

Effect of WC and Si additions on the mechanical properties of ZrB₂-WC-Si based cermet

R.R.Rout^a, B.Mishra^a, N.Sahoo^a, S.K. Karak^{b*}

^aDalmia Institute of Scientific and Industrial Research, Rajgangpur

^bNational Institute of Technology, Rourkela, Odisha, India

Corresponding author E-mail: skkarak@gmail.com

Abstract: The present paper deals with the study of mechanical behavior of ZrB₂-WC-Si cermets with respect to variation in weight percentage of ZrB₂, WC and Si. Pellets are pressed in hydraulic press with a load of 6T followed by sintering through spark plasma at 1800°C under inert atmosphere. Vickers hardness test of the cermet ZrB₂-60-WC-20-Si-20 showed hardness of 27.5 GPa where as it was quite lower in case of cermets ZrB₂-60-WC-10-Si-30 and ZrB₂-60-WC-15-Si-25. Wear test showed that the mass loss became lower in case of ZrB₂-60-WC-20-Si-20 in comparison to other cermets. This was attributed to the formation of metastable phases of WSi₂ and SiC those are responsible for the increase in hardness of the cermet. Resulting matrix became stronger and also intergranular-intragranular region became densified. Furthermore, this effect was supposed to reduce matrix wear of the cermet having composition ZrB₂-60-WC20-Si-20.

1. Introduction

Ultra High Temperature Ceramics (UHTC) like zirconium diboride (ZrB₂) have important properties which includes high melting point (>3000°C), high strength (>500MPa) and electrical conductivity (10⁷ S/m), as well as excellent chemical stability. Due to these useful high temperature advantages, it was applied in different critical areas such as thermal protection systems, cutting tools, high temperature electrodes, and molten metal crucibles [1–5]. But this application became restricted as ZrB₂ ceramics are very much difficult for producing dense ceramic parts with complex shapes. Many researchers have reported that ZrB₂ ceramics are densified by hot pressing [6,7], which are limited to produce specimens with simple shapes. Report showed that ZrB₂ was densified below 2000°C by use of additives such as B₄C [8], MoSi₂ [9], and C [10]. Proper densification was attributed to activation of sintering by removal of surface oxide impurities from the ZrB₂ particle surfaces (B₄C and C) or by liquid phase sintering (MoSi₂). Microwave sintering was another alternative to hot pressing and conventional sintering. Microwave sintering has the advantages of uniform and rapid heating since the energy was directly coupled into the specimen rather than conducted into the specimen from an external heat source [11]. In addition to promote densification of ZrB₂ in pressureless sintering, B₄C was also reported to absorb microwave energy [12]. To aid sintering, a low melting metallic phase such as silicon was added and the effects of Si addition on the microstructure and mechanical properties of SiC–B₄C based cermets was studied [13]. In order to improve the toughness and high-temperature hardness or strength property, various transition metal carbides (WC, NbC, TaC, etc.) are added to improve cermet properties [14]. Wei-Ming Guo et al have done research work on high-temperature deformation of ZrB₂ ceramics with WC additive in four-point bending method through hot-pressing at 1900 °C for 0–60 min in argon atmosphere under a static load of 25 MPa. After 60 min bending deformation, around 8% strain was reached without apparent macroscopic cracks, which showed superplastic behaviour. This was attributed to the presence of a secondary W-containing phase formed by the addition of WC [15].

For low temperature sintering of composite materials, Spark plasma sintering (SPS) was one of the advance sintering technique that densified the composite body within a certain time period. It was also a promising technique for those materials that are difficult to sinter by conventional sintering route. Advantages of SPS over conventional pressureless sintering include faster heating rates, shorter dwell time to retain finer microstructure [16–18]. Due to localized high-temperature spark effect, adsorptive gas and impurities existing on the surface of powder particles can be eliminated. To promote sintering by diffusion, high-speed ion migration between contacting particles were possibly due to the applied

electric field and then transferring material in micro and nano levels [19]. On the contrary, conventional sintering process was carried out at higher temperature with prolonged time, resulting in grain growth and concomitant inferior mechanical properties. Moreover, there are no reports available on the synthesis of ZrB_2 -WC-Si cermets by spark plasma sintering (SPS). Hence, the present study attempts to prepare ZrB_2 -WC-Si cermets by SPS technique followed by its characterization.

2. Experimental Technique

Commercially available ZrB_2 powder (98% purity, particle size $\sim 35\mu\text{m}$, Esk Ceramics, GmbH & Co, Germany), WC powder (98.5% purity, particle size $\sim 30\mu\text{m}$, Hb metals, India) Si (99.5% pure, particle size $\sim 30\mu\text{m}$, BAIDAO silicon metal ind. Ltd China) are used as-received input raw materials. Different compositions containing ZrB_2 , WC and Si are manually blended and ball milled for 50hrs. Optimum composition of different cermets are decided as per variation of metal content (Si) and metallic carbide content (WC) to study the effect on the mechanical properties of ZrB_2 -WC-Si cermet. Optimal composition of ZrB_2 -WC-Si cermets are given in Table-1. Toluene was taken as solvent for wet milling of above mix. After air drying, the milled powders are pressed in uniaxial acting hydraulic press under a load of 6 tons for a dwell time of 120sec. Green pellets were made with 5mm diameter and 3mm thickness. Pellets are dried in oven at temperature of 80°C for overnight. Then dried pellets are sintered at 1800°C for 3min in spark plasma method under inert gas atmosphere. The bulk densities and apparent porosity of sintered pellets are measured by Archimedes principle. Hardness of sintered pellets are measured by vickers hardness test (LM248AT, LECO Corporation, USA) and wear test (TR-208 M1, DUCOM Instrument, USA) was carried out through ball on disc wear method. Wear pattern of different cermets are analysed through optical microscope (SCOPE-A1, Carl Zeiss India). Different phases of the ZrB_2 -WC-Si cermet after ball milling as well as sintered cermets were analysed by X-ray diffraction analysis (XRD) (ULTIMA-IV, Rigaku, Japan). Morphological features of input powder and sintered sample are analysed by scanning electron microscope (SEM) (JSM 6480LV, JEOL, USA).

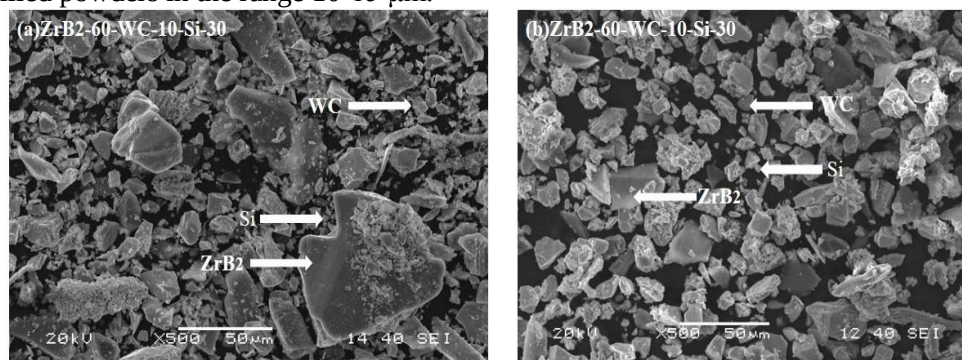
Table.1. Compositions of ZrB_2 -WC-Si cermet

Composition	ZrB_2 Wt %	WC Wt %	Si Wt %
ZrB_2 -60-WC-10-Si-30	60	10	30
ZrB_2 -60-WC-15-Si-25	60	15	25
ZrB_2 -60-WC-20-Si-20	60	20	20

3. Results and discussion

3.1. Morphology of composite powder(before & after milling)

Fig.1 shows the SEM micrographs of ZrB_2 -WC-Si powder at milling time of 0hr and 50hrs for different compositions. Micrograph confirmed the size, shape and morphology of ZrB_2 , WC, and Si powders in different forms. From the figure, it was observed that ZrB_2 and WC powder particles are irregular in shape with sharp edges, whereas Si powders are angular in nature. SEM analysis also confirmed that the size of as received powder of ZrB_2 , WC, and Si are in the range of 30-35 μm and that for milled powders in the range 10-15 μm .



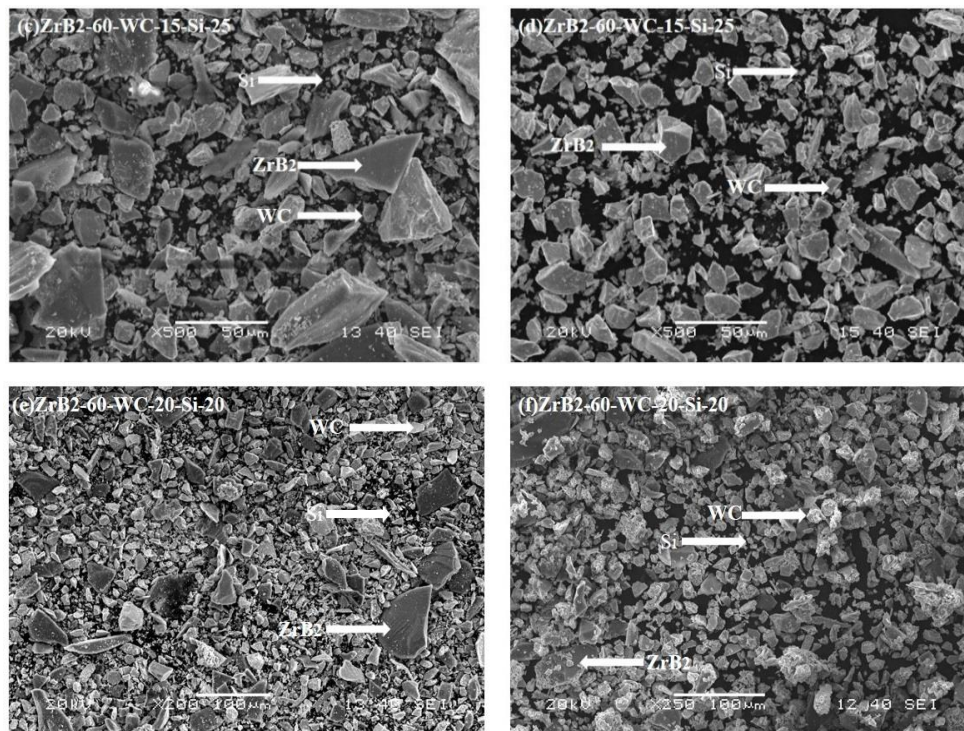


Figure 1. SEM micrographs of unmilled (left) and milled (right) powders: (a) and (b) ZrB₂-60-WC-10-Si-30, (c) and (d) ZrB₂-60-WC-15-Si-25 (e) and (f) ZrB₂-60-WC-20-Si-20

It is also cleared that the particle size of milled powder getting reduced with respect to milling period. Different phases like ZrB₂, WC and Si phases are uniformly distributed throughout whole structure after milling of 50hr. Confirmation of these phases are identified by use of EDS instrument. Same observation could be correlated with XRD pattern of the milled powder.

3.2. Phase analysis

Fig.2 shows the X-ray diffraction pattern of three different cermets having compositions ZrB₂-60-WC-10-Si-30, ZrB₂-60-WC-15-Si-25 and ZrB₂-60-WC-20-Si-20 taken at milling time of 0h and 50 h. It was observed that the peak intensity gradually in reducing manner with respect to milling time and accordingly peak broadened [20]. This was attributed to the reduction in particle size and introduction of lattice strain during milling. The reduction in particle size and lattice strain phenomenon arouse due to different collision took place between different parts of mill and also with particles of powder [21]. Further, even after 50 hrs of milling peaks of ZrB₂, WC, and Si are found with some minor impurity phases.

From the XRD patterns, the presence of ZrB₂, WC and Si phases at each stage of milling are also confirmed. In case of XRD analysis of milled powders at higher milling time (50 h), phenomenon like peak shifting as well broadening were observed upto minimum extent. This might be due to the fact gradual reduction in micron-level particle into sub-micron or nano-metric level fragmentation of particles caused by high energy planetary ball mill.

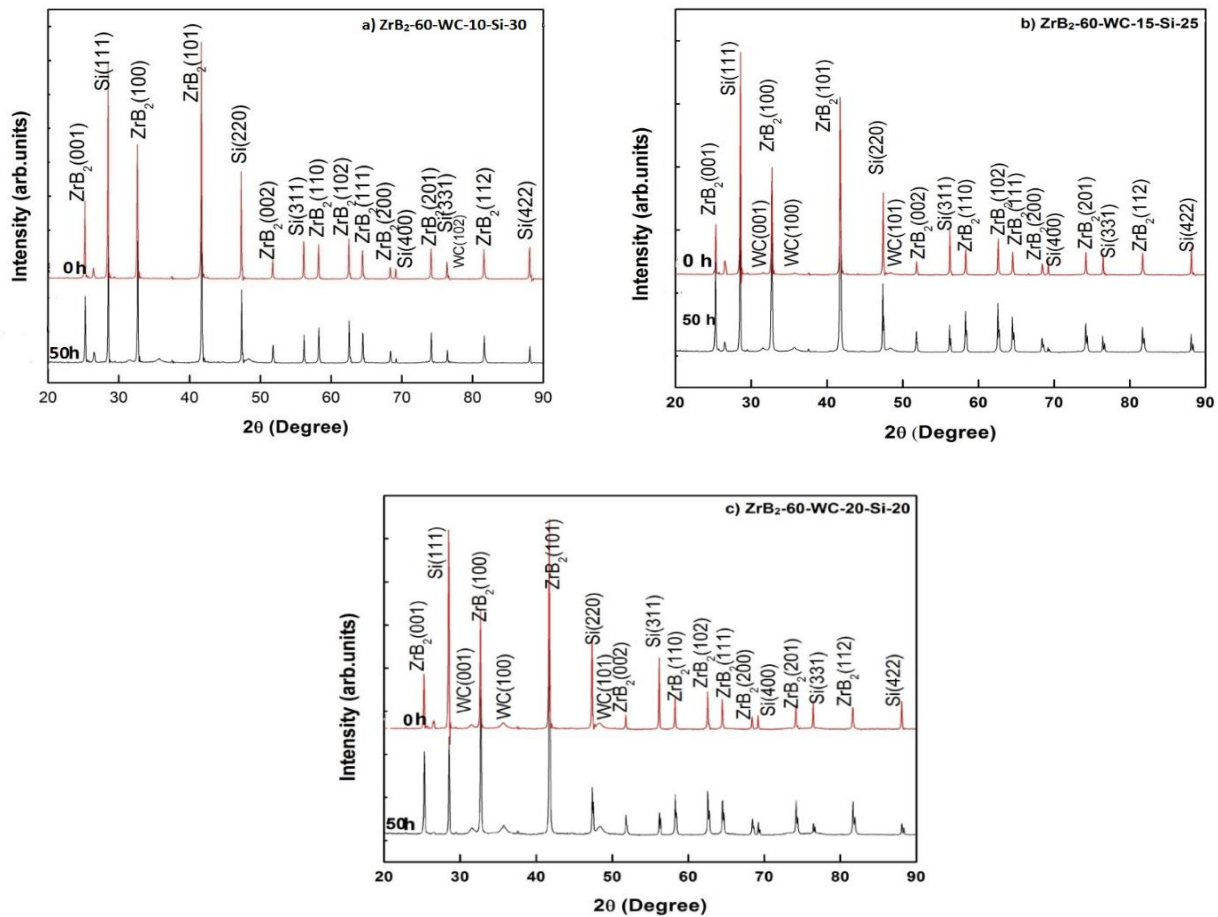


Figure 2. XRD spectra of milled powders of ZrB_2 -WC-Si system at milling time 0h & 50h:
(a) ZrB_2 -60-WC-10-Si-30, (b) ZrB_2 -60-WC-15-Si-25 (c) ZrB_2 -60-WC-20-Si-20

3.3. Characterization of different cermet (after SPS)

3.3.1. Morphology of sintered cermet

Fig.3 shows the microstructures of ZrB_2 -WC-Si cermet sintered at 1800°C through spark plasma sintering method. Due to less holding time during sintering, grain growth was restricted through out the process. However some localized plasma arc was accelerated the liquid phase sintering by the formation of glassy phases (perticularly seen in composition ZrB_2 -60-WC-20-Si-20). Complete structure was densified by the formation of metastable phases (WSi_2) and metallic carbide (SiC) as identified by EDS in that corresponding area. Presence of these phases could also be confirmed from X-ray diffraction pattern of corresponding samples (fig.4).

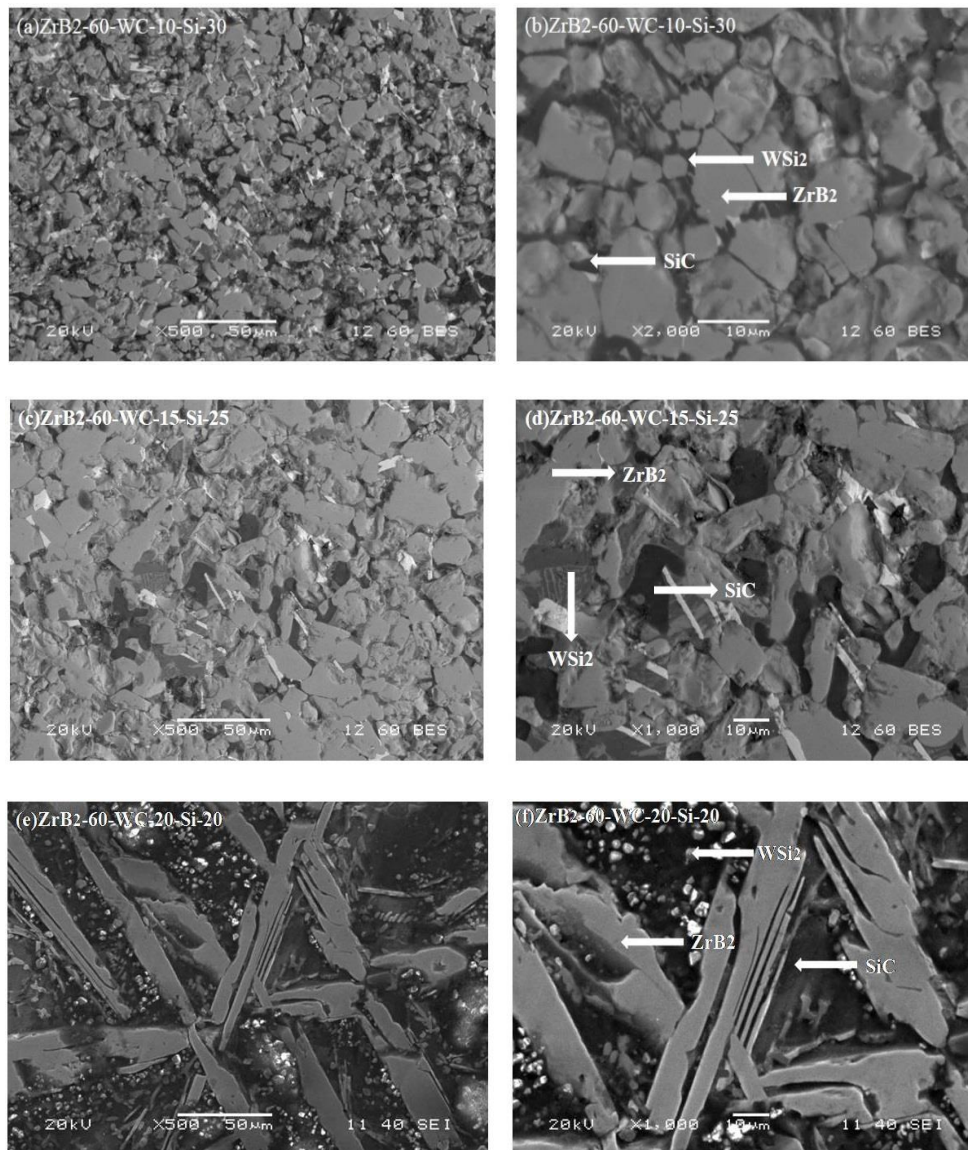


Figure 3. SEM micrographs of ZrB_2 -WC-Si cermets sintered at 1800°C : (a) and (b) for ZrB_2 -60-WC-10-Si-30, (c) and (d) ZrB_2 -60-WC-15-Si-25 (e) and (f) ZrB_2 -60-WC-20-Si-20

3.3.2. Phase analysis of sintered cermets

X-ray diffraction pattern of three different ZrB_2 -WC-Si cermets sintered at 1800°C through plasma sintering technique was shown in fig.4. XRD analysis showed the presence of parent phases like ZrB_2 , WC, Si and product phases of all samples after sintering. As sintering was carried out above the melting point of Si (at 1400°C), hence reaction initiated with C (from WC partially) and finally formed SiC as confirmed from SEM micrograph of corresponding sample. XRD pattern showed the occurrence of primary phases like ZrB_2 , WC, Si and besides these phases some metastable phase like WSi_2 are also present as intermediates. It could also be observed that while increasing WC content from composition ZrB_2 -60-WC-10-Si-30 to ZrB_2 -60-WC-20-Si-20, the formation of SiC was very much effective.

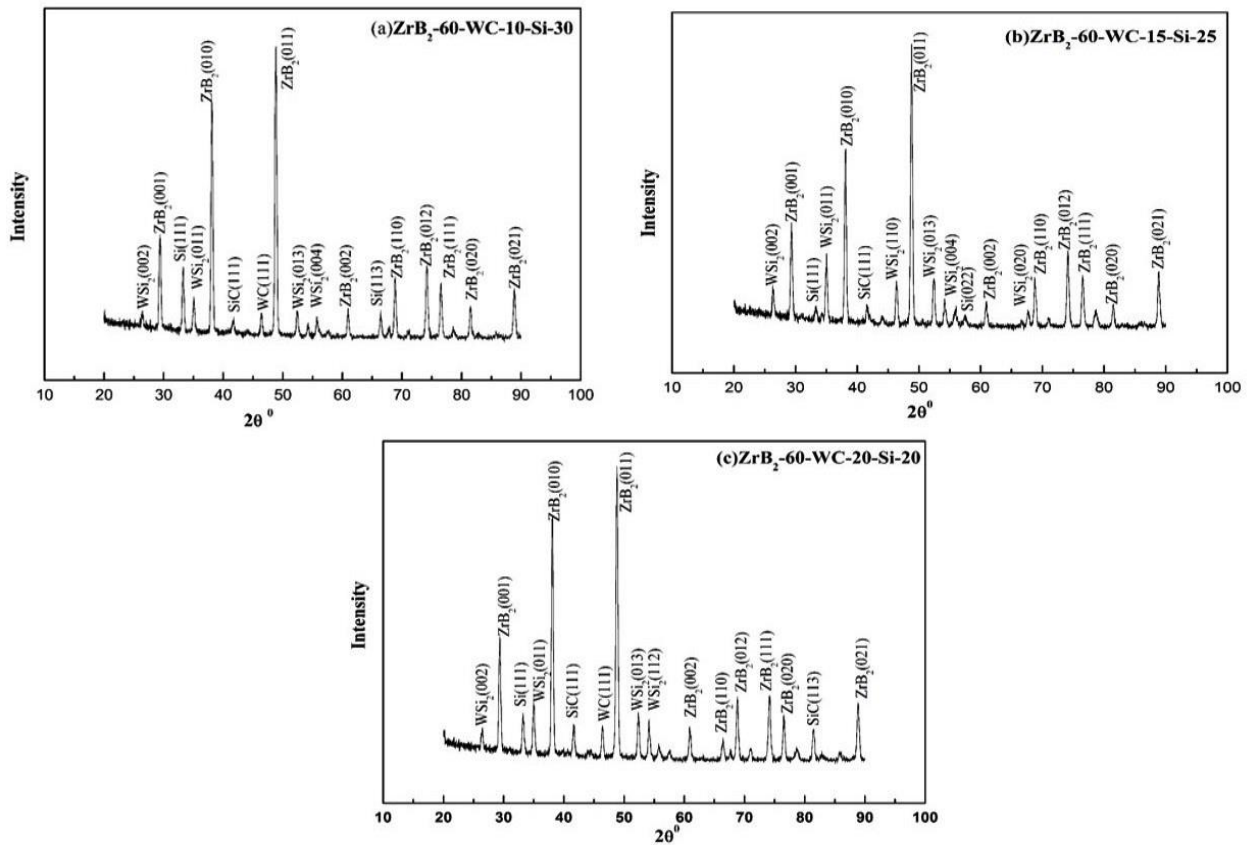


Figure 4. XRD patterns of ZrB₂-WC-Si cermet sintered at 1800°C (a) ZrB₂-60-WC10-Si-30, (b) ZrB₂-60-WC-15-Si-25 and (c) ZrB₂-60-WC-20-Si-20

3.3.3. Densification

Fig.5 shows the variation of apparent porosity and bulk density of different samples of ZrB₂-WC-Si cermets. It was cleared that the apparent porosity of the cermets decreases accordingly with increasing WC content upto 20% and also reducing metallic Si content upto 20%. Similarly bulk density was found higher in case of ZrB₂-60-WC-20-Si-20 in comparison to cermet ZrB₂-60-WC-10-Si-30 and ZrB₂-60-WC-15-Si-25. This might be attributed to the formation of metastable compounds likes WSi₂ and SiC in the matrix part by sealing the pores through liquid phase sintering and hence increasing the bulk density of the cermets even with lower metal content.

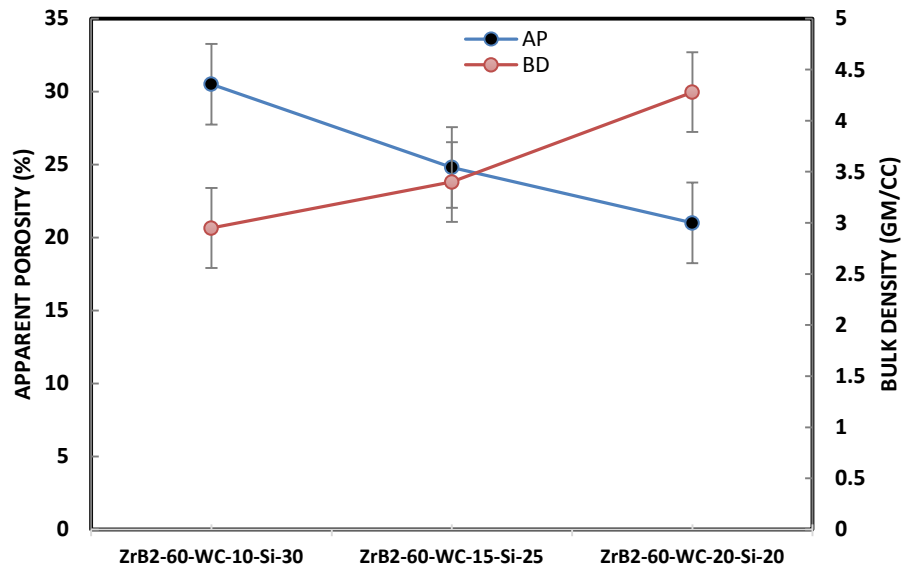


Figure 5. Apparent porosity and bulk density of sintered ZrB₂-WC-Si cermet

3.3.4. Micro-hardness

Fig.6 shows the variation of hardness of the ZrB₂-WC-Si cermets with respect to different compositions. The hardness values of sintered samples showed similar trends like density of corresponding cermets. It was observed that the amounts and distribution of ZrB₂, WC and Si phases along with product phases are affecting the hardness and density of the cermet with respect to sintering temperature. It was evident from the figure that the hardness value linearly increasing with the WC content of the material. The presence of residual porosity in case of cermets containing 10 wt. % and 15 wt. % WC, might be account for the part of decrease in measured hardness in comparison to cermet containing 20 wt. % WC. Residual stresses in sintered product was another factor affecting hardness of cermet. Due to increase in density and lower apparent porosity of the cermet ZrB₂-60-WC-20-Si-20, the hardness value was increasing accordingly. Also due to formation of prominent SiC phases in the ZrB₂ matrix part of ZrB₂-60-WC-20-Si-20 cermet, the hardness value was found to be increasing drastically however same phenomenon observed with lower fraction in case of cermets ZrB₂-60-WC-10-Si-30 and ZrB₂-60-WC-15-Si-25. S. Zhu et al.[11] have observed that the hardness value of ZrB₂ based composites found to be 17.5 GPa while sintering at 1820°C through microwave sintering. Furthermore, the cermet having composition ZrB₂-60-WC-20-Si-20 recorded extraordinary level of improvement of the hardness (i.e. 27.5 GPa).

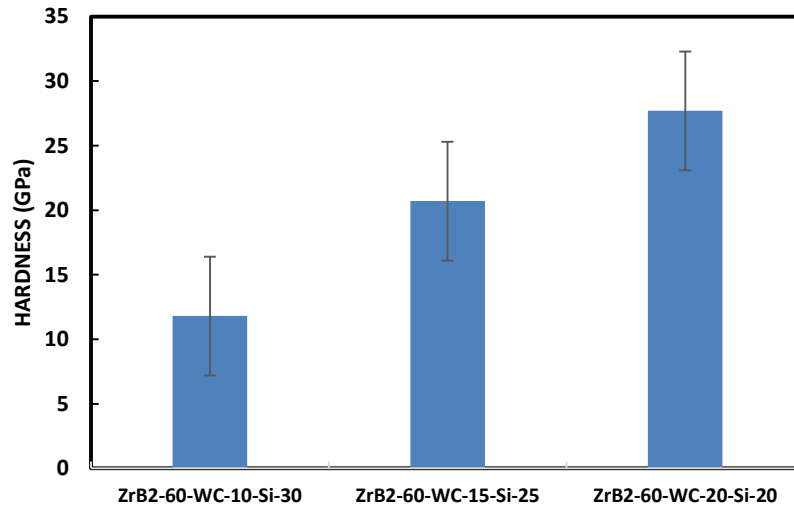


Figure 6. Hardness of ZrB₂-WC-Si cermet with varying compositions

3.3.5. Wear behaviour

Wear behavior of ZrB₂-WC-Si cermet for different compositions are studied by means of graphical representation as shown in fig.7 and fig.8. It was observed that the cermet ZrB₂-60-WC-20-Si-20 showed lower wear depth with respect to time and sliding distance. This might be due to liquid phase sintering of metallic Si in the matrix during SPS and formation of WSi₂ and SiC phases simultaneously enhancing the hardness of the cermet as confirmed from XRD and SEM analysis. As a result of which intergranular and intragranular region became densified resulting less wear of the matrix of the cermet.

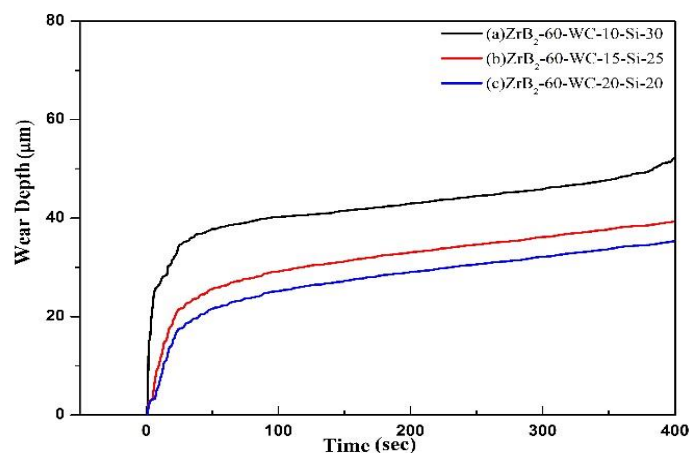


Figure 7. Variation of wear depth with sliding time for different ZrB₂-WC-Si cermets

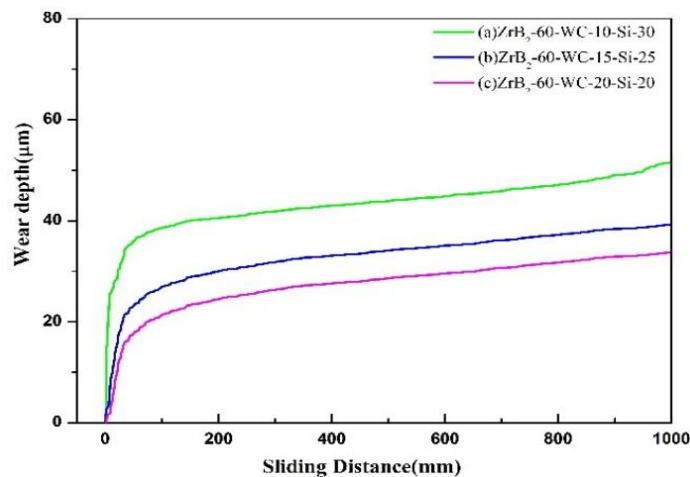


Figure 8. Variation of wear depth with sliding distance for different ZrB₂-WC-Si cermets

From the results discussed earlier, the density and hardness are reached at maximum value in case of cermet ZrB₂-60-WC-20-Si-20. Hence matrix part of corresponding cermet became strengthen and the wear pattern gradually in reducing nature.

4. Conclusion

ZrB₂-WC-Si cermet having different compositions in the form of ZrB₂-60-WC-10-Si-30, ZrB₂-60-WC-15-Si-25 and ZrB₂-60-WC-20-Si-20 are synthesized through SPS technique. XRD analysis of the sintered cermets shows the presence of parent phases along with metastable phase like WSi₂ and also SiC formation in different cermets, however it is most prominent in ZrB₂-60-WC-20-Si-20. It could be correlated with SEM analysis of sintered pellets that confirmed the presence of different phases like ZrB₂, WC in the matrix along with SiC. Lower porosity and higher bulk density are observed in case of sintered ZrB₂-60-WC-20-Si-20 cermet. Hardness of ZrB₂-60-WC-20-Si-20 cermet shows higher value i.e. 27.5 GPa as compared to the other cermets ZrB₂-60-WC-10-Si-30 and ZrB₂-60-WC-15-Si-25. The wear pattern is improving gradually upto maximum level in case of cermet containing 20% WC and 20% Si.

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