Synthesis of complex carbonitrides and boridenitrides by electric discharge assisted mechanical milling

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SYNTHESIS OF COMPLEX METAL CARBONITRIDES AND BORIDENITRIDES BY ELECTRIC DISCHARGE ASSISTED MECHANICAL MILLING

By

IIS SITI AISYAH

A thesis submitted in fulfilment of the requirements for the award of the degree of

PHD IN MATERIALS ENGINEERING

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   I.S. Aisyah, A. Calka, D. Wexler
   *Annual International Conference on Materials Science, Metal and Manufacturing (M3 2011), published by GSTF.*

2. Electric Discharge Assisted Mechanical Milling – New Process of Synthesis TiBN and ZrBN; Microstructure, Phase Transformation and Grain Size (Published poster)
   I.S. Aisyah, A. Calka, D. Wexler
ABREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>BSEI</td>
<td>Back scattering electron imaging</td>
</tr>
<tr>
<td>CHN</td>
<td>Carbon hydrogen nitrogen</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EDAMM</td>
<td>Electric discharge assisted mechanical milling</td>
</tr>
<tr>
<td>FEGSEM</td>
<td>Field emission gun scanning electron microscopy</td>
</tr>
<tr>
<td>HEBM</td>
<td>High energy ball milling</td>
</tr>
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<td>HV</td>
<td>Hardness Vickers</td>
</tr>
<tr>
<td>ICDD PDF</td>
<td>International Centre for Diffraction Data Powder Diffraction Files</td>
</tr>
<tr>
<td>LVSEM</td>
<td>Low vacuum scanning electron microscopy</td>
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<tr>
<td>MeB</td>
<td>Metal boride</td>
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<td>MeBN</td>
<td>Metal boride nitride</td>
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ABSTRACT

Metal carbonitrides and boridenitrides are finding applications as new materials in areas where high temperature, high hardness and/or high pressure properties are critical. In monolithic form, these materials are particularly well suited for increasing the performance of cutting and machining tools due to their high hardness, thermal stability and chemical inertness. In the work presented here, the novel powder synthesis route of Electric Discharge Mechanical Milling (EDAMM) was applied to the synthesis of powders of carbonitrides and boronitrides (boridenitrides) using as precursors: elemental refractory transition metals; Zr Hf, Ta, Mo and W; transition metals, Ti, Va, Cr; and mixed Si and Si-Al -transition metals.

The effects of varying EDAMM process parameters on product were investigated. Variables included; discharge energy under AC and DC milling modes, average gap between electrodes in vibrating mill, and electrical impulse pulse modulation and amplitude. EDAMM processed products were characterized by bulk CHN chemical analysis, metallography, x-ray diffraction, electron microscopy and microhardness investigations in order to understand phase and microstructural evolution, and changes in physical properties. It was found that crystalline MeCN and MeBN powders can be obtained in supersaturated solid solution form, or in the form of ternary intermetallic phases depending on the arrangement of EDAMM processing parameters. It was found that an AC mode of processing, acting at relatively low energies compared to DC mode processing, promoted the formation of interstitial solid solution phases MeC(N) and finer particles. Contrarily, under the higher energy input DC mode the formation of ternary intermetallic phases MeC,N, was promoted, usually taking the form of usually in agglomerated particles. Typically, the nitriding of the powders by EDAMM was found to transform the powder structure and also increases the hardness value. Moreover,
the efficiency of this novel method was evaluated, not only with respect to an improvement of nitriding methods but also in terms of improved mechanical performances in respect to combined compacting and sintering induced in the same time.
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INTRODUCTION

Producing new super-hard materials has usually high cost, and requirements of needing high temperatures, high pressures and expensive equipment. High hardness metal based materials usually take to form in metal carbides, nitride and borides, which are used primarily for refractory applications and applications requiring high hardness. It is well known that carbide and nitride coatings are well suited for increasing the performance of tools due to their high hardness, thermal stability and chemical inertness.

Traditionally, Me-B-N and Me-C-N compounds are fabricated in the form of a coatings by deposition methods, including the various derivations of chemical vapour deposition, such as; magnetron sputtering, cathodic arc plasma deposition, combined magnetron sputtering and ion implantation. Although these methods have improved significantly over the years disadvantages remain including; low deposition rates, lack of thickness, inferior films/substrate adhesion and difficulty in deposition of uniform layers on parts with complicated shapes and also relatively expensive fabrications. Me-B-N and Me-C-N compounds in the powder form can be synthesized by ball milling. The obtained products can be compacted and sintered. However, a disadvantage of this method is the long milling times that can make this process uneconomical.

In this research the new electric discharge assisted mechanical milling method (EDAMM) was applied to the synthesis of Me-C-N and Me-B-N compounds.
In Chapters 4 to 6, the nitriding behaviour of metal carbides and borides of group IV (titanium, zirconium and hafnium), group V (vanadium and tantalum) and group VI (chromium, molybdenum and tungsten) are investigated. Also transformations in Silicon Carbide were studied. The experiments were carried out in using process parameters including AC and DC mode discharges during milling, variations in gap between electrodes, and variations in gases flow rates and milling times. Phase changes and nitrogen content, microstructure and microhardness were analysed by X-ray diffraction, Scanning Electron Microscopy, CHN analysis and Vickers hardness testing.

In Chapter 7, the study focuses on synthesizing metallic composites; Ti-Al and Ti-Al-Si by two different methods; conventional planetary ball milling and EDAMM. Obtained powder samples were subsequently compacted and sintered in SPS.
1 LITERATURE REVIEW AND THEORITICAL BACKGROUND

1.1. INTRODUCTION

This chapter is a review of basic concept of various conventional synthesis methods of compounds Me-C-N and Me-B-N (metal carbonitrde and boronitride). Conventional nitriding processes and mechanisms, and novel electric discharge assisted mechanical milling EDAMM method, are compared and discussed. In this chapter results from published papers relevant to this study are reviewed and discussed.

1.2. REFRACTORY CERAMIC MATERIALS

Metal Carbonitrides and Metal Boridenitrides (further called as Me-C-N and Me-B-N systems) were recognised as high refractory ceramic compounds groups (e.g. carbides, oxides, nitrides, borides and composites based on these compounds) with properties such as extremely high hardness, high temperature stability, high thermal conductivity and good corrosion resistance. They are widely applied in various branches of technology. These materials show attractive mechanical properties for aerospace, military, chemical and metallurgical applications [1] [2]. Conventionally, they can be synthesized by the gas-condensation methods, high energy ball-milling, wet chemical processes, and combustion synthesis. The most applicable method for producing Me-C-N and Me-B-N in thin layers is coating deposition. Using this technique, Me-C-N and Me-B-N have been produced industrially in the world scale. However, this method is known as time-consuming and expensive. On the other hand, mechanical milling has been a one-step successful route as an
inexpensive and faster way for synthesizing refractory compounds in powder form. Therefore this chapter discuss both synthesis methods of Me-C-N and Me-B-N.

1.3. DEPOSITION METHODS

Methods for depositing a thin film of material onto substrate or onto previously deposited layers are usually called “thin film deposition” methods. There are various ways of film deposition, including wet/semimolten and vapour deposition methods. The former is generally appropriate for thick coating and small area configuration applications. The later is usually chosen as a better process for producing highly pure coatings with good structural control and lower processing temperatures. K. L. Choy explain two types of vapour processing, these are Chemical Vapour Deposition (CVD) and Physical Vapour Deposition (PVD) [3]. Chemical Vapour Deposition (CVD) involved the chemical reaction which was obtained from reacted-gaseous on a heated substrate surface.

The CVD reactor is principally build in 3 main parts, these are

1. Reaction chamber for the placement the substrate into the chamber.
2. Substrate holder, and
3. Heating system with temperature control.

The principle process of the CVD reactor is used to heat the substrate to the required deposition temperature. Moreover, K. L. Choy stated that even at low processing temperatures, CVD is capable of producing single layer, multilayer, composite, nanostructured and/or functionally graded coating materials in precise controlled dimensions with unique or complex structures. CVD has also become an important technique in coating technology for broad applications including; production of functional semiconducting thin films, and coatings with improved surface properties such as protection wear, corrosion, oxidation, chemical reaction, thermal shock, and neutron adsorption. These include the
coating of various elements and compounds such as C, B, Si, borides, carbides, nitrides, oxides, silicides, and sulfides. CVD can successfully produce electronic semiconductors and protective coatings for electronic circuits in the early 1970s.

K.L. Choy state that various refractory ceramic materials have been synthesized by this method, include; TiB$_2$, SiC, B$_4$C, BN, TiN, Al$_2$O$_3$, ZrO$_2$, MoSi$_2$, and diamond, which can be used for hard coatings, protection against wear, corrosion protection, oxidation, chemical reaction, thermal shock, neutron adsorption or as diffusion barriers, ceramic fibres (e.g. SiC and C) and ceramic matrix composites (e.g. SiC/SiC, SiC/C).

Based on different heating and type of precursor, there were the different variants of CVD methods, including thermally activated CVD (TACVD), plasma enhanced CVD (PECVD), photo-assisted CVD (PACVD), atomic layer epitaxy process (ALECVD), metalorganic assisted CVD (MOCVD). There are also variants such as fluidised-bed CVD, electrochemical vapour deposition for depositing dense films onto porous substrates; chemical vapour infiltration, Aerosol Assisted Chemical Vapour Deposition (AACVD) and Flame Assisted Chemical Vapour Deposition (FACVD). Another method of vapour depositing is Physical Vapour Deposition (PVD); this method does not involve complex chemistry as in the CVD-based methods, so there are no chemical reactions in this process.

In the past Ti-C-N (titanium carbonitride), has been synthesized by several variants CVD; reactive ion beam assisted deposition, magnetron sputtering, and arc evaporated [4, 5]. The later showed that the TiC$_{1-x}$N$_x$ hardness increases with $x$ up to a maximum at 0.4–0.7 in coatings, and that the hardness of TiC was greater than that of TiN. SJ Bull state that TiCN exists in a broad composition range in a coating form [6] and can be produced with
composition TiC$_{1-x}$N$_x$, where $x$ ranges from 0 to 1; in this range nitrogen is substituted by carbon in the face-centered cubic structure.

ZrCN (zirconium carbonitride) is also applied as wear resistant films on cemented carbide cutting tools, and has additional unique applications, including; deposition films that absorb solar energy, and refractory protective coatings on nuclear fuel elements. Conventionally ZrCN coating is fabricated by deposition methods of chemical vapour deposition [7] magnetron sputtering [8], cathodic arc plasma deposition [9] and combined magnetron sputtering and ion implantation (CMSII) [10].

In 1995 the ternary phase diagrams of ZrCN, TiCN and HfCN were established by Binder, Lengauer and Ettmayer at 1150°C (Figure 1.1) [11].

![Figure 1.1 Tentative phase diagram of the Zr-C-N system at 1150 °C established by Binder, Lengauer and Ettmayer](image)

TiCN, ZrCN and HfCN phase equilibria at 1150°C in the solid regions were investigated by means of arc-melted as well as hot-pressed alloys. The binary carbide system Zr-C is
characterized by an intermediate phase with the B1-type structure (i.e. NaCl) and here mentioned as δ-phase.

Takahashi and coworkers in 1981 succeeded in synthesis of ZrC$_x$N$_y$ films by chemical vapour deposition onto steel and graphite substrates, using a reactant gas mixture of ZrCl$_4$, CH$_4$, N$_2$, H$_2$ and Argon [7]. A homogeneous solid solution of ZrC$_x$N$_{1-x}$ in the binary system ZrC-ZrN was obtained by controlling either CH$_4$:N$_2$ mole ratio in the feed gas or the deposition temperature. They investigated influence of deposition temperature on the lattice constant then concluded that the crystalline of ZrC$_x$N$_y$ increased with an increase in the deposition temperature. Finally, Takahashi state that at 1140˚C a solid solution formed with a high carbon concentration.

Aigner stated that stoichiometric titanium carbonitrides, zirconium carbonitrides and hafnium carbonitrides obey the Vegard rule up to 1473 K [12]. The thermal expansion values of the fcc phases Ti(C$_x$N$_{1-x}$), Zr(C$_x$N$_{1-x}$) and Hf(C$_x$N$_{1-x}$) with [C+N]/[Me] ~ 1 and TiN$_{1-x}$ with [N]/[Ti] = 1.0 to 0.67 were determined from lattice parameter measurements made with high temperature X-ray diffraction (HTXRD).

Spillman et al (2002) used Pulsed Reactive Crossed Beam Laser Ablation (PRCLA deposition method [8] to deposit carbonitride film. They used a zirconium metal and a nitrogen and carbon containing gas pulse mixture. The ZrCN film was deposited on Si and Mg substrates by ablating of Zr using a KrF laser in the presence of a synchronized CH$_4$/N$_2$, C$_2$H$_6$/N$_2$ or C$_2$H$_4$/N$_2$. The result showed that ZrC$_x$N$_y$ thin films can be grown under optimum conditions ($\Delta$t=700 µs, d ≤ 7 mm) even at room temperature when CH$_4$/N$_2$ gas mixtures are used. Above $T_s$ = 400˚C, high quality single crystal-line thin films are successfully produced. However,
Spillman stated that using C$_2$H$_6$ or C$_2$H$_4$ gas will degrade the crystal quality and complicates the control of stoichiometry. Another factor that influenced the chemical composition of ZrC$_x$N$_y$ is the substrate temperature, as found by Berndt et al, in 1995 in their work on synthesis of ZrCN films by plasma assisted metal organic chemical vapour deposition (PACVD) [13].

Zaoui and Ruterana (2005) state that transition metal carbides and nitrides in group IV (ZrC, TiC and HfC) have not been much studied experimentally, therefore the theoretical calculation of the chemical bonding for these systems is a considerable interest [14]. Furthermore they investigated and described the mechanical and electronic behaviour of a series of binary transition metal carbides and nitrides and their ternary alloys. They also investigated variations of chemical bonding character as a function of carbon and nitrogen content in TiC$_x$N$_{1-x}$, Zr$_x$Nb$_{1-x}$C and HfC$_x$N$_{1-x}$ alloys.

Han et al. successfully deposited Hf-C-N (hafnium carbonitride) by pulsed d.c. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) [15]. The result shows highly oriented polycrystalline films in the (111) direction at temperatures as low as 300ºC. They also stated that the flow rate ratio of N$_2$ reactive gas and the He + H$_2$ carrier gas were an important deposition parameter. With a slightly different method Wenwu Wang also succeeded in synthesizing HfCN by MOCVD [16].

Si–C–N nanocomposite thin films were deposited on industrially important substrates like silicon (100), borosilicate glass, and stainless steel (304SS) by radio frequency (RF) magnetron sputtering[17]. In this study SiCN was found to have higher hardness when deposited at stainless steel, followed at glass and silicon by VHN (15 gf) 2123, 1560 and 1434
respectively. Batacharya stated that best adhesion is due to the lowest thickness, which also explains the reason for getting the highest hardness in case of 304SS substrates[17]. Torun et al also synthesized SiCN using magnetron sputtering by varying the composition and nitrogen fraction. In general the SiCN films showed comparable, but slightly lower hardness values to what has been reported for CNx films grown under similar conditions. The highest hardness value for a 1-μm-thick film grown in this study reaches 28 GPa.

Cr-C-N (chromium carbonitrides) systems are generally synthesized by CVD and PVD, using methods including; cathodic arc PVD [18] [19] [20], and Metal Organic CVD [21] [22]. Warcholinsky found that CrCN with less carbon composition (up to 10 at%) has higher hardness, around 30 GPa [18]. Even though he stated that low carbon content in CrCN films are difficult to understand and need a more detailed study.

Preparation of Ta-C-N (tantalum carbonitrides) was conducted by Yeh, using self-propagating high-temperature synthesis (SHS) method [23]. Its study use compacted samples of tantalum and carbon powders ignited in gaseous nitrogen. Then the effects of the carbon content and nitrogen pressure on the combustion characteristics and the degree of nitridation were studied. The other researchers, O. Yu, Khyzhun and Kolyagin indicated that substitution of carbon atoms for nitrogen atoms in the cubic and rhombohedral tantalum carbonitrides, Ta(C,N), led to the increase of metallic and ionic components and the decrease of the covalent component in the chemical bonding [24]. They state that rhombohedral Ta₄C₃ carbide and TaC₀.₅₉N₀.₁₅ carbonitride can be synthesized using high-temperature interaction of refractory metal interstitial alloys with their oxides.
Previous researchers succeeded synthesized Me-B-N (metal boronitrides) system especially on alkaline earth and rare earth boron nitride compounds. Furthermore a series of metal boron nitrogen compounds has been identified as a single phase form and most of their structure types have been evaluated, as table below (Figure 1.2). Rogl stated that generally there is also a small amount of carbon and oxygen impurities that easily stabilise higher order compounds [25].

<table>
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<td>B$_2$N$_4$</td>
<td>B$_2$N$_5$</td>
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<td>$\beta$La$_2$BN$_3$</td>
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<tr>
<td>LaBa$_x$(BN$_y$)$_z$</td>
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<td>$\beta$Sr$_2$BN$_3$</td>
<td>$\gamma$Sr$_2$BN$_3$</td>
</tr>
<tr>
<td>LaEr$_x$(BN$_y$)$_z$</td>
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<td>$\beta$Ba$_2$BN$_3$</td>
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<td>$\alpha$Ce$_2$(BN$_y$)$_z$N</td>
<td>$\alpha$Pr$_2$(BN$_y$)$_z$N</td>
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**Figure 1.2. Classification of crystal structure in the system Me-B-N**

Based on the chemical ability, he classified the metal element to form or not to form binary borides (MeB), binary nitrides (MeN) and/or ternary boron nitride compounds (MeBN). As a result, Figure 1.3 shows the classification of four different groups (A to D).
Metal element of groups A (Me=Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi and Po have inability to form binary borides, then only binary nitrides will form. In group B, the metals have the affinity higher to boron than to nitrogen. A stable two-phase equilibrium between metal borides and boron nitride formed at low temperature and low nitrogen partial pressure. In group C (Me=Ti, Zr, Hf, V, Ta, Sc, Y, Cr, Mo, W Mn and Re), no ternary Me-B-N compounds formed, except for Niobium. Group D (include Niobium) were dominated by the existence of Me-B-N ternary metal boron nitride compounds. The phase equilibria of this group has the large electropositive elements than others group.

Spear et. al established the ternary vanadium-boron-nitrogen (V-B-N) phase with reaction between VN and BN in the presence of nitrogen at a pressure of one atmosphere [26]. No ternary phase was observed in this system. However ternary solutions were concluded to be slight. Other researcher, Badzin et. al. have prepared V–B–N (vanadium boronitride) films, it was deposited by high frequency magnetron sputtering of a composite VB$_2$ as a target in a gaseous mixture of argon and nitrogen [27]. This study stated that using magnetron sputtered, the nitrogen has sufficient energy to replaceboron and to form vanadium nitride VN on the
target surface. Since the energy of diffusion activation $V-N$ (1.48 eV) is lower than for $B-V$ (2.22 eV). As the bond energy of $VB_2$ (~125 eV) lower than $VN$ (~166 eV), then he stated that apparently, a further process is the decomposition of $VB_2$.

Gorishny et. al and Min Zhou have produced Cr-B-N (chromium boronitride) using magnetron sputtering methods [28] [29]. The former used reactive-unbalanced magnetron sputtering, and the later used RF plasma assisted magnetron sputtering methods. Gorishny stated that XRD data of starting powder suggest the films made without nitrogen are polycrystalline and contain only the CrB$_2$ phase. With the addition of nitrogen, BN and Cr$_x$N bonded phases nucleate, which results in a rapid decrease in the grain size and the deposition of nanocrystalline or amorphous films. The later stated that XRD results indicate that a phase transformation from CrB$_2$ to h-BN and $\beta$-CrN occurs in the Cr–B–N films with increasing nitrogen partial pressures. However, Rogl confirmed that in group C no ternary Me-B-N compounds formed, except for Niobium.

Although CVD and PVD have been improved significantly over the years there are still remaining disadvantages such as, low deposition rates, lack of thickness, inferior films/substrate adhesion and difficulty in deposition of uniform layers on parts with complicated shapes. The processing routes also difficult to commercialize, due to economic barriers associated with the very high reaction temperatures and long processing times required. More over some of disadvantages of deposition methods can affect the coating properties, such as the formation of the brittle eta phase at the interface [30], also a high fraction of vacancies can exist on the carbon or nitrogen sites, which will also affect properties such as hardness [31]. There was also difficult to produce film coating in a fixed composition. That why most of commercial coatings show a gradation of the composition
from the interface to the coating surface [6]. Clearly there were some problems in coating application.

Moreover, K.L. Choy concluded the points of drawback of CVD and PVD as describe as below [3].

1. Because of using toxic, corrosive, flammable and explosive precursor gases, it could raised a chemical and safety hazards.
2. Because of different precursors have different vaporization rate, it is difficult to deposit multicomponent materials with well controlled stoichiometry, it will be more difficult when using multi-source precursors.
3. CVD variants which use more sophisticated reactor and/or vacuum system, tends to increase the cost of fabrication

The drawbacks of PVD are:

1. Depositing coatings limited onto a simple shaped component and difficulty in complex shape.
2. Depositing coatings limited onto small area and difficulty for large area deposition.
3. Because of PVD uses solid metal or oxide sources which are tedious and time consuming, it resulted in varying stoichiometry and difficulty to be manufactured and installed.

1.4. MECHANICAL MILLING

Another method used for synthesis of MeCN and MeBN is mechanical milling. In powder metallurgy and mineral processing industries, mechanical milling is a process which is usually
used for crushing rocks and blending powder. If used for mixing and or synthesis of intermetallic from its elemental powder, sometime it called Mechanical Alloying [32]. This method is also used for milling of compound in which induces changes in structure and/or microstructure, in this case it is called Mechanical Milling. Mechanical milling is normally a dry, high-energy ball milling that is used to synthesize a varying of materials. This technique has also been used widely for preparation of nanostructured materials. Beginning from the mid-1980s, a number of research have been conducted to synthesize a variety of stable and metastable phases including supersaturated solid solutions, crystalline and quasicrystalline, intermediate phases and amorphous alloys [33].

The mechanisms of mechanical milling are based on stresses induced to powder particles trapped between colliding balls-powder-ball in the milling equipment [34]. In this process the powders suffered a series of repeated flattening, cold welding, fracturing and re-welding. The force of the impact plastically deforms the powder leading to fracture, the new surfaces formed allow for welding to occur. Figure 1.4 schematically illustrates this process.

**Figure 1.4 Schematic diagram showing the impact process of balls (after Zhang)**
The mechanism can be classified into three groups: ductile-ductile, ductile-brittle and brittle-brittle systems. The mechanism for alloying in ductile-ductile involves the flattening and cold welding of fine powder into the surface, producing a lamella structure of the materials. Then after repeated flattening, fracturing and re-welding, a more homogeneous, equiaxed structure forms [33]. The mechanism for alloying in ductile-brittle systems is as follow, the first ductile phase will flattened and the brittle one will fragmented, then these fragmented brittle particles tend to become occluded by the ductile constituents and trapped in the weld interfaces between in ductile particles, producing in uniform distribution of brittle particles in a ductile phase. The mechanism for alloying in brittle-brittle, firstly during milling the brittle components get fragmented and their particle size continuously reduced until the limit of comminution when further reduction in size is not possible anymore.

Mechanical milling is carried out by varying devices such as ball, attritor, vibration, universal and planetary mills. Otherwise, a range of conventional and new milling and attriting devices have been developed for enhancing the mechanochemical reactions. They include; high energy ball milling, reactive ball milling, cryomilling, rod milling, mechanically activated annealing, double mechanical alloying, and mechanically activated self-propagating high-temperature synthesis (MASHS).

Mechanical milling is relatively low cost in comparison to other fabrication methods, even though the process still faces multiple obstacles. The main problem is the contamination that resulted from grinding media (the milling chamber and rod-end), the inside surface of the mill housing as well as any gases within the mill. However, the contamination can be minimised by milling in high purity inert gases, because inert gases do not react with the powder and also protecting process from the contaminant.
1.4.1 HIGH ENERGY BALL MILLING

High energy ball milling has been shown to be a promising method in producing powder. It was supported by high value of kinetic energy which can be resulted from the strong ball impacts when colliding balls process. High energy ball milling has become one of popular method to produce micropowders and, in some cases, nano structured materials of various materials, and nano composites. Supersaturated crystalline solid solutions, amorphous phases, nano crystalline solids and compounds through in situ solid–solid, gas–solid, and liquid–solid reactions have been produced by high-energy mechanical milling method. Moreover, nano crystalline carbides, nitrides, borides and silicides were also synthesized via high-energy mechanical milling method [35].

Kamarul Zaman discussed the kinetic energy of high energy ball milling, and stated that attritor type mill has kinetic energy ranged between 200 - 400 kW/ton, whilst a ring mill delivers 1690 kW/ton of energy [36]. This study described that high energy ball milling produced more deformation, more fracturing and cold welding and produces smaller particles compared to conventional one. Because it should have high impact velocities and high impact frequencies of the grinding media than conventional ball mill. Others advantage of HEBM is performed at room temperature, which could result in significant economically production cost. Baset on 1993 realised designing the high capacity high energy ball milling, which can process up above 250 g of powder with about 5 kg of balls [37]. Currently, high energy ball milling commercially produce oxide dispersion strengthened (ODS) in higher capacity, it process of 1 ton of powder in a 2 meter diameter mills which contain more than 1 million balls weighing approximately 10 tons [38]. The type of high energy ball milling methods
includes: planetary and vibratory mills (such as the Spex Mill), with an oscillation amplitude of about 20 mm or more, tumbling and attritor mills, attritor and vibratory (with oscillation amplitude up to about 5 mm) mills. Figure 1.5 demonstrates how impact energy in a ball mill is controlled by using magnetic grinding media in conjunction with magnets [39].

![Figure 1.5. Planetary ball mill with magnetic controlled](image)

**Figure 1.5. Planetary ball mill with magnetic controlled**

According to high energy ball milling, Calka et. al. stated the importance of milling conditions for the formation of vanadium carbides (VC and V₂C) [40]. When using high energy ball milling, the resulting carbides were found to be nanocrystalline. When using lower energy conditions gave a vanadium-carbon mixture, which crystallized into the carbides upon annealing.

Until now, high energy ball milling has been proved as efficiently way to produce ceramic and refractory material. Moreover, Patel stated that high-energy mechanical milling is an ideal processing method to form nano-sized particle, such as strong matrix Ti and brittle element such like Si [41]. This study argued that ball milling not only fracture powder particles into smaller particle, but also enable good mixing which result a homogeneously mixed composite.
Furthermore, transition metal carbonitrides, the principal component of cermets, can be obtained by high energy ball milling through a mechanically induced self-sustaining reaction (MSR) and subsequently sintered through a classical pressureless method [42]. In this study Cordoba, from titanium and carbon powders, synthesized TiC_{x}N_{1-x} phase, which was uniform in the whole sample. The sample with very low carbon composition has a d-spacing very similar to TiN (JCPDS Card: 38-1420) while sample with a higher carbon has a d-spacing more similar to TiC (JCPDS Card: 32-1383) [43].

Likewise, Xiang successfully obtained spherical Ti(C,N) particles with average size of below 100 nm via high-energy mechanical milling and subsequent carbothermal reduction–nitridation (CRN) reaction [35]. He stated that high-energy mechanical milling has lower reaction temperature and shorter reaction time compared with low energy one. Jianlin Li succeeded in synthesising of nanocomposite TiB_{2}/TiN/ TiC_{x}N_{1-x} using high energy ball milling and subsequent heat treatment [44]. The formation of TiC and TiN occurs within 10 h of milling. Diffusion of carbon and nitrogen atoms has faster than boron atoms in the titanium matrix. After 30 h of milling, the resulting powder mixtures were mainly composed of nanocrystalline Ti, TiN, TiC and TiB, then transformed into Ti(C_{x}N_{1-x}), TiN and TiB after subsequent heat treatment at 1300°C.

1.4.2 REACTIVE BALL MILLING

Reactive Ball Milling (RBM) is milling process in the presence of reactive solids, or liquids, or gases, which enabling a chemical reaction to take place. It is unique to other solid state processes as reactions which normally require elevated temperatures can be activated at room
temperature. Reactions can occur at room temperature during reactive milling since energy is accumulated as strain defects [45]. This method now regularly employed to synthesize metal oxides, nitrides, and carbides. Principally this method is mechanical alloying process which accompanied by a solid-state reaction. Known as the first inventor of Reactive Ball Milling was Jang in 1975 [33]. This method produce dispersed oxides and carbides in aluminum, it were conducted without any addition of control agent. Only adding a lamp-black or graphite during milling then finally the dispersoid of carbide will be achieved. Producing of titanium nitride also can be conducted by milling of titanium in a nitrogen atmosphere. Milling of tungsten with carbon (graphite) has produced tungsten carbide Otherwise several other compounds have also been produced in a similar way.

Furthermore, Secondi et. al in 1993 created nanoceramics and cermets by ball milling. And stated that using reactive ball milling under N₂ gas, both titanium nitride and TiN-noble metal nanocomposites can be obtained from pure Ti and Ti-noble metal alloys respectively [46]. Ogino et.al obtained TiN and (Ti₁₀.₅Al₀.₅)N with NaCl structure from milling of titanium and Ti₀.₅Al₀.₅ in nitrogen atmosphere. The metastable nitride (Ti₀.₅Al₀.₅)N decompose to stable TiN and AlN phases at 1373 K and above. This study also found composite powder consisted TiN and –iron phases by milling Ti₀.₅Fe₀.₅ powder mixture [47]. Chen Zhenhua et. al developed a set of solid–liquid reactive ball milling devices [48]. This study proved that reactive ball milling is an effective method to prepare nanometer-sized intermetallic Fe–Sn, Fe–Al, Fe–Pb and Ti–Al alloy system.

1.4.3 MECHANICAL ACTIVATION IN NITRIDING OF METAL-CARBIDES AND METAL-BORIDES

Mechanical milling considered to be a chemical reactor in which a wide range of chemical reactions can be easily mechanically initiated, without any heating to higher temperature.
Mechanical energy in this system leads to activate chemical reactions and structural changes. It starts from repeated cold welding and fracturing of powder particles result the formation of a large number of defects. Then because of fracture of the powder particles, a lot of micro-cracks are generated. It provides free surfaces leading to an increase in internal energy. Furthermore repeated fracturing and re-welding of the powder particles, causing the reaction area also increased, resulting in an increase in chemical reactivity during mechanical milling [49].

In the case of EDAMM method [50] the high intensity electric discharge creates a plasma channels with the localized high temperature areas as a result of Joule heating. The high temperatures in plasma channels accelerate diffusion and in consequence lead to fast reaction within short times. Localised-temperature of the powder particles changed dynamically the mechanical milling process. Even though very difficult to directly monitor the temperature during milling, it can be predicted through calculation or observation. Principally temperature is not dominating factor, but it influenced the diffusion rate. Since it is well known that the diffusion rate is a function of the diffusivity, called as D. In general, the diffusivity is a function of temperature, expressed in an Arrhenius type equation:

\[
D = D_0 \exp \left(-\frac{\Delta Q}{RT}\right) \tag{1-1}
\]

where \(D_0\) is a material constant, \(\Delta Q\) is the activation energy, \(R\) is the universal gas constant and \(T\) is the temperature. During diffusion, an interstitial atom is moved to an adjacent interstice. So, a high energy barrier must be overcome. Increasing of free energy is referred to as activation energy. Activation energy for diffusion is equal to the sum of the activation energy to form a vacancy and that to move the vacancy.

\[
\Delta Q = \Delta Q_f - \Delta Q_m \tag{1-2}
\]
where $\Delta Q_f$ is the activation energy for creating vacancies, and $\Delta Q_m$, is the activation energy for moving vacancies [49].

1.5 PLASMAS

When a gas is heated to a higher temperature and lose one or more of its electrons it means plasma was produced. This phenomenon creates positive and negative particles which are freely moving independently of each other within the plasma. They usually exist with dust particles. Generally dust particles attach plasma free electrons leading new plasma equilibrium and the occurrence of new phenomena [51]. Plasmas can be classified into two groups. Thermal or equilibrium plasmas, which are commonly called “hot” plasmas and non-thermal or non-equilibrium plasmas which are commonly called “cold” plasmas [52]. The dust particle in plasma usually form as solid bodies with sizes ranging from a few nm to cm, and then it called dusty (or complex) plasmas, it will be explained later in sub-chapter 1.5.1. In short, plasma is such highly active gas with ionized vibrational excited molecules. Plasma is generating dissociated species into the gaseous phase, which do not require activation energy.

1.5.1 DUSTY PLASMA

The term “dusty or complex plasmas” are plasma containing solid or liquid particles (dust) which are charged. The charges can be negative or positive, depending on the charging mechanisms operating in the plasmas [53]. Dusty plasma is ordinary plasma contaminated with a certain amount of condensed (solid or liquid) particulates (grains). There was currently
no exact definition of plasma in general, that why such a definition is quite sufficient, for instant it was also called as “complex, colloidal, or aerosol plasma” [54].

Solid particles can be formed from reactive gases like silane, methane, or acetylene or material sputtering [51]. Solid particles in the plasma system was usually of micrometric or nanometric dimensions. The particles can enter the plasma either by various methods, such as external injection, erosion of plasma-facing surfaces, heterogeneous surface reactions of plasma species or homogeneous reactions in the plasma volume, or a combination of them. The particles acquire a negative electrical charged, this will strongly influences their behaviour in the plasma volume. The particles will interact with one-another, exhibiting collective movement or forming crystalline structures. The population of dust moreover, changes the properties of the discharge, it was most noticeable where a significant drop in the electron density and a significant increase of the electron temperature [55]. The mechanism of particle growth starts with the formation of negative clusters, that although increasing in size, moreover, they never appear to have more than one excess electron. The mechanism start when negatively charged clusters likely transfer the electron to a positive ion (such as Ar+), it means it lose an electron, then it becoming neutral particles in the process. Furthermore, the growth of the cluster is terminated, as only negative ions engage in growth reactions. Finally when the clusters reach a certain critical size, then the attachment of negative ions becomes more likely than the growth of the original chain of the cluster. Furthermore, accumulating the greater quantities can be reached by electric charge [55].

The gases that are usually used in plasma processing are nitrogen, argon, hydrogen and helium. The common type primary gas is nitrogen, it is known as the cheapest of the gases. It can be applied only nitrogen or combine with others gases, such as NH₃ for instant with
hydrogen. Argon known as the easiest to form plasma and is completely inert, also generally used with a secondary gas to increase the energy. Hydrogen usually used as an additive to other plasma gases, hydrogen also exhibits high energy levels. The other gas is Helium, when using for the plasma energy, it gives a high level of controlling [56]. Figure 1.6 shows the energy content of the gas related to temperature of plasma.

![Energy Content Graph](image)

**Figure 1.6** shows the energy content of the gas related to temperature of plasma.

Nucleation of all phases within the system is always possible in dusty plasma. Synthesizing in this method can reduce the nucleation energy for formation of new phases to nearly zero. Figure 1.7 below shows the steps how the dusty plasma method works, the first step creation of electrons (and ions) through ionisation or dissociation of gases, followed by surface interactions under high energy surface bombardment and finally, clustering and formation of dust with different composition than starting particles.
In deposition methods, it was known Plasma Nitriding, also referred to as ion nitriding, is a diffusion process that improves the wear resistance and fatigue properties of the product being nitried. The process was developed in the 1920's as an alternative to the gas nitriding process. The plasma process in this case is a thermal process performed in a vacuum environment. Plasma nitriding, also known as *ion nitriding*, *plasma ion nitriding* or *glow-discharge nitriding*, is an industrial surface hardening treatment for metallic materials.

El Hossary conducted the experiment on depositing carbonitride on the steel using different radio frequency plasma power [57]. This experiment conclude that the variations in the carbonitriding rate as a function of the plasma processing power for ASS treated for 7 min are shown in Figure 1.8. It can be seen that the carbonitriding rate increases as the plasma power increases up to 520 W. However, with a further increase in the plasma power the rate gradually decreases.
Kazuhiro has investigated plasma nitriding behavior of low carbon alloy steel [58]. This study described that XRD analysis of the diffusion layer at the depth of 100 mm showed the peak broadening and the peak shift to the low angle side as shown in Fig. 1.9, which showed α-Fe (110) peaks comparing before and after nitriding. On the contrary, for plain carbon steel no change was observed.

**Figure 1.8 The rate of carbonitriding as a function of plasma processing power**
In mechanical milling, the reactivity of the nitriding media is due to high localized-temperature but also the gas plasma ionized state. In this technique intense electric fields are used to generate ionized molecules of the gas around the powder to be nitried. The gas used in mechanical milling in plasma nitriding is usually pure nitrogen. In this case, the powder as a dust particle, passing through the nitrogen atmosphere, the particle then physically and
chemically absorb the active nitrogen atoms, which are in the plasma space. After the nitrogen rich particle dissolved into the powder, the physically absorbed nitrogen atoms would diffused into the metal matrix in nitriding temperature. In this case it was proved gradually increasing the nitrogen content as increasing milling duration and definitely further increasing localized-temperature of powder.

1.5.3 SPUTTERING METHODS

Sputtering or it was called as “ion bombardment” is physical ejection of particle from the solid. It only happens when the kinetic energy of the incoming particles is much higher than conventional thermal energies ($\gg 1$ eV). The sputtering method can improve the nitriding rate if the material to be treated has strong tendency to form oxide with residual oxygen in the reactor [59]. However, the disadvantage of sputtering has been reported that particle contaminates grown in the gas phase for several kinds of sputtering targets and plasma sources.

Dai Hong conducted the experiment using magnetron sputtering to synthesis of Ti(CN) in 2 different ways, there are both sputtered homogeneous and gradient Ti(C, N) coatings [5]. The result have the face centered cubic (fcc) structure and dense columnar structures with most of grains extending from the interface to the surface. The homogeneous Ti(C, N) coating exhibits higher nanohardness than that of the gradient Ti(C, N). Moreover, the homogeneous Ti(C, N) coated inserts have better wear resistance than gradient Ti(C, N) coated inserts in continuous turning. However it was obtained result that the gradient Ti(C, N) coated inserts showed the better properties in interrupted cutting.
1.6 ELECTRICAL DISCHARGE ASSISTED MECHANICAL MILLING

Electrical Discharge Assisted Mechanical Milling (EDAMM) is a novel approach using high voltage, low current, electrical discharge in association with rod-end mechanical milling. Within the EDAMM mill, the electrical discharges lead to a molecular breakdown of the controlled atmosphere, followed by the formation of monatomic gases. Furthermore, the aim of the arc discharge is also to locally heat up powders which are subsequently subjected to the plasma treatment. Principally this method combines mechanical milling and an electrical discharge, which enhances chemical reactions in a plasma environment. This is a promising process that produces an advanced material, it was proved successfully to minimise processing times from long hours to a few mere minutes [60]. This method is a new and promising technique for the processing of materials and minerals, the synthesis of fine precursor powder products and for the investigation of novel reaction paths [50].

Even though the mechanisms for spark milling are complex and not fully understood, so far it proved resulted a great achievement in material synthesis. Variation in milling parameters has been shown to influence the phase formation, and it is precisely this method has been shown to form fine particulates and agglomerates in very short milling times[61].

**Figure 1.10 The schematic of EDAMM device (after Calka)**
During EDAMM milling, the vibration leads small gaps between the stainless steel rod and the chamber wall and resulted in an electric discharge (Figure 1.10). Electric discharge induces high chemical reactivity in between the powder particles that are suspended between electrodes (the rod-end and the chamber). The mechanism of chemical reactions between powder particles surfaces induced by electric discharge is complex and poorly understood.

However, the most important factors that contribute to enhanced reactivity are the formation of a plasma environment between the powder particles, formation and acceleration of ions, and bombardment (implantation, sputtering and deep penetration) of ions onto the powder particle surfaces. The powder surfaces have experienced extremes localized temperature via joule heating, furthermore the arc is conducted through the powder [62]. This process causes the formation of channels on the particles surface (Figure 1.11).

\[ \text{Figure 1.11 Illustration of Extreme Localised Temperature on Powder Surfaces (Needham)} \]

Furthermore heat may occur along these channels to induce localised melting, vaporisation and thermal stresses also facilitate rapid fracturing. Moreover it can be resulted increasing the total surface area of the reactants, and therefore also an increasing in the rate of diffusion.
processes. Diffusion obviously was enhanced by locally Joule heating that results from the electric discharges mentioned above. In addition, the powder particles are constantly being mixed and fractured by the impact of the vibrating electrode.

1.6.1 MILLING PARAMETER IN METAL NITRIDING

The most influence parameter particularly in nitriding process by deposition methods, were temperature of substrate, gas pressure and concentration [18]. However, in EDAMM, there was the mechanical impact involved, the amount of energy are one of important parameter, it depend on arrangement of vibration amplitude, power supply mode and average gaps between electrodes. Beside those gas composition and concentration, milling temperature, current intensity, pulse duration, gas flow, gas pressure, also influenced the final result. Previous work, in the application of EDAMM, already observed the effect of vibration amplitude and milling duration to evaluate their role in product composition and morphology. Then in this study, focus investigation was on effect the amount of energy by applying AC or DC mode, and varying of vibration amplitude or gap between electrodes. That mentioned aspect categorizing of the level energy. It is well known that mechanical intensity of the milling action depends on the energy of the collisions. The charge is characterized by the amplitude, or the gap between rod-end electrodes, may be this was similar with BPR (ball and powder ratio) in conventional ball milling. The value of amplitude or gaps of electrode may be approximately proportional to the rate of specific energy input.
ilmenite and carbon. Basically, during the milling procedure, high temperature activation of the chemical reaction from ilmenite to TiC+ Fe₃C is carried out in situ as a result of the electric discharges. The electric discharges replace the traditional annealing treatments that are typically used during carbo-thermal reduction. Using this method on synthesizing hard composite material does not require the removal of excess reactants, or the removal of unwanted product, it is because the reaction is fully complete. The composite product is exclusively composed of TiC and Fe₃C [65].

Previously EDAMM also effectively applied on nitriding process. Titanium powder was converted into titanium nitride powder after short periods of discharge milling. In contrast, under the same milling conditions without a discharge, it means no plasma in it, no TiN was detected after 30 min milling. The nitrogen uptake rate was found to be extremely rapid for both low and high energy discharge milling, however, higher final nitrogen content was obtained when milling using the higher energy input [60].

1.7 NITRIDING OF METALS – THERMODYNAMICAL CONSIDERATIONS

Some previous researchers have been discussed about thermodynamic consideration of nitriding process whether conducted by deposition method or conventional ball milling. However investigation of this matter never been done in EDAMM system, this become important since the complexity of process between mechanical alloying assisted electric discharge combined with ion bombardment in plasma environment it proved powerful to fasten the chemical reaction and higher dissolved nitrogen. Based on thermodynamic reactions, the stability of each element also can be predicted, and the mechanism of nitrogen dissolving will be known.
1.7.1 METAL-CARBON- NITROGEN (ME-C-N) REACTIONS

Firstly, it may be start with production of nitrogen atoms in plasma environment. This confirmed by Czerwiec, that electron impact dissociation of molecular nitrogen will produce nitrogen atoms at low pressure and high plasma densities [59]. Likewise, in this study, EDAMM applied at the low pressure (>1 atm) and high plasma densities. So it will follow the reaction below:

\[ e + N_2 \rightarrow e + 2N \]  \hspace{1cm} (1-3)

\[ e + N_2 \rightarrow 2e + N + N^+ \]  \hspace{1cm} (1-4)

\[ e + N_2^+ \rightarrow 2N \]  \hspace{1cm} (1-5)

However at low pressure the most dominant was reaction number (1-3). Even though sometime following electron-ion recombination reaction during nitriding process (1-5) is also a possible source of N atoms.

In the process of nitriding there are nitrogen sub-ions \( N^- \), \( N^{2-} \), \( N^+ \), and \( N^{2+} \). The existence of ions with different valence in gas and liquid media has been proved in many works [66]. However some researcher stated that neutral nitrogen ion more suitable.

The prediction of thermodynamic reaction of nitriding Metal-Carbide (then called as Me-C), as followed:

\[ e + N_2 \rightarrow e + 2N \]  \hspace{1cm} (1-3)

\[ (\text{MeC}) + N \rightarrow \text{MeC}(N) \]  \hspace{1cm} (1-6)
1.7.2 METAL- BORON-NITROGEN (ME-B-N) REACTIONS

The prediction of thermodynamic reaction of Metal-Boron-Nitrogen as follow, based on Metal Boron generally in the form of MeB$_2$ (the composition in ratio 10:20):

\[ e + N_2 \rightarrow e + 2N \]  \hspace{1cm} (1-3)

\[ (\text{MeB}_2) + N \rightarrow \text{MeB}_2\,(\text{N}) \]  \hspace{1cm} (1-7)

1.7.3 STRUCTURE, PROPERTIES AND APPLICATIONS

ZrC, TiC and TaC exhibit the same FCC structure (their space group is $Fm\bar{3}m$), after milling and nitriding for different times, it was shown that nitrogen atom will interstice or even substitute in the matrix of solvent Me-C. As a result solid solution formed in two ways based on position in the solvent or parent matrix, whether interstitial solid solution or substitutional solid solution.

Interstitial solid solution formed when B atom is so small compared to the atom A, furthermore B can easily enter the interstices of the lattice A. In this step increasing of unit cell volume was always accompanied. Then the single lattice parameter $a$ must increase, if A is cubic. When A is not cubic, then one lattice parameter will increase and the others decrease [67]. Furthermore Cullity describe the density of an interstitial solid solution will follow density equation below:
\[
\rho = \frac{1.66042 \Sigma A}{V'}
\] ................................. (1-8)

Where, \[ \Sigma A = n_s A_s + n_i A_i \] .................................(1-9)

\( n_s \) and \( n_i \) are number of solvent and interstitial atoms per-unit cell, and \( A_s \) and \( A_i \) are atomic weight of solvent and interstitial atoms, respectively.

Random substitutional solid solution some time is directly proportional to the atomic percent solute present. It is well known as Vegard’s Law, but it is not obeyed strictly by metallic solid solution. When \( n \) refers to the number of atom per-cell and \( A \) to the atomic weight, Cullity determine the density of substitutional solid solution as equation (1-8) with \( \Sigma A \) factor being given by :

\[
\Sigma A = n_{\text{solvent}} A_{\text{solvent}} + n_{\text{solute}} A_{\text{solute}}
\] ................................. (1-10)

Finally, solid solution known as interstitial or substitutional may be decided by determining whether the x-ray density calculated according to equation (1-8) agrees with measured density.

Relating determination of solid solution type, Cordoba stated that synthesizing between TiC and TiN which have fcc structure (NaCl type), with nitriding process for 20 min by ball milling, will produce a complete quasi-binary Ti(C, N) solid solution [42]. Moreover as a result TiC(N) formed with the atoms of carbon and nitrogen occupying all the octahedral interstitial sites. Because the contribution of N atoms to the valence electron structure of the ceramic is similar to the role of C atoms. Therefore they act interstitial interchange in metal
matrix. Figure 1.12 shows the schematic crystal structure of TiC(N) solid solution, where C also represents C and N, respectively.

**Figure 1.12 shows the schematic crystal structure of TiC(N)**

The crystal structure should be in the same form for TaC(N), ZrC(N), and HfC(N) which was obtained in the same nitriding process, because they also have the same FCC structure (NaCl type) with space group $Fm\bar{3}m$. These refractory carbonitrides especially Group IV transition metals (Ti, Zr and Hf) have the great possibilities to form solid solution MeC(N) or even the new phases metal carbonitride, which generally known as MeC$_x$N$_y$.

The ternary Me-C-N or Me-B-N have a great properties such as high melting point, high hardness, corrosion resistance, wear/abrasion resistance [13, 68], this suitable for high speed machining used as the hard phase in sintered cermet alloys and for protective layers on hard metals. These materials are also can applied as cutting tools in machining operations where high temperatures are developed due to the intensive tool-workpiece interaction [69].
2. EXPERIMENTAL METHODS

2.1. INTRODUCTION

This chapter provides information about equipment devices, experimental procedures, including, the starting powders and its best matched references which are applied to this study.

2.2. THE MILLING DEVICES

The Spark Milling or EDAMM (Electric Discharge Assisted Mechanical Milling) method is an advanced and novel attrition milling method that was designed and developed by A/Prof Andrzei Calka [50]. It has been designed to generate a milling process that combines repeated impact of a hardened and curved stainless steel rod end, and vibration of stainless steel hemispherical container under electrical conditions of pulsed arc discharge. A photographs of an EDAMM milling cell during operation is shown in Figure 2.1 below:

FIGURE 2.1 ELECTRIC DISCHARGE CELL DURING MILLING (AFTER CALKA)
The hemispherical stainless steel milling chamber has a diameter approximately 20 mm, which is where the powder is placed. The base is connected to the negative terminal of the power supply. Then the stainless steel rod which suspended loosely above the milling chamber is connected via a flexible copper cable to the external positive electrode and power supply. The top and base reactor were locked and tightened by long-bolt which also functioned as pillar reinforcement. This facilitates viewing of the spark and plasma during milling as well as providing insulation to prevent short circuiting and avoid the leakage.

Through the Perspex tube, gases flow directly into the base of the milling unit. The outlet holes were built on milling chamber walls in different position, it was in opposite inlet holes. The setup of the gas facilities allows a choice of either a measurable rate of gas flow during milling or no flowing gas alternatively, it means sealing off the inlet and keeping a static atmosphere throughout milling. Gases used in this project were nitrogen, argon and helium. The gas flow is maintained at a rate of 1.5 cc/min.

The vibration plate facilitated vibratory motion of the stainless steel rod in a vertical direction. This motion forces the rod to smash powder particle during milling, it produce mechanical milling action and mixing the powder. The vibration amplitude can be controlled by varying voltage input to the sieve shaker. This is done in a controlled way using a calibration based on average steel rod oscillation distance measured from a mark on the rod using a digital camera for different voltage inputs. The higher the voltage of the sieve shaker the higher vibration amplitude.

During milling pulsed arc discharges are initiated at the tip of the stainless steel rod and travel through the milling atmosphere and powders before terminating at the stainless steel base in
the centre of the hemispherical milling cell. These arcs are produced by connecting the milling unit to a sophisticated external power supply, custom built specifically for discharge milling. Radio frequency DC or AC impulses can be generated by the unit, with voltages in the kV range and currents in the mA range.

2.3. SPARK MILL SETTINGS

This work was principally aimed at investigating the synthesis of different Me-C-N and Me-B-N compounds and at determining the optimum processing parameters where synthesis was successful. The general setting variables for EDAMM processing are shown below:

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>Nitrogen, Argon and Helium</td>
</tr>
<tr>
<td>Gas flow</td>
<td>1.5 cc/min</td>
</tr>
<tr>
<td>Milling time</td>
<td>0.5 – 20 minutes</td>
</tr>
<tr>
<td>Gap between electrodes</td>
<td>2 – 12 mm</td>
</tr>
<tr>
<td>Target current</td>
<td>2.8 – 3.3 Å</td>
</tr>
<tr>
<td>Voltage</td>
<td>2 - 5 kV</td>
</tr>
<tr>
<td>Milling mode</td>
<td>AC and DC</td>
</tr>
</tbody>
</table>

2.4. SPARK MILLING PROCEDURE

- Cleaning the chamber.

The reactor was cleaned prior to each experiment to avoid contamination of samples from previously processed powders. Because after milling, there were commonly remaining loose material or any material that had got partially welded to the milling surface, it need a carefully cleaning, included scrubbing of the internal chamber walls and rod end surface. The cleaning
steps applied using abrasive paper and using abrasive grinding tool. Then follow by rinsing with ethanol then drying. This improved the milling cell back to fresh, and clean stainless steel surface also avoid the contaminant.

- **Measuring the powder**

To ensure an equal volume of powder was used for all experiments, the powder was measured out using the measuring device shown in Figure 2.2 (a). Then powder sample was placed in the hemispherical milling chamber as shown in Figure 2.2 (b).

![Figure 2.2 EDAMM apparatus (a) Powder measurement (b) Milling chamber.](image)

- **Setting the reactor**

EDAMM reactor settings for vibration amplitude, peak current intensity, impulse duration and time milling duration were selected as required. The milling chamber was kept at atmospheric pressure and gas flow was selected at a rate of 1.5 cc/min. Milling durations of 0.5, 1, 2, 5, 10 and 15 minutes were used for all experiments. After the completion of milling, the chamber was opened and the milled powders collected using a clean spatula. These samples were stored in sealed glass tubes until taken up for XRD, CHN and SEM analysis.
2.5. STARTING POWDER AND REFERENCE SAMPLE

All of the starting powder obtained from Sigma-Aldrich, its properties and matched-JCPDF reference are given in table below:

### TABLE 2.2. STARTING POWDER AND ITS BEST MATCHED-PDF REFERENCE

<table>
<thead>
<tr>
<th>Element</th>
<th>Aldrich Prod. code</th>
<th>Particle size (μm)</th>
<th>Purity</th>
<th>JCPDF No</th>
<th>Molecular weight</th>
<th>Volume</th>
<th>Space group</th>
<th>Lattice</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Carbide/ Me-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(IV)C</td>
<td>307807</td>
<td>&lt;44</td>
<td>98%</td>
<td>32-1383</td>
<td>59.91</td>
<td>81.04</td>
<td>Fm3m</td>
<td>4.327</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr(IV)C</td>
<td>336351</td>
<td>5</td>
<td>99%</td>
<td>19-1487</td>
<td>103.23</td>
<td>103.69</td>
<td>Fm3m</td>
<td>4.698</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HiC</td>
<td>594636</td>
<td>&lt;1.25</td>
<td></td>
<td>06-0510</td>
<td>190.50</td>
<td>99.90</td>
<td>Fm3m</td>
<td>4.64</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BCa</td>
<td>378100</td>
<td>&lt;74</td>
<td>98%</td>
<td>06-0555</td>
<td>55.25</td>
<td>328.98</td>
<td>Fm3m</td>
<td>4.698</td>
<td>-</td>
<td>-</td>
<td>12.07</td>
</tr>
<tr>
<td>TaC</td>
<td>280801</td>
<td>5</td>
<td>99%</td>
<td>02-1023</td>
<td>192.96</td>
<td>87.88</td>
<td>Fm3m</td>
<td>4.446</td>
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<tr>
<td>MoC</td>
<td>399531</td>
<td>&lt;44</td>
<td>99.5%</td>
<td>11-0680</td>
<td>203.89</td>
<td>37.04</td>
<td>P63mme</td>
<td>3.006</td>
<td>4</td>
<td>7.33</td>
<td></td>
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<tr>
<td>W(IV)C</td>
<td>241881</td>
<td>10</td>
<td>99%</td>
<td>05-0728</td>
<td>195.86</td>
<td>20.83</td>
<td>hexa</td>
<td>2.91</td>
<td>-</td>
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<tr>
<td>Cr₃C₂</td>
<td>402680</td>
<td>&lt;44</td>
<td>99.9%</td>
<td>03-0935</td>
<td>180.01</td>
<td>178.45</td>
<td>Pnam</td>
<td>-</td>
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<tr>
<td>SiC</td>
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<td>&lt;37</td>
<td>97.5%</td>
<td>29-1131</td>
<td>40.10</td>
<td>123.33</td>
<td>P63mc</td>
<td>3.073</td>
<td>-</td>
<td>15.08</td>
<td></td>
</tr>
<tr>
<td>Metal Boride Me-B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrB₂</td>
<td>336343</td>
<td>5</td>
<td>95%</td>
<td>06-0610</td>
<td>112.84</td>
<td>30.70</td>
<td>P6/mmm</td>
<td>3.169</td>
<td>3.53</td>
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<td>TiB₂</td>
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<td>&lt;10</td>
<td>-</td>
<td>07-0275</td>
<td>69.52</td>
<td>25.63</td>
<td>P6/mmm</td>
<td>3.028</td>
<td>3.228</td>
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<tr>
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<td>709204</td>
<td>38-1398</td>
<td></td>
<td>200.11</td>
<td>29.73</td>
<td>26.79</td>
<td>P6/mmm</td>
<td>3.142</td>
<td>3.47</td>
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<td>TaB₂</td>
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<td>08-0115</td>
<td></td>
<td>202.57</td>
<td>26.79</td>
<td>26.79</td>
<td>P6/mmm</td>
<td>3.078</td>
<td>3.265</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoB</td>
<td>709182</td>
<td>&lt;44</td>
<td>99.5%</td>
<td>06-0636</td>
<td>106.75</td>
<td>163.92</td>
<td>I4/amd</td>
<td>3.108</td>
<td>16.97</td>
<td>-</td>
<td>-</td>
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<tr>
<td>VB₂</td>
<td>336319</td>
<td>08-0118</td>
<td></td>
<td>72.56</td>
<td>23.82</td>
<td>23.82</td>
<td>P6/mmm</td>
<td>2.998</td>
<td>3.060</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WB</td>
<td>10497</td>
<td>97%</td>
<td>06-0635</td>
<td>194.66</td>
<td>164.28</td>
<td>164.28</td>
<td>I41/amd</td>
<td>3.115</td>
<td>16.93</td>
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</tbody>
</table>

2.6. CHARACTERIZATION METHODS

The starting and milled powders were characterized by varying methods. XRD used for analyzing the structural changes, and phase transformation. SEM used for analyzing of
morphology, and composition of powder, the particle size and its distribution also can be calculated using imageJ software support. CHN combustion analysis used for measured the chemical elemental powder composition.

2.6.1. X-RAY DIFFRACTION (XRD)

The fresh as well as milled Me-C-N and Me-B-N powder were characterized with an x-ray diffractometer (Philips PW 1730). Phase identification was carried out using the International Centre for Diffraction Data (ICDD 2000) Powder Diffraction Files (PDF) which was provided by TRACES™ software, it developed by Diffraction Technology Ltd (Canberra, Australia).

Sample preparation of XRD is done as per the standard practice. Sample packing was carried out by filling the powder on a quartz substrate slit. Precautions were taken to have a tight powder packing on the glass slit and no manual contamination with the powder specimens. The X-ray diffraction measurements were carried out with the help of a Goniometer using Cu Kα radiation (Kα= 1.54056 Å) at an accelerating voltage of 40 kV and a current of 25 mA. In this test the sample was in stationary condition, only the arms of the X-ray tube was rotating in the opposite direction up to 100° of 2θ during the test. The samples were scanned in the range from 10 to 100 ° of 2θ with a scan rate of 2 °/min. The analysis was carried out to find out phase changes. This study presents the X-ray diffraction graph with the note of milling time (in the left side) and sample name identification (in the right side).
2.6.2. SCANNING ELECTRON MICROSCOPY (SEM)

The starting as well as milled powder of Me-C-N and Me-B-N were characterized using SEM in two ways, polished and unpolished. In this study, we used two different SEM machine for analysing of morphology and powder form. They are Low Vacuum SEM (JSM 6490 LV SEM) and Field Emission Gun-SEM (JSM 7001F SEM) or we called FEGSEM.

All samples, polished and unpolished, must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder. The polished sample was addressed for analysis of cross-sectioned powder structure, it included observe the grain boundary, and also measure the compound composition by EDS. Polished sample was prepared by hot mounting process at 4200 kPA, and 150 ºC for 8 minutes. Rough grinding performed by MD-Allegro then followed by diamond polishing performed by MD/DP-Plan (Struers) 6 μm, this was for pre-polishing of hard materials. For intermediate polishing steps, it used MD/DP –Dur 3 μm, and finally finishing steps used 0.25 μm. All polishing process used DP suspension A and the green lubricant. Unpolished sample was addressed for observe powder morphology in particle form. It prepared by dispersing the powder on the sticky-tape on the sample holder.

This study used two types of signals produced by SEM, secondary electron imaging (SEI) and back scattered electrons (BSE). The signal of secondary electron detectors resulted from interactions of the electron beam with atoms at or near the surface of the sample. Secondary electron imaging or SEI, in the most common, can produce very high-resolution images of a sample surface. A wide range of magnifications is possible, especially using the FEGSEM, from about 10 times to more than 500,000 times. Moreover Back-scattered electrons (BSE)
has the signal resulted from beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM, its signal is strongly related to the atomic number (Z) of the specimen. BSE images can perform the different color of different element, it also provide information about the distribution of elements in the sample. It equipped with varying analyzing methods, there were X-ray map for identify elemental composition in a one region, spot analysis to identify the composition just in a small spot, or line analysis to identify the composition in a horizontal or vertical line area.

2.6.3. CARBON HYDROGEN NITROGEN TEST (CHN)

The starting as well as milled powder of Me-C-N and Me-B-N were characterized using CHN combustion test to find weight percent of elemental Carbon, Hydrogen and Nitrogen. Nitrogen contents of as milled powders were estimated using a Carlo Erba 1106 combustion elemental analyser.

2.6.4. MICROHARDNESS

Microhardness was measured with a microhardness tester equipped with a tetragonal diamond pyramid Vickers indenter. The schematic of the pyramid geometry performed below [70].
About 6 measurements on every type of materials were performed in the experiment. Each indent was made focused to the individual particle which was mounted using hard polyfast. Indentations were carried out on the particles with the maximal particle size. The loads was kept constant at 50 gram in all experiment with prolong 5 sec period indentation.
3. SYNTHESESIZING OF GROUP IV– (TITANIUM, ZIRCONIUM AND HAFNIUM) CARBONITRIDE AND BORONITRIDE

3.1. INTRODUCTION

In this chapter, results of nitriding process by EDAMM applied to Group IV transition metals of the periodic table (Titanium, Zirconium and Hafnium) are reported. Phase changes, nitrogen content and powder morphology were examined using XRD, SEM and CHN analysis.

3.2. TITANIUM CARBONITRIDE (TIC\textsubscript{x}N\textsubscript{y})

Titanium Carbonitride (TiCN) obtained by EDAMM processing in nitrogen of Titanium Carbide (Ti(IV)C) powder, as supplied by Aldrich- (production code- 307807 with 98% purity325 mesh and density 4.930 g/mL at 25 °C).

3.2.1. X-RAY DIFFRACTION

A typical XRD pattern for the as-received titanium carbide starting powder is shown in Figure 3.1. The peaks in this pattern give good matches with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) card no 32-1383. This PDF card from the mineral known as Khamrabaevite, Titanium Carbide, has the following details: space group-Fm\textit{3}m, molecular weight- 59.91 g/mole, volume-81.04, cubic structure with lattice a = 4.3274. The EDAMM was performed in DC and AC mode, over milling times of: 0.5, 1, 2, 5 and 10 minutes, with the gap between electrodes of: 6, 7.5 and 12 mm.
Results of EDAMM in DC mode are shown in Figure 3.2. It shows XRD pattern of the starting powder and milling products from 0.5 to 10 minutes, with 7.5 mm gap between electrodes. Detailed analysis of the peaks positions shows shifting to higher angles with increasing milling time. It is believed that this was caused by the increase of dissolved nitrogen content. Shifting of the peak towards positions expected for TiN phases are clearly seen on the Figure 3.3 for the enlarged (220) peaks. It can be also noticed that peaks broaden with increasing nitrogen content, and are significantly broader comparing to the ones of the starting powder. It means that the structure is gaining more nanocrystalline characteristics. There is no XRD evidence of other intermediate phases.
Figure 3.2 XRD pattern of powder milled for different milling time under DC discharges in 7.5 mm gaps between electrodes.

Figure 3.3 The effect of milling time on evolution of (200) TiC peak.
Figure 3.3 presents a single peak in the range of 35-37 degrees 2-theta. From up, it shows the starting powder with a peak perfectly matching ICDD-PDF number 32-1383 contributing to TiC. After being milled for 0.5, 1 and 2 minutes, the peak shifted slightly to the right side which indicates start of phase evolution to the expected TiC_{x}N_{y} intermetallic phases caused by increasing level of dissolved nitrogen. It also revealed presence of unreacted starting powder. Other peaks shifted to the left side are predicted to contribute to TiC(N)solid solution. Furthermore, in the range of 5 to 10 min milling time, peak shift to the new intermetallic phase position occurred, matching ICDD-PDF number 42-1489 and contributing to TiC_{0.7}N_{0.3}. It is thought that under DC system, further milling resulted in shifting, broadening and decreasing the intensity of TiC peaks. Presumably, during 5-10 min milling time range, higher impact of mechanical milling in DC mode produced sharp lighting plasma in arching mode, allowing transfer high localized temperature and faster diffusion of nitrogen in the matrix. Thus, the carbon atoms (r=0,16nm) were substituted by nitrogen ones (r=0,13nm), what was proved by the decrease of lattice parameter from 4.327 to 4.297 nm[71]. Furthermore JE Sundgren stated that substitutional site in the 0-1 range x fraction, cause nitrogen substitution in the face-centred cubic structure. To sum up, usage of DC mode allowed to obtain the new phase of TiC_{x}N_{y}. During DC mode the temperature is much higher in AC mode so obtaining this phase is unlikely to be caused only by vacancies and faster diffusion.

Figure 3.4 show the XRD patterns for TiC milled in AC mode with 6 mm gaps between electrodes. It shows that after milling times respectively from 0.5 to 10 minutes there are significant peak shifts towards lower angles, what can be also seen on the Figure 3.5 for the enlarged (111) peaks.
FIGURE 3.4. XRD PATTERN OF MILLED POWDER FOR DIFFERENT MILLING TIME IN AC DISCHARGES WITH 6 MM GAPS BETWEEN ELECTRODES

FIGURE 3.5 THE EFFECT OF MILLING TIME ON EVOLUTION OF (111) XRD PEAK
Figure 3.4 shows the XRD pattern of powders after milling for 0.5 and 1 minute. The peak is shifted to lower angle, to positions expected for TiC(N) particle (PDF 06-0614). ICDD-PDF card indicates that the lattice parameter increases from 4.3274 to 4.3825 nm with the cell volume increase from 8.04 nm$^3$ to 8.10 nm$^3$. It is believed, the nitrogen molecules with small ionic radius 0.13 nm diffused into interstitial sites of TiC phase, causing the expansion of unit cell and lattice parameter [67]. After being milled for 2 minutes, the peak intensity became broader, meaning smaller cell volume and lattice parameter than product milled for 0.5 and 1 minute. Analysis of further milling times (5 and 10 min) shows slight shift of the peaks towards smaller angles what contributes to higher rate of nitrogen dissolution. It means also that nitrogen content is higher than the one of the starting powder what can be named as interstitial supersaturated solid solution [72].

AC mode transferred lower energy than DC mode. Combined with the lower gap between electrodes of 6 mm, resulted in lower impact, that can transfer the nitrogen only into interstitial site. The longest milling times (5, 10 min) resulted in more nitrogen dissolution and more sufficient high temperature localization. That led to replacement of the carbon in its site and TiC(N) formation in two possible positions: as interstitial and substitutional atom in the carbon site.

Figure 3.6 show the XRD results obtained from TiC EDAMM processed in AC mode using 12 mm average gap between electrodes. The peak shift is clearly seen on Figure 3.7
**Figure 3.6** XRD pattern of milled TiC powder for different milling times under AC mode with 12 mm gaps between electrodes

**Figure 3.7** The effect of milling time on evolution of (111) XRD peak
In case of 12 mm gap between electrodes (Figure 3.6), all peaks shifted slightly to the left, what can be clearly seen on examination of the Figure 3.7 for the enlarged (111) peak. The product of milling in AC mode with 12 mm gaps resulted in higher amount of nitrogen content, as present in Figure 3.1. It is believed that during nitriding for 0.5 to 10 min, nitrogen atom interstices in TiC matrix. Further milling caused more nitrogen dissolution and eventually formed supersaturated interstitial solid solution TiC(N) after being milled for 10 min. At this point however, milling energy was too low to convert all of the substrate what was proved by the presence of unreacted powder. Thermal vibrations were not effective enough to lead to the diffusion, therefore nitrogen could settle just in interstitial position. In case of using the AC mode, plasma was transformed into the cloudy mode, what was the reason of energy being transferred to the powder not in the amount high enough to overcome the activation energy required for the creation of new intermetallic phase Ti$_x$C$_y$N$_z$. The summary of related PDF card is showed below.

<table>
<thead>
<tr>
<th>Card No</th>
<th>PDF name</th>
<th>Space group</th>
<th>Molecular weight (g/mole)</th>
<th>Volume(Å$^3$)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06-0614</td>
<td>Titanium Carbide - TiC</td>
<td>Fm3m</td>
<td>59.91</td>
<td>81.10</td>
<td>4.3285</td>
</tr>
<tr>
<td>32-1383</td>
<td>Titanium Carbide - TiC</td>
<td>Fm3m</td>
<td>59.91</td>
<td>81.04</td>
<td>4.3274</td>
</tr>
<tr>
<td>42-1489</td>
<td>Titanium Carbide Nitride - TiC$<em>{0.3}$N$</em>{0.7}$</td>
<td>Fm3m</td>
<td>60.51</td>
<td>79.35</td>
<td>4.297</td>
</tr>
</tbody>
</table>

Figure 3.8 shows a detailed comparison of the TiC (220) peaks shift for samples EDAMM processed under AC and DC mode in for 10 minutes with 12 mm gap between electrodes. Fig 3.8(a) shows a symmetrical single (220) peak at 2-theta at 60.46 degrees corresponding to cubic structure of the TiC starting powder. Fig. 3.8(b) shows the outcome of EDAMM in AC mode. In this case we can see two overlapping peaks. The strong one is at the same position
as the peak for the starting powder peak (2-theta 60.46 degrees) and is overlapping a lower intensity peak at estimated 2-theta of 60.26 degrees.

**FIGURE 3.8 XRD PATTERNS OF TiC (220) PEAK PROFILE AND POSITION EVOLUTION IN A) STARTING POWDER AND AFTER MILLING FOR 10 MIN WITH GAP BETWEEN ELECTRODES 12 MM IN B) AC AND C) DC MODE.**
The observed shift of the Fm3m peaks towards lower angles is consistent with the formation of a phase of the same structure with larger lattice parameter than that of the TiC starting powder. This set of new peaks is seen on the left side of each peak within the 2-theta angle range between 20-100 degrees. Considering the fact that CHN analysis revealed that the sample contains 2.01 wt% of nitrogen, we may deduce that the new peaks are consistent with the formation of interstitial solid solution TiC(N) type phase. The effect of EDAMM processing in DC mode is different, as seen in Figure 3.8(c). This sample was found to contain 1.8 wt% of nitrogen and in this case the centre of the (220) peak appears at a higher angle (2-theta 60.73 degrees) and the peak itself shows asymmetry indicative of a broadening towards higher angle. From PDF data we know that cubic Ti$_x$C$_y$N$_z$ phase (PDF 01-076-2484) has its (220) peak at 2-theta 61.793 degree. So it appears that the peak shift towards higher angle in the samples processed in DC mode is associated with formation of Ti$_x$C$_y$N$_z$ type phases. The broadening towards higher angles could be attributed to the overlapping of a large number of single peaks coming from small fractions of Ti$_x$C$_y$N$_z$ phase with different a values.

Figure 3.9 shows the XRD pattern of TiC being milled for 10 minutes in DC mode with different gaps between electrodes. The aim of this experiment was to investigate the influence of the average distance between electrodes on the process for vibration amplitudes of 2, 4, 7.5 and 12 mm. The XRD pattern obtained from TiC EDAMM processed at 2 and 4 mm electrodes gaps doesn’t show any noticeable peak shifts what can be also seen on figure 3.10 with enlarged (111) peak. However the peak is broadened and its intensity is lower. The XRD pattern for TiC milled with 7.5 mm electrode gap shows that the peak has shifted to the expected Ti$_x$C$_y$N$_z$ phase position. Interestingly, when using 12 mm gap between electrodes, the XRD pattern shows broadened and shifted peak, comparing to the peak of 7.5 mm gaps between electrodes. It indicates that higher gap results in higher kinetic energy which is
produced by localized, higher temperature. Then presumably acted as sintered, it proved by increasing the peak intensity and shifting to the left.

This can be also by assumed that the larger gap between the electrodes the bigger velocities by can have the nitrogen ions. In other words, bigger gaps mean higher kinetic energy that can produce higher impact of the ion. This leads to producing higher localized temperature to diffuse nitrogen deeper into powders. This conditions also resulted in higher nitrogen content than with smaller electrodes gaps. Higher nitrogen content is also proved on Figure 3.12 which shows results obtained when used a bigger gap between electrodes.

![Figure 3.9 XRD Pattern of TiC Milled Powder for Different Gap Between Electrodes Using DC Mode](image-url)
Synthesizing and nitriding process of TiC in nitrogen atmosphere by EDAMM has the enthalpies of formation for the particular products as followed [43]:

- $\text{TiC} + N \rightarrow \text{TiC}(N), \quad \Delta H = \text{around} \ -184 \text{ kJ/mol (TiC)}$
- $\text{TiC} + N \rightarrow \text{TiC}_x\text{N}_{1-x}, \quad \Delta H = \text{from} \ -184 \text{ kJ/mol (TiC)} \text{ to} \ -338 \text{ kJ/mol (TiN)}$

The energy output for $\text{TiC}_x\text{N}_{1-x}$ synthesis is higher than the one for formation of TiC(N). Thus it can be assumed that interstitial solid solution can be obtained at lower energy process while the new intermetallic phases at higher energy ones.
3.2.2. CHN ANALYSIS

Figure 3.11 shows results of the CHN combustion of TiC powder milled for 0.5, 1, 2, 5 at 10 min in DC and AC system. In this figure nitrogen intake by TiC in AC mode is represented by red solid line while the blue dashed line represents nitrogen intake by TiC in DC mode.

![Graph showing nitrogen content in TiC with milling time](image)[Figure 3.11 Nitrogen content in TiC in different milling time in AC and DC system]

It can be noticed that nitrogen content in both systems increases most rapidly within the first two minutes of milling. Nitrogen intake in TiC in AC mode was higher, around 0.1 wt% higher in each step than in DC system. Extrapolation of both curves to significantly longer times above 10 min might suggest that additional nitrogen intake would be very small or constant. Thus, the maximum solubility of nitrogen in TiC was at 10 min time milling. This step led to creation of supersaturational solution with no further extension of solid solubility. Suryanarayana stated about this as solid solubility limit, as shown in Figure 3.12 [33].
Figure 3.12 Schematic diagram showing the variation of solid solubility with time during mechanical alloying of metal powder mixture

Figure 3.13 show the results of the CHN analysis of TiCN products milled for 10 min with a gap between electrodes varying from 2 to 12 mm, in AC and DC system. In this figure nitrogen uptake by TiC in AC mode is represented by the red solid line and the blue-dash line represents nitrogen uptake by TiC in DC mode. Graph shows that the amount of absorbed nitrogen increases with increased gap between the electrodes. Extrapolation of both curves indicates marginally smaller increases in nitrogen uptake for gaps bigger than 12 mm.

Figure 3.13 Nitrogen content in TiC in different gap between electrodes in AC and DC system
From figure 3.11 and 3.13 it can be concluded that the uptake of nitrogen in TiCN was found to be proportional to longer milling times and average gap between electrodes.

3.2.3. SEM ANALYSIS

Figures 3.14 show SEM secondary electron images of TiC\textsubscript{x}N\textsubscript{y} obtained from a) the titanium carbide starting powders and products formed after discharge milling in DC mode for b) 2 min and c) 10 min with the nitrogen flow. The average gap during milling was 7.5 mm. The SEM micrograph of the TiC starting powder shows a small fraction of large particles with average diameter size of 20-70 μm and a large fraction of small particles below 10 μm. After 2 minutes of discharge milling (Figure 3.14, b) large particles became smaller and the small particles agglomerated. During the first two minutes of milling relatively large powder particles underwent fragmentation, what was presumably caused by ion surface bombardment and mechanical action of the plunger, while the very small powder particles are believed to agglomerate under the influence of strong electrostatic forces. Figure 3.14 (c) shows powder morphology after 10 minutes of milling. SEM micrograph shows only large agglomerated particles with the average size up to 100 micrometers. All small particles have disappeared.

Figures 3.15 show SEM secondary electron images of TiC(N) obtained from products formed after discharge milling in AC mode for a) 2 min, b) 5 min and c) 10 min respectively under flowing nitrogen. The average gap during milling was 6.0 mm. Figures 3.15 shows SEM secondary electron images of TiC(N) obtained from products formed after discharge milling in AC mode under flowing nitrogen for a) 2 min, b) 5 min and c) 10 min respectively. The average gap during milling was 12 mm.
**Figure 3.14** SEM secondary electron images of TiC$_3$N$_2$ obtained from a) starting powder b) products formed after discharge milling in DC mode under flowing nitrogen for 2 min, and c) 10 min. The average gap during milling is 7.5 mm.
FIGURE 3. 15 SEM secondary electron images of TiC(N) obtained after EDAMM in AC mode for a) 2 min, b) 5 min and c) 10 min. The average gap during milling is 6.0 mm.
FIGURE 3. 16 SEM secondary electron images of TiC(N) obtained after EDAMM in AC mode for a) 2 min, b) 5 min and c) 10 min. The average gap during milling is 12 mm.
SEM images of TiC(N) after being milled for 2 min in AC mode under flowing nitrogen with 6 mm average gap between electrodes (Figures 3.15a) with particle size around 5-10 μm, showed no agglomeration. After milling for 5 min (Figures 3.15.b) part of particles became smaller and some of them created large agglomerates up to 25 μm. It is believed that agglomerates were formed under the influence of strong electrostatic forces. 10 minutes milling time (c) resulted in fragmentation of large powder particles what could have been caused by ion surface bombardment and mechanical action of the plunger. Small powder particles are believed to agglomerate under the influence of strong electrostatic forces, cold welding or arc discharge. The last one led to high localized-temperature area and resulted in melting of some of particle’s surface. Agglomerating of particles up to 25 μm can be also observed.

Figures 3.16 show SEM secondary electron images of TiC(N) obtained from products formed after discharge milling in AC mode under flowing nitrogen with 12 mm gap. First, 2 min milling time (a) shows that particles are almost of the same size- around 5-10 μm- with a small fraction of agglomerated particles. After 5 minute milling time (b), the increase of agglomerated particles of 10-30 μm size can be seen. Some of them are believed to be created through fragmentation of bigger ones. Further milling for 10 min (c) resulted in agglomeration of bigger particles up to 50 μm. It is believed that the average gap between electrodes during milling of 12 mm resulted in higher impact of the plunger what enhanced electrostatic forces.

As a result it can be concluded that DC mode tends to produce agglomerated particles, because of higher energy transfer from plasma into the bulk powder in sharp arching mode. It may lead to increase of higher localized-temperature that cause melting even it small fraction
and agglomeration. This was proved by the fact that after 10 minutes milling time no finer particles remained.

The AC mode gave better results, especially when using 6 mm average gap during milling. It resulted in relatively homogeneous finer particles, with small fraction of agglomerates.

3.2.4. MICROHARDNESS

Figure 3.17 shows the indented Ti$_x$C$_y$N$_z$ after 10 min milled by EDAMM, of the average hardness value of 2239 HV. This result is comparable with that obtained by Akihiro et al, of the value of TiCN at around 20 GPa (2039 HV) with 10 N load applied [80]. Thus, it can be concluded that hardness of the material increases with the increase of nitrogen dissolved in its structure.

![Indentation of Ti$_x$C$_y$N$_z$ after milled for 10 min.]

**Figure 3.17 Indentation of Ti$_x$C$_y$N$_z$ after milled for 10 min.**
3.3. ZIRCONIUM CARBONITRIDE (ZRCₓNᵧ)

Zirconium Carbonitride (ZrₓCᵧNₓ) was synthesized by EDAMM from Zirconium Carbide (Zr(IV)C) by Aldrich; the production code- 336351, 99% purity and the average particle size of 5 μm.

3.3.1. X-RAY DIFFRACTION

A typical XRD pattern for titanium carbide starting powder is shown on Figure 3.18. The peak in this pattern gives a match with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) card no 19-1487. This PDF card of Zirconium Carbide gives following information about the molecule: space group- Fm3m, molecular weight- 103.23 g/mole, volume- 103.69 nm³ and a cubic structure with lattice a = 4.698.

![XRD pattern of Zirconium Carbide starting powder](image)

**Figure 3.18 XRD pattern of Zirconium Carbide starting powder (PDF no 19-1487)**
Figure 3.19 shows the ZrC powder after being milled by EDAMM for 1, 2, 5 and 10 minutes, using DC mode and 7.5 mm gap between electrodes. Peaks were observed to shift to slightly higher angles with increasing EDAMM processing times, consistent with the presence of increases in dissolved nitrogen and formation of a structure closer to ZrN.

![XRD Pattern of ZrC Milled Powder for Different Milling Time Using DC Discharges](image)

**FIGURE 3.19 XRD PATTERN OF ZrC MILLED POWDER FOR DIFFERENT MILLING TIME USING DC DISCHARGES**

On Figure 3.20 for the enlarged (220) peak, its shift can be noticed. It indicates formation of new phase Zr\(_x\)C\(_y\) with different composition and physical properties. New position of the peak matches with ICDD-PDF cards (Table 3.2) as follows:
Table 3.2. ICDD-PDF that matched with ZrC milled powder

<table>
<thead>
<tr>
<th>ID Sample</th>
<th>Milling time (min)</th>
<th>Card No</th>
<th>PDF name</th>
<th>Space group</th>
<th>Molecular weight(g/mole)</th>
<th>Volume(nm$^3$)</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrC62</td>
<td>1</td>
<td>19-1487</td>
<td>Zirconium Carbide</td>
<td>Fm3m</td>
<td>103.23</td>
<td>103.69</td>
<td>4.698</td>
</tr>
<tr>
<td>ZrC63</td>
<td>2</td>
<td>19-1487</td>
<td>Zirconium Carbide</td>
<td>Fm3m</td>
<td>103.23</td>
<td>103.69</td>
<td>4.698</td>
</tr>
<tr>
<td>ZrC64</td>
<td>5</td>
<td>11-0110</td>
<td>Zirconium Carbide</td>
<td>Fm3m</td>
<td>103.23</td>
<td>103.56</td>
<td>4.696</td>
</tr>
<tr>
<td>ZrC65</td>
<td>10</td>
<td>73-0477</td>
<td>Zirconium Carbide</td>
<td>Fm3m</td>
<td>103.23</td>
<td>101.78</td>
<td>4.669</td>
</tr>
</tbody>
</table>

Figure 3.20 The effect of milling time on evolution of (200) XRD peak

Table 3.2 shows that volume per-unit cell ratio decreases. If it concerns volume parameter the change is from 103.69 nm$^3$ for ZrC milled for 1 min to 101.78 nm$^3$ for ZrC milled for 10 min. Lattice parameter decreased from 4.698 nm to 4.669 nm. It can indicates that newly formed phase has a smaller carbon content because of nitrogen substitution. This substitution led to creation of a new phase-Zr$_x$C$_y$N$_z$. Because the weight fraction of nitrogen as a second component is too small, or even be undetectable, possibly intermetallic phase of Zr$_x$C$_y$N$_z$ has formed.
XRD pattern of milled ZrC sample with increasing gap between electrodes (0, 1.2, 2, 6.5mm) are shown on Figure 3.21. Peak centres were observed to shift to slightly higher angles with increasing gap, consistent with increasing substitution of nitrogen for carbon in the Fm3m lattice, and the formation of ZrCₙNₙ phase.

![XRD Pattern](image)

**FIGURE 3.21** XRD PATTERN OF ZrC MILLED POWDER FOR 10 MINUTES WITH DIFFERENT GAPS BETWEEN ELECTRODES USING DC MODE

Taking under consideration one enlarged (200) peak, its shift towards higher angles can be noticed (Figure 3.22). It indicates that the lattice parameter has decreased, which is attributed to nitrogen-carbon substitution or formation of new ZrₙCₙNₙ phase.

Inspection of Fig 3.22 reveals detectible peak shifting for gaps greater than 1.2 mm. Mechanical milling with a 1.2 mm gap between electrodes (Figure 3.22) does not result in detectible peak shifting, possibly because the energy associated with this gap is relatively low.
Despite this, combustion analysis revealed incorporation of 0.25 wt% N into the structure in this sample. With 2 mm and 6.5 mm gaps, peaks shifted to right side, presumably associated with the formation of $\text{Zr}_x\text{C}_y\text{N}_z$.

**Figure 3.22 The effect of gap distance between electrodes on evolution of (200) XRD peak**

Figure 3.23 presents XRD patterns obtained from ZrC powder EDAMM processed with 6 mm gap between electrodes, in AC mode. During milling for times ranging from 0.5 until 10 min, peaks which can be associated with the formation of ZrC, $\text{Zr}_x\text{C}_y\text{N}_z$ and/or ZrC(N) are observed. The shift of the peaks to the left is consistent with an increase of lattice parameter consistent with the formation of ZrC(N) solid solution phase. In this case nitrogen is located in the ZrC lattice in interstitial sites and so forms an interstitial-solid solution. Figure 3.24 shows the peak shifting occurred on enlarged (200) single peak for examination. After 10 minutes two newly created heights on the peak can be seen which contributes to solid solution ZrC(N) (left one) while the right peak may correspond to formation of $\text{Zr}_x\text{C}_y\text{N}_z$ phase.
Figure 3.23 XRD pattern of ZrC milled powder for different milling time with 6 mm gap between electrodes, using AC mode.

Figure 3.24 The effect of milling time on evolution of (200) ZrC peak.
Figure 3.25 present XRD pattern of ZrC powder milled with EDAMM with 12 mm gap between electrodes. Not fully shifted peak (Figure 3.26) indicates that there is some unreacted powder left. XRD pattern also means increasing of the lattice parameter and cell volume, it can be due to nitrogen precipitation in ZrC lattice, or the formation of ZrC(N) interstitial solid solution phase what was a result of milling for longer than 2 minutes. Interestingly, after being milled for 10 min, two overlapping peaks can be seen. Left peak represents a solid solution ZrC(N), right peak may correspond to formation of Zr$_x$C$_y$N$_z$ phase. It is believed that using higher energy level together with wider gap between electrodes (12 mm) and longer milling time can lead to higher level of dissolved nitrogen. This effect can be seen due to chemical analysis in Figure 3.27.

![XRD Pattern](image.png)

**Figure 3.25** XRD pattern of ZrC milled powder for different milling time with 12 mm average gap during milling, in AC mode.
Figure 3.26 The effect of milling time on evolution of (200) XRD peak

Figure 3.27 shows (220) peak evolution in ZrC sample. Figure 3.27 (a) shows symmetrical (220) peak at 2-theta 55.3 degrees. Sample after EDAMM in AC mode (1.62 wt% of nitrogen) shows two peaks; on the left side (2-theta 55.3) at the same position as starting powder and new peak on the right side at 2-theta 55.44 degrees, as shown on figure 3.27 (b). Left peak represents a fraction of untransformed ZrC powder while the right peak may correspond to formation of ZrxCyNz phase. Formation of a fraction of solid solution ZrC(N) can’t not be excluded. Figure 3.27 (c) shows outcome of EDAMM in DC mode (1.16wt% of nitrogen). The peak’s shape is very similar to TiC peak after EDAMM in DC. Like in the previous case, it is believed that the peak shape and shift towards higher angle is associated with formation of ZrxCyNz type of phases.
**Figure 3.** 27 XRD patterns of ZrC (220) peak profile and position evolution in a) starting powder and as a result of milling for 10 min with gap between electrodes of 12 mm in b) AC and c) DC mode.
3.3.2. CHN ANALYSIS

Figure 3.28 shows the results of the CHN combustion of ZrC powder milled for 0.5, 1, 2.5 and 10 min in DC and AC system. In this figure nitrogen intake by ZrC in AC mode is represented by red solid line while the blue dashed line represents nitrogen intake by TiC in DC mode.

It can be noticed that nitrogen content in both system increases rapidly up to 5 minutes of milling, then the intake is smaller. Dissolution of nitrogen in ZrC in AC mode is bigger than in DC mode at least by 0.5 wt% when milling time exceeded 2 minutes. Extrapolation of both curves to significantly longer times above 10 min might suggest that additional nitrogen uptake would be very small or will be constant. This means that solid solution might have reached its supersaturation level what is proved by Suryanarayana-the saturation limit (Figure 3.12)

![Figure 3.28 Nitrogen content in ZrC in different milling time in AC and DC system](image-url)
Figure 3.29 shows the results of CHN analysis of ZrCN products, after milling starting powder for 10 min with the gap between electrodes varying from 2 to 12 mm in AC and DC system. In this figure nitrogen uptake by ZrC in AC mode is represented by the red solid line, while the blue dash line represents nitrogen uptake by ZrC in DC mode. The graph shows that the amount of absorbed nitrogen increases with increasing average gap between electrodes. In AC mode the rate of dissolved nitrogen is higher than in DC mode. Each step in AC mode has 0.5 wt% increasing diffused nitrogen, in DC mode it only happened in the first 0.5 min, after that point the increasing slightly at 0.3 wt% dissolved nitrogen in each step. Extrapolation of both curves to larger gap distances indicates marginally smaller increase of nitrogen uptake for gaps larger than 12 mm. It means that no further increase its solubility would occur. From Figure 3.28 and 3.29 it may be concluded that the degree of nitrogen would be proportional to longer milling times and gap between electrodes.

**Figure 3.29 Nitrogen in ZrC in different milling gap in AC and DC system**
3.3.3. SEM ANALYSIS

Figures 3.30 show SEM secondary electron images of ZrCN obtained from a) zirconium carbide starting powders, products formed after discharge milling in nitrogen for b) 2 min and c) 10 min. The average gap during milling is 7.5 mm in DC mode. SEM micrograph of ZrC starting powder shows a homogeneous small grain with average diameter of 1-10 μm (Figure 3.30, a). After 2 minutes of discharge milling majority of small particles agglomerated under the influence of strong electrostatic forces and cold-welding with their average size of 50 μm (Figure 3.31, b). Figure. 3.30, c) shows the powder morphology after 10 minutes of discharge milling. The SEM micrograph shows large agglomerated particles with the average size around 100 μm. It is well known that SEM observations are consistent with the fracturing of relatively large particles in the starting powder and the continuous agglomeration of the smaller particles.
Figure 3. SEM secondary electron images of ZrCN obtained from A) starting powder, product formed after discharge milling for B) 2 min and C) 10 min in DC mode under flowing nitrogen and the average gap during milling-7.5 MM.
Figure 3.1 SEM secondary electron images of ZrCN obtained from products formed after discharge milling for a) 2 min, b) 5 min and 10 min in AC mode under flowing nitrogen and the average gap during milling- 6 mm
Figure 3.32 SEM secondary electron images of ZrCN obtained from products formed after discharge milling for a) 2 min, b) 5 min and 10 min in AC mode under flowing nitrogen for and the average gap during milling- 12 mm
Figure 3.31 shows SEM secondary electron images of ZrCN obtained from products formed after discharge milling in AC mode under flowing nitrogen with the average 6 mm gap between electrodes during milling. After being milled for 2 min (Figure 3.31,a) large fraction of small particles (5 μm) and smaller fraction of large (10-30 μm) agglomerated particles can be noticed. After being milled for 5 min (Figure 3.31,b) part of particles became smaller but majority of them agglomerated. It is believed that agglomeration was increased under the influence of strong electrostatic forces. Further milling for 10 min caused decrease in agglomeration as well as in the size of particles. The size of components of the smaller fraction had diameter around 10 μm whereas large fraction was dominated by homogeneous fine particles.

Figure 3.32 shows SEM secondary electron images of ZrCN obtained from products formed after discharge milling in AC mode under flowing nitrogen and the average gap of 12 mm. After 2 min milling (Figure 3.32,a) it can be seen that particles can be divided into 2 groups: agglomerated particles up to 50 μm and small particles of 5-10 μm. Agglomeration is believed to be influenced by the large gap between electrodes (12mm) which is associated with high energy mechanical impact in collision between plunger and chamber. Interestingly, after being milled for 5 minutes (Figure 3.32,b) the amount of agglomerated particles decreased whereas finer particles of the size around 5-10 μm were sustained. This phenomenon may be caused a tipping of the balance between fracturing (smaller particles) and cold welding (larger particles). Further milling for 10 min (Figure 3.32,c) shows that particles have agglomerated again up to 50 μm size. Thus, it can be concluded that the average gap during milling at 12 mm resulted in higher energy impact of plunger and electrostatic forces what caused fracturing.
It can be also concluded that DC mode tends to produce agglomerated particles because of its high energy which is directly transferred into the bulk powder. This may lead to the increase of a higher localized-temperature that causes melting. In comparison to previous one, the AC mode gave improved results, especially with the usage of 6 mm average gap. It resulted in relatively homogeneous, fine particles without any agglomeration.

Figure 3.33 illustrates the fracturing phenomenon that occurred in ZrCN after 10 min milling in DC mode with 7.5 mm average gap between electrodes. Particles agglomerated and fractured at the same time as the effect of cold-welding. It is thought that fracturing and cold welding competitively influence the powder. Several colours can be seen within the particle’s surface what contributes to different chemical composition of these areas (Figure 3.34).

**Figure 3.33** ZrCN SEM secondary electron images of a particle after 10 min milling with 7.5 mm gap in DC system
Figure 3.34 shows EDS analysis of the particle’s surface produced through discharge milling. Thin, light grey grain boundary phase was found to be a phase rich in Zr, Fe, Ni and Cr. It appears that at least a fraction of the ZrC or ZrCN is reduced during milling to form Zr. Mill base or plunger fragments contain Fe, Ni and Cr, which are β-eutectoid stabilizing elements to Zr. It is worth noting that they react with Zr in the presence of the plasma and lower the melting point, forming a small amount of liquid which, in turn, this appears to play a role in the binding together of adjacent ZrCN grains.
3.4. HAFNIUM CARBO NITRIDE (HFC\textsubscript{x}N\textsubscript{y})

Hafnium Carbide, Hf(IV)C made by Sigma-Aldrich was used as a starting powder to synthesize HfC\textsubscript{x}N\textsubscript{y}. Production code is 594636 with the average size of particles less than 1.25 μm.

3.4.1. X-RAY DIFFRACTION

A typical XRD pattern for the as-received hafnium carbide starting powder is shown on Figure 3.35. The biggest peak in this pattern matched the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) card no 06-0510. PDF card characterizes Hafnium Carbide with space group- Fm3m, molecular weight is 190.50, volume-is 99.90 and a cubic structure with lattice a = 4.64. There is also small amount of contaminants eg. Hafnium oxide- HfO\textsubscript{2} which matched with PDF card no 43-1017.

![XRD pattern](image)

**Figure 3.35 XRD Pattern of Starting Powder (PDF no 06-0510)**

The XRD pattern of HfC powder milled in DC system in different milling times is shown on Figure 3.36. As received HfC was milled for 1, 2 and 5 minutes, with a 7.5 mm gap between
electrodes under flowing nitrogen. The final result of the longest milling times caused transformation of HfC into HfC$_x$N$_y$.

**Figure 3.36** XRD pattern of HfC milled powder in different milling times with the average gaps of 7.5 mm, in DC mode

**Figure 3.37** The effect of milling on evolution of (111) XRD peak
Figure 3.37 shows enlarged peak in the range of 32-35 degrees 2-theta. In comparison to the starting powder, 1 min milling time caused broadening and decrease in intensity of the above mentioned peak. At this point HfC$_x$N$_y$ starts to nucleate. 2 minute milling time shows further broadening of that peak as well as intensification of peaks around 34º, 39º, 57º and 68º. Those peaks correspond to the strongest XRD peak classified as HfC$_x$N$_y$. After 5 minutes of milling XRD pattern shows that peak corresponding to HfC disappeared in favour to HfC$_x$N$_y$ peaks. This stage is therefore optimum for eliminating the HfC phase and obtaining intermetallic HfC$_x$N$_y$ instead.

The XRD pattern of HfC powder milled in AC system in different milling times is shown on Figure 3.38. HfC underwent 1, 2, 5 and 10 minutes milling times, with 7.5 mm gap between electrodes under flowing nitrogen. During milling for 1, 2 and 5 min new HfC$_x$N$_y$ phase started to nucleate but its peak has lower intensity than the one of HfC phase. Nucleation continues until 10 minutes and peak corresponding to HfC$_x$N$_y$ intensifies. The powder was not fully transformed into ternary intermetallic HfC$_x$N$_y$ what is shown on the XRD pattern, showing presence of the peak corresponding to unreacted HfC.
**Figure 3.38** XRD pattern of HfC milled powder for different milling times with 7.5 mm average gap, in DC mode.

**Figure 3.** The effect of milling on evolution of (111) XRD peak.
Figure 3.39 shows enlargement of the 32-35 degrees 2-theta peak. With increasing milling time decrease in intensity of the main peak corresponding to HfC can be observed. Another, newly created peak around 34° indicates obtaining new phase of HfC$_x$N$_y$.

3.4.2. CHN ANALYSIS

Figure 3.40 shows results of the CHN combustion analyses of HfCN product after different milling times. In this figure nitrogen uptake by HfC is represented by the blue solid line while the red dash line represents weight percent of carbon. This graph shows that the amount of absorbed nitrogen increases proportionally to the milling time and gains the value of HfCN with 0.85 wt% N in the first 30 seconds up to 3.42 wt% N after being milled for 10 minutes. Simultaneously, the amount of carbon decreases with increasing milling time what was caused by nitrogen substitution of carbon in the matrix.

![Figure 3.40 Weight % of Nitrogen and Carbon in HfCN in Different Milling Times](image-url)
3.4.3. SEM ANALYSIS

Figure 3.41 shows SEM secondary electron images of a) HfCN starting powder, product particle after EDAMM milled for b) 0.5 min, c) 2 min, d) 5 min and e) 10 min, in DC mode using 7.5 mm average gaps. The SEM micrograph (Figure 3.4, a) of as-received powder shows a small fraction of fine grain with average diameter size up to 1 μm and large fraction of agglomerated particles up to 25 μm. After discharge milling for 0.5 min b) it is shown that agglomerated particles rapidly fractured, however after being milled for 2 min it shows (Figures 3.41, c) small particles agglomerated, it is believed to be caused by influence of strong electrostatic forces and cold-welding. Agglomerated particles had the diameter around 10-25 μm and finer particles up to 5 μm. Figure. 3.41 (c) presents powder after being milled for 5 min. It shows that fracturing is a dominant process which resulted in large fraction of small particles with the average size of 1-5 μm and more. It is also shown that some agglomerated particles were of the size of 25 μm. Further milling for 10 min (Figure 3.41, d) caused small particles to disappear what is believed to be caused by frequent collisions and impact of rod end on the powder and wall chamber that lead to agglomerate. At this point, the particle size range is 5-50 μm.
Figure 3.41 SEM secondary electron images of a) HfCN starting powder, b) particle after milling for 0.5 min, c) 2 min, d) 5 min and e) 10 min in DC mode with 7.5 mm of average gaps.

Figure 3.42 shows SEM secondary image of cross-section of HfC$_x$N$_y$ product obtained from a) after discharge milling in nitrogen for 1 min, b) 2 min, c) 5 min and d) after milling for 10 min respectively. The average gap during milling is 7.5 mm in DC mode. The SEM micrograph of the HfC$_x$N$_y$ after being milled for 1 min (Figure 3.42, a) shows finer grain with average diameter size up to 1 μm. After 2 min (Figure 3.42, b) of discharge milling small
particles agglomerated under the influence of strong electrostatic forces and cold-welding and reached a size of around 1-5 μm. Figure 3.42 (c) shows powder after 5 min milling. It shows large agglomerated particles with the average size around 5-10 μm and even more. It shows some porosity between agglomerated particles. Then after being milled for 10 min (Figure 3.42, d) porosity almost disappear. It is believed that frequent collision and impact of rod end with the powder and wall chamber resulted in dense powder. As a result dense, agglomerated particles were obtained.

**Figure 3.42** SEM secondary electron images of HfCxNy obtained from products formed by discharge milling for a) 1 min, b) 2 min, c) 5 min and d) 10 min in DC mode under flowing nitrogen, and the average gap during milling of 7.5 mm
Figure 3.43 High contrast SEM backscattered image of the HfCN after 10 min milling in DC mode, with 7.5 mm average gap

Figure 3.43 shows the EDS analysis of product after being milled for 10 min. The black region and dark grey were found to be the areas rich in nitrogen with nearly the same composition (91Hf3.5C4.8N and 92Hf4C4N). Light, grey grains have higher carbon content than other grains with the composition of 91Hf5C3.5N. Small fraction of Fe existed in the small white grain boundary phase, it was 89Hf4C2.9N3.5Fe. It is though that the existing Fe comes from mill base or plunger fragments. It can be noticed that the result of EDS was mostly confirmed by CHN results, and it is believed that HfC reached higher nitrogen intake than ZrC and TiC in the same type of processes.

Figure 3.44 present SEM secondary electron images of HfCN product particle after EDAMI milling for a) 1 min, b) 2 min, c) 5 min and d) 10 min, in AC mode, using 7.5 mm average gaps. SEM micrograph of (Figure 3.44, a) powder milled for 1 min shows a small fraction of finer grain with the average diameter size up to 1 μm and large fraction of agglomerated particles up to 50 μm. After 2 min of discharge milling (Figure 3.44, b) agglomerated
particles fractured. This process was occurring up to 5 min of milling time (Figure 3.44, c) what resulted in finer particles. It is believed that fracture was a dominant process, leading to creation of large fraction of small particles with the average size up to 5 μm and small fraction of larger particle up to 20 μm. After being milled for 10 min (Figure 3.44, d) small particles agglomerated under the influence of strong electrostatic forces and cold-welding. Their size was around 10-20 μm. Small particles didn’t disappear entirely and it is believed that frequent collision and impact of rod end to the powder and wall chamber led to agglomeration.

**Figure 3.44** SEM secondary electron images of a) HfCN particle after 1 min, c) 2 min, d) 5 min and e) 10 min milling time, in AC mode with 7.5 mm average gap

Figure 3.45 shows SEM secondary image of HfC₃Nₓ cross-section, obtained from discharge milling in nitrogen for a) 1 min, b) 2 min, c) 5 min and d) 10 min. The average gap during milling was 7.5 mm in AC mode. SEM micrograph of the HfC₃Nₓ after 1 min milling time (Figure 3.45, a) shows finer grain with the average diameter size up to 1 μm. After discharge milling for 2 min (Figure 3.45, b) small particles started to agglomerate under the influence of
strong electrostatic forces and cold-welding with the particle size around 1-3 μm. Figure 3.45(c) shows the powder after 5 min milling time. It shows the increase amount of agglomerated particles with weak bonding with the average size up to 5 μm and more. It also shows some porosity between agglomerated particles. After 10 min milling time (Figure 3.45, d) porosity almost disappeared what is believed to occur due to frequent collision and impact of rod end to the powder and wall chamber resulting in more dense, agglomerated powder. Despite this fact some of finer particles still remained. It was proved that AC mode transfers lower energy than DC mode, because the cloudy plasma doesn’t create localized high temperature spot what is minimizing the melted region that leads to agglomeration of the powder.

Figure 3.45 SEM secondary electron images of HfCxNy obtained by discharge milling for a) 1 min, b) 2 min, c) 5 min and d) 10 min in DC mode, under flowing nitrogen for with the average gap during milling of 7.5 mm
Figure 3.46 shows the EDS analysis of product being milled for 10 min, in AC mode. The dark grey area was found to be rich in carbon with the chemical composition of \(88\text{Hf}9\text{C}3.5\text{N}\) and \(90\text{Hf}6.5\text{C}3.5\text{N}\). Lighter, grey area has higher nitrogen content- \(81\text{Hf}10\text{C}9\text{N}\) and \(85\text{Hf}8.5\text{C}6.5\text{N}\). Presumably dark grey region corresponded to HfC and the light one is HfCN.

![Figure 3.46: High Contrast SEM Backscattered Image of the HfCN after 10 Min Milling Time in AC Mode, with 7.5 mm Gap](image)

3.4.4. MICROHARDNESS

Figure 3.47 shows the indentation of \(\text{Hf}_x\text{C}_y\text{N}_z\) after (a) 5 and (b) 10 min milling by EDAMM. Hardness values are 1808 and 2169, respectively. It is believed that \(\text{Hf}_x\text{C}_y\text{N}_z\) after being milled for 10 min has finer crystallite grain, higher nitrogen content and higher lattice strain what may cause increase in hardness. This fact was confirmed by Zhecheva *et. al* statement, that the microhardness increases with the increase of the time and temperature of nitriding [80].
3.5. ME-B-N SYSTEM OF GROUP IV

Me-B-N system was synthesized from starting powder of ZrB$_2$, TiB$_2$ and HfB$_2$ (Aldrich), the production code- 336343, 336289 and 709204 respectively. Synthesis was done by EDAMM using DC power supply, with 7.5 and 12 mm gaps between electrodes and in different milling times from 1 to 10 minutes.

3.5.1. X-RAY DIFFRACTION

A typical XRD pattern for the as-received zirconium boride, titanium boride and hafnium boride powder is shown in Figure 3.48, 3.49 and 3.50 respectively. Peaks in these patterns give a match with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) of ZrB$_2$, TiB$_2$ and HfB$_2$ number 06-0610, 07-0275 and 38-1398 respectively. Physical properties of these powders, such as space group, molecular weight, volume and atomic structure are presented in Table 3.2.
**Figure 3.48** XRD pattern of ZrB\(_2\) starting powder (PDF no 06-0610)

**Figure 3.49** XRD pattern of TiB\(_2\) starting powder (PDF no 07-0275)
Figure 3.50 XRD pattern of HfB$_2$ starting powder (PDF no 38-1398) with small amount of HfC contaminant (PDF no 06-0510)

Figure 3.51 shows the ZrB$_2$ powder after EDAMM milling for 1, 2, 5 and 10 minutes, with 7.5 mm gap between electrodes, in DC mode. Significant shift of the peak can be noticed for each of milling times. Peaks shift is clearly seen on the pattern with the enlarged (100) peaks (Figure 3.52). It can be noticed that peaks shifted to the left, indicating formation of interstitial solid solutions of ZrB$_2$(N). It is thought that shifting to lower angles indicates increase of lattice parameter; it can be caused by nitrogen interstice in the ZrB$_2$ matrix.
Figure 3.51 XRD pattern of ZrB$_2$ powder milled in DC mode with 7.5 mm gap between electrodes.

Figure 3.52 The effect of milling time on evolution of (100) XRD peak.
Figure 3.53 shows the ZrB$_2$ powder after EDAMM milling for 1, 2, 5 and 10 minutes with 12 mm gap between electrodes, in DC mode. It can be seen that peaks shifted to the right side what is clearly shown by their enlargement on Figure 3.54. Peaks shift on XRD pattern indicate decrease of lattice parameter and cell volume probably due to nitrogen substitute of carbon in carbon site. Presumably ZrB$_x$N$_y$ phase was obtained. After milling for 10 min, the peak presents others phases; ZrN (PDF card 02-0956) and BN (PDF 18-0251). It is believed that further milling time followed by the increase of more localized-temperature creates bigger amount of heat which induces decomposition of ZrB$_2$. Then nitrogen radicals diffuse and can create ZrN and BN phases. Process could be predicted by thermodynamical reaction shown below:

$$2 \text{ZrB}_2 + \text{N}_2 \rightarrow \text{ZrB}_x\text{N}_y + \text{ZrN} + \text{BN},$$

which was obtained during milling for 10 min.

**Figure 3.53 XRD pattern of ZrB$_2$ milled powder for different milling time in DC mode with 12 mm gap between electrodes**
Figure 3.54 The effect of milling time on evolution of (100) XRD peak

Figure 3.55 shows the TiB$_2$ powder after EDAMM milling for 1, 2, 5 and 10 minutes with 12 mm gap between electrodes, in DC mode. It shows, the peak shifts to the right side with increasing milling time, it is believed that it was caused by the increase of dissolved nitrogen content, the shifting peak towards positions expected for TiN phases. These peak shifts indicate formation of intermetallic TiB$_x$N$_y$. After milling for 10 min, there is XRD evidence of other intermediate phases, ZrN (PDF card 06-0642) and BN (PDF card 20-0773). The peak shifts are clearly seen on examination for the enlarged (100) peaks (Figure 3.56).
**Figure 3.55** XRD pattern of TiB milled powder for different milling time in DC system with 12 mm gap between electrodes.

**Figure 3.56** The effect of milling on evolution of (101) XRD peak.
Figure 3.57 shows the TiB₂ powder after EDAMM milling for 1, 2, 5 and 10 minutes with 7.5 mm gap between electrodes, in DC mode. It shows that with the increase of milling time, the peak shifts towards smaller angles what can be clearly seen for the enlarged (100) peak (Figure 3.58). This indicates formation of single phase interstitial solid solutions TiB₂(N).

**Figure 3.57** XRD pattern of TiB powder milled in DC system with 7.5 mm gap between electrodes
Figure 3.58 The effect of milling time on evolution of (101) XRD peak

Figure 3.59 shows the HfB$_2$ powder after EDAMM milling for 10 minutes, using DC power supply with 7.5 mm average gaps between electrodes. Figure 3.60 shows evolution of (100) XRD peak as the effect of milling for several milling times. It is shown, the peak corresponding to HfB$_2$ slightly shifted and drastically decreased in intensity. On the contrary, peak corresponding to HfC shifted towards higher angles what is believed to be caused by dissolved nitrogen content. It is thought that nitrogen reacted and dissolved easier in HfC than HfB$_2$. 
Figure 3.59 XRD pattern of HfB$_2$ (upper) and milled powder after 10 min milling time (lower) in DC system with 7.5 mm gap between electrodes.

Figure 3.60 The effect of milling time on evolution of (100) XRD peak.
3.5.2. CHN ANALYSIS

Figure 3.61 shows the results of the CHN combustion analyses of TiBN and ZrBN powders milled for 1, 2, 5, 10 min, with the average gap during milling of 7.5 and 12 mm. In this figure nitrogen uptake by TiB is represented by the black solid line for 12 mm gaps, while dashed line relates to 7.5 mm average gaps during milling. The red line represents nitrogen uptake by ZrB at 12 mm average gaps between electrodes while red dashed line relates to 7.5 mm average electrodes gaps. This graph shows that the amount of absorbed nitrogen increases with increasing milling time. It was found that TiB have higher level of absorbed nitrogen than ZrB. Furthermore, extrapolation of ZrBN curves to longer milling times would indicate marginally small increases in nitrogen uptake.

**Figure 3.61 Nitrogen content in Ti-B-N and Zr-B-N system in different milling time and gap between electrodes, in DC system**
3.5.3. SEM ANALYSIS

Figure 3.62 shows an SEM backscattered image of a polished cross-section of TiB$_2$(N) after 10 min milling with 7.5 mm average gaps during milling in DC mode. The grey regions are believed to comprise TiB$_2$(N) based product, which is separated by higher atomic number regions of Fe containing milling contamination product. The uniformity of colour of the grey regions is consistent with the premise that the TiB$_2$(N) comprises a homogeneous solid solution phase what was proved by the surface colour being homogeneously grey.

![Figure 3.62 SEM backscattered electron images of TiB$_2$(N) after 10 min milling time with 7.5 mm average gap between electrodes](image)

Figure 3.62 SEM backscattered electron images of TiB$_2$(N) after 10 min milling time with 7.5 mm average gap between electrodes

Figure 3.63 shows the cross-section of ZrB$_2$(N) after 10 min milling time with 7.5 mm average gaps, in DC mode. Shapes of grains are uneven and have irregular, probably incidental shapes. Considering the colour of the surface, in contrary to previous one, it indicates slightly different composition.
Figure 3.63 SEM backscattered electron images of ZrB$_2$(N) after 10 min milling time with 7.5 mm average gap between electrodes.

Figure 3.64 shows HfB$_2$(N) after 10 minutes of milling time. Particle’s structure looks like lamellar form, with the length up to 20 μm (a) in 600 and (b) in 3500 magnification.
Figure 3.64 SEM secondary electron images of HfB$_2$N after milling for 10 min in a) 600x, and b) 3500x magnification

Figure 3.65 shows HfB$_2$(N) in enlarged view specified by EDS analysis. It shows that between big, grey particle, there are small white regions. EDS revealed that it was 97 wt% Hf, and 3 wt% N. The darker grey regions were identified as 85 wt% Hf and 15 wt% B. It is also believed that the grey part is mostly HfB$_2$. 
Figure 3.65 EDS SPOT ANALYSIS AND SPECTRA OF Hf-B-N AFTER MILLING FOR 10 MIN IN DC MODE

Figure 3.66 shows SEM secondary electron images of HfBN starting powder and after 10 min milling time for cross-section particle form. The starting powder (up) has finer particle up to 1 μm and a small fraction of agglomerated particles between 5-10 μm. After being milled for 10 min (down) finer particles disappeared leaving only agglomerated ones with the size of up to 50 μm.
3.5.4. MICROHARDNESS

Figure 3.67 shows hardness indentation of Ti$_3$B$_2$N$_2$ after milling for 10 min. The average Vickers hardness obtained in the test was 2764. From those tests it is known that ternary intermetallic Ti$_3$B$_2$N$_2$ has higher hardness than binary TiN (14.5 GPa) and TiB$_2$ (18.5 GPa) as was also stated by Andrievsky [84].
Figure 3.68 and 3.69 show hardness indentation of $\text{Zr}_x\text{B}_y\text{N}_z$ and $\text{Hf}_x\text{B}_y\text{N}_z$ after milling for 10 min with the average Vickers hardness values obtained during tests- 2043 HV and 2039 HV, respectively.

**Figure 3.67** The hardness indentation of $\text{Tl}_x\text{B}_y\text{N}_z$ after milling for 10 min in DC mode.

**Figure 3.68** The hardness indentation of $\text{Zr}_x\text{B}_y\text{N}_z$ after milling for 10 min in DC mode.
3.6. DISCUSSION

In this chapter, nitriding process of Me-C-N (Me = ZrC, TiC and HfC) and Me-B-N (Me = ZrB₂, TiB₂ and HfB₂) during EDAMM was investigated. Conventionally, they are fabricated by various deposition methods, as described in Chapter 1.3. The aim of this work was to investigate possibilities of EDAMM method for Me-C-N and Me-B-N powders fabrication that could be subsequently sintered to dense, bulk, hard metals using spark plasma sintering or other methods of densification. In nitriding processes assisted by conventional plasma the nitrogen intake is limited to thin surface layer. During EDAMM processing, combination of powder mixed by plunger, powder fracturing and agglomeration is believed to result in new surfaces of nitrogen ions from the plasma. In consequence the powder becomes nitrogenised in the whole its volume.

Furthermore, it is found that the degree of nitrogenation is proportional to both milling times and average gap between electrodes. It is assumed that that larger gap between the electrodes allows the nitrogen ions to achieve higher velocities and so achieve higher energy of...
mechanical milling in general. Plasma surface interactions of arriving nitrogen radicals with associated surface deposition under high energy bombardment will likely lead to the saturation of particle surfaces with nitrogen ions and subsequent diffusion into the bulk of the powder particles. This should result in formation of a relatively uniform solid solution phase.

In the case of Me-C-N EDAMM processed in DC mode, the XRD peaks tend to shift to the right (to the higher angles), which means that the lattice parameter decreased and presumably nitrogen substitutes for carbon atoms. Intermetallic nitride MeC$_x$N$_{1-x}$ phase was successfully produced, with higher nitrogen intake. However, using AC mode, especially in TiC cases, the XRD results tends to shift to the left (to the lower angles). That means that the lattice parameter increased because of addition of nitrogen in the Me-C matrix. That indicates creating supersaturated interstitial solid solution of MeC(N) phase, produced with higher nitrogen intake. In contrary, in ZrC case, longer milling times present two or more overlapping peaks, which contributes to ZrC(N) solid solution and new ternary ZrC$_x$N$_y$ phase in the same time.

Presumably, formation of Me$_x$C$_y$N$_z$ intermetallic phase during milling was believed to occur via complex process which involves rapid particle’s fracturing due to combined effects of milling and electrical discharge, interaction of fine particles with hot nitrogen gas and free radicals generated by the electrical discharge, and thermally activated local diffusion of the nitrogen into the powder particles. In contrast, the interstitial mechanism of nitrogen incorporation is believed to occur without the need a higher energy, when nitrogen enters interstices in the Fm3m lattice. Furthermore, the energy efficiency for Me$_x$C$_y$N$_z$ synthesis is significantly higher than the one for formation of MeC(N) solid solution. It is concluded that lower energy is needed to obtain interstitial solid solution than the new intermetallic phase.
Formation of Me-B-N system was done with DC mode. This decision was based on previous researches in which it was stated that Me-B-N ternary system, known as compound, is relatively difficult to produce even when using high energy. Rogl stated that in group IV no ternary Me-B-N system can be formed except for niobium [25]. EDAMM successfully proved that Me-B-N system can be obtained in the form of intermetallic Me\textsubscript{x}B\textsubscript{y}N\textsubscript{z} phase when combining high energy level (DC mode) and heavy impact (12 mm of average gaps). In this study, XRD pattern tends to shift to the right (to the higher angle), indicating new MeB\textsubscript{x}N\textsubscript{y} phase, with higher nitrogen intake of around 0.8 wt% N for Ti\textsubscript{x}B\textsubscript{y}N\textsubscript{z} and 0.46 wt%N for Zr\textsubscript{x}B\textsubscript{y}N\textsubscript{z}.

When using 7.5 mm average gap during milling to produce Me-B-N, XRD pattern tends to shift to the left (lower angles) what leads to obtaining interstitial solid solution of MeB(N) phase. It can be concluded that using DC mode (which has as higher energy than AC mode) together with 7.5 mm average gap still doesn’t create sufficient energy to transform to the new ternary Me\textsubscript{x}B\textsubscript{y}N\textsubscript{z} phase. Thus, for this process higher energy and larger average gap between electrode is needed.

Comparing two compounds Me-C and Me-B it can be clearly stated that in the first one, nitrogen dissolves easier during EDAMM processing, as evidenced by the fact that for milled under the same parameters, nitrogen incorporation occurs with a lower gap than for Me-B systems. Furthermore, in the Me-C-N system, even though DC mode combined with lower gap, such as 2 mm, it resulted new phase Zr\textsubscript{x}B\textsubscript{y}N\textsubscript{z}, while using 7.5 mm average gaps between electrode resulted Ti\textsubscript{x}B\textsubscript{y}N\textsubscript{z}. 
Taking under consideration morphology of particles and their size, usage of DC mode led to obtaining smaller amount of fine particles that expected. This was caused by the fact that the system creates localised, high temperature in the form of sharp arch what tends melt certain parts of particles that finally leads to their agglomeration.

On the contrary, AC mode transfers plasma in a cloudy mode. Combination of this energy transfer and smaller average gaps during milling leads to particle’s fracturing rather than the presence of melted areas. Thus, AC mode requires lower energy to gain finer particles. Apart from above mentioned facts, AC mode also has its drawbacks. Lower energy used in this mode is not sufficient to obtain new ternary Me-C-N and Me-B-N phases what leaves unreacted products in the powder. In DC mode higher energy resulted in heavy impact and localized, high temperature what caused particle’s agglomeration and obtaining ternary system.

SEM observations of milled powder enabled observation of particle’s fracture as well as agglomerations of the smaller ones. Agglomeration was caused by higher energy that leads to high, localized temperature. Under electrons and ions stream thin, external particle’s surface was heated to temperatures high enough to allow their melting. These thin, melted regions under the additional influence of electrostatic forces led to particle’s agglomeration what could be seen in the SEM micrograph especially after milling in DC mode.

EDAMM milling process causes decrease in crystallite size. In the EDAMM chamber, powder particles are undergo localized, fast heating and fast quenching factors due to the impulse mode of the electrical discharge. Such extreme conditions, involving quenching from high temperatures, are believed to be responsible for crystallite size reductions, as evidenced
by the XRD patterns after EDAMM, which show broadened peaks indicating reduce of crystallite’s size to nanometers.

Hardness values of Me-C-N and Me-B-N of group IV which were obtained by EDAMM are slightly higher than obtained by deposition methods. It was caused by the fact that EDAMM induced particle’s fracturing and also nitrogen dissolving and this additionally supported by high energy activation caused its faster diffusion. Thus, EDAMM caused higher dissolution of nitrogen and finer grain size what led to the increase of hardness value.

Microhardness of EDAMM products increases with the increase of the time and nitriding temperature. Consequently it also increases nitrogen content. It is difficult to compare microhardness values though, because of great influence of the grain size.

3.7. CONCLUSION

- The solubility of nitrogen and phase transformation can be precisely controlled by milling time and gap between electrodes.
- The highest nitrogen solubility occurred in Me-C-N and Me-B-N system of Group IV, after 10 minutes of milling combined with 12 mm gap between electrodes. It can be predicted that further increase of these parameters won’t increase solubility of nitrogen.
- SEM studies show formation of homogeneous solid solution with finer particle, which come from AC mode product. Contrarily, agglomerated particle will be found from DC mode product.
- Almost no additional brittle of nitride phases was observed (except for TiBN and ZrBN), there are small amounts of ZrN, TiN and BN appearing after 10 min milling time.
- The final particle size and composition is dominantly determined by the size and composition of starting powder and also milling time of EDAMM.
4. SYNTHESIS OF GROUP V –VI (TANTALUM, VANADIUM, CHROMIUM, MOLYBDENUM, TUNGSTEN) CARBONITRIDE AND BORONITRIDE

4.1 INTRODUCTION

This chapter investigated nitriding process by EDAMM on group V of periodic table (such as tantalum, vanadium) and group VI (chromium, molybdenum and tungsten). Synthesis parameters based on most optimum ones obtained from chapter 4 which were: 10 min milling time in DC mode with 7.5 average gap between electrodes. Substrates that were used were: carbonitride/Me-C-N and metal boronitride/Me-B-N powder. They were then characterized to identify the phase changes, nitrogen content and morphology of the final powder. It was examined using XRD, SEM and CHN analysis.

4.2 TANTALUM CARBONITRIDE

Tantalum Carbonitride (TaC$_x$N$_y$) synthesized from Tantalum Carbide, Ta(IV)C as a starting powder (Aldrich); production code- 280801 with 99% purity and particle size <5 μm.

4.2.1. X-RAY DIFFRACTION

A typical XRD pattern for the as-received tantalum carbide (TaC) starting powder is shown on Figure 4.1. The peak matched with the International Center for Diffraction Data Powder Diffraction File (ICDD-PDF) card no 06-0524. This PDF card characterizes Tantalum Carbide with the space group- Fm3m, molecular weight- 192.96, volume- 88.48 and a face centered cubic structure (FCC) with lattice a = 4.456.
**Figure 4.1 XRD pattern of TaC starting powder (PDF no 06-0524)**

Figure 4.2 show the powder TaC after being milled by EDAMM for 0.5, 1, 2, 5, 10 minutes, using DC power supply with 7.5 mm gap between electrodes. It shows that the peak shifted to the right side with increasing milling time what resulted in decrease of lattice parameter. That was caused by increasing dissolution of nitrogen content and shifted peak reached the position of TaN phases.

The peak’s shift can be clearly seen on the Figure 4.3 for the enlarged (111) peak. These peak shifts indicate formation of TaC\(_x\)N\(_y\). It is believed that during milling for 10 min, particle refinement occurs and is associated with the accumulation of lattice defects. High impact of mechanical milling resulted in deformation and increase if structure defects, also producing higher localized temperature what allowed nitrogen diffusion. Presumably decrease of lattice parameter occurred because nitrogen has smaller atomic radius than carbon (nitrogen is 0.13...
Å while atomic radius of carbon is 0.16 Å) where the carbon site was substituted by N t [71].

It is believed that high fraction of vacancies also exist on the carbon and nitrogen sites.

Usage of DC mode enabled to obtain new TaC$_x$N$_y$ phase. There is no XRD evidence of other intermediate phases. It can also be noticed from the figure, that peaks broaden with the increase of nitrogen content and are significantly broader comparing to those of the starting powder. After being milled for 10 min peak’s intensity increased indicating presence of localised-temperature and its influence on sintering and growing of the grain. It can be concluded that EDAMM also enhances sintering process. Better results were obtained after 5 min milling time. Peaks had lower intensity, presumably a finer crystallite size as referred to Scherrer’s formula.

![Figure 4. 2 XRD pattern of TaC milled at different milling times, with 7.5 mm gap between electrodes in DC mode](image-url)
To investigate the effect of electrical pulse module and pulse amplitude on product evolution, further investigations were performed in which process parameter are pulse module and pulse amplitude with the value between 70:70 and 90:90, the result as Figure 4.4 below, and the enlargement view on Figure 4.5.
On the Figure 4.5 it shown that pulse module and pulse amplitude do not have any significant influence, however it can be thought that higher average gaps between electrodes emits more power to transform the phases. When the powder was being milled in 70:70 on pulse module and amplitude with gap between electrodes of 4mm (a) it shows slight shift to the right side and so to the higher angle what can presumably mean TaC being transformed to TaC$_x$N$_y$ phase. This was proved by broader peaks and decrease in their intensity. No additional, new peak occurred. When pulse module and pulse amplitude were 90:90 (b and c) and with the different gap (4 and 7.5 mm) then XRD peak to shift more. The same Ta$_x$C$_y$N$_z$ phase was formed with no evidence of intermediate phases. The intensity decreased much more indicating finer crystallite size that was obtained. It is thought that these factors dominantly perform fracturing process. Interestingly, when using 12 mm average gap during milling (d)
with pulse module and pulse amplitude applied at lower value of 70:70 composite Ta₄C₃, TaN and a small amount carbon was obtained. No solid solution of TaCN appeared. It is thought that a bigger gap leads to higher energy which transfers plasma in arching mode to localized spot. Then decomposition occurs resulting in Ta₄C₃, carbon free and TaN to be obtained. Complete transformation into 3 phases that mentioned above occurred.

**Figure 4.5 XRD pattern of enlarged 111 and 200 peaks of TaC milled in different pulse current and duration time, and gaps**

For clearer examination Figure 4.6 shows XRD pattern of TaC that was being milled in 70:70 pulse current and pulse duration time with 12 mm average gap between electrodes. It was obviously shown that composite Ta₄C₃, TaN and free carbon were obtained. Transformation was predicted by the reaction below:

$$6 \text{TaC} + \frac{1}{2} \text{N}_2 \rightarrow \text{TaN} + \text{Ta}_4\text{C}_3 + \text{TaC} + 2\text{C}$$
Nanocomposite phases mentioned previously are a part of TaC phase diagram presented on Figure 4.7. Thereby, TaC powder after being milled for 10 min in DC mode, in 70:70 of pulse current and duration time with 12 mm of the average gap has the ratio of $C/Ta=0.65$ to 1.2. Likewise, atomic percentage of carbon is decreasing from 55 to 40. Referring to TaC phase diagram, it is believed that process of the reaction occurred in localized area at 1430 – 2400ºK. It is believed that carbon percentage decreased as nitrogen dissolved and substituted carbon in the crystalline site.
Figure 4.7 Phase diagram of TaC

4.2.2. CHN ANALYSIS

Figure 4.8 shows results of the CHN combustion analysis of TaCN powders milled in different milling times. In this figure nitrogen uptake by TaC is represented by blue dots, while the red dot represents weight percentage of carbon. This graph shows that the amount of absorbed nitrogen increases with increasing milling time. After being milled for 0.5, 2, 5 and 10 min nitrogen intake increased to 0.04, 0.05, 0.06 and 0.14 wt% N respectively. However on the contrary, the amount of carbon decreased with increasing milling time. It was confirmed again with JS Bull’s statement that carbon-nitrogen can be substitution-interstitial process. It is believed that Ta$_x$C$_y$N$_z$ solid solution was successfully obtained where the nitrogen and carbon can substitute each other in TaC matrix just after being milled by EDAMM for 5 min.
In Table 4.1, nitrogen intake after 10 min milling time with different average gaps between electrodes and different pulse module and amplitude was shown. It is thought that the pulse module and amplitude of 90:90 is not an effective way to get higher nitrogen solubility. On the contrary, comparing to pulse module and amplitude that had lower values than 70:70, it produced enough energy to fracture particles. It means that new surface was obtained what allowed nitrogen to be easily dissolved in TaC matrix.

TABLE 4.1. NITROGEN INTAKE IN TaC MILLED FOR 10 MIN WITH SEVERAL AVERAGE GAPS, PULSE MODULES AND AMPLITUDE

<table>
<thead>
<tr>
<th>Pulse module: amplitude</th>
<th>Average gap between electrode(mm)</th>
<th>Nitrogen content</th>
</tr>
</thead>
<tbody>
<tr>
<td>70:70</td>
<td>4</td>
<td>0.19</td>
</tr>
<tr>
<td>70:70</td>
<td>7.5</td>
<td>0.14</td>
</tr>
<tr>
<td>90:90</td>
<td>4</td>
<td>0.09</td>
</tr>
<tr>
<td>90:90</td>
<td>7.5</td>
<td>0.07</td>
</tr>
</tbody>
</table>
4.2.3. SEM IMAGES

Figures 4.9 show SEM secondary electron images of TaC$_{x}$N$_{1-x}$ obtained from a) starting powder, b) products formed after 2 min discharge milling in nitrogen, c) after 5 min milling and d) after 10 min milling. The average gap during milling was 7.5 mm. SEM micrograph of the TaC$_{x}$N$_{y}$ starting powder shows ligamental-irregular form, around 1-3 μm in size. After milling for 2 min (b) particle’s shape was transformed to more round, with average diameter up to 1 μm. After 5 minutes of discharge milling (c) small particles agglomerated under the influence of strong electrostatic forces and cold-welding. Their size was around 1-3 μm. It is also believed that larger particles fractured into smaller ones of the size of up to 1 μm. Further 10 min milling (d) caused further agglomeration, and all small particles disappeared. At this point, particle’s size was around 2-5 μm.

**Figure 4.9 SEM secondary electron images of TaC$_{x}$N$_{1-x}$ starting powder and product after b) 2 min, c) 5 min and d) 10 min milling time with 7.5 mm average gap between electrodes in DC mode**
4.2.4. MICROHARDNESS

Figure 4.10 shows the hardness indentation of $\text{Ta}_x\text{C}_y\text{N}_z$ after milling for 10 min by EDAMM. The average Vickers hardness obtained during the measurement was 2852 which is higher than the hardness of TaC (1570 HV) [82]. Presumably, increase in hardness is connected with the amount of dissolved nitrogen.

![Figure 4.10. Vickers hardness indentation of $\text{Ta}_x\text{C}_y\text{N}_z$ after 10 min milling time](image)

4.3 TANTALUM BORONITRIDE

Solid solution of Tantalum Boride, $\text{TaB}_2\text{(N)}$ was synthesized from Tantalum Boride ($\text{TaB}_2$) (Aldrich). Production code- 336173.

4.3.1. X-RAY DIFFRACTION

Figure 4.11 shows XRD pattern for the tantalum boride ($\text{TaB}_2$) starting powder. The peak in this pattern gives a match to International Center for Diffraction Data – Powder Diffraction...
File (ICDD-PDF) card no 08-0115. This PDF card characterizes Tantalum Boride with following characteristics: space group- P6/mmm, molecular weight- 202.57, volume- 26.79, in a hexagonal structure with lattice a = 3.078 and c = 3.265

![XRD Pattern](image.png)

**Figure 4.11 XRD Pattern of TaB₂ Starting Powder (PDF no 08-0115)**

Figure 4.12 shows TaB₂ powder after being milled for 10 min, using DC power supply with 7.5 mm gaps between electrodes. It shows that the peak shifted to the left side with increasing milling time what is believed to be caused by increasing dissolved nitrogen content.

The peaks shift is clearly seen on the Figure 4.13 for the enlarged (100) peak. This peaks shift indicates formation of single phase solid solutions of TaB₂(N). There is no XRD evidence of other intermediate phases. It can be also noticed from the figure, that peaks broaden with increasing nitrogen content, and are significantly broader comparing to those of the starting powders.
FIGURE 4.12 XRD PATTERN OF TaB₂ STARTING POWDER AND AFTER 10 MIN MILLING TIME, WITH 7.5 MM GAP BETWEEN ELECTRODES IN DC MODE

FIGURE 4.13 XRD PATTERN OF SINGLE PEAK TaB₂(N) AFTER MILLED FOR 10 MIN IN DC SYSTEM WITH 7.5 MM GAP BETWEEN ELECTRODES
4.3.2. SEM IMAGES

Figure 4.14 shows SEM secondary image of a) TaB$_2$ starting powder and b) product after milled for 10 min with 7.5 mm average gap between electrodes in DC mode. TaB$_2$ starting powder’s particles have irregular shape and their size is up to 5 μm (Figure 5.14, a). Furthermore, products after being milled for 10 min show large fraction of agglomerated particles of the size of around 10-50 μm. It is believed that all finer particles of starting powder agglomerated under the influence of strong electrostatic forces and cold-welding, especially when using DC mode where joule heat is more localized and discharge appears more like an arc discharge, which would likely result in high enough local temperatures to melt the particles.

Figure 4.15 shows the cross-section of TaB$_2$(N) after being milled for 10 min in DC mode. Surface is in majority in the same, grey colour what indicates similar composition of those areas. Small dark grey colour in grain’s boundaries is believed to be a contaminant. Moreover, light region is believed to be a result of plastic deformation caused by EDAMM milling.
FIGURE 4. 14 SEM secondary image of a) TaB₂ starting powder and b) product of 10 min milling with 7.5 mm average gap between electrodes in DC mode
4.4. VANADIUM BORIDENITRIDE

Vanadium Boron Nitride (VB\textsubscript{N\textsubscript{y}}) was synthesized from Vanadium diboride (VB\textsubscript{2}) (Aldrich), the production code- 336319.

4.4.1. X-RAY DIFFRACTION

Figure 4.16 shows XRD pattern of Vanadium diboride (VB\textsubscript{2}) starting powder. Peak gives a match with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) card no 08-0118. This PDF card characterizes Vanadium diboride; space group-P6/mmm, molecular weight- 2.56, volume- 23.82, hexagonal structure with lattice $a = 2.998$ and $c = 3.060$. There is an indication of small amount of contaminant of C\textsubscript{8}H\textsubscript{8} present in the powder.
Figure 4.17 shows XRD pattern of VB$_2$ powder after being milled for 10 min, using DC power supply with 7.5 mm gap between electrodes. It shows that the peak shifted to the left side- to lower angles, with increased milling time. It is believed that shifting was caused by increasing of dissolved nitrogen in solid solution what led to presence of the peak expected for VB$_2$(N) interstitial solid solution. There were also intermediate phases of BN (PDF 09-0012) and VB (PDF 30-1416) formed (Figure 4.18). Additional peak is believed to be a C$_8$H$_8$ contaminant coming from starting powder.
Figure 4.17 XRD pattern of VB$_2$ starting powder and after 10 min milling time with 7.5 mm gap between electrodes in DC mode.

Figure 4.18 The effect of milling time on evolution of (101) XRD peak.
It is believed that after milling the starting powder for 10 min under flowing nitrogen, the nitrogen had sufficient energy to replace boron. Decrease of boron content led to transformation of VB$_2$ into VB. Furthermore, free boron started to bond with nitrogen radicals to finally become BN. No VN compound appeared, even though the energy of diffusion activation of V–N (1.48 eV) is lower than for B–V (2.22 eV) [27]. This due to the fact that decomposition of VB$_2$ is more probable as its bond energy (~125 eV) is smaller than VN (~166 eV). Finally, transformation was supposed to lead to expected products as shown on the reaction path below:

$$3\text{VB}_2 + \text{N}_2 \rightarrow \text{VB}_2 + \text{VB} + \text{BN} + \text{VB}_2(N)$$

Finally, reaction process may occur in the red-area range, as described by Spear et al in the VB phase diagram in Figure 4.19 below [26].
4.4.2. CHN ANALYSIS

CHN combustion analysis of VB$_2$(N) after milled for 10 min reported that nitrogen intake are 0.4 wt%, carbon 0.64 wt% and hydrogen 1.07 wt%. This result confirm with the XRD pattern which there is the peak belonging to carbon hydride (C$_8$H$_8$) as contaminant which come from starting powder. Nitrogen presumably dissolved in the VB$_2$(N) and also BN.

4.4.3. SEM IMAGES

Figure 4.20 shows SEM secondary image of a) VB$_2$ starting powder and b) VB$_2$(N) after milled for 10 min with 7.5 mm average gap between electrodes, in DC mode. Starting powder was received in two fractions a) small particles had spherical form with the size of around 5 μm and other large particles of the size around 10-25 μm. After being milled for 10 min b) large particles became smaller and small particles agglomerated. During milling process, relatively large powder particles underwent fragmentation, presumably because of ion surface that was being bombarded and mechanical action of the plunger. Small powder particles (10-70 μm) are believed to agglomerate under the influence of strong electrostatic forces. On the other hand, large particles tend to fracture into small particles up to 1 μm.

Figure 4.21, a) shows SEM secondary image and b) backscattered electron image, of VB$_2$(N) after being milled for 10 min, in DC mode with average gap during milling of 7.5 mm. The dark grey colour was characterizes as VB$_2$(N) and the black area is believed to be VB phase.
Figure 4. 20 SEM secondary image of a) VB$_2$ starting powder and b) VB$_2$(N) after being milled for 10 min with 7.5 average gap between electrodes, in DC mode.
4.5. CHROMIUM CARBONITRIDE

Chromium Carbonitride (CrC\textsubscript{x}N\textsubscript{y}) was synthesized from Chromium Carbide powder (linear formula: Cr\textsubscript{3}C\textsubscript{2}- Aldrich). It was characterized with following features: production code- 402680 with 99.5% of purity, particle size 325 mesh, density- 6.68 g/mL at 25 °C, respectively.

4.5.1. X-RAY DIFFRACTION

A typical XRD pattern for the as-received titanium carbide starting powder is shown in Figure 4.22. The peak in this pattern gives a match with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) card no 03-0935. This PDF card characterizes Chromium Carbide (Cr\textsubscript{3}C\textsubscript{2}) with the space group- \textit{Fm3m}, molecular weight- 180.01 and volume-178.45.
Figure 4.23 shows the XRD pattern of Cr$_3$C$_2$ after being milled by EDAMM in different milling times, in DC mode, with 7.5 mm average gap during milling. Examination of phase transformation was shown on Figure 4.24 for enlarged peaks, between 30 and 60 degrees 2theta. Powder milled for 10 min included amorphous phase of Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ with small amount of Cr$_7$C$_4$. Similar results have been found by Schuster and Maury. They predicted obtaining amorphous CrCN phase below temperature 450ºC [22]. Furthermore, after being milled for 15 min, both amorphous and crystalline phases of Cr$_{6.2}$C$_{3.5}$N$_{0.3}$, Cr$_7$C$_4$ and Cr$_3$C$_2$ were obtained. Intensification of peaks and amorphous-crystalline transition near 450ºC indicating the grain growth were also confirmed by Schuster and Maury. Furthermore, after being milled for 20 min, amorphous Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ and small amount un-reacted crystalline Cr$_3$C$_2$ were found.
**Figure 4.23** XRD pattern of Cr$_3$C$_2$ after being milled in different milling times, in DC mode

**Figure 4.24** Enlarged XRD pattern in the range of 30-55 degrees 2 theta
Figure 4.25 shows the XRD pattern of Cr$_3$C$_2$ molecule after being milled by EDAMM in different milling times, in AC mode with 7.5 mm average gap during milling. On Figure 4.26 enlarged peak between 37 and 47 degrees 2-theta was shown. Starting powder (a) has a match with PDF no 03-0935 without any noticeable contamination. After 10 min milling (b) some peaks became broader comparing to the ones of the starting powder. There can also be noticed new phase of Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ that was obtained in the range of 42-45 degrees 2-theta. Milling for 15 and 20 min (c and d), didn’t cause any significant changes. Peak contributing to Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ phase was obtained in the same range of 2-theta values. It is thought that AC mode does not have enough energy to transform Cr$_3$C$_2$.

**Figure 4.25** XRD pattern of Cr$_3$C$_2$ after being milled by EDAMM in different milling times, in AC mode
**Figure 4.26 XRD pattern of Cr$_3$C$_2$ in the range of 37-47 degrees 2 theta**

Figure 4.27 shows the XRD pattern of Cr$_3$C$_2$ after being milled with different average gaps during milling in different arrangement of pulse module and pulse amplitude, in DC mode. On Figure 4.28 enlarged peak in the range 37-47 degrees 2-theta was shown. It can be noticed that starting powder (a) has an excellent match with PDF no 03-0935, without any contaminations. When pulse module and amplitude were kept at 70:70 in 5 mm average gaps (b) Cr$_3$C$_2$ was transformed into Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ and small amount of the powder remained unreacted. Moreover, new Cr$_7$C$_4$ phase appeared. Interestingly, when pulse module and amplitude were kept at 80:80 (c) with 5 mm average gap, Cr$_3$C$_2$ phase reacted entirely. That resulted in obtaining nanocrystalline Cr$_7$C$_4$ and small amount of Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ phase.

On the contrary, when pulse module and amplitude were kept at 70:70 with 7.5 mm average gap (d) the same phases and several unreacted Cr$_3$C$_2$ were obtained. When nitrogen was kept in no-flowing condition, both peaks of Cr$_{6.2}$C$_{3.5}$N$_{0.3}$ and Cr$_3$C$_2$ intensified what indicates the crystal growth (e). Thus, it can be concluded that flowing nitrogen preserves smaller grains. It
is thought that the arrangement of pulse module and amplitude has small influence on phase transformation whereas flowing nitrogen is a factor resulting in obtaining finer grains.

**Figure 4.** XRD pattern of milled Cr$_3$C$_2$ with different average gaps and different pulse module and pulse amplitude.
Figure 4.28 XRD pattern of Cr₃C₂ in the range 37-47 degrees 2-theta

Figure 4.29 shows the XRD pattern of Cr₃C₂ after being milled under helium atmosphere in different combinations of pulse module and pulse amplitude, with 7.5 mm of the average gap during milling in DC mode.

On Figure 4.30 enlarged peak in the range 30-55 degrees 2-theta was formed. It shows that starting powder (a) has an excellent match with PDF no 03-0935, without any contamination. When setting parameters of pulse module and amplitude at 70:70, (b) the given result included obtaining of Cr₇C₃ and Cr₆.₂C₃.₅N₀.₃ nano-crystal. Also several peaks appeared that contributes to un-reacted Cr₃C₂. When the pulse module and amplitude were set at 50:50 (c)
the powder had in majority $\text{Cr}_{6.2}\text{C}_{3.5}\text{N}_{0.3}$ and $\text{Cr}_3\text{C}_3$ nano-crystals. Both peaks for these phases intensified, whereas intensity of $\text{Cr}_3\text{C}_2$ peak decreased.

It is believed that in helium atmosphere, when pulse module and amplitude were set at 50:50, particles were more homogeneous than at 70:70. This was confirmed and can be seen on Figure 1.6. In plasma flame theory helium with the same input of energy produces higher temperature than other gases. This is why the peak belonging to $\text{Cr}_{6.2}\text{C}_{3.5}\text{N}_{0.3}$ compound intensified. Nitrogen diffused faster what was the result of higher, localized-temperature produced by helium.

![Figure 4.29 XRD pattern of $\text{Cr}_3\text{C}_2$ after being milled in helium atmosphere, and different parameters of pulse module and pulse amplitude, in DC mode](image-url)

**Figure 4.29** XRD pattern of $\text{Cr}_3\text{C}_2$ after being milled in helium atmosphere, and different parameters of pulse module and pulse amplitude, in DC mode
When EDAMM milling was conducted under nitrogen atmosphere, the transformation of Cr$_3$C$_2$ is supposed to follow the reaction below:

$$24 \text{Cr}_3\text{C}_2 + 1.5 \text{N}_2 \rightarrow \text{Cr}_3\text{C}_2 + \text{Cr}_7\text{C}_4 + 10 \text{Cr}_{6.2}\text{C}_{3.5}\text{N}_{0.3} + 8\text{C}$$

It is believed that the process of the reaction occurred in the red-area range as shown in the Cr-C phase diagram on Figure 4.31 below.
4.5.2. CHN RESULT

CHN combustion analysis of Cr_xC_yN_z system after milling by EDAMM when using DC mode reported that nitrogen intake is in the range of 0.27-0.47 wt% and in AC mode- 0.00-0.08 wt%. This was consistent with XRD results revealed the presence of new phases Cr_xC_yN_z system associated with DC mode processing.

4.5.3. SEM IMAGES

Figure 4.32 shows polished milling product after being milled in DC mode for 10 min (A and B), 15 min (C and D) and 20 min (E and F) at different magnifications, between left and right side and with the nitrogen content of 0.29, 0.47 and 0.27 wt% respectively. It shows that milling for 10 min (Fig 4.32 B) led to obtaining diffusion zones of nitrides having large, needle-like shape settling in grain boundaries. Further milling for 15 min resulted in appearance of darker areas in the cross-section (Fig 4.32 D) caused by bigger amount of
dissolved nitrogen. This fact was confirmed by higher nitrogen content. While regions in the surface also be observed, the diffusion zones become wider extending into the interior of matrix. After milling for 20 min (Fig 4.32 E) it seems that results are similar to the B sample. It was confirmed by the CHN analysis that nitrogen intake in both B and E sample differed slightly (0.27 and 0.29 wt% N).

**Figure 4.32** SEM backscattered image of Cr2C2 after being milled in DC mode with 7.5 mm average gap for A) 10 min with 0.29 wt% N, C) 15 min with 0.47 wt% N, and E) 20 min with 0.29 wt% N. B), D) and F) are in bigger magnifications; left-100x and right-1000x
4.5.4. MICROHARDNESS

Figure 4.33 shows indentation of Cr$_x$C$_y$N$_z$ after (a) 15 and (b) 20 min of milling. The average hardness obtained through microhardness measurements were 2092 and 1824 respectively. The result is comparable to the hardness of CrCN, what was confirmed by Schuster and Maury by OMCVD method [81]. Value obtained were: 1700 for Cr$_{0.062}$N$_{0.08}$C$_{0.03}$ and 1900 for Cr$_{0.064}$N$_{0.17}$C$_{0.19}$.

![Figure 4.33. Hardness indentation of Cr$_x$C$_y$N$_z$ after (a) 15 min and (b) 20 min milling](image)

4.6. MOLIBDENUM CARBONITRIDE AND BORIDENITRIDE

Molybdenum carbide (Mo$_2$C) and molybdenum boride (MoB) powder was purchased from Aldrich. It’s characteristics are: production code- 399531 and 709182 respectively, particle’s size -325 mesh with 99.5% of purity (for both).
4.6.1. X-RAY DIFFRACTION

Figure 4.34 shows XRD pattern of the as-received Molybdenum carbide (Mo$_2$C) starting powder. The peak gives a match with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) no 11-0680. This PDF card gives following characteristics of molybdenum carbide: space group- P63mmc, molecular weight- 203.89, volume- 37.04 and hexagonal structure with lattice a = 3.006 and c = 4.733.

![XRD pattern for Molybdenum Carbide (Mo$_2$C) starting powder (PDF 11-0680)](image)

**Figure 4.34 XRD pattern for Molybdenum Carbide (Mo$_2$C) starting powder (PDF 11-0680)**

Figure 4.35 shows the XRD pattern for the as-received Molybdenum boride (MoB) starting powder. The peak in this pattern gives a match with the International Center for Diffraction Data – Powder Diffraction File (ICDD-PDF) card no 06-0636 for predominant hexagonal-MoB. There is also small amount of orthorhombic MoB- PDF card no 06-0644. The predominant molybdenum boride has space group- I4/amd, molecular weight- 106.75, volume- 163.92 and a hexagonal structure with lattice a = 3.108 and c = 16.97.
Figure 4.36 shows the XRD spectra of Mo$_2$C milled by EDAMM for 10 minutes, with 7.5 mm average gap between electrodes, in DC mode. Peaks shifted to the right, indicating Mo$_x$C$_y$N$_z$ formation. It was also shown that peak’s intensity decreased drastically (Figure 4.37) what proved fracturing. It is worth noticing that no crystalline Mo was detected in the XRD patterns. There is an indication of changes in the composition where atomic percentage of Mo is decreasing and carbon increasing. The nitrogen is difficult to be observed, due to small atom nitrogen interstice in carbon site.
Figure 4.36 XRD pattern of Mo-C milled for 10 min, with 7.5 mm average gap between electrodes, in DC mode.

Figure 4.37 XRD pattern of peaks evolution of Mo-C milled for 10 min, with 7.5 mm average gap between electrodes, in DC mode.
Figure 4.38 shows phase diagram with outlined red-box, being area of prediction where the transformation may occur. It is highly probable that the transformation has quite localized temperature in the range of around 1658°C -1964°C.

![Figure 4.38 Mo-C phase diagram](image)

Figure 4.39 shows the XRD pattern of MoB milled by EDAMM for 10 minutes, with 7.5 mm average gap between electrodes, in DC mode. Peak belonging to hexagonal MoB drastically decreased in intensity. On the contrary, orthorhombic-MoB intensified what means that it was rapidly formed. For clearer examination on Figure 4.40 peaks between 31 to 37 degrees 2-theta were shown in enlargement.
Figure 4.39 XRD pattern of MoB milled for 10 min, with 7.5 mm average gap between electrodes, in DC mode.

Figure 4.40 XRD pattern including 31-37 degrees 2-theta peaks of milled MoB.
4.6.2. CHN ANALYSIS

CHN analysis of MoC(N) after 10 min milling time revealed that nitrogen intake is 0.47 wt%, and 5.93 wt% of carbon. No nitrogen intake in MoB was reported.

4.6.3. SEM IMAGES

Figure 4.41 shows unpolished MoC starting powder (a) and the powder after 10 min milling (b). As-received powders consist of large fraction of small particles with the average diameter of 2-5 μm, and small fraction of bigger particles up to 15 μm. Then, after being milled for 10 min(b) all particles are believed to agglomerate under the influence of strong electrostatic forces.

![SEM Image of unpolished and milled MoC powder](image)

**Figure 4.41 SEM image of unpolished (a) and after milling for 10 min (b) of MoCN starting powder**

Figure 4.42 presents SEM secondary electron (a) and backscattered (b) image of MoC after milling for 10 min. It appears that nitrogen was primarily nucleated on the Mo$_2$C grain boundaries,
Figure 4.42. SEM secondary electron (a) and backscattered (b) image of MoCN after milling for 10 min.

4.6.4. Microhardness

Figure 4.43 shows hardness indentation of $\text{Mo}_x\text{B}_y\text{N}_z$ after milling for 10 min. The average Vickers hardness obtained was 1948 HV.

Figure 4.43. Hardness indentation of $\text{Mo}_x\text{B}_y\text{N}_z$ after milling for 10 min in DC mode.
4.7. TUNGSTEN CARBONITRIDE AND BORIDENITRIDE

As a starting powder Tungsten Carbide, W(IV)C (Aldrich) was used with following characteristics: product number- 241881, the particle size- 10 μm with 99 % purity and molecular weight- 195.85.

4.7.1. XRD ANALYSIS

WC powder matched with JCPDF number 05-0728 (Figure 4.44, a) which has a hexagonal structure, molecular weight- 195.86, volume-20.83, lattice parameter a=2.91 and c=2.84.

![XRD Pattern](image)

**Figure 4.44 XRD pattern of as-received WC a) and after 10 min milling time b) with 7.5 mm average gap between electrodes, in DC mode**
The XRD pattern of WC after milled by EDAMM for 10 min shown in Figure 4.44 (b), it appear the new peak W$_2$C that matched with JCPDF 02-1134 with hexagonal structure. The molecular weight =379.71, volume = 36.54 and lattice parameter a=2.99 and c=4.72. The peak belonging to hexagonal-WC looks drastically decreased its intensity. Contrarily the hexagonal W$_2$C shown nucleated, apparently nitriding process in WC has the complex mechanism. Presumably nitrogen dissolved into WC matrix, induced the strain between lattice, it noted that W$_2$C has “c” lattice longer than WC. It confirmed with Cullity statement, when interstitial solid solution obtained, then increasing of unit cell volume was always accompanied. The single lattice parameter “a” must increase, if powder structure is cubic. When it is not cubic, such as hexagonal, then one lattice parameter will increase and the others decrease [69].

Presumably the reaction occurred as below:

$$4WC + N_2 \rightarrow 2WC + W_2C + (CN)_2 \text{ gas}$$

Figure 4.45 (a) shows the as-received Tungsten Boride (WB) powder obtained from Aldrich, with the product number 10497, and has 97% of purity. Molecular weight = 194.651 g/mol. It also confirmed with JCPDF number 06-0635 in all of peak. Furthermore after milled by EDAMM for 10 minutes shown in Figure 4.45 (b), it exhibit that WB transform to some peak that matched with 06-0541 (WB) also some peak matched with W$_2$B JCPDF 06-0591.
Figure 4.45 XRD pattern of a) as-received WB and b) after milled for 10 min in 7.5 mm average gap between electrodes, in DC mode.

Figure 4.46 shows phase diagram of WC with the outlined red-box where the transformation might have occurred. It is probable that very high localized temperature combined with mechanical milling induced the transformation in the temperature range of 1523-2657°K.
4.7.2. CHN ANALYSIS

CHN combustion analysis of WB after 10 min milling time revealed only 0.04 wt% of nitrogen intake. This proved, that metal boride is relatively difficult to synthesize and instead Me-B-N compound was obtained.

4.7.3. SEM IMAGES

Figure 4.47 shows the SEM image of WC after being milled for 5 (a) and 10 min (b). It exhibit rapid decrease of the particle’s size. Manufacturer-Aldrich-states that the particle’s size of as-received WC is around 10 μm or bigger. After 5 min, as shown on figure 4.47 (a) almost 80% of starting powder particles fractured to around 5-10 μm. Sample being milled for 10 min exhibit finer agglomerated particles of the size around 1-5 μm (b).
Figure 4.47 SEM backscattered image of WC after milled for 5 (a) and 10 min (b).

Figure 4.48 shows SEM secondary image of unpolished starting powder of WB (a) of the average size of around 1-5 μm, then after 10 min milling (b) large fraction of agglomerated particles up to 100 μm and small particles up to 10 μm can be seen.

Figure 4.48 SEM secondary image of unpolished starting powder of WB (a) and after being milled for 10 min.
4.7.4. MICROHARDNESS

Figure 4.49 shows hardness indentation of WₓCᵧNₓ after a) 5 and b) 10 min of milling with the average hardness obtained: 1936 and 2207. It is believed that the block-like shapes (grey regions) in Figure 4.49 (a) are softer than light regions. After milling for 10 min, softer regions fractured, and seemingly (Figure 5.49 (b)) became more dense and harder. However, Akihiro states that the hardness value of WC is 27 GPa (2753 HV). When carbon content decreases as WₓC is forming, the hardness decreases to 17.5 GPa (1784 HV) [83]. It can be predicted that hardness value of WₓCᵧNₓ is higher than WₓC and may be also higher than the one of the starting powder-WC.

Figure 4.50 shows hardness indentation of WₓBᵧNₓ after milling for 10 min with the average hardness obtained- 2653 HV.
**Figure 4.49.** The hardness indentation of $\text{WSiN}_x$ after (a) 5 and (b) 10 min milling in DC mode

**Figure 4.50.** The hardness indentation of $\text{WBN}_x$ after milled 10 min in DC mode
4.8. DISCUSSION

In this chapter, nitriding of Me-C-N (Me = TaC, CrC, MoC and WC) and Me-B-N (Me = TaB, VB, MoB and WB) during EDAMM was investigated. After being milled in EDAMM for several minutes, each material has different trend.

Ta-C-N, Ta-B-N and V-B-N system have similar trend to Group IV (ZrC, TiC and HfC), where shifting of the peak indicates forming new intermetallic phase of TaC$_x$N$_y$, and TaB$_2$(N) and VB$_2$(N) solid solutions. However, in Ta-C-N case, when the arrangement of pulse module and duration were kept at 70:70 and average gap between electrodes was 12 mm, it gave different transformation resulting in formation of TaN, Ta$_4$C$_3$, TaC(N) composite and a small amount of carbon. Presumably the mechanism occurred in very complex route between diffusion of nitrogen and decomposition of TaC.

Moreover, in Mo-C-N and W-C-N systems, after being milled by EDAMM for 10 minutes, they have the same phenomenon of decreasing amount of carbon caused by nitrogen diffusion. Because of very small size of nitrogen atom it couldn’t be clearly detected. Seemingly, metal carbide only limited transformed into less-carbon composition phases. however, nitrogen atom contributed in phase transformation, as detected by CHN test, that there is some amount dissolved nitrogen in milled product.

Amorphous CrCN was obtained after 10 min of milling in predicted temperature below 450ºC. Increased milling energy (usually in DC mode, and sometimes achieved by bigger average gap between electrodes) is normally expected to introduce more strain and increase defect concentration in the powder what leads to easier amorphization process. On the other
hand, higher milling energies also produce more heat (higher temperatures) and this can result in crystallization of the amorphous phase. Therefore, a balance between these two effects will determine the nature of the final phase product.

When it comes to morphology and particle size, DC mode is not an effective way to obtain fine particles due to its high energy and transferring plasma in sharp arching mode. That induces very high localized temperature what leads to melting of particle’s surface causing agglomeration.

4.9. CONCLUSION

- It has been observed that in some cases the final phase is different from the one that was expected. During the nitriding reactions of MoC and WC, no ternary intermetallic or solid solution phases were formed but Mo$_2$C and W$_2$C as intermediate phases formed instead. The highest nitrogen solubility in Me-C-N and Me-B-N system of Group V and VI were obtained after 10 minutes of milling.

- SEM revealed that formation of homogeneous solid solution in fine particles, can be obtained with AC mode. Contrarily, agglomerated particles will be found in DC mode products.
5 SYNTHESIZING OF SILICON CARBONITRIDE

5.1 INTRODUCTION

This chapter will characterize nitriding process by EDAMM in different types of gases. Synthesizing of silicon carbonitride was done with following parameters: milling in flowing nitrogen, argon and helium gases, pulse module and duration kept at 70:70, average gap between electrodes: 5 and 7.5 mm. Si-C-N powder obtained by this method will then be characterized to identify phase changes, nitrogen content and morphology of powder.

5.2 SILICON CARBONITRIDE

Hexagonal SiC was used as a starting powder (Aldrich) having following parameters: product number- 357391, ≥ 97.5 % purity, particle size- 400 mesh, density- 3.22 g/mL at 25ºC. As advised by Aldrich SiC powder was synthesized by reduction of silica with coke (and salt as flux) at high temperature in an electric furnace.

5.2.1. X-RAY DIFFRACTION

XRD pattern of as-received silicon carbide (SiC) is shown on Figure 5.1. It indexed to two hexagonal SiC phases, dominantly H-SiC PDF card number 29-1131 (a =3.073 nm, c= 15.08 nm) and H-SiC PDF card number 22-1317 (a =3.073 nm, c = 10.053 nm ).
Figure 5.1. XRD pattern of hexagonal SiC powder.

Figure 5.2 shows XRD pattern of SiC after being milled by EDAMM for 0.5 to 10 min, under flowing nitrogen in DC mode, using pulse module and duration kept at 70:70 and with 7.5 mm gap average between electrodes. As-received powder has two types of hexagonal SiC as shown on Figure 5.2 (a). After 0.5 min, peak’s intensity drastically decreases what proves efficient fracturing, as shown on Figure 5.2 (b). Longer milling times; 1, 2 and 5 min (Figure 5.2 (c-d)), resulted in peaks belonging to H-SiC PDF card 22-1317 to fully disappear. After being milled for 5 min, hexagonal SiC peak slightly shifted to the left. It is believed that structural transformation from hexagonal to cubic structure of C-SiC PDF card 02-1050 occurred. After being milled for 10 min, transformation was successfully accomplished as shown on Figure 5.2 (f). Transformation was more clearly shown on peak’s enlargement on Figure 5.3 below.
**Figure 5.2.** XRD pattern of hexagonal to Cubic SiC transformation during milling for 0.5 to 10 min.

**Figure 5.3.** The effect of milling time on evolution of XRD peak.
The structural transformation of SiC is believed to be caused by nitrogen gas which dissolved in SiC solid solution. Presumably the reaction occurred between room temperature and around 1415°C according to phase diagram below (Figure 5.4). This was also confirmed by other researchers, such as Okojie et al who successfully transformed H-SiC into C-SiC by highly doped oxidation [73]. However, Yang et al found the cubic β-SiC after ball-milled of hexagonal α-SiC for 60 hours in argon at room temperature [74]. This study successfully transformed it in only 10 min.

![Phase Diagram of SiC](image)

**Figure 5.4. Phase Diagram of SiC**

Figure 5.5 shows XRD pattern of SiC after being milled by EDAMM for 5, 10 and 15 min, under flowing argon in AC mode, pulse module and duration kept at 70:70 and 7.5 mm gap between electrodes. As-received powder with two types of hexagonal SiC is shown on Figure 5.5 (a). After 5 min milling, peak’s intensity drastically decreased what proved that fracturing occurred efficiently (Figure 5.5 (b)). Milling for 10 min (Figure 5.5 (c) resulted in peak’s transformation from H-SiC (PDF29-1131) to H-SiC (PDF 29-1128). There is also indication that small amount of FeSi₂ contamination present (PDF 35-0822). Furthermore, after being
milled for 15 min (Figure 5.5 (d), both of as-received H-SiC peaks fully disappeared and only new H-SiC (PDF 29-1128) and FeSi$_2$ remained.

Figure 5.5. XRD pattern of SiC after being milled by EDAMM for 5, 10 and 15 min, in argon, in AC mode, pulse module and duration in 70:70 and 7.5 mm gap average between electrodes.

Figure 5.6 shows XRD spectra of SiC after being milled by EDAMM for 5, 10 and 15 min, in Helium, in AC mode, pulse module and duration- 70:70 and 7.5 mm gap between electrodes. Powder peaks were almost the same as of the powder processed in flowing argon. The difference is in the presence of FeSi$_2$ which appeared faster than in argon gases. After 5 min FeSi$_2$ nucleated. The process is likely to be caused by helium’s higher temperature in the same energy content comparing with others gases (Figure 1.6.). Furthermore, peak’s intensity
drastically decreased what proved that fracturing occurred efficiently (Figure 5.6 (b)). Longer milling time for 10 min (Figure 5.6 (c)) resulted in transformation of the peaks belonging to H-SiC (PDF29-1131) to H-SiC (PDF 29-1128). There is also an indication of small amount of FeSi₂ contamination (PDF 35-0822). Furthermore, after being milled for 15 min (Figure 5.6 (d)), both of as-received H-SiC peaks disappeared entirely and only new H-SiC (PDF 29-1128) and FeSi₂ remained.

![XRD Pattern](image)

**Figure 5.6. XRD Pattern of SiC after being milled by EDAMM for 5, 10 and 15 min, in Helium, in AC mode, pulse module and duration- 70:70 and 7.5 mm average gap between electrodes.**

Figure 5.7 shows XRD spectra of SiC after being milled by EDAMM for 5, 10 and 15 min, in nitrogen, in AC mode, 70:70 pulse module and duration and 7.5 mm average gap between electrodes. After 5 min (Figure 5.7(b)), as-received powder transformed into new cubic SiC but also small amount of FeSi₂ contaminant was left. On the contrary, longer milling time in
10 and 15 min presented un-reacted SiC (Figure 5.7(c) and (d)). It is believed that this happened because of plasma transfer in AC mode (cloudy plasma) which tends to distribute the plasma much wider than in DC mode. Presumably only at the centre maximum temperature could be reached. Thus, particles being on the border are more likely to remain unreacted.

**Figure 5.7. XRD pattern of SiC after being milled by EDAMM for 5, 10 and 15 min, in nitrogen, in AC mode, pulse module and duration in 70:70 and 7.5 mm average gap between electrodes**

Figure 5.8 shows the XRD spectra of SiC after being milled by EDAMM for 5 and 10 min, in nitrogen, in AC mode, with pulse module and duration kept at 70:50 and 7.5 mm gap average between electrodes. As a result, un-reacted SiC and small amount of FeSi₂ still remained.
5.2.2. CHN ANALYSIS

Figure 5.9 shows results of the CHN combustion analysis of SiCN powders milled in different milling times. On this figure nitrogen uptake by SiC is represented by the red line, while the blue line represents weight percent of carbon. This graph shows that the amount of absorbed nitrogen increases with increasing milling times. After being milled for 0.5, 1, 2, 5 and 10 min the nitrogen intake increased as follows: 0.54, 0.57, 0.66, 0.80 and 0.89 wt% N, respectively. The amount of carbon decreased with increased milling time. It is probable that we succeeded
producing cubic SiC(N) solid solutions with nitrogen and carbon that can substitute each other in the SiC matrix just after 10 min milling by EDAMM.

**Figure 5.9. CHN combustion result of SiCN powders milled in different milling time in nitrogen gas in DC mode.**

5.2.3. SEM

Figure 5.10 compare SEM secondary electron images obtained from a) hexagonal SiC starting powder called H-SiC, with products formed after discharge milling in nitrogen for b) 5 min and c) 10 min respectively. The SEM micrograph of the H- SiC starting powder (a) shows large particles with the average diameter of 20-40 \( \mu \)m and a fraction of small particles below 20 \( \mu \)m. After 5 minutes of discharge milling (b) large particles became smaller whereas small particles agglomerated. During first 5 minutes of milling relatively large powder particles underwent fragmentation what could be caused by ion surface bombardment and mechanical action of the plunger. Small powder particles are believed to agglomerate under the influence
of strong electrostatic forces. Figure 5.10 (c) shows the powder morphology after 10 minutes of milling. The SEM micrograph shows mixture of large, agglomerated particles with the average size of around 50 µm as well as small (1-5µm) particles.

![Figure 5.10](image)

**FIGURE 5.10.** SEM SECONDARY ELECTRON IMAGES OF A) AS-RECEIVED SiC POWDER, AFTER MILLED FOR B) 5 MIN AND C) 10 MIN IN NITROGEN GAS IN DC MODE.

5.2.4. MICROHARDNESS

Figure 5.11 shows hardness indentations of Si₃CₓNₙ after milling for 10 min in DC mode by EDAMM. The average Vickers hardness obtained was 3657. This result is higher than a value of Hv (50g) = 2777, obtained by Badzian [27] for SiCN synthesised by microwave plasma studied [27]. It is possible that EDAMM processing has introduced heavy defect densities into the particles. Then a variety of crystal defects possible include: dislocations, vacancies, stacking faults, and increased number of grain boundaries. The presence of this such a heavily deformed structure might enhance diffusion of nitrogen and also result in increases the hardness compared to that obtained from the phase in near-equilibrium thin film form.
5.3 DISCUSSION

When nitriding of SiC was carried out in DC mode, structural transformation of two types from hexagonal SiC to single phase cubic SiC was obtained. The mechanism is believed to have started when as-received hexagonal SiC peak shifted to the left after 5 min of milling. Then structural transformation occurred, probably being induced by nitrogen dissolving from gas and migrating into SiC solid solution. The structural transformation from hexagonal into cubic C-SiC (PDF card 02-1050) was successfully accomplished after milling for 10 min. This reaction probably occurred in between room temperature to around 1415°C. However, when SiC was being milled under flowing nitrogen in AC mode, the structural transformation was obtained after longer milling time- 10 min. Also peaks contributing to contaminants such as FeSi2 and some un-reacted hexagonal SiC appeared. It is believed that higher energy to fully transform the structure into the cubic SiC is needed.
In argon and helium gases, milling of SiC has the same trend. Part of as-received two types hexagonal SiC (PDF 22-1317 and 29-1131) transformed to hexagonal SiC (PDF 29-1128). There is also an indication that a small amount of contamination of FeSi$_2$ (PDF 35-0822) is present. H-SiC is fully disappeared after longer milling time and new H-SiC (PDF 29-1128) and FeSi$_2$ remained.

Even though argon and helium are known as inert gases, the contaminant still remained. This is due to the fact that the contaminant comes from the chamber base. The contaminant in gases form, such as oxide, etc didn’t appear.

5.4 CONCLUSION

- The solubility of nitrogen and phase transformation can be accurately controlled by milling time, AC/DC modes and atmosphere gas.
- The amount of absorbed nitrogen increases with increasing milling times.
- The average Vickers hardness obtained was 3657. This is slightly higher than the one obtained by Badzian, which was measured in the same load- 50 gr. It is believed that EDAMM milling induced the strain and finer crystallite size that increase the hardness.
- The structural transformation from hexagonal to cubic SiC was fully accomplished in 5 min in DC mode and 10 min in AC mode.
6. SYNTHESIZING, COMPACTION AND SINTERING OF TiAlSiN AND TiAlN

6.1 INTRODUCTION

This chapter investigated synthesizing of Ti-Al-Si and Ti-Al composites by conventional planetary ball milling followed by nitriding by EDAMM method. The synthesized product was densified and sintered by SPS. Obtained product was characterized using XRD, SEM, CHN and its microhardness was measured by Vickers method.

6.2 STARTING POWDER

The starting powder -Ti (99.5%), Al (99%) and Si (99.3%)- was obtained from Aldrich with the particle size smaller than 45 μm (compositions are given in Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alloy</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Titanium</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Premix KC1</td>
<td>Ti-Al-Si</td>
<td>62</td>
<td>26</td>
</tr>
<tr>
<td>Premix KC2</td>
<td>Ti-Al</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

The initial stage of mixing the Ti-Al powder for 1 hour revealed sharp Bragg-peaks corresponding to h.c.p.-Ti (PDF card 44-1294), and f.c.c.-Al crystals (PDF card 04-0787) shown in Fig 6.1 (a).
Ti-Al-Si system, at the initial stage of mixed powder for 1 hours shown revealed sharp Bragg-peaks corresponding to h.c.p.-Ti (PDF card 44-1294), f.c.c.-Al crystals (PDF card 04-0787) and f.c.c-Si (PDF card 27-1482). Shown in Fig 6.2 (a).

6.3 PLANETARY BALL MILLING

Figure 6.1 show XRD patterns of Ti and Al mixed and milled by planetary ball milling in different time intervals. It shows that Ti and Al reflections became wider and their intensities drastically decreased during milling at 90 hrs (Fig 6.1.b). It clearly indicates that Al atoms diffused into Ti lattice. Peak between 75-80 degrees 2-theta indicates the formation of a solid solution of aluminum and/or nitrogen in titanium, identified as 0.6Ti–0.4Al-N. This nanocrystalline binary substitutional solid solution was formed after 90 hrs and the process continued until 190th hour of milling time. Broadening of the peak was observed, which is characteristic for mechanically milled structures. After 330th hour of milling, aluminum peak cannot be seen in the XRD pattern, indicating complete dissolution of aluminum in titanium. A small peak of amorphous phase was obtained after complete dissolution of Al in titanium; especially at 60-65 and 70-75 degrees 2-theta.

Broadening of the Ti–Al solid solution peak in the course of milling may be attributed to the effect of both small particle size and substitution of Ti atoms (atomic radius = 0.86˚) by smaller Al atoms (atomic radius=0.53˚). The shifting and broadening phenomenon continued up to 560th hour what is believed to be caused by the effect of both lattice strain development due to constant fracture and re-welding mechanism. As a result particle’s size decreased. This indicates presence of major Ti(Al,N) nanocrystalline solid solution and amorphous phase. Small amount of Ti peaks can be seen on XRD pattern meaning, un-reacted Ti is still present.
Figure 6.1 shows XRD pattern of Ti, Al and Si mixed and milled by planetary ball milling in different time intervals.
Figure 6.2 (a) shows Ti-Al-Si powders at the initial stage of mixed powder for 1 hr. It revealed sharp Bragg peaks corresponding to h.c.p.-Ti (PDF card 44-1294), f.c.c.-Al crystals (PDF card 04-0787) and f.c.c-Si (PDF card 27-1482).

After being milled for 90 hrs there were no significant phase changes, all peaks contributed to 3 major elements of powders in crystalline structure, however the peak is wider and broader. After 190 hrs of milling it was confirmed that Ti, Al and Si were still present and that they started formation of metastable solid solution phase Ti(Al,Si,N). Formation of solid solution Ti(Al,Si,N) continued up to 330\textsuperscript{th} hr while Si peak disappeared completely. It is believed that a small-sized silicon atom moved into the lattice of TiAlN hardening the solid solution what was also confirmed by Rebouta [75]. Furthermore at the time range of 450- 560 hrs of milling, powder is a homogeneous nanocrystalline solid solution Ti-Al-Si-N phase with small amount of un-reacted Ti.
In order to clarify the phase formation, microstructural evolution, and thermal stability of the phase, Differential Thermal Analysis (DTA) measurement was done. Details of the development of the microstructure have been studied by SEM and the phase transformation was analysed by XRD measurement.
The DTA slope of Ti-Al-N, after being milled for 560 hrs, shows two exothermic and one endothermic peak (Fig 6.3). First peak (between 487 – 601°C) indicates exothermic reaction of dissolution of aluminum in titanium. It led to formation of Ti(Al) solid solution. Second peak means that there was an endothermic reaction, where the nitrogen absorbed energy to break the bonds and became an interstitial component in the lattice of Ti(Al,N) solid solution. The last peak between 1026-1149°C is recrystallization process of Ti(Al,N) solid solution, transforming to nanocrystalline TiN, AlN, TiO and intermetallic Ti$_3$AlN. Phase evolution was confirmed X-ray diffraction (Fig 6.4).

**Figure 6.3. DTA graph of Ti-Al-N which was annealed at 1200°C**
Ti-40%Al powder milled for 560 hr after annealing in DTA machine at 1200°C shows recrystallization of metastable phase Ti(Al,N) and its transformation into TiN, AlN, Ti$_3$AlN and TiO which could be also seen on SEM images on Fig. 6.11 (d).

6.4 EDAMM METHOD

Fig 6.5 shows XRD patterns of the powders produced in different time intervals, at the initial stage of mixed powder for 1 hr by ball milling. It revealed sharp Bragg peaks corresponding to h.c.p.-Ti (PDF card 01-0787) and f.c.c.-Al crystals (PDF card 01-1176). After being milled by EDAMM for 1 minute under nitrogen atmosphere, Ti and Al peaks disappeared and new phases was created: TiN(PDF card 38-1420), AlN (PDF card 25-1133), Ti$_3$AlN (PDF card 37-1140), Ti$_2$AlN (PDF card 18-0070) and Al$_3$Ti (PDF card 26-0038).
1 min of the process resulted in large areas being exposed to nitrogen molecules. Nitrogen decomposed into individual atoms, by combination of mechanical milling and electrical discharges what led to rapid formation of five main phases mentioned above. The phase formation mechanism needs further examination. The XRD pattern of powder milled for 2 minutes didn’t show any significant changes except of peak of Ti$_2$AlN which became broader.
and some of them disappeared. After 5 and 10 minutes of milling, Al₃Ti peak completely disappeared. A detailed analysis revealed that intensity of AlN diffraction decreased slightly.

Fig. 6.6 shows XRD pattern of Ti-Al-N milled with the amplitude and pulse module- 70% , time of milling 10 until 20 minutes (two steps of 10 minutes) with the same process parameter, the last is milled for 10 min with the amplitude and pulse module 50%. Both later present the formation of new phase of Al₂O₃.

**Figure 6.6. XRD Patterns of the Ti-Al-N Powders Produced by EDAM in Different Time Intervals**

Fig. 6.7 show the XRD patterns of the powders at the initial stage of mixed by ball milling in 1 hr reveal sharp Bragg-peaks corresponding to h.c.p.-Ti, f.c.c.-Si and f.c.c.-Al crystals. After
milling for 1 and 2 minutes, main phases: TiN (PDF card 38-1420), AlN (PDF card 25-1133) and Ti₇Al₅Si₁₂ (PDF card 22-0502) are present. After 5 min of milling by EDAMM the intensity of Ti₇Al₅Si₁₂ peak decreased while a new Al peak appeared at 50° and 66 ° (20). It is believed that Ti₇Al₅Si₁₂ decomposed, and Si incorporated into AlN and TiN in small fraction. It was not detected by XRD but existence of Si was shown by EDS measurement. However, the incorporation of a smaller silicon atom into the lattice of TiAlN (solid-solution hardening) led to creation of a local tensile stress (lattice distortion), which contributes to higher hardness [76]. As a proven that Si incorporated into AlN and TiN is shown that their peak intensified, as presented in Fig above. In 10 min EDAMM, completely Ti₇Al₅Si₁₂ peak disappeared as Ti₂AlN appeared.
Figure 6.7. show the XRD patterns of Ti-Al-Si-N powders produced by EDAMM in different time intervals

6.5 CHN RESULT

Figure 6.8 shows the CHN combustion elemental analyses of Ti-Al-N and Ti-Al-Si-N powders milled for 89.75, 189.92, 330.67, 450 and 560 hours. The average nitrogen concentration varies (in wt%) depending on the milling time. Red line on the figure represents Ti-Al-Si-N and black line is Ti-Al-N system.
Both Al-Si-N and Ti-Al-N show the same trend. Up to 100 hrs concentration of nitrogen is relatively low. It increases at 200th hr to 2.31% for TiAlN and to 2.58%N for TiAlSiN. After that point, nitrogen content increases drastically to 13.91% in TiAlSiN and 10.91%N in TiAlN in 330 hrs of milling. As predicted, rapid fracturing resulted in reducing grain’s size and creation of crystallites. Surfaces are highly reactive towards gas so the nitrogen molecules are absorbed. Moreover, in 300-500 hours range no significant nitrogen did dissolve and its increase reached the level of around 10%. Thus, it can be concluded that longer milling time resulted in a supersaturation of nitrogen in titanium. It was examined that dissolved nitrogen in Ti-Al-Si-N system is by 27% higher than in Ti-Al-N. Extrapolation of both Ti-Al-N and Ti-Al-Si-N curves to significantly longer times above 560 h might suggest that additional nitrogen uptake would be very small for both Ti-Al-N and Ti-Al-Si-N. Comparison of
nitrogen concentration between this work and Chen and Calka’s work are described on Fig 6.9 [77].

![Figure 6.9. Comparison of Nitrogen Concentration between Ti-75 at% Al by Chen et. al and Ti-40 at% Al (This Work)](image)

It is shown that higher energy (HE) of ball-milling has a point above which the increase of nitrogen absorption is not so significant. Higher energy conditions led to rapid increase of the intake in the first 100 hours of milling time. This can be explained, assuming that higher energy allows nitrogen ions to achieve higher velocities what will likely lead to the saturation of particle’s surfaces with nitrogen ions and subsequent diffusion into the bulk of the powder’s particles. Composition of starting powder has small influence what was confirmed by Ogino, who reported that nitriding reaction kinetics for titanium and Ti-Al system in nitrogen atmosphere are a function of the milling conditions [78]. It can be concluded that mechanism of phase formation depends on milling conditions. In the previous work, Chen et al produced Ti-Al-N after milling for 86 hrs by high-energy ball milling using Ti-75 at% Al.
and Ti-25 at% Al as a starting powder. Bhaskar using Ti-10 at% Al as a starting powder obtained Ti-Al-N in just 1 hr [79] using the same equipment. It can be stated that the higher energy level, the faster synthesis of Ti-Al-N compound. On the other hand, low-energy ball milling has advantages such as more homogeneous phases and economical production.

Figure 6.10 shows the average nitrogen concentration in Ti-Al and Ti-Al-Si milled by EDAMM. The red line represents Ti-Al-Si-N and black line is Ti-Al-N compound. It shows different trend that the one shown on Figure 6.8 and has also higher concentration of the nitrogen. After milled by EDAMM for 1 min, nitrogen content was considered equal to 330 hrs milled by PBM. Increase of dissolved nitrogen is 4.8 % in 10 min by EDAMM. The mechanisms of decomposition of nitrogen and subsequent reaction which occurred during conventional high pressure plasma nitriding may be produced from some combination of
decomposition, catalytic dissociation and plasma induced dissociation. Diffusion of highly reactive forms of nitrogen into the metallic structure might also occur, being thermally activated by localized temperature that increased as a result of Joule heating of the elemental molecules generated by the electric arch discharge. The relative contributions of all these factors to reaction in the current series of experiments are unknown. However, the homogeneous distribution of nitrogen in Ti-Al system can be shown on X-ray mapping as presented on Figure 6.13.

6.6 SEM IMAGES

Figure 6.11 (a) is the first stage of premix by ball milling for 1 hr. The powder contains a mixture of random size elemental Ti and Al with the grain size of around 3-10 μm. Figure 6.11 (b) shows Ti-Al-N powder after 330 hrs of milling where its crystal structure disappears and forms spherical agglomerates in the range 0.5 to 5 μm. Furthermore, Figure 6.11 (c) shows Ti-Al-N powder after being milled for 560 hours after which finer particles (＜0.25 μm) could be gained. It is believed that the fracturing process was possible because of longer milling times and dissolution of nitrogen that finally led to obtaining homogeneous Ti(Al,N) supersaturated solid solution.

Figure 6.11(d) shows particles of the powder milled for 560 hours. It underwent annealing process in argon gas for 1 hr at 1200°C, with the speed of 20 °C /min. Structural evolution of the initial state(c) and after annealing(d) is shown. Finer particles disappeared and instead melted structure was obtained, with separated small amount of TiO.
Figure 6.11. Ti-Al-N a) starting powder b) milled for 330 h, c) milled for 560 h, and d) after subjected DTA testing.

Figure 6.12 shows SEM of Ti-Al-Si-N compound as a (a) starting powder- irregular morphology, particle’s size of around 20-45 μm. Figure 6.13 (b) showed polished cross-section powder after premix for 1 h. Till this stage the powder did not completely mix. The cross-section of particles show 3 different colours what indicates the presence of Ti (grey), Al (black) and Si (white).
Figure 6.12. Ti-Al-Si-N a) starting powder, b) cross section polished powder after mixing for 1 h, c) unpolished powder after milling for 330 h, and d) cross-section of c)

Figure 6.12 (c) shows Ti-Al-Si-N after being milled for 330 h. It shows the decrease in particle’s size to 2-5 μm and some agglomerates. Figure 6.12 (d) shows cross-section of Ti-Al-Si-N compound after being milled for 330 h on which 2 different colours can be noticed indicating different compounds: Ti-Al-Si-N (dark grey) and Ti (light grey) what was also confirmed by XRD result.
Figure 6.13. SEM of Ti-Al-Si-N after being milled for 330 hr by BM, followed by 10 min by EDAMM, and their spectra of EDS-spot analysis.

Figure 6.13 shows polished sample of Ti-Al-Si after being milled by PBM for 330 hrs, followed by milling in EDAMM for 10 min. It can be seen that fragmentation occurred. Investigation at this point, by spot analysis gave information about types of phases, that matched also XRD results: nr 1 (dark grey) is TiN, nr 2 (light grey) is Ti$_2$AlN, nr 3 (white region) is AlN, and nr 4 (black region) is Ti$_7$Al$_3$Si$_{12}$. 
6.7 DISCUSSION

This chapter described the applicability of combined Low Energy (LE) Planetary ball milling and EDAMM method for fabrication of TiAlN and TiAlSiN composite. Powders were subsequently sintered to fully compacted, bulk hard metals using spark plasma sintering, then, we measured the hardness of compacted powder. In conventional plasma assisted nitriding processes, the nitrogen intake is only limited to thin surface layer. In this method, combination of conventional planetary ball milling was followed by EDAMM and resulted in more fractured powder and nitrogen present in the entire particle’s volume. In consequence the powder became also more homogeneous.

6.8 CONCLUSION

Present work demonstrates that nanostructured Ti-Al-N and Ti-Al-Si-N were successfully obtained by low energy ball milling followed EDAMM. Furthermore:

1. In low energy ball milling system, dissolution of aluminum, silicon and/or nitrogen in titanium-based results in nanocrystal Ti(Al,N) and Ti(Al,Si,N), starting from 89.75 h and became more homogeneous at 450 h.

2. Powder milled by LE BM (without EDAMM) and annealed at 1200ºC resulted in phase changes to nanocrystalline TiN, AlN and intermetallic Ti3AlN, and TiO

3. Nanocrystalline TiN, AlN and Ti3AlN were successfully formed in only 1 min by EDAMM.
4. This research proved that low energy planetary ball milling offer the economical manufacturing process of homogeneous Ti(Al,N) powder while EDAMM produces finer grain and faster reaction that leads to obtaining nanocomposite.
7. CONCLUSIONS AND RECOMMENDATIONS

7.1. CONCLUSIONS

- In current research some fundamental dependencies of Me-C-N and Me-B-N product formation on processing parameters were established.

- Significant differences in product evolution were obtained when applying AC and DC modes of electrical impulses during EDAMM processing.

- In case of DC mode, plasma was transferred in a sharp arching mode, melting some areas of particles what led to their agglomeration. Higher localized temperature led to rapid diffusion and as a consequence higher level of dissolved nitrogen and new intermetallic Me-C-N and Me-B-N phase were obtained.

- In the case of AC mode, plasma transferred in wider cloudy mode. Thus, the amount of energy transferred to the powder was not high enough to overcome the activation energy required for obtaining new intermetallic phase of Me-C-N and Me-B-N.

- Bigger gaps between electrodes and DC mode induced higher energy activation that can produce new ternary phases.

- This proved that EDAMM is a simple but powerful method which allowed to control the formation of the final product.

- Applicability of EDAMM method on synthesizing Me-C-N and Me-B-N does not require removal of excess reactants or unwanted products. It is due to the fact that reaction is includes almost all of the starting product, especially when using DC mode.
- The application of electric discharge in mechanical milling dramatically enhances reaction rate presumably to high, localised temperatures generated by electric discharge what in consequence speeds up diffusion.
- Nitrogen uptake rate was found to be extremely high for both low (AC mode) and high energy (DC mode) discharge milling, however, higher final nitrogen content was obtained when milling was combined with bigger energy impact altered by the average gap between electrodes.

7.2. RECOMMENDATIONS

The aim of this method is to develop new materials for advanced products that must be explored further in more sophisticated experiments and analysis methods such as studies on temperature influence during milling process. The experiment should be carried on, in controllable temperature. It is thought that EDAMM may be also promising when synthesizing more complex MeCN and MeBN compounds, which combine one or more metallic carbides or nitrides, such as TiN-ZrC, CrC-SiN, etc. Also examination of capability of EDAMM in material’s compacting and sintering has to be investigated thoroughly.
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