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Preparation of ZrB_2 -SiC based ceramics using $MoSi_2$ as sintering aids and explanation using electronic theory of sintering – an elementary literature review

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ABSTRACT
ZrB_2 (zirconium diboride)-based ceramics reinforced by 15vol.% whiskers with high density were successfully prepared using $MoSi_2$ as sintering aids. The effects of sintering condition and $MoSi_2$ content on densification behavior, phase composition, and mechanical properties of$_w$/ZrB_2 composites were studied. Nearly, fully dense materials (relative density >99%) were obtained by hot-pressing (HP) at 1700°C–1800°C in flow argon atmosphere. The grain size of ZrB_2 phase in the samples sintered by HP at 1700°C–1800°C were very fine, with mean size below 5 μm. Mechanical properties (such as flexural strength, fracture toughness, and Vickers hardness) of the sintered samples were measured. The sample with 15vol.% $MoSi_2$ addition sintered by HP at 1750°C displayed the best mechanical properties.

Keywords: zirconium diboride (ZrB_2) $MoSi_2$ sintering aids mechanical properties, Spark plasma sintering(SPS)

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I. INTRODUCTION

Zirconium diboride (ZrB_2) ceramics have been widelystudied due to their combination of physical properties,such as high melting temperature (3245°C), high strength,high electrical and thermal conductivity, chemical inert-ness against molten metals of nonbasic slags, and superthermal shock resistance [1,2]. These properties makethem currently considered as ultra-high temperatureceramics (UHTCs). However, there are three main barrierslimiting the application development of ZrB_2-basedceramics: relatively poor mechanical properties includinglow strength and fracture toughness, poor intrinsicsinterability because of the strong covalent bonds betweenZr and B, and the poor oxidation resistance at hightemperature.A lot of studies have been done in order to address thebarriers limiting the application development of ZrB_2-based ceramics. To improve the strength and fracturetoughness of ZrB_2ceramics, particles [3], whiskers [4,5], or carbonfibers [6] were used asreinforcements. However, a large amount of reinforce-ments will inhibit the sintering densification of ZrB_2ceramics, which affects the mechanical properties of theceramics. To improve the sintering densification of ZrB_2,very high sintering temperatures (2100°C–2300°C), pressure-assisted sintering procedures, and sintering additivesare usually adopted. So far, a lot of metals (e.g., Cr and Fe)and ceramic powders(e.g., Si_3N_4, AlN, WC, and $MoSi_2$)were used to promote the sinterability of ZrB_2[7–11].$MoSi_2$was found to be an effective additive to improveboth sinterability and oxidation resistance of ZrB_2ceramics [12–14].In this study, $MoSi_2$was selected as sintering aids, andSiC whisker was selected as toughness phase. The aim ofthis work is to study preparation and properties of thecomposites in the system ZrB_2-15vol.%SiC whisker-(10vol.%–20vol.%) $MoSi_2$. The densification behavior,phase composition, mechanical properties, and micro-structure of sintered materials were investigated.

Motivation

Transition metal diborides, especially zirconium and hafnium diboride are potential ceramic material for ultra high temperature applications above 1800°C. These borides are characterized by high melting point, formation of high melting point oxides, good oxidation resistance and excellent thermo-mechanical properties. In this present exploration, zirconium diboride (ZrB_2) has been selected for its moderate density (6.09 gm/cc) and better oxidation resistance compared to high density hafnium diboride (11.2 gm/cc). .SiC and $MoSi_2$ were added to improve the thermal shock resistance and sinterability of the ultra high temperature ceramics (UHTCs).

Experiment

Commercial powders were used to prepare the ceramics. ZrB_2, particle size: 10-15m, purity: 99.5%;, particle size: 2 m, purity: 99.9 %; $MoSi_2$, particle size: 2 m, purity: 99.9 %. The powder mixtures mixed with a certain volume proportion (ZrB2:: MoSi2=7:3:2 for ZSM; ZrB2:=7:3 for ZS) were filled into the ZrO2jar and ball milled for 6 h using ZrO2media. Subsequently, the slurries were dried in a rotary evaporator. The dried powder mixtures were filled into a graphite die, which was then put into the SPS furnace under argon atmosphere to sinter for 5 min at 1900 0C, with a heating rate of 100 0C/min and an applied pressure of 30 MPa.

II. RESULTS AND DISCUSSION

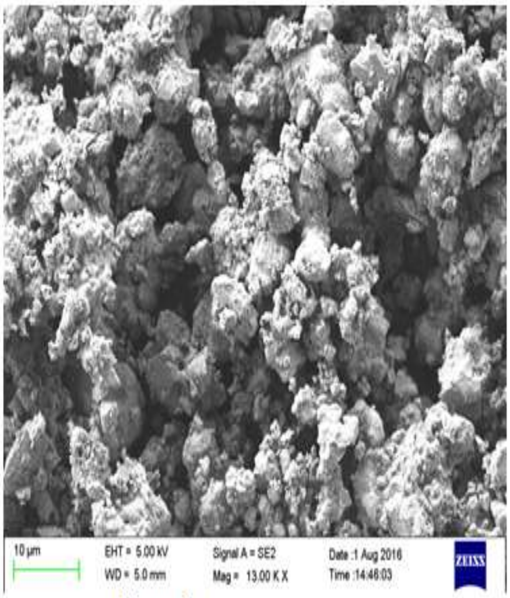

Figure 1. a

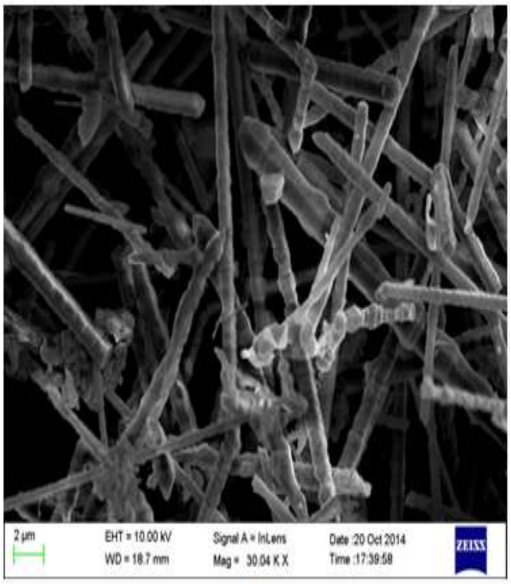

Figure 1. b

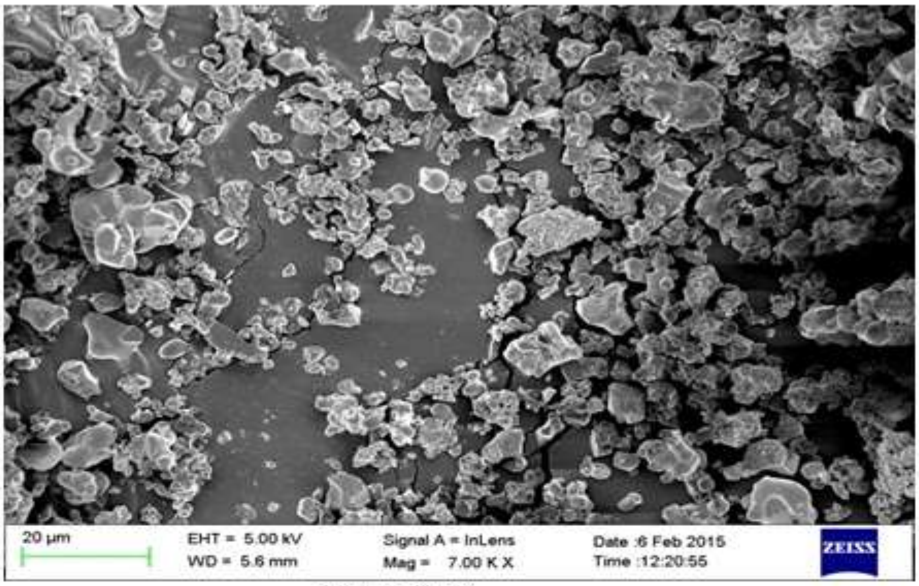

Figure 1. C

Figure 1. a SEM image of at 13000X Figure 1. b SEM image of SiC-Wat 3040XFigure 1.c SEM image of ZrB_2at 7000X

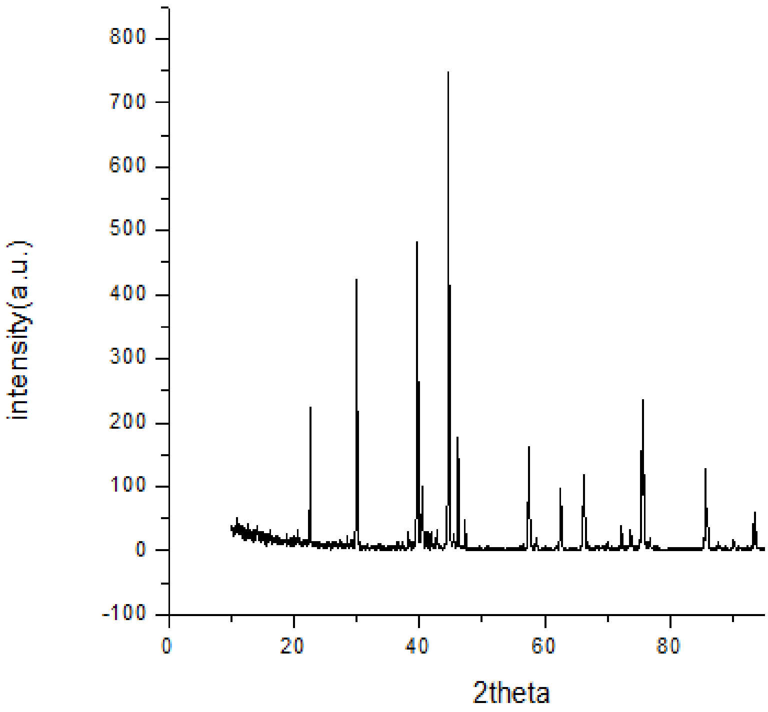

Fig 2.a X-Ray Diffractogram of $MoSi_2$

a = 0.32112 nm, b = 0.32112 nm, c = 0.45236 nm

2theta	(h k l)
22.98	0 0 2
29.98	1 0 1
39.66	1 1 0
44.635	1 0 3
46.38	0 0 4
47.252	1 1 2
57.512	2 0 0
62.48	2 0 2
66.58	1 0 5
75.36	2 1 3
85.62	2 2 0
99.079	3 1 0

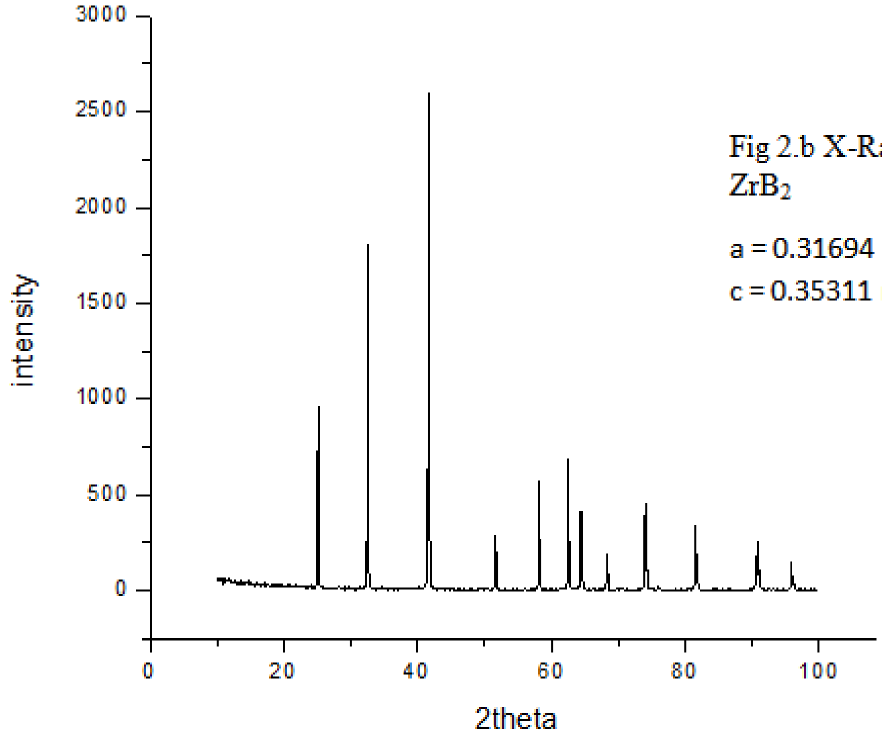

Fig 2.b X-Ray Diffractogram of ZrB_2

a = 0.31694 nm, b = 0.31694 nm, c = 0.35311 nm

2theta	(h k i l)
25.596	0 0 0 1
32.38	1 0 -1 0
41.69	1 0 -1 1
51.35	0 0 0 2
58.38	1 1 -2 0
62.77	1 0 -1 2
64.254	1 1 -2 1
68.036	2 0 -2 0
73.906	2 0 -2 1
81.52	1 1 -2 2
91.17	1 0 -1 3
95.85	2 1 -3 0

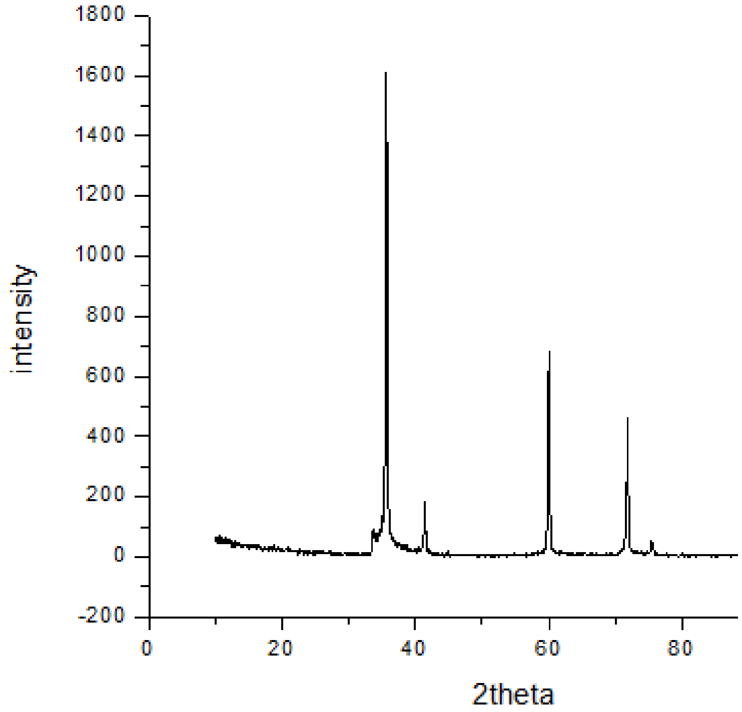

Fig 2.c X-Ray Diffractogram of SiC

a = 0.307 nm, b = 0.307 nm, c = 5.287 nm

2theta	(h k l)
35.27	1 1 1
41.117	2 0 0
60.447	2 2 0
71.7435	3 1 1
75.43	2 2 2
89.98	4 0 0

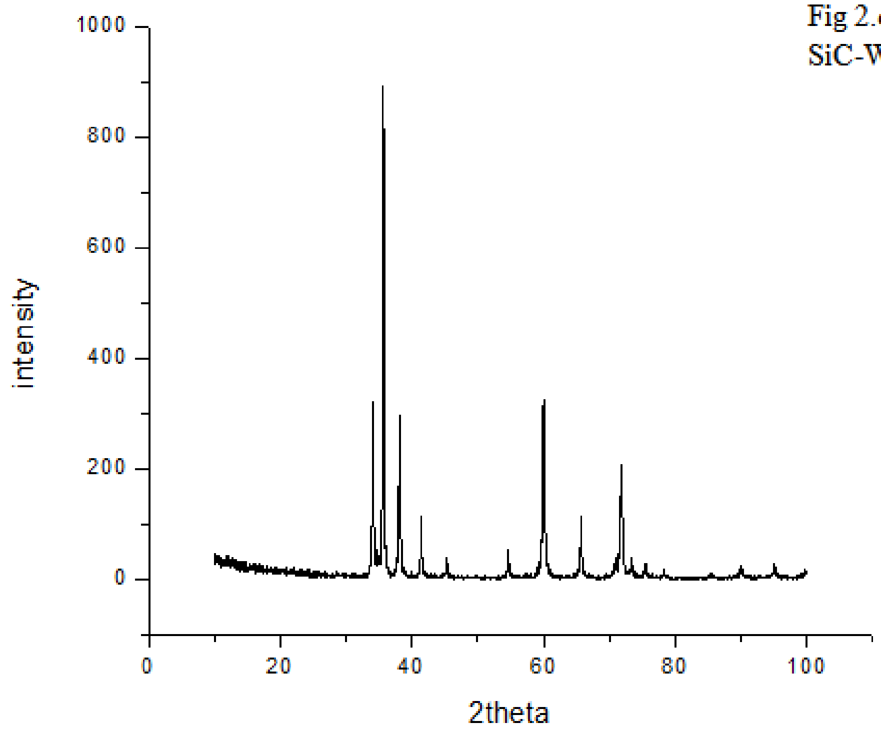

Fig 2.d X-Ray Diffractogram of SiC-W

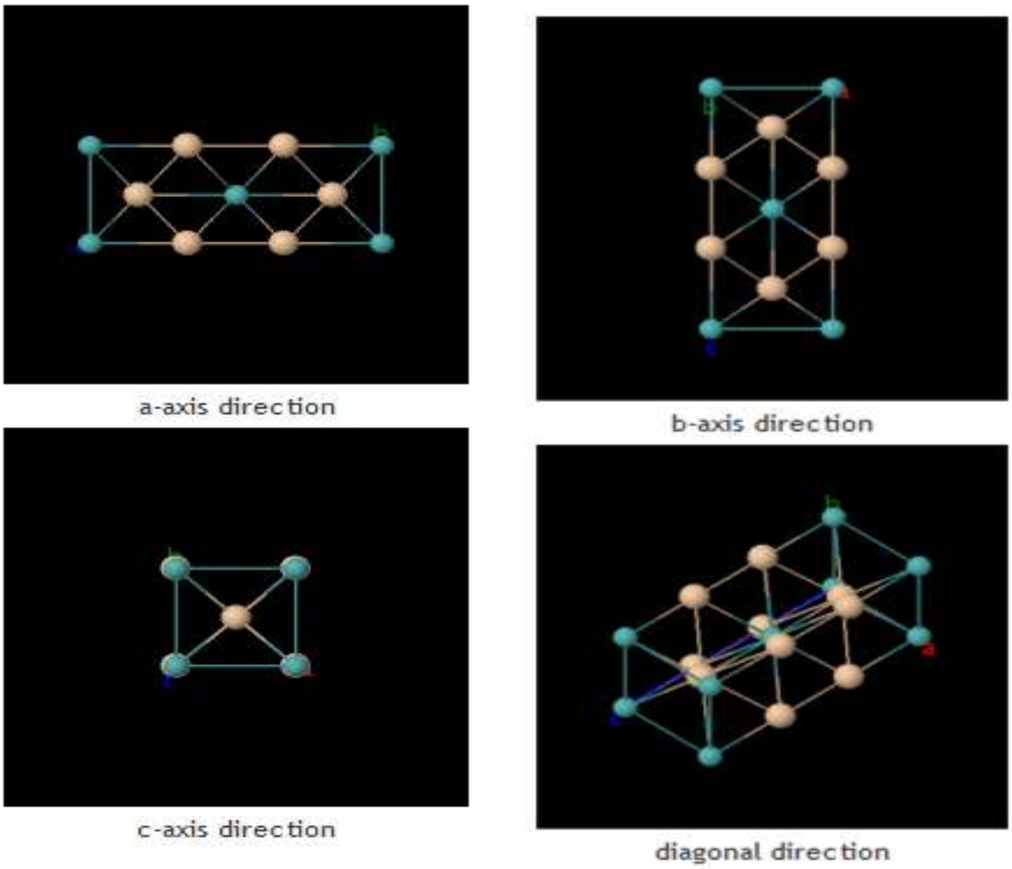

Fig 3 Tetragonal structure of $MoSi_2$ (Courtesy: NIST, Japan)

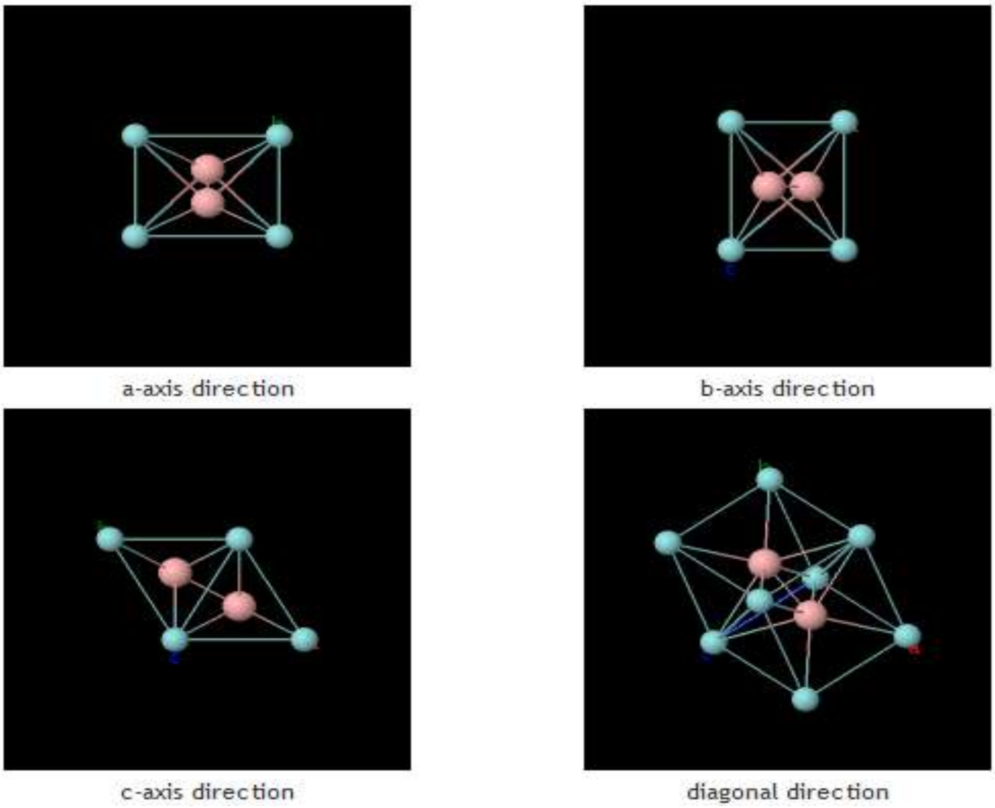

Fig 4. HCP structure of ZrB_2 (Courtesy: NIST, Japan)

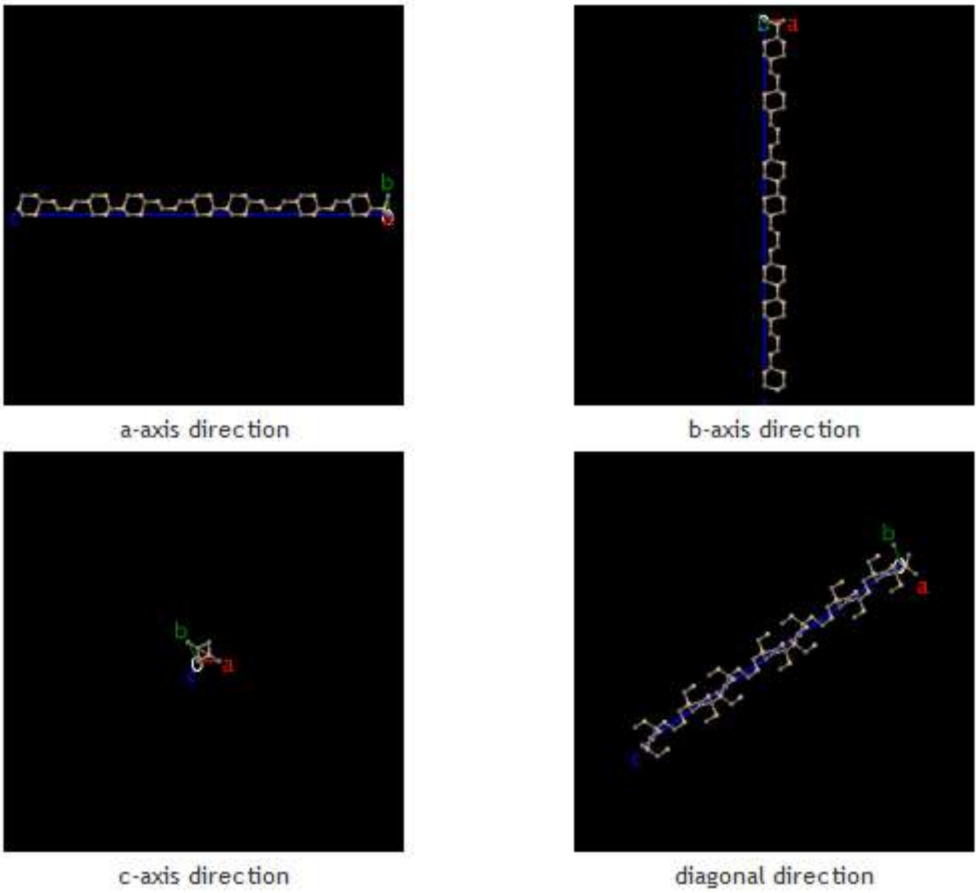

Fig 5. HCP structure of (Courtesy: NIST, Japan)

Table 1. Table for calculating microstructural features of $MoSi_2$particles(dimensions: μm, using imageJ software)

Count	Total Area 0.406	Avg size %Area 40.511	%Area Mean Median 255 255	mean Average Size	median
3915	1588.667	0.406	40.511	255	255

Table 2. Table for calculating microstructural features of ZrB_2particles(dimensions: μmusing imageJ software)

Count	Total Area 0.406	Avg size %Area 40.511	%Area Mean Median 255 255	mean Average Size	median
3724	4665.027	1.253	34.41	255	255

Table 3. Table for calculating microstructural features ofparticles(dimensions: μmusing imageJ software)

Count	Total Area 0.406	Avg size %Area 40.511	%Area Mean Median 255 255	mean Average Size	median
571	213.68	0.374	29.622	255	255

Hypothesis

From spdf configuration of atoms

C: [He]$2s^2$ $2p^2$
B: [He]$2s^2$ $2p^1$
Si: [Ne]$3s^2$ $3p^2$
Zr: [Kr]$4d^2$ $5s^2$
Mo: [Kr]$4d^5$ $5s^1$

Addition of $MoSi_2$ with ZrB_2-SiC is hypothesized to reduce the sintering temperature for Spark Plasma Sintering (SPS) as compared to that for ZrB_2-SiC due to presence of unpaired electron each in Zr and Mo atoms after hybridization. As a result, the 2 unpaired electrons may pair up with each other, thus, making the system more reactive for sintering from atomistic point of view.

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