Spark Plasma Sintering of Ceramic Matrix Composite of TiC: Microstructure, Densification, and Mechanical Properties: A Review

Samson Dare Oguntuyi[1(✉)], Oluwagbenga Johnson[2,3], and Mxolisi Brendon Shongwe[1]

[1] Institute for Nano Engineering Research, Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa
ShongweMB@tut.ac.za

[2] Department of Mining and Metallurgical Engineering, University of Namibia, Private Bag, Ongwediva 13301, Namibia
Ojohnson@unam.na

[3] Department of Metallurgy, School of Mining, Metallurgy and Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, PO Box 524, Johannesburg, South Africa

Abstract. The application of monolithic/un-doped/single-phase ceramics has been limited due to their difficulty in sintering and low fracture toughness. Ceramic matrix composites have gained predominant attention in the past decades in comparison to monolithic/un-doped/single phase ceramics, this is as a result of the high fracture toughness, good wear resistance, and high hardness that they (ceramic matrix composite) possess. Also, the use of sintering additives in collaboration with the application of modern consolidation viz spark plasma sintering (SPS) has gained high prominence to nullify these challenges faced by ceramics. Although, previous review has highlighted the use of diverse techniques (hot press, hot isostatic, pressureless sintering, and SPS) on the consolidation of ceramics and its composites. Amidst all these techniques, SPS has stood to be an effective powder metallurgy route for achieving good microstructure and excellent mechanical properties. This review takes a research on the effects of nitrides based sintering additives on the microstructure, densification, and mechanical properties of titanium carbides ceramic matrix by SPS. The review finally concludes on the potential research importance on the types of sintering additives inclusion that should be in further research processes for improvement in material properties of titanium carbides.

Keywords: SPS · TiC · Microstructure · Densification · Mechanical properties

1 Introduction

Titanium carbide usually demonstrates metallic and ceramic-like features, with a typical crystal structure as depicted in Fig. 1. It has lately grown high interest as a result of its

M. Awang and S. S. Emamian (Eds.): *Advances in Material Science and Engineering*, LNME, pp. 93–101, 2021.
https://doi.org/10.1007/978-981-16-3641-7_13

combined unique properties viz significant elastic modulus (~400 GPa), high melting point (3,160 °C), high hardness, high oxidation resistance, excellent wear-resistance, low thermal expansion, high electrical conductivity, and considerable chemical stability [1–5]. These outstanding properties have made Titanium carbide a high potential material for elevated temperature applications including wear-resistance coatings, corrosion resistance parts, impact- barrier armors, ceramic cutting tools, crucibles, etc., [4–6]. Although monolithically, the sinterability of titanium carbide is challenging in achieving the desired results. These challenges of titanium carbide are due to the solid covalent bond, low self-diffusion coefficient, and oxide layers which are mostly B_2O_3 and TiO_2 [4, 5, 7, 8]. Therefore, consolidation of monolithic TiC with enhanced densification required an elevated sintering temperature greater than 2000 °C with high pressure. These sintering parameters usually resulted in uncontrolled grain growth, poor microstructure, and inefficient mechanical properties [6, 8].

To nullify the aforementioned challenges, sintering additive and/or sintering aid are usually applied to lower the sintering temperature [9, 10]. B_4C, $TiSi_2$, Si_3Ni_4, TiC, $MoSi_2$, WC, TaC, AlN, SiC are examples of non-metallic sintering aids/additives that are being added to ceramic matrix composite to inhibit grain growth and reduce consolidation temperature [11–13]. Additionally, applying metallic additives viz Co, Ni, Fe, Mo also enhances the sinterability and fracture toughness of the manufactured ceramic materials this is attributed to the toughening stimulation mechanism and the creation of liquid phase [12–15]. The improvement of combined fracture toughness, hardness, modulus strength with enhanced performance and densification are prompted by the use of ceramic matrix composites (CMC). CMC also ensures that sintering temperatures are lowered compared to undoped ceramics which usually involves the use of high temperatures for sintering [16–18]. As a substitute route, spark plasma sintering (SPS) is an important method for the consolidation of ceramics, SPS enables the production of fine microstructure which consequently improves mechanical properties, these attributes were as a result of its fast heating and short holding time in comparison with conventional sintering viz, hot pressing, hot isostatic pressing, flash sintering, etc. [19–21]. In the SPS technique, the ceramics materials are introduced in the graphite die, then using a pulsed electric current under an externally applied pressure, the sintering process is accomplished [23, 24]. This article gives a critical review on TiC reinforced with sintering additives consolidated by SPS. An observation will be carried out on how nitride-based material additives have had an influence on the densification, microstructure, and mechanical properties of a TiC ceramic-based matrix.

1.1 Limitations and Challenges of TiC

Difficulty in densification as a result of poor sinterability and high covalent nature of TiC has created some challenges in sintering it, Monolithic application of TiC is limited owning to poor fracture toughness, brittle-like nature, and poor thermal shock resistance [25–30]. Hence, the use of sintering additive in addition to the use of modern techniques of sintering has been observed to minimize these challenges [30–33].

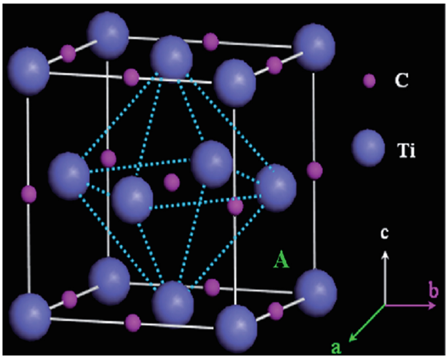

Fig. 1. A crystal structure of TiC [34].

2 Effects of Sintering Additives

Various sintering additives have different influences on the sinterability, microstructure, densification, and mechanical properties of various ceramic materials. The types, quantity, and proper dissipation of these sintering additives go a long way in achieving enhanced properties of the ceramic matrix composites. More also, the individual properties of the sintering additives which are reinforced in the ceramic matrix contribute to the whole properties of the sintered ceramic matrix composites. Some sintering additives have depreciating or enhancing effects on the overall properties of c ceramic matrix composite which are largely attributed to the properties of the reinforcing additives [34].

2.1 Spark Plasma Sintering of TiC Matrix Composites Using Nitrides Based Material as Sintering Additive

Nitrides-based additives such as AlN, TiN, etc., reduced the hardness of TiC ceramic matrix to some percentage but enhances the fracture toughness which has been a challenge for ceramics generally. More also, the reduction in the flexural strength of some TiC ceramic composites was as a result of higher hardness of TiC than the nitrides based sintering additives, therefore the percentage increment of these nitrides based additives reduces the hardness and strength of the TiC ceramics composites but consequently enhances fracture toughness [35, 36].

Pazhouhanfar et al. [37], observed the effects of 5wt.% TiN on the microstructural and mechanical properties of TiC composites. The composites were consolidated at 1900 °C for 10 min under 40 MPa. Densification of 97% was reported for the doped TiC which was 1.6% greater than the relative density of the monolithic (95.5%). Figure 2(a) shows the graphical representation of the relative density of these samples. But densification of 98% and 99% was achieved for a monolithic TiC when sintered by SPS at 1600 °C and 1900 °C respectively, the achievement of the later densification was attributed to the use of fine size particle powder (<2 μm) [30, 38]. The introduction of TiN in the composites as a secondary phase was reported to inhibit grain growth.

The addition of 5wt% TiN to the monolithic TiC reduced the Vickers hardness by 12% compared to the undoped TiC Fig. 2(b) showed this graphically. The formation

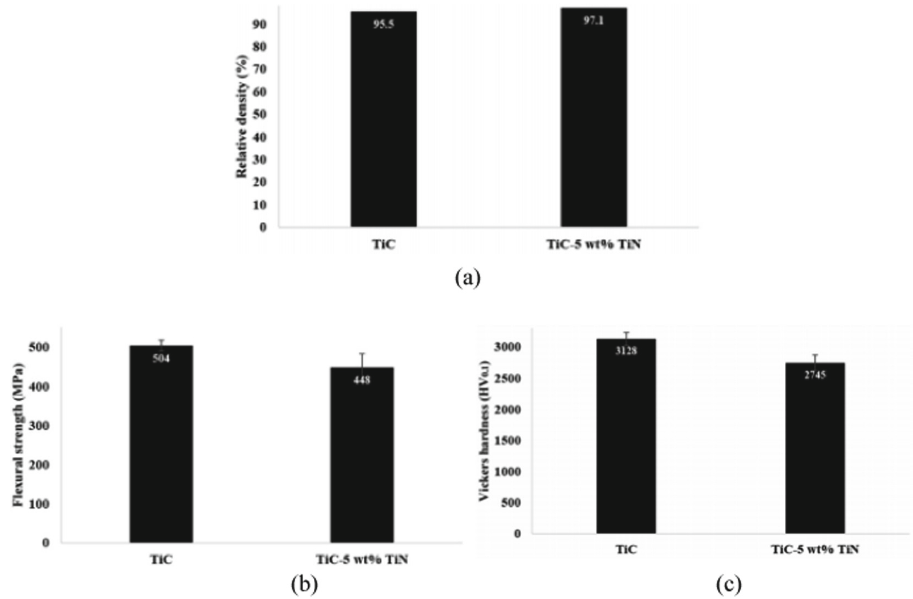

Fig. 2. Shows the densification for undoped TiC and doped TiC with 5wt% of TiN [37]. (b) and (c) showing the flexural strength and Vickers hardness of monolithic TiC and doped TiC with 5wt% TiN respectively [37].

of solid solution phase of Ti(C, N) in the absence of bonding phase contributed to the reduction of the hardness of the doped TiC, similar observations were made in previous works [39, 40]. The flexural strength of the undoped TiC was reported to be greater than the doped TiC, as seen in Fig. 2(c), the existence of the in-situ brittle phase of Ti(C, N) formed was said to contribute to the reduced flexural strength of the doped TiC.

Russias et al. [36] studied the effects of TiN in TiC cermets. It was reported that the addition of TiN to the cermets resulted in grain growth inhibition and transforms the repartition of diverse phases. The existence of TiN reduces the cermet hardness but consequently enhances the cermet's toughness. The hardness reduction was as a result of the lower hardness of TiN as a reinforcement in the cermet which at the same proportion promoted the fracture toughness. This outcome has mostly been observed that the corresponding improvement in hardness and fracture toughness is hard to achieve when sintering additives are being added to a ceramic matrix, as the increase in one leads to the decrease of the other and vice versa [35, 41].

Fattahi et al. [42], reported improved densification and flexural strength when TiC based composites were doped with 5wt% AlN at a sintering temperature of 1900 °C for 10 min under 40 MPa. The addition of AlN and the in-situ Ti_3 Al was reported to influence the full densification of the composites, but its Vickers hardness reduced by 2% in comparison to the monolithic TiC due to the phases of AlN and Ti_3 Al present in the composites whose hardness are lower than TiC, [43, 44], Fig. 3(b) the light- gray color in the micrograph depicted phases of the TiC matrix, while the dark-gray-color were the secondary in-situ formed phases or AlN [43, 44]. The reported flexural strength for the monolithic and doped TiC was 504 MPa and 688 MPa grain size. The enhanced relative density of the doped sample and the formation of the in-situ phase created a clean interface between the secondary phases and the matrix all quantified to the improved flexural strength. The microstructural observation as shown in (Fig. 3a), depicted that the monolithic TiC contained some pores, suggesting inadequate sintering temperature to fully densify the material, while the doped sample with 5 wt% AlN showed highly full densification without any visible porosity in the microstructure (Fig. 3b).

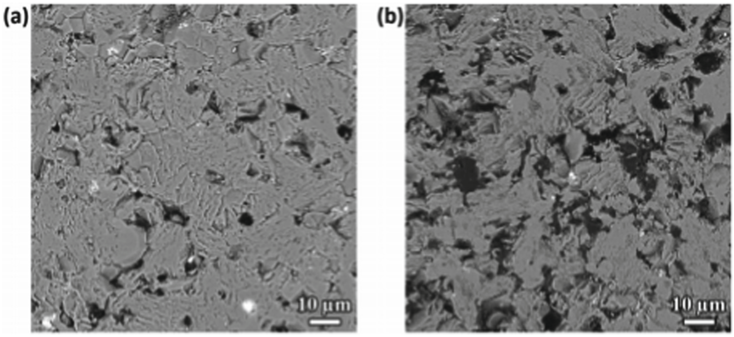

Fig. 3. A SEM graphs of the sintered (a) undoped TiC and (b) doped TiC with 5 wt% AlN [42].

Shaddel et al. [41] reported contrasting densification and mechanical properties of TiC composites when it was doped 5 wt% BN in comparison to Fattahi et al. experiment [42] under the same sintering condition. The addition of BN did not influence the densification of the samples, that both the doped and undoped TiC achieved similar results of approximately 95%. More also, the sintering additive had a depreciating effect on the mechanical properties such that the flexural strength and Vickers hardness reduced at around 15% and 7%, respectively, in comparison to the acquired values for the monolithic samples. The content and texture composites and the in-situ carbonic phases formed when TiC was doped with BN were said to be the cause for the drop in hardness [45], more also, the non-provision by the remaining BN particles in cleaning the interface with TiC had a poor impact on the flexural strength of the doped samples compared with the monolithic sample.

3 Comparison of Different Nitrides in Terms of Properties (Densification and Mechanical Properties)

Different nitrides based have been studied on the microstructure, densification, and mechanical property of TiC (as depicted in graph 1), it was observed that AlN provided improvement in achieving good densification and combined excellent mechanical properties (Table 1). The Fig. 4, majorly showed the influences of sintering additives on the densification and mechanical properties of TiC compared to undoped TiC.

Table 1. Showing the effects of different nitrides sintering additives with TiC using Spark Plasma Sintering for consolidation.

Material composition	Processing condition	Sintered density	Hardness (GPa)	Fracture toughness (MPa m$^{1/2}$)	Flexural Strength (MPa)	References
TiC–5wt% TiN	1900 °C, 40 MPa, 10 min	97	274.5 (HV0.1)	–	450	[37]
Monolithic TiC	1900 °C, 40 MPa, 10 min	99.9	25.7	–	–	[38]
TiC-5wt% AlN	1900 °C, 40 MPa, 10 min	101.27	3050 (HV100)	–	688	[42]
TiC-5wt% BN	1900 °C 40 MPa, 7 min	95	2914 (HV100)	–	429	[41]
Monolithic TiC	1650 °C, 100 MPa, 5 min	97.9	28	5.9	–	[46]

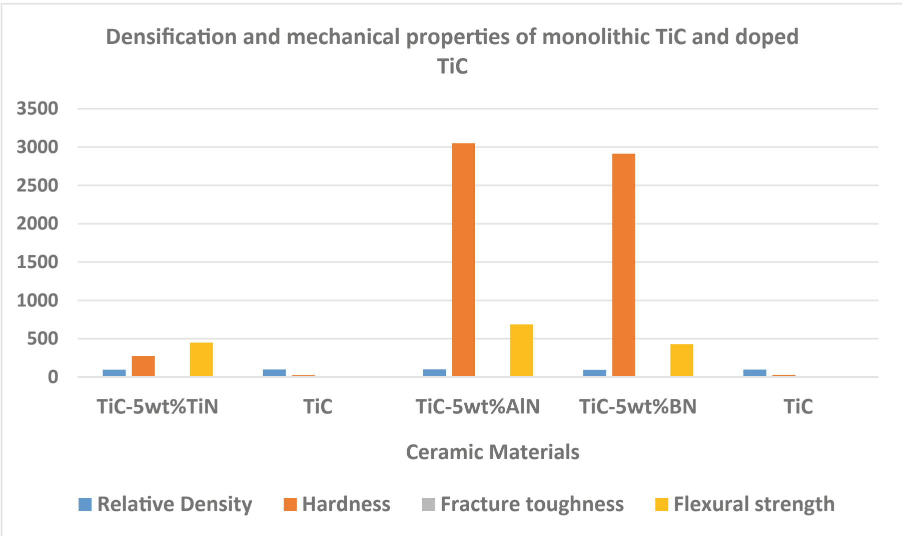

Fig. 4. Relative density and mechanical properties of TiC ceramic materials.

4 Conclusion

The addition of nitrides based on titanium carbides ceramic composites has been observed to produce some contrasting results in the densification and mechanical properties of TiC matrix. It can be inferred that not all nitrides based additives yielded good improvement on the properties of ceramics based matrix, as some of the (nitrides additives) have a depreciating effect while others produce enhancement in the properties of TiC based matrix composites. Therefore, more works should undertake more in adding non-metallic ceramics together with nitrides additive whose hardness is not far less than the parent composites, with this concept an improved combined mechanical properties can be attained without any depreciating effect in any of the desired properties.

Acknowledgments. Appreciation goes to all the author for their contributions to the success of this review.

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