

EFFECT OF NdB_6 ADDITION ON DENSIFICATION AND PROPERTIES OF ZrB_2

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This paper reports on the effect of NdB_6 addition on densification and properties of ZrB_2 . NdB_6 powder (2.5, 5 and 10 wt. %) was added to ZrB_2 powder and consolidated by hot pressing. It was found that NdB_6 addition assisted in densification of ZrB_2 at lower hot pressing temperature of 1750°C. Formation of solid solution was observed at the interface of ZrB_2 and NdB_6 phases. Hardness was found to be slightly increased by 2.5 wt. % NdB_6 addition but decreased by 5 and 10 % NdB_6 addition. Fracture toughness of composite is found to be higher than the monolithic ceramic. It was found that composite samples have excellent oxidation resistance at 900°C in air.

INTRODUCTION

Zirconium diboride has attracted extensive attention due to excellent combination of properties as high melting point, high hardness, high thermal and electrical conductivity, high temperature strength and thermal shock resistance [1-3]. It is considered a potential material for hypersonic flight, atmospheric re-entry and rocket propulsion [1, 4]. It is a highly promising candidate for the leading edges of future re-entry vehicles which will have sharp edges for better flight performance [1, 3-5]. It is expected to be used for electrode application in Hall-Heroult cell and electric discharge machining due to its good electrical conductivity [6-8]. It is also considered a suitable material for neutron absorber in nuclear reactors. [9-10]

Despite of attractive properties of ZrB_2 , its applicability is limited due to its poor sinterability and low fracture toughness. Poor sinterability of ZrB_2 is due to low self diffusivity and strong covalent bonding. Dense ZrB_2 shapes can be fabricated by hot pressing or spark plasma sintering at high temperatures (~ 1900°C) [1, 11]. Previous studies have shown improved sintering behavior and properties by the addition of second phase [12-15]. Carbon and carbide additions were reported to accelerate densification by reacting with the oxide layer present in the surface of ZrB_2 particles [16-20]. Addition of silicides such as TiSi_2 , ZrSi_2 , CrSi_2 and TaSi_2 improved the densification of ZrB_2 by formation of liquid phases

during sintering. [21-23]. Metallic addition such as Ni is also reported to improve the densification by liquid phase sintering [19]. Though, metal and silicide additions lower the hot pressing temperature, they are also expected to deteriorate the mechanical properties.

Rare earth hexaborides are remarkable materials due to their refractory nature and good physical properties such as high thermal and electrical conductivity. Moreover these hexaborides are expected to form solid solution with ZrB_2 and assist in densification. As per author's knowledge there is no literature on the application of NdB_6 as sinter additive for ZrB_2 . NdB_6 has high melting point and thus would be a promising additive for high temperature application. The purpose of the present study is to elucidate the effect of NdB_6 on processing and properties of ZrB_2 . Salient properties of ZrB_2 and NdB_6 are given in Table 1.

Table 1. Salient properties of ZrB_2 and NdB_6 *.

Property	ZrB_2	NdB_6
Crystal structure	Hexagonal	Cubic
Density	6.1	4.95
Melting point	3245	2610
Thermal expansion coefficient ($^{\circ}\text{C}^{-1}$)	5.9×10^{-6}	7.3×10^{-6}
Thermal conductivity	57.9	47
Elastic modulus (GPa)	489	–
Hardness (GPa)	23.91	24.9

EXPERIMENTAL

Starting material

In house prepared ZrB_2 (D_{50} : 2.7 μm , 'C': 0.6 wt. %, 'O': 0.5 wt. %) and NdB_6 (D_{50} : 2.5 μm , 'C': 0.8, 'O': 0.7 wt. %) powders were used as starting materials. Preparation details of ZrB_2 powder is presented elsewhere [24]. NdB_6 was prepared by boron carbide

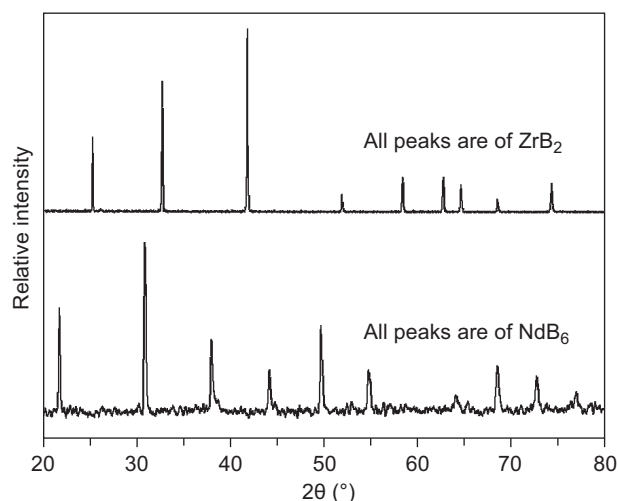
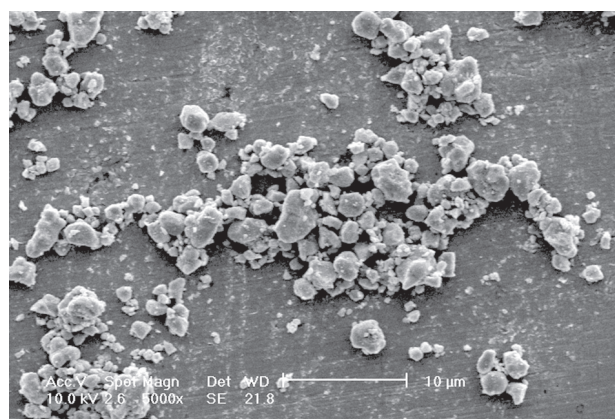
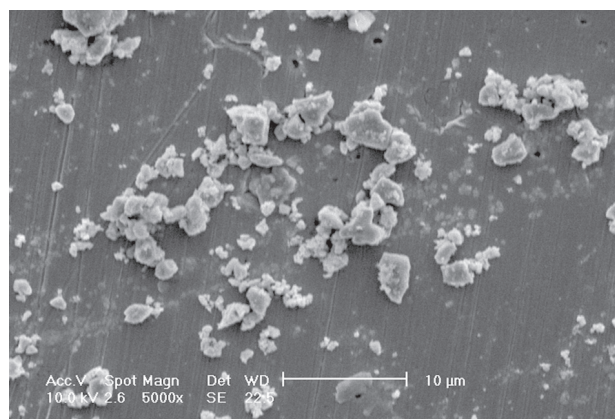


Figure 1. XRD pattern of starting materials: a) ZrB_2 , b) NdB_6 .



a) ZrB_2



b) NdB_6

Figure 2. SEM image of starting powders: a) ZrB_2 , b) NdB_6 .

reduction of Nd_2O_3 . Mean particle diameters of starting powders were measured by laser diffraction method (CILAS PSA 1064L). Figure 1 presents the XRD pattern of the starting powders. Figure 2 presents the SEM images of powder which show that both ZrB_2 and NdB_6 particles are equiaxular and in the range of 2 - 4 μm . No agglomerations were observed in the starting powders.

Densification and characterization

For densification, weighed quantities of fine zirconium diboride and neodymium hexaboride were mixed thoroughly using a motorized mortar and pestle in dry condition for 1 h to obtain samples of different compositions. The powders were then loaded in a high density graphite die (12 mm diameter) and hot pressed at a temperature of 1750°C under a pressure of 35 MPa for 2 hour in a high vacuum (1×10^{-5} mbar) chamber. The pellets were ejected from the die after cooling and the density measured by liquid displacement method. Densified samples were polished to mirror finish using diamond powder of various grades from 15 to 0.25 μm in an auto polisher (laboforce-3, Struers). Microhardness was measured for polished samples under a load of 100 g and dwell time of 10 s. The indentation fracture toughness (K_{IC}) data were evaluated by crack length measurement of the crack pattern formed around Vickers indents (using 10 Kg load), adopting the model formulation proposed by Anstis et al. [25], $K_{IC} = 0.016(E/H)^{1/2}P/c^{3/2}$, where E is the Young's modulus, H the Vickers's hardness, P the applied indentation load, and c the half crack length. Young's moduli (E) of the samples were measured by ultrasonic method as per ASTM C1419 procedure. The reported value of hardness and fracture toughness are the average of five measured values. Polished and fractured surfaces of dense pellets were analyzed by scanning electron microscope and Energy dispersive spectroscopy (EDS).

Oxidation

Oxidation study of the composite was carried out at a temperature of 900°C. Hot pressed pellet of diameter 12 mm was cut into thin slice of 3 mm thickness. All the surfaces of the cut sample were polished with emery papers (1/0, 2/0, 3/0, 4/0) and finally with diamond paste up to 1 μm finish. Oxidation tests were conducted in a resistance heated furnace. In order to avoid oxidation during heating, the sample was directly inserted into the furnace on reaching the required temperature. Samples were placed in an alumina crucible kept into the furnace. The samples were oxidized for different time intervals (0.5, 1, 2, 4, 8, 16, 32 and 64 h) at the set temperature of 900°C. The samples were carefully weighed before and after exposure, to determine the weight change during the oxidation process. The morphology and nature of oxide layer was understood by observing the surface in a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Densification and characterization

Effect of NdB_6 addition on densification and properties were studied. Hot pressing conditions, relative densities, hardness and fracture toughness obtained for the ZrB_2 composites are presented in Table.2.

It was found that addition of 2.5 wt. % NdB_6 resulted in densification of 99.3 % ρ_{th} at a temperature of 1750°C and a pressure of 35 MPa. Under identical hot pressing conditions, a density of 96.5 % and 95.4 % TD was obtained in composites with 5 % and 10 % NdB_6 respectively. In case of monolithic ZrB_2 , a near full

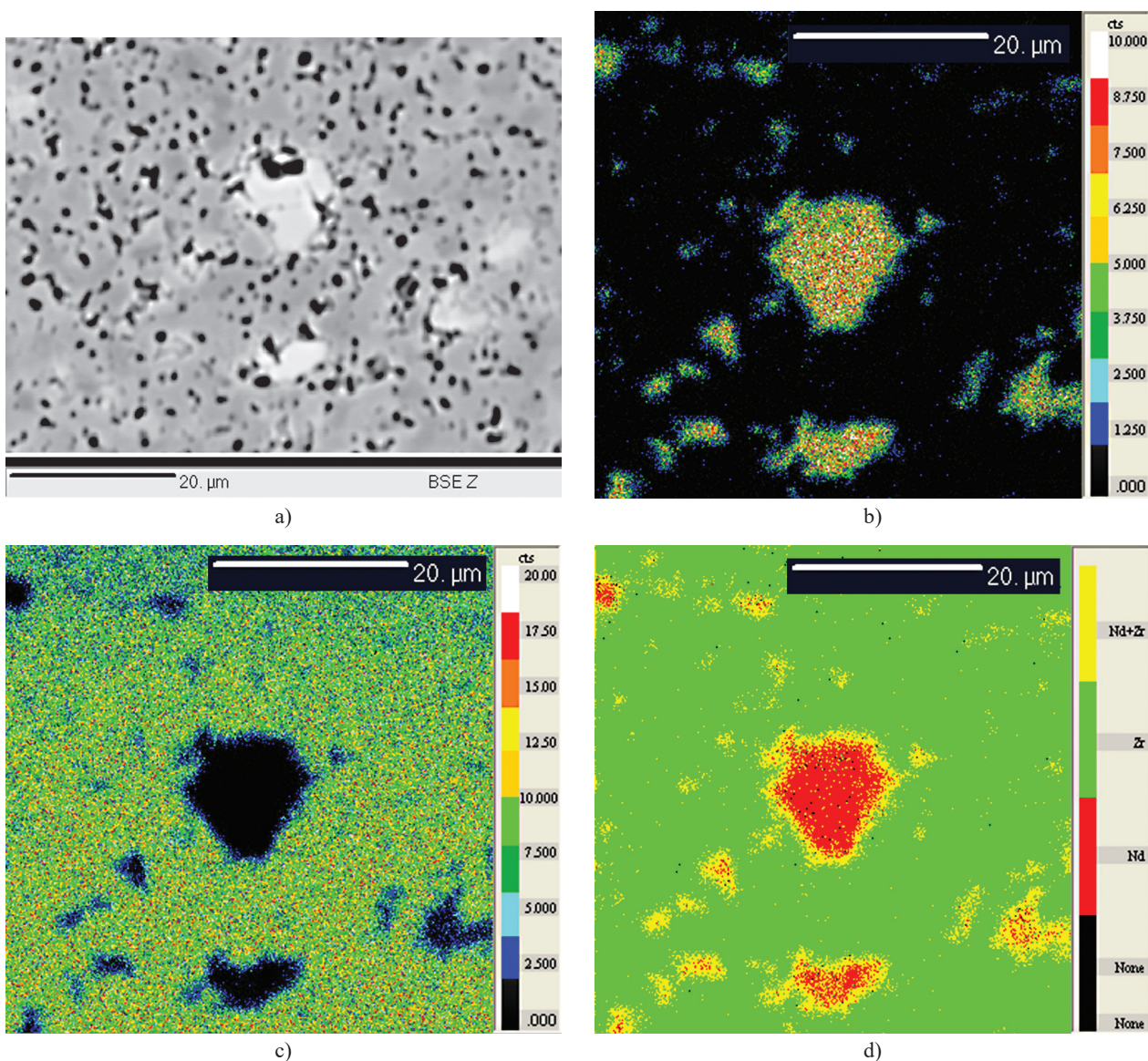


Figure 3. a) Back scattered image of $\text{ZrB}_2 + 10\% \text{NdB}_6$; b) Distribution of Nd; c) Distribution of Zr; d) Overlay of Zr and Nd distribution.

Table 2. Hot pressing conditions and properties of the ZrB_2 composites.

Sample	Temp. (°C)	Pressure (MPa)	Density (%)	Hardness (GPa) (100 gm)	K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)
ZrB_2^*	1850	35	99.8	23.91	3.31
ZrB_2	1750	35	80.3	–	–
$\text{ZrB}_2 + 2.5\% \text{NdB}_6$	1750	35	99.3	26.4 ± 2	4.25 ± 0.5
$\text{ZrB}_2 + 5\% \text{NdB}_6$	1750	35	96.5	21.7 ± 2	4.62 ± 0.5
$\text{ZrB}_2 + 10\% \text{NdB}_6$	1750	35	95.4	22.6 ± 2	4.74 ± 0.5

* Reference [20]

density (99.8 % TD) was obtained at a higher temperature and pressure of 1850°C and 35 MPa [24]. In the present study, the hot pressing temperature was lower by 100°C. For the purpose of comparison, monolithic ZrB₂ was hot pressed at 1750°C and a density of merely 80.3 % TD is achieved. Addition of NdB₆ to ZrB₂ may result in the solid solution formation of ZrB₂ and NdB₆. On the formation of ZrB₂-NdB₆ solid solution, Nd takes Zr atom positions and boron occupies boron positions in the crystal structure. Due to large number of boron atoms from NdB₆, there will be generation of point defects in ZrB₂. The point defects are known to enhance the diffusional mass transfer and thus assist in densification at slightly reduced temperature. Formation of solid solution was confirmed by elemental analysis (EDS) of phases present in microstructure, which is discussed in the next paragraph.

Back scattered image of ZrB₂ + 10 % NdB₆ sample hot pressed at 1750°C is presented in Figure 3a. Distribution of Nd and Zr in the microstructure is presented in Figure 3b-d. It is obvious that the matrix is Zr rich and indeed it is ZrB₂. A second phase with white shades was found in the BSE image. Elemental mapping has revealed that the white shades are Nd rich and it must be NdB₆. Figure 3d presents the overlay distribution of Zr and Nd in the microstructure. In this image presence of three distinct phases were noticed. Apart from ZrB₂ (green regions) and NdB₆ (red regions) there are yellow regions, which were analysed to contain both Zr and Nd. This suggested the formation of ZrB₂-NdB₆ solid solution. However, ZrB₂ and NdB₆ do not form complete solid solution and NdB₆ is also present as second phase in the composite as observed in the XRD pattern of the dense pellet of ZrB₂ + 10 % NdB₆ sample which is shown in Figure 4. It indicated the presence of crystalline ZrB₂ and NdB₆. One peak of ZrO₂ is also found in the XRD pattern which could be due to the oxygen pickup

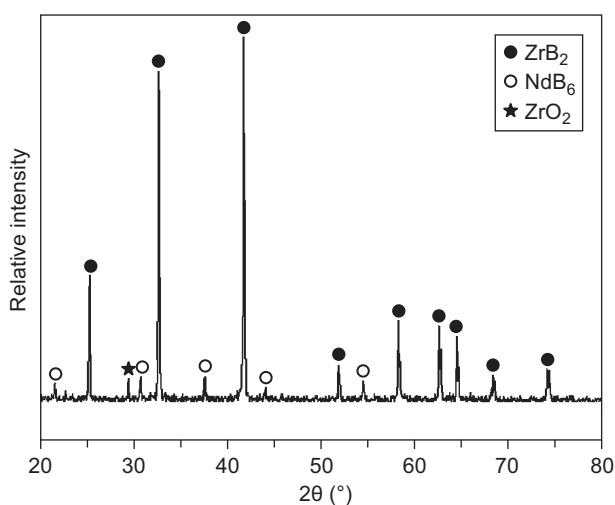
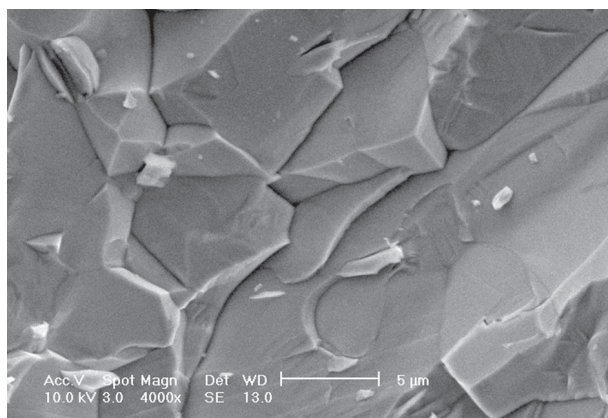


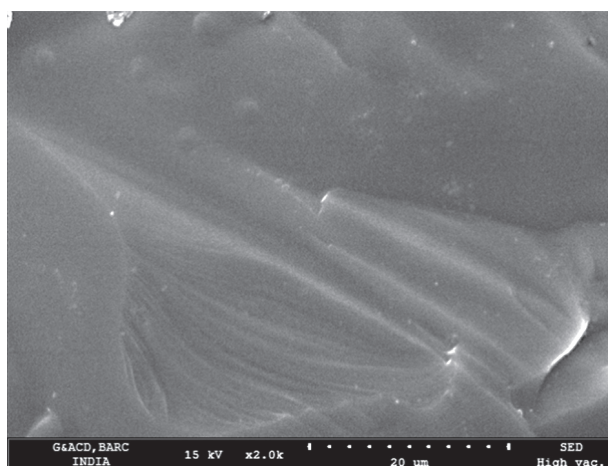
Figure 4. XRD pattern of Hot pressed ZrB₂ + 10 % NdB₆ sample.

during mixing of ZrB₂ and NdB₆. Usually fine non oxide ceramics are associated with thin oxide layer as coating on the particles.

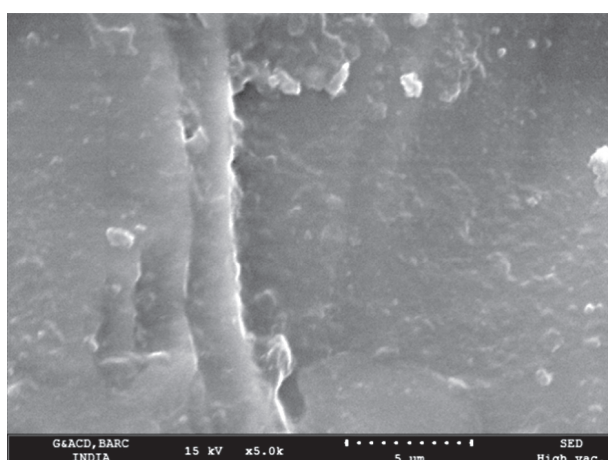
Comparison of other sinter additives from literature is discussed below. Guo et al. [26] have reported that addition of 5 % Re₂O₃ (Re = Y, Yb, La, Nd) to ZrB₂-20 % SiC results in > 99 % TD on hot pressing at 1900°C.



a)



b)



c)

Figure 5. Fractured surfaces of ZrB₂ composites: a) ZrB₂ + 2.5 % NdB₆; b) ZrB₂ + 5 % NdB₆; c) ZrB₂ + 10 % NdB₆.

La_2O_3 and Nd_2O_3 react with surface oxides to form a liquid phase and promote densification of ZrB_2 -SiC ceramics. Wang et al.[27] have reported that 10 % Mo addition gives a density of 98.9 % TD on hot pressing at 1950°C and 20 MPa. Zhu *et al* [28] have observed that addition of 3 - 10 % Al_2O_3 and Y_2O_3 and 20 % SiC_w to ZrB_2 gives a density > 97 % TD on hot pressing at 1800°C. From the above it is clear that addition of NdB_6 in the present investigation is found to be very effective in lowering the hot pressing temperature to 1750°C.

Mechanical properties and fractography

Variation in Vickers hardness and fracture toughness of ZrB_2 composites are presented in Table 2. Hardness of monolithic sample was measured as 23.9 ± 2 GPa [1], which increases to 26.4 ± 2 GPa with the addition of 2.5 wt. % NdB_6 . The increase in hardness is attributed to the solid solution hardening by formation of ZrB_2 - NdB_6 solid solution. On formation of solid solution the parent lattice gets strained and results in hardening of material. The hardness value of composite with 5 and 10 % NdB_6 addition was measured as 21.7 ± 2 and 22.6 ± 2 GPa respectively. The relatively lower hardness is due to the lower density of the hot pressed composite. Hardness of monolithic ZrB_2 has been reported to be in the range of 22 - 23 GPa [1, 2, 29]. Chamberlain et al. [29] have reported a hardness of 23 GPa for hot pressed ZrB_2 . Silvestroni et al [30] have reported a hardness of 18.3 GPa for hot pressed $\text{ZrB}_2 + 15$ vol. % WSi_2 . Hardness of $\text{ZrB}_2 + \text{EuB}_6$ composite has been reported in the range of 21 - 25 GPa [14].

Fracture surfaces of $\text{ZrB}_2 + \text{NdB}_6$ composites are presented in Figure 5. It is obviously seen that the mode of fracture is transgranular in all the three composites. Fracture toughness of $\text{ZrB}_2 + 2.5$ % NdB_6 sample was measured as $4.25 \text{ MPa}\cdot\text{m}^{1/2}$. With increased addition of NdB_6 , fracture toughness increased gradually to 4.62 and $4.74 \text{ MPa}\cdot\text{m}^{1/2}$ for composites containing 5 and 10 % NdB_6 respectively. The fracture toughness values obtained in the composite samples are found to be greater than the values reported for monolithic ZrB_2 in literature. Fracture toughness of monolithic ZrB_2 has been reported as $3.5 \text{ MPa}\cdot\text{m}^{1/2}$ [1]. Ran et al [31] have reported the enhancement of fracture toughness to $4.2 \text{ MPa}\cdot\text{m}^{1/2}$ by 5 % SiC and 5 % ZrH_2 addition.

Oxidation study

The weight gain data obtained during oxidation at 900°C as a function of time for $\text{ZrB}_2 + 2.5$ % NdB_6 , $\text{ZrB}_2 + 5$ % NdB_6 and $\text{ZrB}_2 + 10$ % NdB_6 samples are presented in Figure 6. All the three samples have shown continuous weight gain with time. On progress of oxidation it was observed that the rate of oxidation (slope of the curve) gets decreased. Figure 7 presents the rate of

weight gain with time for $\text{ZrB}_2 + 10$ % NdB_6 sample. It shows sharp decrease in rate of oxidation just after initial oxidation. The decrease in rate of oxidation is credited to the formation of a protective layer. In the previous study [1], oxidation rate was found to be constant in case of monolithic ZrB_2 . The enhancement of oxidation resistance of ZrB_2 by NdB_6 addition could be attributed to the formation of protective layer which could be a glassy layer based on boron, oxygen, Neodymium and zirconium.

Figure 8 presents the XRD pattern of oxidized surface. It shows the presence of ZrO_2 and Nd_2O_3 phase in crystalline form. One small peak of B_2O_3 is also present. Figure 9 presents the SEM microstructures of the oxidized surface. Presence of protective layer is evidently visible. Figure 10 presents the typical EDS pattern of oxide layer which indicates presence of Zr, Nd and O elements in the protective layer, which suggest the formation of Zr-Nd-B-O glassy phase which imparts resistance to oxidation by limiting the diffusion of oxygen through it. Presence of crystalline ZrO_2 and Nd_2O_3 phase

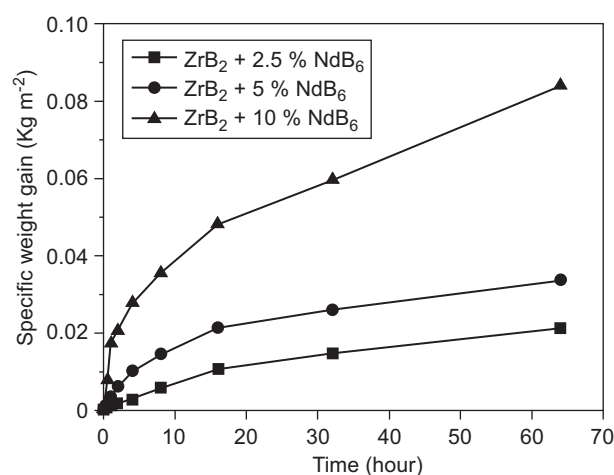


Figure 6. Specific weight gain vs time plot for ZrB_2 based composites after oxidation at 900°C for 64 hour.

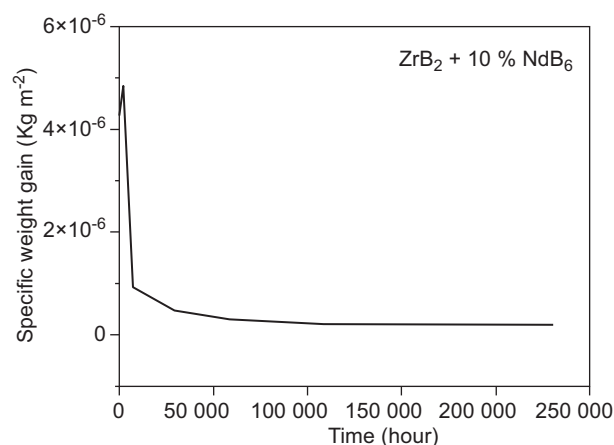


Figure 7. Rate of weight gain with time during oxidation of $\text{ZrB}_2 + 10$ % NdB_6 at 900°C in air.

in XRD pattern suggests that very fine zirconium oxide and neodymium oxide crystals could be present in the glassy layer.

The observations of other researchers on oxidation of ZrB₂ based material is discussed below. Sciti et al. [32] have found that on oxidation of ZrB₂ + 20 % MoSi₂ at 700°C, the extent of oxidation is very limited. Samples oxidized at temperature range 1200 - 1400°C was found to be covered by a continuous silica-rich glassy layer, in

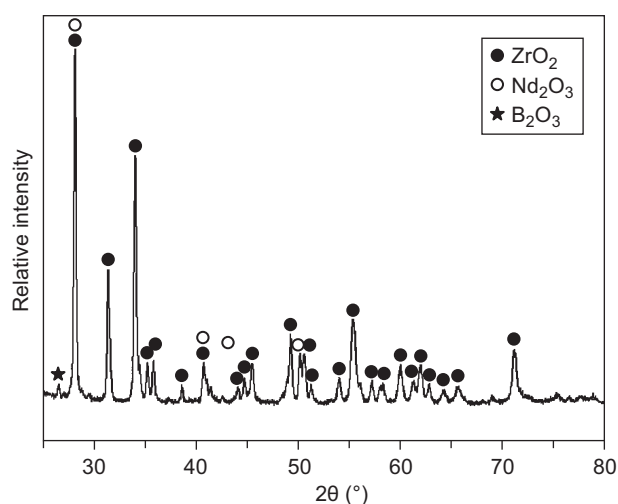


Figure 8. XRD pattern of ZrB₂ + 10 % NdB₆ sample after oxidation at 900°C for 64 hour.

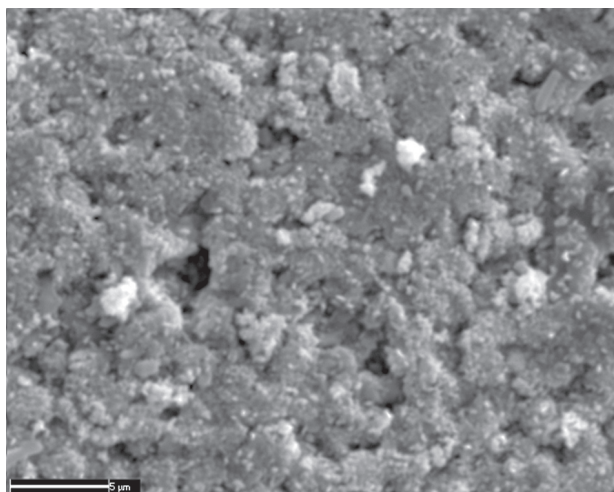


Figure 9. SEM image of ZrB₂ + 10 % NdB₆ composite after oxidation at 900°C for 64 hour.

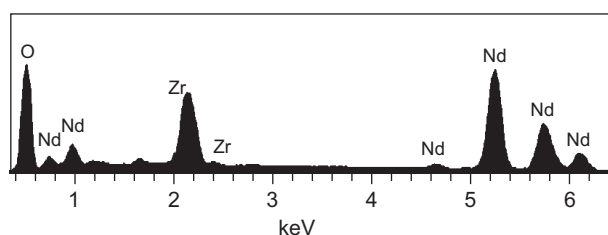


Figure 10. Typical EDS pattern of oxidized surface of ZrB₂ + 10 % NdB₆.

which small zirconia and/or zircon grains are embedded. Peng et al. [33] have studied the oxidation behaviour of ZrB₂ ceramic containing B₄C, SiC, TaB₂ and TaSi₂ by scanning thermogravimetry in the temperature range of 1150 to 1550°C. SiC additions improved oxidation resistance over a broadening range of temperatures. Tantalum additions to ZrB₂-B₄C-SiC in the form of TaB₂ and/or TaSi₂ increased oxidation resistance over the entire evaluated spectrum of temperatures. Dehdashti et al. [34] have studied the effect of tungsten addition on oxidation of ZrB₂. For pure ZrB₂, the protective liquid/glassy layer covering the surface as a result of oxidation was evaporated above 1500°C. For (Zr,W)B₂ specimens, the liquid/glassy layer was present after exposure up to 1600°C. Zhao et al [35] studied the effect of AlB₂ addition on oxidation of ZrB₂ at 1500°C. The oxidation tests revealed that the AlB₂ phase improved the oxidation resistance for the ZrB₂ based ceramics, owing to the Al-B-O liquid phase formed on the surface of the oxidized specimen, which slows down the oxygen transportation velocity.

In this study, NdB₆ addition to ZrB₂ was found effective in improving the oxidation resistance at 900°C in ambient air.

CONCLUSION

Neodymium hexaboride was found to be an effective sintering aid for densification of ZrB₂. Addition of 2.5 % NdB₆ assisted in sintering and lowered the hot pressing temperature to 1750°C from 1850°C for monolithic ZrB₂. A mechanism was proposed to explain the reduction in sintering temperature. Formation of solid solution of ZrB₂ and NdB₆ was observed in microstructure analysis. As there is more number of boron atoms in NdB₆ there was formation of point defects in ZrB₂, which assisted in sintering. Addition of merely 2.5 % NdB₆ was found to enhance the hardness due to solid solution formation. Fracture toughness of the composite is found to be higher than that of monolithic ceramic. Oxidation resistance of ZrB₂ at the temperature of 900°C was improved by NdB₆ addition by the formation of protective oxide layer.

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