Abstract

The present investigation attempts to synthesize ZrB_2 powder in the form of whiskers and nanocrystalline particles, study their sintering behaviour and compare the same with properties of commercial high purity ZrB_2 powder. Attempts have also been made to study the production of ZrB_2-Cu composite and evaluate their performance as an electrical discharge machining (EDM) cutting tool.

The thesis is divided into 5 chapters. The first chapter introduces the borides as futuristic high temperature structural materials and elaborates on the problems involved in the production of boride powders and the difficulties in producing dense borides. The chapter defines the present problem and its relevance. The second chapter deals with detailed literature review, which is presented in four different sections. The first section describes the production of borides (TiB_2, ZrB_2 and HfB_2) in general. The detailed production of ZrB_2 by different processes and their advantages, limitations etc. are explained. This section also includes a short overview on SHS process for the synthesis of advanced ceramics. The next section is concerned with pressureless sintering of ZrB_2 and the difficulties occurring during sintering of various ZrB_2 based composites. The third section deals with the oxidation behaviour of ZrB_2 and its various composites. The fourth section explains the EDM of ceramics materials, property changes due to EDM and improvement of EDM performance by incorporating tool materials by powder metallurgy route. The details of experimental procedures, materials used for present study and details of technique used for characterization of products etc. are delineated in chapter-III. The chapter-IV is concerned with various results obtained from different experiments and discussion of results. Relevant conclusions are drawn in chapter-V.

Zirconium diboride due to its high temperature strength, thermal stability and good electrical and thermal conductivity could be an excellent high temperature structural material. The ZrB_2 whiskers could find application as reinforcement in the composite production. Attempts have been made to produce ZrB_2 whiskers through a carbothermal reduction of a mixture of ZrO_2, H_3BO_3 and carbon. Effects of various catalysts and additives on the process of whisker formation have been investigated in detail.

Nanocrystalline ZrB_2 powder is produced through a magnesiothermic reduction (SHS) process using a mixture of ZrO_2, H_3BO_3 and Mg as the starting material. It is a highly exothermic process and can't be controlled easily. The heat generated also tends to produce dense semi molten mass of ZrO_2, ZrB_2, $B_{51}Zr$ and MgO mixture. Attempts have been made to develop

methods for controlling the process through appropriate additives and in the process to control the particle size of the ZrB_2 produced. The process parameters have been optimized to produce nanocrystalline sinterable grade powder and obtain a high yield of ZrB_2 powder. A process of double SHS (DSHS) has been developed for this purpose.

The synthesized ZrB_2 powders are used for pressureless sintering study and its sintering behaviour is compared with the commercial ZrB_2 powder. The sintered samples are free from cracks and other defects and show high shrinkage rates. Excessive weight loss during sintering of synthesized ZrB_2 powder has been observed and its causes are identified. The currently produced ZrB_2 shows a higher densification rate than the commercial powder and the sintered samples made from DSHS powder also show higher hardness.

The DSHS powder contains significant amount of ZrO_2 (~18wt%), which decreases the purity of product as compared to high pure commercial ZrB_2 powder. But after sintering the purity of dense compact made from the DSHS powder is increased due to reaction between unreacted ZrO_2 and $B_{51}Zr$. Negligible weight loss of sintered sample upon HF solution reflects the purity of DSHS samples.

The cyclic oxidation of dense ZrB_2 is investigated over the temperature range of 700-1200^{0}C in static air condition. Thermal analysis shows two types of oxidation products forming during oxidation. The O_2 diffusion profile measured from SEM/EDS study confirms an oxide layer (~25μm) formation at 800^{0}C in the case of DSHS ZrB_2 whereas under similar condition entire cross section is found to oxidize in case of commercial powder sintered. The oxidized surface at 1200^{0}C becomes porous possibly due to evaporation of B_2O_3 phases and the presences of cracks are often found under SEM. The XRD result shows presence of only ZrO_2 phase at all temperatures and presence of B_2O_3 is not detected by XRD study (possibly due to evaporation or its amorphous nature).

The ZrB_2-Cu composite is developed by pressureless sintering of different types of ZrB_2 powders (SSHS, DSHS and commercial) with addition of different amounts of Cu. A maximum density of the composite is found after sintering at 1250^{0}C and maximum hardness of the composites is found at 30 wt% of Cu addition and beyond this level the hardness is found to decrease with Cu addition. The coefficient of thermal expansion of DSHS ZrB_2-Cu composites if found to be larger than that of commercial powder.

Out of different ZrB_2-Cu composites, the ZrB_2-40wt% Cu composite is found to show better performance as a tool material during EDM study. Both the composites (DSHS and commercial) show better metal removal rate and less tool removal rate than the conventionally used copper tool. But copper tool shows lower average surface roughness and diameteral overcut than composite tools. The various types of debris containing satellite, dents, crack and burnt core etc. are formed at different processing condition of EDM.

The overall study tends to suggest that the currently developed DSHS powder seems to yield high density products in comparison to the commercial ZrB_2 powder. The temperature of synthesis of ZrB_2 is as low as ~800^0C, which indicates the possibility of large cost saving.