TiC–TiB2 composites: A review of processing, properties and applications

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Abstract:- Ceramic-matrix composites (CMCs) based on TiC-TiB2 have attracted enormous interest during recent years because, in comparison to single phase ceramics, they exhibit superior properties including high hardness, good wear resistance and high fracture toughness. This paper presents the properties and application of TiB2-TiC. Much of the research effort has therefore focused on the synthesis, processing and fabrication of TiC-TiB2 is based primarily on self-propagating high-temperature synthesis (SHS).

Keywords: Composites; TiC–TiB₂; Self propagation High-temperature Synthesis (SHS).

I. INTRODUCTION

The development of ceramic-matrix composites (CMCs) is of increasing interest because they can enhance the intrinsically low fracture resistance of monolithic ceramics. Typical ceramic systems that are of such interest are carbide–boride composites of transition metals as they are recognized as valid candidates for technological applications under extreme conditions due to their excellent combination of mechanical and electrical properties as well as their good corrosion and oxidation resistance at high temperatures[1]. Titanium diboride/titanium carbide (TiC-TiB₂) is covalent compounds and possess excellent hardness and corrosion resistance. This composites are suitable for applications such as wear parts and high-temperature structural components. This composite has many characteristics such as high melting point and hardness, good thermal shock resistance and high temperature stability [2]. In comparison to conventional cermets based on WC and TiC, cermets based on TiC–TiB₂ composites, exhibit a higher hardness and chemical stability at high temperatures and are regarded as a good alternative for wear-resistant applications[3].

In addition, the use of TiC–TiB₂ in non-structural applications like wall tiles in nuclear fusion reactors, cathodes in Hall–Heroult cells and vaporizing elements in vacuum-metal deposition installations has been under investigation[4, 5]. It has also been shown that the fracture toughness and wear resistance of TiC–TiB₂ composites prepared from premixed TiB₂ and TiC powders were significantly higher than those of TiB₂ and TiCsingle phases [6]. Table 1 compares measurements of the Vickers hardness between TiC–TiB₂ and singlephase TiC and TiB₂[7]. It is apparent that the TiC–TiB₂ hardness measured at room temperature was lower than that of the single-phase materials. However, at 600 C the hardness of the composite exceeds the hardness of monolithic TiC and TiB₂.

Material	Vickers Hard	Vickers Hardness (Gpa)	
	25°C	600°C	
TiC	27.5	6.8	
TiB ₂	28.5	7.8	
TiC-TiB ₂	23.0	8.3	

TABLE 1 Vickers hardness at room and high temperature for TiC-TiB₂ composites and monolithic materials

Self propagation High- temperature Synthesis (SHS) densification is an attractive alternative technique for the preparation of dense composites [4]. It is known that the formation of liquid phases during the process increases the densification rate of ceramic composites. The SHS process is based on high-temperature exothermic reactions between reactants to achieve highly pure products. The pressure-assisted SHS technology includes two stages that are carried out simultaneously: [1] synthesis of a porous ceramic material by a self-sustaining reaction and [2] its densification by the application of mechanical pressure. The main advantages of the SHS technique are the high cost-effectiveness associated with the utilization of reaction heat instead of electric power, simplicity of facilities and high quality of the products. Many papers have been published devoted to the fabrication of TiC–TiB₂ composites by SHS-densification [5, 6, 7 and 8]. However, it was shown that the SHS composites obtained had poor mechanical properties due to the coarse-grained microstructure exhibited [7, 8]. In the present study, TiC–TiB₂ composites and the production of bulk TiC–TiB₂ ceramics by pressure-assisted SHS have been investigated.

1.1 Properties and applications of TiC

Titanium carbide (TiC) has recently been receiving high commercial attention, due to a number of desirable properties. It is extremely hard, one of the hardest known metal carbides [8]. TiC shows excellent thermal stability and has a very high melting temperature of approximately 3100°C [9, 10 and 11]. Besides, this material displays relatively high thermal and electrical conductivity. Good thermal conductivity results in low temperature gradients, which reduces thermal stresses and cracking, making it suitable for high speed cutting tool applications [12, 13]. Furthermore, this material has good electrical conductivity that makes it suitable for electrical discharge machining, which helps overcome the problem of shaping such hard material [13]. TiC has a lower density, which is desirable for applications that demand lightweight materials. It also exhibits excellent chemical stability, so it reduces the type of chemical interaction between the cutting tool and the work piece which typically causes crater wear [14, 15].

TABLE 2 Bulk properties at room temperature of titanium carbide (disordered state) with FCC structure and composition pear 50 at% C [16]

Lattice parameter (nm)	0.43	
Density (g/cm ³)	4.93	
Melting point (C)	3067	
Micro-hardness (GPa)	28	
Young Modulus (GPa)	450	
Heat conductivity $(Wm^{-1} C^{-1})$	28.9	
Linear thermal expansion coefficient (10^{-6} C^{-1})	8.5	
Electrical resistivity (μ cm)	100	

Due to the many characteristics of this material such as very high hardness, high melting temperature and excellent thermal and chemical stability, TiC is a suitable material for many commercial applications such as abrasive materials, cutting tools, grinding wheels and coated cutting tips [9, 10 and 11]. An overview of the most important properties of titanium carbide is presented in Table 2. TiC ceramic has been used worldwide as a high temperature ceramic in the cutting tools industry, in the form of a hard metal or cermets [17, 18 and 19]. In reality, TiC-based materials form the most important group of cutting tools after tungsten carbide-cobalt [20], conducting diffusion barriers in mechanical chemistry and the microelectronics industry, especially as a hardening phase of super alloys or reinforced particles in composites [17, 18 and 19].

TiC ceramic was traditionally synthesized and fabricated by various methods such as carbothermal reduction synthesis at elevated temperatures, powder metallurgy, mechanical alloying, reactive sintering and so on [17, 18 and 19]. However, most of these methods lead to the complexity of process and equipment, contamination of products, and even high temperatures being required for TiC-formation because of the relatively coarse raw powder mixtures [17, 18 and 19].

Despite the many advantages of this material, there are some limitations which obstruct its application. One limitation is difficulty in the production. Moreover, this material needs intensive energy and requires expensive, high temperature equipment for its production. For instance, current production methods involve reactions carried out at temperatures well above the melting point of titanium (1670°C). These high temperature production processes include carbothermal reduction of titanium dioxide, carburization of titanium by heating in the vapor of a suitable hydrocarbon and the direct reaction of titanium with carbon [10, 14 and 21].

1.2 Properties and applications of (TiB2)

TiB₂ ceramics are of interest for applications such as cutting tools, wear resistant parts, armor material and electrode materials in metal melting, because of their excellent combination of properties including high hardness, elastic modulus, better strength to weight ratio, wear resistance, good thermal and electrical conductivity. From the perspective of oxidation resistance, TiB₂ samples show parabolic oxidation kinetics below 1000°C as a result of the formation of TiO₂ and B₂O₃ [22] and linear oxidation kinetics above 1000°C in the presence of crystalline TiO₂ and volatile B₂O₃. TiB₂ is one of the choices for high temperature applications, because of its refractoriness and high strength at elevated temperatures. In particular, TiB₂ ceramics are characterized by an excellent combination of properties including high values of melting point, hardness, wear resistance, electrical and thermal conductivity, good creep resistance and excellent chemical stability. Such unique combination of properties makes TiB₂ a candidate material for heavy duty wear applications, cutting tools, impact resistant armor and electrode material, etc [23, 24].

 TiB_2 exhibits superior mechanical properties with the lowest density and a relatively high coefficient of thermal expansion. However, poor sinter ability and relatively low fracture toughness of monolithic TiB_2 limit its wider use in many engineering applications [25].

TiB₂ melts congruently at 3225° C. Both TiB and TiB₂ phases have a narrow homogeneity range. TiB₂ exists over a stoichiometry range of 28.5-30wt% B. The characteristics of high melting point and stability of TiB₂ make it suitable for high temperature structural applications [17, 26]. Important factors that control the composition of borides are the ratio of atomic sizes of boron (B) to metal (M) atoms, and in general the B:M ratios vary from 1:4 to 12:1 [7, 27]. Table 3 summarizes some of the properties of TiB₂.

TABLE 3 Properties of T_1B_2 [7, 28]	
Lattice parameter (nm)	a = 0.3028; c =
	0.3228
Density (g/cm ³)	4.52
Melting point (C)	3225
Hardness $HK_{0,1}$ (kg/mm ²) (>95% dense)	2600 (25 C)
	2400 (200 C)
	1800 (400 C)
	1050 (600 C)
	460 (1000 C)
Young Modulus (GPa)	560
Heat conductivity $(Wm^{-1} C^{-1})$	24-59
Linear thermal expansion coefficient (10^{-6} C^{-1})	5.107+1.997×10 ⁻³ T
Electrical resistivity (μ cm)	20.4 (25 C)
	26 (200 C)
	36 (400 C)
	46 (700 C)
Friction coefficient	0.9
Wear coefficient	1.7×10^{-3}
Weibull modulus	11

Increasing the number of B atoms leads to an increase in the B-B bond strength and results in an increase in melting temperature, hardness, strength and chemical stability. The M-B bond strength in diborides depends on the degree of electron localization around the M atoms. In metal borides, the outer electron configurations are sp2 and sp3, which promote strong covalent bonding [29]. Densification of monolithic TiB_2 also depends on the purity of the starting powders. Several investigators have carried out a comparative study on the sinter ability of TiB_2 powders produced by various processing techniques [30]. Khanra reported that a maximum of 97% theoretical density was achievable with the nano-sized TiB₂ powders (obtained by SHS technique) after pressure less sintering at 1950°C for 30min [31]. Such high density is attributable to the finer particle size and high defect concentration of the SHS produced TiB₂ powders. Wang and his co-workers investigated the influence of hot pressing temperature and sintering time on densification, microstructure and mechanical properties of TiB₂ ceramics [19]. Baik and Becher analyzed the detrimental effect of oxygen contamination, which gets introduced during synthesis and/or subsequent processing, on the densification of TiB₂[32]. Ferber et all reported that the materials with anisotropic coefficient of thermal expansion (CTE), such as TiB₂, often develop micro-cracks, relieving localized residual stresses generated during cooling from hot pressing temperature [33]. Such stresses arise primarily from the mismatch of thermal expansion between individual grains and anisotropic thermal expansion coefficient.

TiB₂-based cermets typically contain TiB₂ as a major phase, bonded with a non-metallic phase (silicides, carbides) and a metallic phase (Co/Ni). These materials are expected to be a novel lower density (having potentially higher hardness) substitute for the WC/Co system. With respect to chemical stability, an important factor in high temperature machining applications, TiB₂ is more stable in contact with pure iron than WC and Si₃N₄. Therefore, the machining behavior or tribological properties of TiB₂ against a steel counter face should expectedly be better than that of competing ceramics. The chemical inertness at high temperatures and good electrical conductivity of TiB₂ make it an excellent candidate for special electrical applications, e.g. cathodes used in aluminum electros melting or vaporizing elements for vacuum metal deposition installations. An important requirement of cathode material for aluminum reduction cells is that the material be wetted by aluminum. TiB₂ is a very attractive material for the aluminum industry because of its easier wet ability by molten aluminum, low solubility in molten aluminum and good electrical conductivity [34, 35]. Beside that,

pure hot-pressed TiB_2 was found to be completely wetted by aluminum with a contact angle of zero in a cryolite melt at 980°C. As far as armor applications are concerned, TiB_2 exhibits favorable properties such as high impact velocity for dwell/penetration transition and deformation induced hardening [36, 37].

These composites have been used as wear parts, cutting tools and heat exchangers. These electro-conductive toughened ceramics can be shaped by electro discharge machining to manufacture complex components, largely increasing number of industrial applications of these ceramic materials. Other applications of TiB_2 were also attempted, such as electrical contact barrier for Si in the semiconductor industry [38].

II. PROPERTIES AND APPLICATIONS OF TIC-TIB2 COMPOSITES

It is widely known that ceramic materials exhibit superior properties when compared to metals, in terms of thermal stability, corrosion and wear resistance. The ceramic-ceramic composites that combine boride and carbide offer an attractive combination of excellent mechanical and electrical properties and corrosion resistance, particularly at relatively high temperatures and/or in corrosive environments [39]. A summary of the mechanical properties of $TiC-TiB_2$ obtained by various processing routes and reported in the literature is summarized in Table 4.

 TiB_2 and TiC are covalent compounds and possess excellent hardness and corrosion resistance. TiB_2 and TiC are important materials for high-temperature applications because of their high melting points, hardness, elastic modulus and electrical conductivity, and relatively low coefficient of thermal expansion [32,40 and41].

Among these ceramics, TiB_2 and TiC have been proposed as components for high refractory cermets and for super-hard cutting tools.

Several investigators reported the use of reactive sintering/in situ densification techniques to produce TiB_2 -based composites [42, 43and 44].

Such processes are developed with an aim to lower the sintering temperature, densify the materials with or without use of sintering additives and reduce the processing costs, etc. Reactive sintering is a technique wherein both the chemical reactions of the starting powders and the densification occur in a single step [45] processed TiB₂-TiC composites via reactive sintering by the chemical reaction between Ti and B₄C powders after sintering at 1500°C for 1 hour. In another work, in situ toughened TiB₂-TiC_x composites were fabricated using reactive hot pressing of B₄C and Ti powders at high temperatures (1700-1800°C) for 1 hour [44]. The composites possessed very high relative density and high fracture toughness of 12.2MPa/m^{1/2}. Gotman produced in situ dense TiB₂/TiC and TiB₂/TiN composites from 2BN-3Ti and B₄C-3Ti powder blends with or without the addition of Ni via reactive synthesis techniques at temperatures of 1100°C [42].

The fabrication of TiB_2 and TiC ceramics by conventional sintering, hot pressing or hot isostatic pressing of TiB_2 and TiC powders is costly because of the time-consuming and facility-intensive nature of these processes [5, 39 and 43]. Cermets are produced traditionally by sintering which generally lasts for several hours. They are attractive for application in aircraft propulsion systems and space thermal protection systems, because of their high melting point, good thermal shock resistance and excellent high-temperature stability. They are also potential candidates for application in cutting tools, die, machine tool inserts, wear-resistant parts and lighter armor materials because of their high hardness, elastic modulus and light weight. Moreover, they can be used as cathodes for the Hall-Heroult cell due to their good electrical conductivity [32, 45].

The available data provide evidence that the combination of good wear resistance and relatively high thermal shock and oxidation resistance renders $TiC-TiB_2$ composites. However, no actual application of these materials is commercially available due to the fact that a cost-effective and reliable processing route allowing an accurate control of the microstructure has still to be established for this class of materials. Regarding this, the SHS process seems to offer a promising way provided an accurate control of the process parameters is achieved.

III. TIC-TIB2 SYNTHESIS AND PROCESSING

Ceramic-matrix composites are usually prepared by the densification of mechanically mixed component powders. Since the melting temperatures of TiB_2 and TiC are extremely high, their fabrication to full density requires long exposures at high sintering or hot-pressing temperatures. The densification of such materials is made even more difficult due to their high degree of covalent bonding and the low self-diffusion coefficients of the constituent elements. The high processing temperatures adversely affect the microstructure due to grain growth and also lead to high production costs. As a consequence, there is an increasing need for a more practical route of fabricating $TiC-TiB_2$ parts [46]. There are abundant amounts of processing data available in the industry to process the ceramic composites. However, they are often kept proprietary and not released in the

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public domain. More so than other materials, its manufacturing processes significantly affect the properties of TiB_2 -TiC. In conventional methods, ceramic are produced by compaction and sintering of chemically inert powders at high temperature to give consolidated products. Also considering production of TiB_2 -TiC composite for industrial purposes, near net shape fabrication processes are preferred due to the limited machine ability of the alloy. Furthermore Powder Metallurgy (PM) is a well-known process for its ability of providing semifinished and net-shaped products. In addition to, material savings, energy savings, process automation, as well as precise control of the chemical compositions can be achieved by PM while avoiding problems associated with the melting procedures like segregation. Fabrication techniques for conventional processing method by metallurgy powder of this product can be categorized in four groups conventional sintering (CS), Hot Isostatic Pressing (HIP), Spark Plasma Sintering (SPS) and Self-propagating High Temperature Synthesis (SHS).

In conventional sintering (CS), a green compact of elemental Ti, B and C powders is prepared and further sintered at near melting temperature of TiB_2 to yield in binary TiB from diffusion of Ti and B elements, because the melting point of TiB_2 is higher than TiC. So conventional sintering requires long heating times and samples are limited in shape and pore size. The porous structure is shown to be of small size and irregular shape. Maximum porosity of 40% has been achieved with this procedure [47, 48].

Hot Isostatic Pressing (HIP) is a process that subjects a material simultaneously to both high temperature and high gas pressure. HIP can close internal porosity in a material without distorting the external geometry, consolidate powder materials to 100% of theoretical density or form perfect diffusion bonds between similar or dissimilar materials. The mixture of elemental powder particles is encapsulated in an evacuated gas-tight welded canister and undergoes simultaneous isostatic pressure and elevated temperature. Other than that, Argon gas can be used as an inert environment without the need for the airtight chamber. In this case, HIP can be used to compress and trap Ar gas bubbles in between the elemental powders. A subsequent high-pressure diffusion stage leads to Ar-filled pores. Sintering the product at reduced pressures causes the gas to expand and bring about near-spherical pores in the final product.

Typically, the temperature is selected to permit limited plastic deformation of the material being processed in the solid state at an argon gas pressure of 15,000, 30,000, or at times, 45,000 psi (1,000 to 3,000 atmospheres) is isostatically exerted on the heated parts for a period of time. The chamber is then slowly cooled, depressurized and the parts removed. Fig. 1 is shown the schematic of HIP.



Fig.1. Schematic drawing of the HIP device.

Likewise all raw materials contain microscopic voids and "bubbles" of gas, from that standpoint, So It can be considered Titanium, Boride and Carbon porous. The advantages of the HIP for the fabrication of this composite is to eliminate of all internal porosity in simple or complex shapes with resulting improvement of mechanical properties such as ductility and fatigue life. A typical heating and pressurizing procedure for HIP is shown in Fig.2 [49].



The capsule-free HIP process was shown to produce homogenous porous TiB2-TiC with near-spherical pores. The structure could show acceptable pseudo elasticity due to the removal of stress concentration in near-spherical pores. Controlling the porosity characteristics in a porous material has a great influence on the mechanical properties of the products [50].

HIP products now include automotive parts, pump bodies, valves, vacuum chambers, bearings, sterile enclosures, etc. anywhere residual porosity cause high rejection rates, unacceptable property levels and surface finishing problems after machining. Commercial alloy applications include steel, stainless steel and aluminum castings. Not limited to metals, the process is very versatile, having been used to densify ceramics, plastics, glasses and many other materials.

Generally the advantages of HIP processes include shorter solid state diffusion time, good control over the pore size (microstructure), and ability to manipulate various geometries, resulting in a thermodynamically stable.

So Hot Isostatic Pressing can provide many benefits by stabilizing a material, removing residual stresses, densifying and eliminating voids and occlusions. The process "homogenizes" an alloy and in most cases, the properties of the material are enhanced, providing greater stability and wear characteristics [51].

Spark plasma sintering (SPS) is a newly developed process-a synthesis and processing technique-which makes possible sintering and sinter-bonding at low temperatures and short periods by charging the intervals between powder particles with electrical energy and effectively applying a high temperature spark plasma generated momentarily [51,52 and 53]. In the SPS method, raw powders are loaded in a graphite die, and a uniaxial pressure is applied during sintering. The heating is accomplished by spark discharges in the voids between the particles. Due to these discharges, the particle surface is activated and purified, and a self-heating phenomenon is generated between the particles. As a result, heat-transfer and mass-transfer can be completed instantaneously.Therefore, SPS technique can be used for sintering ceramic particulates reinforced composite quickly to its full density at relatively low temperature [54]. Fig. 3 is a schematic drawing of the SPS device.



SPS systems offer many advantages over conventional systems using hot press (HP) sintering, hot isostatic pressing (HIP) or atmospheric furnaces, including ease of operation and accurate control of sintering energy as well as high sintering speed, high reproducibility, safety and reliability [55, 56]. The SPS process is expected to find increased use in the fabrication of functionally graded materials (FGMs), intermetallic compounds, fiber reinforced ceramics (FRC), metal matrix composites (MMC) and nanocrystalline materials, which are difficult to sinter by conventional sintering methods. However, little work has been done on the TiB_2 -TiC composites produced by SPS technique. Fig. 4 shows the materials covered by SPS processing.



Fig.4 .Typical examples of materials covered by SPS processing (Source: SPS Forum survey)

According to, high-temperature, short-period SPS sintering is expected to provide almost all ceramic materials with new characteristics and sintered effects which are different from those obtained by the HP and HIP processes [56-58]. The ceramic materials which can be sintered at high density include oxides such as $A1_20_3$, mullite, Zr0₂, MgO, Hf0₂ and SO₂, carbides such **as** Sic, B₄C, TaC and TiC, borides such as TiB₂ and HfB₂ and nitrides such as Si₃N₄, TaN, TiN and AIN.

Self propagation high temperature synthesis (SHS) is an alternative method to the conventional one in producing advanced materials such as ceramics, ceramic-composites and intermetallic compounds. The underlying basis of SHS relies on the ability of highly exothermic reactions to be self-sustaining and, therefore, energetically

efficient. One of the difficulties with SHS is the inability to control the intermetallic phases [59]. A schematic representation of the SHS process is shown in Fig. 5.



Fig. 5. Schematic representation of the SHS process

The porosity of the SHS product depends on the original porosity of the green compact and synthesis parameters such as the change in the molar volume, the combustion front thermal gradients, and the gas evolution as a result of volatile impurity expulsion. The porosity and the mean pore size and the distribution of that can, to some extent, be controlled in SHS. Performing the reaction under a reduced pressure or adding a gasifying agent increases the porosity. Manipulating the reaction temperature by adding diluents to the initial mixture can be a way to control the pore size. Uniformity of the temperature profile within the sample greatly affects the homogeneity of the product.

The products of the combustion synthesis reaction are normally extremely porous, e.g. typically 50% of theoretical density of such porous materials may have some applications such as filters and catalytic support structures, and perform for liquid metal infiltration in the production of ceramic-metal composites [60].

The synthesis of TiB_2 -TiC with this method requires preheating of the sample to achieve self-sustained combustion since the exothermicity of the reaction is relatively low [61]. The preheating temperature affects the amount of transient liquid phase present at the combustion front. Excessive pre-heating has been shown to have detrimental effects such as anisotropy in the pore structure [62]. The SHS reaction can be performed in two different approaches; first by locally initiating the reaction which will further propagate along the sample [59,62] and second by volume combustion [63] i.e., heating the entire sample up to the reaction temperature which will let the reaction take place simultaneously throughout the whole sample [62].

A bulk porous TiB_2 -TiC has been produced via SHS from Ti, B and c green compact with a pre-heating temperature of 1200 °C. The porosity of the green compact, the transient liquid phase, and the volatilization of the impurities followed by the escape of absorbed gases left three dimensionally interconnected pores in the product which formed banded channel structures along the propagation direction of the reaction [59].

As outlined by Merzhanov [64], the main advantages of SHS method are less energy and time consuming, the products are high purity. Also The process can be used not only for producing refractory powders but also to make near net-shape components by utilizing the exothermic heat with processes such as casting, consolidation and coating.

Beside the benefits of this method it has some limitation. Since this method is difficult to control because of the high reaction rates. However, some controls are possible by adding diluents which do not join in the reaction, but increase the thermal mass of the system and lower adiabatic temperature. This leads to a decrease in combustion wave velocity, and the reaction rate decreases as expected for solid-solid reactions [65].

So among these fabrication techniques for synthesizing the composites, SHS technology has attached much attention, because of its low energy consumption, high time efficiency and high product purity [66].

IV. CONCLUSIONS

The fabrication of TiC–TiB₂ composites is difficult. SHS and its derivatives where pressure has been applied are capable of yielding products in excess of 95% theoretical density. A lot of the reported studies using SHS have been carried out aiming for a product of eutectic composition in order to promote liquid-phase formation that will assist the sintering process. The variation in the composition of the material can yield significant differences in microstructure. In addition to the eutectic microstructure, spherical TiC grains coexisting with a eutectic mixture are possible at higher TiC content. Products with a higher TiB₂ level have been reported to form prismatic TiB₂ grains together with the eutectic phase. The particle size of the reactant materials plays an important role in the SHS process. Reduction of the reactant particle size leads to an increase in the combustion

rate. Reduction of the cooling rate following SHS has been observed to lead to grain growth. An interesting development is the use of the SHS-quench process which results in the formation of a met stable product. Upon heat treatment, morphological evolution of nanocrystalline phases has been observed. Evaluation of the properties of samples produced by these processes, have shown very promising improvements, principally with regard to wear resistance and fracture toughness.

REFERENCES

- Y. Yorozu, M. Hirano, K. Oka, and Y. Tagawa, "Electron spectroscopy studies on magneto-optical media and plastic substrate interface," IEEE Transl. J. Magn. Japan, vol. 2, pp. 740–741, August 1987
- H. Zhao, Y. Cheng, "Formation of TiB₂-TiC composites by reactive sintering," Ceram. Int 1999, vol. 25, pp. 353–358.
- [3] R. Licheri, R. Orrù, G. Cao, "Chemically activated combustion synthesis of TiC-Ti composites," Mater. Sci. Eng., A, vol. 2,pp. 185–97, 2004.
- [4] E.Y. Gutmanas, I.J. Gotman, "Dense high-temperature ceramics by thermal explosion under pressure," . Eur. Ceram. Soc, vol. 19, pp. 2381–2393, 1999.
- [5] X. Zhou, S. Zhang, M. Zhu, B. Chen," Investigation of TiB₂–TiC composites produced by SHS and their application in Hall–Heroult cells for aluminum electrolysis," . *Int. J. Self-Propag. High-Temp Synth*, vol. 7, pp. 403–408, 1979.
- [6] D. Brodkin, S. Kalidindi, M. Barsoum, M. Zavaliangos, "Microstructural evolution during transient plastic phase processing of titanium carbide–titanium boride composites," A. J. Am. Ceram. Soc, vol. 79, pp. 1945–1952, 1996.
- [7] G. Wen, SB. Li, BS. Zhang, ZX. Guo, "Reaction synthesis of TiB₂ –TiC composites with enhanced toughness," *Acta Metall*, vol. 41, pp.1463-1470, 2001.
- [8] L. Contreras, X. Turrillas, GB. Vaughan, A. Kvick, MA, "Rodriguez XRD study of TiC-TiB₂ composites obtained by SHS," Acta Mater, vol. 52, pp. 4783–4790, 2004.
- [9] LL. Ye, MX. Quan Synthesis of nanocrystalline TiC powders by mechanical alloying," *Nanostructured mater*, vol. 5, pp. 25-31, 1995.
- [10] M. Eskandarany, EL. Sherif, "Synthesis of nanocrystalline titanium carbide alloy powders by mechanical solid state reaction," *Metall. Mater. Trans. A*, vol. 27A, pp.2374-2382, 1996.
- [11] M. Eskandarany, EL. Sherif, "Structure and properties of nanocrystaline TiC full-density bulk alloy consolidate from mechanically reacted powders," J. Alloys Compd, vol.305,pp. 225-238, 2000.
- [12] R. Koc, C. Meng, GA. Swift. Sintering properties of submicron TiC powders from carbon coated titanium precursor J. Mater. Sci. Lett 2000, 35, 3131-3141.
- [13] HSP. Fard, HR. Baharvandi, H. Abdizadeh, B. Shahbahrami, "Chemical synthesis of nano-titanium diboride powders by borothermic reduction," *Int. J. Mod Phys B*, vol. 22, pp. 3179–84, 2008.
- [14] EY. Gutmanas, I. Gotman, "Dense high-temperature ceramics by thermal explosion under pressure". J. Eur. Ceram. Soc, vol. 19, pp. 2381-2393, 1999.
- [15] JL. Ellis, CG. Goetzel , Cermets, ASM Metals Handbook, p. 978-1007, 1990.
- [16] AM. Santhanam, P. Tierny, JL. Hunt, Cemented Carbides, ASM Metals Handbook, p. 950-977, 1990.
- [17] LB. Nikzada, R. Licheria, MR. Vaezib, R. Orrùa, G. Caoa, "Chemically and mechanically activated combustion synthesis of B₄C-TiB₂ composites," Int. J. Refract. Met. Hard Mater, vol. 35, pp. 41–48, 2012.
- [18] RR. Taylor, SA. Pirzada, "Ceramic carbide powder synthesis in a non-transferred arc plasma flow reactor," *Mater. Manuf. Processe, vol.* 8, pp. 501-507, 2007.
- [19] A. Biedunkiewicz, P. Figiel, U. Gabriel, M. Sabara, S. Lenart," Synthesis and characteristics of nanocrystalline materials in Ti, B, C and N containing system," Eur. J. Solid State Inorg. Chem, vol. 9, pp. 417–22, 2011.
- [20] W. Wang, Z. Fu, H. Wang, R. Yuan, "Influence of hot pressing sintering temperature and time on microstructure and mechanical properties of TiB₂ ceramics," *Bioinformatics*, vol. 22, pp. 1045-1049, 2002.
- [21] M. Razavi, R. Ghaderi, MR. Rahimipour, R. Ostad Shabni, "Synthesis of TiC Master Alloy in Nanometer Scale by Mechanical Milling Mater," Manuf. Processes, vol. 27, pp. 1310-1314, 2012.
- [22] L. Khusboo, VA. Sherbakov, "Fabrication of in-situ Ti–Si–C fine grained composite by the self propagating high temperature synthesis (SHS) process," Int. J. Refract. Met. Hard Mater, vol. 29, pp. 209-213, 2011.
- [23] SR. Levine, EJ. Opila, MC. Halbig, JD. Kiser, M. Singh, JA. Salem, "Evaluation of ultra-high temperature ceramics for aero propulsion use," J. Eur. Ceram. Soc, vol. 22, pp. 2757-2767, 2012.
- [24] B. Ghosh, SK. Pradhan," Microstructure characterization of nanocrystalline TiC synthesized by mechanical alloying," Mater. Chem. Physics, vol. 120, pp. 537–45, 2010.
- [25] R. Telle, G. Petzow, "Densification and Mechanical Properties of B₄C with Al₂O₃ as a Sintering Aid," J. Am. Ceram. Soc, vol. 2, pp. 1155-1201, 2011.
- [26] B. Basu, GB. Raju, AK. Suri, "Processing and properties of monolithic TiB₂-based Materials," Int. Mater. Rev, vol. 51, pp. 352-374, 2006.
- [27] L. Guanghua, L. Jiangtao, C. Kexin, "Combustion synthesis of refractory and hard materials: A review," Int. J. Refract. Met. Hard Mater, vol. 39, pp. 90-102, 2013.
- [28] RA. Cutler, Engineering Properties of borides, in Engineered materials handbook, vol. 4, 1991.
- [29] RG. Munro, "Material properties of titanium diboride," J. Reinf. Plast. Compos, vol. 105, pp. 709–720, 2012.
- [30] W. Georg, "Electron deformation density in titanium diboride chemical bonding in TiB₂," J. Solid State Chem, vol. 177, pp. 628-631, 2004.

- [31] AK. Khanra, MA. Godkhindi, LC. Pathak, "Process for in-situ preparation of aluminia-(Ti, Zr) borides composite," *Mater. Sci. Eng.*, A, vol. 281-287, pp. 454-455, 2007.
- [32] AK Khanra, MM. Godkhindi, LC. Pathak, "Comparative Studies on Sintering Behavior of Self-Propagating High-Temperature Synthesized Ultra-Fine Titanium Diboride Powder," J. Am. Ceram. Soc, vol. 88, pp. 1619-1621, 2005.
- [33] M. Selva Kumar, P. Chandrasekar, Chandramohan, M. Mohanraj, "Characterisation of titanium-titanium boride composites processed by powder metallurgy techniques," Mater. Charact, vol. 73, pp. 43-51, 2012.
- [34] LU. Jianbang, S. Shili, Q. Feng, W. Yawei, J. Qichuan," Compression properties and abrasive wear behavior of high volume fraction TiCx-TiB₂/Cu composites fabricated by combustion synthesis and hot press consolidation," Mater. Des, vol. 40, pp. 157-162, 2012.
- [35] KD. Watson, JM. Toguri,"The wettability of carbon-titanium diboride composite materials by aluminum in cryolite melts," *Metall. Mater. Trans. B*, vol. 22, pp. 617-621, 1991.
- [36] M. Dionne, G. L'esperance, A. Mirchi, "Microscopic characterization of a TiB₂-Carbon material composite: Raw materials and composite characterization," Metall. Mater. Trans. A, vol. 32, pp. 2649-2656, 2001.
- [37] [36] DP. Dandekar, DC. Benfanti, "Strength of titanium diboride under shock wave loading," J. Appl. Phys, vol. 73, pp.673-679, 1993.
- [38] AR. Keller, M. Zhou,"Effect of microstructure on dynamic failure resistance of titanium diboride/alumina ceramics," J. Am. Ceram. Soc, vol. 86, pp. 449-457, 2003.
- [39] BS. Du, P. Sameer, R. Narendra, B. Dahotrea,"Phase constituents and microstructure of laser synthesized TiB₂– TiC reinforced composite coating on steel," Scripta Mater, vol. 59, pp. 1147–50, 2008.
- [40] MA. Janney, "Mechanical properties and oxidation behaviors of a hot-pressed SiC-15vol%-TiB₂ Composite" J. Am. Ceram. Soc, vol. 66, pp. 322-324, 1987.
- [41] Z. Lei, S. Ping, J. Qichuan, "The mechanism of combustion synthesis of (TiCx Ny-TiB₂)/Ni from a Ni-Ti-C-BN system," Powder Technol, vol. 205, pp.52–60, 2011.
- [42] MW. Barsoum, B. Houng," Transient plastic phase processing of titanium-boron-carbon composites," J. Am. Ceram. Soc, vol. 76, pp. 1445-1451, 1993.
- [43] G. Zhang,"Preparation of TiB₂-TiC_{0.5} N_{0.5} ceramic composite by reactive hot-pressing and its microstructure," Ceram. Int, vol. 21, pp. 29-31, 1995.
- [44] SP. Chen, QS. Meng, W. Liu, ZA. Munir," Titanium diboride–nickel graded materials prepared by field-activated, pressure-assisted synthesis process," J. Mater. Sci. Lett, vol. 44, pp. 1121–1126, 2009.
- [45] G. Wen, Li. SB, BS. Zhang, ZX. Guo, "Reaction synthesis of TiB₂ –TiC composites with enhanced toughness," Acta Mater, vol. 49, pp. 1463-1470, 2000.
- [46] P. Shen, BL. Zou, SB. Jin, QS. Jiang," Reaction mechanism in self-propagating high temperature synthesis of TiC-TiB₂/Al composites from an Al-Ti-B-C system," Mater. Sci. Eng., A , vol. 300-309, pp. 454–455, 2007.
- [47] I. Gotman, NA. Travitzky, EY. Gutmanas," Dense in situ TiB₂–TiN and TiB₂–TiC ceramic matrix composites: reactive synthesis and properties," Mater. Sci. Eng., A, vol. 244, pp. 127–137, 1998.
- [48] F. Hong, MH. Lewis," Ceramic-matrix composites via in-situ reaction sintering," Ceramic Engineering and Science Proceedings, vol. 14, pp. 699-706, 1993.
- [49] FJ. Akhtar," Microstructure evolution and wear properties of in situ synthesized TiB₂ and TiC reinforced steel matrix composites," J. Alloys Compd, vol. 459, pp.491–7, 2008.
- [50] B. Yuan, CY. Chung, XP. Zhang, MQ. Zen, GM. Zhu, "Control of porosity and superelasticity of porous TiC-TiB shape by hot isostatic pressing," Smart Mater. Struct, vol. 14, pp. S201–6, 2005.
- [51] M. Bram, A. Ahmad-Khanloua, A. Heckmannb, B. Fuchsa, HP. Buchkremera, D. Stovera," Powder metallurgical fabrication processes for NiTi shape memory alloy parts," *Mater. Sci. Eng.*, A, vol. 337, pp. 254–63, 2009.
- [52] FH. Froesa, J. Hebeisenb., Hot isostatic pressing of titanium based materials, 1994, Pages 71-90.
- [53] KQ. Feng, Y. Yang, M. Hong, JL. Wu, SS. Lan," Intensified sintering of iron powders under the action of an electric field: effect of technologic parameter on sintering densification," J. Mater. Process. Technol, vol. 208, pp. 264–269, 2008.
- [54] Sh. Shili, Q. Feng, J. Shenbao, L. Jianbang, J. Qichuan," Compression properties and work-hardening behavior of Ti₂AlC/TiAl composites fabricated by combustion synthesis and hot press consolidation in the Ti–Al–Nb–C system," J. Mater. Des, vol. 32, pp. 5061-5065, 2011.
- [55] ZA. Munir, U. Anselmi-Tamburini, M. Ohyanagi," The effect of electric field and pressure on the synthesis and consolidation of materials: a review of the spark plasma sintering method," Mater. Des, vol. 20, pp. 41763–777, 2006.
- [56] I. Song, L. Wang, M. Wixom,"Self-propagating high temperature synthesis and dynamic compaction of titanium diboride/titanium carbide composites," J. Mater. Sci. Lett, vol. 35, pp. 2611-2617, 2003.
- [57] N. Tamari, T. Tanaka, K. Tanaka, M. Kawahara, M. Tokitn., "Effect of Spark Plasma Sintering on Densification and Mechanical Properties of Silicon Carbide," J. Mater. Res, vol. 103, pp. 740-746, 1995.
- [58] T. Nishimura, M. Mitomo, H. Hirotsuru, M. Kawahara, "Fabication of Silicon Nitride Nano-ceramics by Spark Plasma Sintering," J. Mater. Sci. Lett, vol. 13, pp. 1046-1047, 2001.
- [59] D. Vallauri, IC. At'ıas Adrian'a, A. Chrysanthou, "TiC–TiB₂ composites: A review of phase relationships, processing and properties," J. Eur. Ceram. Soc, vol. 28, pp. 1697–1713, 2008.
- [60] A. Biswas," Porous TiB₂ by thermal explosion mode of SHS: processing, mechanism and generation of single phase microstructure," Acta Mater, vol. 53, pp. 4015–25, 2005.
- [61] BY. Li, LJ. Rong, YY. Li, VE. Gjunter," Synthesis of porous Ti-C shape-memory alloys by self propagating hightemperature synthesis: reaction mechanism and anisotropy in pore structure," *Acta Mater*, vol. 48, pp. 3895–904, 2001.

- [62] C. Greiner, SM. Oppenheimer, DC. Dunand High strength, low stiffness, porous TiB_2 with superelastic properties . Acta Biotechnol 2005, 1, 705–16.
- [63] AG. Merzhanov.," History and recent developments in SHS," Ceram. Int, vol. 21, pp. 371-379, 1995.
- [64] AG. Merzhanov, "Solid flames: discovery, concepts and horizons of cognition," *Combust. Sci. Technol*, vol. 98, pp. 307–336, 1994.
- [65] ZA. Munir, U. Anselmi-Tamburini, M. Ohyanagi.," The effect of electric field and pressure on the synthesis and consolidation of materials: a review of the spark plasma sintering method," J. Membr. Sci, vol. 41, pp. 763–777, 2006.