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Advances in Powder Metallurgy & Particulate Materials—2017

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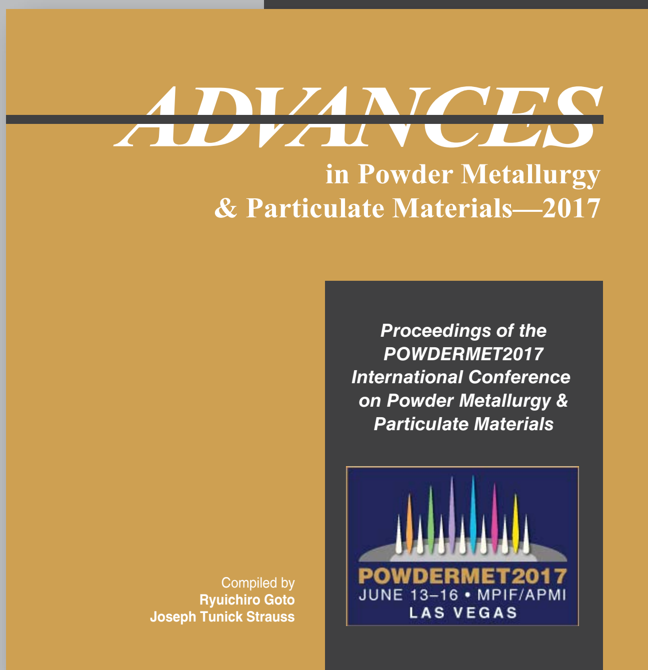

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TECHNICAL SESSIONS

04: CERMETS

VAN GOGH 2

Session Chairman:
Rajendra Sadangi, U.S. Armament Research Laboratory

053 *Canada* 9:30 a.m.
Microstructure Development and Sintering Response of Intermetallic Cermets with Molybdenum Carbide Additions
Marciel Gaier, Dalhousie University

111 *Germany* 9:55 a.m.
Influence of Refractory Elements on the Mechanical Properties and Morphology of TiC Hard Particles in Metal Matrix Composites
Andreas Mohr, Ruhr Universtiy Bochum

279 *USA* 10:20 a.m.
Process Control and Production Efficiency through Particle-Size Distribution
Jeff DeNigris, Malvern Instruments

SPECIAL INTEREST PROGRAM
(See page 37 for details)
9:30–10:45 a.m.
SIP 1: Materials for Extreme Applications

TECHNICAL SESSIONS
Wednesday Afternoon
2:45–4:00 p.m.

05: PARTICULATE PRODUCTION I

DEGAS 1

Session Chairman:
Arthur E. Jones, Symmco, Inc.

103 *USA* 2:45 p.m.
Screen Processing to Prepare Powder Metals for AM
Greg Riter, Elcan Industries

197 *USA & Canada* 3:10 p.m.
Advancements of Carbonyl Metal Powder Production: An Overview
Lou Koehler, Koehler Associates, LLC

No presentation scheduled at this time 3:35 p.m.

06: MANAGEMENT ISSUES

DEGAS 2

Session Chairman:
Keith Fleming, Engineered Sintered Components

101 *USA* 2:45 p.m.
Metal Dusts Explosion Hazards and Protection
Jérôme R. Taveau, Fike Corporation

234 *USA* 3:10 p.m.
Portable Vacuums for AM/PM Operations: The Good, the Bad and the Ugly
Alfonso Ibarreta, Exponent, Inc.

278 *USA* 3:35 p.m.
Nurturing Value in the PM Industry
Michael Benson, Stout Risius Ross Advisors, LLC

07: MIM II: STAINLESS STEEL & SUPERALLOYS

VAN GOGH 1

Session Chairman:
Stefan Joens, Elnik Systems, LLC

058 *United Kingdom, USA & Dominican Republic* 2:45 p.m.
Processing and Properties of MIM 430L Made by Prealloy and Master Alloy Routes
Martin A. Kearns, Sandvik Osprey Limited

242 *Switzerland* 3:10 p.m.
Biocompatible Austenitic Stainless Steel Processed by MIM of Biopolymer-Based Feedstock
Efrain Carreño-Morelli, University of Applied Sciences and Arts Western Switzerland

009 *Germany* 3:35 p.m.
Metal Injection Molding of Nickel-Base Superalloy CM 247 LC: Influence of Heat Treatment on the Micro-structure and Mechanical Properties
Andreas Meyer, Friedrich-Alexander-Universität Erlangen-Nürnberg

08: CERAMIC-BASED COMPOSITES

VAN GOGH 2

Session Chairman:
John Johnson, Elmet Technologies, LLC

085 *Germany* 2:45 p.m.
Carbide-Oxide Composites Made from Nanoscaled Tungsten Carbide, Alumina and Zirconia Powders
Johannes Pötschke, Fraunhofer IKTS

075 *USA* 3:10 p.m.
Hot Pressing vs Pressing and Sintering: Some Striking Contrasts While Dealing with Boron Carbide Based Ceramic Blends
Arun K. Chattopadhyay, Etimine USA, Inc.

No presentation scheduled at this time 3:35 p.m.

HOT PRESSING VERSUS SINTERING: SOME STRIKING CONTRASTS WHILE DEALING WITH BORON CARBIDE BASED CERAMIC BLENDS

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ABSTRACT.

Strength and fracture toughness of boron carbide based ceramic composites seemingly showed improvement if the PM parts were submitted to the conventional pressing and sintering versus direct hot pressing. Continuing efforts to find practical means to strengthen boron carbide using Ti, Zr and Si inclusions have shown that the sintering at elevated temperatures maybe helpful to achieve similar properties as those of hot-pressing methods, which are expensive and not-so-easy for complex parts.

INTRODUCTION.

The use of borides and boride based alloys have been the subject of research in powder metallurgy for a long time for their specialty industrial use and particularly for the great advantages of their super high strength; yet lightweight properties. However, despite its fascinating properties and usefulness, it is found that there are some properties which limit and compromise the use of boron carbide (BC) as a structural ceramic, such as low fracture toughness, low tensile strength and problematic sintering that still need to be resolved amongst many other hindrances.

BC is a low density (2.52 g/cm^3) covalently bonded material with very high hardness (770 kg/mm^2) and melting point (2427°C). It is mainly used in the industries of lightweight ceramic armors and wear-resistant parts like blasting nozzles, grinding wheels etc., and it is also used in control rods for nuclear reactors.

In order to achieve high density BC powders, the process of sintering has always proven to be difficult, for which certain sintering aids, or additives like carbon, aluminum oxide, titanium di-boride (TB), titanium carbide (TC), silicon carbide (SC) etc. are found to be helpful. BC powders are typically hot-pressed at 2100-2150°C and 30–40 MPa to obtain desired densities. Hot pressing followed by sintering are also used to achieve near full density of BC. Hot pressing using hot isostatic pressing (HIP) method followed by sintering, or post-sintered HIPed, has been applied to carbon-doped BC to reach full theoretical density in order to improve flexural strength, modulus of elasticity, wear resistance etc. Pressure-less sintering of BC is often preferable in comparison to hot-pressing. Pressure-less sintering minimizes the requirement for expensive machining while making complex shapes or forms. However, to reach full theoretical density using pressure-less sintering is found rather difficult. 92-95% of theoretical density could only be achieved so far with pressure-less sintering at temperatures ranging between 2100-2250°C. Various additives were also tried to promote densification of BC using pressure-less sintering like TB, TC, SC, Si, Al_2O_3, AlF_3, W_2B_5 etc. in order to enhance fracture toughness and other mechanical properties of boron carbide. Although many of those additives were helpful to densify BC, they also reduced the fracture strength due to excessive grain growth.

The hot pressings are generally performed under vacuum at 2150–2200 ºC temperature. Pressure-less sintering of BC, as reported elsewhere [1-19], is generally carried out around 2200 ºC. Sintering a BC system is trickier than hot pressing. Due to the presence of >90% covalent bonding in BC, the movement of particles and diffusion across the grain boundaries, which eventually reduce or eliminate pores in the compact body. It does not occur unless it is near its melting point (2450 ºC). Therefore it is to be noted that for pressure-less sintering, a temperature between 2100 and 2350 ºC is very suitable for effective diffusion to occur. In the case of hot pressing, a sintering temperature of 2000–2200 ºC at a pressure around 25–40 MPa under vacuum or under Ar atmosphere is used. Vacuum or inert atmosphere is required to prevent crystal structure rearrangements that BC is known to undergo above 600 ºC. Hot-pressing at high pressure and temperature, besides densification, allows BC and dopant metal to go through physicochemical changes. It forms BC- metal composites in situ and undergoes complex structural rearrangements. It also goes through considerable plastic deformation. Otherwise it requires pressures >100 MPa for BC alone in order to improve its hardness by densification eliminating voids [1-12].

The purpose and significance of this paper is to review the conventional industrial practices of sintering BC in relation to a common goal and objective - how to reduce the manufacturing costs without compromising quality. While reviewing various methods along with some limited studies on ensuing material properties, the results have been encouraging enough to merit further investigation on pressure-less sintering as a cost effective method for large scale sintering of geometrically complicated large ceramic bodies.

However, the quality of pressure-less sintered boron carbide still falls short compared to those of hot pressed or post-sintered hot isostatic pressed (HIPed) compacts. It also goes without saying, each independent method has its own frailty to address all issues with BC. Unfortunately research into pressure-less sintering of BC is yet to find an answer to the problem - what is really acting against the densification of BC in pressure-less sintering that cannot replace hot pressing or other techniques?

It was delineated in our previous work about the selective role of additives to improve fracture toughness in BC. It was demonstrated that at an optimum level of usage of a specific additive, the additive functionally reduces the level of free carbon present in BC, which effectively improves wetting properties at the inter-particle interfaces. Good wetting at the interface helps to achieve strong inter-particle bonding through direct interaction between the additive metal and BC while going through the liquid phase rearrangements during hot pressing or sintering.

EXPERIMENTAL.

Additives were chosen as a continuation of our previous studies. In our previous studies Silicon (Si), Titanium (Ti), and Zirconium (Zr) were found to be the most effective ones at around 2% level of addition to bring about maximum strength by migrating into the BC crystal lattice. Metals as dopants in BC essentially act as binders and enable the composite to densify at a lower working pressure.

As starting materials, BC powder (~99% purity) of average particle size <5–10 mm was used for the study of metal doped BC systems. The powder blends are prepared by pick-up free tumble mixing. For the powder blends theoretical densities of each component are used to estimate the desired weight percentages of each additive.

Samples for pressure-less sintering were prepared by weighing the powders to make pellets of dimensions 13x2 mm using theoretical density estimates. Uniaxial pressing at 60 MPa was employed to create green pellets. The dimensions of the pallets were subsequently measured and weighed to calculate their green density. The pellets were then sintered in a graphite element furnace at 2150 ºC, 2250 ºC and 2350°C with a fixed heating regime of 30 °C/min.

In order to compare against the hot-pressed (HP) BC, only one commercial type hot-pressed BC sample with known Ti content was used. The general properties of the sample are used as obtained. The total level of Ti impurity was approximately 1%.

Sintering Fundamentals:

There are multimode mechanisms of inter-particle diffusions that can occur during sintering. Diffusions across the grain boundary can take place from surface and lattice through plastic flow by dislocation motion, and through vapor transport. Figure 1 shows those possible ways diffusional transport can take place. All of those transportation processes can cause two types of effects to the sintering particles. In case of diffusions that occurs across the grain boundaries, and also through the dislocations during plastic flow, shrinkage can take place. Whereas, in the case of diffusion through surface, lattice or vapor, it can cause grain growth. Therefore, in multimode diffusion mechanism both shrinkage as well as growth can happen concurrently.

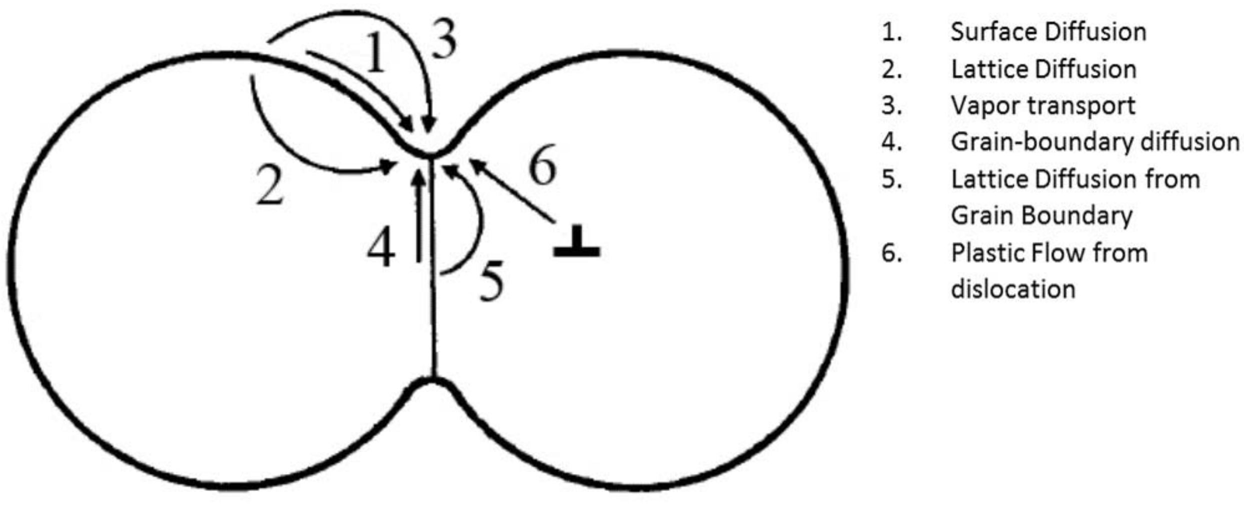

Figure 1: Sintering mechanisms of a two particle system [8].

While viewing the sintering aspects of BC, it is realized that many factors can work against the densification of boron carbide. From its own characteristic nature, BC's strong covalent bonding hinders self-diffusion and resists grain boundary sliding strongly. An excessive grain growth in BC is known to occur above 2250-2300 ºC, which would indicate a vapor transport route such as evaporation-condensation of BC [7, 8]. It is also suggested that the growth in BC can also happen upon sintering above 2150 ºC. Sintering above 2150 ºC can volatilize the non-stoichiometric fractions of BC that can virtually decompose BC and form graphite particles around the grain boundaries [12].

In contrast to the pressure-less sintering, hot pressing is one of the most popular ceramic processing routes due to its ability to sinter highly dense components at lower temperatures. This is achieved by the application of force via a ram that impinges a mechanical driving force acting towards a reduction in porosity. The coarsening or grain growth can be avoided by using reactive metals like Si, Ti, Zr etc. that can convert free carbon particles [1, 2] to their respective borides or carbides avoiding grain growth.

$$Si + C = SiC \qquad \text{(i)}$$
$$Ti + C + B_4C = TiC + TiB_2 \qquad \text{(ii)}$$

The impinged pressure rather drives the BC particles to rearrange instead.

The ease at which hot pressing can reach near theoretical density (TD), pressure-less sintering seldom can achieve that fit.

Results and Discussions:

As we discussed in our previous publications [1, 2], there are many dopants for BC reported for the improvement of the fracture property of BC; however, amongst all dopants tried, Si, Ti, and Zr are by far the most effective to bring about the changes in the nature of compaction of BC and structural property through solid-state reaction during sintering. It is also important to point out that the inclusion of dopants does not require a very high addition. Those inclusions of appropriate dopant metals in BC are very effective at a lower addition level ranging within 1-3 wt% depending upon the nature of metals used for inclusion. The improvements in flexural strength and fracture toughness have been observed in B4C with the presence of secondary phases like TiB2 and ZrB2 [10-12]. The higher flexural strength is generally attributed to the enhanced density and the refined microstructure [4, 15], while the improved fracture toughness is related to the controlled addition of other phases by promoting crack deflection and associated crack bridging [16].

In this study, figure 2 shows the densities of the sintered BC with the inclusions of additives at various addition levels. The trend in variation of sintered density at 2350 ºC was surprisingly very similar to the trends observed with the compressive strength and impact elasticity as shown in figure 3 [1, 2]. The maximum attainable density in BC was found with Zr addition, which is approximately 97% of the theoretical density of BC. The hot pressed sample of BC had a density of 98.5%, which suggests that with a proper selection of dopant metals and using a suitable compressive force, BC can reach very similar density as those of the hot-pressed versions.

The limited microstructure studies with the Zr-BC sample with 2.5% of Zr (figure 4) sintered at 2350 ºC showed minimum porosity compared to BC alone, which corroborates very well with its higher density and hardness values. The visible contrast between BC and Zr-BC microstructures is the conspicuous presence of Zr phases with diminishing voids and free carbon particles, which are very common impurities present in BC. While comparing with the highly polished and electrochemically etched hot-pressed sample of BC, secondary phases and metal inclusions can also be noticed. Most of the grain boundaries also show bright contrast, which is believed to be the result from the effect of etching at the grain boundary [17].

Recent work on strengthening BC [1, 2, 5, 18] developed some fundamental understanding on the probable functions and mechanisms of metal inclusions through controlled usage and proper selection. Incorporating inclusion materials at a higher level may not necessarily improve the strength and fracture properties of BC as such, rather in most cases they only show mixed properties of each components. The studies with 10-20% addition levels of hard metal borides of Ti, La, Ce etc. [19, 20] to improve hardness and fracture toughness of BC, indicated that those borides stayed distinctly as two phase systems. La and Ce in particular, could not even be substituted in the BC crystal structure due to their bulkier ionic sizes, >110 pm vis-a-vis 80 pm for B [1, 2]. As the microstructures revealed, there is very little free carbon left after metallic inclusions. This may eventually cause the rearrangement of boron carbide crystals where carbon particles are mostly exhausted either to form metal borides or carbides, or to remove the oxide layers.

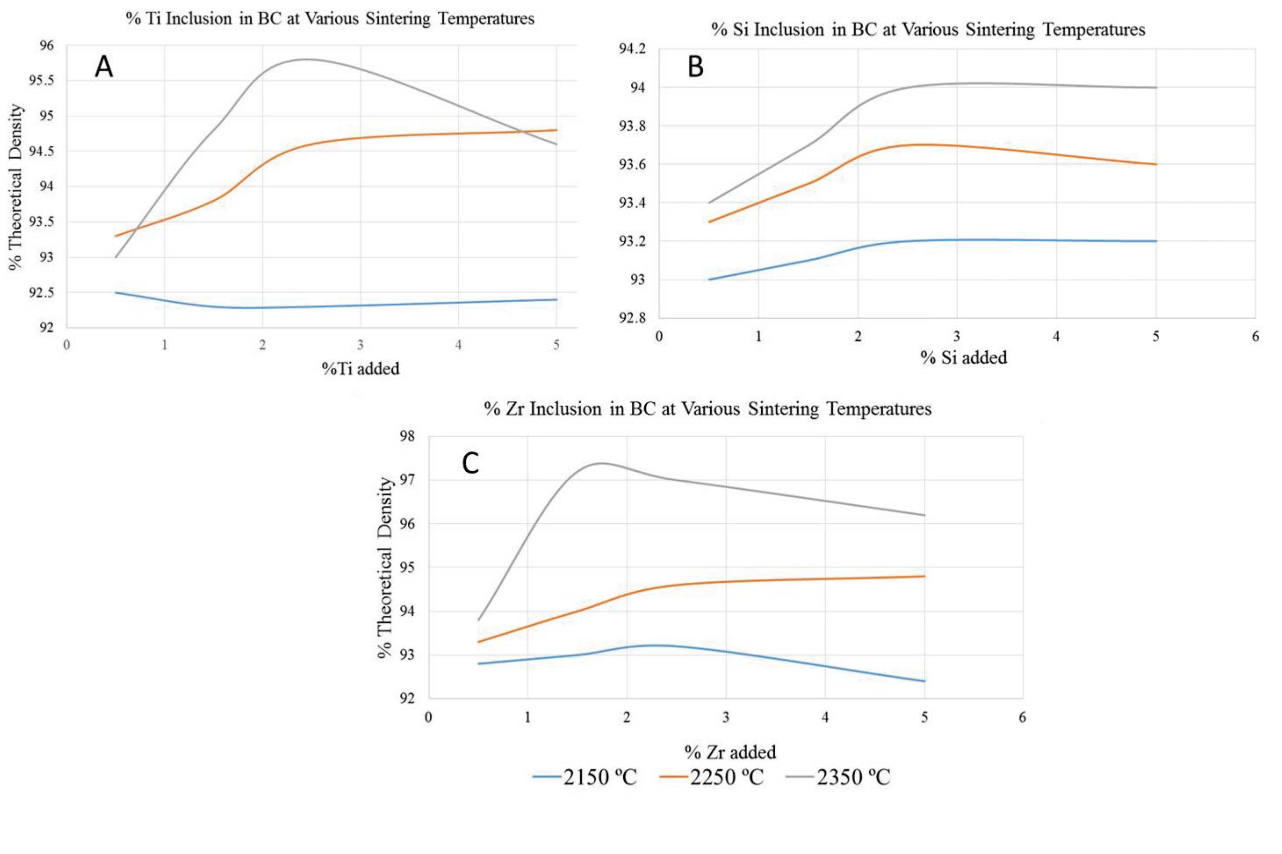

Figure 2: Density trend of BC at various levels of inclusion of Ti (A), Si (B) and Zr (C).

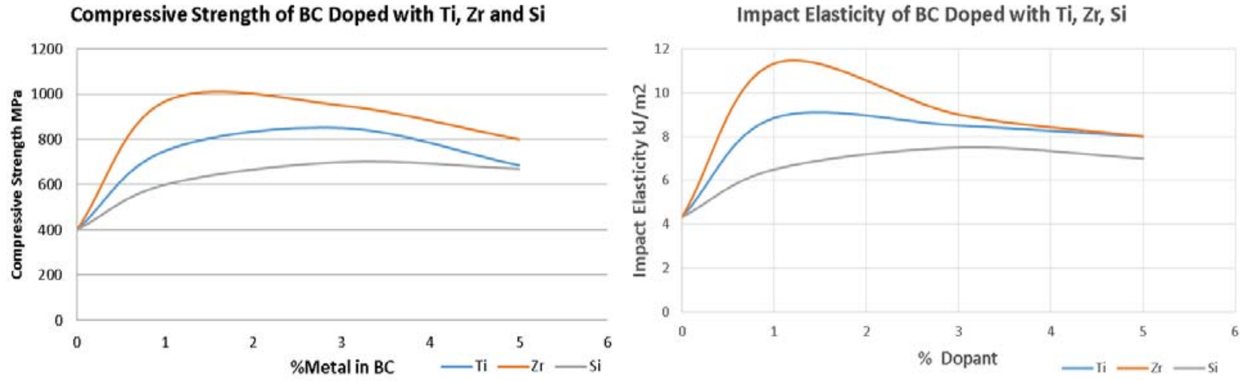

Figure 3: Compressive Strength and Impact Elasticity variations with the changes in metal inclusions in BC [1, 2].

This explained the rise in density as the inclusions reached an optimum level of addition. This is also probably due to the fact that the densification of particles at 2350 ºC must be occurring at a higher rate in comparison to the other competing factors of growth that also occurs during sintering as explained above.

Figures 5 shows the hardness of Si, Ti and Zr impregnated BC relative to their densities. The trend of results clearly show that, regardless of the type of inclusion, the increase in density translates to an increase in hardness.

Considering all the results, it appeared, as it was demonstrated before [1, 2], Zr is the most effective additive with respect to improving properties of BC. The mechanism to remove free carbon particles and oxide layers in BC in the presence of Zr, generates more borides and boron carbide, which also causes simultaneous substitution of Zr into the BC crystal lattice.

Along with this advantage, Zr also reached the highest density sintered compacts at 2350 ºC and produced the highest hardness compacts, the values of which were found to be much closer compared to the hot-pressed sample.

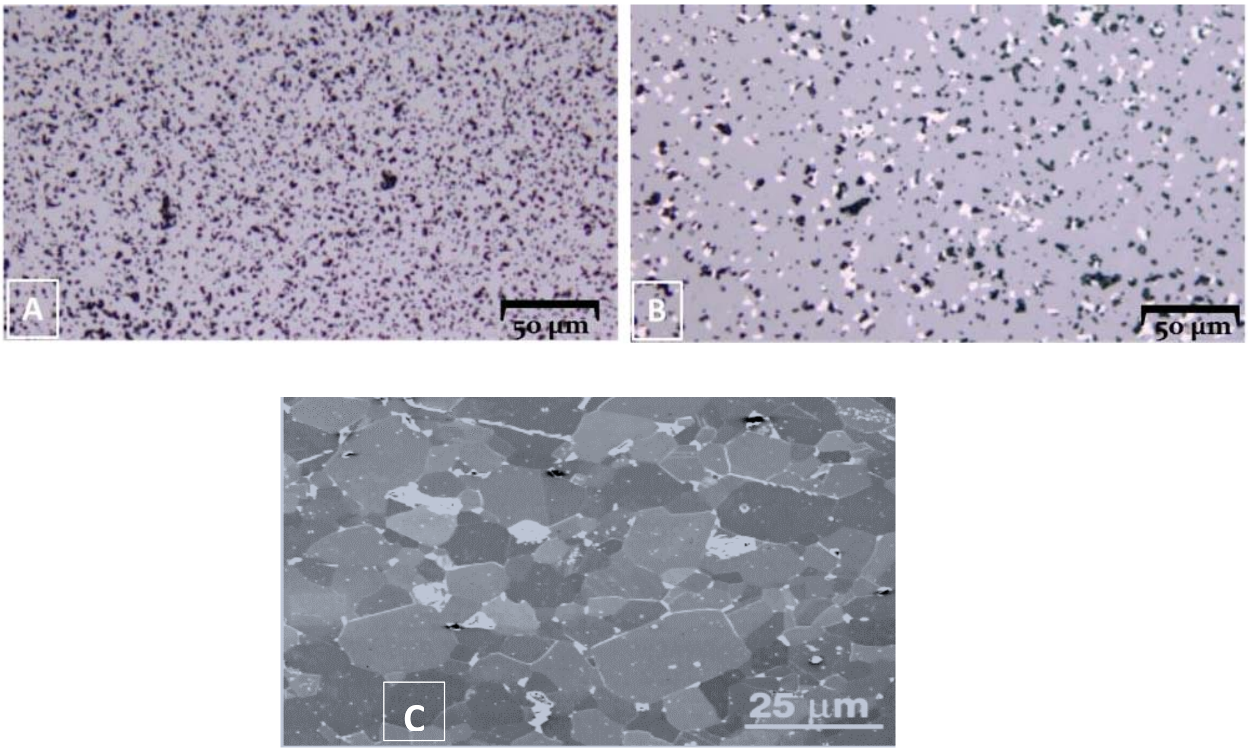

Figure 4: (A) Microstructure of boron carbide and (B) microstructure of Zr doped boron carbide sintered at 2350 ºC. (C) Highly polished and etched hot-pressed sample of boron carbide demonstrating secondary metal inclusions at the grain boundaries [17].

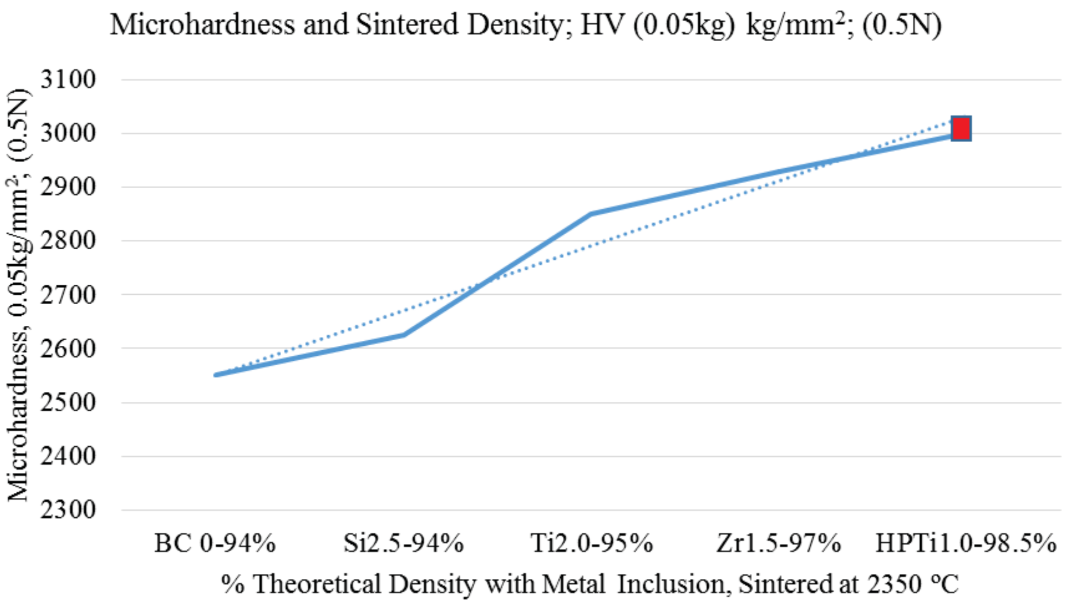

Figure 5: Microhardness of sintered boron carbide with metal inclusions with reference to Hot-pressed boron carbide with 1% Ti [17].

CONCLUSIONS.

In continuation to our previous investigations on the effect of Si, Ti and Zr as dopants in BC, their effect and advantages in pressure-less sintering of boron carbide were further reviewed. Pressure-less sintering of BC is very tricky. As it appeared, high temperature sintering (near melting point) with faster heating rates can be helpful to achieve similar density as that of hot-pressed BC. For pressure-less sintering, most of the published literatures dealt with the sintering temperatures around 2150-2200 ºC using relatively higher concentration of dopants. Low-temperature sintering of boron carbide with higher percentage of metal inclusions tend to produce segregated enlarged metal rich phases. Our investigation suggests, there are ample scopes to fine tune the conditions further to be able to achieve properties similar to hot-pressed BC. The use of Zr at a lower level of addition (~1.5 wt%), was found to be the most effective sintering additive to produce parts very similar in hardness and density as those of hot-pressed BC. In order to accomplish high-strength and high-density compressed parts, care must be taken in selecting the optimum weight percent of the metal inclusions [12].

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