahedra, *AIP Conf. Proc.*, AIP, 1986, pp. 70-86.
- [42] S. Xiang, Q. Yang, H.M. Lien, K. Shial, E. Grounske, R. Haber, K.Y. Xie, The effect of boron and aluminum additions on the microstructure of arc-melted boron carbide, *J. Am. Ceram. Soc.*
- [43] D.R. Tallant, T.L. Aselage, A.N. Campbell, D. Emin, Boron carbide structure by Raman spectroscopy, *Phys Rev B Condens Matter* 40(8) (1989) 5649-5656. 10.1103/PhysRevB.40.5649.
- [44] C. Cheng, K.M. Reddy, A. Hirata, T. Fujita, M.E. Chen, Structure and mechanical properties of boron-rich boron carbides, *J. Eur. Ceram. Soc.* 37(15) (2017) 4514-4523. 10.1016/j.jeurceramsoc.2017.06.017.
- [45] H. Werheit, V. Filipov, U. Kuhlmann, U. Schwarz, M. Armbruster, A. Leithe-Jasper, T. Tanaka, I. Higashi, T. Lundstrom, V.N. Gurin, M.M. Korsukova, Raman effect in icosahedral boron-rich solids, *Sci Technol Adv Mater* 11(2) (2010) 023001. 10.1088/1468-6996/11/2/023001.
- [46] K.Y. Xie, V. Domnich, L. Farbaniec, B. Chen, K. Kuwelkar, L.N. Ma, G.W. McCauley, R.A. Haber, K.T. Ramesh, M.W. Chen, K.J. Hemker, Microstructural characterization of boron-rich boron carbide, *Acta Mater.* 136 (2017) 202-214. 10.1016/j.actamat.2017.06.063.
- [47] Q. An, Prediction of superstrong τ -boron carbide phase from quantum mechanics, *Phys. Rev. B* 95(10) (2017) 100101.
- [48] Q. An, W.A. Goddard, Nanotwins soften boron-rich boron carbide (B₁₃C₂), *Appl. Phys. Lett.* 110(11) (2017) 111902. 10.1063/1.4978644.
- [49] B. Morosin, G.H. Kwei, A.C. Lawson, T.L. Aselage, D. Emin, Neutron Powder Diffraction Refinement of Boron Carbides - Nature of Intericosahedral Chains, *Journal of Alloys and Compounds* 226(1-2) (1995) 121-125. Doi 10.1016/0925-8388(95)01585-X.
- [50] G.H. Kwei, B. Morosin, Structures of the boron-rich boron carbides from neutron powder diffraction: Implications for the nature of the inter-icosahedral chains, *J. Phys. Chem.* 100(19) (1996) 8031-8039. 10.1021/jp953235j.

- [51] T. Page, L. Riester, S. Hainsworth, The plasticity response of 6H-SiC and related isostructural materials to nanoindentation: slip vs densification, MRS Online Proceedings Library Archive 522 (1998).
- [52] T.F. Page, W.C. Oliver, C.J. McHargue, The deformation behavior of ceramic crystals subjected to very low load (nano) indentations, J. Mater. Res. 7(2) (1992) 450-473.
- [53] N. Bertin, C. Tomé, I. Beyerlein, M. Barnett, L. Capolungo, On the strength of dislocation interactions and their effect on latent hardening in pure magnesium, International Journal of Plasticity 62 (2014) 72-92.

Figures

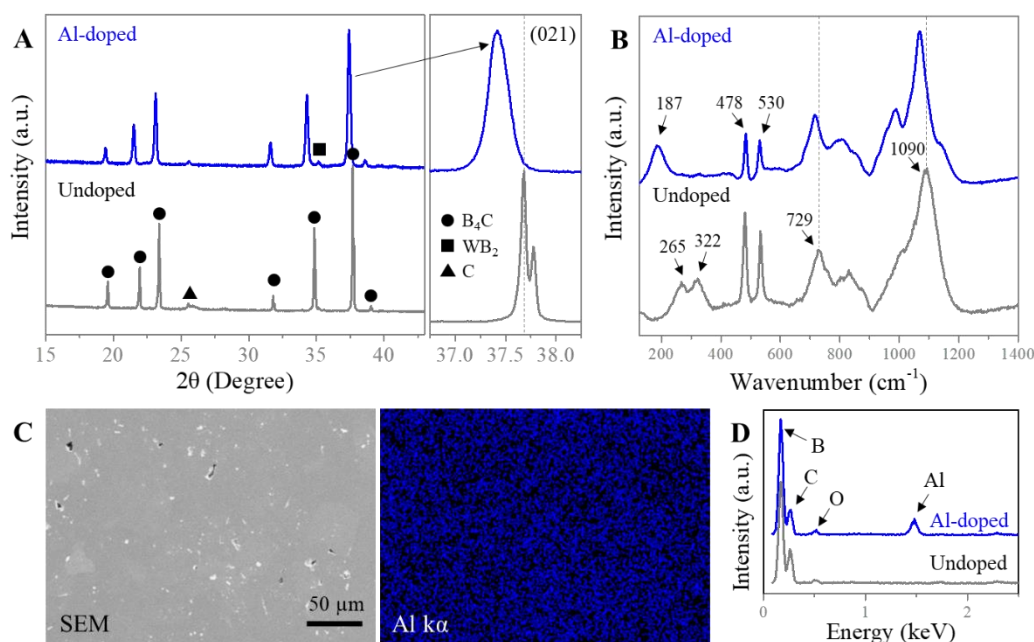


Fig. 1. (A) X-ray diffraction patterns of Al-doped and undoped boron carbide. The enlarge region from 2θ 36.5–38.5 depicts the (021) peak position shift due to Al-doping. (B) Raman spectra of Al-doped and undoped boron carbide. A reduction in the 478 cm^{-1} peak intensity is associated with the modification of the 3-atom chain due to Al-doping. The new peak at 187 cm^{-1} is related to an increase in the lattice defects as a result of chain modification. (C) Depicts scanning electron micrograph and distribution of Al $K\alpha$ acquired using Energy-dispersive spectroscopy (EDS). (D) STEM-EDS spectra show the Al peak in the Al-doped sample.

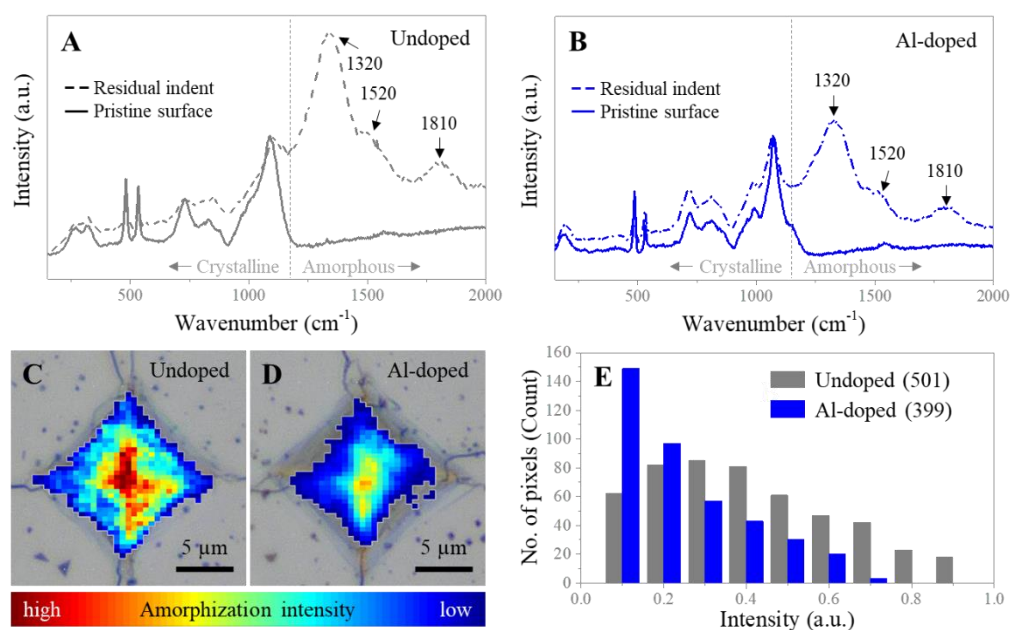


Fig. 2. Raman spectra acquired from the pristine and indented boron carbide of (A) undoped and (B) Al-doped boron carbide. Amorphization intensity heat map of (C) undoped and (D) Al-doped boron carbide. The integrated pixel intensity shows a reduction of 44% in the total amorphization intensity due to Al-doping. Each pixel is $0.5 \times 0.5 \mu\text{m}$ and each map is $20 \times 20 \mu\text{m}$. The heat map was constructed from 5 independent results. (E) Histogram of pixels by intensity.

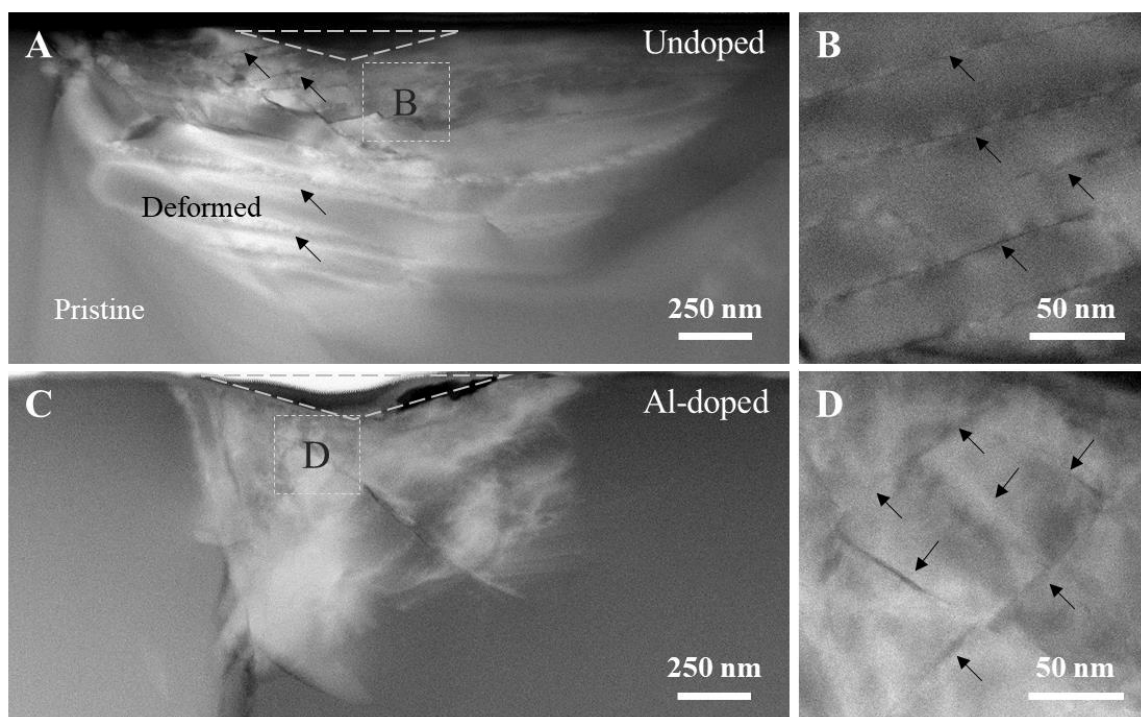


Fig. 3. Low angle annular dark-field scanning transmission electron microscopy (LAADF-STEM) images of deformation zones under Berkovich indentation (marked by the dashed triangle) of (A) Undoped and (C) Al-doped boron carbide. Long, near-parallel shear faults are visible in the undoped boron carbide. High-resolution images of (B) Undoped boron carbide depicts long and parallel shear faults whereas (D) Al-doped boron carbide exhibits diffused micro-cracks.

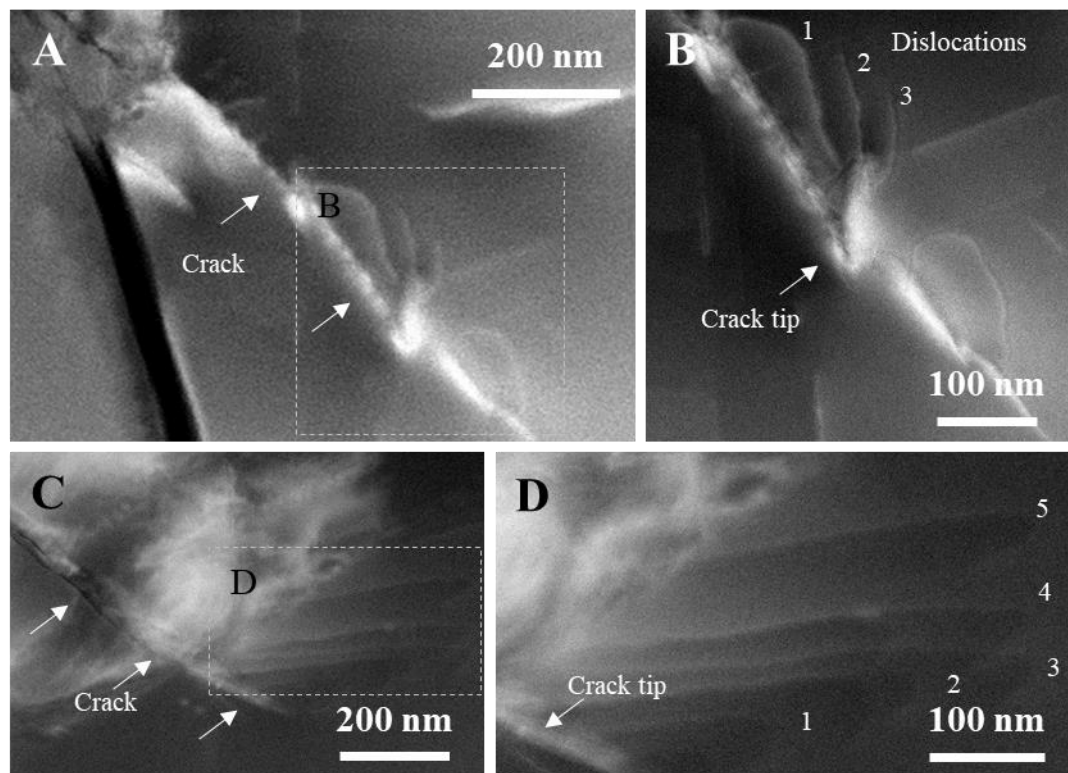


Fig. 4. (A) and (C) illustrate low angle annular dark-field scanning transmission electron microscopy (LAADF-STEM) images of dislocations emanating from crack tips in two different Al-doped boron carbide specimens. The enlarged images are shown in (B) and (D). Cracks are labeled with arrows and dislocation are numbered.

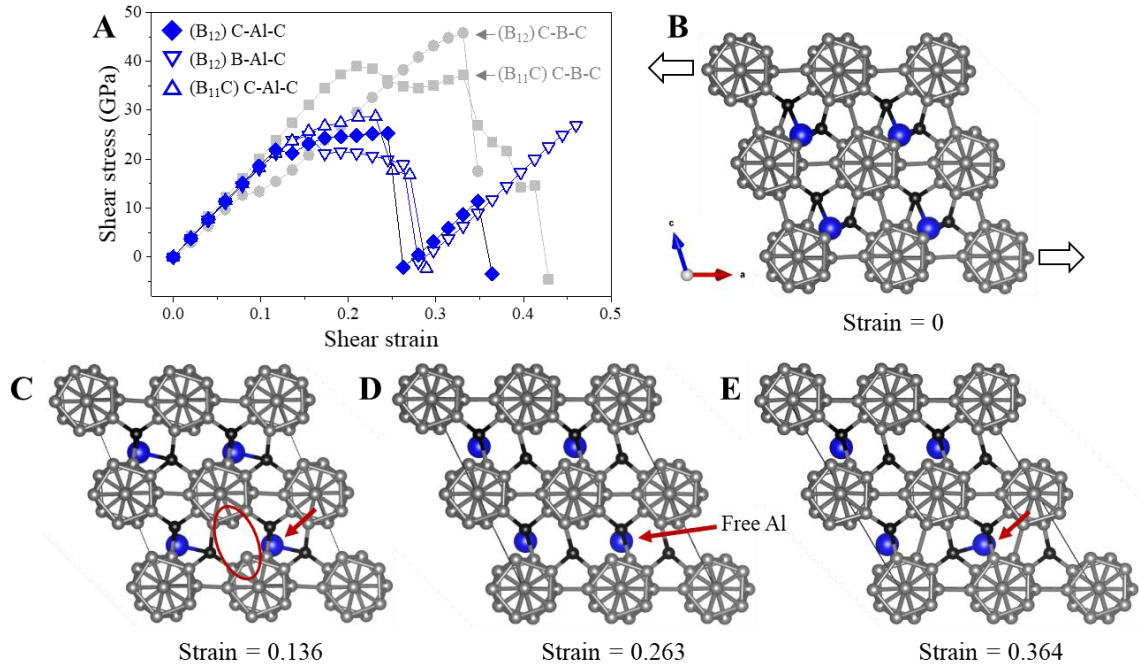


Fig. 5. (A) The shear-stress and shear-strength relation of the stable Al-doped boron carbide structures, (B₁₂) C-Al-C, and (B₁₂) B-Al-C, and (B₁₁C) C-Al-C, sheared in the easiest slip system (001)_r/[001]_r. Deformation mechanism of the most stable Al-doped structure, B₁₂(C-Al-C), shear along easiest slip system (001)_r/[001]_r is illustrated in (B)-(E). (B) The B₁₂ (C-Al-C) structure at 0 strain. (C) At 0.136 strain, the inter-icosahedra bonds break between the shear planes creating an opening. The Al in the C-Al-C kicked chain kinked towards the opening (black arrow). (D) At 0.263 strain, the Al atom is broken free and enters the opening. (E) At 0.364 strain, the Al atom enters the opening and forms a new C-Al-C. New inter-icosahedral bonds are formed and the overall structure is restored resulting in displaced icosahedra.

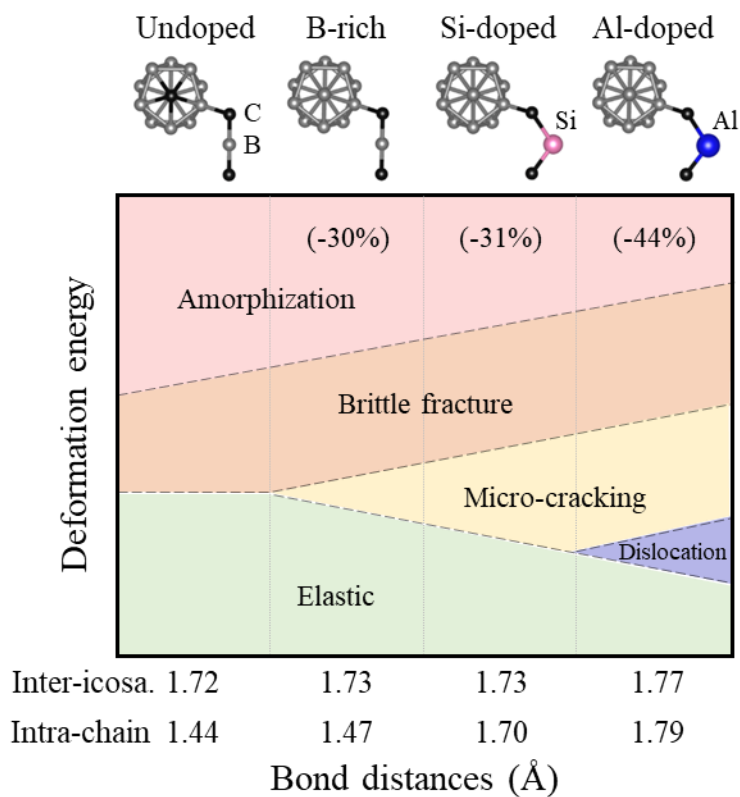


Fig. 6. Schematic showing the domains of deformation mechanisms of various boron carbide solid-solution systems. Micro-cracking has been reported to dissipate strain energy in B-rich and Si-doped boron carbide, leading to a 30-31% reduction in amorphization. Al doping activates dislocation movement and micro-cracking to dissipate deformation energy, which leads to further suppression of amorphization (44%).

Supporting information

Enabling dislocation mediated plasticity in boron carbide (B_4C) via Al-doping

This document contains:

Figures S1-S13

Table S1

Contents:

Fig. S1: SEM and EDS map	41
Fig. S2: ζ-factor analysis.....	42
Fig. S3: Corresponding HADDF and BF images of Fig. 3A and 3C	43
Fig. S4: Corresponding HAADF and BF images of Fig. 3B and 3D	44
Fig. S5: Additional supporting HRTEM images of deformation behaviors.....	45
Fig. S6: Amorphous shear bands in undoped boron carbide	46
Fig. S8-S10: Examination of possible Al-doped structure	48
Table S1: Formation energy and chemistry of all stable Al-doped boron carbide structures	51
Fig. S11: Detailed deformation and failure process of (B_{12}) C-Al-C	52
Fig. S12: Detailed deformation and failure process of (B_{12}) B-Al-C	54
Fig. S13: Detailed deformation and failure process of $(B_{11}C)$ C-Al-C	56
References	58

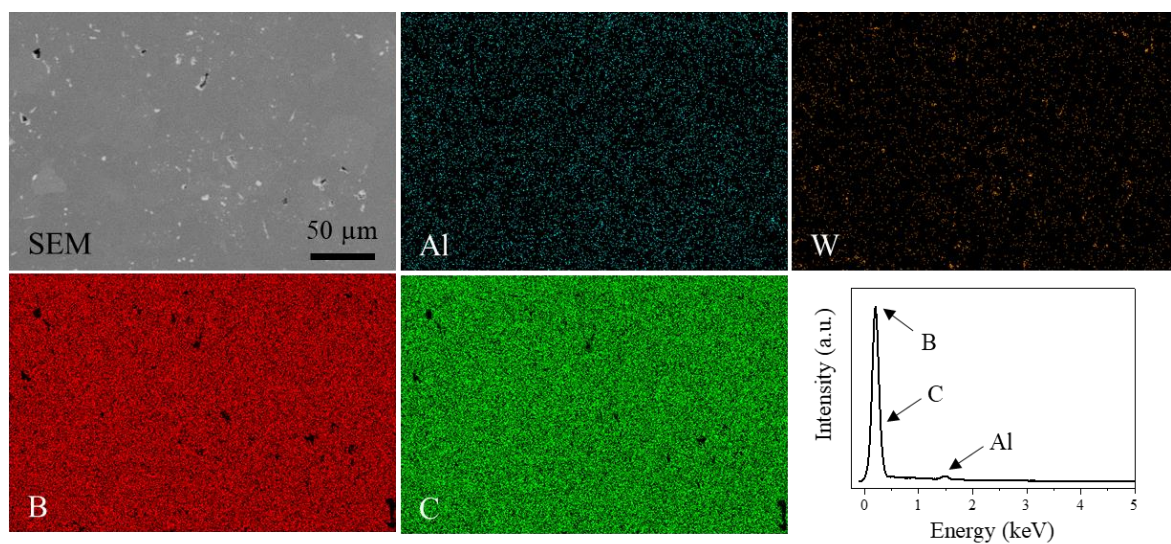
Fig. S1: SEM and EDS map

Fig. S1. Scanning electron microscopy (SEM) image and the associated Energy-dispersive spectroscopy (EDS) maps and EDS spectrum of Al-doped boron carbide. The major chemical signatures are from B, C, and Al. Traces of W is also identified.

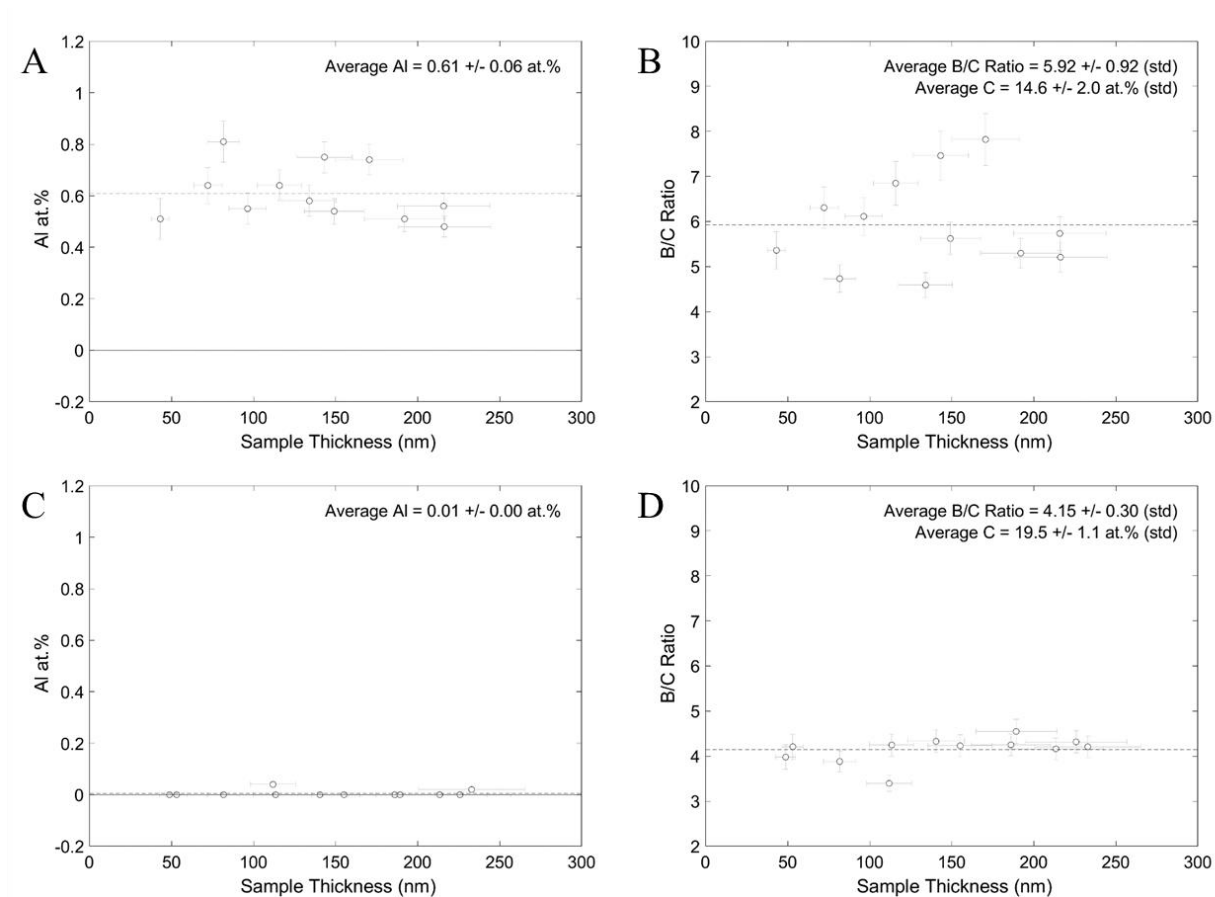
Fig. S2: ζ -factor analysis

Fig. S2. Al, B, and C contents vs TEM sample thickness of (A and B) Al-doped and (C and D) undoped boron carbide.

Fig. S3: Corresponding HADDF and BF images of Fig. 3A and 3C

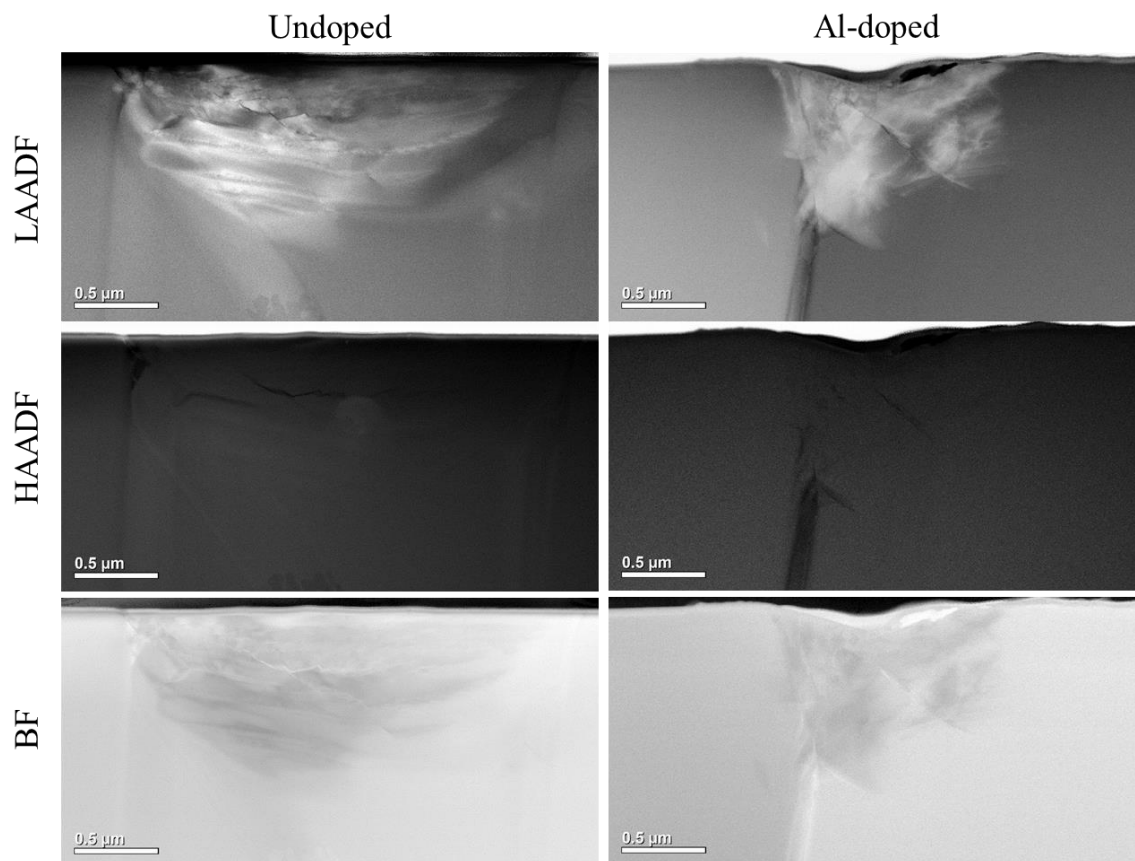


Fig. S3. The corresponding low angle annular dark field (LAADF), high angle annular dark-field (HAADF), and bright-field (BF) images to Fig. 3A and 3C. The images depict the deformation zone beneath the Berkovich indentation in Al-doped and undoped boron carbide.

Fig. S4: Corresponding HAADF and BF images of Fig. 3B and 3D

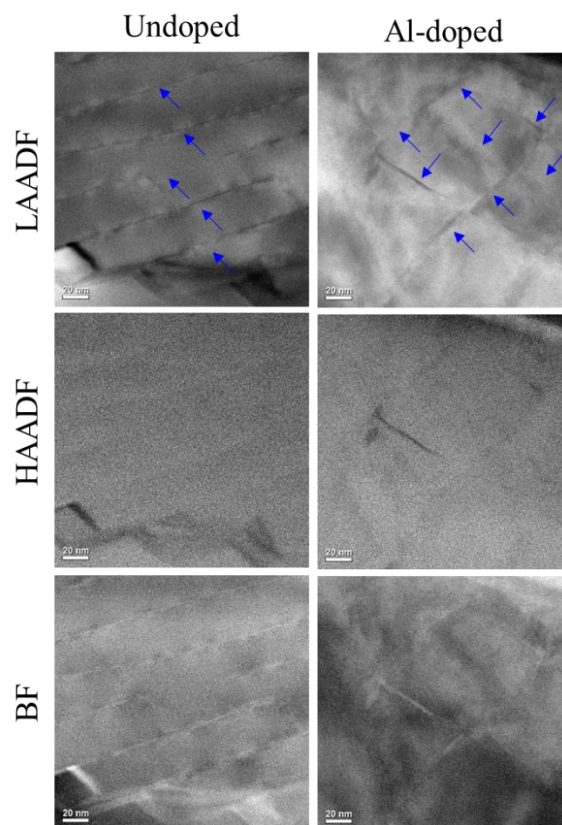


Fig. S4. The corresponding low angle annular dark field (LAADF), high angle annular dark-field (HAADF), and bright-field (BF) images to Fig. 3B and 3D. The images depict the differences in detail deformation behavior between Al-doped and undoped boron carbide.

Fig. S5: Additional supporting HRTEM images of deformation behaviors

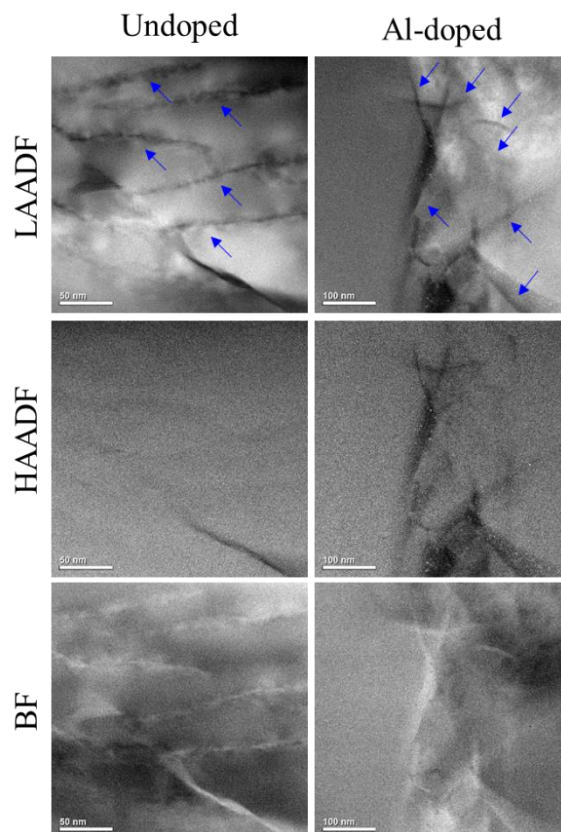


Fig. S5. Additional low angle annular dark-field (LAADF), high angle annular dark-field (HAADF), and bright-field (BF) images depicting the differences deformation behavior between Al-doped and undoped boron carbide. Short and diffused fracture behaviors are visible in the Al-doped boron carbide whereas long and distinct shear bands are found in the undoped boron carbide.

Fig. S6: Amorphous shear bands in undoped boron carbide

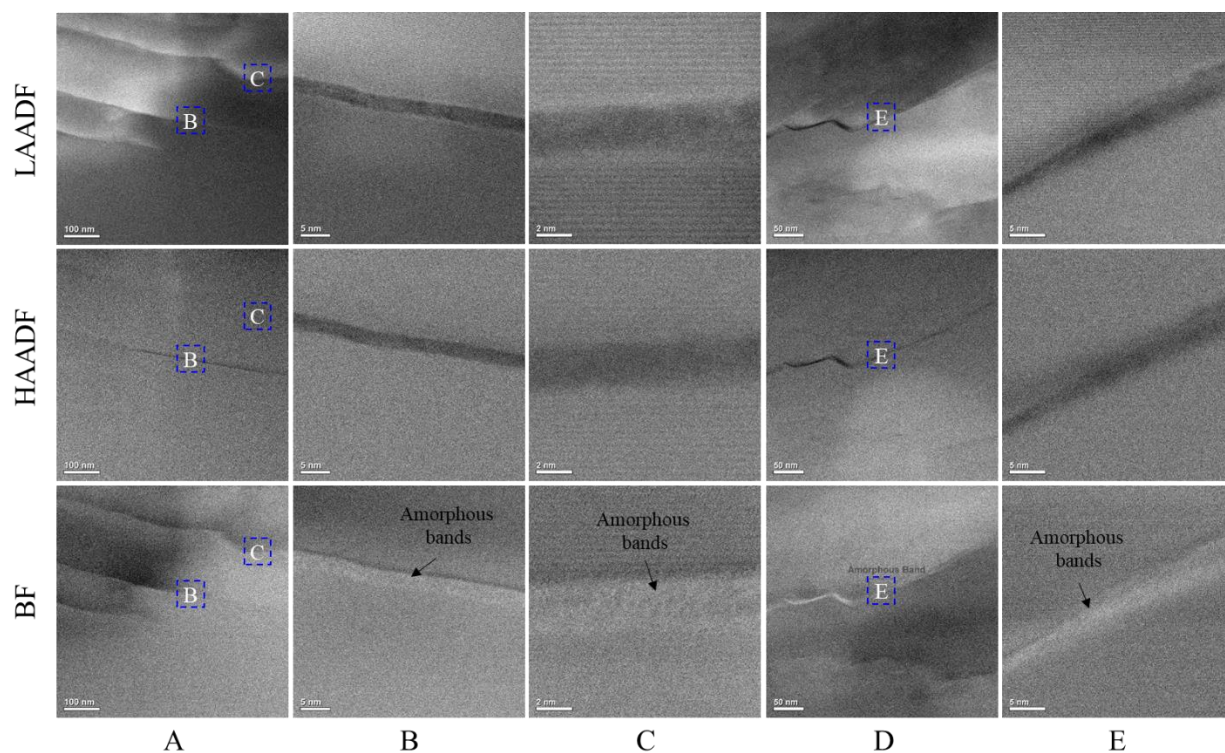


Fig. S6. Numerous amorphous bands were identified in the shear bands in undoped boron carbide. Low angle annular dark-field (LAADF), high angle annular dark-field (HAADF), and bright-field (BF) images depict the shear bands and amorphous bands containing inside the shear bands.

Fig. S7. Corresponding HAADF and BF images of Fig. 4

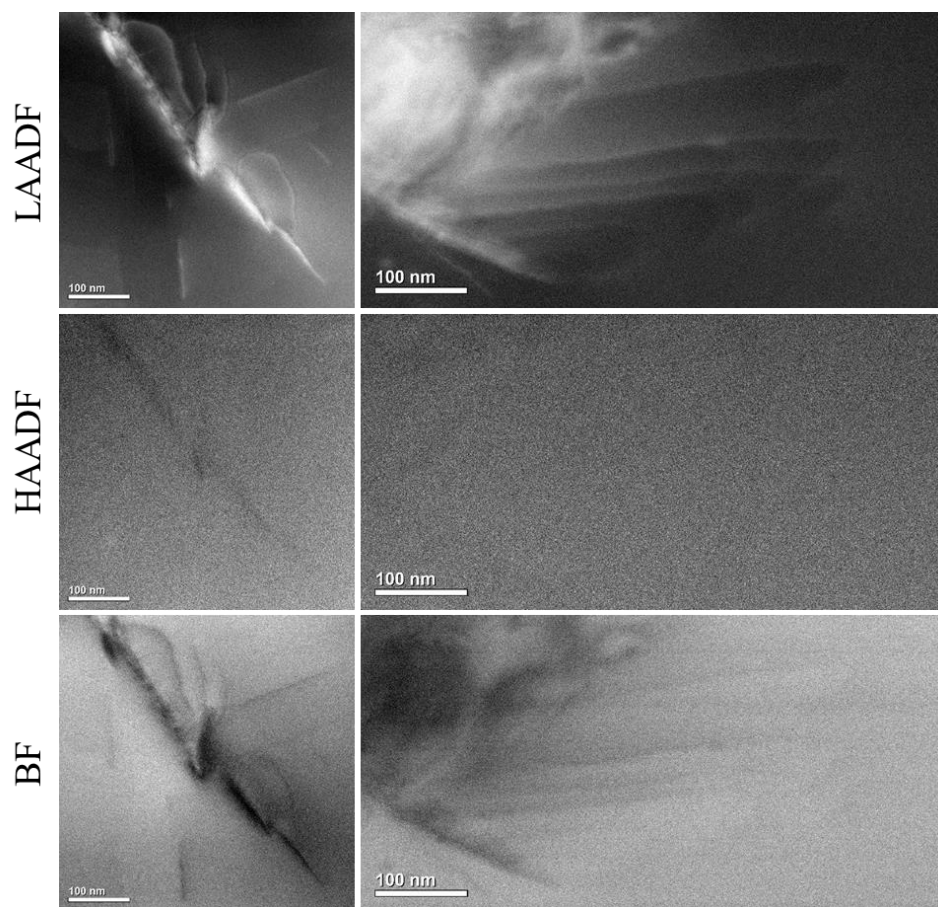


Fig. S7. The corresponding low angle annular dark-field (LAADF), high angle annular dark-field (HAADF), and bright-field (BF) images to Fig. 4B and 4D. The images depict dislocations unclogging from a crack for two difference TEM samples.

Fig. S8-S10: Examination of possible Al-doped structure

The possibility of Al atoms in boron carbide is debated. Three possible sites have been proposed, namely C-Al-C linear [1], X-Al-X kinked [2], or X-Al₂-X double Al chain [3], where X=C or B. The most stable boron carbide consists of B₁₂ or B₁₁C icosahedra [4], which is also true for Al-doped boron carbide [2]. Thus, we concluded that there are a total of 13 combinations of possible Al-doped boron carbide structures.

The (B₁₂) C-Al-C linear chain is shown in Fig. S8. After structural relaxation, the center Al atom pops out to form a C-Al-C kinked chain with an angle of 124.4°. The kinked chain configuration is similar to what is proposed by Neidhard [2] thus we exclude the possibility of having linear chains.

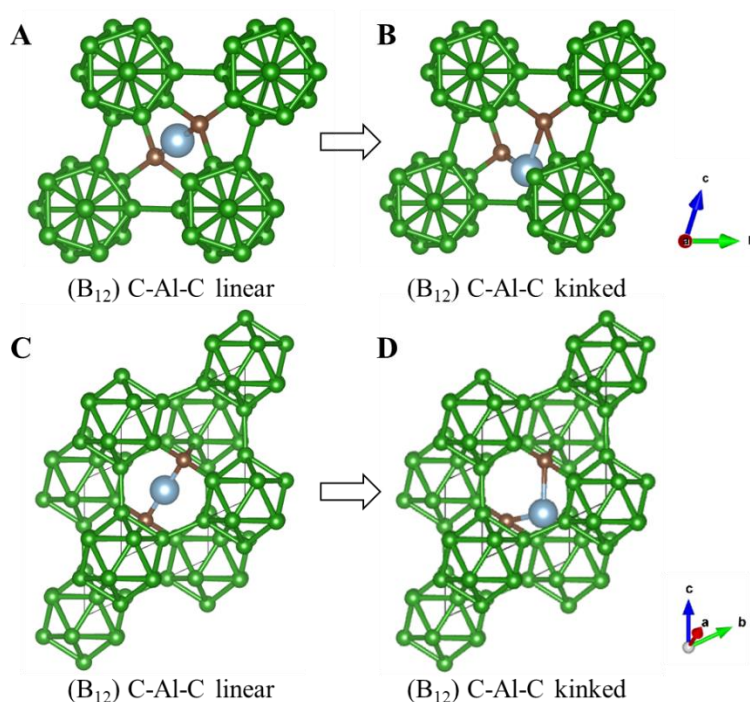


Fig. S8. (A) and (C) depict the Al-doped boron carbide structure proposed by Lipp [1] viewed in different directions. The structure composes B₁₂ icosahedra and a linear C-Al-C

chain. After structure relaxation, the center Al atom pops out and forms a kinked C-Al-C chain.

There are a total of 6 combinations of B_{12} or $B_{11}C$ kinked chain structures, as shown in Fig. S9. We excluded the (B_{12}) B-Al-B because the structure does not contain a C atom, thus it cannot be a boron carbide structure. $(B_{11}C)$ B-Al-B is also excluded from further investigations as the chain must contain a C atom [2].

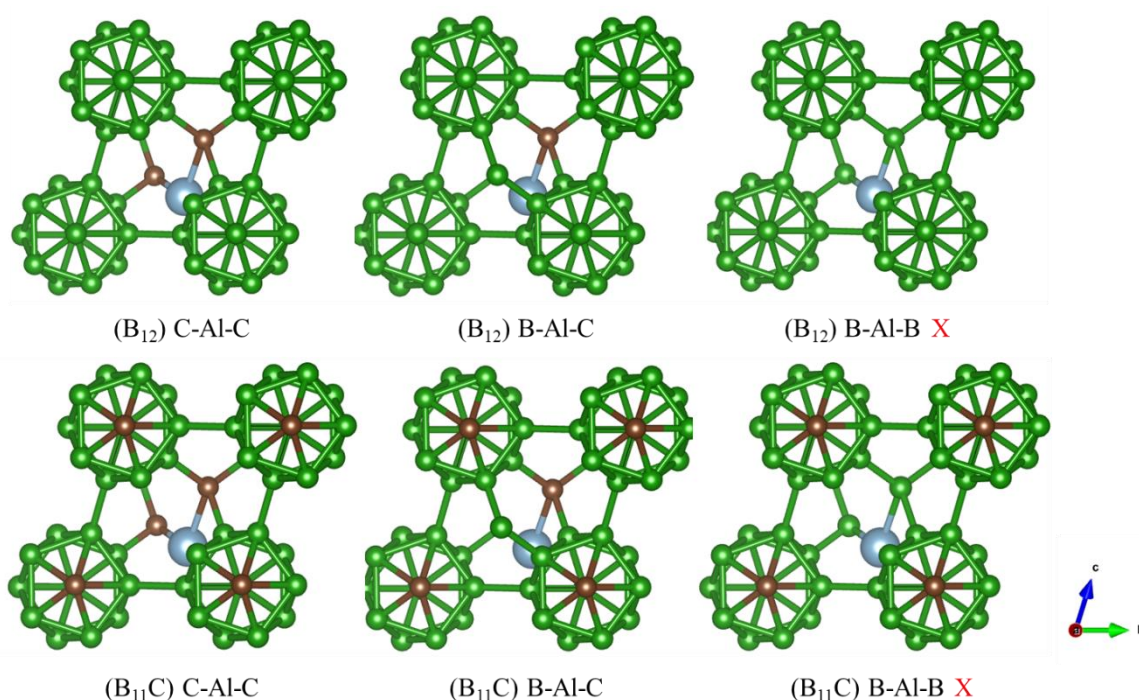


Fig. S9. The 6 configurations of Al-doped boron carbide with a kinked chain. (B_{12}) B-Al-B is excluded from simulation because the structure does not contain C. $(B_{11}C)$ B-Al-B configuration is also excluded as the chain must contain a C atom.

Six total combinations of B_{12} or $B_{11}C$ double Al chain structures are interrogated (Fig. S10). The (B_{12}) B-Al₂-B and $(B_{11}C)$ B-Al₂-B are eliminated from further consideration following the same logic as for kinked chain configuration. We found icosahedra in $(B_{11}C)$

C-Al₂-C and (B₁₁C) B-Al₂-C disintegrated after DFT relaxation, suggesting B₁₁C is less stable to Al-doping compared to B₁₂.

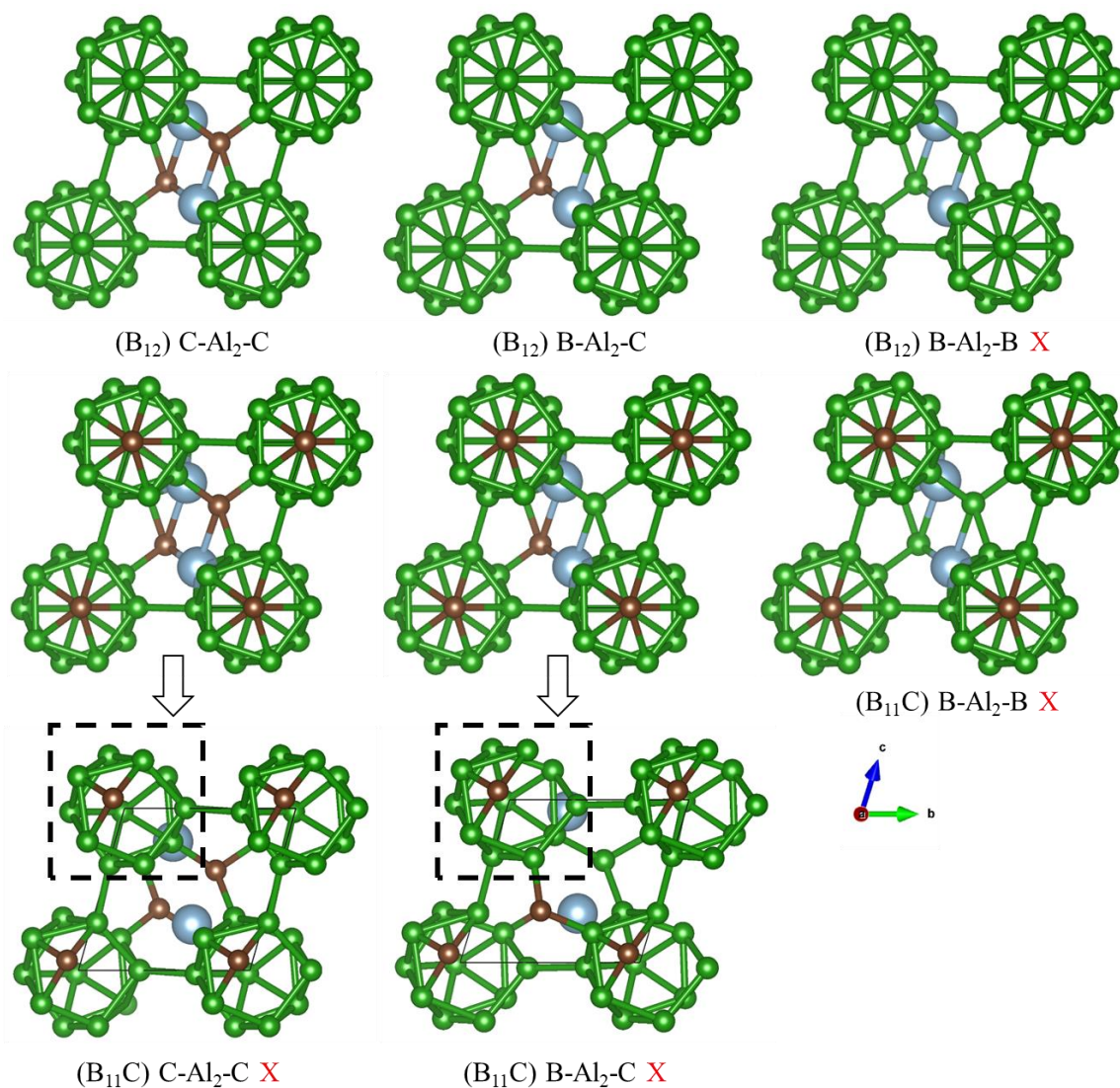


Fig. S10. The 6 configurations of Al-doped boron carbide with double Al chain, as suggested by Schmechel [3] (B₁₂) B-Al₂-B is excluded from simulation because the structure does not contain C. (B₁₁C) B-Al₂-B configuration is also excluded because the chain must contain C, as suggested by Neidhard [2]. The remaining (B₁₁C) icosahedra deconstructed after relaxation.

Table S1: Formation energy and chemistry of all stable Al-doped boron carbide structures

The formation energy of the 6 remaining configurations was computed using the equation:

$$\text{Formation Energy} = (E_{\text{mix}} - E_{\text{Al}} - E_{\text{B}_{12}} - E_{\text{graphite}})$$

where E_{mix} , E_{Al} , $E_{\text{B}_{12}}$, and E_{graphite} are the electronic energies of the doped structure, FCC Al, alpha B_{12} , and graphite crystal. Although $\beta\text{-B}_{106}$ is more stable, the alpha- B_{12} is used since its crystal structure is similar to B_4C . The formation energies for the six structures, listed in Table S1 indicated that three configurations, $(\text{B}_{12}) \text{C-Al-C}$, $(\text{B}_{12}) \text{B-Al-C}$, and $(\text{B}_{11}\text{C}) \text{C-Al-C}$, are possibly present because of negative formation energy. Fig. S9. (a-c) displays the three optimized structures from DFT.

Table S1. Chemical composition and formation energy for stable Al-doped boron carbide configuration

Configuration	Stoichiometry	C at. %	Energy(eV)	Formation Energy (eV)
$(\text{B}_{12}) \text{C-Al-C}$	B_6C	14.29	-103.9	-1.276
$(\text{B}_{12}) \text{C-Al-B}$	B_{13}C	7.14	-100.9	-0.816
$(\text{B}_{11}\text{C}) \text{C-Al-C}$	$\text{B}_{3.67}\text{C}$	21.41	-105.4	-0.236
$(\text{B}_{11}\text{C}) \text{B-Al-C}$	B_6C	14.29	-101.4	1.263
$(\text{B}_{12}) \text{C-Al}_2\text{-C}$	B_6C	14.29	-104.0	1.391
$(\text{B}_{12}) \text{B-Al}_2\text{-C}$	B_{13}C	7.14	-102.5	1.374

Fig. S11: Detailed deformation and failure process of (B₁₂) C-Al-C

The most plausible slip system of pure boron carbide is $(001)_r/\langle 001 \rangle_r$ according to a previous theoretical study [5]. Shear deformation was first applied to the most stable Al-doped structure, (B₁₂) C-Al-C in the same slip system. The ideal shear strength of (B₁₂) C-Al-C is 25.27 GPa and the structure appears to recover after the initial failure (Fig. S9D). We investigated the deformation failure mechanism of (B₁₂) C-Al-C shown in Fig. S11. Fig. S11A displays an intact structure. As shear strain increases to 0.136, the B-B bonds connecting two adjacent icosahedra are stretched from 1.73 Å to 2.12 Å and breaks (S11B), leading to a slight decrease of shear stress from 21.90 GPa to 21.22 GPa. When the shear strain continuously increases to 0.245, the Al4-C7 chain bond is stretched from the original 1.89 Å to 2.10 Å without breaking, as shown in S11C. However, this Al4-C7 bond is drastically stretched to 2.67 Å and breaks as the shear strain further increases to 0.263 (S11D). This Al-C bond breaking also significantly releases the shear stress from the maximum of 25.27 GPa to 2.07 GPa. It is worth noting that the icosahedra are not deconstructed in the stress release (S11D). After the shear stress relaxation, we further increase the shear strain up to 0.348 leads to an increase in shear stress. At 0.348 strain, the icosahedral-chain C8-B45 and C7-B39 bonds are stretched from 1.60 Å and 1.55 Å to 1.73 Å and 1.76 Å, respectively. However, they are not broken at this strain (S11E). When shear strain increases to 0.364, these two bonds are broken C8-B45 and C7-B39 bonds are broken (S11F), releasing the shear stress from 11.42 GPa to -3.43 GPa. Meanwhile, the new C7-B4, B45-B39 and C8-B10 bonds form, leading to half of the structure transforms back to its original structure. Again, no icosahedra are deconstructed at this shear strain, suggesting that the structure is not failed.

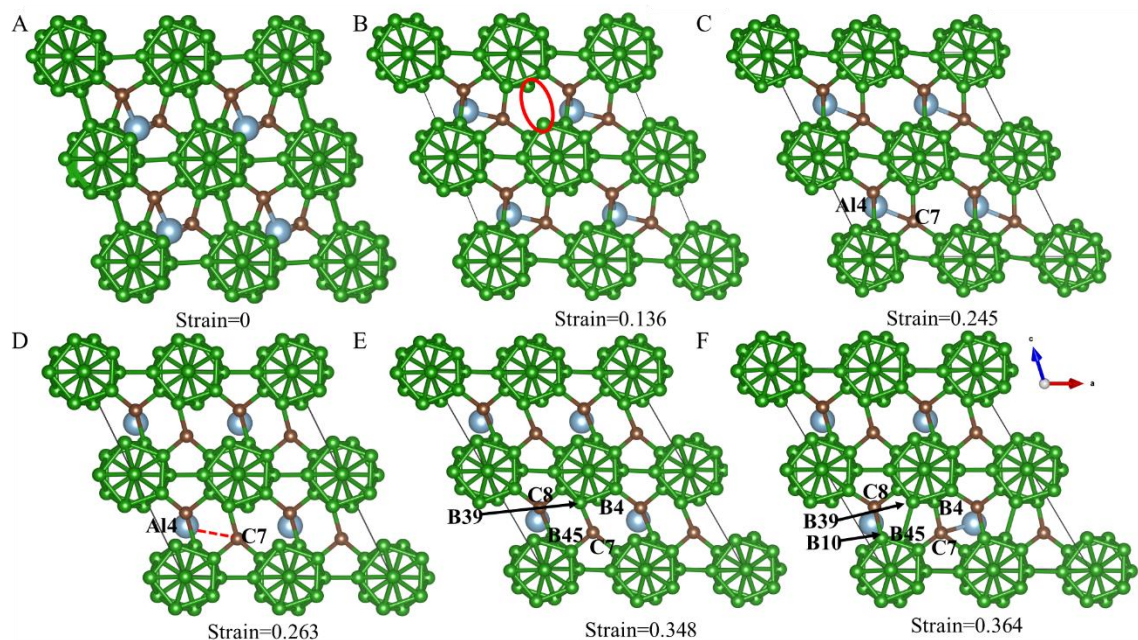


Fig. S11. The deformation and failure process of (B₁₂) C-Al-C under ideal shear deformation: (A) the intact structure. (B) the structure at 0.136 strain in which B-B bonds connecting two adjacent icosahedra break. (C) the structure at 0.245 strain in which chain Al4-C7 bond is stretched to 2.10 Å without breaking. (D) the structure at 0.263 strain in which chain Al-C7 bond is broken, releasing the shear stress. (E) the structure at 0.348 strain before the icosahedra slip. (F) the structure at 0.364 strain after icosahedra slip.

Fig. S12: Detailed deformation and failure process of (B₁₂) B-Al-C

The deformation and failure mechanism of (B₁₂) B-Al-C is shown in Fig. S12. Fig. S12A shows an intact structure. At 0.155 shear strain, the B-B bonds connecting two adjacent icosahedra are stretched from 1.70 Å to 1.92 Å without breaking, as shown in Fig. S12B. As shear strain increases to 0.173, the B-B bonds are drastically stretched to 2.30 Å and break, releasing the shear stress from 24.86 GPa to 21.16 GPa, as shown in Fig. S12C. Further increasing the shear strain to 0.263, the chain Al4-B14 bond is stretched from the original 2.01 Å to 2.42 Å and breaks, which slightly decreases the stress to 18.92 GPa. Meanwhile, both C7-B88 and B17-B14 bonds are slightly distorted and stretched. However, they are not broken at this strain with the bond length of 1.59 Å for C7-B88 and 1.69 Å for B17-B14, respectively, which are comparable to their original length (1.64 Å for C7-B88 and 1.63 Å for B17-B14), as shown in Fig. S12D. However, at 0.280 strain, the C7-B88 and B17-B14 bonds are drastically stretched to 1.74 Å and 1.79 Å, respectively, as shown in Fig. S12E. This releases the shear stress from 18.92 GPa to -1.03 GPa. Next, continuing increasing the shear strain up to 0.460, the shear stress gradually increases to 26.95 GPa. Particularly, at 0.460 shear strain, new B14-B31 and C7-B76 bonds form, suggesting the icosahedra slip, as shown in Fig. S12F. Meanwhile, no icosahedron is deconstructed at this strain.

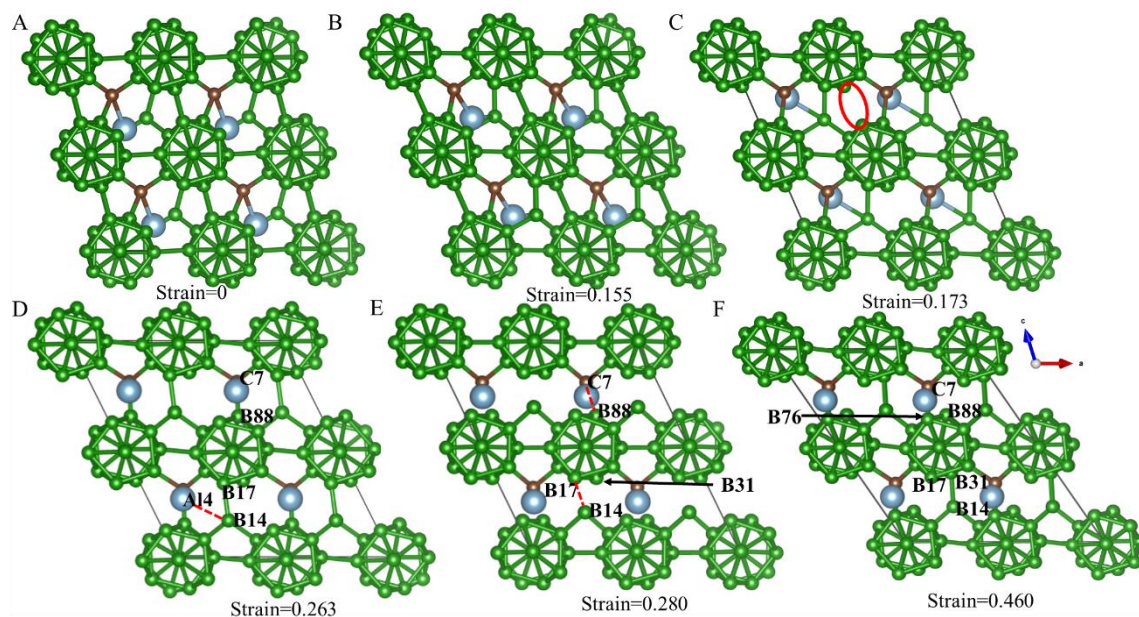


Fig S12. The deformation and failure process of (B₁₂) B-Al-C under ideal shear deformation: (A) The intact structures. (B) the structure at 0.155 strain. (C) the structure at 0.173 strain corresponding to the breaking of B-B bonds which connect two icosahedra. (D) the structure at 0.263 strain in which chain Al14-B14 bond breaks. (E) the structure at 0.280 strain in which B14-B17 and C7-B88 bonds break. (F) the structure at 0.460 strain corresponding to the icosahedral slip.

Fig. S13: Detailed deformation and failure process of (B₁₁C) C-Al-C

The deformation and failure mechanism of (B₁₁C) C-Al-C is different from both (B₁₂) C-Al-C and (B₁₂) B-Al-C. S13A shows the intact structure of (B₁₁C) C-Al-C. As shear strain increases to 0.231 corresponding to the ideal shear strength of 28.65 GPa, the B-B bonds connecting two icosahedra are stretched from the original 1.83 Å to 2.96 Å and break, as shown in Fig. S13B. At 0.251 shear strain, the C-B bonds within the icosahedra break, which initiates the deconstruction of icosahedra, as shown in Fig. S13C. In addition, the C-Al bond in the chain is also stretched from 2.00 Å to 2.56 Å. The breaking of the bond releases the shear stress from 28.65 GPa to 17.67 GPa. At 0.290 shear strain, the C14-B52 bond connecting the chain and icosahedra is stretched from 1.58 Å to 1.77 Å (Fig. S13D, which further releases the shear stress to -2.34 GPa.

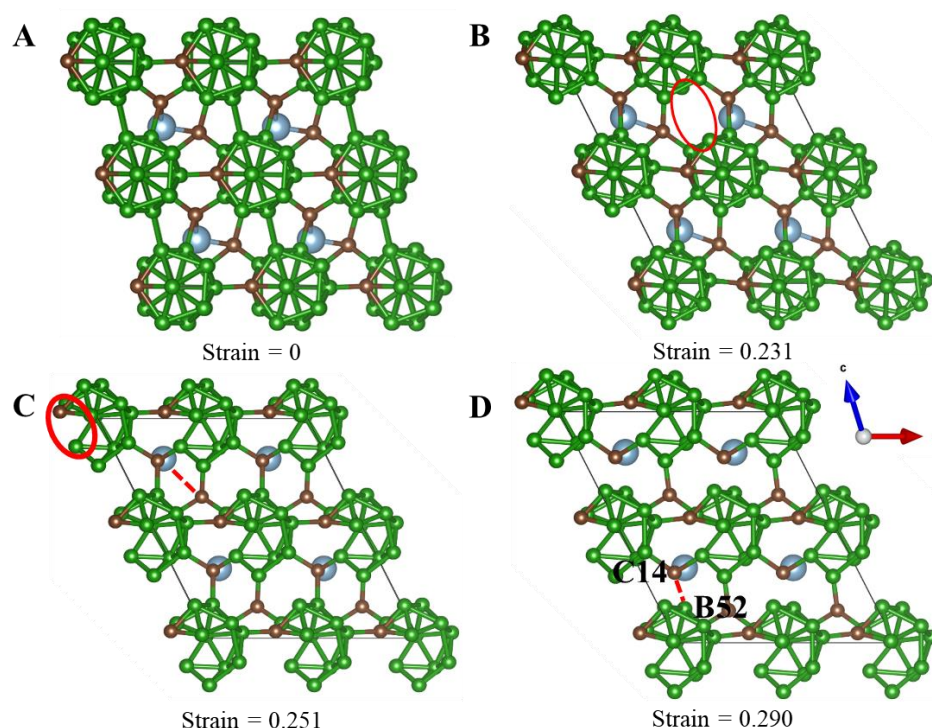


Fig. S13. The deformation and failure process of (B₁₁C) C-Al-C under ideal shear deformation: (A) The intact structure. (B) the structure at 0.231 strain in which B-B bonds connecting two icosahedra break. (C) the structure at 0.251 strain in which chain Al-C bonds break. (D) the structure at 0.290 strain in which C14-B52 bonds connecting chain and icosahedra break.

References

- [1] A. Lipp, M. Röder, Über ein aluminiumhaltiges Borcarbid, Zeitschrift für anorganische und allgemeine Chemie 343(1-2) (1966) 1-5.
- [2] H. Neidhard, R. Mattes, H. Becher, Zur Darstellung und Struktur eines aluminiumhaltigen Borcarbids, Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry 26(4) (1970) 315-317.
- [3] R. Schmechel, H. Werheit, K. Robberding, T. Lundström, H. Bolmgren, IR Active Phonon Spectra of B–C–Al Compounds with Boron Carbide Structure, Journal of Solid State Chemistry 133(1) (1997) 254-259.
- [4] V. Domnich, S. Reynaud, R.A. Haber, M. Chhowalla, Boron Carbide: Structure, Properties, and Stability under Stress, J. Am. Ceram. Soc. 94(11) (2011) 3605-3628. 10.1111/j.1551-2916.2011.04865.x.
- [5] Q. An, W.A. Goddard, 3rd, T. Cheng, Atomistic explanation of shear-induced amorphous band formation in boron carbide, Phys. Rev. Lett. 113(9) (2014) 095501. 10.1103/PhysRevLett.113.095501.

CHAPTER 3

Anisotropy and Residual Stress in B₄C-ZrB₂ Eutectic

Qirong Yang, Chawon Hwang, Atta U. Khan, Vladislav Domnich, Eric D. Gronske, and

Richard A. Haber*

Department of Material Sciences and Engineering, Rutgers, The State University of New

Jersey, Piscataway, NJ 08854, USA

*Corresponding author email: rich.haber@rutgers.edu and address: 607 Taylor Road, Piscataway, NJ 08854, USA. Tel: +1(848) 445-5924, Fax: +1(732) 445-5926.

Abstract

Microstructure texturing in eutectic composites is known for contributing to anisotropic materials properties. Although B_4C - ZrB_2 eutectic has long been discovered, very little is known about how the highly textured microstructure and the crystallographic orientation of the constituent phases affect the mechanical properties of the composite. In this study, B_4C - ZrB_2 eutectic is prepared via arc melting to investigate the hardness and toughness anisotropy due to microstructure texturing and crystallographic orientations. In addition, residual stresses responsible for the observed toughening mechanism was elucidated using the theoretical model and Raman stress mapping.

Keywords: Eutectic composite; Carbide; Boride; Hardness anisotropy; Residual stresses

Introduction

Monolithic boron carbide (B_4C) is remarkable for its combination of high hardness (28-37 GPa) and low density (2.52 g/cm^3), making it applicable for sand-blasting nozzles, grinding materials, and armor ceramics [1-4]. However, its covalent nature makes B_4C intrinsically brittle and difficult to sinter. Metal borides, such as ZrB_2 , are often used as sintering aids for B_4C not only for their ability to enhance the sintering behavior but also to improve the fracture toughness [5]. Mestvirishvili et al. reported a small improvement in fracture toughness, e.g. from 2.6 to $2.8 \text{ MPa}\cdot\text{m}^{1/2}$, with a 3 wt% incorporation of ZrB_2 in B_4C [6]. Han et al. showed a significant improvement in toughness, 6.3 and $7.0 \text{ MPa}\cdot\text{m}^{1/2}$, with 38 and 51 wt% addition of ZrB_2 , respectively [7]. In addition to the aforementioned benefits from the particulate composite, eutectic composites also acquire superior mechanical properties. Waku et al. showed a significant improvement of flexural strength, from 100 to 700 MPa at 1500°C , between the Al_2O_3 - $GdAlO_3$ hot-pressed and eutectic

composites [8]. Anisotropic material properties due to strong microstructure texturing are commonly found in eutectic materials [9]. For example, ZrC-ZrB₂ eutectic shows higher hardness values transverse to the solidification direction while higher fracture toughness in the longitudinal direction [10].

Rudy et al. constructed B₄C-ZrB₂ pseudobinary phase diagram using experimental data and theoretical calculation in 1969 [11]. They estimated that a eutectic composition contains 58-68 mol% B₄C with a eutectic point at 2220 ± 20 °C. Experimentally, the B₄C-ZrB₂ eutectic system was first verified by Ordan'yan et al. and the composition was estimated to have 70-75 mol% of B₄C and the eutectic point found around 2280 ± 30 °C [12]. Kovalev et al. later conducted a detailed study and determined that the exact composition was 71.5 mol% B₄C and 28.5 mol% ZrB₂ with a eutectic point of 2200 °C [13]. The B₄C-ZrB₂ phase diagram and the proposed eutectic compositions are summarized in Fig. 1. Kovalev et al. found that B₄C-ZrB₂ eutectic formed a highly textured microstructure consisting of ZrB₂ plates (lamellar) or rods in the matrix of B₄C depending on the solidification rate [13]. Namely, slow solidification rates resulted in plate-like morphology whereas fast solidification rates were prone to result in rod-like structures. Kovalev et al. determined that Vickers hardness value of the eutectic was $31-33 \pm 0.75$ GPa, which is roughly in agreement with Ordan'yan's findings, 32.2-34.3 GPa, for a 100g load [13]. Although it is well established that microstructure texturing and crystallographic orientation relationships between the constituent phases can lead to anisotropic material properties, neither study considered the effect of plate/rod orientation on the hardness values. The crystallographic orientation relationship between the ZrB₂ rods and the B₄C matrix was not determined and its contribution to hardness and toughness were never

assessed. Furthermore, toughening by changing the fracture behavior (from transgranular to intergranular) has been documented for many eutectic B_4C carbide containing systems, however it has never been examined for the B_4C - ZrB_2 eutectic system [9].

Therefore, to further our understanding of the B_4C - ZrB_2 eutectic system, this work aims to accomplish the following tasks: 1) identify the crystallographic orientation relationship between the constituent phases, 2) evaluate if microstructural texturing and crystallographic orientation contributes to hardness and toughness anisotropy, 3) evaluate crack propagation behavior in the eutectic composite, and 4) estimate residual stress using theoretical calculation and verify it using Raman spectroscopy to explain crack deflection behavior.

Material and Methods

Powders of B_4C (Grade HD20, H.C. Starck) and ZrB_2 (Grade B, H.C. Starck) were mixed according to the eutectic composition (28.5 mol% ZrB_2 and 71.5 mol% B_4C) and then cold-pressed without a binder. The pellet was melted under argon flow multiple times using a benchtop arc melter (5SA, Centorr Vacuum Industries) to ensure uniform mixing. The melt was allowed to cool on a water-cooled copper hearth to room temperature and flipped between each melting. A schematic of the melt device is depicted in Fig. 2a.

The ingot was sectioned longitudinal and latitudinal to the base of the ingot (Fig. 2b) and polished down to mirror finish using 9, 6, 1 and 0.25 μm diamond embedded pads. Powder diffraction was done on pulverized ingot with/without silicon standard (SRM 640e; NIST) using an X'Pert Pro diffractometer (PANalytical) with $Cu\ K\alpha$ radiations. The Vickers hardness was obtained using a VH3300 automatic tester (Wilson) with 0.1g-2kg

loads following ASTM standard C1327-15. The indents were selectively placed parallel and perpendicular to the c-axis of the ZrB_2 rods to examine anisotropy. 1 kg load indents were also placed on a polycrystalline B_4C dense body prepared by hot press apparatus. Cracks resulting from the 1 kg indents from both specimens were used to evaluate indentation fracture toughness using the equation $K_{IC} = 0.018 \times (E/H)^{0.5} (Pc^{-1.5})$ [14], where E is Young's modulus in GPa, H is Vickers hardness in GPa, P is load in Newton (9.81 N), and c is the median crack length from the center of the indent to crack tip in meter. E is obtained using the rule of mixture taking the eutectic volume fraction and the E of the constituent phases, $E_{\text{B}_4\text{C}} = 430$ GPa [2] and $E_{\text{ZrB}_2} = 489$ GPa [15]. A field emission scanning electron microscope (FE-SEM; SIGMA Zeiss), equipped with energy-dispersive X-ray spectroscopy (EDS; Oxford Instruments) and electron backscattered diffraction detector (EBSD; Nordlys), was used to reveal the microstructure and examine the crack propagating behaviors. The cross-sectional diameter and the length of the rod-like grains, as well as the spacing between the grains were measured using an image analysis software (Lince 2.4.2) according to the linear intercept method (ASTM E112-13). EDS was used to identify the chemical composition between the constituent phases. EBSD was employed to resolve the crystallographic orientation of the constituent phases. Raman spectroscopy was used to map out the residual stresses in the matrix of B_4C . Raman data was collected using an inVia Reflex Raman microscope (Renishaw) equipped with 532 nm laser at 100x objective.

Results and Discussion

Microstructure

The arc melter prepared B_4C - ZrB_2 eutectic ingot was sectioned longitudinally and latitudinally to the base of the copper hearth, as shown in Fig. 2b. Although arc melting is not a directional process, the overall cooling direction is roughly longitudinal since a water-cooled hearth is the main source of cooling. The local cooling direction, however, can vary from the overall cooling direction as it can be influenced by local thermal gradients, composition, pores, and impurities [9]. This overall cooling direction dramatically changed the morphology of the eutectic colonies. When examining the overall microstructure on the longitudinal cross-section, the colonies formed are much longer in height than in width, aligning with the fastest cooling direction (Fig. S1). The morphology within the same colony is similar while varying substantially from one colony to another. The morphologies between the colonies are random and often consist of hypereutectic, hypoeutectic, mixture of lamellar and rod-like structures, large grains of ZrB_2 , and pure B_4C .

The microstructure at the center of the well-developed colonies consists of ZrB_2 rod-like grains embedded in the B_4C matrix (Fig. S2). The diameter of the rods are $0.68 \pm 0.14 \mu m$ and the matrix spacing between the rods is $0.62 \pm 0.27 \mu m$. The average length of the rods is determined to be $18.45 \pm 4.27 \mu m$ although it is expected that the measurements underestimate the actual length of the rods. The exact length of the rods is difficult to determine because the long axis of the rods do not align perfectly parallel with the cutting plane. Any misalignment between the long axis of the rods and the cutting plane would make the rods appear shorter.

Hardness anisotropy due to microstructure texturing

Vickers hardness was obtained on the well-developed rod-like regions parallel and perpendicular to the long axis of the ZrB_2 to examine the potential anisotropy (Fig. 2c and 2d). Across all indentation loads, the hardness values were consistently 2-3 GPa higher parallel to the rods and the difference exists outside of the error bars (Fig. 3a). The hardness values at 100g load were in agreement with the findings of Ordan'yan and Kovalev. Their hardness values averaged out and exist within the range of hardness values determined in this study since they did not consider the microstructural texturing or the crystallographic orientation.

The anisotropy in hardness can partly be explained by the high aspect ratio between the rod's length and the cross-section, e.g. smaller radial cross-section yields a higher hardness (Hall-Petch relationship) [16]. ZrB_2 and B_4C have different hardness values, hence the difference in the indented volume fraction could also explain the observed hardness disparity. The indents were placed in the well-developed eutectic area, and thus the total integrated volume fraction for each constituent phases is constant for either indentation direction. However, given a fixed indent size (25.3 μm diameter for 9.8N Vickers indent), the cross-sectional area of ZrB_2 on the parallel and perpendicular directions do not have the same area fraction, namely 22.2 and 53.2 area % parallel vs. perpendicular. The limited size of the indents and the shallow penetration of Vickers indenter (136° cross the opposite facets), means that the actual deformed volume fractions of the constituent phases are also different in the two directions. The deformed volume fractions were estimated to be 22.2% ZrB_2 in the parallel direction and 27.0% in the perpendicular direction (Table 1). The method for approximating area and volume fractions

is detailed in Supplementary work. Using the rule of mixtures [17], hardness values at 1 kg load are estimated to be 28.2 GPa and 27.7 GPa in the parallel and perpendicular directions, respectively (Fig. 3a). The calculated hardness values are similar to the measured values. More importantly, the difference in indented volume fraction offers an explanation for the observed hardness anisotropy.

Crystallographic orientation and its effect on the hardness anisotropy

The hardness difference between the calculated values ($\Delta=0.5$ GPa) is smaller than the difference in the measured values ($\Delta=1.8$ GPa) at 1 kg load. The rule of mixtures utilizes the hardness values acquired from the polycrystalline ZrB_2 (19.6 GPa) [18] and B_4C (30.7 GPa). Therefore, the calculated values do not reflect the already existing anisotropy in single crystal ZrB_2 and B_4C . In order to examine if the already existing anisotropy in the constituent phases contributes to the observed hardness anisotropy, the crystallographic orientation relationship between the ZrB_2 rods and the B_4C matrix was identified using EBSD mapping (Fig. 4a). Using the hexagonal system notation, we identified the crystal orientation relationship of B_4C $(0\bar{1}11) \parallel \text{ZrB}_2 (0001)_{\text{basal}}$ and $\text{B}_4\text{C} (01\bar{1}1) \parallel \text{ZrB}_2 (\bar{1}2\bar{1}0)_{\text{prismatic}}$.

Domnich et al. found a minor hardness anisotropy in single crystal boron carbide using Berkovich indenters, namely the hardness value on the $(10\bar{1}1)$ plane was ~ 1 GPa higher than that of the (0001) plane [19]. It is important to point out that the $(10\bar{1}1)$ plane on boron carbide and the $(01\bar{1}1)$ matrix planes identified in this study are symmetrically equivalent, both belong to the pyramidal (π) planes using the hexagonal notation (Fig. 4b). This means that the matrix has a higher hardness value when the indents were made in the

perpendicular direction. Nakano et al. found that the basal plane in ZrB_2 single crystal has a higher Knoop hardness value than the prismatic planes [20]. Using nano-indentation (Berkovich), Csanadi et al. also found the basal plane of ZrB_2 is ~ 5 GPa harder than the prismatic planes [21]. This implies the rods yield a higher hardness when the indents were made in the parallel direction, contrary to the assessment of the matrix. It is important to note that the hardness difference obtained using nano-indentation does not scale linearly due to indentation-size effect [22], thus it is difficult to approximate the exact hardness difference at higher loads. Furthermore, the hardness values for single crystal boron carbide or ZrB_2 at 1 kg load are also unknown. Nevertheless, the hardness anisotropy in the single crystals, no matter the values, could contribute to the small difference observed between the calculated and the measured hardness values.

Toughness anisotropy and crack propagating behaviors

Cracks emanating from the 1 kg load indents were used to evaluate the indentation fracture toughness. In the parallel indentation direction, we obtained $3.54 \pm 0.62 \text{ MPa}\cdot\text{m}^{0.5}$ compared to monolithic B_4C at $2.4\text{-}2.6 \text{ MPa}\cdot\text{m}^{0.5}$ [6, 23] (Fig. 5). The improvement in the toughness can be explained by the crack deflection observed at the B_4C - ZrB_2 interfaces (Fig 6a). When the crack meets an interface, the crack first changes direction then travels around the ZrB_2 grain. The frequent change of direction shortens the overall crack length, which improves the indentation toughness values. The crack deflection observed in the eutectic is likely caused by residual stress due to the mismatch between the linear thermal expansion coefficients and elastic moduli of the constituent phases (discussed in residual stress calculation). Since the microstructure is consistent in the parallel indentation direction, no toughness anisotropy was identified.

In the perpendicular indentation direction, two crack propagation directions were evaluated to examine fracture toughness due to microstructure texturing, namely along the long axis and transverse to the long axis of ZrB₂. We measured $3.11 \pm 0.57 \text{ MPa}\cdot\text{m}^{0.5}$ along the long axis and $5.03 \pm 1.23 \text{ MPa}\cdot\text{m}^{0.5}$ transverse to the long axis (Fig. 5). Compared to monolithic B₄C, an indentation toughness improvement of 24% was observed along the long axis of ZrB₂. We attribute this to the occasional deflection between the B₄C-ZrB₂ interfaces as shown in Fig. 6c. The crack deflects twice when it interacts with the ZrB₂ phase, once as it enters the ZrB₂ phase and once more as it leaves the ZrB₂ phase (marked in red). The crack travels unimpeded within the B₄C matrix and often travels along the B₄C-ZrB₂ interfaces (marked in blue), an indication for weak grain boundaries. The observation of crack deflection at the B₄C-ZrB₂ interface and the lattice and thermal expansion mismatch between the constituent phases is good evidence for weak boundaries. This is further evident by examining the fracture surface along the long axis as shown in Fig. 7a. When the crack intersects the ZrB₂ rod, it deflects along the matrix-rod interface until the rod fractures at a weak point and debonds [24].

The indentation toughness improvement is substantial, about 100% improvement, when the crack travels transversely to the long axis of ZrB₂. This is expected because more B₄C-ZrB₂ interfaces provide more crack deflection (Fig. 6c). However, it is important to note that the deflection does not happen at every interface. The enhancement in the indentation toughness can also be attributed to the higher toughness value of ZrB₂, 3.5-3.7 $\text{MPa}\cdot\text{m}^{1/2}$ [25, 26] compared to 2.4-2.6 $\text{MPa}\cdot\text{m}^{1/2}$ for B₄C [6, 23]. The tougher ZrB₂ requires more energy to fracture, thus resulting in shorter overall crack lengths. Contrary to the fracture surface along the long axis, we did not observe ZrB₂ rod pullouts on the

transverse direction (Fig. 7b). In addition, fragments of ZrB_2 rods are commonly seen when the fracture surface is parallel to the c-axis of the rods and not seen on the transverse direction. Taken together, microstructure texturing plays a significant role in toughness anisotropy. The effect of crystallographic orientation of the constituent phases on the toughness anisotropy is not examined in this study because there is no report on the toughness anisotropy in single crystal B_4C or ZrB_2 .

Residual stress calculation

The crack deflection observed in our work can be partly explained by the presence of residual stress as B_4C and ZrB_2 have very different linear thermal expansion coefficients and elastic moduli. The residual stress in the matrix can be modeled using the Shrink-fit of hollow cylinder onto a solid cylinder model [24]:

$$P_m = -\sigma_{\theta\theta} = \sigma_{rr} = \frac{E_f E_m (\alpha_m - \alpha_f) (1 + \nu_f) (T_o - T_A)}{(1 + \nu_f) E_m (1 - 2\nu_f) + E_f (1 + \nu_m)}$$

$$\sigma_{zz} = -2\nu_f P_m + E_f (\alpha_f - \alpha_m) (T_o - T_A)$$

where σ_{rr} , $\sigma_{\theta\theta}$, and σ_{zz} refer to radial, hoop/circumferential, axial stress components, respectively (Fig. 7). Subscripts f and m refer to the fiber and matrix, α is the linear thermal expansion coefficient, ν is the Poisson's ratio, E is the elastic moduli, T_A is the temperature at which the misfit stresses start to arise, and T_o is the final ambient temperature [24]. In this work, we take α , ν and E to be $4.5 \times 10^{-6} \text{ K}^{-1}$, 0.18, 430 GPa respectively for B_4C [2, 27, 28], $6.66 - 6.93 \times 10^{-6} \text{ K}^{-1}$ (for a- and c-axis directions respectively), 0.119, 489 GPa respectively for ZrB_2 [15, 29, 30], $T_A = 1200 \text{ }^\circ\text{C}$, and T_o to be $25 \text{ }^\circ\text{C}$. The T_A is assumed to be roughly half of the T_{melt} of B_4C because at temperatures higher than that materials can “flow” and stresses can be relaxed [24]. Using the two different elastic modulus values for

a- and c-axis for ZrB_2 , the residual stress in the matrix has the radial component of 630-710 MPa in tension, hoop component of 630-710 MPa in compression, and axial stress component around 1.4-1.57 GPa in tension. The localized nature of the stress fields fall off rapidly following the $\frac{1}{r^2}$ relationship [24]. However, the spatial proximity between the rod-like ZrB_2 grains implies the effective residual compression stressed in the B_4C matrix should be higher, between 875 and 985 MPa, as illustrated in (Fig. 8). As the crack propagates the rod-matrix interface, it orients itself parallel to the axis of the local compressive stress and perpendicular to the axis of the local tensile stress in the surrounding matrix [31]. This results in crack deflection around the ZrB_2 rod as seen in Fig. 6a.

Raman stress mapping

Raman spectroscopy was used to further elucidate the magnitude and spatial distribution of the residual stress in the B_4C matrix. An example of a Raman spectrum of B_4C is shown in Fig. 9a. Peak shifting of the nominally 1080 cm^{-1} Raman band for B_4C can be interpreted as a change in a stress state. For example, an upshift of 1 cm^{-1} in the 1080 cm^{-1} Raman band corresponds to a volume reduction or an equivalent of compressive stress of 278 MPa [27]. Conversely, a downshift of 1 cm^{-1} is associated with volume expansion either due to doping or tensile stress of the same magnitude [32-34]. Raman mapping was done on the longitudinal and latitudinal cross-section in the well-developed eutectic regions. An upshift of $3\text{-}4\text{ cm}^{-1}$ was observed at the interface of B_4C and ZrB_2 suggesting a compressive state (Fig 9b and 9c). Although Zr-doped B_xC ($x \approx 3.75\text{-}10.1$ for solid solution) is thermodynamically stable between $2300\text{-}2450\text{ }^\circ\text{C}$, it has not been observed in the $\text{B}_4\text{C}\text{-ZrB}_2$ eutectic system [11, 12, 35]. In addition, X-ray diffraction data

does not support the doping explanation since the peak positions of the boron carbide phase were indexed to that of stoichiometric B_4C (Fig. 10). This result is expected since B_4C is in equilibrium with ZrB_2 at elevated temperatures and Zr-doping can only occur when the B/C ratio is greater than 4, e.g. $B_{13}C_2$ [11]. Furthermore, doping would result in lattice expansion and a downshift in the 1080 cm^{-1} peak, opposite to what was found. It's important to note that the spatial resolution of Raman spectroscopy and the analysis technique is not high enough to measure the absolute values of residual stress. The step size ($0.5\text{ }\mu\text{m}$) and the Raman laser spot size ($\sim 0.5\text{ }\mu\text{m}$) are roughly the same sizes as the diameter of the rods ($0.68\text{ }\mu\text{m}$) and the matrix spacing ($0.62\text{ }\mu\text{m}$) between the rods. Nevertheless, it is discernable that there is an upshift in the 1080 cm^{-1} Raman band when the spectra were acquired between the ZrB_2 grains, indicating a compressive state. The color intensity of the Raman mapping suggested that the upshift is around $3\text{-}4\text{ cm}^{-1}$, which is equivalent to $830\text{-}1110\text{ MPa}$ of compressive residual stress. The values are in agreement with the effective residual stress ($875\text{-}985\text{ MPa}$) calculated using the Shrink-fit of hollow cylinder onto a solid cylinder model.

The obvious sharpening of the 1580 cm^{-1} peak (carbon G peak) near or at the rods indicated that graphitization has occurred [36-38]. In general, free amorphous carbon is expected in commercial boron carbide powder [39]. Yet, the sharpening of the peak is only observed near the ZrB_2 phase. Since boron carbide is a solid-solution and has a higher carbon solubility at higher temperatures, the free carbon can dissolve into boron carbide at the eutectic temperature ($\sim 2200\text{ }^\circ\text{C}$) [35]. However, carbon solubility significantly decreases at lower temperatures. It is possible to infer that as the melt cooled, carbon precipitated and nucleated as graphitic carbon at the interfaces of B_4C and ZrB_2 .

Conclusions

A B_4C - ZrB_2 eutectic ceramic composite was prepared using an arc melter. The overall morphology consists of colonies of rod-like ZrB_2 in B_4C matrix, separated by non-eutectic morphology. The Vickers hardness parallel to the c-axis of the rods was 2-3 GPa higher compared to the perpendicular direction. The hardness anisotropy is mostly attributed to microstructure texturing and the difference in the indented ZrB_2 and B_4C volume fraction in the different indentation direction. The already existing hardness anisotropy in the constituent phases also has a minor contribution to the observed hardness disparity. The crystallographic orientation relationship between the ZrB_2 rods and the B_4C matrix was determined to be ZrB_2 (0001) $\parallel$ B_4C (0 $\bar{1}$ 11) and ZrB_2 ($\bar{1}$ 2 $\bar{1}$ 0) $\parallel$ B_4C (01 $\bar{1}$ 1). Crack deflection was commonly observed at the B_4C - ZrB_2 interface. Overall, the eutectic composite showed higher indentation toughness than monolithic B_4C . Toughness anisotropy was observed with higher indentation toughness value transverse to the long axis of the ZrB_2 rods than for parallel. The mechanism responsible for the observed crack propagation behavior was residual stress, which was estimated using theoretical calculations and verified experimentally using Raman stress mapping.

Acknowledgment

This work was supported by the Army Research Laboratory under Cooperative Agreement [W911NF-12-2-0022]; and the Defense Advanced Research Projects Agency [Grant No. W31P4Q-13-1-000].

References

- [1] V. Domnich, S. Reynaud, R.A. Haber, M. Chhowalla, Boron Carbide: Structure, Properties, and Stability under Stress, *J. Am. Ceram. Soc.* 94(11) (2011) 3605-3628.
- [2] F. Thevenot, Boron carbide—a comprehensive review, *J. Eur. Ceram. Soc.* 6(4) (1990) 205-225.
- [3] A.U. Khan, V. Domnich, R.A. Haber, Boron carbide-based armors: Problems and possible solutions, *Am. Ceram. Soc. Bull.* 96(6) (2017) 30-35.
- [4] A.U. Khan, A.M. Etzold, X.K. Yang, V. Domnich, K.Y. Xie, C. Hwang, K.D. Behler, M.W. Chen, Q. An, J.C. LaSalvia, K.J. Hemker, W.A. Goddard, R.A. Haber, Locating Si atoms in Si-doped boron carbide: A route to understand amorphization mitigation mechanism, *Acta Mater.* 157 (2018) 106-113.
- [5] H.B. Ma, H.L. Liu, J. Zhao, F.F. Xu, G.J. Zhang, Pressureless sintering, mechanical properties and oxidation behavior of ZrB₂ ceramics doped with B₄C, *J. Eur. Ceram. Soc.* 35(10) (2015) 2699-2705.
- [6] Z. Mestvirishvili, I. Bairamashvili, V. Kvatchadze, N. Rekhviashvili, Thermal and Mechanical Properties of B₄C-ZrB₂ Ceramic Composite, *Journal of Materials Science and Engineering B* 5(9) (2015) 9.
- [7] H. Wenbo, G. Jiaxing, Z. Jihong, Y. Jiliang, Microstructure and properties of B₄C-ZrB₂ ceramic composites, *Int. J. Eng. Innov. Technol* 3(1) (2013) 163-166.
- [8] Y. Waku, N. Nakagawa, T. Wakamoto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, A ductile ceramic eutectic composite with high strength at 1,873 K, *Nature* 389(6646) (1997) 49-52.
- [9] W.T. Chen, R.M. White, T. Goto, E.C. Dickey, Directionally Solidified Boride and Carbide Eutectic Ceramics, *J. Am. Ceram. Soc.* 99(6) (2016) 1837-1851.
- [10] C.C. Sorrell, V.S. Stubican, R.C. Bradt, Mechanical properties of ZrC-ZrB₂ and ZrC-TiB₂ directionally solidified eutectics, *J. Am. Ceram. Soc.* 69(4) (1986) 317-321.
- [11] E. Rudy, D. Harmon, Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems. Part 1. Related Binary Systems., Aerojet-General Corp Sacramento CA Materials Research Lab, 1965.
- [12] S. Ordan'Yan, A. Dmitriev, K. Bizhev, E. Stepanenko, Interaction in the system B₄C-ZrB₂, *Sov. Powder Metall. Met. Ceram.* 27(1) (1988) 38-40.
- [13] A.V. Kovalev, E.M. Dudnik, O.N. Grigor'ev, T.I. Shaposhnikova, I.S. Martsynyuk, Directionally solidified eutectic of the B₄C-ZrB₂ system, *Powder Metal. Met. Ceram.* 39(1-2) (2000) 63-66.
- [14] H. Lee, R.F. Speyer, Hardness and fracture toughness of pressureless-sintered boron carbide (B₄C), *J. Am. Ceram. Soc.* 85(5) (2002) 1291-1293.
- [15] D. Wiley, W. Manning, O. Hunter Jr, Elastic properties of polycrystalline TiB₂, ZrB₂ and HfB₂ from room temperature to 1300 K, *J. Less-Common Met.* 18(2) (1969) 149-157.

- [16] B.M. Moshtaghioun, D. Gomez-Garcia, A. Dominguez-Rodriguez, R.I. Todd, Grain size dependence of hardness and fracture toughness in pure near fully-dense boron carbide ceramics, *J. Eur. Ceram. Soc.* 36(7) (2016) 1829-1834.
- [17] H.S. Kim, On the rule of mixtures for the hardness of particle reinforced composites, *Mat Sci Eng a-Struct* 289(1-2) (2000) 30-33.
- [18] S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, Pressureless sintering of zirconium diboride using boron carbide and carbon additions, *J. Am. Ceram. Soc.* 90(11) (2007) 3660-3663.
- [19] V. Domnich, Y. Gogotsi, M. Trenary, T. Tanaka, Nanoindentation and Raman spectroscopy studies of boron carbide single crystals, *Appl. Phys. Lett.* 81(20) (2002) 3783-3785.
- [20] K. Nakano, T. Imura, S. Takeuchi, Hardness anisotropy of single crystals of IVa-diborides, *Jpn. J. Appl. Phys.* 12(2) (1973) 186.
- [21] T. Csanadi, S. Grasso, A. Kovalcikova, J. Dusza, M. Reece, Nanohardness and elastic anisotropy of ZrB₂ crystals, *J. Eur. Ceram. Soc.* 36(1) (2016) 239-242.
- [22] Y.V. Milman, A.A. Golubenko, S.N. Dub, Indentation size effect in nanohardness, *Acta Mater.* 59(20) (2011) 7480-7487.
- [23] K. Sairam, J. Sonber, T.C. Murthy, C. Subramanian, R. Hubli, A. Suri, Development of B₄C–HfB₂ composites by reaction hot pressing, *Int. J. Refract. Met. H.* 35 (2012) 32-40.
- [24] D.J. Green, An introduction to the mechanical properties of ceramics, Cambridge University Press 1998.
- [25] A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, D.T. Ellerby, High-strength zirconium diboride-based ceramics, *J. Am. Ceram. Soc.* 87(6) (2004) 1170-1172.
- [26] R. Telle, L. Sigl, K. Takagi, Boride-based hard materials, *Handbook of ceramic hard materials* (2000) 802-945.
- [27] M.H. Manghnani, Y. Wang, F. Li, P. Zinin, W. Rafaniello, Elastic and vibrational properties of B₄C to 21 GPa, *Sci. Technol. High Pressure* 2 (2000) 25-30.
- [28] K.Y. Xie, Q. An, T. Sato, A.J. Breen, S.P. Ringer, W.A. Goddard, 3rd, J.M. Cairney, K.J. Hemker, Breaking the icosahedra in boron carbide, *Proc Natl Acad Sci U S A* 113(43) (2016) 12012-12016.
- [29] J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, R.B. Dinwiddie, W.D. Porter, H. Wang, Thermophysical properties of ZrB₂ and ZrB₂–SiC ceramics, *J. Am. Ceram. Soc.* 91(5) (2008) 1405-1411.
- [30] N.L. Okamoto, M. Kusakari, K. Tanaka, H. Inui, M. Yamaguchi, S. Otani, Temperature dependence of thermal expansion and elastic constants of single crystals of ZrB₂ and the suitability of ZrB₂ as a substrate for GaN film, *J. Appl. Phys.* 93(1) (2003) 88-93.

- [31] G.C. Wei, P.F. Becher, Improvements in Mechanical-Properties in Sic by the Addition of Tic Particles, *J. Am. Ceram. Soc.* 67(8) (1984) 571-574.
- [32] X.Q. Yan, Z. Tang, L. Zhang, J.J. Guo, C.Q. Jin, Y. Zhang, T. Goto, J.W. McCauley, M.W. Chen, Depressurization amorphization of single-crystal boron carbide, *Phys. Rev. Lett.* 102(7) (2009) 075505.
- [33] J. Sandler, M.S.P. Shaffer, A.H. Windle, M.P. Halsall, M.A. Montes-Moran, C.A. Cooper, R.J. Young, Variations in the Raman peak shift as a function of hydrostatic pressure for various carbon nanostructures: A simple geometric effect, *Phys. Rev. B* 67(3) (2003) 035417.
- [34] V.P. Pham, G.Y. Yeom, Recent Advances in Doping of Molybdenum Disulfide: Industrial Applications and Future Prospects, *Adv. Mater.* 28(41) (2016) 9024-9059.
- [35] M. Beauvy, Stoichiometric Limits of Carbon-Rich Boron-Carbide Phases, *J Less-Common Met* 90(2) (1983) 169-175.
- [36] D. Ghosh, G. Subhash, T.S. Sudarshan, R. Radhakrishnan, X.L. Gao, Dynamic indentation response of fine-grained boron carbide, *J. Am. Ceram. Soc.* 90(6) (2007) 1850-1857.
- [37] A. Erdemir, C. Bindal, G.R. Fenske, Formation of ultralow friction surface films on boron carbide, *Appl. Phys. Lett.* 68(12) (1996) 1637-1639.
- [38] A.C. Ferrari, Raman spectroscopy of graphene and graphite: disorder, electron-phonon coupling, doping and nonadiabatic effects, *Solid State Commun.* 143(1-2) (2007) 47-57.
- [39] M. Chen, J. McCauley, J. LaSalvia, K. Hemker, Microstructural Characterization of Commercial Hot-Pressed Boron Carbide Ceramics, *J. Am. Ceram. Soc.* 88(7) (2005) 1935-1942.

Tables

Table 1. Estimated area and volume fractions for each under the Vickers imprint and the hardness corresponding to each indentation direction.

ZrB ₂ (area %)	22.2	53.2	---
B ₄ C (area %)	77.8	46.8	---
ZrB ₂ (vol. %)	22.2	27.0	25.2
B ₄ C (vol. %)	77.8	73.0	74.8
Measured Hv (1 kg)	28.6	26.8	---
Calculated Hv	28.2	27.7	---

Rule of mixtures: $H = f_m H_m + f_f H_f$ [17]

B₄C Hv: 30.7 GPa

ZrB₂ Hv: 19.6 GPa [18]

Figures

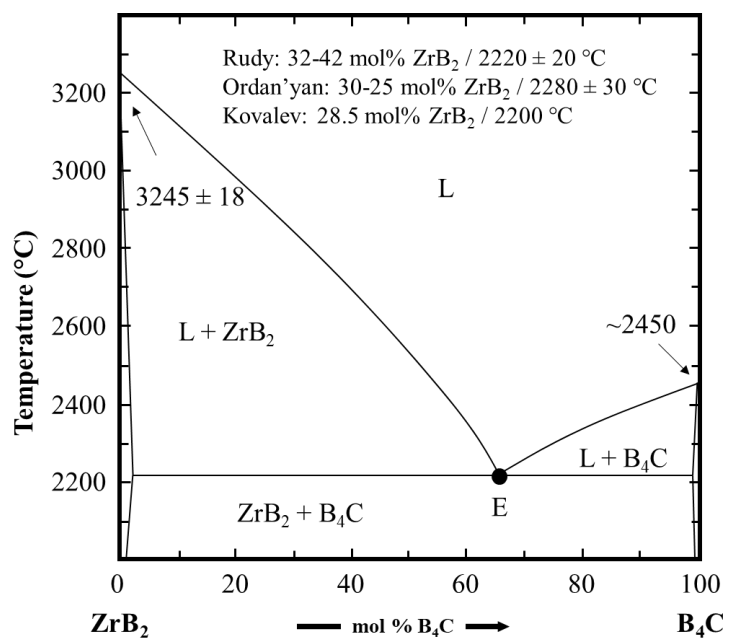


Fig. 1. Phase diagram of the B_4C - ZrB_2 system, adapted from Rudy [11], and the proposed eutectic points by Rudy [11], Ordan'yan [12], and Kovalev [13].

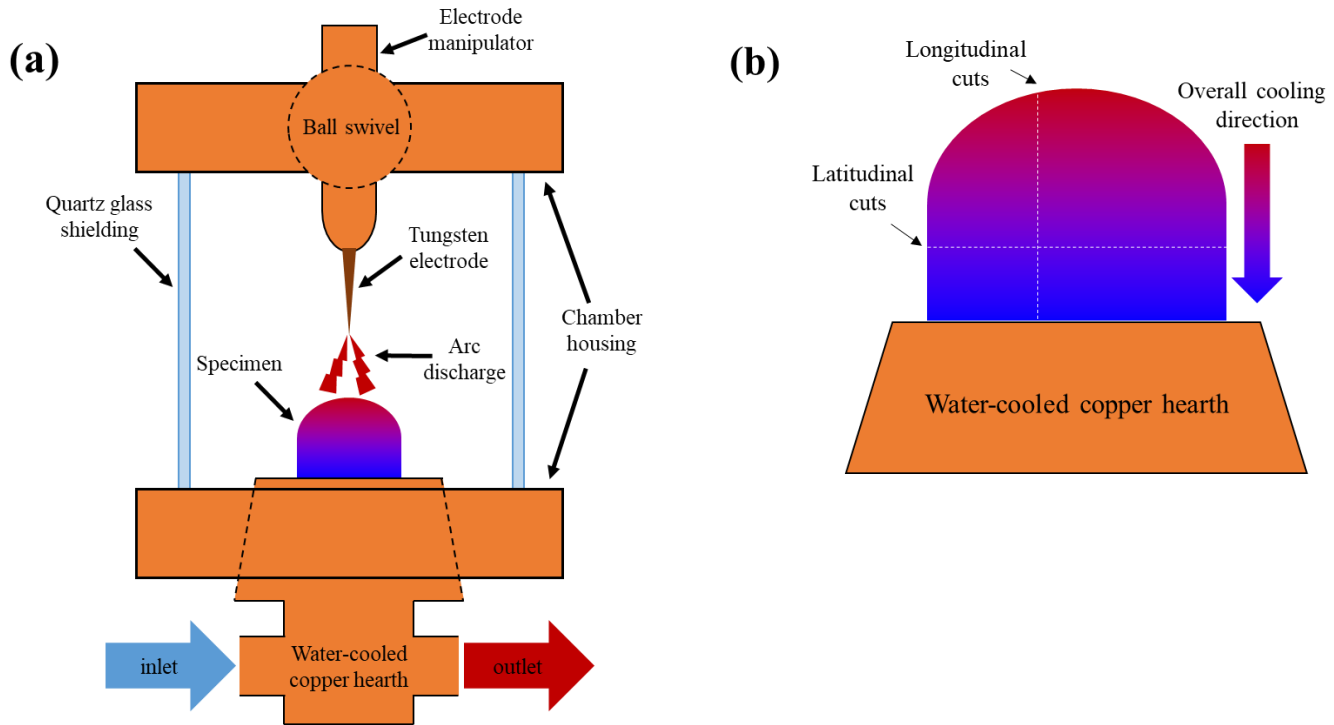


Fig. 2. (a) Schematic depicting the bench-top arc melter and (b) a close-up view of the specimen with associated cutting and overall cooling directions.

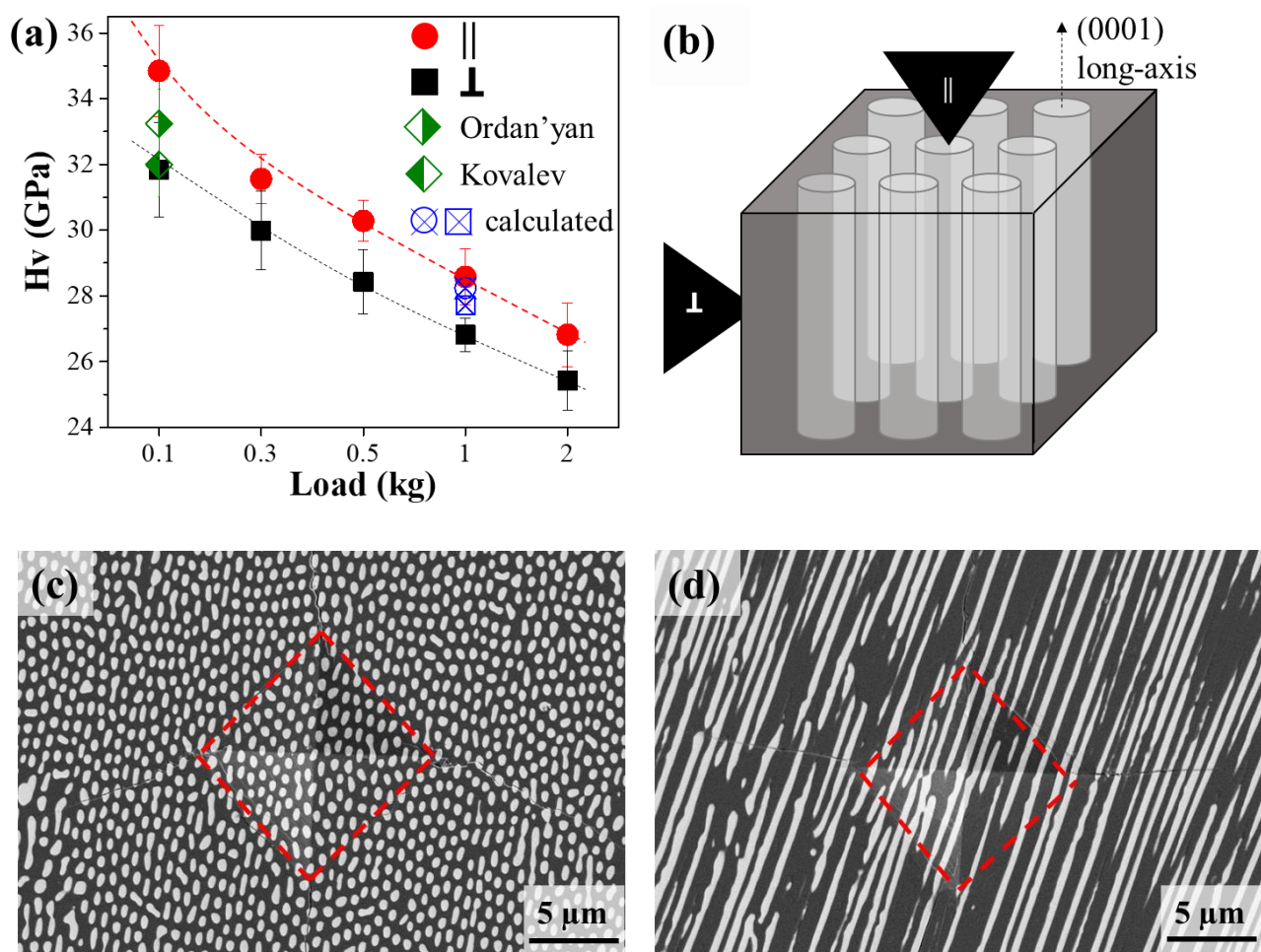


Figure 3. (a) Load vs. hardness values acquired parallel and perpendicular to the long axis of ZrB_2 rod-like grains. (b) Schematic illustrating the indentation direction with respect to rod orientation. SEM images of 0.5kg load indents parallel and perpendicular to the long axis of the rods in (c) and (d) respectively.

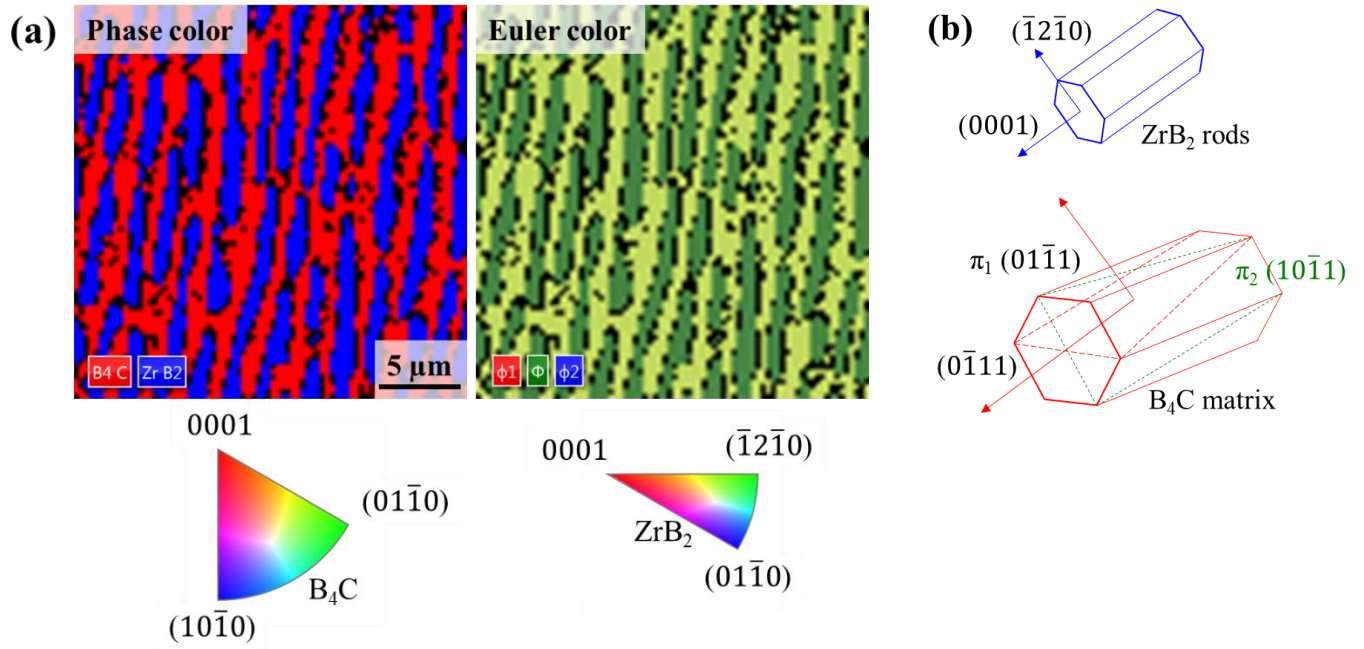


Figure 4. (a) EBSD mapping of the highly textured B₄C-ZrB₂ eutectic microstructure showing rod-like ZrB₂ grains in the B₄C matrix. (b) Schematics of the crystal orientation for ZrB₂ rods and B₄C matrix in the eutectic composite.

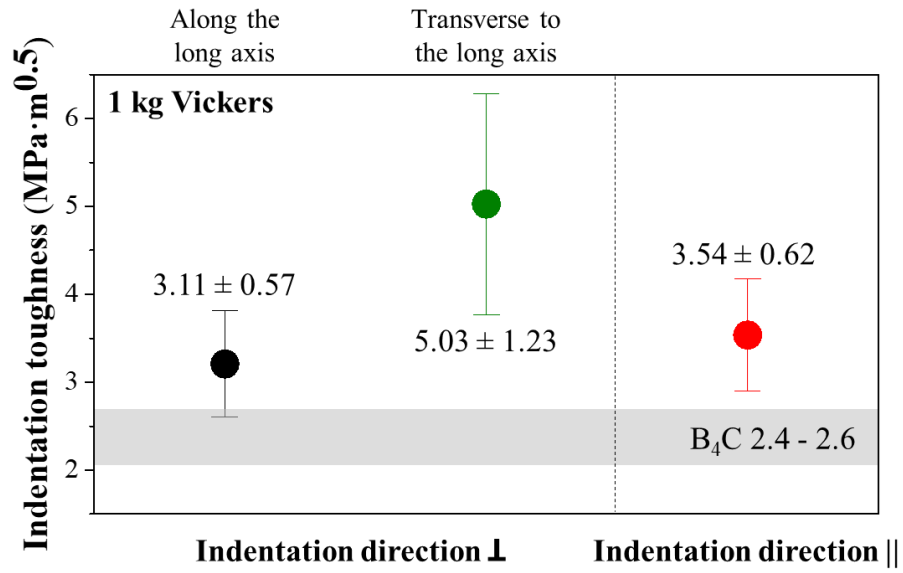


Figure 5. Indenation fracture toughness of B₄C-ZrB₂ eutectic composite and monolithic B₄C [6, 23].

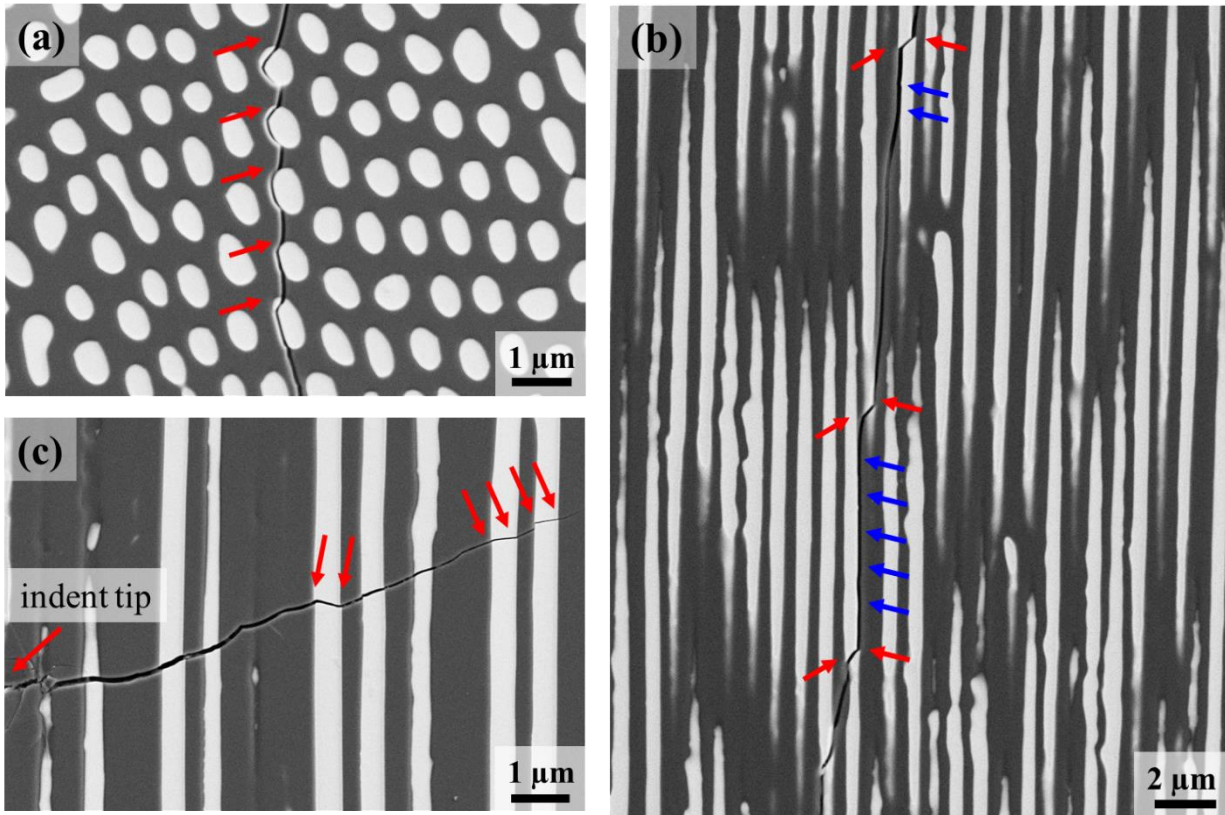


Figure 6. (a) Crack deflects around the ZrB_2 grains when the indent was placed parallel to the long axis of the ZrB_2 rod. When the indent was placed perpendicular to the long axis, crack is longer (b) along the long axis and shorter (c) transverse to the long axis of the ZrB_2 rod.

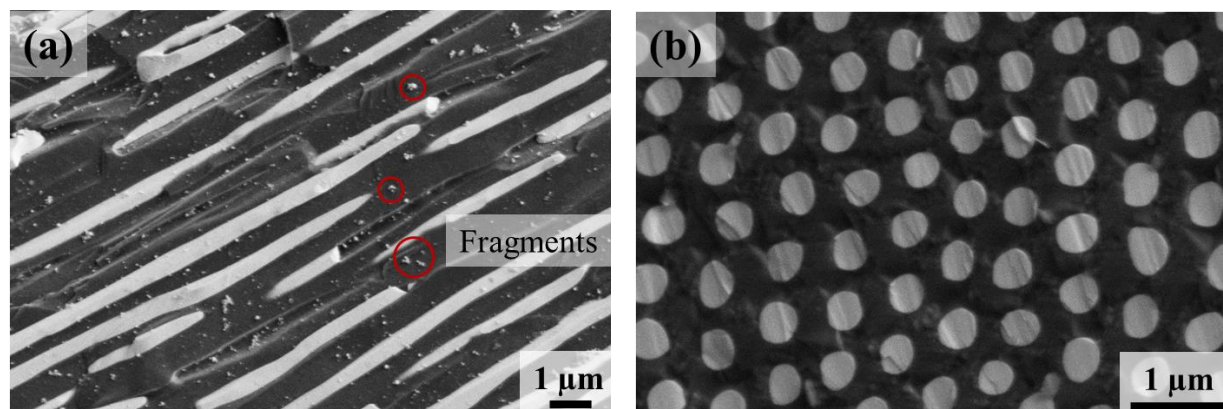


Figure 7. Fracture surface (a) along and (b) transverse to the long axis of ZrB₂ rods. ZrB₂ fragments are commonly seen on the parallel surface when the rods fractured and delaminated from the matrix.

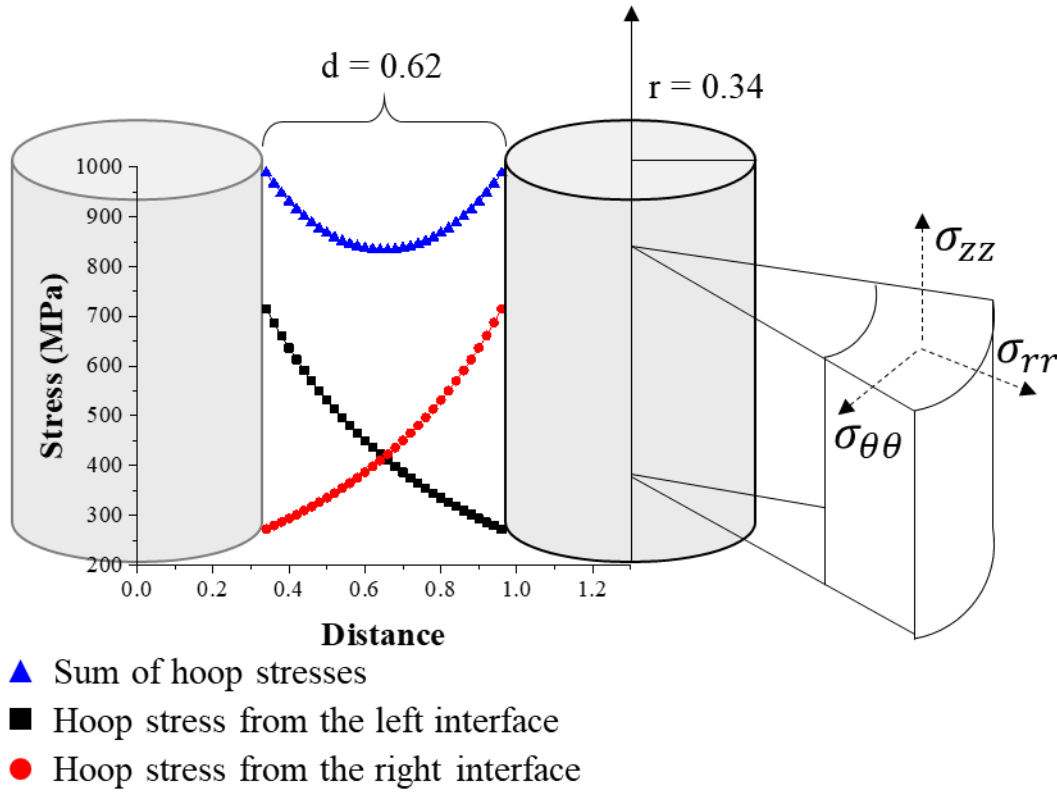


Figure 8. Cylindrical polar coordinates used to describe the stress components. Spatial distribution of hoop stresses in the matrix are plotted in the area between the grain. The maximum calculated hoop stress (710 MPa) is located at the grain-matrix interface and falls off rapidly following the $\frac{1}{r^2}$ relationship. The sum of the stresses, or the effective stress, between the two grains is higher (875-985 MPa) due to the proximity of ZrB_2 rods.

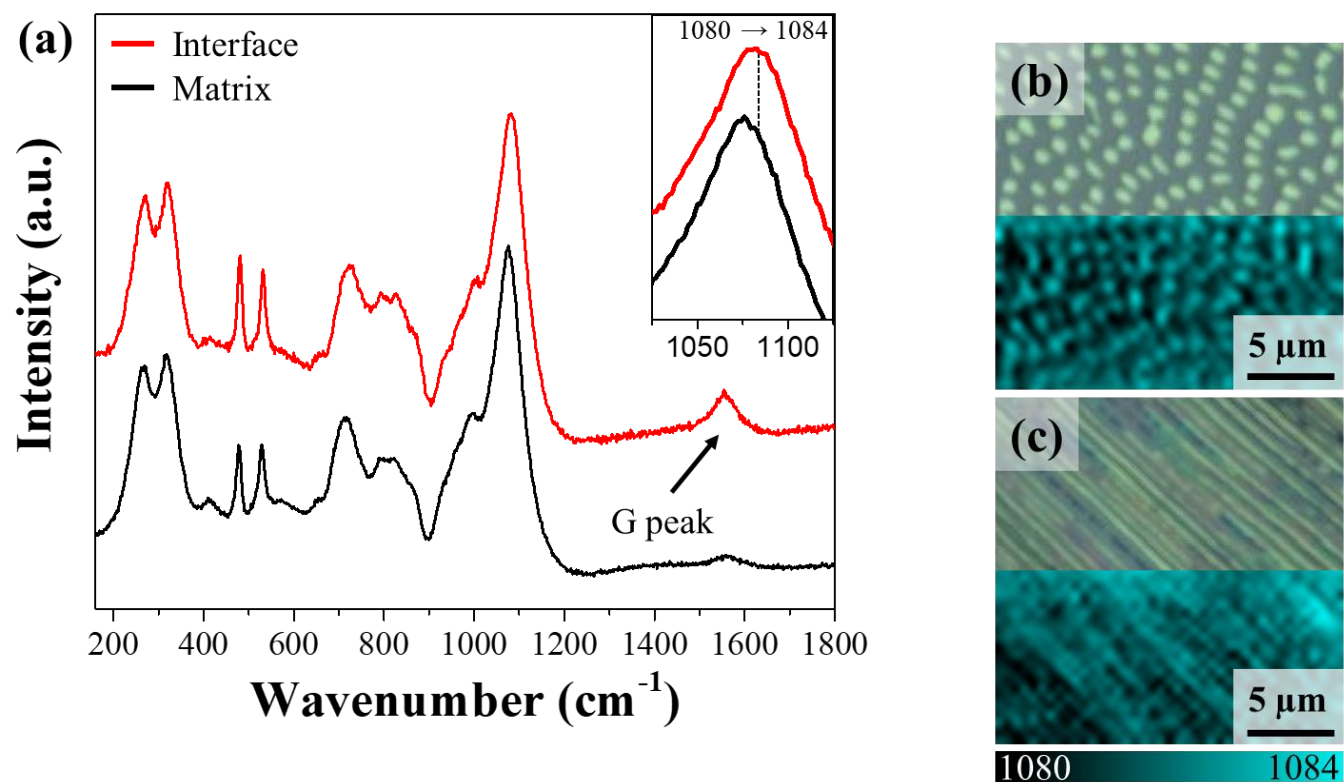


Figure 9. (a) Raman spectra acquired from longitudinal and transverse section showing an upshift near the ZrB_2 regions. Raman stress mapping and the corresponding optical image (b) parallel and (c) perpendicular to the c-axis of the rods.

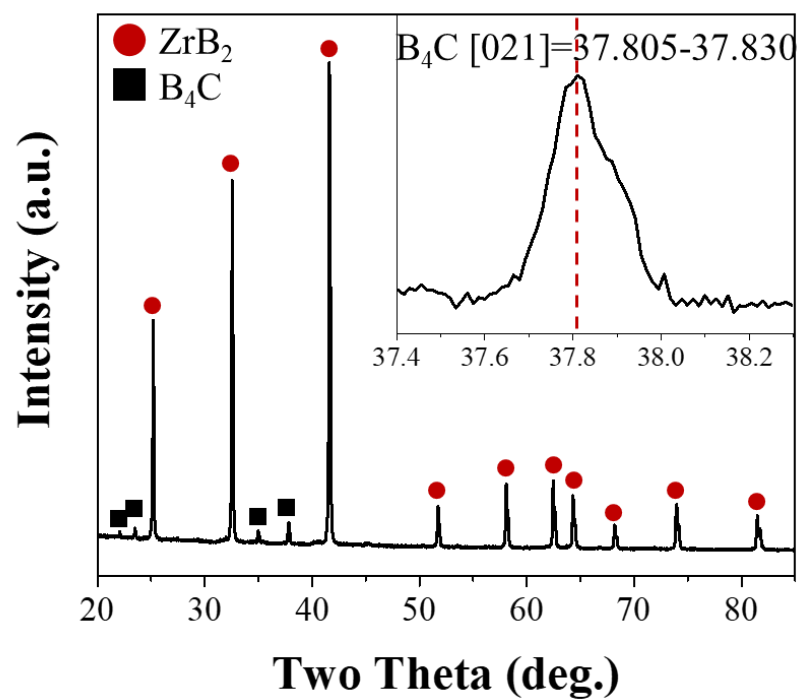
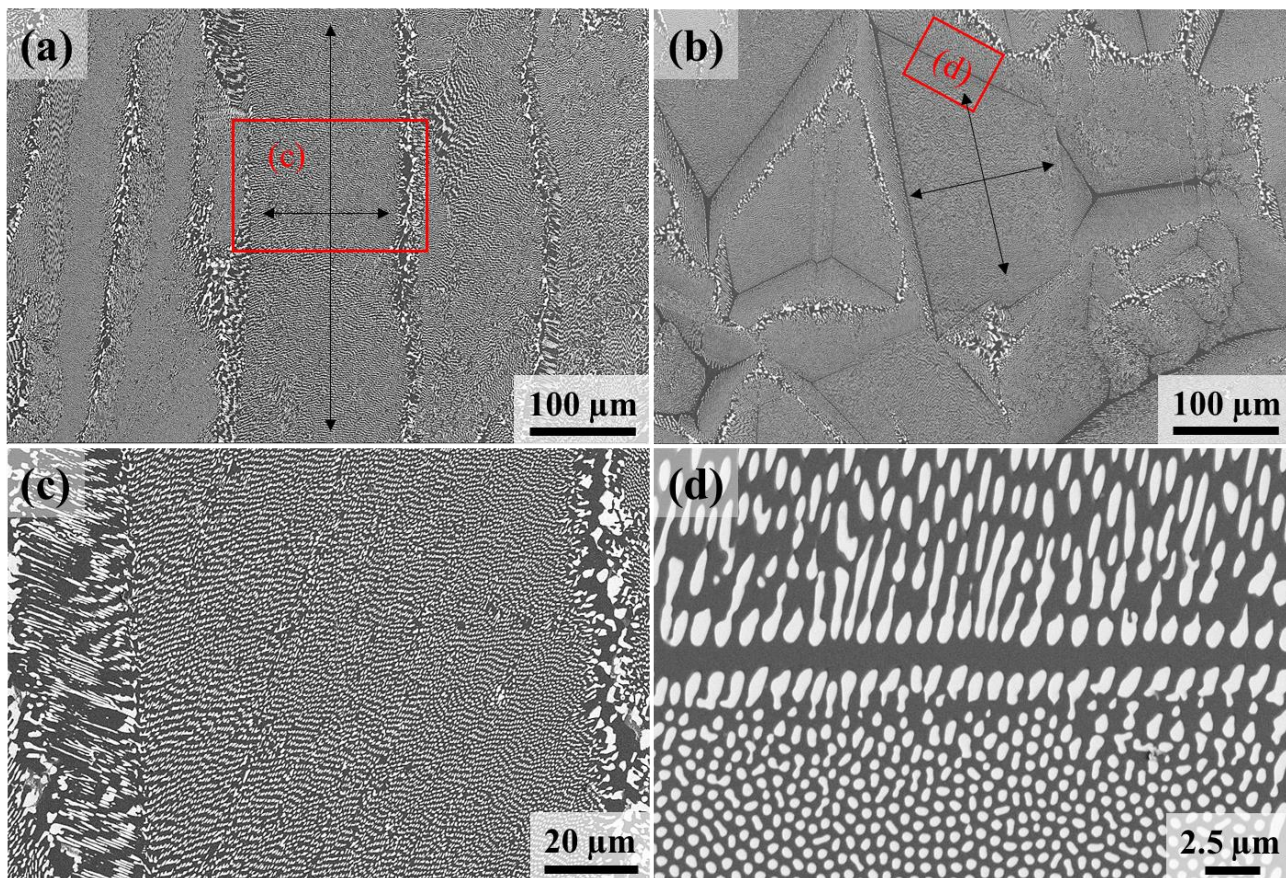
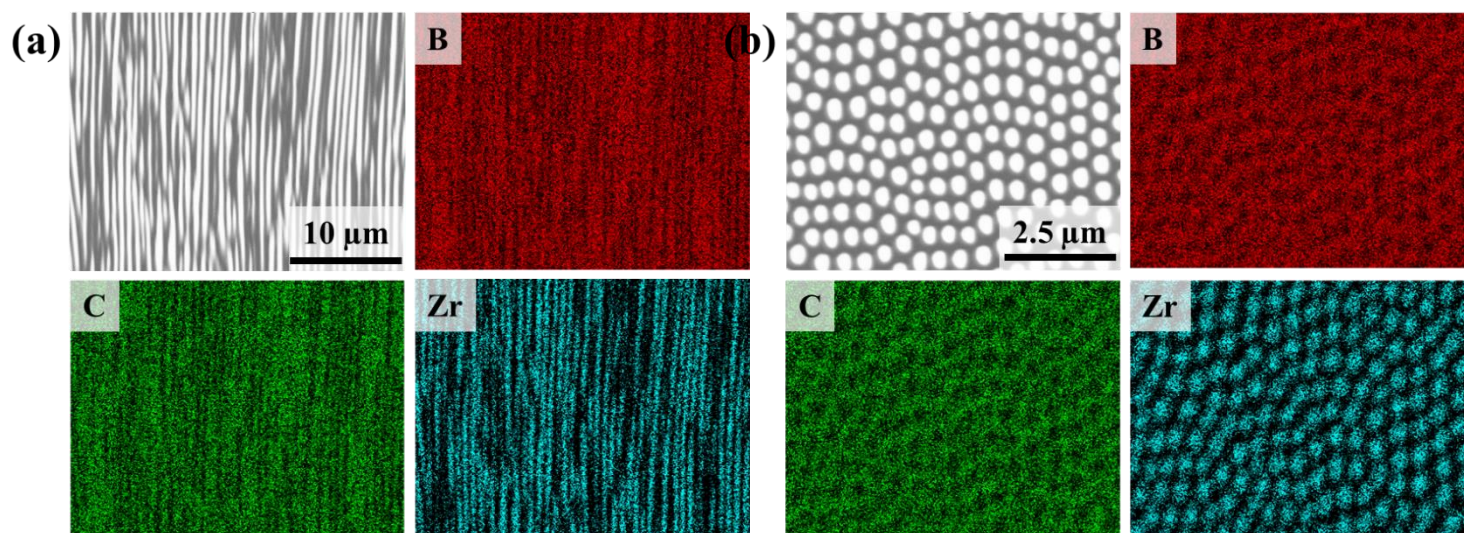


Figure 10. XRD pattern for B_4C - ZrB_2 eutectic composite. The [021] peak position of boron carbide is indexed to be stoichiometric B_4C suggesting no doping occurred.

Supplementary Figures



Supplementary figure 1. SEM images of the (a) longitudinal and (b) latitudinal section of the specimen. The colonies are much longer in height than in width suggesting the overall cooling direction is longitudinal. The morphologies between the colonies (c) and (d) are random, consist of hyper- or hypoeutectic, large agglomerates of ZrB_2 , and pure B_4C .

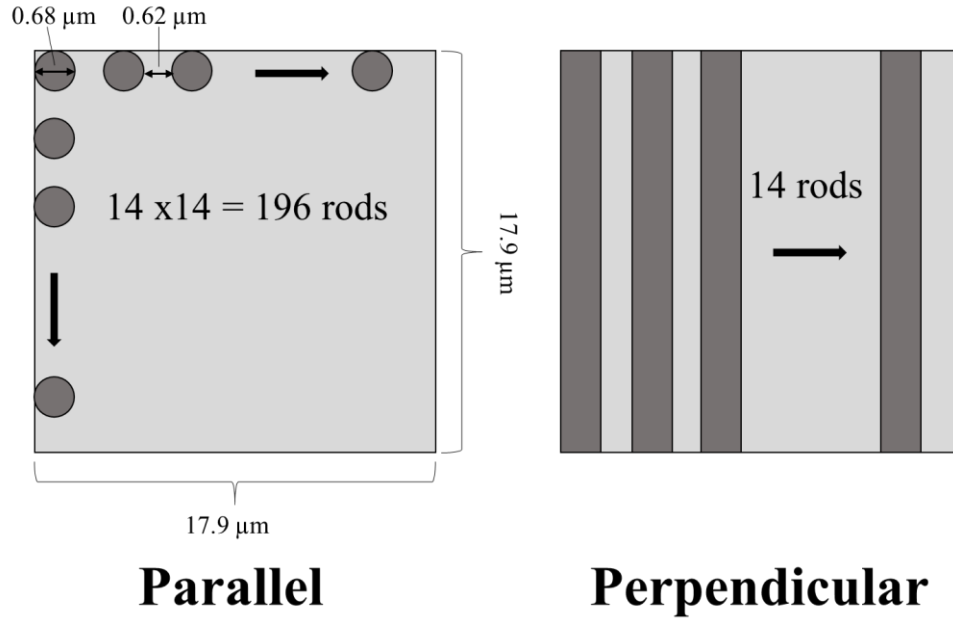


Supplementary figure 2. EDS elemental mapping of the microstructure showing ZrB_2 rods in the B_4C matrix taken parallel (a) and perpendicular (b) to the c-axis of the rods.

Supplementary Information

Area fraction calculation

Since the hardness values were acquired on the well-developed regions, we can assume that the total integrated volume fraction of each constituent phase is constant. However, Vickers indent penetration is shallow at 136° across the opposite facets. Using 9.8N Vickers indent as an example, this implies that the indented volume may not have a consistent volume fraction in both indentation directions. This is evident by examination of area fraction on the cross-section area of the imprints. In the parallel direction, 22.2% of the cross-section is ZrB_2 whereas 53.2% are found on the perpendicular direction. ZrB_2 is considerably softer than B_4C , thus it is likely that simply having more ZrB_2 is the leading cause for the observed hardness anisotropy. Hardness is the ability to resist deformation. When an indenter penetrates beyond the surface, the bulk material is doing the work to stop deformation. Thus, it is important to evaluate the volume fraction of the constituent phases as opposed to area fraction.



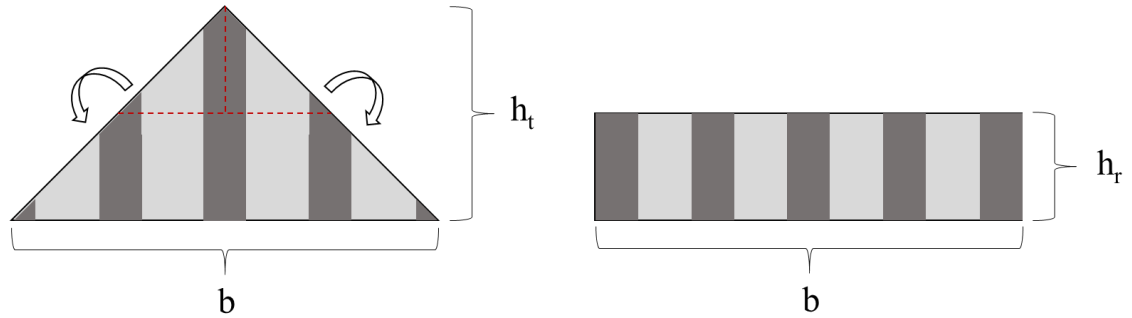
$$\text{Parallel: } \frac{196 \text{ rods} \times \pi r^2}{\text{total area } (17.9 \times 17.9)} = 22.2\% \text{ area}$$

$$\text{Perpendicular: } \frac{14 \text{ rods} \times 0.68 \times 17.9}{\text{total area } (17.9 \times 17.9)} = 53.2\% \text{ area}$$

Model assumptions and deformed volume equivalent

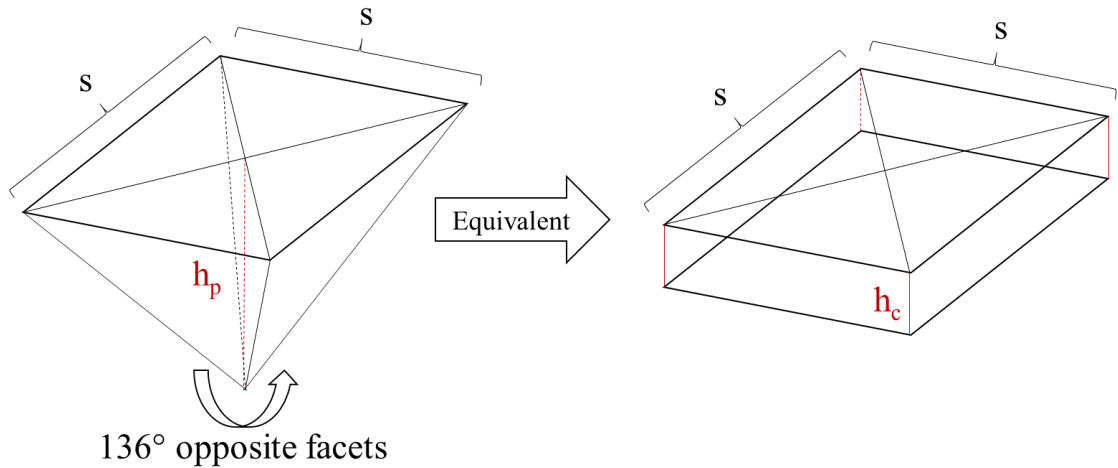
The deformed material volume in this work is defined as the total volume deformed by the indenter. The deformed or the indented volume assumes the geometry of the indenter. For simplicity, this work does not account for the elastic recovery of the material or the pile-up which occurs to accommodate material displacement. This work assumes the indented material exhibits perfect plasticity. This model also does not account for the deformed volume beneath the apparent imprint or the effect fracture has on hardness. The ZrB₂ phase is assumed to be perfect cylinders.

Determining the volume fraction of ZrB_2 within the indented volume can be complicated. A geometric equivalent is made to simplify the approximation. This can be illustrated in the diagram below.



$$A_t = \frac{1}{2}bh_t = bh_r = A_r$$

Where subscript t and r are for triangle and rectangle, A is the area, h is the height, and b is the base for both geometries. The area of a triangle can be redistributed to form a rectangle with the same base while conserving the area fraction of the constituent parts. This analogy can be applied directly to a 3D solid, such as a pyramid, since a triangle is a 2D cross-section of a pyramid.



$$V_p = \frac{1}{3}s^2h_p = s^2h_c = V_c$$

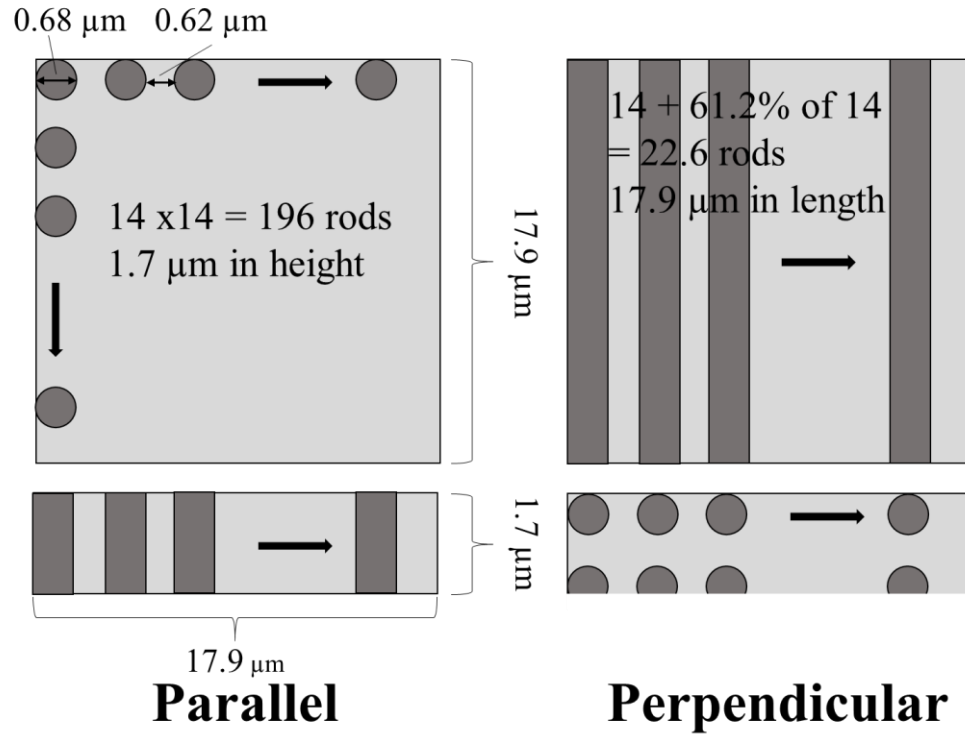
$$\frac{1}{3}h_p = h_c$$

Where subscript p and c are for pyramid and cuboid, V is the volume, h is the height, and s is the side for both geometries.

The volume of a pyramid (Vickers indenter) is precisely 1/3 that of a cuboid with identical side dimensions. In other words, a cuboid with sides identical to the sides of the pyramid but 1/3 the height. The volume fraction of the ZrB_2 is also conserved in this equivalent. This modification dramatically simplifies the approximation. Instead of calculating the volume of cylinders inscribed inside a pyramid, now we are calculating the same volume inside a cuboid. In this case, the height of the cylinder is the height of the cuboid in the parallel direction and the length of the cylinder is the side of the cuboid in the perpendicular direction.

Volume fraction calculation

At 1 kg load (9.8N), the Vickers indenter imprints are on average 25.3 μm across the imprint diagonals. Using the geometry of Vickers indenter, we can estimate that the sides of the imprint are 17.9 μm and have a depth of 5.1 μm . Using the volume equivalent we previously established, this volume is equal to a cuboid with a height of 1.7 μm . ZrB_2 rods inside the volume are displayed below. The dimensions of the rods are values acquired from measuring the length and cross-section.



Using the assumed arrangements above, we can estimate that the volume fraction of the ZrB_2 phases is 22.2% in the parallel direction and 27% in the perpendicular direction. These values represent the deformed volume fraction of each constituent phase during indentation.

CHAPTER 4

Small amount TiB₂ addition into B₄C through sputter deposition and hot pressing

Chawon Hwang^{1,*}, Stephen DiPietro², Kelvin Y. Xie^{3,†}, Qirong Yang¹, Azmi M. Celik¹,
Atta U. Khan¹, Vladislav Domnich¹, Scott Walck⁴, Kevin J. Hemker³, Richard A.
Haber^{1,*}

¹ *Department of Materials Science and Engineering, Rutgers, The State University of
New Jersey, Piscataway, NJ 08854, USA*

² *Exothermics, Inc., Amherst, NH 03031, USA*

³ *Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD
21218, USA*

⁴ *SURVICE Engineering Co., U.S. Army Research Laboratory, Aberdeen Proving
Ground, MD 21005, USA*

[†] Author's present address: *Department of Materials Science and Engineering, Texas
A&M University, College Station, TX 77843, USA*

*Corresponding author e-mail: chawon.hwang@rutgers.edu, rich.haber@rutgers.edu and
address: 607 Taylor Road, Piscataway, NJ 08854, USA. Tel: +1 (848) 445-5924, FAX:
+1 (732) 445-5926

Abstract

A small amount of TiB_2 (< 5 wt%) was added into B_4C through a novel method that combines the use of sputter deposition and hot pressing. Sputter deposition provided more uniform dispersion of TiB_2 grains with smaller grain sizes as compared to the conventional particulate mixing. A small amount of TiB_2 addition demonstrated to be an effective way for improving the fracture behavior and toughness of B_4C while not sacrificing its outstanding lightweight property to a large extent: 2.3 wt% TiB_2 addition brought 15% improvement in indentation fracture toughness while resulting in less than 2% increase in density. The improvement can be attributed to the combination of crack impeding by TiB_2 grains and crack deflection at the B_4C - TiB_2 interfaces. TiB_2 also played as grain growth inhibitor resulting in a slight increase (2%) in Vickers hardness. Another intention of employing sputter deposition was to modify the grain boundary of B_4C ; however, neither formation of Ti-containing phase nor Ti segregation has been observed at grain boundaries likely due to the poor wettability of B_4C .

Keywords: Boron carbide; Titanium diboride; Small amount addition; Sputter deposition; Hot pressing;

Introduction

Boron carbide displays an excellent hardness (29-45 GPa) while being lightweight (density: 2.52 g/cm³).⁽¹⁻⁵⁾ Thus, it has been one of the materials of choice as an armor ceramic for the protection of personnel and vehicles. ⁽¹⁾ Furthermore, it has found a variety of applications such as abrasives for grinding hard materials, wear-resistant components for water-jet cutting, neutron absorbent/detecting materials for nuclear reactors, and thermoelectric materials for thermoelectric energy generation.⁽⁶⁻⁸⁾ However, further widespread application of boron carbide is hindered by its poor fracture behavior and toughness.⁽⁹⁾ It fails catastrophically when subjected to high-velocity impact over its Hugoniot elastic limit (HEL, 17-20 GPa) and shows transgranular fracture mode.^(10, 11)

One of the approaches to improve the fracture behavior and/or the toughness of boron carbide (B₄C) is by adding a reinforcement such as silicon carbide (SiC) and transition metal (group IV) diborides (Me^{IV}B₂, Me is Ti, Zr, and Hf).⁽¹²⁻¹⁶⁾ While the addition of SiC does enhance the toughness of B₄C, it does not necessarily result in a preferred intergranular fracture mode, except when SiC grains have platelet, whisker or fiber morphologies. ^(12, 13) On the other hand, when Me^{IV}B₂ is added, cracks deflect at the reinforcement-matrix interfaces leading to a combination of transgranular and intergranular fracture modes.⁽¹⁴⁻¹⁶⁾

Though the addition of Me^{IV}B₂ improves the fracture behavior and toughness of B₄C, it bears a significant density penalty which nullifies the lightweight property of B₄C. For example, TiB₂, ZrB₂, and HfB₂ have densities of 4.52, 6.08, and 10.5 g/cm³, respectively, compared to B₄C (2.52 g/cm³).^(4, 17) Being the lightest among all Me^{IV}B₂, small amount TiB₂ addition is preferred in search of ways to improve the fracture behavior

and toughness of B_4C . TiB_2 additions between 5 and 88 wt% have been fabricated using the conventional particulate mixing methods such as ball milling, through which the dispersion of TiB_2 particulate in B_4C becomes difficult when the addition amount and particle size of TiB_2 become small.(15, 20, 21)

Here, we investigated the TiB_2 addition of < 5 wt% by applying a novel method that combines the use of sputter deposition and hot pressing. The purpose of this study was to 1) demonstrate the viability of sputter deposition as a means to incorporate TiB_2 into B_4C , 2) identify the efficacy of small amounts of TiB_2 addition for improving the fracture behavior and toughness of B_4C while not causing a significant density penalty, and 3) examine if the sputter deposition of TiB_2 on B_4C powder leads to a modification of grain boundaries.

Materials and Methods

Sputter deposition and sintering processes

B₄C powder (Grade HD 20, D50=0.3-0.6 μm on the data sheet; H.C. Starck, MA, USA) was used as the base powder. To wash off the surface oxide ($\text{H}_3\text{BO}_3/\text{B}_2\text{O}_3$), the base powder was put into a dilute HCl (pH 3.5) for 12-24 h, rinsed with DI water, and put into methanol for 12-24 h.(18) After decanting excess methanol, the powder was introduced as wet into a sputter deposition system. A DC magnetron sputter deposition system coupled with a rotating drum (Balzers BAF 260 chamber and Sierra cathode) was used. After being introduced into the drum, the powder was dried under vacuum for 48 h, followed by a tumble drying at 250°C for 24h, and subjected to RF etching in an argon-helium atmosphere ($\text{Ar-5\%H}_2$). Then, TiB₂ was sputtered onto the powder in argon (Ar) gas using a TiB₂ disk as the sputtering target. The TiB₂ disk was hot pressed using TiB₂ powder (Grade G; H.C. Starck, MA, USA). The sputtering power ranged from 3 to 14 kWh. The sputter coated powder was stored either in air or in an inert environment. For the inert environment storing, the coated powder was put in hexane and stored in a glove box under Ar gas. B₄C/TiB₂ particulate mixture was prepared through wet ball milling using SiC balls and ethanol media (TiB₂ powder: H.C. Starck Grade F, D50=1.5-2.5 μm on the data sheet). The mixture was mixed for 2 hours followed by drying at 100°C. The sputter deposited powder and particulate mixture were filled into a graphite die (25x45 mm) and sintered using a hot press (Thermal Technology LLC, CA, USA) at 1975-2100°C for 15-60 min under a uniaxial pressure of 50 MPa in Ar gas. The sintering profile consists of a hold step at 1500°C for 30 min under 20 MPa before reaching the sintering condition at a heating rate of 5°C/min. The inert-environment stored powder was filled into a graphite die as wet

and loaded into the hot press chamber to mitigate the oxidation of the powder. As a comparison sample, the un-coated B₄C powder was also sintered at the constant conditions.

Characterizations and mechanical properties evaluation

Density measurements were carried out using the Archimedes method. Specimens were sectioned into smaller pieces with diamond coated blades to proceed with the following analyses, observations, and measurements. XRD patterns were obtained on crushed powder using the X'Pert Pro Diffractometer (PANalytical, Netherlands) at 45kV and 40 mA with Cu $K\alpha$ ($\lambda=1.540598$ Å) radiation at a scanning rate of 0.04°/min. The peak positions of XRD patterns were corrected using the silicon standard (SRM 640e; NIST). Phase identification and quantification (Rietveld refinement) were performed using the JADE program (Jade 9; Materials Data, Inc., CA, USA). Relative sintering density was calculated by dividing the measured density by theoretical density, which is obtained from the phase quantification results and the rule of mixtures. SEM observation was performed on ion milled cross-sections (IM 4000+ ion milling system; Hitachi America, Ltd., NY, USA) using SIGMA FE-SEM (ZEISS, Germany). Bright-field transmission electron microscopy (TEM), high angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDX) were performed on the mechanically polished then Ar ion beam thinned specimens using a JEOL 2100F equipped with an Oxford Inca XEDS system. A Gatan Tridiem GIF electron energy loss spectroscopy (EELS) detector was used to identify the bonding characteristics of the surface coating. The grain size was measured using an image analysis software (Lince 2.4.2, NAW, Germany) according to the linear intercept method (ASTM E112-13). Vickers hardness (H_v) measurements were performed on polished cross-sections using an M400-G3 microhardness tester (LECO, MI,

USA) following ASTM C1327-15 (1 kgf, 10 sec dwell time). Indentation fracture toughness (K_{IC}) was calculated using the equation, $K_{IC} = 0.018 \times (E/H)^{0.5}(Pc^{-1.5})$, where E is Young's modulus in GPa, H is Vickers hardness in GPa, P is load in Newton (9.81 N), and c is the median crack length from the center of the indent to crack tip in meters.(19) The values of H_v and indentation K_{IC} are averaged from ten reliable indentations.

Results and Discussion

TiB₂ sputter-deposited B₄C powder

Fig. 1a shows the XRD pattern of sputter-deposited B₄C powder as compared to the as-received. The as-received B₄C powder contained surface oxide (boric acid, H₃BO₃) and free carbon (graphitic) as additional phases. After the sputter deposition, it showed an additional weak and broad peak around 45° two thetas, which matches to TiB₂ or Ti. TEM coupled with EDX was employed to confirm the presence of a surface coating on the B₄C powder (Fig. 1b). The elemental maps revealed the presence of Ti that continuously covers B₄C powders, indicating that a surface coating containing Ti was formed on B₄C powders. The thickness of the surface coating was estimated to be several nanometers according to the high magnification elemental analysis focused on the edge of powders (Supplementary Fig. 1). It should be noted that oxygen was also detected from the surface coating. The origin and the treatment of the oxygen are discussed later.

The sintered body of sputter-deposited B₄C powder and comparison to the conventional particulate mixing method

The sputter-deposited powder was hot-pressed at 2100°C for 60 min under 50 MPa in Ar gas, of which the XRD pattern and SEM micrograph are shown in Fig. 2 (2a and 2b). It is evident by the XRD pattern that TiB₂ is formed during sintering. Phase quantification (Rietveld refinement) reveals 2.3 wt% of TiB₂ was incorporated into the composite. As a comparison, a B₄C-TiB₂ composite was prepared by ball milling B₄C/TiB₂ particulate mixture and hot pressing at the same conditions (Fig. 2c). For consistency, the TiB₂ amount (2.4 wt%) was designed to be close to that of the sputter deposition sample. The sputter deposition sample (Fig. 2b) showed more uniform dispersion of TiB₂ with finer particle

size ($0.47 \pm 0.05 \mu\text{m}$) compared to the ball milling sample ($1.78 \pm 0.2 \mu\text{m}$; Fig. 2c). When mechanical properties compared, no significant differences were observed between the sputter deposition sample and the ball milling sample: indentation fracture toughness, 2.54 ± 0.14 vs $2.55 \pm 0.09 \text{ MPa}\cdot\text{m}^{1/2}$; hardness, 30.5 ± 1.1 vs $30.3 \pm 0.9 \text{ GPa}$. The above results indicate that sputter deposition can serve as a route to add a small amount of TiB_2 into B_4C .

Effect of small amount TiB_2 addition

To investigate the effect of small amount TiB_2 addition on the fracture behavior, toughness, and density of B_4C , variations in TiB_2 addition were made by adjusting sputtering power. Fig. 3a shows the crack propagation behavior observed. Cracks frequently deflect at the B_4C - TiB_2 interfaces, likely due to the residual stress which is estimated to be 480-660 MPa (See the supplementary information Calculation of the residual stress). Fig. 3b shows the indentation fracture toughness and Vickers hardness as a function of TiB_2 addition amount. TiB_2 amount was analyzed using Rietveld refinement of XRD pattern (the reliability factors were less than 5%). TiB_2 addition of 2 wt% and more brought improvements in indentation fracture toughness (for 2.3 wt% TiB_2 , 15% improvement compared to monolithic B_4C). The improvements can be attributed to the combination of crack impeding by TiB_2 grains and crack deflections at the B_4C - TiB_2 interface. TiB_2 addition also resulted in a slight increase in hardness within the margins of standard deviations (for 2.3 wt% TiB_2 , 2% improvement). We attribute the increase in hardness to the decrease in grain size as shown in Fig. 7c and 7d. TiB_2 -added B_4C (7c) showed smaller grains ($730 \pm 60 \text{ nm}$) compared to monolithic B_4C ($930 \pm 90 \text{ nm}$). TiB_2 played as a grain growth inhibitor as well as reinforcement for B_4C . The above results suggest that a small amount TiB_2 addition is an effective way to improve the fracture

behavior and toughness of B_4C while not sacrificing its outstanding lightweight property to a large extent. 2.3 wt% TiB_2 addition showed a 15% improvement in indentation fracture toughness while resulting in a $< 2\%$ increase in density.

Another purpose of this study was to examine the effect of TiB_2 addition through sputter deposition on the grain boundary of B_4C . Fig. 4 shows TEM micrographs and Ti-elemental maps of TiB_2 -added B_4C through sputter deposition and hot pressing. Neither formation of the Ti-containing phase nor Ti segregation at grain boundary was observed. This result indicates that the surface coating formed by sputter deposition does not stay at the grain boundary during sintering likely due to the poor wettability of B_4C .(20)

Challenges in obtaining dense bodies of TiB_2 sputter-deposited B_4C

We encountered several technical challenges while fabricating B_4C - TiB_2 composites using sputter deposition and hot pressing. The oxygen-enriched layer was found on the surface of the sputter-deposited powder (Fig. 1b). The EELS spectrum of the surface coating showed distinctive L_2 and L_3 edges of Ti that are close to what is reported for TiO_2 (Supplementary Fig. 2). (21, 22) These results suggest that sputter-deposited TiB_2 surface coating has oxidized to TiO_2 and H_3BO_3 upon exposure to air. The presence of oxides typically hinders the densification of B_4C by contributing to both the evaporation-condensation process and the formation of closed pores. (23-25) Thus, the surface oxide of base B_4C powder was washed off before sputter deposition and the sputter-deposited powder was stored in an inert environment. The thus obtained powder showed reduced oxygen content: O:Ti changed from 3.6:1 to 2:1 (Supplementary Fig. 3). The fully dense microstructure shown in Fig. 2b was achieved after reducing the oxygen content in the

surface coating. The microstructure of the sintered body before reducing the oxygen content can be found in Supplementary Fig. 4.

Summary

In search of ways to improve the fracture behavior and toughness of B₄C while not sacrificing its outstanding lightweight property to a large extent, a small amount TiB₂ addition (< 5 wt%) was investigated through sputter deposition combined with hot pressing. According to crystallographic and microstructural characterizations and mechanical properties evaluation, the following conclusions have been made.

- a) Sputter deposition can serve as a route to add small amount TiB₂ into B₄C, showing more uniform dispersion of TiB₂ grains with smaller sizes ($0.47 \pm 0.05 \mu\text{m}$) as compared to the conventional ball milling ($1.78 \pm 0.2 \mu\text{m}$). Dense bodies of TiB₂ sputter-deposited B₄C have been achieved by reducing the oxygen content in the surface coating by means of washing base B₄C powder and storing the sputter-deposited powder in an inert environment.
- b) 2.3 wt% TiB₂ addition showed a 15% improvement in indentation fracture toughness while resulting in less than 2% increase in density. The improvement can be attributed to the combination of crack impeding by TiB₂ grains and crack deflection at the B₄C-TiB₂ interface. TiB₂ also played as a grain growth inhibitor resulting in a slight increase (2%) in Vickers hardness.
- c) No formation of the Ti-containing phase or Ti segregation at grain boundary has been observed, indicating that the surface coating formed by sputter deposition does not stay at the grain boundary during sintering likely due to the poor wettability of B₄C.

Acknowledgments

This study was sponsored by the Defense Advanced Research Projects Agency under Grant No. W31P4Q-13-1-0001 and the Army Research Laboratory under Cooperative Agreement No. W911NF-12-2-0022 with additional support from the National Science Foundation I/UCRC Award No.1540027.

References

1. Lionel VG, F. SR, James C. Flexural Strength, Fracture Toughness, and Hardness of Silicon Carbide and Boron Carbide Armor Ceramics. *International Journal of Applied Ceramic Technology*. 2010;7(5):643-51.
2. Solozhenko VL, Kurakevych OO, Andrault D, Le Godec Y, Mezouar M. Ultimate metastable solubility of boron in diamond: synthesis of superhard diamondlike BC₅. *Physical review letters*. 2009;102(1):015506.
3. Niihara K, Nakahira A, Hirai T. The effect of stoichiometry on mechanical properties of boron carbide. *Journal of the American Ceramic Society*. 1984;67(1):C-13-C-4.
4. Domnich V, Reynaud S, Haber RA, Manish C. Boron Carbide: Structure, Properties, and Stability under Stress. *Journal of the American Ceramic Society*. 2011;94(11):3605-28.
5. Ridgway RR. Boron Carbide A New Crystalline Abrasive and Wear-Resisting Product. *Transactions of The Electrochemical Society*. 1934;66(1):117-33.
6. Thévenot F. Boron carbide - A comprehensive review. *Journal of the European Ceramic Society*. 1990;6(4):205-25.
7. Suri AK, Subramanian C, Sonber JK, Murthy TSRC. Synthesis and consolidation of boron carbide: a review. *International Materials Reviews*. 2010;55(1):4-40.
8. Innocent J-L, Portehault D, Gouget G, Maruyama S, Ohkubo I, Mori T. Thermoelectric properties of boron carbide/HfB₂ composites. *Materials for Renewable and Sustainable Energy*. 2017;6(2):6.
9. Khan AU, Domnich V, Haber RA. Boron carbide-based armors: problems and possible solutions. *American Ceramic Society Bulletin*. 2017;96(6):30-5.
10. Grady DE. Shock-wave strength properties of boron carbide and silicon carbide. *Le Journal de Physique IV*. 1994;4(C8):C8-385-C8-91.
11. Roy T, Subramanian C, Suri A. Pressureless sintering of boron carbide. *Ceramics international*. 2006;32(3):227-33.
12. Dariel MP, Frage N. Reaction bonded boron carbide: recent developments. *Advances in Applied Ceramics*. 2012;111(5-6):301-10.
13. Zhang Z, Du X, Wang W, Fu Z, Wang H. Preparation of B₄C–SiC composite ceramics through hot pressing assisted by mechanical alloying. *International journal of refractory metals and hard materials*. 2013;41:270-5.
14. Huang SG, Vanmeensel K, Malek OJA, Van der Biest O, Vleugels J. Microstructure and mechanical properties of pulsed electric current sintered B₄C–TiB₂ composites. *Materials Science and Engineering: A*. 2011;528(3):1302-9.

15. Wenbo H, Jiaying G, Jihong Z, Jiliang Y. Microstructure and properties of B₄C-ZrB₂ ceramic composites. *Int J Eng Innov Technol*. 2013;3(1):163-6.
16. Sairam K, Sonber J, Murthy TC, Subramanian C, Hubli R, Suri A. Development of B₄C–HfB₂ composites by reaction hot pressing. *International Journal of Refractory Metals and Hard Materials*. 2012;35:32-40.
17. Cotton J. Ultra-high-temperature ceramics. *Advanced Materials & Processes*. 2010;168(6):26-8.
18. Hwang C, Yang Q, Xiang S, Domnich V, Khan AU, Xie KY, et al. Fabrication of dense B₄C-preceramic polymer derived SiC composite. *Journal of the European Ceramic Society*. 2019;39(4):718-25.
19. Lee H, Speyer RF. Hardness and Fracture Toughness of Pressureless-Sintered Boron Carbide (B₄C). *Journal of the American Ceramic Society*. 2002;85(5):1291-3.
20. Manning JR. CR, Gurganus TB. Wetting of Binary Aluminum Alloys in Contact with Be, B₄C, and Graphite. *Journal of the American Ceramic Society*. 1969;52(3):115-8.
21. Tsai C-H, Chen S-Y, Song J-M, Gloter A. Spontaneous growth of ultra-thin titanium oxides shell on Ag nanowires: an electron energy loss spectroscopy observation. *Chemical Communications*. 2015;51(94):16825-8.
22. Huang C-N, Bow J-S, Zheng Y, Chen S-Y, Ho N, Shen P. Nonstoichiometric titanium oxides via pulsed laser ablation in water. *Nanoscale research letters*. 2010;5(6):972.
23. Dole SL, Prochazka S, Doremus RH. Microstructural Coarsening During Sintering of Boron Carbide. *Journal of the American Ceramic Society*. 1989;72(6):958-66.
24. Lee H, Speyer RF. Pressureless sintering of boron carbide. *Journal of the American Ceramic Society*. 2003;86(9):1468-73.
25. Kim KH, Chae JH, Park JS, Ahn JP, Shim KB. Sintering behavior and mechanical properties of B₄C ceramics fabricated by spark plasma sintering. *Journal of Ceramic Processing Research*. 2009;10(6):716-20.

Figures

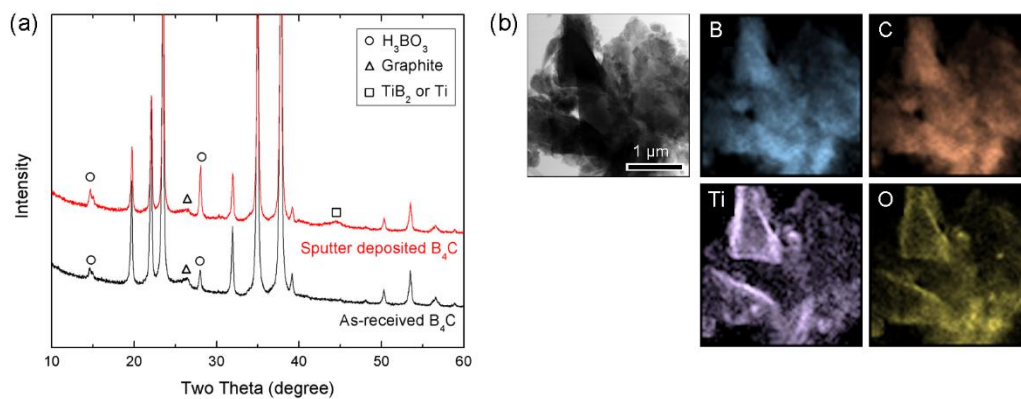


Fig. 1. (a) XRD pattern of TiB₂ sputter-deposited B₄C powder as compared to as-received. (b) TEM micrograph and corresponding elemental maps of sputter-deposited powder.

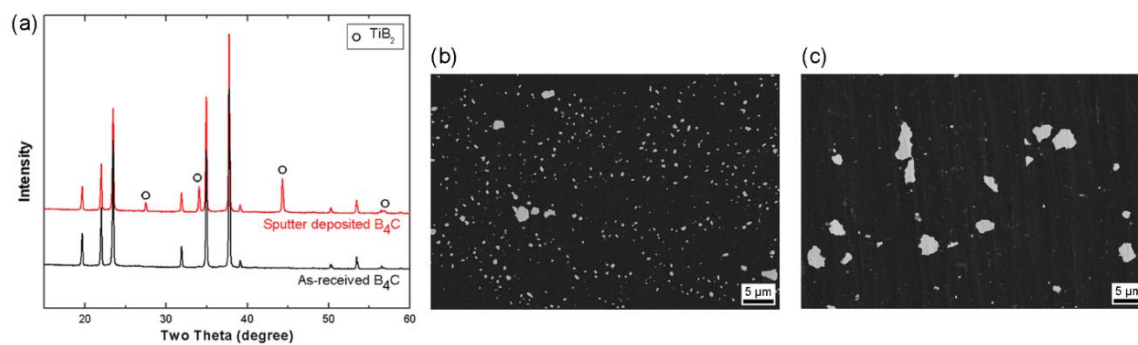


Fig. 2. (a) XRD pattern of the sintered body of TiB₂ sputter-deposited B₄C as compared to that of as-received B₄C. (b) SEM micrograph of the sintered body (sintering conditions: 2100°C for 60 min under 50 MPa). (c) B₄C-TiB₂ prepared through conventional particulate mixing (sintering conditions: 2100°C for 60 min under 50 MPa).

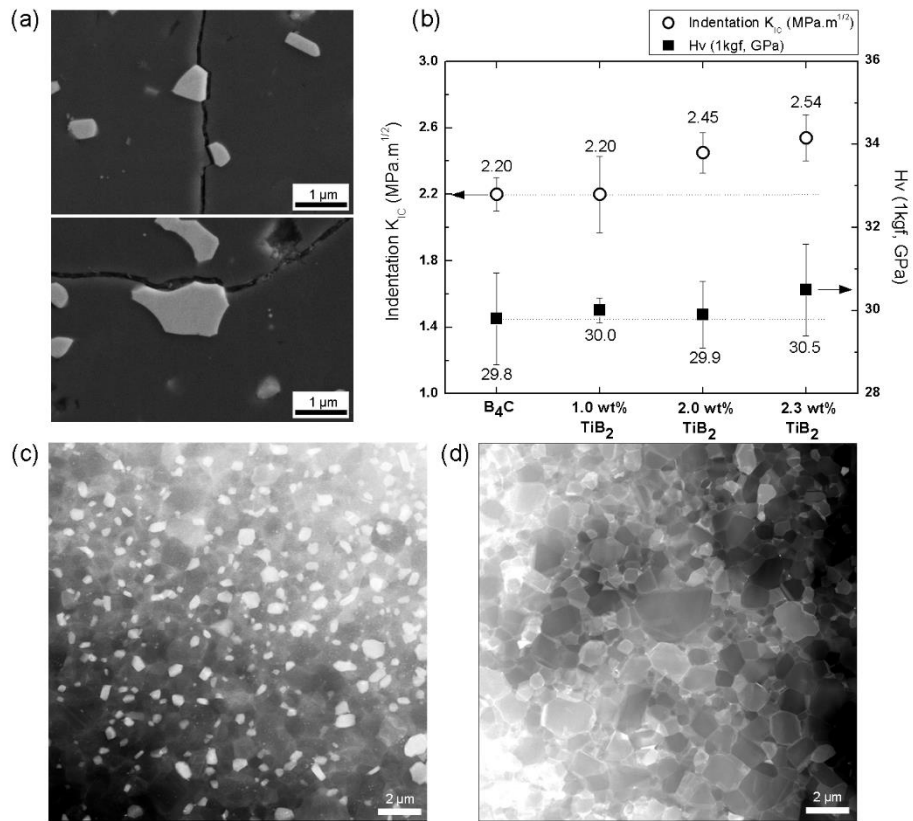


Fig. 3. Effect of small amount TiB₂ addition into B₄C on (a) the crack propagation behavior and (b) the indentation fracture toughness and Vickers hardness. (c) and (d) show TEM micrographs of TiB₂-added B₄C (TiB₂ addition: 2.3 wt%) and (d) Monolithic B₄C, respectively. The bright phase in (c) is TiB₂.

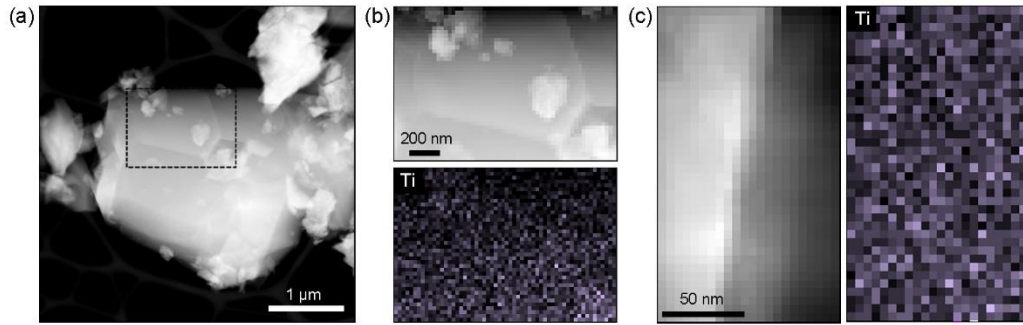
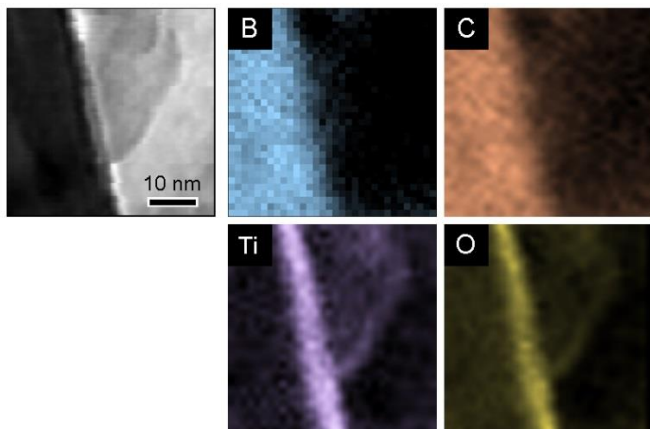
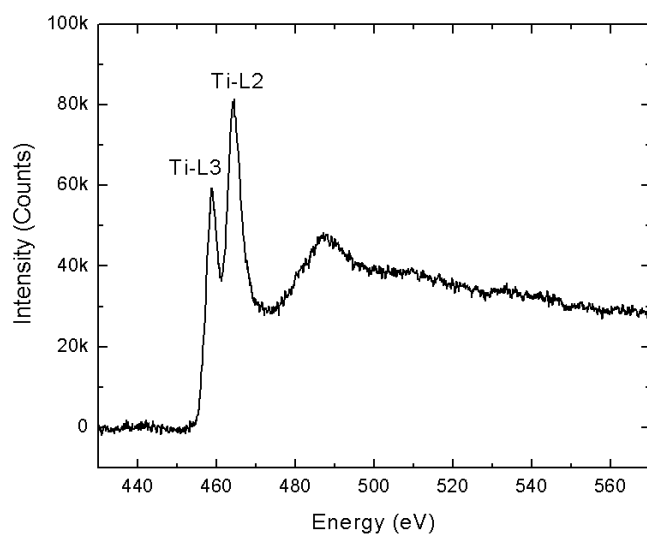


Fig. 4. TEM micrographs and Ti-elemental maps focusing on grain boundaries of TiB_2 added B_4C through sputter deposition and hot pressing. (a) TEM micrograph of the sintered body. (b) the area marked in (a) and corresponding Ti-elemental map, which shows a whole grain of B_4C . (c) Zoomed-in grain boundary and corresponding Ti-elemental map.

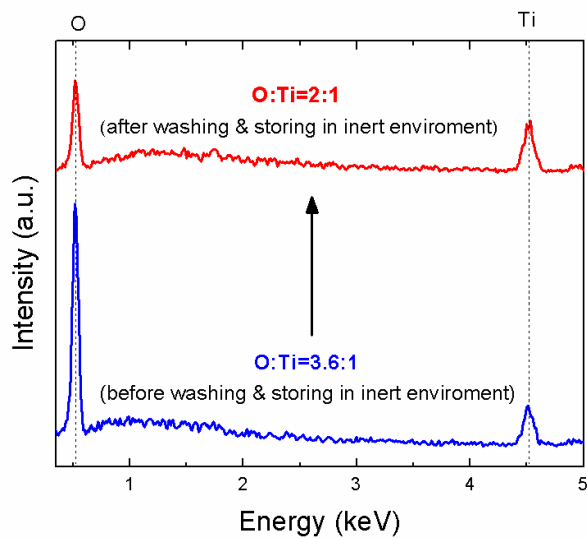
Supplementary Figures



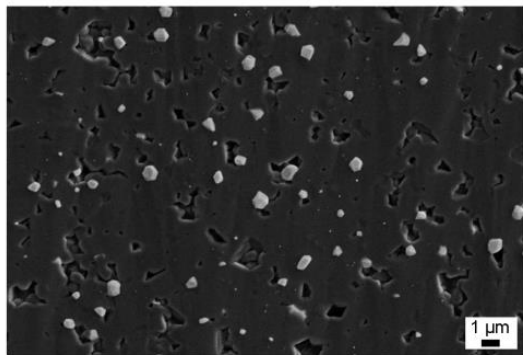
Supplementary Figure 1. TEM micrograph and corresponding elemental maps of sputter-deposited powder focusing on the surface coating formed on B_4C powder.



Supplementary Figure 2. EELS spectrum obtained from the surface coating on the B₄C powder after sputter deposition.



Supplementary Figure 3. EDX spectra obtained from the sputter-deposited powder before (blue) and after (red) washing the base powder and storing the sputter-deposited powder in an inert environment. The spectra were taken using EDX spectroscopy equipped in FE-SEM.



Supplementary Figure 4. The microstructure of the sintered body of sputter-deposited B₄C powder before reducing the oxygen content in the surface coating (sintering conditions: 2100°C for 60 min under 50 MPa).

Supplementary Information

Calculation of the residual stress

The residual stress at the B₄C-TiB₂ interface using the following equation. (1)

$$\sigma_m = -\frac{1}{2} \times \frac{(\alpha_p - \alpha_m) \times \Delta T}{\left[\frac{(1 + \nu_m)}{2E_m} \right] + \left[\frac{(1 - 2\nu_p)}{E_p} \right]}$$

where the subscripts *m* and *p* refer to the matrix and particulate, respectively, α is the thermal expansion coefficient, ΔT is the temperature range over which stresses are not relieved by a diffusive process, ν is the Poisson's ratio, and E is Young's modulus. By taking $7.4 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ and $4.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for α_p (TiB₂)(2) and α_m (B₄C)(3), 0.108 and 0.18 for ν_p (TiB₂)(2) and ν_m (B₄C)(4), 565 GPa and 430 GPa for E_p (TiB₂)(2) and E_m (B₄C)(5), one finds that for $\Delta T = 800 \sim 1000^\circ\text{C}$ compressive residual stress between 480-600 MPa can develop in the B₄C matrix around TiB₂ grains. The values are close to that for SiC-TiC composite (500 MPa for $\Delta T = 1000^\circ\text{C}$), which shows crack deflections at the interface due to residual stress. (1)

References

1. Wei GC, Becher PF. Improvements in mechanical properties in SiC by the addition of TiC particles. *Journal of the American Ceramic Society*. 1984;67(8):571-4.
2. Munro RG. Material properties of titanium diboride. *Journal of Research of the National Institute of Standards and Technology*. 2000;105(5):709.
3. Ridgway RR. Boron Carbide A New Crystalline Abrasive and Wear-Resisting Product. *Transactions of The Electrochemical Society*. 1934;66(1):117-33.
4. Thévenot F. Boron carbide - A comprehensive review. *Journal of the European Ceramic Society*. 1990;6(4):205-25.

5. Xie KY, Kuwelkar K, Haber RA, LaSalvia JC, Hemker KJ. Microstructural Characterization of a Commercial Hot-Pressed Boron Carbide Armor Plate. *Journal of the American Ceramic Society*. 2016;99(8):2834-41.

CHAPTER 5

Fabrication and Characterization of Arc Melted Si/B Co-doped Boron Carbide

Qirong Yang¹, Chawon Hwang^{1,*}, Christopher J. Marvel², Ankur Chauhan³, Vladislav Domnich¹, Atta U. Khan¹, Jerry C. LaSalvia⁴, Martin P. Harmer², Kevin J. Hemker³, and Richard A. Haber^{1,*}

¹Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA

²Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA

³Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD 21218, USA

⁴Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

*Corresponding authors' emails: ch596@soe.rutgers.edu & rich.haber@rutgers.edu

Address: 607 Taylor Road, Piscataway, NJ 08854, USA. Tel: +1(848) 445-5924, Fax: +1(732) 445-5926.

Abstract

Boron carbide undergoes stress-induced amorphization when subjected to large non-hydrostatic stresses that exceed its elastic limit. This has been proposed as the source for the abrupt loss of shear strength in boron carbide which limits its engineering applications. Si/B co-doping was suggested as one of the means to suppress stress-induced amorphization but this has not been experimentally verified. Here, by utilizing arc melting, we prepared Si/B co-doped boron carbide with increased Si content as compared to conventional methods. Through Raman analysis in conjunction with an indentation and elemental analyses based on SEM and STEM (ζ -factor microanalysis), it is suggested that Si/B co-doping is a promising avenue for suppressing stress-induced amorphization. A comprehensive characterization of microstructure, chemistry, and structural change of boron carbide as a result of Si/B co-doping was elucidated.

Keywords: Boron carbide, Arc melting, Si/B co-doping, Stress-induced amorphization, Transmission electron microscopy

Introduction

The remarkably high hardness (~ 40 GPa) and low density (2.52 g/cm^3) of boron carbide are rooted in its strong covalent bonds and crystal structure. It is comprised of 12-atom icosahedra located at the vertices of a rhombohedral crystal ($R\bar{3}m$ space group) and a 3-atom linear chain along the longest diagonal [1-5]. Although boron carbide is most notably used as a armor ceramic, it suffers from localized stress-induced amorphization during high impact events which limit its effectiveness against high-velocity projectiles [6, 7]. Stress-induced amorphization in boron carbide has been described as the inhomogeneous loss of crystalline order in localized zones scattered within a crystalline volume, forming nano-scale bands with large aspect ratios [6, 8, 9]. Experimentally, stress-induced amorphization has been observed in high-pressure events including ballistic impacts [6], laser shock compression [10], diamond anvil cell compression [11-13], mechanical scratching [9, 14], as well as dynamic and quasi-static indentations [15-17].

The mechanism of stress-induced amorphization in boron carbide has been extensively modeled by numerous studies [7, 12, 18-21]. This solid-state transition is thought to be initiated by the bending of the 3-atom chain [12, 20-22]. An et al. [7] found that breaking of the intra-icosahedra initiates the failure process but also emphasized that the bending of the 3-atom chain created a strong covalent bond between the center C atom of the chain and B atom in the icosahedra. The bond distorted the icosahedra, resulting in irreversible structural damage and the total decomposition. Using laser-assisted atom probe tomography, Xie et al. [23] demonstrated that the inter-icosahedra bonds are the weakest, suggesting breakage in the icosahedra could be a source for triggering amorphization. Using the Gibbs free-energy approach, Fanchini et al. [24] found that boron carbide

composed of $B_{11}C$ icosahedra and C-B-C chain denoted as $B_{11}C(CBC)$, can subsequently transform into $B_{12}(CCC)$ through atom swapping at elevated pressures. The $B_{12}(CCC)$ polymorph further degenerates into alternating layers of graphite and B_{12} icosahedra which is what the authors of the study presume an amorphous band contains. Localized melting has also been suggested as the origin of the amorphization [25]. Mechanical scratch tests performed on boron carbide submerged in water (a medium to remove heat) resulted in less amorphization, suggesting a rise in temperature played a role in facilitating amorphization. Based on strain energy to thermal energy relationship, Zhao et al. [10] estimated that localized melting for boron carbide is plausible at elevated pressures. Awasthi et al. [26] further added that defects and inhomogeneity present in the material act as sources for stress-concentrations, causing a spike in local pressure which leads to localized melting.

Despite having mixed views on the origin of amorphization, atomistic fine-tuning the structure and chemistry of boron carbide remain the most promising pathways for the mitigation of stress-induced amorphization. Using density functional theory (DFT) simulation, Fanchini et al. [27] proposed that replacing the C atom in the icosahedra with a Si atom can lower the abundance of $B_{12}(CCC)$ polymorph, believed to be the most susceptible to the loss of crystallinity, and thus minimize amorphization. An et al. [18] suggested, based on DFT simulation, that amorphization could be prevented by replacing the C-B-C chain with a Si-Si pair. However, Rietveld refinement of XRD data for an experimentally prepared Si-doped boron carbide indicated that Si occupies an interstitial site adjacent to the vacancy in the $X-\square-X$ chain ($\square$ for vacancy, $X = B$ or C), resulting in a kinked chain [28]. Based on this finding, Khan et al. [28] hypothesized that vacancy sites are the weak points that facilitate amorphization [28]. Computational work by Taylor [29]

also suggested that the presence of vacancies lowers the energy barrier for the solid-state phase transition, e.g. amorphization. Khan et al. [28] further asserted that the benefit of substituting the vacancy with Si is two-fold: (1) Si reinforces the structure by creating new covalent bonds with the chain ends and nearby icosahedra and (2) Si donates an electron to stabilize the electron-deficient icosahedra. Given the prevalence of vacancies in boron carbide, up to 25% across its stoichiometric range [30], it is desirable to incorporate as much Si into the structure as possible.

There are numerous ways Si can be incorporated into the structure of boron carbide, forming a solid solution generally referred to as $B_{12}(B,C,Si)_3$. Reaction bonded boron carbide with silicon has been reported to form a boron carbide core and Si-doped rim structure [31, 32]. Si-doping can also be achieved using high-energy ball-milling with boron carbide and Si powders [33] and through growing nanorods via a solid-liquid-solid process [34]. These processes achieve 1.2 and 0.38 at.% of Si in boron carbide, respectively. Proctor et al. [13] produced 0.6-1.6 at.% Si-doped boron carbide in the bulk by first growing the Si-doped nanorods and then consolidating them using spark plasma sintering. Moreover, they were the first to demonstrate that Si-doped boron carbide bulk can withstand higher pressure than undoped boron carbide before experiencing amorphization through a diamond anvil cell (DAC) compression study [13]. The aforementioned studies, however, have a low B/C ratio by design (4/1) which does not allow for high Si content in $B_{12}(B,C,Si)_3$. The experimental phase diagram suggests that Si content is the highest in $B_{12}(B,C,Si)_3$ when the B/C ratio is approximately 6.5 and diminishes as the composition moves toward either the carbon-rich end ($B/C \sim 4$) or the boron-rich end ($B/C \sim 10$) [35]. To increase the Si content in $B_{12}(B,C,Si)_3$, many authors

[28, 35, 36] deliberately included excess B in their experiments. In particular, Khan et al. [28] achieved 1.1 at.% Si in boron carbide by using reactive sintering of boron carbide, silicon hexaboride, and amorphous B powders. It should be noted that B-doping (without Si) is also speculated to reduce stress-induced amorphization. Quantum molecular dynamics (MD) simulations demonstrated that B-doped boron carbide has a higher shear strength than the stoichiometric “B₄C” (when B/C = 4) [37] which in turn impedes the stress-induced amorphization. Furthermore, Si- and B-doped (denoted as Si/B co-doped) boron carbide is also conjectured to suppress stress-induced amorphization [28], possibly benefiting from both Si- and B-doping, but this hypothesis remains to be experimentally verified.

The amount of Si content in the B₁₂(B,C,Si)₃ also depends on the processing temperature. According to Kieffer et al. [36], the Si content increases with an increase in processing temperature. Telle et al. [35] determined that the maximum solubility of Si is 2.5 ± 0.3 at.% at 2050 °C. For the purpose of increasing the Si content in B₁₂(B,C,Si)₃, it is desirable to seek new processing methods that can reach temperatures higher than the conventional methods. Here, arc melting is used as a new avenue for the synthesis of Si/B co-doped boron carbide for its high processing temperature. We aim to i) to demonstrate the feasibility of arc melting as an avenue to synthesize B₁₂(B,C,Si)₃ with increased Si content, ii) experimentally verify the supposed amorphization mitigation due to Si/B co-doping, and iii) provide a comprehensive understanding of the microstructure, chemistry, and structural change of boron carbide as a result of Si/B co-doping.

Materials and Methods

Processing

Powders of boron carbide (Grade HD20, H.C. Starck), amorphous boron (Grade I, H.C. Starck), and silicon (Acros Organics) were mixed according to B:C:Si atomic ratio of 78:12:10. A starting Si content of 10 at.% was chosen because it was anticipated that some would be lost to vaporization at the arc melting temperature ($>3000\text{ }^{\circ}\text{C}$). A total of 0.5g powder mixture was then cold-pressed in a 6 mm steel diameter die without binder additive. The pellet was melted under argon (99.999% purity) flow using a lab-scale benchtop arc melter (5SA, Centorr Vacuum Industries). The melt was allowed to recrystallize and cool to room temperature and melted again a total of 5 times to ensure homogeneous mixing. An unmixed 0.5 g of pure boron carbide powder was also cold-pressed and melted in an identical fashion to serve as a control group. Ingots were sectioned using a diamond wheel and polished using diamond embedded pads down to $0.25\text{ }\mu\text{m}$.

X-ray diffraction

For XRD, part of the sectioned ingots was crushed into powders using a steel mortar. Powder diffraction was performed using an X'Pert Pro diffractometer (PANalytical) with Cu $K\alpha$ radiation. The peak positions were corrected using a silicon standard (SRM 640e, NIST) [38].

Microstructural imaging and composition semi-quantification

Mirror finished samples were imaged using a field emission scanning electron microscope (FE-SEM; SIGMA Zeiss) equipped with energy-dispersive X-ray spectroscopy detector (EDS; Oxford Instruments). Elemental mapping and chemical compositions were revealed using SEM-EDS spectrum imaging. Transmission electrode

microscope (TEM) specimens were prepared from Si/B co-doped and undoped samples by tripod polished using diamond embedded pads and then thinned to electron transparency using argon ion polishing (PIPS, Gatan). Submicron features were subsequently imaged using a transmission electron microscope (Technai TF30) with 300 kV electron accelerating voltage.

Chemical quantification

High resolution chemical compositional analysis was conducted by employing ζ -factor microanalysis, which is an analytical transmission electron microscopy EDS approach that enables X-ray absorption corrections [39]. This approach has recently been applied accurately to the B-C-Si system [40] and detailed explanations of the ζ -factor method can be found in several publications [39, 41, 42]. First, thin specimens were prepared using the in-situ lift-out method within a focused ion beam (FIB, FEI SCIOS). The specimens were subsequently imaged and STEM-EDS spectrum imaging was conducted using an aberration-corrected instrument (JEOL ARM-200CF) equipped with a JEOL 100 mm² silicon drift detector. The B and C K-lines and Si K α ζ -factors were determined using SiB₆, high purity SiC, and a standard glass film (NIST SRM 2063a [43]), respectively [40].

Raman spectroscopy and amorphization analysis

Vickers indents were placed in Si/B co-doped and undoped polished surfaces to activate stress-induced amorphization using an automatic hardness tester (VH3300, Wilson) with 4.9 N force. Raman data was collected using an inVia Reflex Raman microscope (Renishaw) equipped with 532, 622, and 830 nm lasers. Amorphous zone distributions within the hardness indents were evaluated using a 532 nm laser with a spatial

resolution of 0.5 μm (100x objective). The Raman spectra were deconvoluted using WIRE 4.2 software. Fig. 1 depicts Raman spectra in the high-frequency regime of pristine boron carbide (p-BC), amorphous boron carbide (a-BC), and boron carbide with graphitic features. The p-BC spectrum is characterized by 4 or more convoluted crystalline peaks, namely around 930, 960, 1000, and 1090 cm^{-1} . The a-BC is characterized by 3 broad bands at 1330, 1520, and 1810 cm^{-1} in addition to the crystalline features. Graphitic contamination is often observed in boron carbide, which is indicated by the D and G peaks in addition to the a- or p-BC Raman peaks [44]. Since the graphitic peaks share similar wavenumber positions with the 1330 and 1520 cm^{-1} amorphous boron carbide peaks, only the 1810 cm^{-1} peak is considered when determining the presence of amorphous boron carbide. The intensity of amorphization is obtained by normalizing the 1810 cm^{-1} amorphous peak with respect to the sum of the pristine boron carbide peaks. A pseudocolor map was used to illustrate the relative distribution of amorphization intensity inside the indent imprints. Amorphization intensity is semi-quantified by summing over the pseudocolor map and then dividing by the probed area in order to account for the difference in indent size. A total of 5 indents were analyzed for Si/B co-doped and undoped boron carbide in order to compare the effect of doping on the suppression of amorphization.

Results and Discussion

Bulk phase identification

Fig. 2 shows XRD patterns of arc melted Si/B co-doped boron carbide and undoped boron carbide. Only stoichiometric “B₄C” (when B/C = 4) is identified in the undoped sample while Si, SiB₆, and doped boron carbide phases are found in the Si/B co-doped sample. The presence of SiB₆ and free Si suggests that not all B and Si participated in doping of boron carbide, but instead part of them reacted to form SiB₆. According to Clark et al. [45], position shift in the (201) peak (37.805° two thetas) indicates contraction or expansion of the crystal lattice [45, 46]. For the Si/B co-doped sample, this peak is shifted towards lower two thetas indicating that the incorporation of B, Si, or both leads to an expansion of boron carbide crystal lattice. In addition, the broadening of the peaks suggests that the dopant content is nonuniform because a single-phase homogeneous sample would result in a clear peak separation between K α -1 and K α -2 doublet. Peak broadening may also result from an increase in planar defects such as twins and/or stacking faults [47].

Microstructural characterization

Dense single-phase and multiphase microstructures are found in undoped and Si/B co-doped samples, respectively, as shown in Fig. 3a and 3b. Large cracks formed in the undoped sample while only smaller cracks form in the Si/B co-doped sample. The cracks are likely due to thermal shock as a result of the fast cooling rate inherent to the arc melting process. In the multiphase material, the cracks are impeded by the secondary phases, especially by a more ductile material such as Si. SEM-EDS mapping was performed on the Si/B co-doped sample to highlight the elemental distribution, shown in Fig. 3c. It is apparent that the spatial distribution of elements is not uniform, including at least three

distinct phases with varying levels of Si concentration (Z contrast), thus confirming the findings of XRD. Regions deficient of Si are common and typically correlated with large areas of B and C, suggesting these regions as undoped boron carbide (white circles). Locally, pockets, where Si, B, and C coexist, are interpreted as Si/B co-doped boron carbide (yellow circles).

Microstructures of both the undoped and Si/B co-doped specimens were examined by TEM and are shown in Fig. 4a and 4b. The most striking difference between the samples is the presence of a high density of planar defects in the Si/B co-doped sample. In contrast very few were observed in the undoped sample. Higher magnification images (Fig. 4c and 4d) show the planar defects found in the Si/B co-doped sample are stacking faults and that the stacking fault density varies substantially. EDS was performed in Si/B co-doped boron carbide and confirmed the area of interest was Si and B co-doped. The high density of stacking faults have been documented for B enriched boron carbide [48]. However, B-rich boron carbide is also accompanied by a high density of twins, which is not found in the Si/B co-doped boron sample. The differences in the microstructure are unlikely caused by the processing method (melting and fast cooling) as both samples were fabricated in the same way. This suggests that the incorporation of Si and B lowers the stacking fault energy in boron carbide. Though the addition of alloying elements is reported to lower the stacking fault energy in metals, for example in Cu-Al alloys [49], this phenomenon is not well understood in ceramics.

Phase identification using Raman spectroscopy

While microstructure-phase correlation can be established through a combined analysis of XRD and EDS mapping, Raman spectroscopy can readily provide this

information over a large area of the microstructure as well as additional insight into the compositional variation within a phase. In Fig. 5, only “B₄C” spectra [48] were found in the undoped sample while numerous phases were identified in the Si/B co-doped sample. These phases include SiB₆, B-doped Si, undoped boron carbide, B-doped boron carbide, and Si/B co-doped boron carbide. SiB₆ is characterized by the presence of the 175 cm⁻¹ band [28]. The presence of a 300 cm⁻¹ peak and the formation of a minimum at 496 cm⁻¹ found in the B-doped Si spectrum are indications for B-doping with [B] > 2x10²¹ cm⁻³ [50]. B-doped boron carbide is characterized by a drop in intensity of the 270 cm⁻¹ band and a visible downshifting in the 1090 cm⁻¹ band [51]. Si/B co-doped boron carbide (denoted as Si/B BC₂₄₀) is marked by the absence of the 270 and 320 cm⁻¹ doublets and the formation of the 240 cm⁻¹ peak [28]. A small shoulder, to the left of the 240 cm⁻¹, is attributed to the formation of the 210 cm⁻¹ peak. The intensity of the 210 cm⁻¹ shoulder intensifies and becomes a distinct peak (denoted as Si/B BC₂₁₀) as the probed regions move closer to the Si source. The apparent correlation between 210/240 cm⁻¹ and Si source has been mentioned by Jannotti et al. [31], when they performed a Raman line scan across an undoped boron carbide core-Si-doped rim structure in a Si infiltrated boron carbide ceramics. This correlation will be further investigated in the later text.

Structural modification due to Si/B co-doping

In order to investigate the structural modification due to B and Si doping, a region varying in B/C ratio and Si contents was identified using SEM-EDS and Raman line scans, labeled “line scans” in Fig. 5a. Fig. 6a shows enlarged optical and SEM images of the area of interest, along with a marked line representing the Raman scan originating from the center of grain I (Si-BC₂₄₀), across grain II (Si-BC₂₁₀), and into B-doped Si. B/C ratio and

Si contents are displayed in Fig. 6b and 6c, respectively. The selected Raman spectra acquired from the line scan are plotted in Fig. 6g. In a typical boron carbide Raman spectrum at ambient conditions (undoped reference), the peaks in the high-frequency regime ($530\text{-}1300\text{ cm}^{-1}$) are attributed to the vibration modes originating from the icosahedra [4, 48, 52, 53]. The narrow band at 480 cm^{-1} is associated with the stretching of the 3-atom chain [52, 54]. The low-frequency Raman bands in boron carbide, such as the 320 and 270 cm^{-1} doublets, are attributed to disorder-activated acoustic phonons [1, 48, 54]. Modifications in icosahedra and the 3-atom chains would result in noticeable peak position changes in the Raman spectra. Fig. 6d-6f depicts the peak positions and intensities of the 480 , 530 , and 1090 cm^{-1} Raman bands with respect to the B/C ratio and Si content. (Analysis in “Grain II” was not possible and was removed due to the abnormally high 210 cm^{-1} peak intensity, as shown in Fig. 6g.) As the B/C increases, particularly in the transition, we observe a sharp decrease in the 1090 cm^{-1} peak position (Fig. 6d), consistent with the findings in the literature [48, 51, 55]. This observation has been attributed to volume expansion due to B substitutions in the icosahedra [48, 51], but the downshift of the 1090 cm^{-1} peak could also be attributed to an increase in lattice constant to accommodate Si atoms. We also like to point out that the downshifting in the 1090 cm^{-1} peak could also be interpreted as an accumulation of local residual stress [56], specifically tension. Since there is a large chemical gradient across a narrow region, the mismatch in the lattice constants between boron carbide with higher B/Si contents and those with lower contents could result in a stress gradient. We observed a downshift in the 530 cm^{-1} peak as the B content increases (Fig. 6e). The new position of the 530 cm^{-1} peak closely resembles the 527 cm^{-1} in alpha-B [52], which are made of B_{12} icosahedra, further indicating the

proliferation of B_{12} icosahedra. The upshift in the 480 cm^{-1} peak position (Fig. 6f) would indicate a stronger inter-chain bonding, possibly due to the newly formed covalent bonds between Si and the atoms at the chain ends (X-Si-X kinked chains). These observations are accompanied by the formation of the 1170 cm^{-1} band, which is commonly found in B-doped boron carbide [48, 51].

Correlation between $210/240\text{ cm}^{-1}$ Raman peak intensities and Si content

As compared to the reference undoped boron carbide spectrum (Fig. 6g), grain I is Si/B co-doped, evident by the absence of the 270 and 320 cm^{-1} doublets and the formation of the 240 and 210 cm^{-1} bands [28], along with a downshift in the 1090 cm^{-1} peak. As the line scan approaches the transition between the two grains (scan distance of $5\text{-}6.5\text{ }\mu\text{m}$ in Fig. 6g), the 210 cm^{-1} band intensifies significantly. Grain II is mainly defined by the 210 cm^{-1} peak. We attribute the formation of 210 cm^{-1} band to heavy Si-doped boron carbide since this peak was only found near the Si source and cannot be assigned to other phases identified in this specimen. Upon reaching the Si source at $13.5\text{ }\mu\text{m}$, characteristics of heavily B-doped Si appear, such as the formation of the 300 cm^{-1} peak and the development of the local minimum at 495 cm^{-1} . Partial 210 cm^{-1} peak intensity is visible in the free Si spectrum since some Si/B co-doped boron carbide remains inside the free Si, marked with red circles in Fig. 6a.

The correlation between the peak intensities of the 210 and 240 cm^{-1} bands and Si content was studied by comparing their normalized peak intensities to Si content. The normalized intensities of the 210 , 240 , and 300 cm^{-1} peaks, with respect to the 1090 cm^{-1} peak, were plotted as a function of scanned distance in Fig. 7. Si content acquired from the SEM-EDS line scan was superimposed over the intensity plot to understand the correlation

between the two results. The data at the transitions as well as in the Si grain were removed in order to focus on the correlation between the 210 and 240 cm^{-1} peak intensities and the Si content. It appears that the lower Si content (<1.5 at.%) is characterized by the mainly 240 cm^{-1} peak while higher Si content (>1.5 at.%) is predominately 210 cm^{-1} peak. The Raman spectrum acquired from Grain I, with low silicon content (<1.5 at.%), is similar to that of the reported Si/B co-doped boron carbide with 1.1 at.% [28], which also only showed the 240 cm^{-1} peak.

Implication for lattice defects due to Si-doping

As mentioned previously, 320 and 270 cm^{-1} doublets are attributed to disorder-activated acoustic phonons [1, 48, 54]. The intensities of the doublets scale strongly with excitation energy, particularly for the near-IR lasers. Given the similarity in wavenumber position of the Si-doped peaks (210 and 240 cm^{-1}) to the disorder-activated doublets and the unusually high intensity of the 210 cm^{-1} peak, Si-doped Raman spectra were investigated using lasers with various wavelengths: 532, 633, and 830 nm. Raman spectra acquired from undoped boron carbide, grain I, and grain II, using various lasers, are plotted in Fig. 8. Similar to the literature [17, 48], the 270 and 320 cm^{-1} peak intensities scale positively with an increase in incident laser wavelength (decrease in laser energy). This is evident by comparing the peak intensities of the 270 and 320 cm^{-1} peaks with that of the 1090 cm^{-1} peak in the same Raman spectrum. Likewise, the 240 and 210 cm^{-1} peaks also show intensity dependency with excitation energy, but more strongly in 210 compared to 240 cm^{-1} . This finding suggests that the 210 and 240 cm^{-1} Raman bands are also related to disorder-induced acoustic phonons as opposed to Khan et al.'s assertion that the 240 cm^{-1} band originates from a new vibrational mode as a result of a new bond created between Si

and the adjacent icosahedron [28]. From this, we deduce that Si-doping is responsible for creating more lattice defects, possibly by forming kinked chains as identified by Khan et al. [28]. It is also possible that as Si atoms saturate the X-□-X (X for C or B) vacancies, the additional Si atoms occupy a new location further disrupting the lattice order, indicated by an intense increase in the 210 cm^{-1} peak intensity beyond about 1.5 at.% Si. The possible location of the second site for the Si atom has been speculated, such as in the Si-Si-X (X for C or B) 3-atom chain [27] or in the Si-X-Si-X 4-atom chain [35], where the second Si takes an interstitial space between neighboring icosahedra just above the linear chain. It's important to note that the linear chain lies along the c-axis (hexagonal notation) in boron carbide. A sharp increase in the c-lattice parameter has been measured in the $\text{B}_{12}(\text{B,C,Si})_3$ as the Si content increases [35], making the latter speculation promising. a- and c-lattice parameters vs B content from B-doped and Si/B co-doped boron carbide are summarized in Fig. S1. DFT simulations combined with in-depth crystallographic analysis would be required to confirm the stability of the suggested structure modifications.

Absolute elemental quantification of $\text{B}_{12}(\text{B,C,Si})_3$

Elemental quantification of Si/B co-doped boron carbide was further characterized using STEM-EDS and ζ -factor microanalysis for their high spatial resolution and accurate absorption correction, respectively. A specimen near a Si source was extracted using FIB to be evaluated for the maximum Si content in boron carbide. Fig. 9a shows a high-angle annular dark-field image of the cross-sectional specimen. STEM-EDS spectrum images were acquired in the location marked by the blue arrows and integrated line scans, in the direction of the blue arrows, were extracted to determine the Si gradient leading to the B-doped Si grain. In Fig. 9b, the Si content at the beginning of the scan is around 2.5 at.%

and increases marginally to around 2.8 at. % at around 3.8 μm . This trend is accompanied by a slight increase in the B/C ratio from 7.5 to 8. From 3.8-4.5 μm , the Si and B/C ratio increased considerably to 3.5 at.% and 10.5, respectively. EDS scan II, in Fig. 9c, shows the mirror image of scan I, a decrease of Si and B/C ratio as the scan moves away from the Si source. The Si and B/C ratio increase again as the scan moves closer to the second Si source at the right side of the EDS scan II. Si content in EDS scan I is slightly higher, attributed to having a larger Si source engulfing the region.

There are two factors that govern the elemental contents in boron carbide, namely processing temperature and cooling rate. As Kieffer [36] and Telle [35] pointed out, the solubility of Si in boron carbide increases with processing temperature. During the arc melting temperature ($>3500\text{ }^{\circ}\text{C}$), boron carbide, B, and Si exist as a supersaturated $\text{B}_{12}(\text{B,C,Si})_3$ liquid. As the liquid cools, Si and B exsolve from the liquid to form SiB_6 and B-doped Si. Because the cooling rate is not instantaneous, evident by the gradients in Si and B contents, some B and Si are in a transient state nearest to the Si sources, which give rise to the high Si and B.

Suggested amorphization mitigation by Si/B co-doping

Si/B co-doped boron carbide has been predicted to reduce stress-induced amorphization [28] but this hypothesis has yet to be experimentally verified. To validate this claim, Si/B co-doped regions were first identified using SEM-EDS and Raman point analysis. Next, 0.49 N Vickers indents were selectively placed in those regions in the Si/B co-doped sample, as shown in Fig. S2, and randomly placed in the undoped sample to activate stress-induced amorphization. The intensity of amorphization is obtained by normalizing the 1810 cm^{-1} amorphous peak with respect to the sum of the crystalline peaks

after accounting for the size of the imprints. Fig. 10 illustrates the pseudocolor map of the amorphous distribution and intensity inside the indent imprints, after evaluating 5 indents for each specimen. Both pseudocolor maps show that the highest amorphization intensity is found near the center of the indents. This finding is expected since the apex of the indenter yields the highest pressure. The undoped pseudocolor map, on average, showed higher intensities inside the indent. Since each pixel carries an intensity, we can obtain a total amorphization intensity by summing each pixel intensity and dividing it over the scanned area. We found a 31% reduction of total amorphization intensity in the Si/B co-doped sample. By counting the number of pixels in each indent, we can estimate the size of the amorphous area. We found a 25% decrease in the amorphous area in the Si/B co-doped specimen. We want to emphasize that our semi-quantitative assessment using Raman phase mapping is limited to only the surface of the imprint. The quasi-plastic zone extends far beneath the probing volume of the Raman laser (532 nm) employed in our study [15, 57]. Thus, our results only suggest that Si/B co-doping could alleviate amorphization on the surface and allude that it could possibly mitigate amorphization throughout the entire quasi-plastic zone. A separate TEM study that examines the role(s) Si/B co-doping has on the deformation behavior of boron carbide beneath the surface was conducted concurrently with this study and the results were submitted as a separate publication.

There are several possible reasons why Si/B co-doping could alleviate stress-induced amorphization in boron carbide. The onset of amorphization is thought to initiate by the bending of the 3-atom chains, followed by the formation of a strong covalent bond between the C atoms in the icosahedra with the center B atoms in the 3-atom chains [7]. B-doping substitutes C atoms in the icosahedra with B atoms [58, 59], which eliminates

the strong C-B interaction required to initiate amorphization. On the other hand, Si atoms occupy the interstitial sites adjacent to vacancies in the X-□-X chain (X = B or C), and form new bonds with the X atoms at the chain ends and with neighboring icosahedra [28]. This substitution reduces the prevalence of vacancies, which is thought to have a propensity for amorphization [29]. The formation of the new covalent bonds could further deter the bending of the chains that initiates the amorphization process [7]. The presence of Si also donates extra electrons to the electron-deficient icosahedra (-2 for B₁₂ and -1 for B₁₁C) [30, 60], further stabilizing the structure. As such, the modification of both icosahedra and the chains due to B- and Si-doping, respectively, could lead to the reduction of amorphization in boron carbide. Atomistic details responsible for the reduction of amorphization in Si/B co-doped boron carbide remain unsolved due to the lack of reasonable quantum molecular dynamics (MD) simulations. We believe a model comprising of the modification of stoichiometry, addition of Si, and possibly residual stress as a result of atomic substitution are required to explain the interplay between the involvements of Si/B and the observed reduction in amorphization.

Conclusions

Si/B co-doped boron carbide was synthesized by arc melting a blend of commercial boron carbide, silicon, and amorphous boron carbide powders. We proceeded to characterize its microstructure, chemical composition, and the ability to suppress amorphization due to Si/B co-doping. The key conclusions are summarized below:

1. Arc melting was utilized to successfully synthesize Si/B co-doped boron carbide by melting a blend of commercial boron carbide, Si, and amorphous B powders. A dense, heterogeneous microstructure was achieved with phases including B-doped Si, SiB₆, undoped boron carbide, B-doped boron carbide, and Si/B co-doped boron carbide.
2. Raman phase mapping suggested that Si/B co-doping in boron carbide could be a promising strategy for reducing amorphization in boron carbide. However, due to the probing limitation of the technique, a direct observation beneath the surface using TEM is necessary to further validate our findings.
3. TEM observation revealed a high density of stacking faults in the Si/B co-doped sample, suggesting complex chemistry may lower the stacking fault energy in ceramics.
4. Two low-frequency Raman peaks, 210 and 240 cm⁻¹, are associated with lattice disorder due to Si-doping and their intensities are correlated with Si content in boron carbide.
5. Absolute composition quantification (ζ -factor method) showed that 3.0 - 3.5 at.% Si doping could be achieved in the transient state of boron carbide.

Acknowledgment

This work was supported by the Army Research Laboratory under Cooperative Agreement [W911NF-12-2-0022]; and the Defense Advanced Research Projects [Grant No. W31P4Q-13-1-000].

References

- [1] V. Domnich, S. Reynaud, R.A. Haber, M. Chhowalla, Boron Carbide: Structure, Properties, and Stability under Stress, *J. Am. Ceram. Soc.* 94(11) (2011) 3605-3628. <https://doi.org/10.1111/j.1551-2916.2011.04865.x>.
- [2] A. Lipp, Boron carbide: production properties and applications, *Technische Rundschau* (1966).
- [3] F. Thevenot, Boron carbide—a comprehensive review, *J. Eur. Ceram. Soc.* 6(4) (1990) 205-225. [https://doi.org/10.1016/0955-2219\(90\)90048-K](https://doi.org/10.1016/0955-2219(90)90048-K).
- [4] K. Shirai, S. Emura, Lattice vibrations and the bonding nature of boron carbide, *J Phys-Condens Mat* 8(50) (1996) 10919-10929. <https://doi.org/10.1088/0953-8984/8/50/018>.
- [5] A.K. Suri, C. Subramanian, J.K. Sonber, T.S.R.C. Murthy, Synthesis and consolidation of boron carbide: a review, *International Materials Reviews* 55(1) (2010) 4-40. <https://doi.org/10.1179/095066009x12506721665211>.
- [6] M. Chen, J.W. McCauley, K.J. Hemker, Shock-induced localized amorphization in boron carbide, *Science* 299(5612) (2003) 1563-6. <https://doi.org/10.1126/science.1080819>.
- [7] Q. An, W.A. Goddard, 3rd, T. Cheng, Atomistic explanation of shear-induced amorphous band formation in boron carbide, *Phys. Rev. Lett.* 113(9) (2014) 095501. <https://doi.org/10.1103/PhysRevLett.113.095501>.
- [8] G. Subhash, A.P. Awasthi, C. Kunka, P. Jannotti, M. DeVries, In search of amorphization-resistant boron carbide, *Scripta Materialia* 123 (2016) 158-162. <https://doi.org/10.1016/j.scriptamat.2016.06.012>.
- [9] D. Ge, V. Domnich, T. Juliano, E.A. Stach, Y. Gogotsi, Structural damage in boron carbide under contact loading, *Acta Mater.* 52(13) (2004) 3921-3927. <https://doi.org/10.1016/j.actamat.2004.05.007>.
- [10] S. Zhao, B. Kad, B.A. Remington, J.C. LaSalvia, C.E. Wehrenberg, K.D. Behler, M.A. Meyers, Directional amorphization of boron carbide subjected to laser shock compression, *Pro. Nat. Acad. Sci.* 113(43) (2016) 12088-12093.
- [11] X.Q. Yan, W.J. Li, T. Goto, M.W. Chen, Raman spectroscopy of pressure-induced amorphous boron carbide, *Appl. Phys. Lett.* 88(13) (2006) 131905. <https://doi.org/10.1063/1.2189826>.
- [12] X.Q. Yan, Z. Tang, L. Zhang, J.J. Guo, C.Q. Jin, Y. Zhang, T. Goto, J.W. McCauley, M.W. Chen, Depressurization amorphization of single-crystal boron carbide, *Phys. Rev. Lett.* 102(7) (2009) 075505. <https://doi.org/10.1103/PhysRevLett.102.075505>.
- [13] J.E. Proctor, V. Bhakhri, R. Hao, T.J. Prior, T. Scheler, E. Gregoryanz, M. Chhowalla, F. Giuliani, Stabilization of boron carbide via silicon doping, *J Phys Condens Matter* 27(1) (2015) 015401. <https://doi.org/10.1088/0953-8984/27/1/015401>.

- [14] M.W. Chen, J.W. McCauley, Mechanical scratching induced phase transitions and reactions of boron carbide, *J. Appl. Phys.* 100(12) (2006) 123517. <https://doi.org/10.1063/1.2405742>.
- [15] G. Parsard, G. Subhash, Raman spectroscopy mapping of amorphized zones beneath static and dynamic Vickers indentations on boron carbide, *J. Eur. Ceram. Soc.* 37(5) (2017) 1945-1953. <https://doi.org/10.1016/j.jeurceramsoc.2016.12.045>.
- [16] V. Domnich, Y. Gogotsi, M. Trenary, Identification of pressure-induced phase transformations using nanoindentation, *MRS Online Proceedings Library Archive* 649 (2000).
- [17] V. Domnich, Y. Gogotsi, M. Trenary, T. Tanaka, Nanoindentation and Raman spectroscopy studies of boron carbide single crystals, *Appl. Phys. Lett.* 81(20) (2002) 3783-3785. <https://doi.org/10.1063/1.1521580>.
- [18] Q. An, W.A. Goddard III, Microalloying Boron Carbide with Silicon to Achieve Dramatically Improved Ductility, *The journal of physical chemistry letters* 5(23) (2014) 4169-4174. <https://doi.org/10.1021/jz5022697>.
- [19] Q. An, W.A. Goddard III, Atomistic origin of brittle failure of boron carbide from large-scale reactive dynamics simulations: suggestions toward improved ductility, *Phys. Rev. Lett.* 115(10) (2015) 105501. <https://doi.org/10.1103/PhysRevLett.115.105501>.
- [20] P. Korotaev, P. Pokatashkin, A. Yanilkin, Structural phase transitions in boron carbide under stress, *Modelling and Simulation in Materials Science and Engineering* 24(1) (2015) 015004.
- [21] P. Korotaev, P. Pokatashkin, A. Yanilkin, The role of non-hydrostatic stresses in phase transitions in boron carbide, *Computational Materials Science* 121 (2016) 106-112.
- [22] S. Aryal, P. Rulis, W. Ching, Mechanism for amorphization of boron carbide B₄C under uniaxial compression, *Phys. Rev. B* 84(18) (2011) 184112.
- [23] K.Y. Xie, Q. An, T. Sato, A.J. Breen, S.P. Ringer, W.A. Goddard, 3rd, J.M. Cairney, K.J. Hemker, Breaking the icosahedra in boron carbide, *Proc Natl Acad Sci U S A* 113(43) (2016) 12012-12016. <https://doi.org/10.1073/pnas.1607980113>.
- [24] G. Fanchini, J.W. McCauley, M. Chhowalla, Behavior of disordered boron carbide under stress, *Phys. Rev. Lett.* 97(3) (2006) 035502. <https://doi.org/10.1103/PhysRevLett.97.035502>.
- [25] D.E. Grady, Shock-Wave Strength Properties of Boron-Carbide and Silicon-Carbide, *J Phys Iv* 4(C8) (1994) 385-391. <https://doi.org/DOI 10.1051/jp4:1994859>.
- [26] A.P. Awasthi, G. Subhash, High-pressure deformation and amorphization in boron carbide, *J. Appl. Phys.* 125(21) (2019) 215901.
- [27] G. Fanchini, D.E. Niesz, R.A. Haber, J.W. McCauley, M. Chhowalla, Root causes of the performance of boron carbide under stress, *Advances in Ceramic Armor II: Ceramic Engineering and Science Proceedings, Volume 27, Issue 7* (2008) 179-188. <https://doi.org/10.1002/9780470291368.ch15>.

- [28] A.U. Khan, A.M. Etzold, X.K. Yang, V. Domnich, K.Y. Xie, C. Hwang, K.D. Behler, M.W. Chen, Q. An, J.C. LaSalvia, K.J. Hemker, W.A. Goddard, R.A. Haber, Locating Si atoms in Si-doped boron carbide: A route to understand amorphization mitigation mechanism, *Acta Mater.* 157 (2018) 106-113. <https://doi.org/10.1016/j.actamat.2018.07.021>.
- [29] D.E. Taylor, Shock Compression of Boron Carbide: A Quantum Mechanical Analysis, *J. Am. Ceram. Soc.* 98(10) (2015) 3308-3318. <https://doi.org/10.1111/jace.13711>.
- [30] G.H. Kwei, B. Morosin, Structures of the boron-rich boron carbides from neutron powder diffraction: Implications for the nature of the inter-icosahedral chains, *J. Phys. Chem.* 100(19) (1996) 8031-8039. <https://doi.org/10.1021/jp953235j>.
- [31] P. Jannotti, G. Subhash, J.Q. Zheng, V. Halls, P.G. Karandikar, S. Salamone, M.K. Aghajanian, Raman spectroscopic characterization of the core-rim structure in reaction bonded boron carbide ceramics, *Appl. Phys. Lett.* 106(4) (2015) 041903. <https://doi.org/10.1063/1.4906969>.
- [32] S. Hayun, A. Weizmann, M.P. Dariel, N. Frage, Microstructural evolution during the infiltration of boron carbide with molten silicon, *J. Eur. Ceram. Soc.* 30(4) (2010) 1007-1014. <https://doi.org/10.1016/j.jeurceramsoc.2009.09.021>.
- [33] M.K. Kolel-Veetil, R.M. Gamache, N. Bernstein, R. Goswami, S.B. Qadri, K.P. Fears, J.B. Miller, E.R. Glaser, T.M. Keller, Substitution of silicon within the rhombohedral boron carbide (B₄C) crystal lattice through high-energy ball-milling, *Journal of Materials Chemistry C* 3(44) (2015) 11705-11716. <https://doi.org/10.1039/C5TC02956B>.
- [34] W.Q. Han, Silicon doped boron carbide nanorod growth via a solid-liquid-solid process, *Appl. Phys. Lett.* 88(13) (2006) 133118. <https://doi.org/10.1063/1.2190468>.
- [35] R. Telle, Structure and properties of Si-doped boron carbide, *The Physics and Chemistry of Carbides, Nitrides and Borides*, Springer 1990, pp. 249-267.
- [36] R. Kieffer, E. Gugel, G. Leimer, P. Ettmayer, Investigations on the system boron-carbon silicon, (1983).
- [37] Q. An, W.A. Goddard, Nanotwins soften boron-rich boron carbide (B₁₃C₂), *Appl. Phys. Lett.* 110(11) (2017) 111902. <https://doi.org/10.1063/1.4978644>.
- [38] M. Mendenhall, Powder diffraction SRMs, (2016).
- [39] M. Watanabe, D.B. Williams, The quantitative analysis of thin specimens: a review of progress from the Cliff-Lorimer to the new zeta-factor methods, *J Microsc* 221(Pt 2) (2006) 89-109. <https://doi.org/10.1111/j.1365-2818.2006.01549.x>.
- [40] C. Marvel, K. Behler, J. LaSalvia, V. Domnich, R. Haber, M. Watanabe, M. Harmer, Extending ζ -factor microanalysis to boron-rich ceramics: Quantification of bulk stoichiometry and grain boundary composition, *Ultramicroscopy* (2019). <https://doi.org/10.1016/j.ultramic.2019.04.008>.

- [41] M. Watanabe, Microscopy Hacks: development of various techniques to assist quantitative nanoanalysis and advanced electron microscopy, *Microscopy* 62(2) (2013) 217-241. <https://doi.org/10.1093/jmicro/dfs085>.
- [42] M. Watanabe, D.W. Ackland, A. Burrows, C.J. Kiely, D.B. Williams, O.L. Krivanek, N. Dellby, M.F. Murfitt, Z. Szilagy, Improvements in the X-ray analytical capabilities of a scanning transmission electron microscope by spherical-aberration correction, *Microsc Microanal* 12(6) (2006) 515-26. <https://doi.org/10.1017/S1431927606060703>.
- [43] R.B. Marinenko, NIST Standards for Microanalysis and the Certification Process, *J Res Natl Inst Stand Technol* 107(6) (2002) 687-91. <https://doi.org/10.6028/jres.107.055>.
- [44] M. Chen, J. McCauley, J. LaSalvia, K. Hemker, Microstructural Characterization of Commercial Hot-Pressed Boron Carbide Ceramics, *J. Am. Ceram. Soc.* 88(7) (2005) 1935-1942. <https://doi.org/10.1111/j.1551-2916.2005.00346.x>.
- [45] H. Clark, J. Hoard, The crystal structure of boron carbide, *J. Am. Chem. Soc.* 65(11) (1943) 2115-2119. <https://doi.org/10.1021/ja01251a026>.
- [46] H.L. Yakel, The crystal structure of a boron-rich boron carbide, *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* 31(7) (1975) 1797-1806. <https://doi.org/10.1021/jp953235j>.
- [47] U. Anselmi-Tamburini, Z.A. Munir, Y. Kodera, T. Imai, M. Ohyanagi, Influence of synthesis temperature on the defect structure of boron carbide: Experimental and modeling studies, *J. Am. Ceram. Soc.* 88(6) (2005) 1382-1387. <https://doi.org/10.1111/j.1551-2916.2005.00245.x>.
- [48] K.Y. Xie, V. Domnich, L. Farbaniec, B. Chen, K. Kuwelkar, L.N. Ma, G.W. McCauley, R.A. Haber, K.T. Ramesh, M.W. Chen, K.J. Hemker, Microstructural characterization of boron-rich boron carbide, *Acta Mater.* 136 (2017) 202-214. <https://doi.org/10.1016/j.actamat.2017.06.063>.
- [49] J. Venables, The electron microscopy of deformation twinning, *Journal of Physics and Chemistry of Solids* 25(7) (1964) 685-692. [https://doi.org/10.1016/0022-3697\(64\)90177-5](https://doi.org/10.1016/0022-3697(64)90177-5).
- [50] N.H. Nickel, P. Lengsfeld, I. Sieber, Raman spectroscopy of heavily doped polycrystalline silicon thin films, *Phys. Rev. B* 61(23) (2000) 15558-15561. <https://doi.org/10.1103/PhysRevB.61.15558>.
- [51] C. Cheng, K.M. Reddy, A. Hirata, T. Fujita, M.E. Chen, Structure and mechanical properties of boron-rich boron carbides, *J. Eur. Ceram. Soc.* 37(15) (2017) 4514-4523. <https://doi.org/10.1016/j.jeurceramsoc.2017.06.017>.
- [52] D.R. Tallant, T.L. Aselage, A.N. Campbell, D. Emin, Boron carbide structure by Raman spectroscopy, *Phys Rev B Condens Matter* 40(8) (1989) 5649-5656. <https://doi.org/10.1103/PhysRevB.40.5649>.
- [53] H. Werheit, V. Filipov, K. Shirai, H. Dekura, N. Shitsevalova, U. Schwarz, M. Armbruster, Raman scattering and isotopic phonon effects in dodecaborides, *J Phys Condens Matter* 23(6) (2011) 065403. <https://doi.org/10.1088/0953-8984/23/6/065403>.

- [54] R. Lazzari, N. Vast, J. Besson, S. Baroni, A. Dal Corso, Atomic structure and vibrational properties of icosahedral B₄C boron carbide, *Phys. Rev. Lett.* 83(16) (1999) 3230. [https://doi.org/10.1016/S0927-0256\(00\)00009-4](https://doi.org/10.1016/S0927-0256(00)00009-4).
- [55] U. Kuhlmann, H. Werheit, Raman effect of boron carbide (B₄C to B₁₀C₃₇), *Journal of alloys and compounds* 205(1-2) (1994) 87-91. [https://doi.org/10.1016/0925-8388\(94\)90771-4](https://doi.org/10.1016/0925-8388(94)90771-4).
- [56] M.H. Manghnani, Y. Wang, F. Li, P. Zinin, W. Rafaniello, Elastic and vibrational properties of B₄C to 21 GPa, *Sci. Technol. High Pressure* 2 (2000) 25-30.
- [57] G. Subhash, D. Ghosh, J. Blaber, J.Q. Zheng, V. Halls, K. Masters, Characterization of the 3-D amorphized zone beneath a Vickers indentation in boron carbide using Raman spectroscopy, *Acta Mater.* 61(10) (2013) 3888-3896. <https://doi.org/10.1016/j.actamat.2013.03.028>.
- [58] D. Emin, Structure and single-phase regime of boron carbides, *Phys Rev B Condens Matter* 38(9) (1988) 6041-6055. <https://doi.org/10.1103/PhysRevB.38.6041>.
- [59] T.L. Aselage, S.B. Vandeusen, B. Morosin, Solution Growth, Structure and Composition of Boron-Carbide Crystals, *J Less-Common Met* 166(1) (1990) 29-44. [https://doi.org/10.1016/0022-5088\(90\)90363-O](https://doi.org/10.1016/0022-5088(90)90363-O).
- [60] A.C. Larson, Comments concerning the crystal structure of B₄C, *AIP Conf. Proc.*, AIP, 1986, pp. 109-113.

Figures

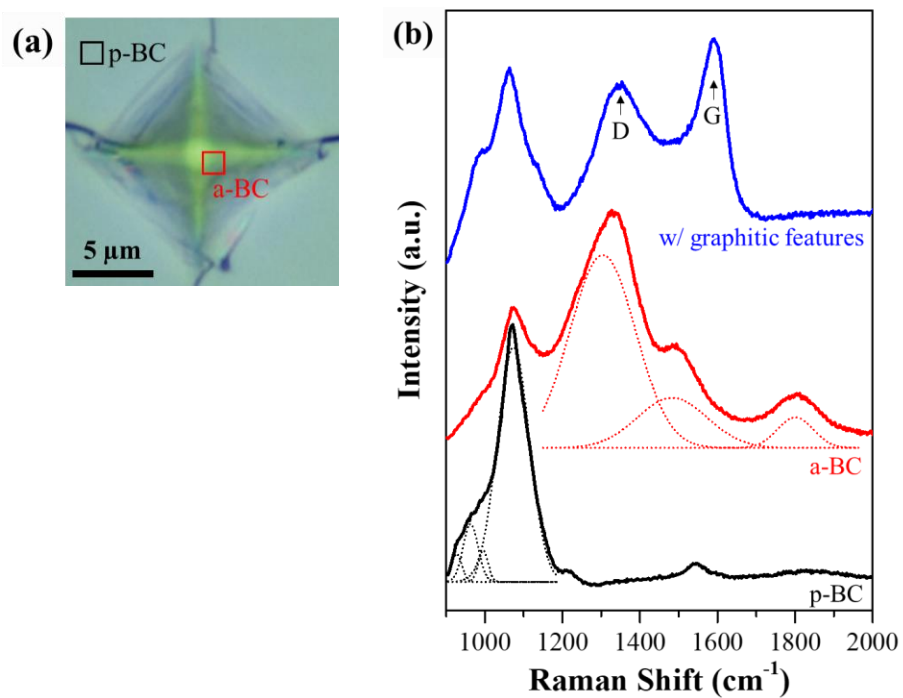


Fig. 1. (a) Optical image of a 4.9N Vickers indent on Si/B co-doped boron carbide. (b) Raman spectra of pristine (p-BC), amorphous boron carbide (a-BC), as well as boron carbide with graphitic features.

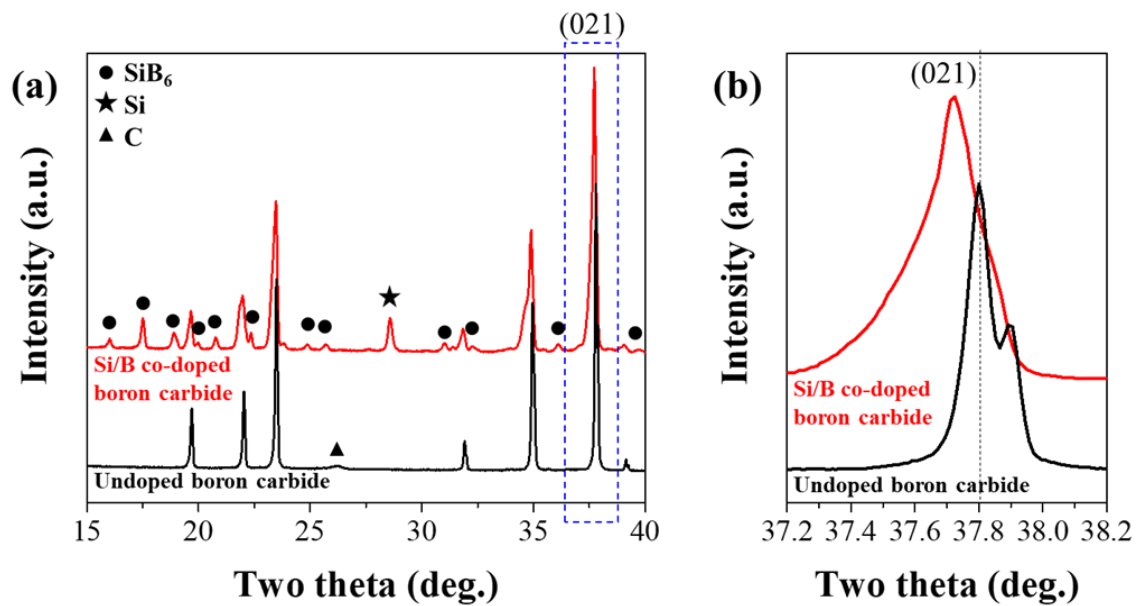


Fig. 2. XRD patterns of arc melted undoped and Si/B co-doped boron carbide from (a) 15-40 and (b) 37.2-38.2 two thetas.

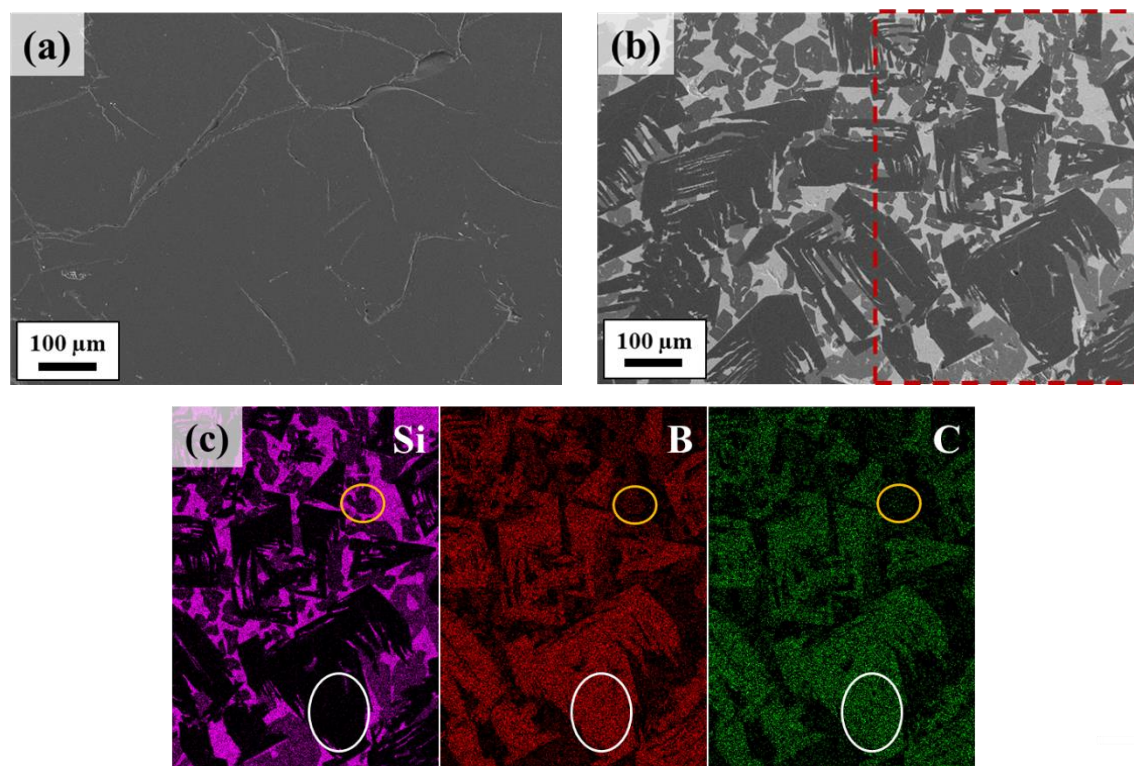


Fig. 3. SEM images of (a) a dense monolithic boron carbide and (b) a multiphase Si/B co-doped boron carbide after arc melting. (c) Elemental mapping of Si, B, and C of the selected area in (b).

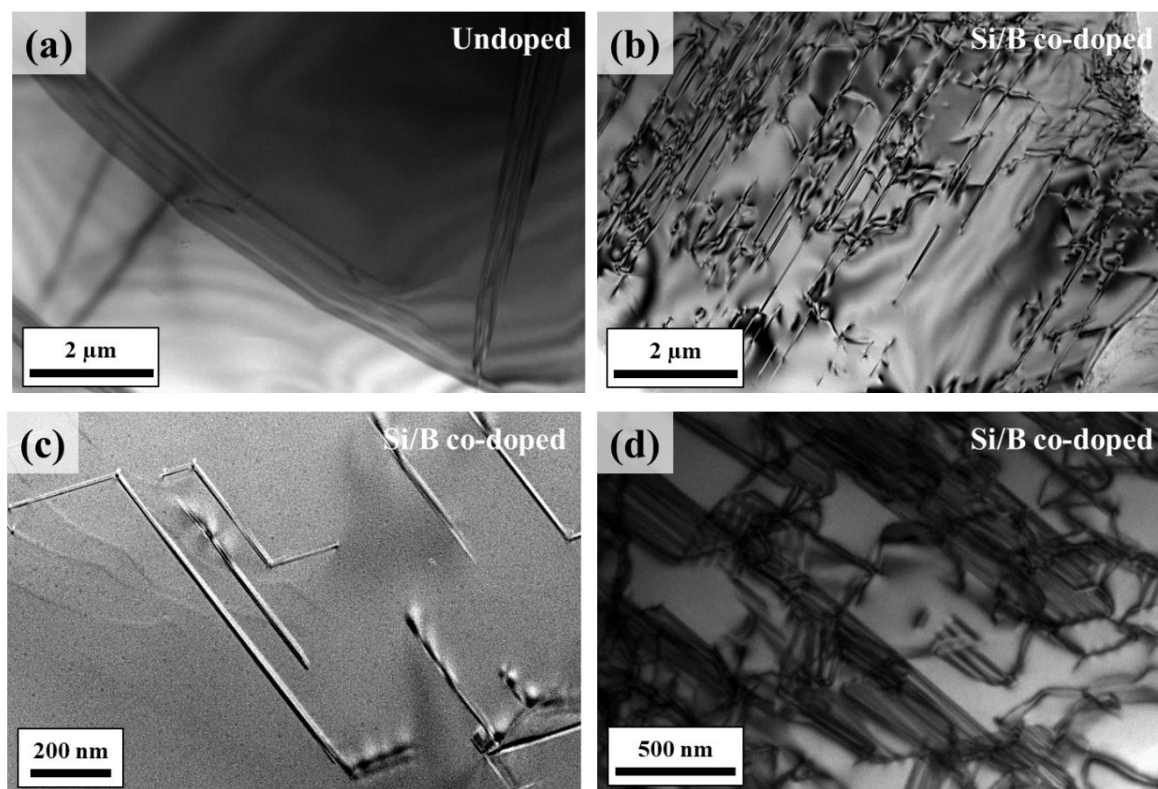


Fig. 4. Bright-field TEM images of arc melted (a) undoped and (b-d) Si/B co-doped boron

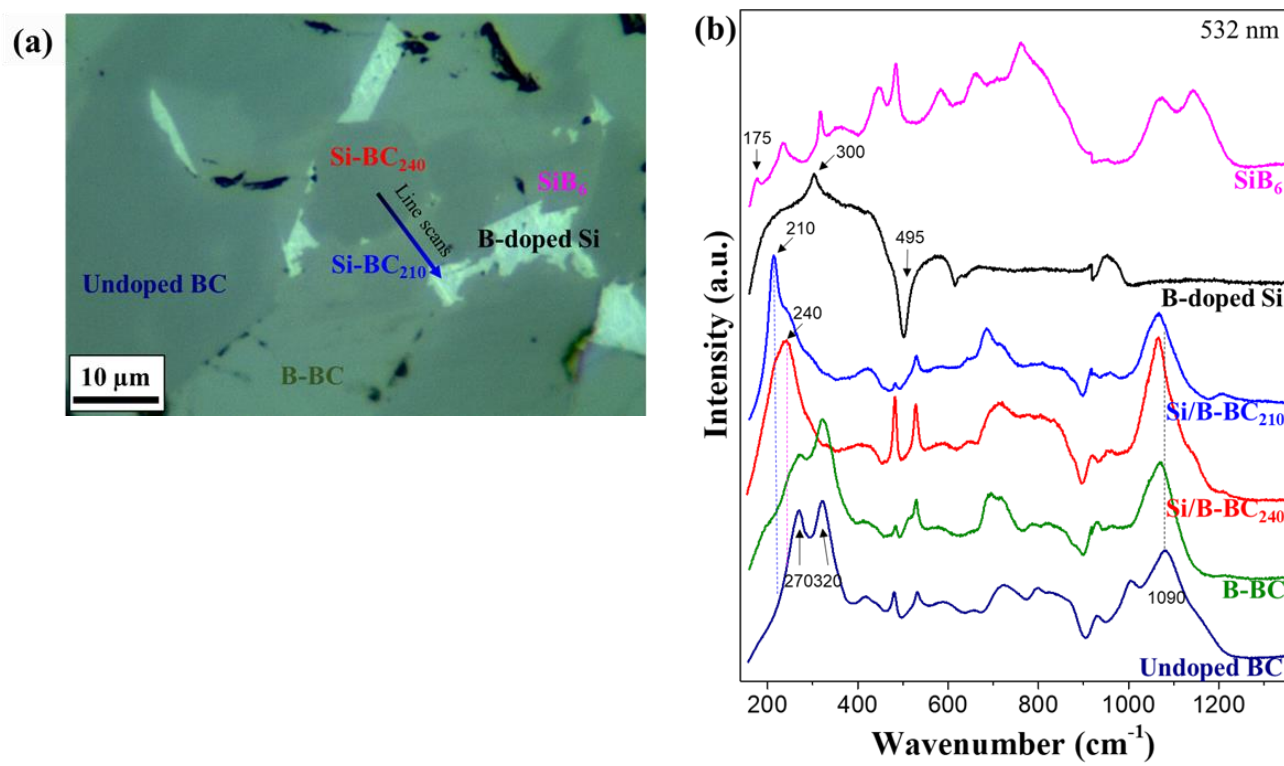


Fig. 5. Optical image of the (a) Si/B co-doped boron carbide and (b) the corresponding phases identified using Raman spectroscopy.

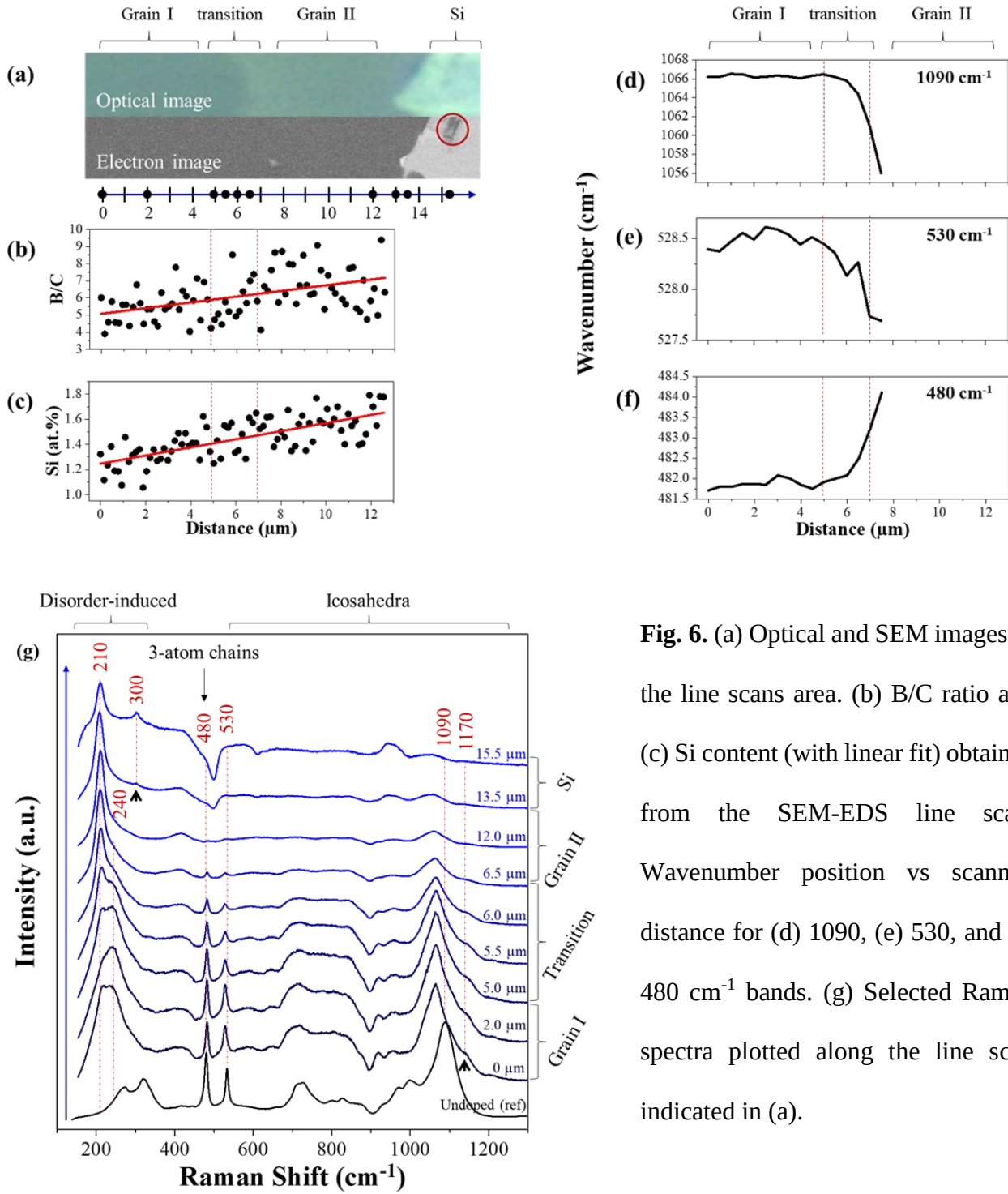


Fig. 6. (a) Optical and SEM images of the line scans area. (b) B/C ratio and (c) Si content (with linear fit) obtained from the SEM-EDS line scan. Wavenumber position vs scanned distance for (d) 1090, (e) 530, and (f) 480 cm^{-1} bands. (g) Selected Raman spectra plotted along the line scan indicated in (a).

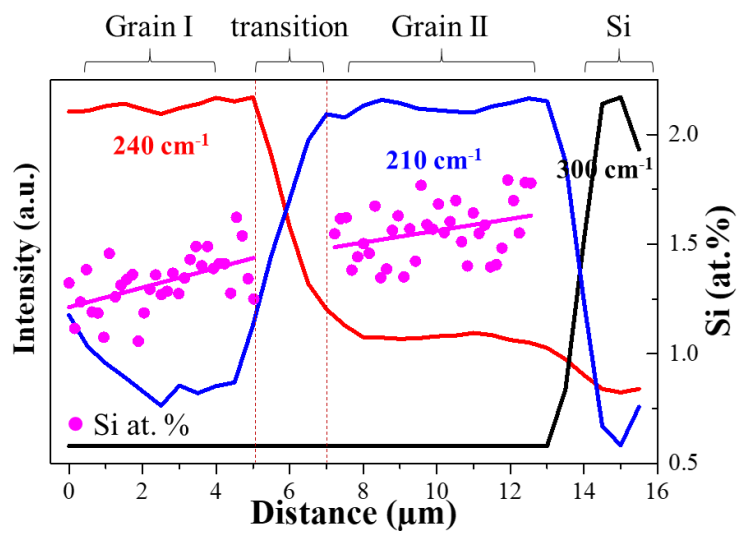


Fig. 7. SEM-EDS Si content superimposed on the normalized 240, 210, and 300 cm⁻¹ peak intensities.

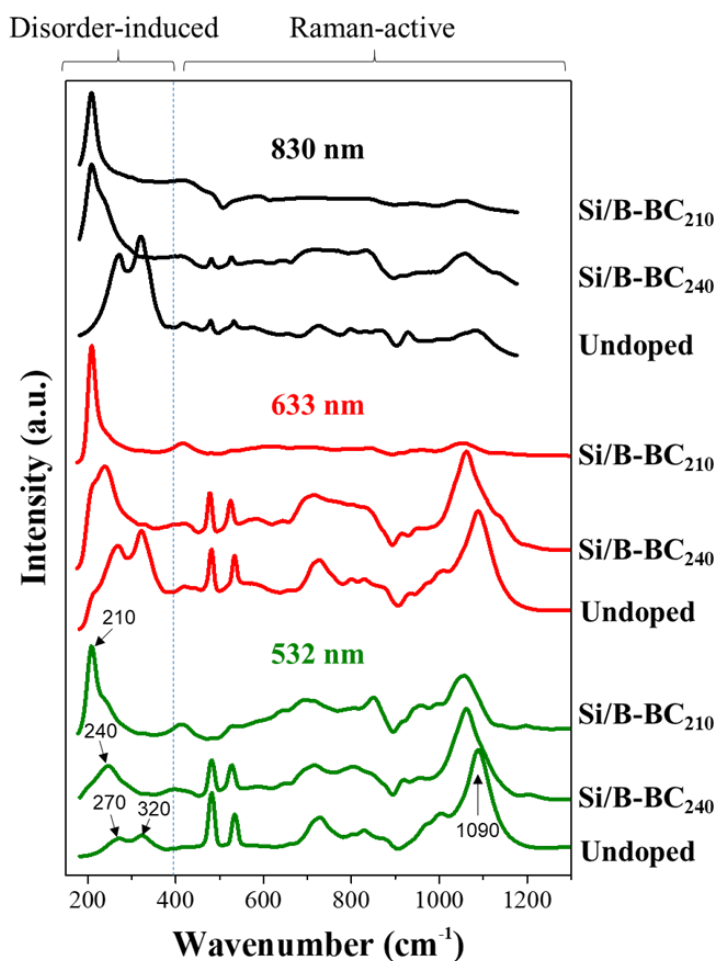


Fig. 8. Raman spectra of undoped, Si-doped₂₄₀, and Si-doped₂₁₀ boron carbide acquired using 532, 633, and 830 nm lasers. Low frequency peaks (210, 240, 270 and 320 cm⁻¹) show strong intensity dependence with excitation energy.

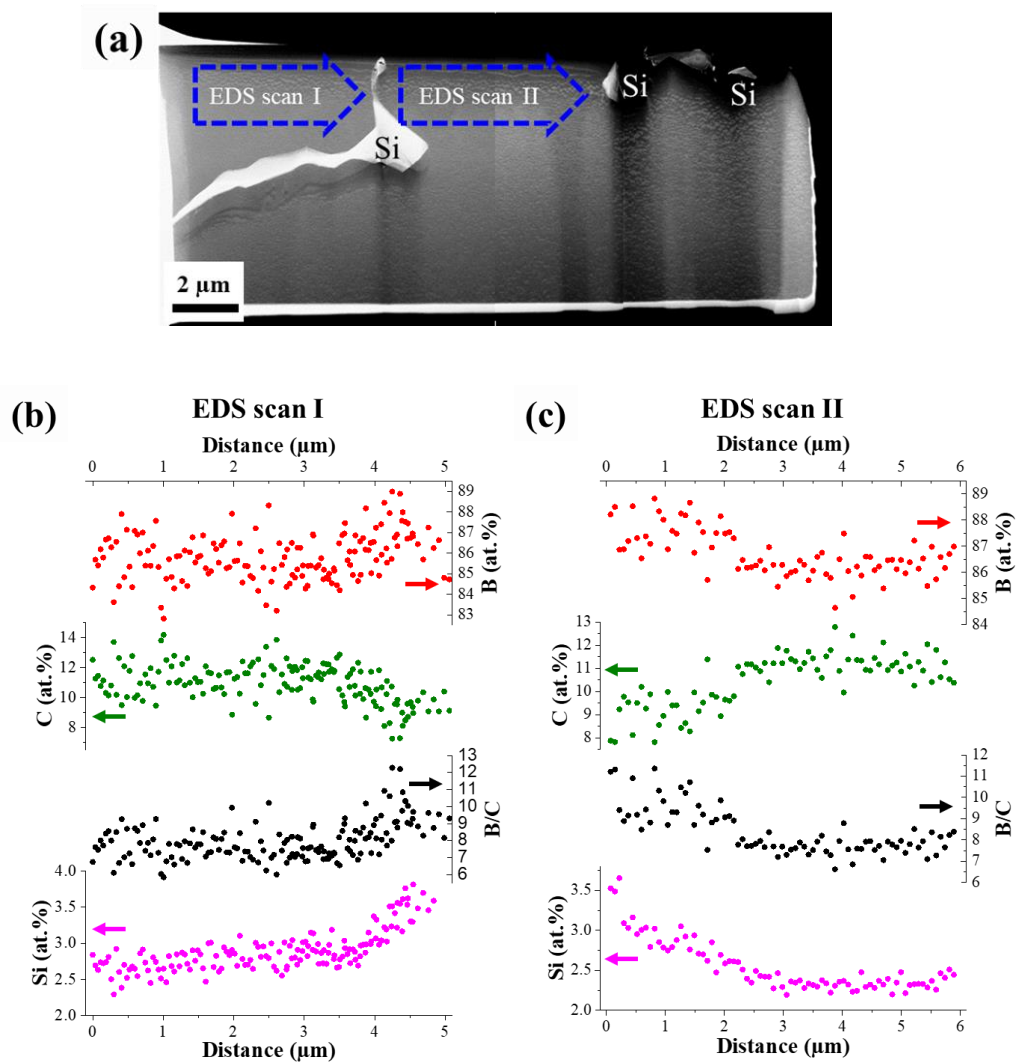


Fig. 9. (a) HAADF-STEM image of the FIB prepared Si/B co-doped specimen. (b) and (c) chemical analysis of EDS scan I and II, respectively.

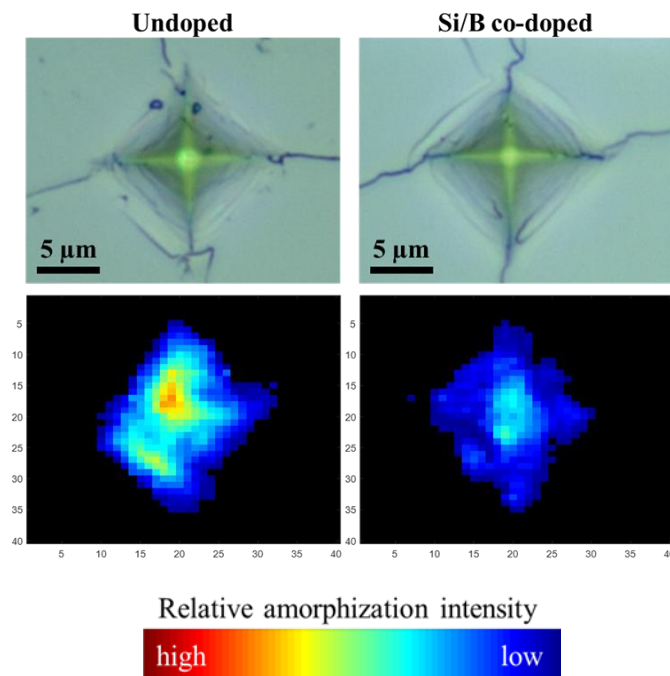


Fig. 10. Optical images of 4.9 N Vickers indents and the corresponding amorphization intensity map for undoped and Si/B co-doped boron carbide. The color maps are averaged of 5 independent results.

Supplementary Figures

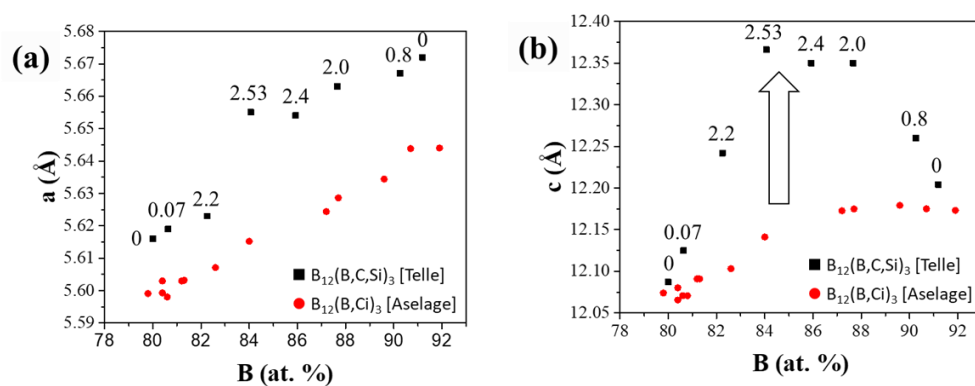


Fig. S1. Boron carbide's (a) *a* and (b) *c* lattice parameters (hexagonal notation) vs B content from Aselage [52] in red and Telle [35] in black. Si at. % content is labeled in black. The arrow in (b) indicates a sharp increase in the *c*-axis due to Si-doping.

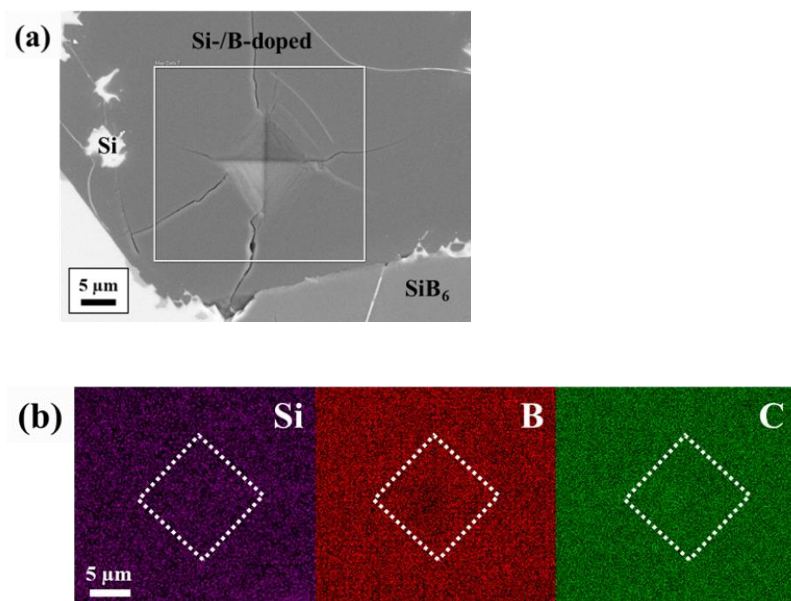


Fig. S2. (a) SEM image of a 4.9 N Vickers indent placed in the Si/B co-doped boron carbide. (b) The corresponding elemental mapping.

CHAPTER 6

Tuning the Deformation Mechanisms of Boron Carbide via Silicon

Doping

Sisi Xiang,¹ Luoning Ma,² Qirong Yang,³ Yvonne Dieudonne,¹ George M. Pharr,¹ Jing Lu,⁴ Digvijay Yadav,¹ Chawon Hwang,³ Jerry C. LaSalvia,⁵ Richard A. Haber,³ Kevin J. Hemker,² Kelvin Y. Xie¹ *

¹ Department of Materials Science and Engineering, Texas A & M University, College Station, Texas 77843, USA.

² Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland 21218, USA.

³ Department of Materials Science and Engineering, Rutgers University, Piscataway, New Jersey 08854, USA.

⁴ NanoMEGAS USA, Tempe, Arizona 85281, USA.

⁵ U.S. Army Research Lab, Aberdeen Proving Ground, Aberdeen, Maryland 21005, USA.

*Corresponding author e-mail: kelvin_xie@tamu.edu

Abstract

Boron carbide suffers from a loss of strength and toughness when subjected to high shear stresses due to amorphization. Here, we report a small amount of Si doping (~ 1 at.%) leads to a significant decrease in stress-induced amorphization due to a noticeable change of the deformation mechanisms in boron carbide. In the undoped boron carbide, the Berkovich indentation-induced quasi-plasticity is dominated by amorphization and micro-cracking along the amorphous shear bands. This mechanism resulted in long, distinct, and single-variant shear faults. In contrast, substantial fragmentation with limited amorphization was activated in the Si-doped boron carbide, manifested by the short, diffuse, and multi-variant shear faults. Micro-cracking via fragmentation competed with and subsequently mitigated amorphization. This work highlights the significant roles that solute atoms play on the structural stability of boron carbide and opens up new avenues to tune deformation mechanisms of ceramics via doping.

Introduction

Boron carbide is widely used in body armor and other engineering applications due to its lightweight and high hardness (1-4). However, consolidated boron carbide loses its strength and toughness when subjected to high-velocity threats (4, 5). The deterioration of the mechanical properties is attributed to the formation of amorphous shear bands, nucleated by high shear stresses generated under impact and sharp-contact loading conditions. These amorphous shear bands act as nucleation sites for microcracks and ‘the path of the least resistance’ for crack propagation, leading to comminuted fracture at much lower stress levels than expected (4). Therefore, the ability to control and mitigate amorphization could guide the design of boron carbide-based armor materials with improved ballistic performance.

The susceptibility of amorphization in boron carbide with B₄C stoichiometry could be explained by its atomic configuration. B₄C can be described using a rhombohedral unit cell, consisting of the 12-atom icosahedra connected via the 3-atom chains. The dominant polymorph is thought to be B₁₁Cp(CBC), where the C atom in the icosahedra occupies the polar sites (6-11). Density functional theory (DFT) simulations suggest that the onset of shear-driven amorphization is triggered by the strong interactions of the polar site C atoms in the icosahedra and the B atoms in the chains, which facilitates the unzipping of icosahedra and the destruction of the crystallinity (6, 12). Molecular dynamics (MD) simulations predicted that the amorphous B₄C has a higher density than the crystalline phase. When the volume is conserved due to constraints, nano-scale voids/cavities will form and coalesce in the amorphous shear bands, leading to crack opening (13). Therefore, tailoring the chain chemistry to reduce the icosahedron-chain interactions offers a

promising pathway for mitigating amorphization and subsequently suppressing the anomalous failure in boron carbide.

One effective strategy to modify the chain chemistry and structure is microalloying, such as Si doping (14-19). Recently, Khan et al. successfully synthesized bulk single-phase Si-doped boron carbide. Rietveld refinement analysis of the X-ray diffraction results revealed that Si atoms occupied the chain sites, forming kinked CSiC chains (16). DFT simulations predicted that Si-doping stabilizes icosahedra from collapsing upon shearing and should lead to improved amorphization resistance (15, 16). However, experimental evidence that verifies this prediction has not been conducted, although some encouraging preliminary observations have been made (17). Moreover, the underpinning mechanisms of how Si-doping mitigates amorphization at the microstructure-level are unknown.

In the present work, we experimentally characterized the effects of Si-doping on the deformation behavior of boron carbide. We created a diffusion couple using boron carbide (with millimeter grain sizes) and silicon hexaboride (SiB₆) to achieve a Si concentration gradient within one boron carbide grain. We then employed nanoindentation to induce amorphization and applied advanced microscopy techniques to uncover the microstructure of the quasi-plastic zones from both the undoped and Si-doped regions. We observed that a small amount of Si doping (~ 1 at.%) led to a substantial decrease in stress-induced amorphization. More surprisingly, Si doping also dramatically changed the deformation mechanisms in boron carbide.

Materials and Methods

Bulk boron carbide was prepared using a commercial (5SA) bench-top 300 Amp arc melter. 0.5 g of commercial (Starck, Grade HD20) boron carbide powder was first cold-pressed into a pellet and then melted in an argon flow. As the liquid cooled, millimeter-sized boron carbide crystals were formed on the surface of the ingot (Fig. S1A). A 5 mm x 5 mm x 5 mm cube was sectioned from the ingot and polished to mirror finish using diamond suspensions. The boron carbide cube was coupled with a cold-pressed SiB6 (Starck, Grade A) pellet and heat treated in a spark plasma sintering apparatus at 1700 °C for 4 hr under 50 MPa (the schematic see Fig. S1B). After heating, the diffusion couple was sectioned parallel to the diffusion direction and polished to mirror finish for further microscopy analyses.

Raman spectroscopy equipped with a 633 nm HeNe laser (InVia Reflex, Renishaw, UK) was used to identify the phases present within the diffusion zone and the material on either side of the zone as well as the amorphized materials in the indents (Figs. 1 and 2). WIRE 4.2 software was employed to deconvolute the Raman spectra and assess the extent of amorphization. Electron Backscatter Diffraction (EBSD) was performed to measure the boron carbide grain size after diffusion had taken place. EDS was used to semi-quantitatively measure the Si content in the diffusion zone. The exact Si content is difficult to obtain using EDS due to the presence of light elements such as B and C in the specimen. Before nanoindentation, the diffusion couple sample polished to mirror finish using diamond lapping film (from 30 μm to 1 μm). Nanoindentation was performed at room temperature using both Vickers and Berkovich indenters. 1 kg Vickers indents and 500 mN Berkovich indents (constant loading rate of 25 mN/s) were placed across the Si-doped

diffusion zone and the undoped boron carbide. When measuring the degree of amorphization, Raman spectroscopy was only performed on the Vickers indents as the Berkovich indents are too small. Some of the Berkovich indents were used for TEM observations.

The cross-sectional TEM samples of undoped and Si-doped boron carbide were prepared from the residual indents using a Tescan LYRA-3 Model GMH dual-beam focused ion beam (FIB) instrument. TEM observation was conducted in an FEI Tecnai G2 F20 Super-Twin FE-TEM operating at 200 kV. Elemental analyses of the TEM samples were carried out using EDS in the TEM. The Si-contents were measured in both Si-free and Si-doped specimens to ensure the Si signal is indeed from doping not from the Si present in the EDS detector. Again, EDS is not the ideal chemical analysis technique in this study. Nevertheless, it serves as a semi-quantitative method to estimate the Si content in the Si-doped boron carbide.

The precession electron diffraction (PED) experiments were performed using an FEI Tecnai TF30 transmission electron microscope equipped with a NanoMEGAS ASTAR system (32, 33). Three types of maps (orientation, reliability, and correlation coefficient) were constructed from the PED results with the 5 nm scanning step size in all samples. The orientation maps are similar to the inverse pole figures in EBSD scans, in which the color of each pixel represents its orientation. In reliability maps, the experimentally acquired diffraction pattern was compared to the simulated pattern in the database. Low brightness indicates a poor match. Poor matches can be caused by the lack of diffraction spots (e.g. amorphous phase and micro-cracks) and multiple sets of diffraction spots (e.g. crystals overlapping). In the correlation coefficient maps, the diffraction pattern of each pixel is

compared to the patterns of its nearest neighbors, and changes in microstructure, such as amorphous phase, micro-cracks, grain boundaries, and elastic strain are highlighted.

Results and Discussion

Energy dispersive x-ray spectroscopy (EDS) revealed that the Si-diffused zone is approximately 250 μm in the boron carbide -SiB₆ diffusion couple (Figs. 1A and S2). The millimeter boron carbide grains and $\sim 250\ \mu\text{m}$ diffusion zone allow a Si concentration gradient in single grains. All the nanoindentation tests, microstructural analyses, and comparisons were carried out in the same boron carbide grain. This experimental design ensures that the observed differences can be dominantly attributed to Si-doping. The roles of other variables such as crystal orientation and grain boundaries are precluded.

Representative Raman spectra obtained from the undoped boron carbide and Si-doped boron carbide highlighted the differences in their chemical bonding (Fig 1B). A typical Raman spectrum of the undoped boron carbide displays major peaks at 270, 320, and 1082 cm^{-1} . The Raman spectra acquired from the Si diffusion zone also showed a significant peak at 1082 cm^{-1} . However, the intensities of the 270 and 320 cm^{-1} peaks were much lower. A new peak at 214 cm^{-1} was also observed. It is suggested that, for boron carbide, the high-frequency peaks (e.g. 1082 cm^{-1}) are attributed to the “breathing” mode of icosahedra, while the low-frequency peaks (e.g. 200 to 350 cm^{-1}) correspond to the chains (9, 11, 20, 21). The fact that the high-frequency peak remained the same but the low-frequency peaks changed dramatically indicates that the icosahedra were retained while the chains were modified via Si doping. The observed Raman spectra for both undoped boron carbide and Si-doped boron carbide are similar to what have been reported in the literature (16, 20). An atomic model describing the B, C, and Si atomic occupancy in the Si-doped boron carbide is provided in Fig. 1C, where some of the CBC chains are replaced by kinked CSiC chains, as described by Khan et al (16).

Having both the undoped and Si-doped regions in the same boron carbide grain, we then employed Vickers indentation and Raman mapping to assess whether Si-doping could mitigate amorphization. Indentation with sharp indenter tips (such as Vickers and Berkovich) is a common technique to impose large shear stress and to trigger stress-induced amorphization in boron carbide (15, 22-26). Raman spectroscopy was then performed on the residual imprints. New peaks (such as 1320, 1520, and 1800 cm^{-1}) associated with amorphization were noted in all indents but were less prominent for the indents in the Si-doped region (Figs. 2A and 2B). Figures 2C and 2D depict the amorphization intensity maps, where each pixel is plotted based on the normalized intensity of the bands at $\sim 1800 \text{ cm}^{-1}$ from the indents and the regions in the vicinity of the indents (22, 27). 1320 and 1520 cm^{-1} bands were excluded from this analysis due to their shared peak positions with the graphitic carbon peaks. It is evident that the degree and extent of amorphization were dramatically reduced in the Si-doped area compared to the undoped boron carbide. This observation is in good agreement with the DFT predictions (14, 16) and prior non-hydrostatic diamond-anvil experimental results, where non-hydrostatic stresses were applied on the undoped and Si-doped boron carbide (17).

To understand why Si-doping facilitates amorphization mitigation at the microstructure-level, cross-sectional transmission electron microscopy (TEM) foils were prepared from the Berkovich nanoindentations using the focused ion beam (FIB) lift-out method. This approach was not attempted on the Vickers indents because previous experience has shown that large residual stresses and numerous cracks prohibit a successful lift-out. Nonetheless, nanoindentation tests with Berkovich tips could also effectively induce amorphization in boron carbide (24-26, 28). Moreover, nanoindentation offers

insight on the mechanical properties (29). The hardness of Si-doped boron carbide at 500 mN (~ 50 GPa) is comparable to that of the undoped counterpart (details see Fig. S3A). Compared with the undoped boron carbide, the Si-doped boron carbide has become slightly softer, which was shown in typical nanoindentation load-displacement curves for undoped and Si-doped boron carbides (Fig. S3B). TEM foils were prepared from the indents at ~ 300 μm (undoped) and ~ 120 μm (Si-doped) away from the diffusion interface. The Si content present in the Si-doped specimens was measured using EDS and semi-quantitatively estimated to be 1 at.%.

Quasi-plastic zones induced by Berkovich nanoindentation were observed in both the undoped and Si-doped boron carbide (for example from the same grain see Fig. 3; for the corresponding bright-field STEM images see Fig. S4). A quick inspection of their microstructure may leave the impression that they are similar. All quasi-plastic zones exhibit complicated diffraction contrast due to the large plastic deformation and elastic residual strain. However, imaging with higher magnification revealed that the characteristics of the amorphous shear bands and micro-cracks in the quasi-plastic zones are strikingly different. Careful inspection of the indented undoped boron carbide showed many long, distinct, and dominantly single-variant shear faults (i.e. amorphous shear bands and micro-cracks) as shown in Figs. 3C. This finding is consistent with the literature (15, 26). In contrast, short and multi-variant shear faults contributed to the quasi-plasticity in the Si-doped sample (Figs. 3D). The prominent differences suggest that as low as 1 at.% Si-doping may dramatically change the deformation mechanisms in boron carbide. However, we encounter a predicament here. Lower magnification TEM images offer an overall view, whereas higher magnification only reveals a very localized microstructure.

While the former makes it difficult to discern the complicated contrast, the latter makes it difficult to confirm whether the observed features are representative. To overcome this challenge, we employed an advanced TEM-based diffraction technique - precession electron diffraction (PED) to simultaneously obtain the global and local microstructure of the quasi-plastic zones.

The orientation, reliability, and correlation coefficient information derived from the PED results highlighted the microstructural similarities and differences of the quasi-plastic zones in the undoped and Si-doped boron carbide. Crystal reorientation was observed in all quasi-plastic zones compared to the corresponding pristine zones (Figs. 4A and 4B), which can be attributed to the amorphous shear bands and micro-cracks (4, 24, 30). Orientation maps viewed in all three principal directions can be found in Fig. S5. Closer inspections unveiled the differences. In the reliability maps (superimposed with the orientation maps, details see Materials and Methods), we note that most pixels in the quasi-plastic zones of the undoped boron carbide display high reliability. The low-reliability pixels are generally associated with the long and distinct amorphous bands and micro-cracks (Fig. 4A). They are better illuminated in the correlation coefficient maps (Fig. 4B), confirming that these long, distinct, and single-variant shear faults (along each side of the indent impression) are indeed the prevailing microstructural features in the quasi-plastic zones in undoped boron carbide. On the contrary, for the Si-doped boron carbide, most amorphous shear bands and micro-cracks are much more diffuse and difficult to distinguish (Figs. 4C and 4D). Although some shear faults are still present in the quasi-plastic zones (such as the top left region near the impression surface in Figs. 4C and 4D), they are no longer the predominant features. Combined with the higher magnification bright-field

TEM observations, we can deduce that short, diffuse, and multi-variant shear faults are prevalent in the quasi-plastic zones of Si-doped boron carbide samples. In addition, a number of low-reliability regions are evident (Fig. 4C). More detailed analysis showed that they are caused by multiple sets of diffraction patterns through the thickness of the TEM foil (Figs. 4E-G). This observation infers many shear faults have large proportions of fault planes contained within the TEM foil. Overlapping crystals were not observed in undoped boron carbide. This further confirms the multi-variant nature of the shear faults in the Si-doped samples. As been described previously, the indents we examined were from the same boron carbide grain but with varied chemistry. Therefore, the differences in deformation behavior are primarily caused by Si doping.

To explain the remarkable differences in microstructure and to deduce the active deformation mechanisms, we quantified the densities of shear faults (dividing the total shear fault length by the area) from the same regions in the undoped and Si-doped quasi-plastic zones. The average length density of shear faults was measured to be $9.3 \pm 3.5 \text{ } \mu\text{m}^{-1}$ in the undoped boron carbide and $10.8 \pm 2.4 \text{ } \mu\text{m}^{-1}$ in the Si-doped boron carbide. Two-sample t-test suggested the shear fault densities are statistically the same in both samples. (The calculated $|T|$ is equal to 1.23, which is less than the critical value of $t_{1-\alpha/2, v} = 2.365$ for the two-tailed t distribution.) It is interesting to note that the Raman results indicated that Si-doping significant amorphization mitigation, but the TEM observation revealed that Si-doping did not reduce the shear fault density. The seeming ambivalence suggests that many micro-cracks in the Si-doped samples are caused by direct fragmentation rather than amorphization. The change in mechanism is also manifested by morphologies of shear faults. The shear faults in the undoped boron carbide quasi-plastic zones are long, straight,

distinct, and dominantly single-variant, indicating they started as amorphous shear bands and evolved in micro-cracks. The high planarity of the shear faults is dictated by the fact that amorphous shear bands generally grow along specific crystallographic planes (4, 24). In contrast, the shear faults in the Si-doped boron carbide are short, meandering, diffuse, and multi-variant, suggesting many of them were not evolved from amorphous shear bands but directly formed from fragmentation. The hardness values of the undoped and Si-doped boron carbide regions are comparable. This implies that at similar stress levels, amorphization was dominant in the undoped boron carbide, whereas both amorphization and fragmentation were activated in the Si-doped boron carbide. The presence of Si in the lattice may have stabilized the icosahedra against amorphization (15, 16) and lowered the energy barrier for fragmentation via atomic-level local lattice distortion (16). Since amorphization could lead to a sudden deterioration of mechanical properties (4) while regular fragmentation does not (5, 31), Si-doping may present itself as a promising strategy to design boron carbide exhibiting superior ballistic performance.

Summary

In summary, we discovered that even a small amount of Si doping (~ 1 at.%) in boron carbide resulted in a dramatic change in the deformation mechanisms. Si doping led to a reduction of stress-induced amorphization in boron carbide. We also observed that long, distinct, and dominantly single-variant shear faults formed in the quasi-plastic zones of the undoped boron carbide; short, diffuse, and multi-variant shear faults contributed to the quasi-plasticity in the Si-doped sample. The mitigation of amorphization and the change in deformation mechanisms are likely caused by the atomic-level structural stabilization and lowering energy barrier for fragmentation from Si doping. These discoveries could guide the design of next-generation amorphization-resistant body armor. Moreover, the insight gained from this work opens up pathways for tuning the deformation mechanisms of ceramics via solute doping.

Acknowledgments

Funding: Research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-12-2-0022. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein. Additional supports are from the Defense Advanced Research Projects Agency under grant no. W31P4Q-13-1-0001 and K.Y.X.'s start-up grant from Texas A&M Engineering Experiment Station (TEES).

References

1. V. Domnich, S. Reynaud, R. A. Haber, M. Chhowalla, Boron Carbide: Structure, Properties, and Stability under Stress. *Journal of the American Ceramic Society* **94**, 3605-3628 (2011).
2. K. Y. Xie, K. Kuwelkar, R. A. Haber, J. C. LaSalvia, K. J. Hemker, Microstructural Characterization of a Commercial Hot - pressed Boron Carbide Armor Plate. *Journal of the American Ceramic Society*, (2016).
3. M. Chen, J. McCauley, J. LaSalvia, K. Hemker, Microstructural Characterization of Commercial Hot - Pressed Boron Carbide Ceramics. *Journal of the American Ceramic Society* **88**, 1935-1942 (2005).
4. M. Chen, J. W. McCauley, K. J. Hemker, Shock-induced localized amorphization in boron carbide. *Science* **299**, 1563-1566 (2003).
5. D. Grady, Shock-wave strength properties of boron carbide and silicon carbide. *Le Journal de Physique IV* **4**, C8-385-C388-391 (1994).
6. Q. An, W. A. Goddard, T. Cheng, Atomistic Explanation of Shear-Induced Amorphous Band Formation in Boron Carbide. *Physical Review Letters* **113**, 095501 (2014).
7. G. Fanchini, J. W. McCauley, M. Chhowalla, Behavior of disordered boron carbide under stress. *Physical review letters* **97**, 035502 (2006).
8. C. Kunka, A. Awasthi, G. Subhash, Crystallographic and spectral equivalence of boron-carbide polymorphs. *Scripta Materialia* **122**, 82-85 (2016).
9. H. Werheit, Boron carbide: Consistency of components, lattice parameters, fine structure and chemical composition makes the complex structure reasonable. *Solid State Sciences* **60**, 45-54 (2016).
10. H. Werheit, A. Leithe-Jasper, T. Tanaka, H. W. Rotter, K. A. Schwetz, Some properties of single-crystal boron carbide. *Journal of Solid State Chemistry* **177**, 575-579 (2004).
11. H. Werheit, S. Shalamberidze, Advanced microstructure of boron carbide. *Journal of Physics: Condensed Matter* **24**, 385406 (2012).
12. K. Y. Xie *et al.*, Breaking the icosahedra in boron carbide. *Proceedings of the National Academy of Sciences* **113**, 12012-12016 (2016).
13. Q. An, W. A. Goddard, Atomistic Origin of Brittle Failure of Boron Carbide from Large-Scale Reactive Dynamics Simulations: Suggestions toward Improved Ductility. *Physical Review Letters* **115**, 105501 (2015).
14. Q. An, W. A. Goddard III, Microalloying Boron Carbide with Silicon to Achieve Dramatically Improved Ductility. *The Journal of Physical Chemistry Letters* **5**, 4169-4174 (2014).

15. G. Subhash, A. P. Awasthi, C. Kunka, P. Jannotti, M. DeVries, In search of amorphization-resistant boron carbide. *Scripta Materialia* **123**, 158-162 (2016).
16. A. U. Khan *et al.*, Locating Si atoms in Si-doped boron carbide: A route to understand amorphization mitigation mechanism. *Acta Materialia* **157**, 106-113 (2018).
17. J. Proctor *et al.*, Stabilization of boron carbide via silicon doping. *Journal of Physics: Condensed Matter* **27**, 015401 (2014).
18. M. K. Kolel-Veetil *et al.*, Substitution of silicon within the rhombohedral boron carbide (B₄C) crystal lattice through high-energy ball-milling. *Journal of Materials Chemistry C* **3**, 11705-11716 (2015).
19. C. J. Marvel *et al.*, Extending ζ -factor microanalysis to boron-rich ceramics: Quantification of bulk stoichiometry and grain boundary composition. *Ultramicroscopy* **202**, 163-172 (2019).
20. K. Y. Xie *et al.*, Microstructural characterization of boron-rich boron carbide. *Acta Materialia* **136**, 202-214 (2017).
21. H. Werheit, A. Leithe-Jasper, T. Tanaka, H. Rotter, K. Schwetz, Some properties of single-crystal boron carbide. *Journal of Solid State Chemistry* **177**, 575-579 (2004).
22. G. Parsard, G. Subhash, Raman spectroscopy mapping of amorphized zones beneath static and dynamic Vickers indentations on boron carbide. *Journal of the European Ceramic Society* **37**, 1945-1953 (2017).
23. G. Parsard, G. Subhash, P. Jannotti, Amorphization - induced volume change and residual stresses in boron carbide. *Journal of the American Ceramic Society* **101**, 2606-2615 (2018).
24. K. M. Reddy, P. Liu, A. Hirata, T. Fujita, M. Chen, Atomic structure of amorphous shear bands in boron carbide. *Nature communications* **4**, 2483 (2013).
25. V. Domnich, Y. Gogotsi, M. Trenary, T. Tanaka, Nanoindentation and Raman spectroscopy studies of boron carbide single crystals. *Applied Physics Letters* **81**, 3783-3785 (2002).
26. D. Ge, V. Domnich, T. Juliano, E. Stach, Y. Gogotsi, Structural damage in boron carbide under contact loading. *Acta Materialia* **52**, 3921-3927 (2004).
27. G. Subhash *et al.*, Characterization of the 3-D amorphized zone beneath a Vickers indentation in boron carbide using Raman spectroscopy. *Acta Materialia* **61**, 3888-3896 (2013).
28. V. Domnich, Y. Gogotsi, S. Dub, Effect of phase transformations on the shape of the unloading curve in the nanoindentation of silicon. *Applied Physics Letters* **76**, 2214-2216 (2000).

29. W. C. Oliver, G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of materials research* **7**, 1564-1583 (1992).
30. C. Kunka *et al.*, Nanotwinning and amorphization of boron suboxide. *Acta Materialia* **147**, 195-202 (2018).
31. D. E. Grady, Hugoniot equation of state and dynamic strength of boron carbide. *Journal of Applied Physics* **117**, 165904 (2015).
32. E. F. Rauch, M. Veron, Coupled microstructural observations and local texture measurements with an automated crystallographic orientation mapping tool attached to a tem. *Materialwissenschaft und Werkstofftechnik* **36**, 552-556 (2005).
33. F. Rauch Edgar *et al.*, in *Zeitschrift für Kristallographie International journal for structural, physical, and chemical aspects of crystalline materials*. (2010), vol. 225, pp. 103.

Figures

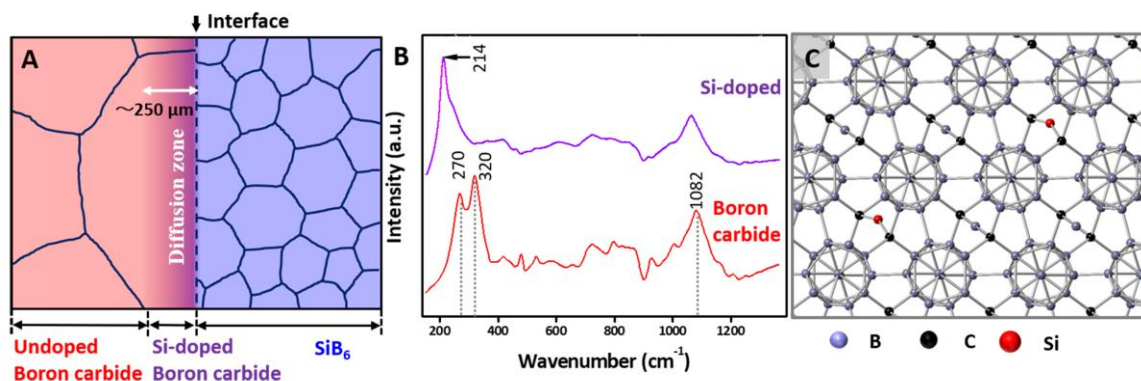


Fig. 1. Structure characteristics of the arc-melted sample after diffusion. (A) Schematic of the arc-melted sample after diffusion has taken place. **(B)** Raman spectra for undoped boron carbide and Si-doped boron carbide. **(C)** A possible atomic model of the Si-doped boron carbide. Some of the CBC chains are replaced by kinked CSiC chains. (The model is adopted from ([16](#)))

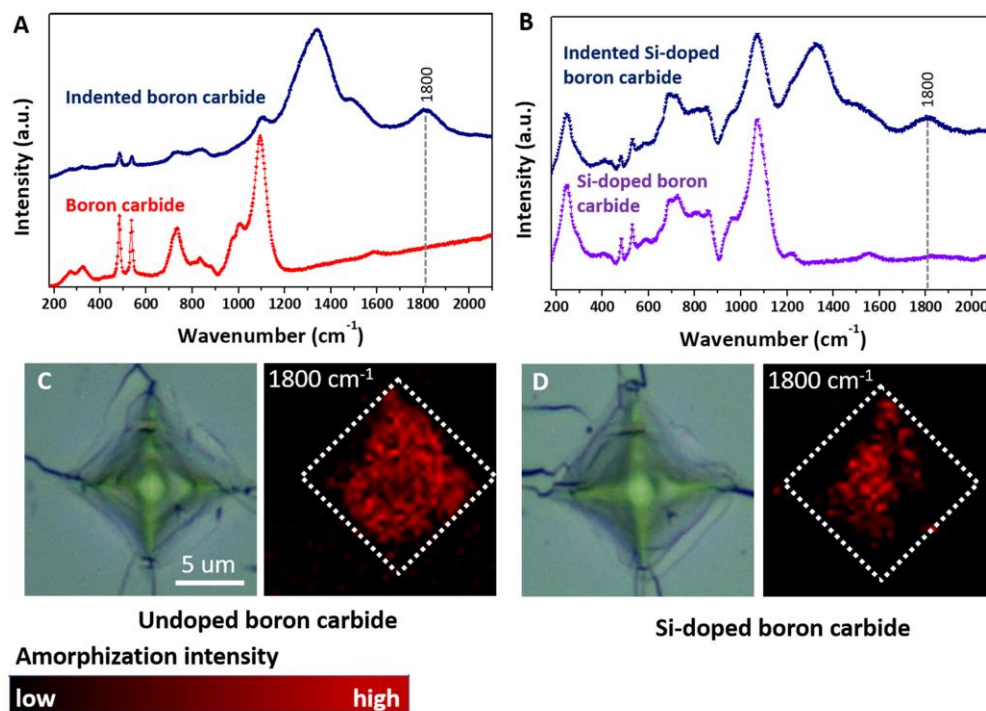


Fig. 2. Comparison of the Raman spectra of indented undoped and Si-doped boron carbides underneath the Vickers indents. Raman spectra of indented (A) undoped boron carbide and (B) Si-doped boron carbide compared to their pristine counterparts. Raman mapping of the amorphous phase in Vickers hardness impressions in (C) undoped boron carbide and within the diffusion zone and (D) in Si-doped single crystal boron carbide.

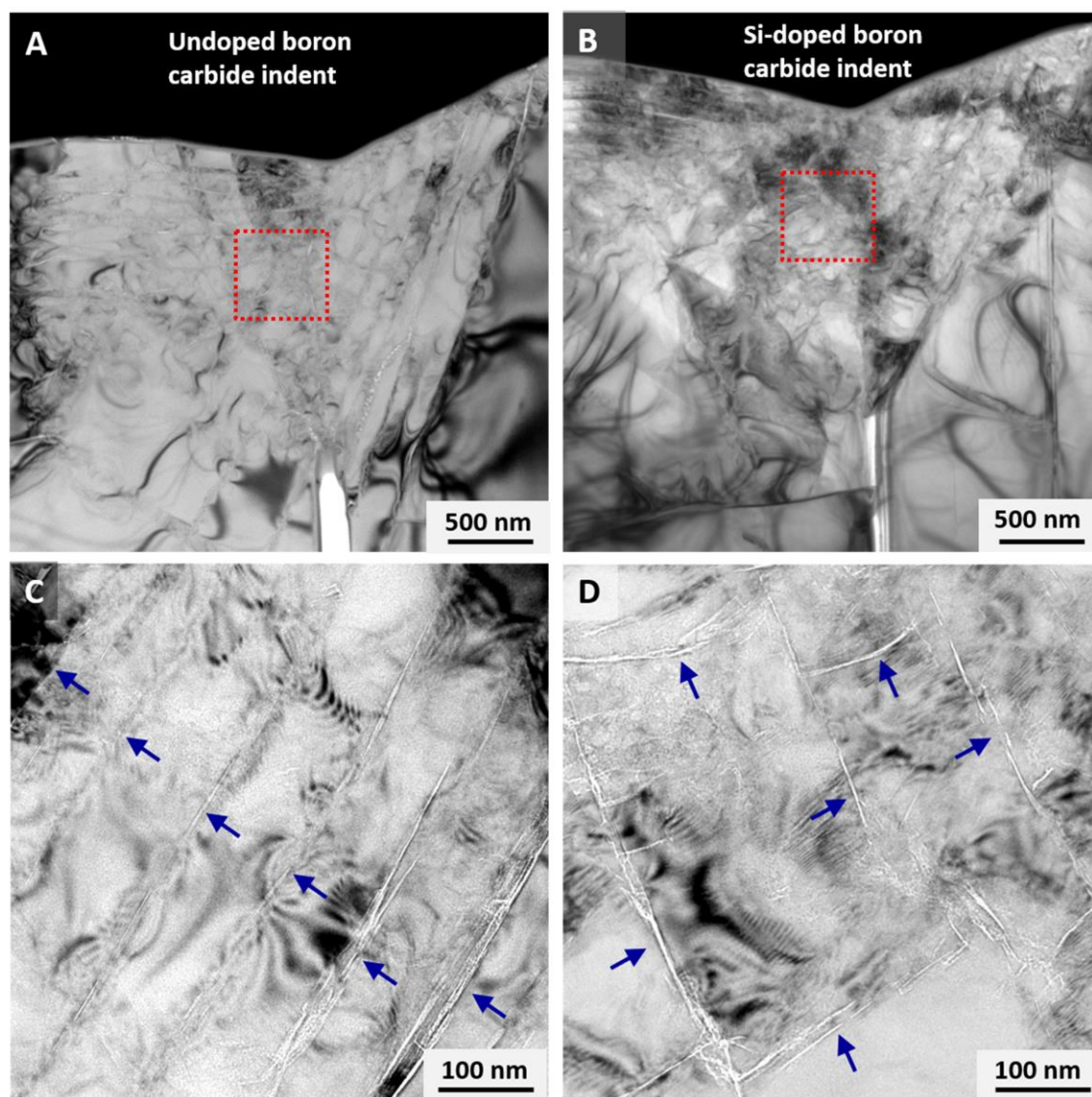


Fig. 3. Bright-field TEM images of indented undoped and Si-doped boron carbides. Low magnification TEM images of indented (A) undoped and (B) Si-doped boron carbides, with higher magnification images showing shear faults in (C) and (D), respectively. The shear faults (consisting of amorphous bands and micro-cracks) are indicated by the arrows.

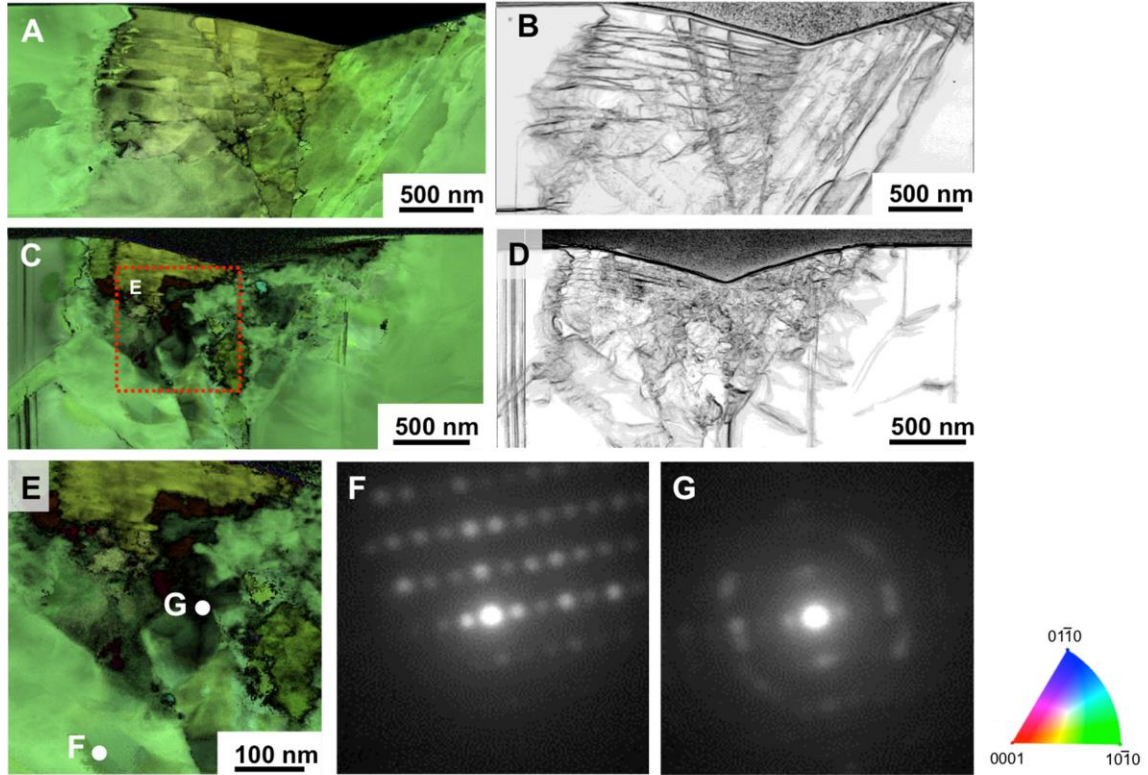


Fig. 4. Microstructure of the quasi-plastic zones revealed by PED with a step size of 5 nm. (A) Orientation map overlapped with reliability map and (B) correlation coefficient map of undoped boron carbide. (C) Orientation map overlapped with reliability map and (D) correlation coefficient map of Si-doped boron carbide. (E) Orientation and reliability map containing part of the quasi-plastic zone of a Si-doped boron carbide sample. The corresponding diffraction patterns from the regions (F) outside and (G) inside the quasi-plastic zone, as labeled in (E). The orientation maps are viewed along the out-of-plane direction. (Note that the intensity of diffuse ring from the narrow amorphous shear bands is overpowered by the diffraction spots from the crystalline phase. The amorphous nature of the shear bands is best revealed by HRTEM rather than PED.)

Supplementary Figures

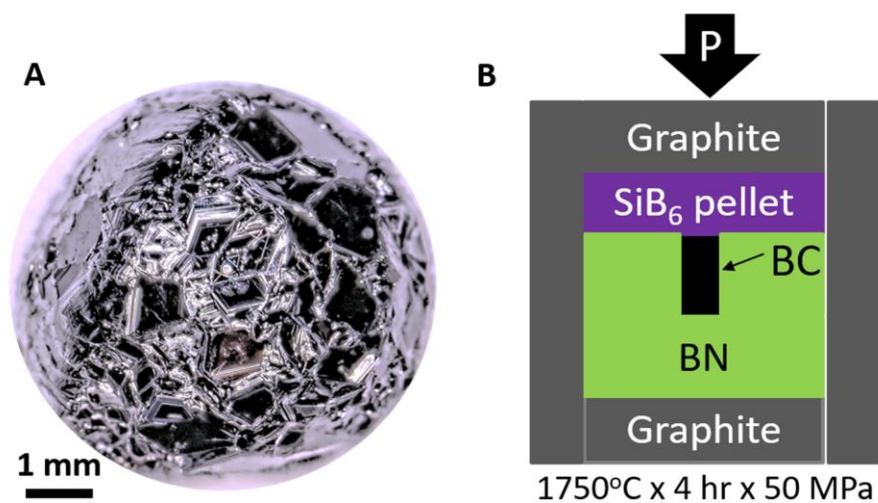


Fig. S1. Preparation of the diffusion couple. (A) Optical image (top view) of the as-melted boron carbide. Millimeter-sized crystals are visible on the top surface of the ingot. (B) Schematic of the die set up used to diffuse Si into boron carbide.

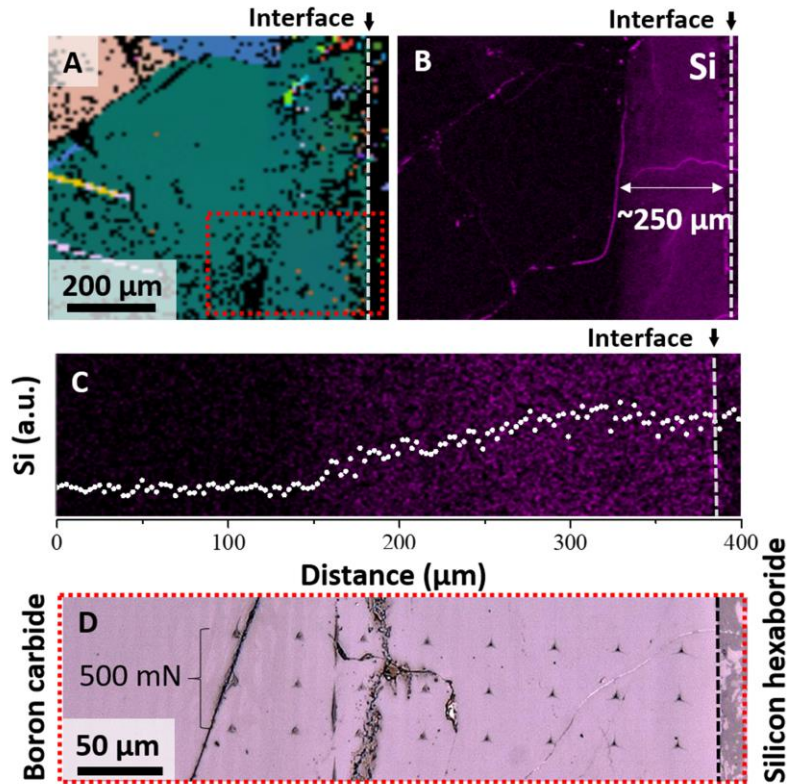


Fig. S2. Berkovich nanoindentation was performed across the Si diffusion zone and the undoped boron carbide within one boron carbide grain. (A) EBSD mapping of the interface showing the same crystal orientation, suggesting a single crystal grain. (B) Si EDS mapping of the corresponding location clearly shows that Si diffused roughly 250 μm into boron carbide. (C) EDS mapping on the diffusion zone and superimposed normalized Si count. (D) Optical image of the indented area showing 3 rows of 8 500 mN Berkovich indents across the diffusion zone. The dashed lines indicate the diffusion interfaces.

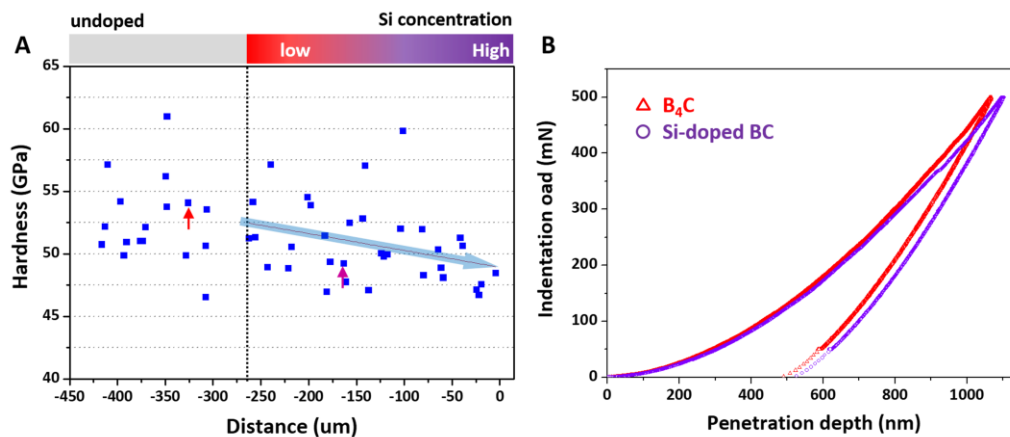


Fig. S3. Berkovich nanoindentation results for undoped and Si-doped boron carbides. (A) Berkovich hardness across the diffusion zone in boron carbide - SiB_6 couple. Zero on the x-axis indicates where the interface of SiB_6 and Si-doped BC is. (B) Typical nanoindentation load-displacement curves for undoped and Si-doped boron carbides.

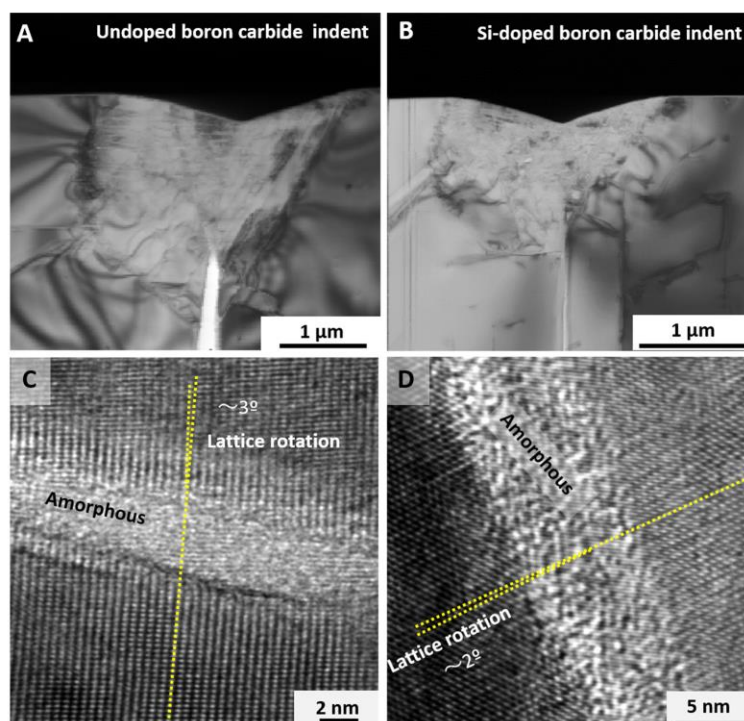


Fig. S4. TEM observation of indented undoped and Si-doped boron carbides. Low magnification virtual bright-field STEM images of indented (A) undoped boron carbide and (B) Si-doped boron carbide. HRTEM images of amorphous shear bands in (C) undoped boron carbide and (D) Si-doped boron carbide.

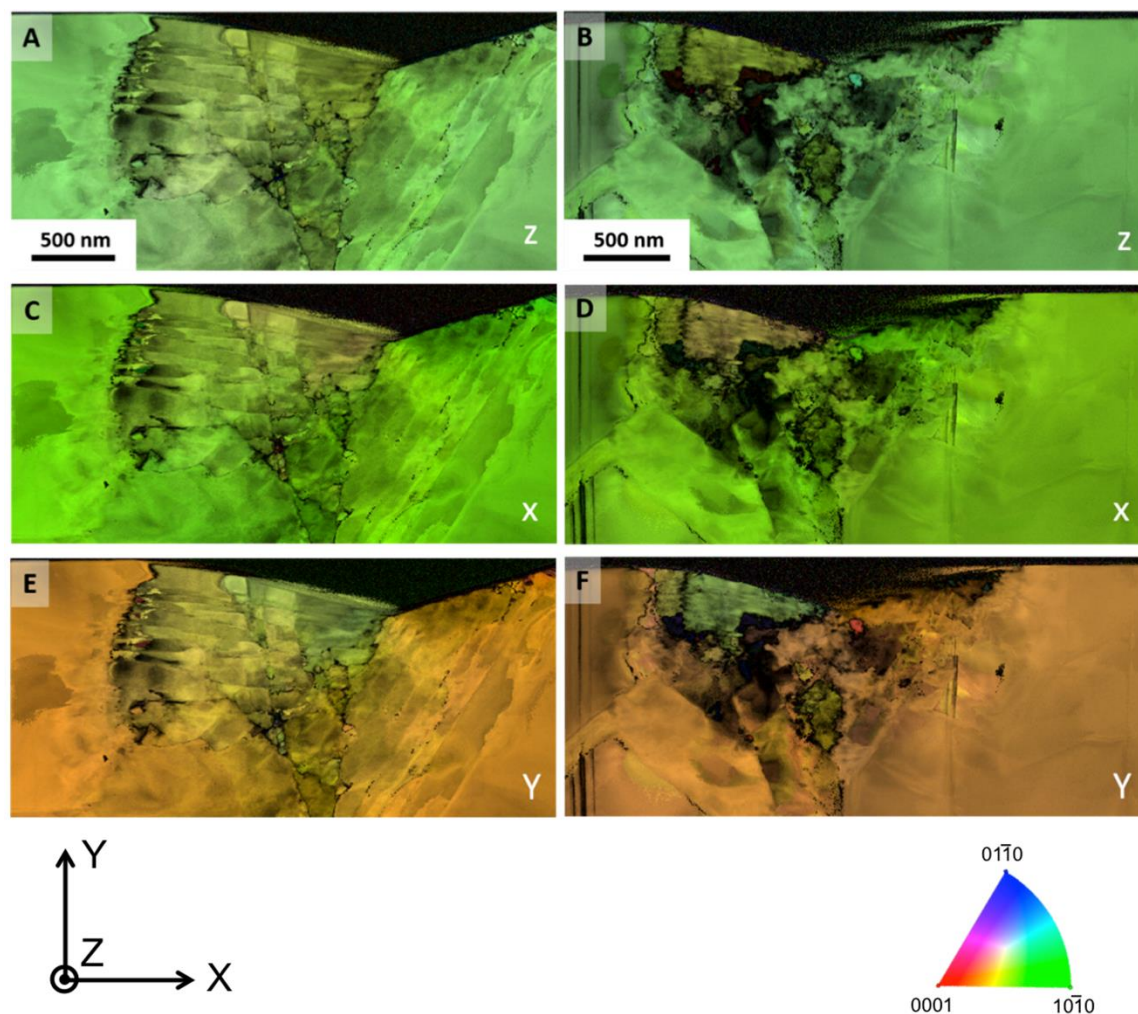


Fig. S5. Orientation maps of the quasi-plastic zones of undoped and Si-doped boron carbides. Orientation maps from Z, X and Y directions overlapped with reliability maps of (A, C and E) undoped and (B, D and F) Si-doped boron carbide.

CHAPTER 7

Notes: This chapter encompasses data that will be written for a journal publication in the near future. This chapter takes a deep dive into characterizing 3-D amorphous volume using Raman spectroscopy and isolating the effect of Si-doping from B-doping.

Introduction

Often the term “Si-doping” is used to describe boron carbide with elevated Si content as a solid solution. However, “Si-doping” is a misnomer because, according to the experimental phase diagram, Si can only be incorporated into boron carbide when the B/C ratio is greater than 4. In another word, the stoichiometric B_4C , the most stable phase of boron carbide, cannot accommodate Si but $B_{6.5}C$ can. The stoichiometric shift from $B_{6.5}C$ to B_4C is referred to as B-doping in boron carbide. The effect of pure Si-doping is put into question when recently B-doping is discovered to also mitigate amorphization [1]. The discovery complicates the assessment of the ability to suppress amorphization. The assessment is further complicated by grain size effect as smaller grain size in boron carbide can lead to higher resistance to amorphization [2, 3].

It is necessary to design an experiment that has boron carbide with a range of B/C ratio and Si/B co-doped boron carbide with the same B/C ratio and grain size. To accomplish the design requirement, a B- B_4C and a SiB_6 - B_4C diffusion couples were fabricated. The B and the Si/B diffuse into the dense B_4C side to form a diffusion gradient. The effect of grain size can be eliminated since the grain size in the diffusion zone is the same. Several thin foils were extracted across the diffusion zone using a focused ion beam (FIB) to characterize its chemical content. Next, TEM based EDS ζ -factor microanalysis was used to determine the chemical content. SEM-based EDS line scan was also performed

across the diffusion zone to get an overall chemical trend and calibrated to the findings of TEM EDS results, as shown in Fig. 1.

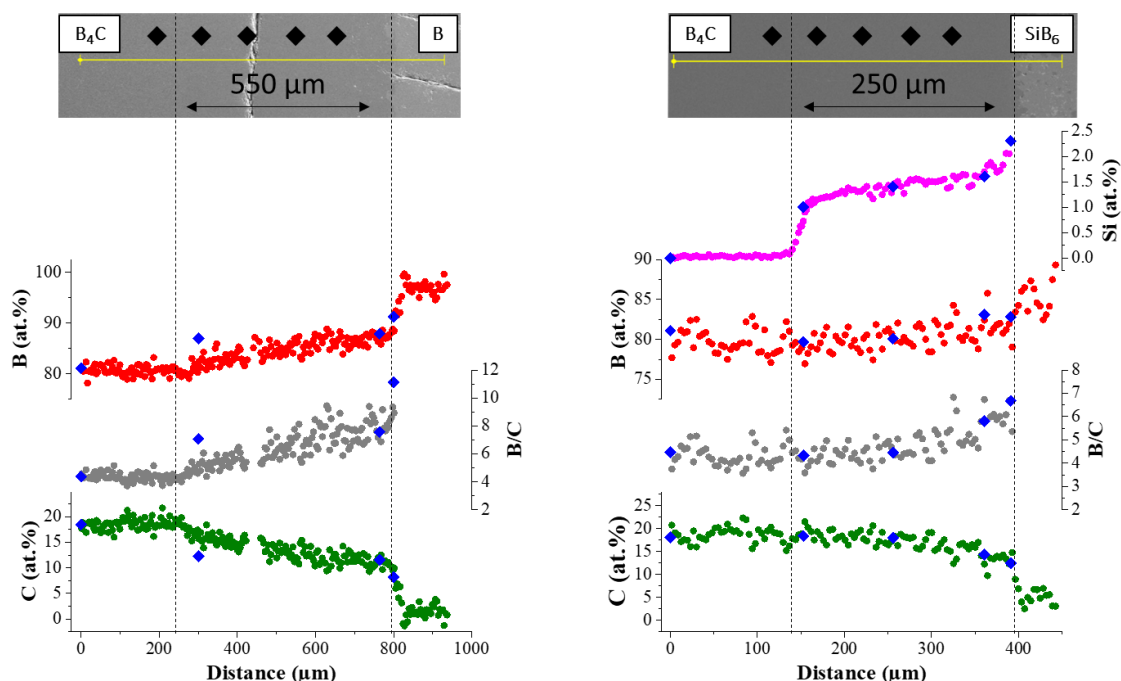


Fig 1. SEM-EDS line scan results across the B-B₄C and SiB₆-B₄C diffusion couple. Blue markers are chemical content calibration standards acquired using TEM-EDS. In the B-B₄C diffusion couple, the B/C ratio roughly covers from 4-9 and SiB₆-B₄C diffusion covers 4-6.5.

Vickers indentations were placed across the diffusion zones as a means to activate stress-induced amorphization. Amorphization mapping on the surface was carried out in the same fashion as described in Chapters 2 and 4. Raman spectroscopy has limited probing size ($\sim 0.5 \mu\text{m}$), which means amorphization in the bulk material is not determined. To better understand the 3-D volume of the amorphous zone, a technique of successive polishing and Raman imaging was employed, as described here [4] and illustrated in Fig. 2. Polishing was carried out using $1 \mu\text{m}$ diamond suspensions. Tracking indents were put

down in the vicinity of the indentations being studied. Polishing was carried out in increments of 5 minutes to ensure over polishing does not occur. Polishing was conducted until only the apex of the imprint remained before a new set of tracking indents was placed. AFM was used to measure the profile of the tracking indents before and after the polishing procedures to obtain the depth of moved material. Raman mapping was conducted on each polished surface. 5-7 indents were surveyed for each chemical content for each layer to ensure the data is statistically significant.

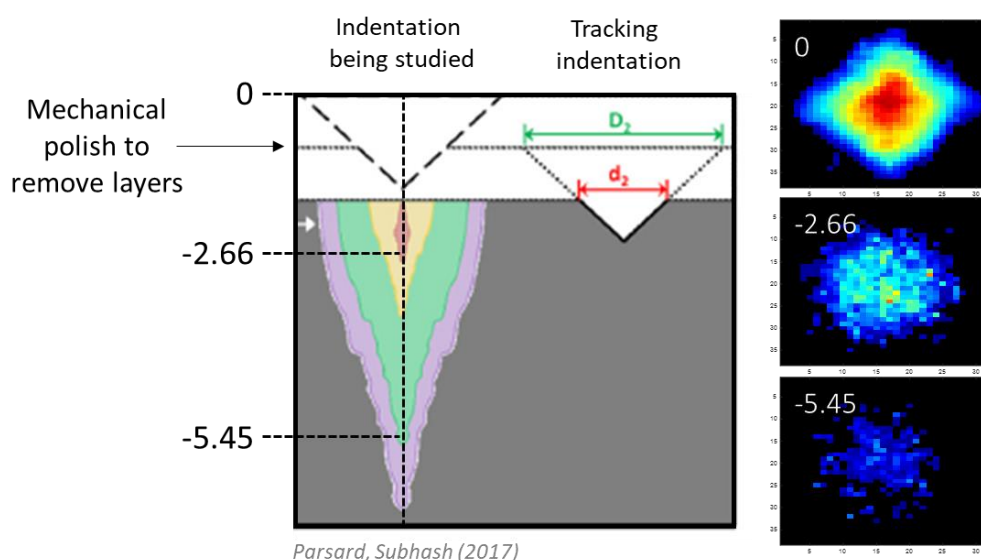


Fig. 2. Illustration of successive polishing and Raman imaging procedure. The amorphous cross-sectional area decreases as the depth increases.

Establishing confidence in comparison:

The first set of the indents was placed in the B_4C , or the undoped side, for both samples. The amorphous intensity map on the surface and at different depths were used to establish confidence in comparing both samples. The Raman map of B_4C on both samples is shown in Fig. 3. It is clear that as the depth increases, the extent of amorphization

decreases, following the trends in the literature [4]. The map acquired from a similar depth shows similar amorphization map intensity and distribution.

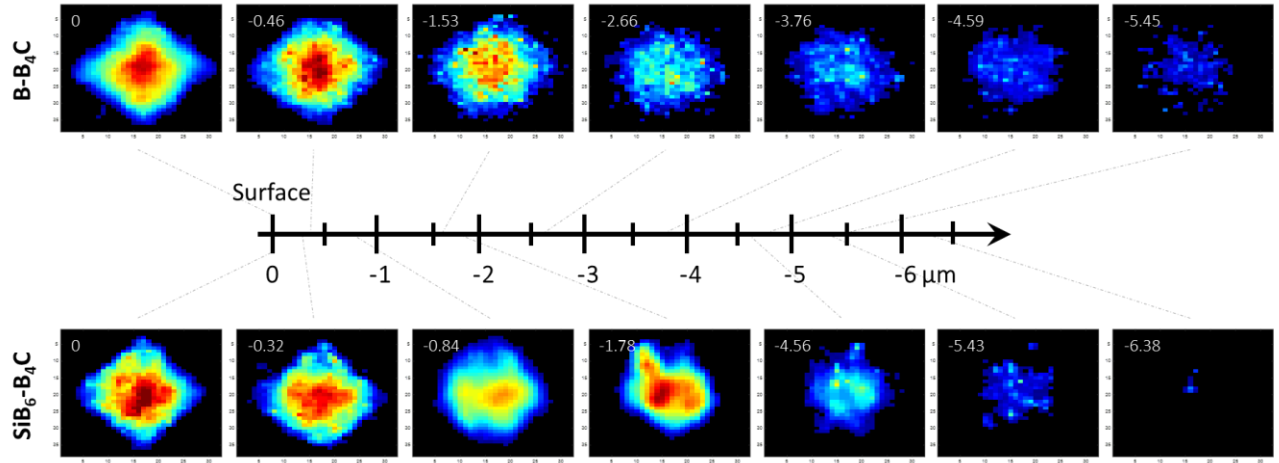


Fig. 3. Raman amorphization intensity map of B₄C composition for B-B₄C and SiB₆-B₄C diffusion couples. A diminishing in amorphization is correlated with an increase in depth. The size of the amorphous area also decreases with depth.

To understand the maps more quantitatively, the summation of the pixels at different depths were compared in Fig. 4. The trend lines for both samples show an identical reduction in amorphization as a function of depth. In the B₄C composition, both materials show the amorphous volume extending to ~6.5 μm beneath the surface. The diameters 1 and 2 of the Vickers imprint were averaged to illustrate the size of the amorphous area. The amorphous areas from both samples show a similar reduction rate. At this point, it is clear to say the B₄C material in both samples is equivalent and they can be compared directly to each other.

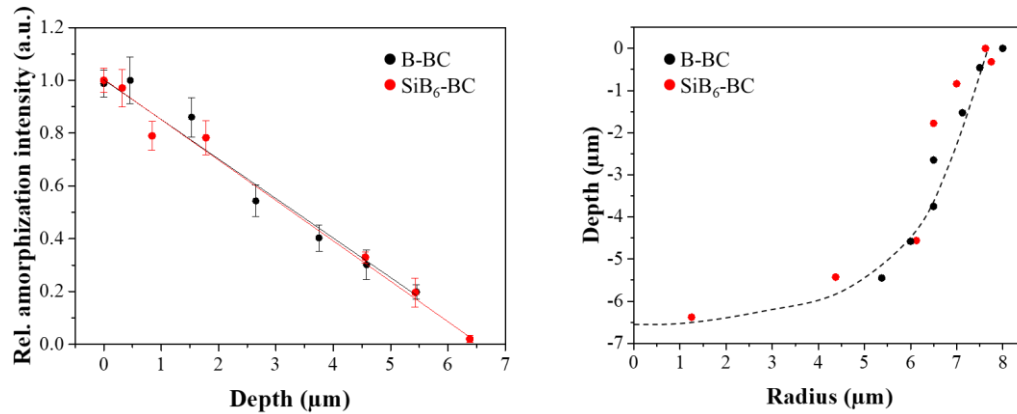


Fig. 4. Quantitatively comparing the amorphization intensity of B_4C composition for B- B_4C and SiB_6 - B_4C diffusion couples. The intensity and area of the amorphous area at the same depth are similar for both samples. The result implies that the baseline B_4C in both samples are equivalent.

Amorphization vs chemistry on the surface

The amorphous map of different chemistry on the surface is displayed in Fig. 5. It's clear that an increase in the B/C ratio reduces amorphization but the increase in Si as well as B/C ratio indeed shows more reduction. Quantitatively, the normalized amorphization intensity trend lines show a substantial reduction due to pure Si-doping when the B/C ratio is fixed.

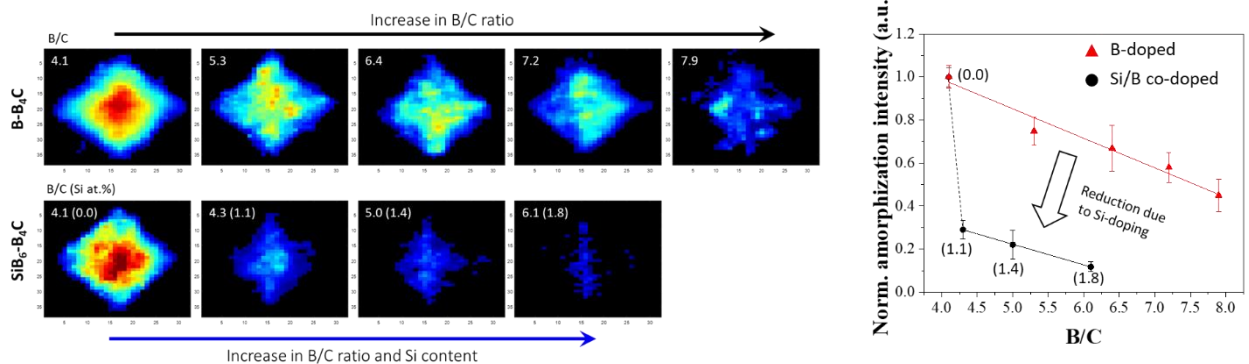


Fig. 5. Comparison of the amorphization intensity map on the surface across the diffusion zone in B-B₄C and SiB₆-B₄C diffusion couples. The normalized intensity shows a substantial reduction in amorphization due to pure Si-doping.

Amorphization vs chemistry at depth

The reduction of amorphization vs depth as a function of chemical content across the diffusion zone is plotted in Fig. 6. It's clear that a decreasing trend is observed for every composition. In general, the trend lines with a higher B/C ratio have less amorphization and the line with Si has substantially less amorphization. It is worth noting that all the trend lines approach zero at roughly the same depth. This suggests the effect of amorphization reduction due to B or Si/B-doping is less efficient deeper into the material. For example, the B/C ratio 5.3-7.9 shows the same level of amorphization at 4.5-5.5 μm beneath the surface. A similar observation can be found for the Si/B co-doped boron carbide at Si content of 1.1-1.8.

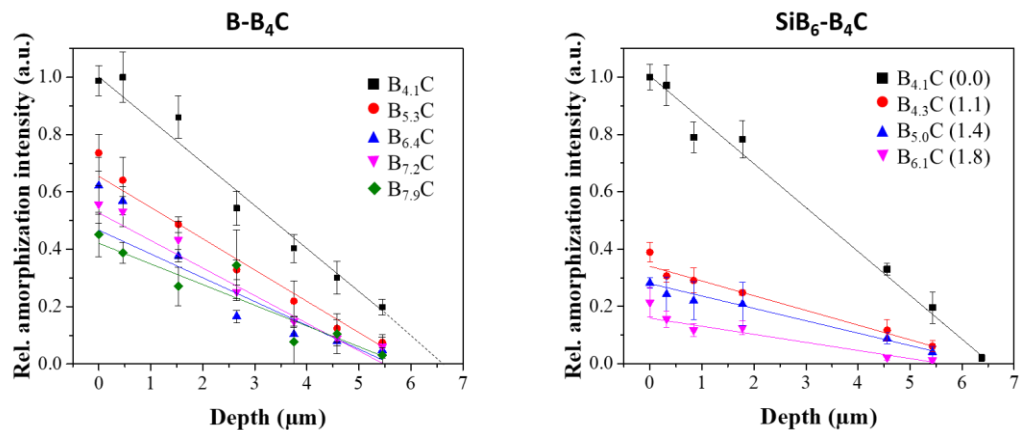


Fig. 6. Relative amorphization intensity of B-doped and B/Si co-doped boron carbide as a function of depth beneath the indentation and chemistry.

The size of the amorphous area is the smallest when the B/C and Si content are the highest, as shown in Fig. 7. The reduction in the amorphous area isn't so clear when the B/C ratio is between 6.4-7.2. The reduction in intensity is evident in Fig. 6. The reduction in area is only evident when comparing the two extreme conditions when B/C is 4.1 and 7.9. The reduction in the amorphous area is clear when Si is increased.

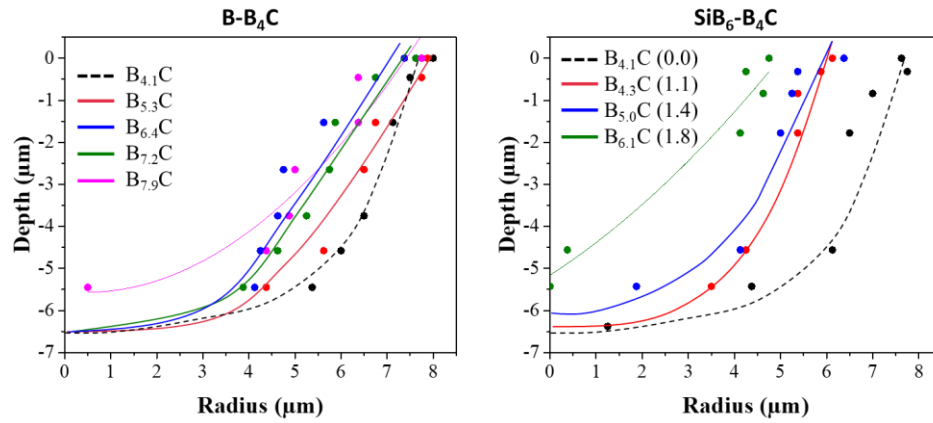


Fig. 7. Comparison of the amorphous radius of B-doped and Si/B co-doped boron carbide as a function of depth and chemistry.

Conclusion

This chapter was carefully designed to compare and decouple the effect of B and Si-doping for reducing amorphization in boron carbide. We found an increase in the B/C ratio is correlated with a steady increase in amorphization. More importantly, as little as ~1 at.% Si can dramatically reduce the amorphization intensity compared to boron carbide of the same B/C ratio. The ~1% number is consistent with the finding in Chapter 6. Si-doping is most effective at suppressing the area of amorphization, in terms of the total intensity.

References

- [1] A. Chauhan, M.C. Schaefer, R.A. Haber, K.J. Hemker, Observed Mitigation of Local Amorphization in Boron-Rich Boron Carbide, Available at SSRN 3414007 (2019).
- [2] G. Subhash, A.P. Awasthi, C. Kunka, P. Jannotti, M. DeVries, In search of amorphization-resistant boron carbide, *Scripta Materialia* 123 (2016) 158-162. 10.1016/j.scriptamat.2016.06.012.
- [3] B.M. Moshtaghioun, D. Gomez-Garcia, A. Dominguez-Rodriguez, R.I. Todd, Grain size dependence of hardness and fracture toughness in pure near fully-dense boron carbide ceramics, *J. Eur. Ceram. Soc.* 36(7) (2016) 1829-1834. 10.1016/j.jeurceramsoc.2016.01.017.
- [4] G. Subhash, D. Ghosh, J. Blaber, J.Q. Zheng, V. Halls, K. Masters, Characterization of the 3-D amorphized zone beneath a Vickers indentation in boron carbide using Raman spectroscopy, *Acta Mater.* 61(10) (2013) 3888-3896. 10.1016/j.actamat.2013.03.028.

CHAPTER 8

Advancing the mechanical properties of Si/B co-doped boron carbide through TiB₂ reinforcement

Qirong Yang¹, Azmi Mert Çelik¹, Jun Du¹, Jerry C. LaSalvia², Chawon Hwang^{1,†}, and Richard A. Haber^{1,†}

¹*Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA*

²*CCDC Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA*

† Corresponding authors' emails: rich.haber@rutgers.edu & chawon.hwang@rutgers.edu and address: 607 Taylor Road, Piscataway, NJ 08854, USA. Tel: +1(848) 445-5924, Fax: +1(732) 445-5926.

Abstract

Boron carbide experiences glass-like brittle behavior when subjected to high shear stresses due to stress-induced amorphization. Strategies to mitigate amorphization have primarily focused on Si/B co-doping. However, the overall mechanical properties of Si/B co-doped boron carbide are unknown. Here, we delivered a comprehensive report on the mechanical properties of Si/B co-doped boron carbide; and proposed an effective strategy to improve the mechanical properties through TiB₂ reinforcement. Vickers hardness of 25.0 GPa, indentation toughness of 2.1 MPa·m^{0.5}, Young's modulus of 430 GPa, and flexural strength of 338 MPa were measured for Si/B co-doped boron carbide. The reinforcement

with TiB_2 increased the overall mechanical properties to 26.6 GPa for hardness, $2.3 \text{ MPa}\cdot\text{m}^{0.5}$ for indentation toughness, and 410 MPa and flexural strength. The improvements were attributed to the combined effects of grain size refinement and crack propagation alteration due to TiB_2 addition.

Keywords: Boron carbide; Si/B co-doping; Titanium diboride; Ceramic composites; Indentation and hardness;

Introduction

Boron carbide is notably used in armor ceramics and other engineering utilities owing to a combination of excellent mechanical properties and low density [1-3]. Nonetheless, boron carbide experiences glass-like fracture behavior when subjected to impact pressures exceeding its Hugoniot Elastic Limit ($\sim 17\text{-}20$ GPa) [3], as occurs during a ballistic event. The anomaly is attributed to the formation of nano-scale amorphous bands nucleated by high shear stresses generated during high-velocity impacts ($\sim 750\text{-}800$ m/s) [4]. The amorphous bands act as crack nucleation sites and crack propagation paths to accelerate the comminute behavior [4, 5].

Strategies to mitigate amorphization have primarily focused on modifying the composition of boron carbide by atomic doping, e.g. B-doping and Si/B co-doping [6, 7]. However, B-doping diminishes mechanical properties of boron carbide due to lengthening/weakening of the covalent bonds and the propensity for rapid grain growth [8, 9]. Similar adverse effects can be anticipated for Si/B co-doping; however, to our best knowledge, the overall mechanical properties have not yet been reported. To improve the mechanical properties of Si/B co-doped boron carbide, we propose reinforcement with titanium diboride (TiB_2) because it possesses the lowest density and the highest toughness among $\text{Me}^{\text{IV}}\text{B}_2$ reinforcement phases, e.g. HfB_2 and ZrB_2 [10]. Furthermore, one report found that TiB_2 inhibits rapid grain growth in boron carbide, leading to a higher hardness [11]. Others found the addition of TiB_2 resulted in an increase in strength and toughness in boron carbide [12, 13].

In general, high hardness is regarded as the best predictor for stopping ballistic penetration while strength and toughness are important factors for rough handling of armor

ceramics [14]. Therefore, understanding the mechanical properties Si/B co-doped boron carbide and its composite with TiB_2 is imperative for them to be considered as potential armor ceramics. Here, we deliver a comprehensive report on the mechanical properties of Si/B co-doped boron carbide and its composite with TiB_2 .

Materials and Methods

Commercially available (H.C. Starck) powders of boron carbide, silicon hexaboride, amorphous boron, and titanium diboride were mixed according to compositions listed in Table 1. The powder mixtures were loaded into a 107 x 107 mm graphite die and reaction hot-pressed at 1950°C at 20 MPa for 3 hrs in Ar.

Phase identification of the consolidated materials was characterized using X-ray diffraction (XRD) and Raman spectroscopy. Microstructure and chemical analysis were carried out using a Field-Emission Scanning Electron Microscope (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS), respectively. The grain size was measured according to the linear intercept method per ASTM E112-13. Density was determined using the Archimedes' principle. The theoretical density of the TiB_2 (4.52 g/cm³) reinforced Si/B co-doped boron carbide (2.50 g/cm³ [15]) composite was determined by the rule of mixture. Methods for obtaining Young's modulus (E), hardness (H_v), and indentation toughness (K_{Ic}) were outlined elsewhere [11]. The consolidated tiles were machined into 3 x 4 x 45 mm bars according to ASTM C1161-18 for a 4-point bending test to acquire flexural strength (σ_f). 10-12 measurements were taken for H_v , K_{Ic} , and σ_f . An armor grade boron carbide (PAD B₄C, CoorsTek; noted as CBC) was used as the baseline for the study.

Results and Discussion

Bulk ceramic tiles (107 x 107 x 13 mm) of Si/B co-doped boron carbide (SBC) and TiB₂ reinforced Si/B co-doped boron carbide (TSBC) are pictured in Fig. S1. The densities are 2.49 and 2.59 g/cm³, corresponding to 99.6 and 99.2% TD for SBC and TSBC, respectively. Fig. 1a illustrates the XRD patterns of SBC, TSBC, and CBC. Only the boron carbide phase was identified in the SBC sample whereas TiB₂ and boron carbide phases were found in the TSBC sample. Minor impurities such as C, BN, and AlN were found in CBC in addition to the major boron carbide phase. The enlarged image depicts the (021) peak position of boron carbide. Relative to CBC, both doped samples show a downshift in the (021) peak position, an indication of expanded crystal lattices due to doping [7, 16]. Raman analysis, shown in Fig. 1b, reveals that SBC and TSBC are Si/B co-doped, evident by the formation of the 210/240 cm⁻¹ doublet and 1170 cm⁻¹ peak [7]. Additionally, the downshift in the 1090 cm⁻¹ Raman band with respect to CBC also indicates larger lattice parameters [7].

The microstructures of SBC and TSBC are shown in Fig. 1c-1f. Although both samples use the same boron carbide powder with an average starting particle size of 0.5 μm, the final grain size is drastically different. SBC has a unimodal grain size distribution with an average of 79.8 ± 11.0 μm. Contrarily, TSBC has bimodal grain sizes with predominantly smaller grains of 1.5 ± 0.2 μm and some larger grains of 32.5 ± 9.2 μm, as shown in Fig. 1f. The exaggerated grain growth is likely due to the formation of Si and/or B containing melts during reactive sintering [16]. The smaller grain sizes in TSBC can be attributed to grain pinning by TiB₂ as reported in the previous study [11]. TiB₂ polishing pull-outs are common in the TSBC sample, marked in black arrows in Fig 1e. A secondary phase rich

in Si and O was found throughout the microstructure of both samples. Due to the lack of the diffraction peaks, we speculate that the second phase is a SiO₂-rich glassy phase likely introduced by SiB₆ as SiO₂ surface oxide in the starting mixtures. A closer inspection reveals that the SiO₂-rich phase is uniformly distributed in the microstructure of SBC, as seen in Fig. 1d. Oppositely, a higher concentration of the SiO₂-rich is intermittently covering the abnormally large boron carbide grain in the TSBC sample, as shown in Fig. S2. This wetting behavior is an example of incomplete or pseudopartial wetting when the second phase content is high and the contact angle between the SiO₂-rich phase and boron carbide grain is nonzero. Such examples can be found in the WC-Co [17], Al-Zn [18], and Fe-Si [19] systems.

The mechanical properties and densities of CBC, SBC, and TSBC are summarized in Fig. 2. Overall, SBC shows inferior mechanical properties compared to CBC and TSBC with an exception of Young's modulus. The diminished mechanical properties have been reported in B-doped boron carbide due to weakening in the atomic bonds [8]. Similarly, Si/B co-doping stretches the covalent bonds, as evident by the downshift in the XRD patterns and Raman spectrum in Fig. 1a-1b, leading to weaker atomic bonds. The larger grains in Si/B co-doping also has an adverse effect on the mechanical properties of boron carbide according to the Hall-Petch relationship [20]. Lastly, the SiO₂-rich glassy phase found in the microstructure of SBC further degrades the overall mechanical properties.

TSBC shows an overall improvement in the mechanical properties compared to SBC, notably +6% H_v, +10% K_{IC}, and +21% σ_f. The improvement in the strength is attributed to smaller grain sizes in TSBC. However, the variation in the grain size distribution expanded the variation in strength values. The Weibull modulus values of SBC and TSBC are 7.5

and 5.7, respectively. The incorporation of TiB_2 enhances the overall toughness in two ways. The tougher TiB_2 ($K_{\text{Ic}} = 6.2 \text{ MPa}\cdot\text{m}^{0.5}$ [21]) requires more energy for a crack to travel through than boron carbide ($K_{\text{Ic}} = 2.7\text{-}2.9 \text{ MPa}\cdot\text{m}^{0.5}$ [14]) thus reducing the overall crack length. Fig. 3a illustrates the termination of crack by a TiB_2 grain. The addition of TiB_2 also changes the crack propagation behavior of boron carbide from intergranular to mixed modes of intergranular and transgranular as shown in Fig. 3b. Residual stress ($\sim 480\text{-}660 \text{ MPa}$) as a result of the lattice parameters and thermal expansion mismatch could cause the observed crack deflection [11, 13]. Furthermore, the weakened grain boundaries due to the presence of incomplete SiO_2 -rich boundary layer could also aid in intergranular crack propagation behavior.

Conclusions

Large-size (107 x 107 x 13 mm) tiles of Si/B co-doped boron carbide and 10 wt.% TiB₂ reinforced Si/B co-doped boron carbide were fabricated through reaction hot-pressing in order to report their mechanical properties. Si/B co-doped boron carbide acquires $H_v = 25.0 \pm 0.9$ GPa, $K_{Ic} = 2.1 \pm 0.2$ MPa·m^{0.5}, $E = 430 \pm 1.7$ MPa, and $\sigma_f = 338 \pm 30$ MPa. TiB₂ reinforced composite has $H_v = 26.6 \pm 0.9$ GPa, $K_{Ic} = 2.3 \pm 0.2$ MPa·m^{0.5}, $E = 427 \pm 2.0$ GPa, and $\sigma_f = 410 \pm 52$ MPa, comparable to the commercially available armor-grade PAD B₄C. The values correspond to an improvement of 6% in H_v , 10% in K_{Ic} , and 21% in σ_f due to TiB₂ addition. The improvement in the mechanical properties is attributed to the combined effects of grain size inhibition and crack propagation alteration due to TiB₂ addition.

Acknowledgment

This work was supported by the Defense Advanced Research Projects Agency [Grant No. W31P4Q-13-1-000] and the Army Research Laboratory [W911NF-12-2-0022].

References

- [1] F. Thevenot, J. Eur. Ceram. Soc., 6 (1990), pp. 205-225
- [2] V. Domnich, S. Reynaud, R.A. Haber, et al., J. Am. Ceram. Soc., 94 (2011), pp. 3605-3628
- [3] D.E. Grady, J. Phys. IV, 4 (1994), pp. 385-391
- [4] M. Chen, J.W. McCauley, K.J. Hemker, Science, 299 (2003), pp. 1563-6
- [5] Q. An, W.A. Goddard III, Phys. Rev. Lett., 115 (2015), pp. 105501
- [6] S. Xiang, L. Ma, B. Yang, et al., Sci. Adv., 5 (2019), pp. eaay0352
- [7] Q. Yang, C. Hwang, C.J. Marvel, et al., J. Eur. Ceram. Soc., 39 (2019), pp. 5156-5166
- [8] K. Niihara, A. Nakahira, T. Hirai, J. Am. Ceram. Soc., 67 (1984), pp. C-13-C-14
- [9] C. Cheng, K.M. Reddy, A. Hirata, et al., J. Eur. Ceram. Soc., 37 (2017), pp. 4514-4523
- [10] W.G. Fahrenholtz, E.J. Wuchina, W.E. Lee, et al., Ultra-high temperature ceramics: materials for extreme environment applications, John Wiley & Sons 2014.
- [11] C. Hwang, S. DiPietro, K.Y. Xie, et al., J. Am. Ceram. Soc., (2019), pp. 4421-4426
- [12] V. Skorokhod, M. Vlajic, V. Krstic, J. Mater. Sci. Lett., 15 (1996), pp. 1337-1339
- [13] S. Yamada, K. Hirao, Y. Yamauchi, et al., J. Eur. Ceram. Soc., 23 (2003), pp. 1123-1130
- [14] L. Vargas-Gonzalez, R.F. Speyer, J. Campbell, Int. J. Appl. Ceram. Technol., 7 (2010), pp. 643-651
- [15] A.U. Khan, A.M. Etzold, X.K. Yang, et al., Acta Mater., 157 (2018), pp. 106-113
- [16] H. Clark, J. Hoard, J. Am. Chem. Soc., 65 (1943), pp. 2115-2119
- [17] B. Straumal, I. Konyashin, B. Ries, et al., Materials Letters, 147 (2015), pp. 105-108
- [18] B. Straumal, X. Sauvage, B. Baretzky, et al., Scripta Materialia, 70 (2014), pp. 59-62
- [19] B. Straumal, E. Rabkin, W. Łojkowski, et al., Acta Mater., 45 (1997), pp. 1931-1940
- [20] B.M. Moshtaghioun, D. Gomez-Garcia, A. Dominguez-Rodriguez, et al., J. Eur. Ceram. Soc., 36 (2016), pp. 1829-1834
- [21] R.G. Munro, J. Res. Natl. Inst. Stan., 105 (2000), pp. 709

Tables

Table 1. Nominal composition and weight fraction of powder mixtures

Sample	Nominal composition	B ₄ C (wt.%)	SiB ₆ (wt.%)	Amorphous B (wt.%)	TiB ₂ (wt.%)
SBC	1.5 at.% Si B _{6.5} C	64.6	12.4	23	0
	10 wt% TiB ₂				
TSBC	1.5 at.% Si B _{6.5} C	58.2	11.2	20.6	10.0

Figures

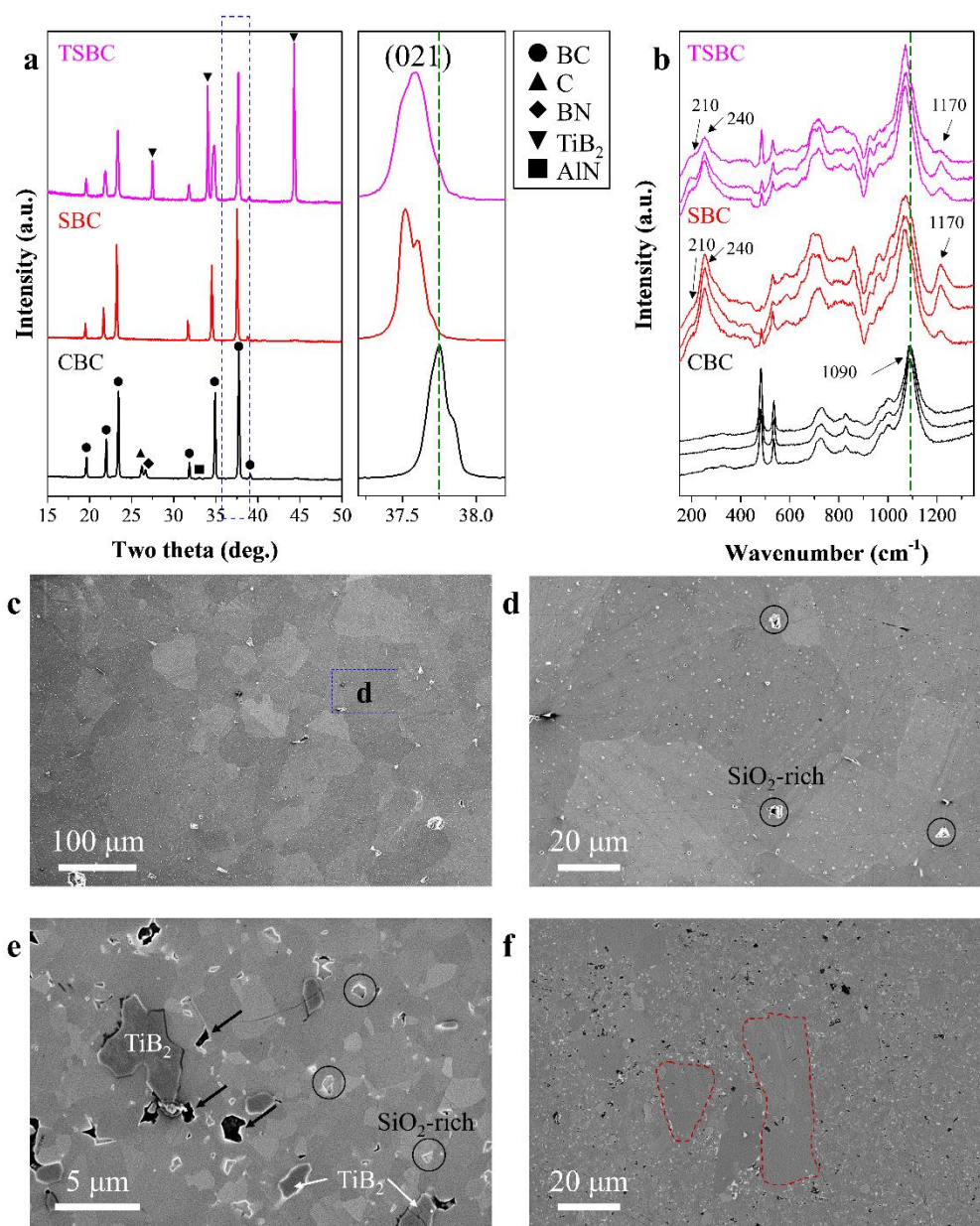


Fig. 1. (a) XRD patterns of TSBC, SBC, and CBC from 15-50° two-theta. The enlarged section depicts the region from 37.3-38.3° two-theta. (b) Raman spectra of TSBC, SBC, and CBC. SEM images of (c)-(d) SBC and (e)-(f) TSBC. The red dashed lines outline the large grains in TSBC. The SiO_2 -rich phase is circled in (d) and (e). Polishing pull-outs in TSBC are marked with black arrows in (e).

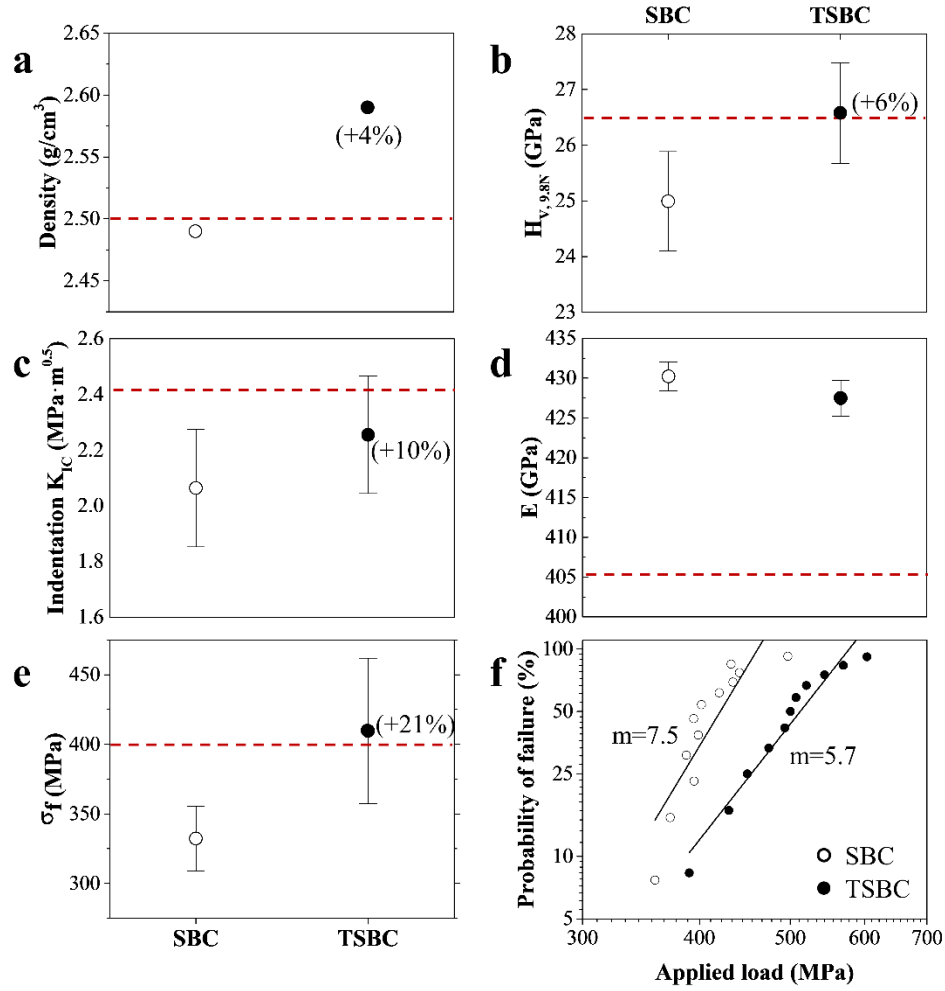


Fig. 2. (a) Density, (b) Vickers hardness, (c) indentation toughness, (d) Young's modulus, (e) fracture strength, and (f) Weibull plots of SBC and TSBC. Properties of CBC are illustrated by the red dashed line. The relative change compared to SBC is indicated in parentheses. Flexural strength of CBC in (e) is taken from Ref. [14]

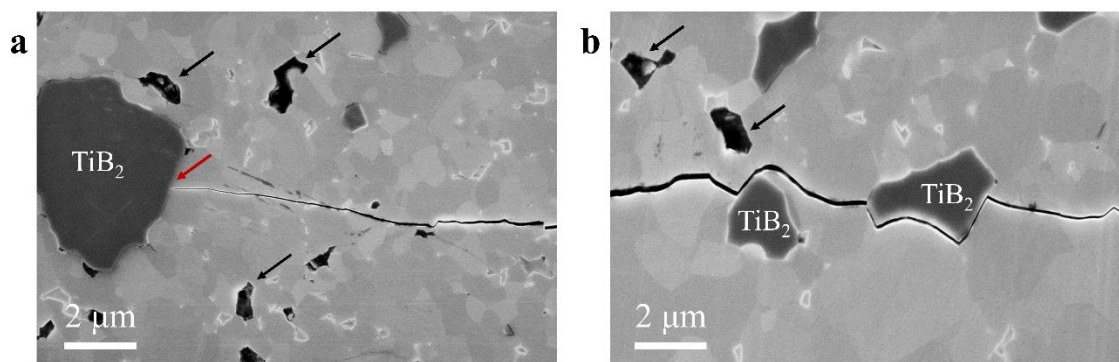


Fig. 3. Examples of crack (a) termination (red arrow) and (b) deflection by TiB₂ in the TSBC sample. TiB₂ polishing pull-outs are marked with black arrows.

CHAPTER 9

Conclusions

Let's revisit the main goal objectives of this thesis:

The goal of this thesis is to address brittleness and susceptibility to stress-induced amorphization of boron carbide, and consequently, propose a path for designing boron carbide ceramics with enhanced toughness and resistance to stress-induced amorphization.

In doing so, 6 objectives were established:

1. Promote room temperature dislocation movement in boron carbide
2. Increase the toughness of boron carbide by secondary reinforcement (ZrB_2 and TiB_2)
3. Mitigate pressure-induced amorphization in boron carbide by foreign atom doping (B and Si)
4. Understand the deformation behaviors of undoped and Si/B co-doped boron carbide
5. Investigate and isolate the effect of Si-doping from B-doping
6. Propose a materials design strategy for next-generation boron carbide with enhanced toughness and resistance to stress-induced amorphization

Objective 1 was achieved in Chapter 2: We found that dislocations can be mobilized by incorporating Al into boron carbide's chain structure. The presence of Al-C bonds increases the overall ionic bond characteristic which in turn lowers the lattice friction. This profound result indicates that deformation behaviors of ceramics can be tuned through atomic doping. The newly activated deformation mechanism dissipated deformation energy and thus also mitigates amorphization.

Objective 2 was accomplished in Chapters 3 and 4: Processing boron carbide composites with ZrB_2 and TiB_2 can improve the overall toughness. The residual stress accumulated at the phase boundaries due to mismatch in elastic modulus and thermal expansion facilitated crack deflection. TiB_2 also pinned the grain growth of boron carbide, thus further improving the overall mechanical properties.

Objective 3 was addressed in Chapter 5: Si/B co-doped boron carbide was processed by melting a blend of Si, B, and B_4C . Through Raman analysis in conjunction with an indentation and elemental analyses based on SEM and STEM (ζ -factor microanalysis), it is suggested that Si/B co-doping is a promising avenue for suppressing stress-induced amorphization.

Objective 4 was achieved in Chapter 6: The deformation zone of single-crystal Si/B co-doped and undoped boron carbide were compared using the state-of-the-art precession electron diffraction (PED) technique. We found that as little as ~1 at.% Si can lead to a substantial decrease in stress-induced amorphization due to a noticeable change of the deformation mechanisms in boron carbide. The undoped boron carbide displays amorphization and microcracking along the amorphous shear bands. This mechanism resulted in long, distinct, and single-variant shear faults. In contrast, substantial

fragmentation with limited amorphization was activated in the Si/B co-doped boron carbide, manifested by the short, diffuse, and multi-variant shear faults. Microcracking via fragmentation competed with and subsequently mitigated amorphization.

Objective 5 was addressed in Chapter 7: We found that an increase in B content correlated with an increase in the reduction of amorphization. More importantly, the involvement of Si, at the same B/C ratio, substantially suppressed amorphization. This study decoupled the effectiveness of the amorphization reduction of B from Si.

Objective 6 was achieved in Chapter 8: We reported the overall mechanical properties of Si/B co-doped boron carbide. A reduction of overall mechanical properties was attributed to weakening in the atomic bond strength due to atomic doping. Most importantly, Si/B co-doped boron carbide composite with 10 wt% TiB_2 compensated for the loss in mechanical properties to a level comparable to that of a commercial boron carbide ceramic tiles, while retaining 44% reduction in amorphization.

Perspective

The two main deformation mechanisms of boron carbide beyond elastic deformation are brittle fracture and amorphization. A fracture occurs when a brittle material is strained to its elastic limit and, consequently, bonds break but the overall bond order is retained. Under high pressure and energy, boron carbide experiences amorphization where bonds not only break but also lose their long-range order. The interstitial doping of Si creates kinked chains in boron carbide that allow the local strain to accumulate. Since the prevalence of Si is sparsely distributed, a network strained lattice act as a weak point for cracks to travel on a sub-micron level. It's plausible that pervasive sub-micro fragmentation found in the Si/B co-doped deformation zone is facilitated by the local strain caused by Si-doping (as suggested in Chapter 6). In other words, Si-doping lowers the energy required to access localized fragmentation. The rationale is further bolstered by examining the lattice constants of Si/B co-doped and undoped boron carbide, $a = 5.63$ and $c = 12.26$ vs $a = 5.60$ and $c = 12.07$ Å, respectively. In a covalently bonded solid, such as boron carbide, longer bonds are weaker. Si/B co-doping undoubtedly contributed to the weakening in the bond strength, and consequently, elastic modulus and toughness as we discovered in Chapters 6 and 8. The lowered energy barrier for fragmentation allowed more localized fragmentation, thus consuming deformation energy before amorphization could occur.

A new form of deformation behavior (localized dislocation glide) was found in Al-doped boron carbide in addition to the similar deformation behavior and the loss in bond strength in Si/B co-doped boron carbide. Compared to Si/B co-doped boron carbide, Al-doping further stretches the lattice constants to $a = 5.64$ and $c = 12.33$ Å. The c-axis (in the

direction of the 3-atom chain) is further weakened to allow inter-planer slip. This gives rise to the dislocation glide, which consists of planes of intact icosahedra, observed in Al-doped boron carbide. The newly added deformation mechanism consumes deformation energy, thus also mitigates amorphization.

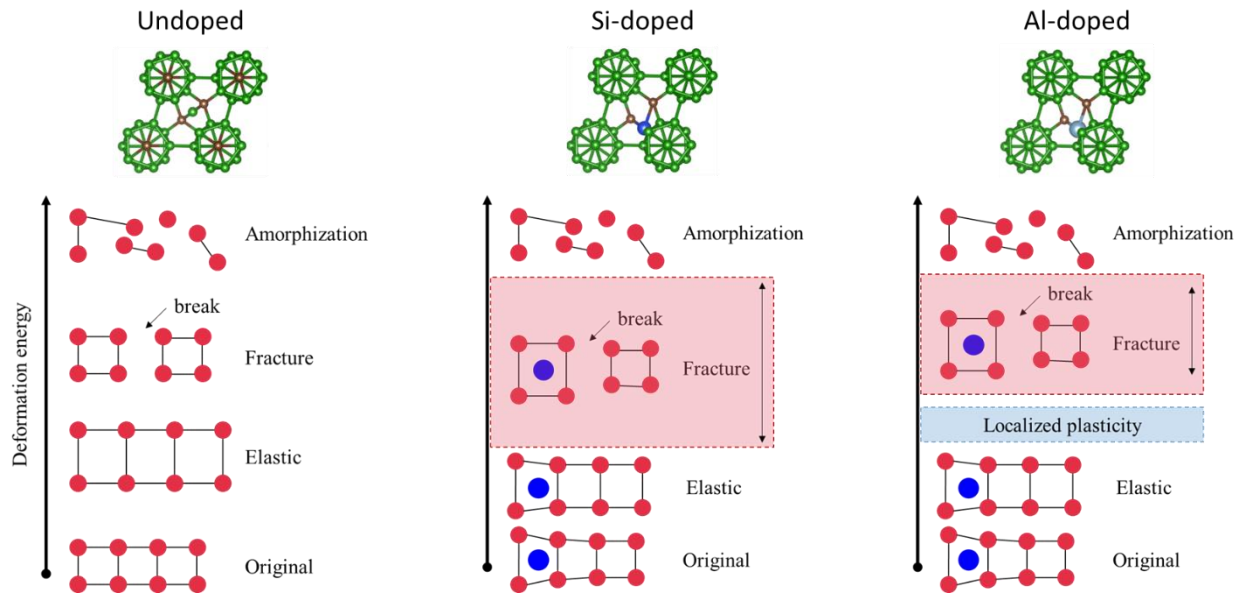


Fig. 1. Comparing deformation mechanisms of undoped, Si-doped, and Al-doped boron carbide. The substitution of Si weakens the atomic bonds of boron carbide and thus lowers the energy barrier for elastic and fracture deformation. Al-doping adds a new deformation mechanism through localized dislocation slip. In both cases, deformation energy is consumed by the deformation mechanism below the threshold of amorphization, thus mitigating amorphization.

Taken together, the idiom “there ain’t no such thing as a free lunch” perfectly summarizes the interplay between material properties and the ability to suppress amorphization. The law of conservation of energy dictates the outcome: either the deformation energy is dissipated through amorphization or other means such as

fragmentation and localized dislocation movement. A loss in mechanical properties (hardness, elastic modulus, and toughness) is a tradeoff necessary to achieve amorphization mitigation in doped boron carbide.

As demonstrated in Chapters 3, 4, and 9, secondary phase reinforcement is a promising strategy to overcome the loss of mechanical properties in boron carbide without effecting the suppression of amorphization, as shown in Fig. 2. The $\text{ZrB}_2\text{-B}_4\text{C}$ eutectic composite greatly improved the toughness of boron carbide. The $\text{TiB}_2\text{-B}_4\text{C}$ composite not only increased toughness, but also hardness by restricting the grain development of boron carbide. The tradeoff here, however, is the increased overall density.

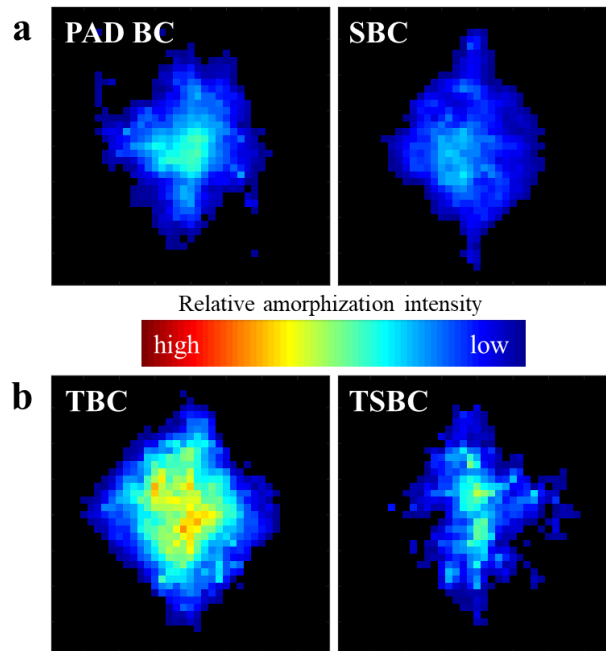


Fig. 2. Amorphization intensity color map of (a) a commercial PAD B_4C vs Si-doped BC (SBC) and (b) TiB_2 reinforced B_4C (TBC) vs TiB_2 reinforced Si-doped BC (TSBC). A reduction of 34% in the amorphization area from PAD BC to SBC and 31% from TBC to TSBC was recorded. A reduction of 44% in amorphization intensity from PAD BC and

TBC their Si/B co-doped counterpart was found. Cross comparison between (a) and (b) is invalid. Each image is 20 x 20 μm .

CHAPTER 10

Future work

- Determine the nature of amorphous boron carbide

The two main techniques used to study amorphization are transmission electron microscopy (TEM) and Raman spectroscopy. Each technique presents a limitation to that complicates the assessment of amorphization in boron carbide. TEM studies are time-consuming, expensive, and can only examine few and localized deformation zones. Raman spectroscopy can survey a larger area but the nature of so-called “amorphous Raman peaks” is highly debated.

1. A dedicated experimental study is necessary to uncover the origin of amorphous Raman peaks. The amorphous Raman peaks of boron carbide acquired from an indentation experiment should be compared to that of amorphous C, B, their mixtures, and boron carbide powders to establish a reliable experimental rationale for their origin.
2. Resolve the short-range order of amorphous material using the pair distribution function (PDF). Election pair distribution function (ePDF) could be directly carried in the amorphous bands of boron carbide using TEM.
3. Alternatively, total scattering could be carried on amorphous boron carbide powders using a high energy X-ray source. This opens an avenue for directly assessing mitigation of amorphization of B-rich, Si-doped, and Al-doped boron carbide provided we can make amorphous powders.

- Enable dislocation mediated plasticity in B-rich icosahedral ceramics

The revolutionary discovery of dislocation movement at room temperature suggests “dislocation engineering” could be applied to boron carbide and other B-rich icosahedral ceramic systems.

1. Explore solid-solution structures using Density Functional Theory (DFT) for B-C-X or higher-order systems
2. Establish the thermodynamic database of the said system
3. Experimentally synthesize suggested the compositions of interest
4. Evaluate the deformation behavior

- Al-doped boron carbide

While Al-doped boron carbide exhibits dislocation movement and amorphization mitigation, little is known about its processing and bulk properties.

1. A comprehensive report on its bulk mechanical properties such as Young’s modulus, hardness, toughness, tensile and compressive strength would be valuable.
2. A consolidation study is necessary to understand its sinterability with and without sintering aids.
3. In-depth microstructure and grain boundary analysis using TEM.
4. Understanding of the thermal stability of Al in boron carbide by heat-treating Al-doped boron carbide at elevated temperatures.

5. Determine the optimal Al content for mitigating amorphization while retaining mechanical properties
 6. Further improving its toughness by making composites with metals or ceramic reinforcement phases.
- Optimizing microstructure and mechanical properties of TiB_2 reinforced Si-doped boron carbide

The goal of this thesis is to explore options to improve toughness and resistance to amorphization. We showed that Si/B co-doping and TiB_2 reinforcement are valid solutions to achieve the goal. However, the microstructure and mechanical properties of 10 wt% TiB_2 reinforce Si/B co-doped boron carbide are not optimized.

1. Vary the TiB_2 content to minimize weight gain while achieving better mechanical properties
2. Optimize the Si and B content to achieve maximum reduction of amorphization while retaining mechanical properties (1-2.5 at% Si across the entire B/C ratio range)
3. The exaggerated grain growth of boron carbide could further be hindered through sintering protocol optimization such as lower temperature or time.