MATERIAL GENOMICS: PROCESSING-PROPERTIES-PERFORMANCE MAPS FOR ADVANCED CERAMICS (HAFNIUM CARBIDE)

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1. Introduction

1.1 Materials genomics

A genome is a bunch of information encoded in the language of DNA that fills in as a plan for an organism's development and improvement. The word genome, when applied in non-natural settings, implies a basic structure block toward a bigger reason. This new coordinated plan continuum — consolidating more prominent utilization of processing and information advances combined with propels in portrayal and analysis — will essentially accelerate the time and number of materials sent by supplanting long and expensive experimental investigations with numerical models and computational recreations. Presently is the ideal opportunity to sanction this activity; the registering limit important to accomplish these advances exists and related innovations, for example, nanotechnology and biotechnology have developed to empower us to gain incredible ground in decreasing chance to advertise at an exceptionally ease.

Different global elements have perceived these issues and various far off nations have just set out on projects to address them. The National Research Council of the National Academies of Sciences, in its report on Integrated Computational Materials Engineering, portrays the likely result: Integrating materials computational instruments and information with modern computational and investigative apparatuses effectively being used in designing fields… [promises] to abbreviate the materials improvement cycle from its flow 10-20 years to 2 or 3 years. While it is hard to envision the genuine decrease being developed time that will result from this activity, we will likely accomplish a period decrease of more noteworthy than 50%.

1.2 Analogy with DNA

Deoxyribonucleic corrosive (DNA) is one of the most notable biomolecules because of its significant function as the genetic information transporter for every single living organism. Basically, it is a biopolymer (polynucleotide) contained various monomers called nucleotides (Vo-Dinh, 2017). Every nucleotide includes a phosphate gathering, a sugar called deoxyribose, and one of the four nitrogen-containing nucleobases, to be specific, cytosine (C), guanine (G), adenine (A), or thymine (T). The phosphate gathering and deoxyribose structure the foundation of the DNA atom, wherein they are covalently binded through 3', 5' -phosphodiester bonds. Typically, a solitary line of such polynucleotides is known as a solitary abandoned DNA (ssDNA).

Two ssDNAs can frame the popular twofold helix structure through Watson-Crick base blending, in which the nucleobases on one strand tie to their integral bases (A to T, C to G) on the other strand by means of hydrogen bonds [5], as appeared in Fig. 1.1. The two integral ssDNAs in a helix are arranged in an enemy of equal design, implying that the 3', 5' - phosphodiester obligations of them run in inverse ways. Such duplex is known as a twofold abandoned DNA (dsDNA) particle (Baltz, 2018). Other than the hydrogen bonds, the base-stacking connections, i.e., dipole-dipole and van der Waals cooperations between the adjoining bases, additionally add to the soundness of the dsDNA atom.

Double-abandoned DNA can frame different helical structures, specifically A-DNA, BDNA and Z-DNA. In living organisms the most widely recognized type of dsDNA is B-DNA, which embrace the Watson-Crick base matching and is a right-gave helix with 2 nm breadth, generally 10.5 bases per helical turn and 0.34 nm separation between neighboring bases, as appeared in Fig. 1.1b. Contrasted and B-DNA, A-DNA is a thicker right-gave duplex with a more limited separation between the base sets. It happens when a B-DNA is dried out just as in RNA-DNA and RNA-RNA duplexes (Jablonka*et al.* 2020).

1.3 Discussion with size

Because of its vigour, nanometer measurement, and in particular, the sub-atomic acknowledgment because of Watson-Crick base blending, DNA particle is one of the most encouraging contenders for base up self-get together. Empowered by the progression of atomic biotechnology, e.g., subjective grouping oligonucleotide combination, polymerase chain response (PCR) strategy for enhancement, and different compounds for ligation, extracting and so on, an entire field alluded as DNA nanotechnology has been committed to utilizing DNA particles as building material for creation of nanoscale gadgets (Orlov and Baranova, 2020). Despite the fact that there exist many organic applications, the basic properties and programmable self-get together of DNA instead of its genetic information are in the focal point of the investigations.

The start of the field is regularly ascribed to Ned Seeman's proposition to utilize DNA particles to shape an unbending cross section to outline proteins, which are difficult to solidify for crystallography [9]. After over 30 years of advancement, there is a plenty of techniques to program and assemble DNA nanostructures and the potential applications have been extended to different fields in science, plasmonics and sub-atomic gadgets. In this segment, the current DNA self-gathered structure themes and the latest thing of their applications would be quickly looked into (Springer *et al.* 2018).

1.4 Genomic Sequencing

Genome sequencing gives fundamental information about structure of genetic information encoded in atomic DNA. Arrangement of nucleotides in DNA chain stores is next to other people, information about succession of amino acids in proteins. Consequently, accessibility of top-notch reference arrangement could hugy affect crop improvement. It likewise empowers phylogenetic investigation, investigation of transformative history, practical examination of protein-coding genes, genetic change, and so forth The recognition of genetic variety, ID of genes and quantitative characteristic loci (QTLs) and expectation of aggregates from genotypes will consistently be a significant portion of plant reproducing (Varshney et al., 2009). Cutting edge sequencing and bioinformatic information handling are advancements that could rearrange, accelerate and decline the expense of these methods.

Bread wheat Bread wheat (Triticumaestivum) is monocot grass species having a place with Poaceae family. It is allohexaploid species (2n=6x=42), which implies that the genome was made up from three fundamentally the same as subgenomes that come from three diploid species (AA=Triticumurartu, BB=Aegilopsspeltoides, DD=Aegilopstauschii). The basic predecessor for all diploid species arose 2.5 – 4.5 million years back (Huang et al., 2003). The primary hybridization between Triticumurartu and Aegilopsspeltoides happened roughly 0.5 million years back (Dvorák and Zhang, 1990) and prompted tetraploid emmer wheat (AABB=Triticumturgidum). Hexaploid bread wheat (AABBDD) emerged from the second hybridization between Triticumturgidum and Aegilopstauschii genomes around 10,000 years back.

1.5 Advance Ceramic processing Analysis

Advanced ceramic processing is categorised in various methods in which gelation is one of essential ways with presence of two parallel reactions into it. Traditional form of ceramic includes several steps such as-

- Pressing
- Plastic forming
- Slip, followed by tape casting

- Sintering
- Firing

Polymerisation of FA and sol-gel reaction between "ZTB and TEOS" is useful for managing compatibility in moieties. After carbonization process, yielding properties of carbon in ceramics are activated with prior susceptibility (Sairam*et al.* 2016). Aim of this process to prepare low density, followed by high porous substance in ceramic formation process. Preparation of a hybrid solution with organic-inorganic salutation is necessary to incorporate polymerization process of FA and sol-gel process as well. After that, solvent was removed from ambient drying temperature to gain hybrid gel with maintenance of all properties. Involvement of "in-situ polycondensation", FA plays an essential role to become a monomer of that process and facilitates progression of that process (Zhang *et al.* 2017). This entire process is useful for preparation of simple ceramics in processing units rather than preparing complex ceramics. Several other operations, including colloidal processing, can be included for preparation of complex ceramics from fine powders. Therefore, advanced processing of ceramics can be a complex process to work with hafnium carbide powder and deal with them at a higher temperature.

Carbides and nitrides of hafnium are connected with a reservoir of refractory material to be predicted as higher-melting points. Therefore, these components are essential for processing of ceramic culture. In this process, NaCl-type rock salt shares higher thermal and conductivity in ceramic processing (Ushakov*et al.* 2019). Colloidal processing is helpful for preparation of both micro and macro ceramic structure through use of dry processing. With help of colloidal processing, shaping and controlling of ceramics can be easier to produce more complex and function-able ceramic system. Besides colloidal processing, tape casting can be used for production of thin ceramics. "Polymer drive ceramics" (PDCs) are manufactured with help of this process by involvement of wet-shaping process and several polymer structures in process level. This process is advantageous in ceramic processing because it conventionally replaces raw materials with silicon-based polymers such as polysiloxanes, followed by polysilazanes (Zhou *et al.* 2017). In this process, PCPs are treated within lower temperature with a contradictory way of sintering process for preparation of ceramics. With production of polymeric precursors, hybrids, followed by ceramic composites are obtained.

1.6 Composition of Hafnium Carbide

Hafnium and carbide are composed together at melting temperature of 3890 °C to create hafnium carbon. This compound has a resistible chemical background to exist as one of essential refractory compounds. In processing of hafnium carbide, oxidation of hafnium carbide (HfC) begins with 430 °C (Zhang *et al.* 2017). Carbon deficiency is relatable in this compound; therefore, hafnium carbide is expressed with HfCx where X value lies between 05 to 1.0. Therefore, this composition is present as rock salt with a composition of a cubic crystal. Powder of hafnium carbide can be yielded with reduction in hafnium oxide at temperature of 1800 to 2000 °C. Pure coating of HfC can be obtained from chemical vaporization from gas mixture; therefore, methane mixture is used to vaporize HfC and hydrogen as well (Wang *et al.* 2017). In this scenario, HfC is categorised with ultra-high temperature ceramics and appropriate for aerospace application with acquiring high temperature.

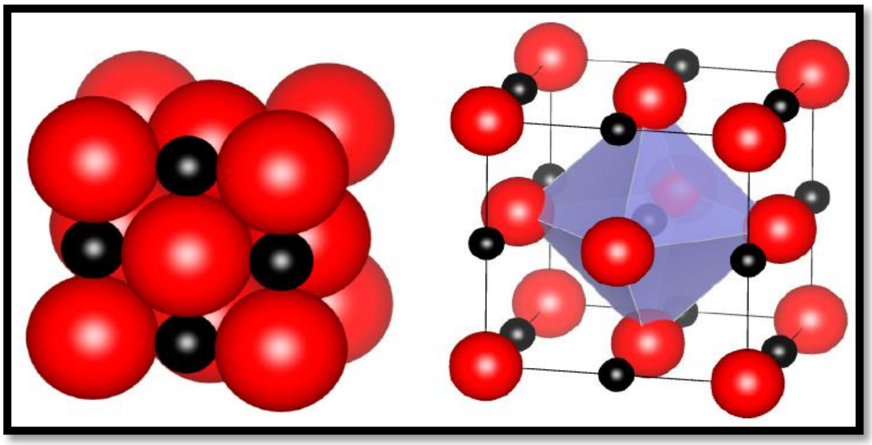

Figure 1.1: Structure of rock salt

(Source: Ushakov*et al.* 2019)

Hypersonic aerospace vehicles, followed by scramjet propulsion, are suitable for unison HfC with their high-temperature structural susceptibility. Hafnium carbide has a superior performance level for ablation activities to enrich their high melting temperature and coat ceramics with better grip. Electrophoretic deposition (EPD) establishes two electrodes within colloidal solutions for preparation of ceramics. Hafnium carbide has one molecule of hafnium and four molecules of chlorine; therefore, IUPAC name is marked as ***hafnium (4+) tetracarbon***(Wang *et al.* 2017)**.** Ceramic formation needs HfC as a primary agent to hold structure of ceramics with polymerisation of both inorganic, followed by organic meiotic. Various forms are present in hafnium carbide such as-

- Granules
- Pellets
- Pieces
- Sputtering target
- Ingot

Due to presence of higher melting temperature at preparation level, it can be suitable for HfC to be applicable through high-temperature application and monoisotopic mass of 191.946549 (Wang *et al.* 2017).

1.7 Analysis of composites of Hafnium carbide

In previous days, silicon carbide is used in air-based vehicles such as "rocket engine nozzles" and "hypersonic air-breathing jet engines". However, hafnium carbide made up of hafnium and carbon is becoming an alternative for ceramic processing with involvement of higher temperature. This HfC is ultra-refractory material with characterisation of higher melting point and phase stability as well. Another essential composite property is stability in chemical level and efficiency at mechanical level as well. Both hafnium and HfC are resistant to corrosion, followed by thermal shock. HfC is composed of-

- 18.55 wt% of hafnium
- 6.24 wt% of carbon (Rueschhoff*et al.* 2020)
- 75.21 wt% of Ta

Density of powder granules is 0.02 m2/g and particles are very much lesser with 200 µm; although, carbon black has a surface area of 15 m2/g and particle size is 0.2 micron. Melting point and boiling point of hafnium is 2150 °C and 5400 °C respectively. For manufacturing of HfC, the needed density of hafnium is 13.1 g/cm3. Along with carbon black, hafnium carbide is present as a higher surface area in presence of tinting strength. Following this, carbon can be used as higher conductive material with greater jetness. Higher surface area is advantageous for ceramic processing because weather ability is increased with greater viscosity level; therefore, requirement of dispersion energy is greater (Patra*et al.* 2016). Composites of HfC include the presence of carbon black into it because it has an oxidised surface with segment wetting and higher level of dispersion. In this scenario, particle size of carbon is a determining factor for blackness and dispensability. The more the structure size is, the more the dispensability because larger structures of carbon exhibit conductivity level.

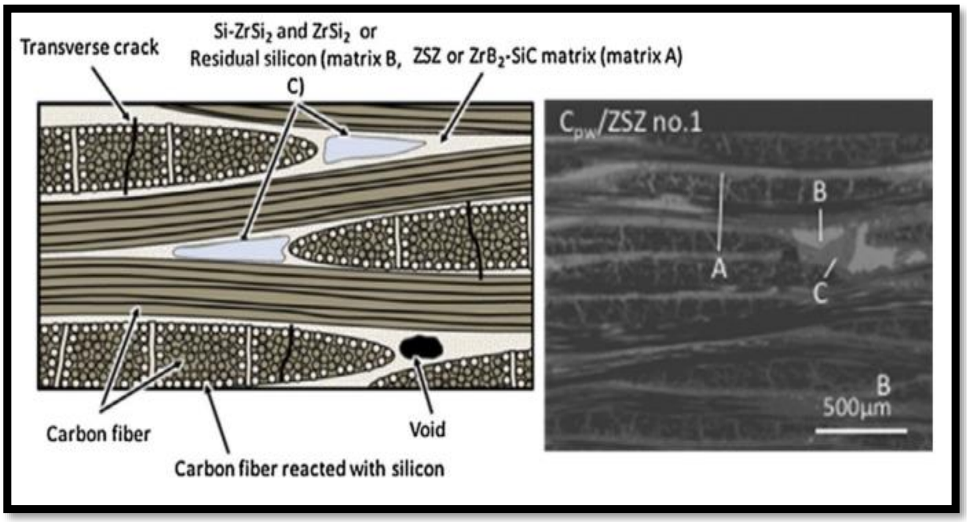

Figure 1.2: Microstructure of ceramic composites

(Source: Rueschhoff*et al.* 2020)

1.8 Comparison of different properties

Effective method for manufacturing of Hafnium Carbide (HfC) become one most in researched topic in present context, especially in industrial research purposes. One of common method for manufacturing of Hafnium Carbides is "Single-Phase Binary HfC" production; however, due to provision of long-term sintering is recommended for effective diffusion process, this process is regarded as difficult and time-consuming in today's era (Kurbatkina*et al.* 2018). Due to this long period of sintering formation of TaC-HfC cannot be formed. It is evident that refractory carbide can be produced by using carbothermal reduction process, in which temperature for production kept within 1800 to 2500 °C. This carbothermal process is then followed by thermodynamic stimulation into Ta_2O_5-7_C system (Li *et al.* 2020).

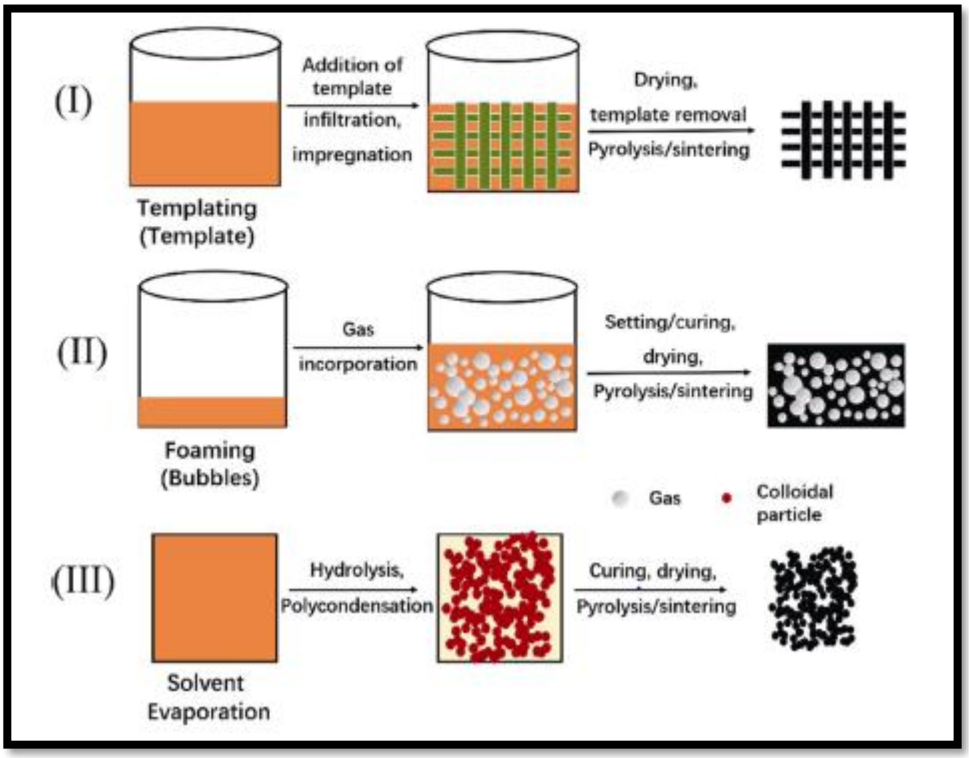

Figure 1.3: Sol-gel; Method of HfC manufacturing

(Source: Li *et al.* 2020)

Process significantly indicates that formation of HfC can be occulted within pressure and temperature ranges from 1/100000 MPa and 727 °C, respectively (Kurbatkina*et al.* 2018). Modern method for HfC manufacturing focuses towards method of hybridisation. Hybridisation process starts with nano-crystalline carbides synthesis, depending on which composition of end HfC products vary widely. This stage is followed by precursor identification and hydrolysis. A carbon source is used in the form of polymeric carbon for gel formation; which in turn undergoes drying process for improved thermal penetration. As stated by Franks *et al.* (2017), this overall hybridisation process for HfC manufacturing results in formation of highly dispersed metal oxide-carbon mixture, which followed by electrolyte decomposition process within a fused bath of chlorides for ultimate formation of HfC.

Formation of HfC by using high melting temperature can affect quality of product, which in turn increases risk for development of non-utility of metallurgy power in single-phase state. Possible reason behind this is difference in diffusion co-efficient rates and chemical activities of metals within carbide mixtures. Therefore, development of "***Self-Propagating High-***

Temperature Synthesis (SHS)" is found to be effective for manufacturing of refractory metal-carbides. SHS serves as an efficient process for HfC fabrication due to its cost-effectiveness, eco-friendliness, and simplicity (Kurbatkina*et al.* 2018). Based on research of Hotza*et al.* (2019), it is evident that Tape Casting is used from lasts 20 years for effective manufacturing of "polymer-derived ceramics (PDCs)". These are utilised as precursors or binders in conventional methodologies of ceramic production.

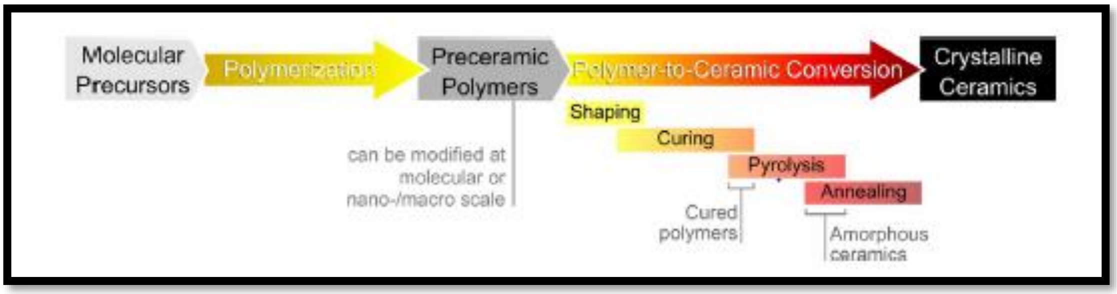

Figure 1.4: Process of Tape Casting

(Source: Hotza*et al.* 2019)

Nitrogenous atmosphere is highly evident for development of effective HfC manufacturing process. SHS method is highly beneficial for HfC ceramic production with a provision of lack of porosity within the product. Along with carbon diffusion in solid-phase, the carbon and tantalum are transferred to surface of product by utilising both Carbon Di-oxide (CO_2) and Carbon Monoxide (CO). This transformation is elevated and terminates by bell-boudoir reaction process (Jenkins and Salem, 2017). Moreover, provisions of steady combustion and mechanical activation for development of different chemical and structural changes in HfC compounds are subjected to further investigation. Therefore, it is clear that effectiveness of different methodologies for production of HfC exerts different properties within end product.

2. Literature Review

2.1 Examples of Advance Ceramic processing

Advanced ceramicprocessing has gain immense attention in recent decades, due to availability of certain properties, such as high corrosion resistance, high tolerance of tear and wear, temperature, as well as refractoriness. Advanced Ceramic is nothing; however, advancement upon traditional Ceramic in industrial purposes. Application of advanced scientific technologies, new material combinations, is efficiently used for development of new variation of ceramics with advanced properties, encountered as advanced Ceramic. Due to presence of these properties, advance Ceramic is particularly withstood with different processing techniques, which most of time fail to develop adequate shape of end material. According to Kiss and Panić (2019), Electro-Discharge Machining is one effective method for advance ceramic processing and shaping, as this method significantly contributes towards disintegration of complex geometric structure of ceramics.

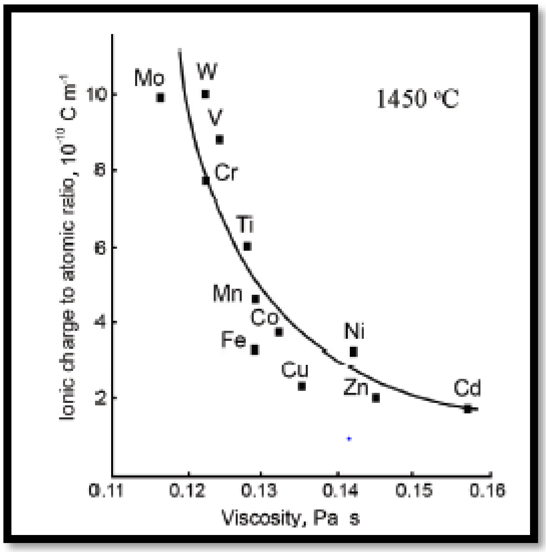

Figure 2.1: Ionic Charge and velocity

(Source: Kiss and Panić, 2019)

In this process, carbon layer with copper tools is utilised as an assistant and main electrodes, respectively. Due to positive attraction property of electrodes, this polarity significantly utilised for production of conductive layer on insulating surface of ceramic workpiece. This results in formation of electrically conductive thick layer of Ceramic via application of powdered electrodes (Kiss and Panić, 2019). Research of Wang *et al.* (2017) suggested this electrolysis and conduction method is useful for development of effective machining of ceramic surface; therefore, aids in processing and production of end material. Metal oxides, such as ZrO2 are used in electrolyte trunk that reacted with dielectric media; resulting in formation of conductive layer over ceramic piece (Li *et al.* 2020).

Among various methods that can be adapted for processing of advanced ceramics, "Laser Shock Processing (LSP)" is found to be most effective one (Wang *et al.* 2017). Research findings of different journals on LSP suggest that LSP is effectively utilised for formulation of polycrystalline ceramic compounds, including α-Al_2O_3. LSP serves X-ray like characterisations, which in turn affiliated with formation of residual pressure that can be expanded up to 12.2 nm (Sairam*et al.* 2016). Adaptation of LSP methodology for processing of advanced ceramics makes this material particularly resistance to indentation cracking. Innovative methodologies focus towards development and adaptation of "High-Energy Laser Pulses" as processing technology to improve irritation level of surface material.

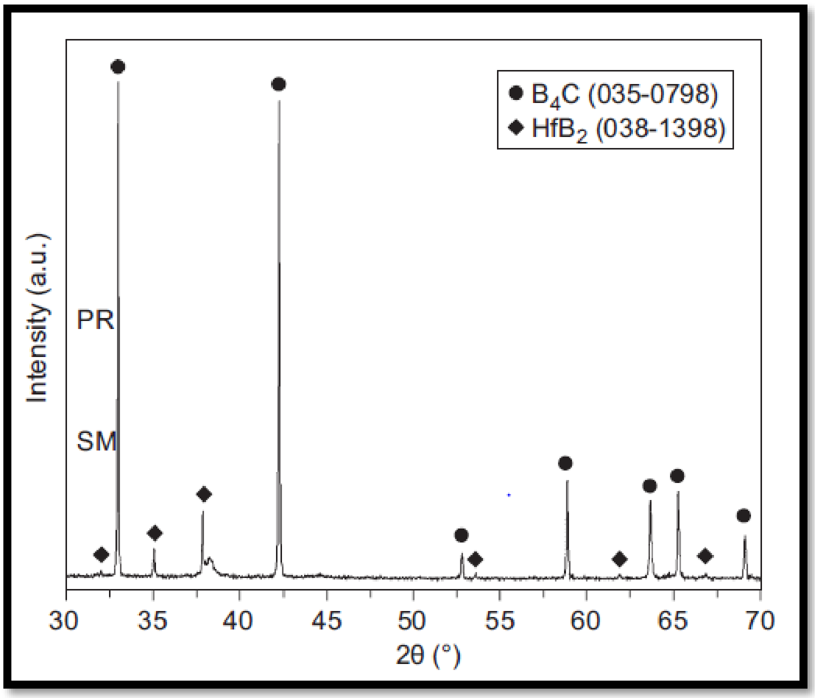

Figure 2.2: X-ray Diffraction of Hafnium compound

(Source: Sairam*et al.* 2016)

Plasma expansion and exploring of compressive Residual Pressures is effective in formation of Shack wave, which in turn effective to formulate high penetration capabilities within plasma of material; therefore, leads to development of compressive residual stresses (Ushakov*et al.* 2019). Using of different combustion calorimetric in oxygen bomb is effective for analysis Hf carbide formation effectively. Shock wave production, in turn, effective for development of sacrificial coating of advance ceramic that is leading towards production of desirable material from product that gets heated. Understanding ofmelting capabilities of atomic carbon and hafnium carbides are effective for acknowledging ability of shack wave in processing and production criteria.

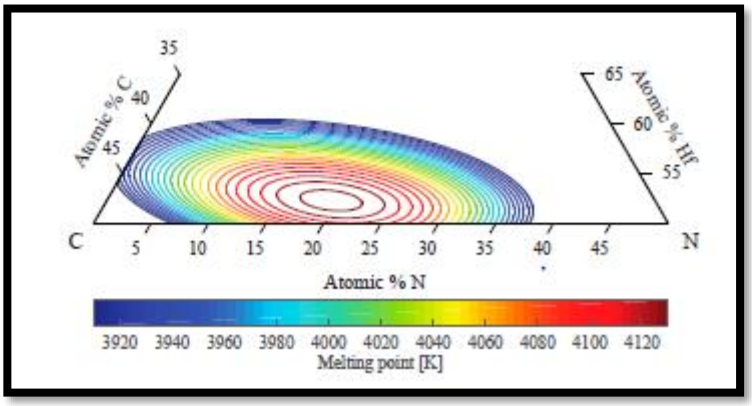

Figure 2.3: Melting Point of atomic C and Hf

(Source: Ushakov*et al.* 2019)

2.2 Colloidal processing for Ceramic production

Colloidal processing is one of fundamental processing method associated with effective development of Ceramic with improved properties, such as more durability, reliability, and functionality of end material. Colloidal method, in comparison with dry processing techniques for ceramic processing, results in production of practice compactness with effective controlling over the operation. This theory of utilising colloidal process for production of ceramics was developed as early as 1960 to 1970s. Colloidal processing from its early days is effectively counteracting with particle interaction within colloidal mixture in the presence of Silicon Carbides (SiC) and different forms of oxides (Kumari, 2016).

According to research production of finer ceramic grains with provision of minimum porosity, higher and uniform density of finer powder production is highly necessary, which in turn effectively achieved by adaptation of colloidal processing (Kumari, 2016). Colloidal principle is depending on suspension rheology along with chemistry affiliated with surface of product, which helps in production of finer ceramic powder from advanced ceramics. Colloidal process helps in aggregation of ceramic particles; along with developing reinforcement properties for formation of complex ceramic shapes with higher densities in green bodies (Wang *et al.* 2017). Colloidal technique is effective in conversion of nano-materials of carbons into ceramic matrices.

A number of methodologies of colloidal process are relevant towards industrialist; however, choice of colloidal process is crucial and significant to type and complexity of Ceramic. In majority of manufacturing industry, concentrated and thick colloidal gel is used for production of ceramics. Such colloidal gel gets extruded in non-wetting oil bath; therefore effective for prevention of product to become dry (Franks *et al.* 2017). This process, therefore allow the formation of finer ceramic properties with presence of "Clogging if Nozzle". Colloidal processing helps in maintenance of effective near-net shaping capabilities of ceramic product; therefore, effectively benefited production of micro-porous structure of ceramics compounds. Consolidation and locking-in structure of ceramic design is also affiliated through colloidal processing. As per the requirement of industrial need; this method is effective for development and accommodation of salts, macromolecules, air bubbles, droplets, solvents, and polymers with ceramic compound to improve properties and quality of desirable end material (Franks *et al.* 2017).

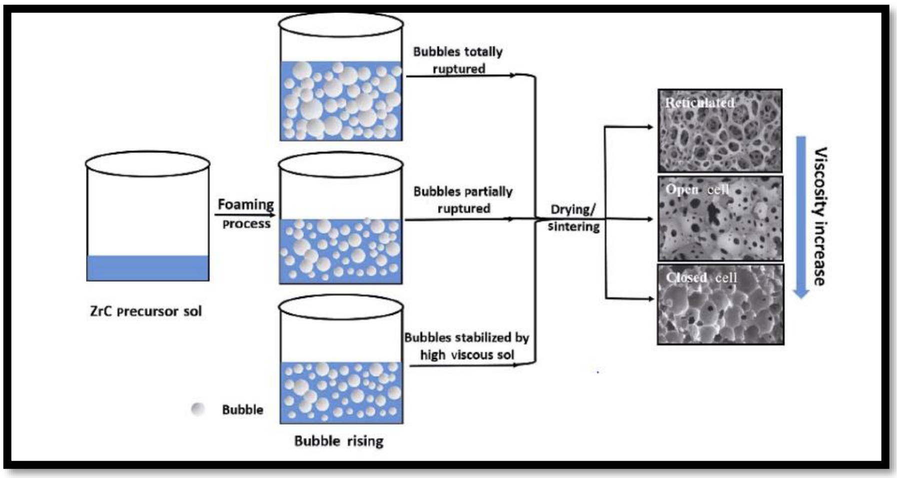

Figure 2.4: Bubble Growth and Stabilisation Process

(Source: Li *et al.* 2020)

2.3 Colloidal processing for Hafnium Carbide production

Hafnium Carbide is characterised as one of most potential Ceramic with efficiently higher melting point; therefore, classified as Ultra-High-Temperature Ceramics (UHTCs). HfC exerts superior ablation properties with high melting point; hence, subjected to high utility in different industries. Colloidal processing, such as Electrophoretic Deposition (EPD) is highly relevant for applying different UHTCMS hybridisation processes. This process is developed through provision of electrophoresis (Zhou *et al.* 2017). Two relevant electrodes are immersing into colloidal gel with presence of Ultra-high temperature that catalyses separation of ions; therefore, facilities coating process. During this process, stainless steels are fundamentally utilised as electrode, which in turn coated with thick layer of conductive material to carryout electrophoresis (Zhou *et al.* 2017).

Mechanical property can be determined and for that high-density shapes required. Research must use analysis technique such as TEM, EDS and XRD. Blockage in nozzle is an issue that should be mitigated. Two of the most important properties of colloidal paste are better solid content as well as better viscoelastic response. Fused deposition can be done through ceramic blend. Entire process is possible to be done through constant rate as polymer filament is used. High temperature helps of melts metal so that organic fluid can be filled through heated liquefier. Low temperature of colloidal solution can extrude for better production of Hafnium carbide ceramic.

Due to presence of direct current and UHT in electrical field, rapid movement of charged particles are developed towards working electrodes; therefore, facilitated development of thick layer of coating. Ceramic powder as raw material along with colloidal processing of electrophoresis technique is highly utilised for obtaining UHTCs, such as HfC. Methods, such as foaming, freezing, gelling can be utilised for the same purpose as well (Li *et al.* 2020). Majority of colloidal processing is affiliated with application of less pressure and sintering along with temperature ranges from 1000 to 2500 °C. Due to provision of mechanical strength, formation of colloidal practices is eventually high and more resistant.

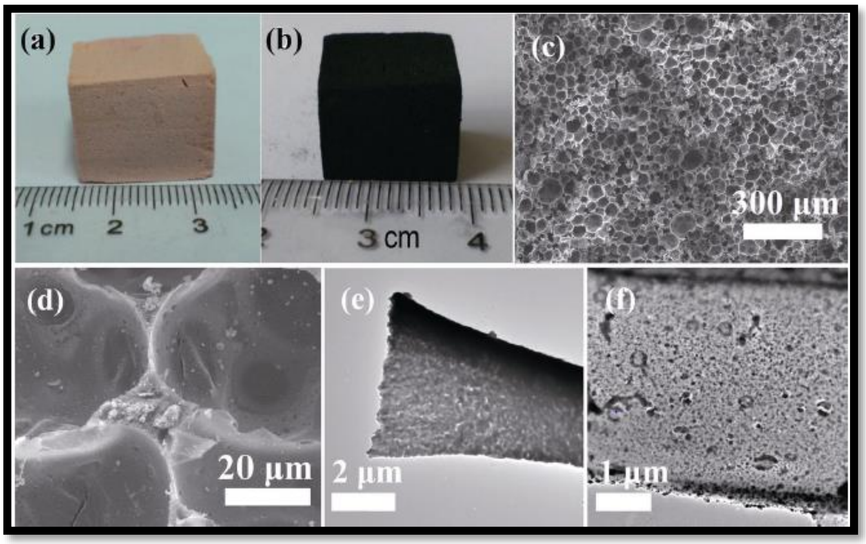

Figure 2.5: Green body of Formed ceramics

(Source: Li *et al.* 2020)

However, likewise, all practical technologies of formation of certain products colloidal process of HfC production are also affiliated with a major risk, which in formation or larger gains due to application of high temperature during processing. According to Li *et al.* (2017), foaming method is found to be one of best method for formation of HfC. Foaming method includes a process that focuses on formation of bubble stabilisation within wet foam; therefore, significantly contributes to effective and enhanced porous structure of HfC end product. According to Patra*et al.* (2016), the incorporation of volatile agents and air within colloidal suspension is effective for formation of porous structure within HfC molecules.

Colloidal Mixture for this process is developed through using mechanical techniques, while n case of bubble stabilisation process is developed through cross-linkage techniques of gelation process. Generally, consolidated forms are heated at higher temperature for development of desirable porosity within the ceramic compounds. Different forms are utilised for effective manufacturing of porous UHTCs, such as HfC (Rueschhoff*et al.* 2020). For instances, a mixture of phenolic resin and zirconia solution is utilised for development of efficient HfC foams in laboratories.

2.4 Various oxidation properties of colloidal production

Properties of ceramic products are most effectively defined in accordance with properties they are exerting into environment. It is evident that different processing products serve different characteristics as compared to original raw material. Chances in properties of end products are mostly found in term of hardness, resistant capabilities, strengths, formation time while utilising colloidal processing. Different temperatures are used for improved management of colloidal products. This temperature ranges from room temperature up to 1400°C. It is evident from different research that oxidation properties of both raw and end material significantly affiliates with capabilities and characterisation of processing products.

According to Kiss and Panić (2019), oxidation capacity of ceramic material can be delayed for treating the elements at more than 750°C. Majority of research suggested that pure HfC is formulated with a theoretical density of 12.21 gm/cm^{3}aswell as a densification level up to 98.5%. According to research, majority of articles are accounting for a particle size of 2.3 to 3.0 micrometres (Zhang *et al.* 2017). On the other than research also suggests that oxidation resistance of purely oxidised HfC is higher as compared to untreated ones. According to serves research, it is estimated that integrity of HfC been after oxidation process can results in break downs due to improper maintenance of processing temperature and pressures.

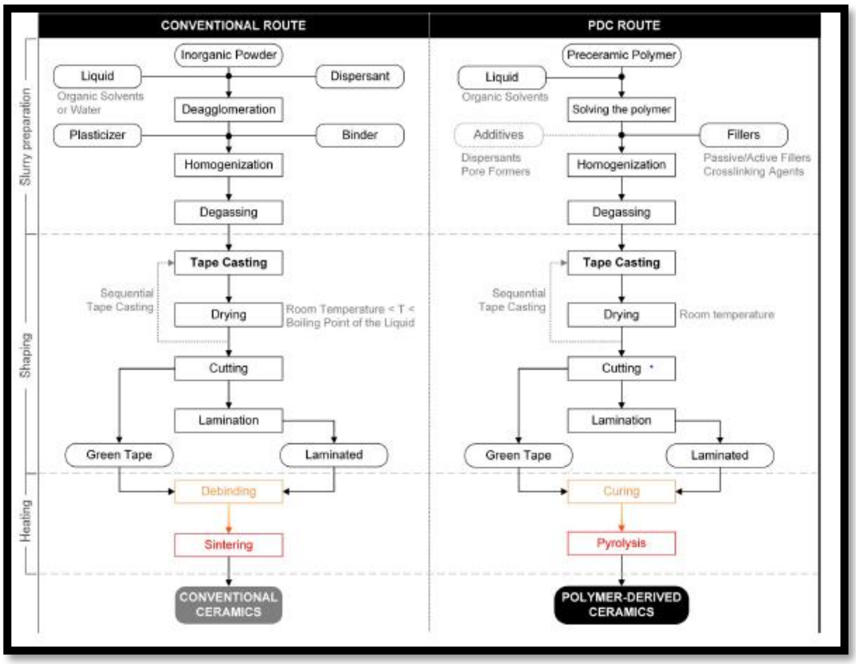

Figure 2.6: Conventional and PDC Methods

(Source: Hotza*et al.* 2019)

For example, in colloidal sample solution of T80H2O, large amount of powdery substances with several solid broken pieces are identified, which indicates that oxidised HfC also undergoes breakdown if not produced effectively. On other hand, TaC shows fewer resistance properties towards oxidation process as compared to HfC. According to Zhang *et al.* (2017), it is observed that T50H50 does not undergo delamination and spallation; therefore, indicating high mechanical integrity to product. Oxidation properties also varied depending on temperature used during colloidal process. For example, research developed by Jenkins and Salem (2017), indicates that oxidation temperature for HfC is started around 800 °C; whereas temperature required starting oxidation process for TaC ranges from 750 °C. Therefore, it is understood that effective knowledge related to temperature used in different stages of processing and production is highly relevant for manufacturing of HfC wit desirable characteristics.

2.5 Colloidal Processing for Hafnium Carbide Ceramic production

Colloidal processes are most effective processes for production and processing of HfC; however, developed products indicates that obtaining of desirable density and characteristics are complex and difficult. Henceforth, modern technologies are focuses on development of adequate responsiveness to improve structural integrity of HfC through provision of additives in colloidal solution for the formation of either paste of slurry of raw material. These additives are effective for formation of Green bodies with higher density in contrast to process of drying packaging of powders (Franks *et al.* 2017). On of example of additives in processing and production process of HfC is Direct Ink Writing. This is essentially attributed with Robocasting process (Kiss and Panić, 2019).

In colloidal process, several ways are there that responsible for Hafnium production. In this process, different types of technique can be involved in obtaining product. Robocasting is involved in manufacturing additives for freeze extrusion. It is possible to have 50 per cent to 65 per cent colloidal slurry for the Robocasting process (Kiss and Panić, 2019). Apart from that, it has been observed that structural integrity must be maintained in the concerned process as it can help for integrity. Another essential factor of the entire process is nozzle that is responsible for repositioning slurry. Different types of concentrated gels are available for extruding oil bath.

Polymer as natural, synthetic substance that huge bigger molecule, used for longer shelf life. This type of substance has lower viscosity so that it can be applied in the implementation process (Franks *et al.* 2017). Another process is colloidal technique that can be used for extrusion of fabrication. Research needs to mitigate formation of ice crystal. More than one process is there including addition of glycerol. Cryoprotectant is included in this process to make it better. Hafnium carbide can be found in disks shapes, and its effect can be observed through hot pressing variables. Time, pressure, as well as temperature, can work as hot pressuring variable. This is effective for maintenance of rheological structure and integrity of end material.

Fused Diffusion techniques are significantly utilised for extrusion of colloidal material affiliated with polymer filaments. This can occur through the evaluation of ceramic blending process within a constraint rate. During this process, heating and melting of liquefiable material help in melting of raw precursor material as well; therefore, effectively contributes to development of particle, which is in turn filled with organic fluids. Moreover, utilisation of extrusion results in the development of solidification on coiling; therefore, effective in controlling ceramic deformations as well. Therefore, it is highly evident that effective management of colloidal process with provision of additive incorporation is effective for Hafnium Carbide Ceramic production.

2.6 Brief on LR findings

2.6.1 Year and Numbers of Publications

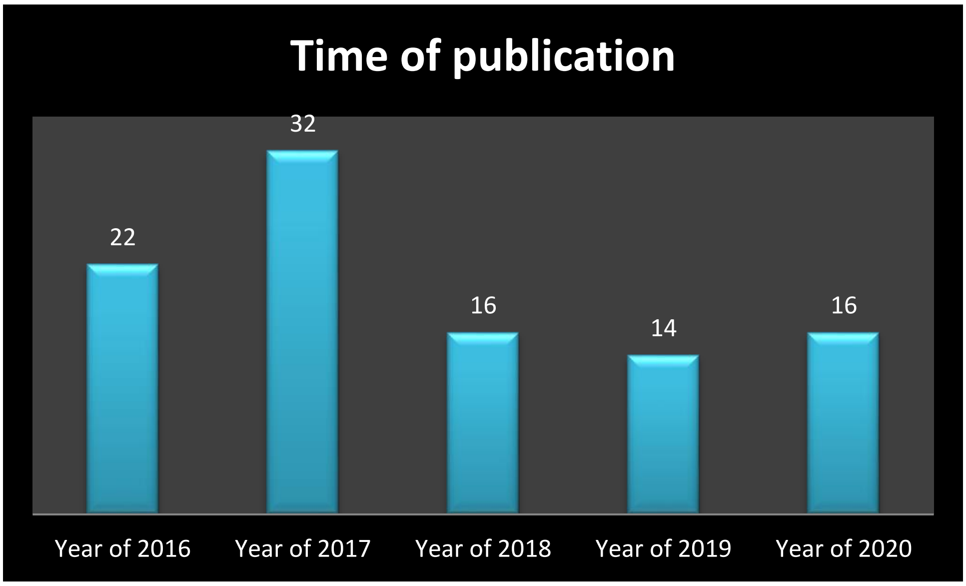

Figure 2.7: Year and Numbers of Publications

It is evident from results of literature review that interest towards ceramic manufacturing and HfC production is developed in previous decades; however, due to inclusion criteria of this research 50 article published within 2016-2020 are taken into account. Results suggest that majority of article (32%) are published in 2017, followed by 22%, 16%, and 14% in 2016, 2018, 2020, and 2019, respectively.

2.6.2 Temperatures used during Manufacturing

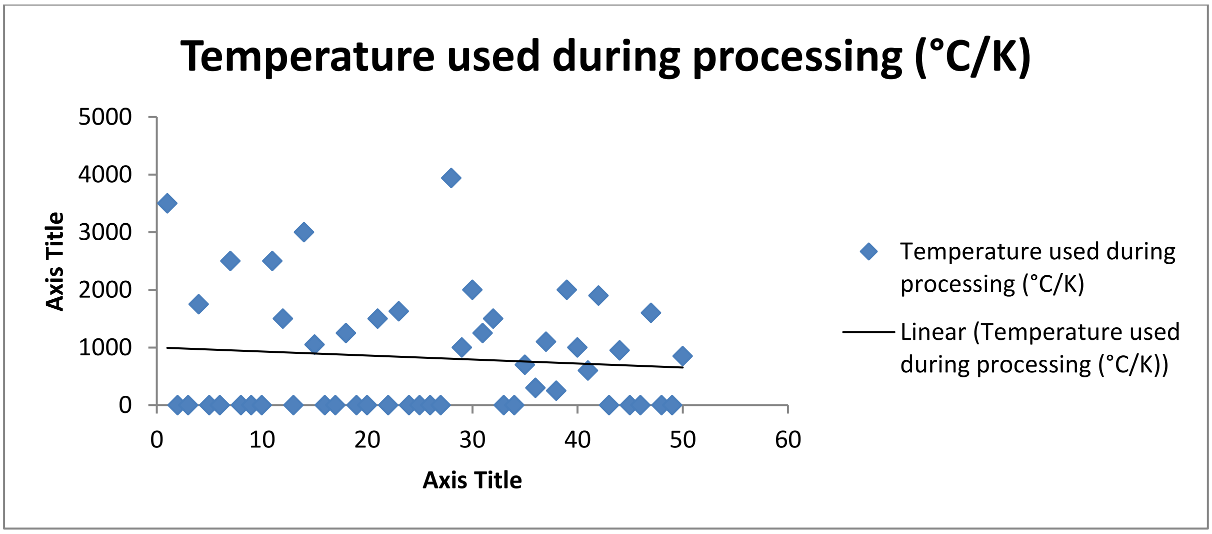

Figure 2.8: Temperatures used during Manufacturing

Results developed from literature review suggest that majority of publication or manufacturing process focuses on temperature range of 1001-2000 °C (65%). The range of 250-1000 ° C, 3001-4000 ° C, and 4001-5000 ° C, respectively follows this. Indicating that temperature range from 500-2000°C is adequate for processing and production of HfC.

2.6.3 Molecular weight

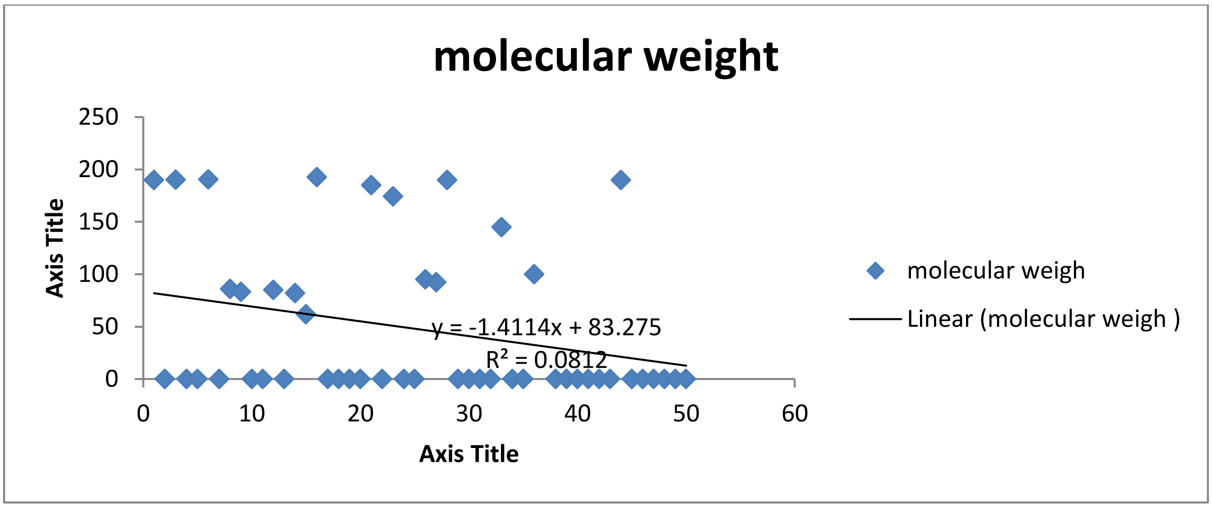

Figure 2.9: Molecular weight

Literature review focuses on time holding aspects during processing of HfC as well. Finding of 50 articles suggested holding time is highly and significantly depends on temperature ranged used during formulation of HfC compounds. About 54% and 34% of journals suggest that holding time ranges from 1 to 120 minutes. However, some of article are accounted for some seconds up 10 hours of holding time (4%).

2.6.4 Density range of final product

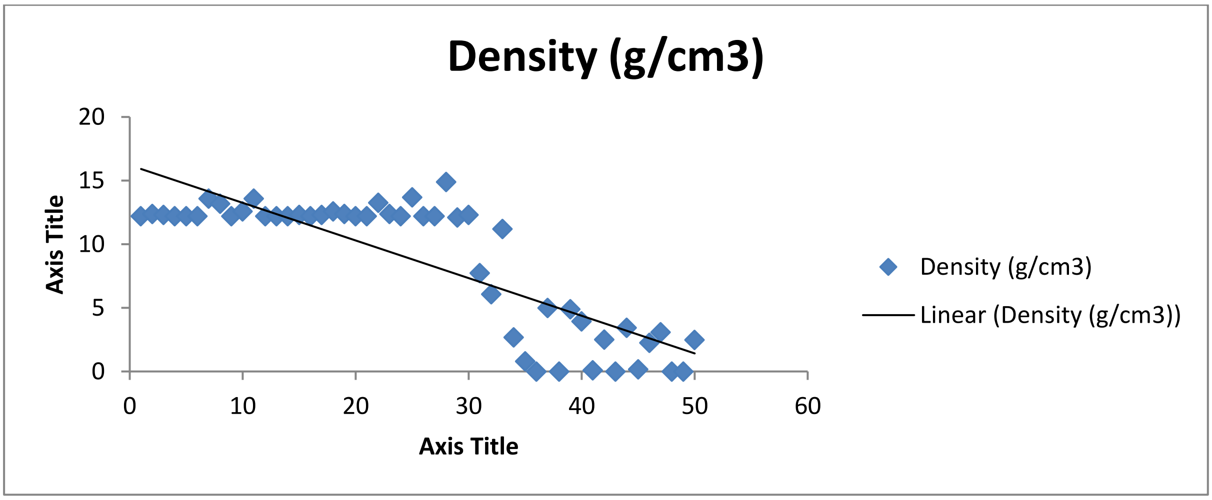

Figure 2.10: Density range of final product

Understanding end product density helps in determination of quality of product. Majority of journals suggested that 64% of end product density ranges from 10 to 20 g/cm^3, while 26% is accounting for density less than 10 g/cm^3. Majority articles shows to achieve density range that is similar to that of actual density of HfC (12.21 g/cm^3). Here oxidation temperature is necessary to understand, which is as follows:

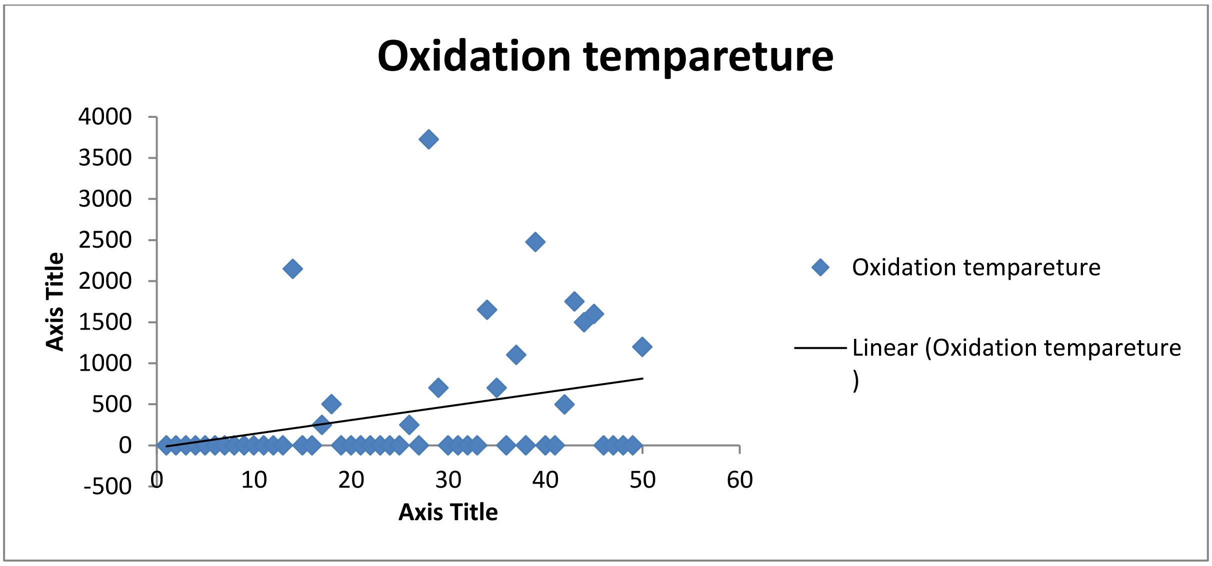

Figure 2.10: Oxidation temperature

3. Methodology

Research on Material Genomics and properties, performance and processing analysis is based on secondary process that is effective and relevant information on topic are gather from articles and journals that are previously available. Primarily, Google Scholar as well as ProQuest, is used for identifying and analysing relevant information related to research topic. Certain criteria have followed to research and identify relevant articles, including

- Journals age are not more than five years that is all journals are published within 2016-2020
- All journals publish and provide information in English language
- Journals are primary focuses on different methods of ceramic as well as hafnium processing with their relevant application in different fields
- Journals provide adequate information regarding physical properties, processing temperature and time

4. Discussion of findings

Hafnium Carbide (HfC) in recent era of increased industrialisation presented as one of potential candidate of "Ultra High-Temperature Ceramics (UHTCs)"; therefore, significantly gaining interest in both research and industrial field (Liang *et al.* 2020). UHTCs serve as potentially protected material in areas that required higher tempter for carrying out an operation, such as atmospheric re-entry,hypersonic flights, rocket propulsion, and so on due to their higher melting point above 3000 °C. Among different forms of ceramics in term of transition-metal nitrides, borides, carbides, HfC is found to be used in different industries due to its significantly higher melting point of 3900 °C (Liang *et al.* 2020). Due to its uses in crucial services, development of higher quality chemical powers, high mechanical resistance, and bulk/film HfC materials is one of potential technological and scientific challenges, which seeks an immediate solution.

A number of methods with advance technologies are now relevant to produce effective HfC powders or material with desirable thermochemical, mechanical, and physical properties. According to Savvatimskiy*et al.* (2020), thermophysical properties of heat conductive materials are significantly gaining interest in aviation, rocket, and nuclear power industries. Temperature used for processing HfC processing difference considerably with time of its holding. Increasing processing temperature generally, decreased holding time of chemical compound. The "High-Temperature Shorter Holding Time" process for HfC production and processing provides a number of benefits including relatively smaller thermal losses, which in turn aid in measurement of thermal properties of resultant products, measurement of thermo physical properties, such as liquefaction and solidification time of product and so on (Ghelich*et al.* 2020).

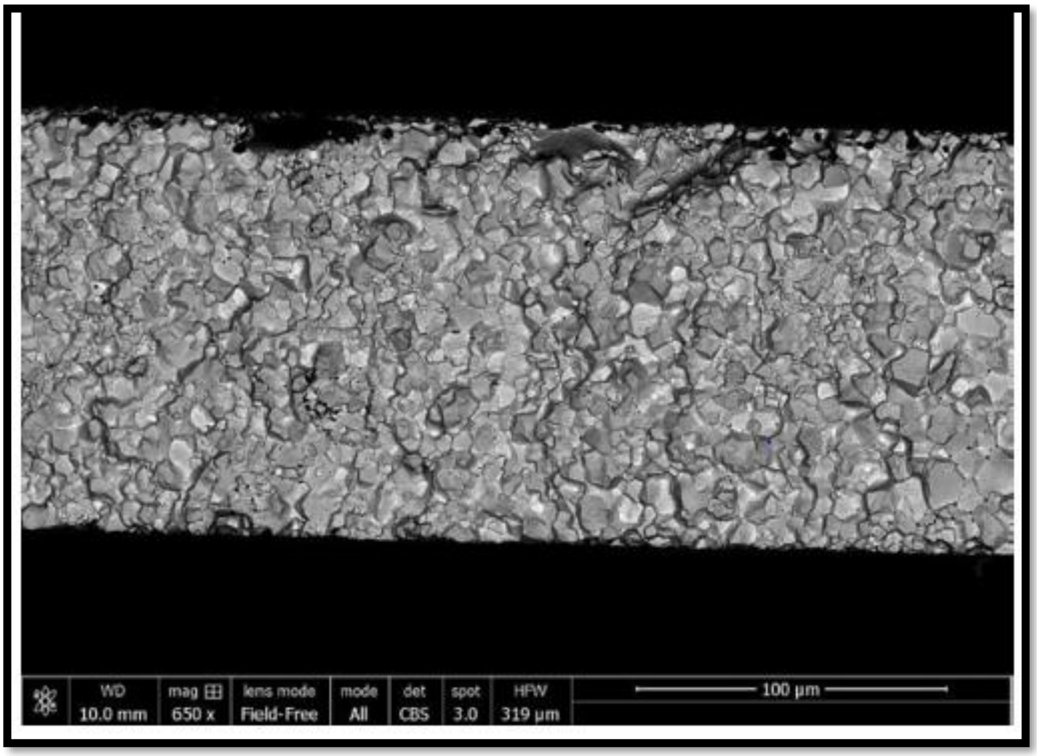

Figure 4.1:Thickness of hafnium carbide (130nm)

(Source: Savvatimskiy*et al.* 2020)

This indicates that HFC compound are relevantly adequate increased heat capacity and electrical resistance up to temperature of 5000 K. Understanding of 2D structure of chemical compounds are essential for analysing their chemical properties (Tuleushev*et al.* 2019). In an experimental research of Zhou *et al.* (2017), a power composed of Hf-Al-C and Hf3[Al(Si)]4C6 is formulated from situ reaction by using "Pulsed Electric Current Sintering (PECS)". According to authors this compound is effectively exerting adhesive energy and facilitates Si-etching process (Zhou *et al.* 2017). A thermogravimetric analysis developed by Zhang *et al.* (2017), provides great information related to thermo resistance power of HfC. An improved thermo chemical property exerts when HfC is composed of TaC.

Among different combination of sample mixture, T50H50 samples highest resistance power against oxidation as well as retention of carbide is also evidently apparent. This is due to mechanical integrity of T50H50 sample that helps in prevention of oxidation of carbide solution (Zhang *et al.* 2017). Moreover, results also indicate that volume changed, and gaseous production within solution is significantly affected by reaction developed within Ta2O5 and HfC. As stated by Wang *et al.* (2017), hafnium dioxide is generally utilised as primary sources for production of HfC along with requirement of higher degree of temperature. However, using of much lower temperature than that of melting point of HfC can help different organisation to product Nano-particles of this compound within limited cost and energy consumption.

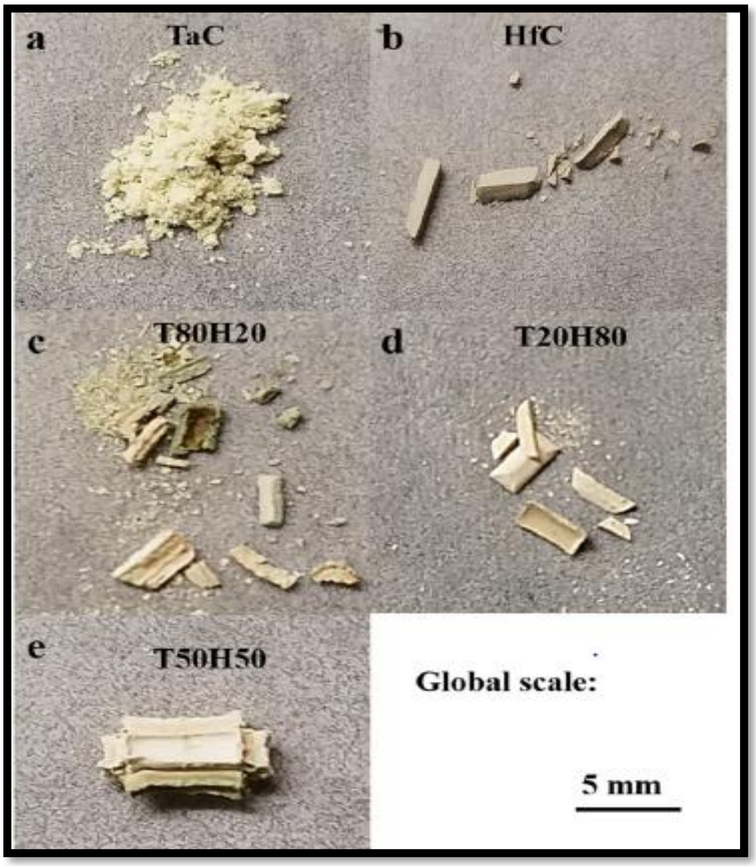

Figure 4.2: Post-oxidation samples of different combination

(Source: Zhang *et al.* 2017)

Hafnium dioxide can undergo "Solid State Reaction" for successful development of nanoparticle of HfC with temperature and time requirement of 700 °C and 10 hours, respectively (Wang *et al.* 2017). Results suggested that nanoparticle produced through "Solid State Reaction" are more-or-less equal in size with an average of 10 nm. Moreover, oxidation and mechanical resistance of this HfC particle are also found to be highly desirable and adequate for use in industrial purpose (Lyakhov*et al.* 2018). "Self-Propagating High Temperature Synthesis (SHS)" deliberately utilised for manufacturing of "single-phase binary carbide (Ta,Hf)C". According to Kurbatkina*et al.* (2018), this process is done in a relatively lower temperature of actual melting point of compound that is 2127 °C and 3001°C, respectively.

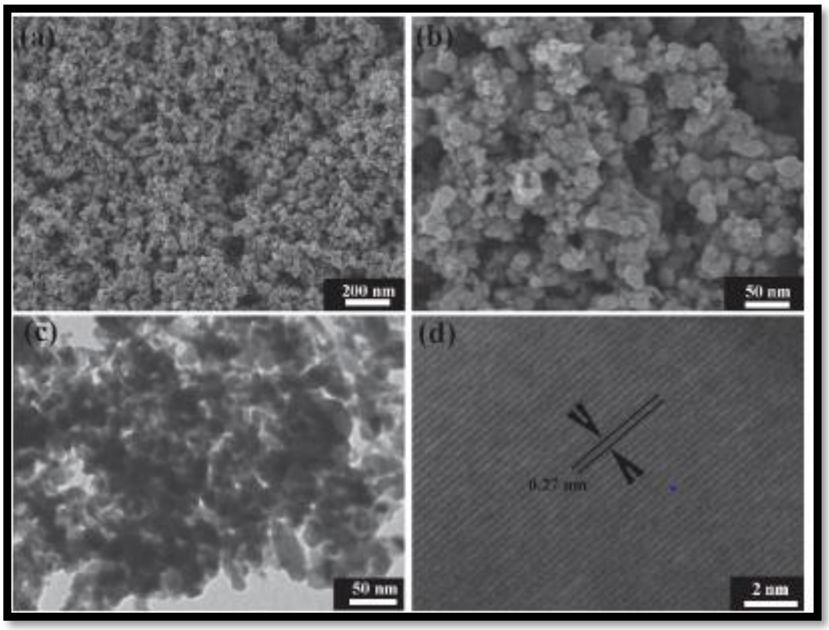

Figure 4.3: SME Image of HfC after Soli-state-Reaction

(Source: Wang *et al.* 2017)

However, this process of HfC manufacturing can be affiliated with higher chances of gaseous losses during combustion; therefore, increasing chances of thermal contact losses in-between a briquette and thermocouple (Kurbatkina*et al.* 2018). However, resultant particles come with a size of fewer than 10 μm with a relative density of 90 to 95%, indicating that compound can effectively as genomic material in different industries (Rasaki*et al.* 2018). As stated by Patra*et al.* (2016), Pyrolysis at 1300 °C can result in formation of HfC by combining Orthorhombic and monoclinic hafnia. This process through provides a relatively smaller yield of Hfc accounting for around 62%; however, come up with an effective particle size ranging at 50 nm (Patra*et al.* 2016).

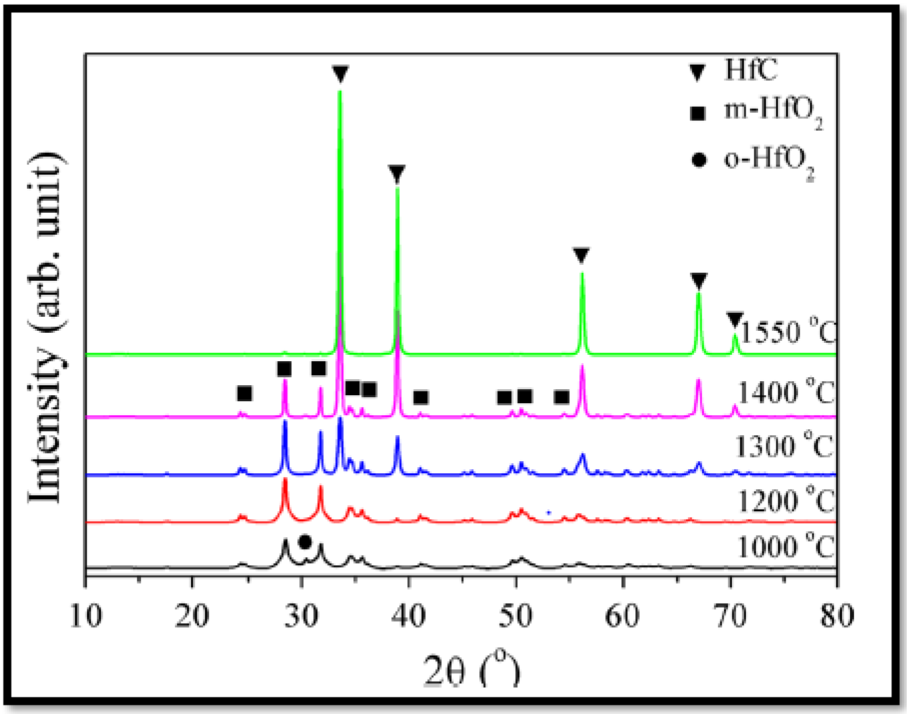

Figure 4.4: Intensity of HFC at different temperature

(Source: Patra*et al.* 2016)

Sol-gel Process, in combination with "high-temperature rapid heat treatment", is one of well-known method for formulation of HfC. Wu *et al.* (2018) stated hafnium tetrachloride and citric acid are needed to be utilised for development of HfC. HfO2-C powders, which has ununiformed structure with relatively smaller particle, which in turn manage by maintaining holding time. Final product comes with a particle size of 500 nm (Wu *et al.* 2018). Development of consolidated HfC powder can be done by modifying a relatively lower temperature at 1600 °C. However, the relative density achieved in this method accounts ranging from 75-98%. According to Mukherjee *et al.* (2016), "spark plasma sintering (SPS)" technique for production of HfC powder can mitigate this risk and provide a relative density of particles accounting for as much as 96%.

High melting point, as well as high hardness, is present in tantalum carbide and for that interest is growing (Dusza*et al.* 2018). Different types of importance are there, including lining materials and reentry vehicles. Oxidation resistance is one of the main factors in this situation that helps in the application. Several products, such as co2 and co, can be formed in this situation (Wang *et al.* 2017). Hafnium carbide and tantalum have high melting point, and for that high hardness can be observed. It has also been observed that solid solution should be used in the oxidation process as it is better resistance compared to carbide.

Hafnium and citric acid can be used as raw material for synthesised Nano hafnium carbide powder. It can be identified from the experiment that that concerned particle has smaller particle along with good uniformity (Wu *et al.* 2018). Size of this type of powder can be 225 nm to 380 nm, and vacuum level can be appropriate. As a reactant, HfO2 can grow by decreasing temperature. It can be observed that particle size can be obtained from HfC powder. It is recommended to use HfC powder instead of commercial powder as it has better sinter ability (Lu *et al.* 2016). Noval method is possible to use for synthesising ultra-fine hafnium carbide.

This method can be done along with plasma-activated sintering as well as liquid precursor conversion. In PAS process, fast formation is done in the solution-based process. This mixture is used for liquid precursor conversion. Low temperature can be obtained in by using HfOCl2 and HfC powder. Carbon source can be demonstrated so that particle size can be identified (Lu *et al.* 2016). Both covalent bond, as well as metallic, can be exhibited with the help of hafnium carbide. In high temperature, high hardness can be observed in hafnium carbide. One of the most important alternative methods is precursor method in this situation.

One of primary functions of HfC is development of strong and strength resistance coating for different materials. Temperature, holding time and crystalline size of particles that are developed by different processing methods of HfC influences of thickness of its coating. Bi-directional and surface diffusion processes are confirming improved reactivity and sustainability of products (Zhu *et al.* 2017). As stated by Li *et al.* (2017), using catalyst and adequate temperature for organometallic polymer development is one of essential criteria required to develop during formation of HfC. Patsera*et al.* (2018), introduce and investigates on effects of mechanical-activation (MA) on development process of TaHfC compounds as well as on "self-propagating high-temperature synthesis (SHS)".

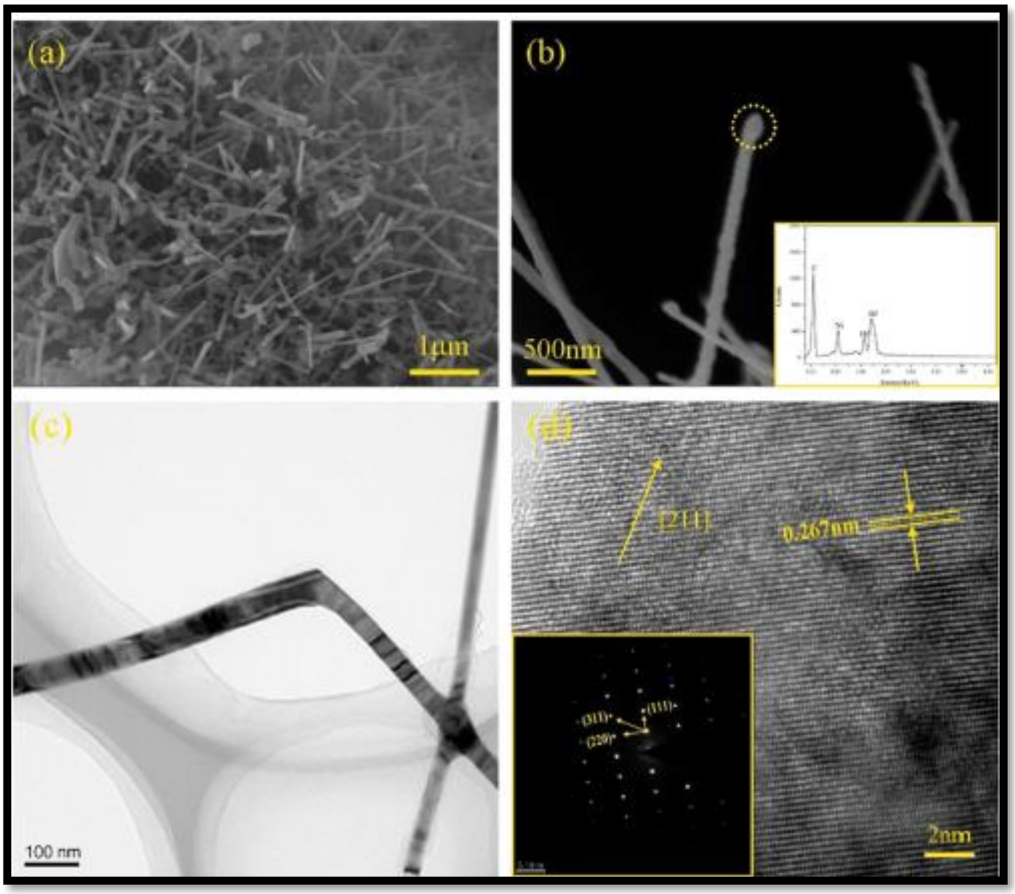

Figure 4.5: HfC nanowires synthesis

(Source: Li *et al.* 2018)

Results from this study suggested that imitation of SHS for production of TaHfC is impossible at it earlier stages as hafnium oxide content will unable to exceed 1% in such processes (Patsera*et al.* 2018). "Vacuum plasma spray system (VPS)" is serving as an effective method for development of a pure HfC coating deposited within the composite made by carbon/carbon (C.C). VPS, along with SiC buffer, effectively improves thickness of coating by 110 μm (Yoo*et al.* 2016). Simonenko*et al.* (2019) suggested that sol-gel technology is effectively utilised for development of finer degree of Ta2O5–HfO2–C powder. This process can be done with a lower temperature (200–1300°C) along with Dynamic vacuum process that helps in formation of protective coating of material within 2 to 4 hours.

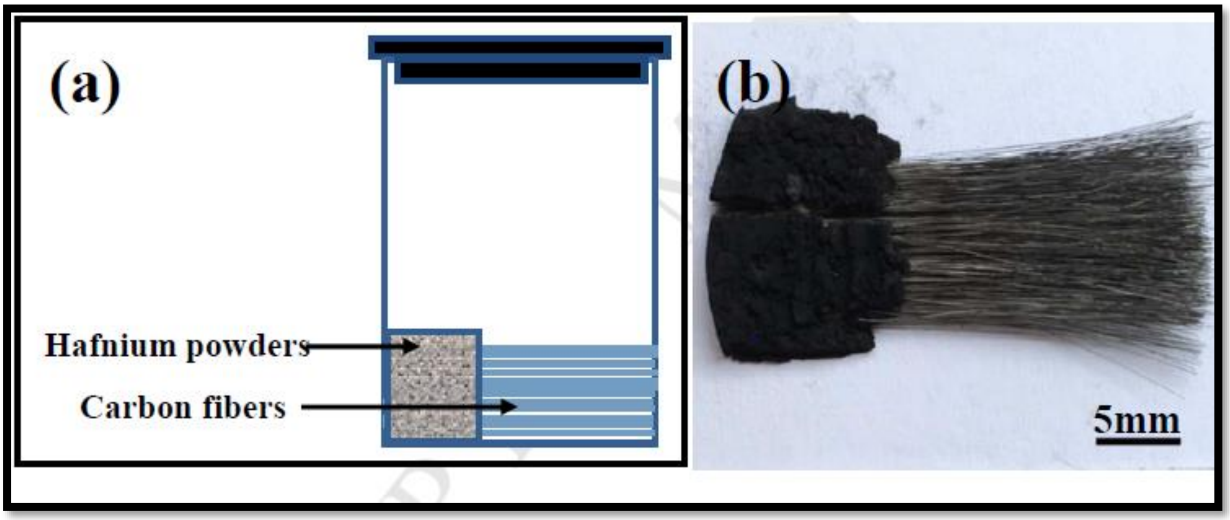

Figure 4.6: Confirmatory Experiment with HfC powder

(Source: Zhu *et al.* 2017)

Improved management and developing HfC system is significantly utilised in different industries, such as planetary ball mill due to its high mechanical activities and irradiation-assisted fabrication process (Grigoreva*et al.* 2017). "Nonstoichiometric hafnium carbonitrides (HfCxNy)" is a variable compound of HfC and developed through higher energy and shorter time operation process. This allows the formation of rock-salt crystal-like structure, along with parameter of particles ranges up to 0.4606 nm (Buinevich*et al.* 2020). Zig-zag nature of HfC is thoroughly investigated in recent era to acknowledge sub-eutectic growth of compound, primarily through using transmission electron microscopy process.

Accounting result of Tian*et al.* (2017), suggested that 125° is primarily found in zigzag structure of HfC followed by 45° and 90° angle is supposed to be rarest angle found in zigzag behavioural growth in HfC compounds. In laboratories, Oxygen deficient film of hafnium oxide is combined with carbon oxide for manufacturing of HfC. Results suggested that oxygen vacancies present inside carbon compound effectively attack hafnium oxide; therefore, accounting for lowering energy required for formation of HfC (Rodenbücher*et al.* 2016).

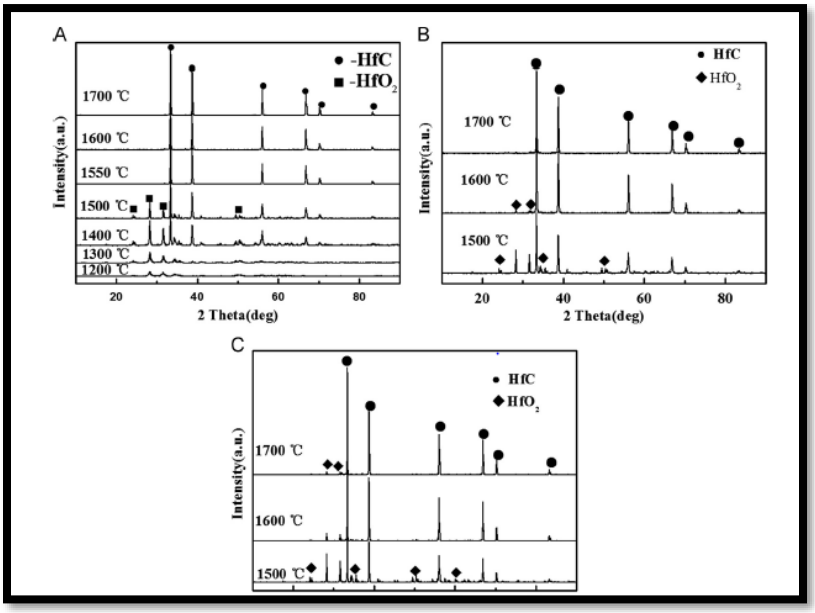

Figure 4.7: HfC in different temperature

(Source: Lu *et al.* 2016)

Hot Pressing is another novel method utilised by Filippov and Skovorodin (2019), for formation of refractory and superhard compounds for protective materials. Results suggested that during period of shrinkage more active and effective sintering in Hot Pressing method as compared to Thermal Expansion Processes (Filippov and Skovorodin, 2019). Detail analysis regarding impact of temperature and pressure ranges utilised for development of HfC system indicates that under isothermal condition transformation of chemical vapour into HfC is done by hafnium fluorides. These fluorides are eventually increasing with an increased temperature, declining pressure within reaction system (Lozanov*et al.* 2016).

Molten hafnium carbide is emerging as a new area of investigation in recent decades, to understand its probability to provide effective products that can be used in protective purposes (Ancharov*et al.* 2019). Lower toughness and increased chances of damaging are evident in modern techniques of HfC production. Incorporation of silicon carbonitride can enhance toughness and damage resistance power of HfC compounds (Hao*et al.* 2020).

Betke*et al.* (2019), in their study, indicated that reticulated pores are evident in ceramics. Such an occurrence is evident after use of dispersed infiltration. Hollow struts have to be taken and passed through this process to acquire better ceramics. Akin to hafnium carbide, Zirconyl nitrate provides similar properties. Density is higher, and higher temperatures are evident, indicating that there is need for more energy for production. Conversion processes are providing evidences for 91.6% porosity. Ceramic nature retains and provides longevity as well.

Fedorov*et al.* (2016), in their research, provided evidence of material genomics effectively. Akin to nature, where species have multiple layers of epidermis for better connectivity and structure ceramics have to contain multiple layers to attain better strength. Hence, their study pointed out that higher temperatures and lower density can lead to corrosion of ceramic material. Hence, they chose water-resistant coats on base materials of their ceramics. This aided in provision of better structural layers. Further, they provide for low energy consumption. The multi-component coating has been incorporated in its ceramic structure that provided additional structure and strength to Hf molecules and cross-linking structure as well.

Previous article provided evidence for coating and indicated that effective coating materials could aid in better structure. Materials such as "Tantalum carbide (TaC), hafnium carbide (HfC)" provide requisite coating properties. Similar notion is achieved from study of Guzmán*et al.* (2017), as they provide evidence for material coating with as well as without gold-based coating in ceramics. Their process uses low energy-consuming materials. Apart from this, pitting corrosion lowered and rate of deterioration decreased substantially as well. This indicates that such coating materials are providing economic importance and are opening a better roadmap for future studies as well.

Higher temperature can provide a process with better strength; however, it is evident in previous studies that it can promote corrosion in ceramic products as well. However, use of doping elements can help in reducing costs. Akin to tungsten crucibles, hafnium crucibles may use doping for effective strengths. Doped elements react with materials such as tungsten carbides and hafnium carbides to provide ceramics of higher standards. Hu *et al.* (2016), provides this process in their study and indicate that optimised higher temperatures are capable of providing better strength. Studying this article provided evidence that materials such as hafnium, are capable of receiving better structure with doping elements and higher temperatures at correct density.

Jenek*et al.* (2016) indicated similar ideas as evident in articles earlier. Multiple layers provide better strength to ceramic materials. Hence, this research can correlate ideas of material genomics with ceramic products. Akin to multiple layers in cell membrane, DNA and RNA, ceramic materials require layer at certain temperature. New and better phase compounds can be made at thin films to provide increased strength and longevity. Apart from this, ceramic materials, made with HfC, can provide corrosion-free structures.

As indicated in the study of Mohammadzadeh*et al.* (2020), it is indicative that ceramic materials are used in airline industries. Such materials are capable of withstanding wear and tear. Apart from this, they can retain their structure and molecular integrity at higher temperatures as well. In this research, authors provided evidence for potential application in wings of aeroplanes. Assessment can be done with the help of a model named "Finite Element Model". Higher melting point, Good transport facilities, high hardness, and relatively lower cost for formulation process are primary areas that increase interest in development of metal carbide through different industries (Vernieri and Santos, 2016).

According to "chemo-mechanical coupling model", the temperature range from 1200-1800°C is most effective for formation of ceramic compound due to its high absorptivity and oxidising changes (Wang and Shen, 2017). Analysis of microstructures of Mechanical Properties of ceramic compounds highly affects additive process during formation of HfC (Yi *et al.* 2018). Development of binary and ternary films through using corrosion properties is evident in study of Yate and Aperador (2017). Results suggested that "ternary Ta-Hf-C alloy films" delivers an effective elasticity, higher hardness, excellent resistance and low nanowear properties.

Conclusion

Hafnium Carbide being and excellent thermo-resistant compound with melting point as much as 3900 °C gains high importance in Material Genomics and industrial investigations. Advanced management of effective processes for manufacturing or processing of HfC is highly relevant in today's era. It is evident that effectiveness of different process varies considerably and accounting for resultant compound with different porosity, thermo-physical properties, resistance properties, relative density, and particle size, depending on which functionality and effectiveness of HfC compound are determined. For example, a temperature ranging from 1000-2000°C is found to be ideal for manufacturing of HfC development from other compounds.

The primary reason behind management of effective temperature, while formulating an extensive and highly resistant HfC compound is prevention of oxidation process of carbide naturally present within raw material. Results suggested that utilisation of "single-phase binary carbide (Ta, Hf)C" are difficult o used for long0term processing due to its inadequacy in diffusion process. Therefore, majority of conventional technologies are utilised for addressing reduction rate of carbo-thermal oxides while developing refractory carbides. Hybrid process of different compounds is utilised in synthesis process of HfC in under modern technologies. Identification of carbon resources for development of HfC compounds are effectively undertaken these days as carbon resources contribute towards formation of paste or gel easily for coating process in different industries.

Due to highly developed melting temperature of HfC is serve as a potential aerospace compound in protective organisation; therefore, organisation pay great interest for development of adequate preparation and manufacturing process of HfC, which will provide higher and desirable quality of product as well as contributes to financial benefits. Beside all effective process of manufacturing or processing of HfC colloidal processing found to be majorly distributed in manufacturing companies. Through colloidal method of HfC processing is a new concept; however, due to its numerous benefits and cost-effectiveness, researcher and analysts are opt for this method eventually. This process evolves as an effective method as this develops resistance, temperature, and reliability of resultant product more than any other method available in market.

"High Temperature Shorter Holding Time, Pulsed Electric Current Sintering (PECS), Solid State Reaction, Self-Propagating High Temperature Synthesis (SHS), spark plasma sintering (SPS)" is certain process that is significant utilised for production of HfC along with higher desirable properties with resultant compound. However, research also suggested that dry manufacturing methods for HfC production come with a number of disadvantages, which can be in turn mitigated by using wet-technologies, which in turn develop assistances for thinner sheet production. Therefore, finally, it can be concluded that development of effective process along with variation of temperature used for production and processing of HfC compounds with maintenances and/or improvement of properties of HfC compounds is highly necessary and require effective investigation at academic and industrial level.

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