THE PRODUCTION OF HfO$_2$-HfB$_2$ COMPOSITE POWDER FROM HfO$_2$, B$_2$O$_3$ AND Mg BY SOLID STATE REACTION AND SUBSEQUENT ANNEALING

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ABSTRACT

Hafnium dioxide-hafnium diboride (HfO$_2$-HfB$_2$) composite powder was synthesized by high-energy ball milling and subsequent annealing of powder mixtures containing stoichiometric amounts of HfO$_2$, B$_2$O$_3$ and Mg. Milling was carried out in various durations by using vibratory ball-mill with a ball-to-powder weight ratio of 10:1. The milled products were annealed in tube furnace with a heating and cooling rate of 10°C/min. under flowing Argon atmosphere. After annealing, the HfO$_2$-HfB$_2$ composite powder is obtained in the presence of magnesium oxide (MgO). The milled and annealed products were analyzed by X-ray diffraction (XRD) technique and scanning electron microscope (SEM).

INTRODUCTION

Milling is commonly defined as the fracturing of relatively coarse materials to the ultimate fineness. It is also a simple room temperature process in which solid state reactions take place between the fresh powder surfaces of the reactant materials by repeated fracturing and repeated welding of powder particles [1]. Hafnium diboride can be synthesized by various methods such as self-propagating high temperature synthesis (SHS), metallothermic reduction, hot-pressing and chemical vapor deposition (CVD) [2]. Moreover, it can be obtained by solid state reactions named as mechanical alloying and mechanochemical synthesis using the powder mixtures of Hf/B and HfO$_2$/B$_2$O$_3$/Mg, respectively [3].

In the current literature, there has been a limited amount of studies related with the production of HfB$_2$ powder and HfO$_2$-HfB$_2$ composite powder. In previous literature findings, HfB$_2$ and its composite powders were synthesized by hot pressing method and the optimum reaction temperature was held about 1900°C [4]. The resistance to oxidation of HfB$_2$-SiC composite was described [5]. HfB$_2$ was also synthesized by carbothermal and borothermal reduction of HfO$_2$ at relatively low temperatures [6-7]. Solid state reactions of HfB$_2$ originated from HfO$_2$-B$_2$O$_3$-Mg system have not been sufficiently discussed up to now. The recent significant study is related with production of HfB$_2$ nanorod from HfCl$_4$ and B-based powder mixtures by mechanochemical synthesis and following annealing [8]. However, selected raw materials such as HfCl$_4$ and B are more expensive than oxide-based raw materials. Therefore, this study will be the first example of this investigation topic.

Within the scope of this study, HfO_2-HfB_2 composite powder was synthesized by high-energy ball milling of powder mixtures containing stoichiometric amounts of HfO_2, B_2O_3 and Mg powders in different milling durations and by subsequent heat treatment.

EXPERIMENTAL DETAILS

The raw materials used in this study were HfO_2 (Alfa Aesar, particle size 285 μm, tech. grade), B_2O_3 (ETI Mine, particle size 467 μm, purity 98 %) and Mg (MME, particle size 143 μm, purity 99,7 %). 3.150 g HfO_2, 1.038 g B_2O_3 and 1.812 g Mg were used to prepare totally 6 g of powder mixture in regard of the reaction shown in Eq. (1).

$$HfO_2 + B_2O_3 + 5Mg \rightarrow HfB_2 + 5MgO \qquad (1)$$

The prepared powder mixtures were milled in a high-energy ball-mill named as Spex 8000 D Mixer/Mill at 1200 rpm during 5, 7, 11 and 30 h milling time. Milling container was hardened steel vial with capacity of 50 ml and milling media was hardened steel balls with diameter of 6 mm. Ball-to-powder weight ratio was chosen as 10:1. Before milling, vial was evacuated to 10^{-2} Pa, back-filled with 99.999 % Argon gas and sealed in a glove-box.

After milled powders (5, 7, 11 and 30 h) were unloaded in glove-box, they were placed in quartz boats and heated up to 900°C, 1100°C and 1300°C in a Protherm tube furnace with a heating and cooling rate of 10°C/min. Annealing was conducted during 6 h under Argon gas flow rate of 2000 ml/min. Selected powders were also annealed for 12 and 18 h. The phase analyses of milled and annealed powders were carried out by Bruker[TM] D8 Advanced Series Powder Diffractometer with Cu Kα radiation in the 2θ range of 10-80° at a rate of 2°/min. The morphologies of the milled and annealed products were characterized by Hitachi[TM] TM-1000 Scanning Electron Microscopy (SEM) operated at 15 kV.

RESULTS AND DISCUSSION

XRD patterns of 5, 7, 11 and 30 h milled powder mixtures are shown in Figure 1. The main phenomena revealed by the XRD patterns are these: B_2O_3 phase is not present due to the amorphization; there is a slight reduction in crystal size of HfO_2 and Mg; and HfB_2 phase does not occur in the reaction process up to 30 h milling duration. Significant differences in HfO_2 and Mg peaks should be actually expected with extended milling time. However, there are slight decreases in the intensities of the peaks and also there are small broadenings that indicates the minor reduction in crystal size. It is obviously seen from Figure 1 that HfB_2 phase will arise over 30 h milling duration. It is considered as a non-economical method. Eventually, it can be said that this reaction needs heat treatment in order to obtain HfB_2 phase and the subsequent annealing process is preferred.
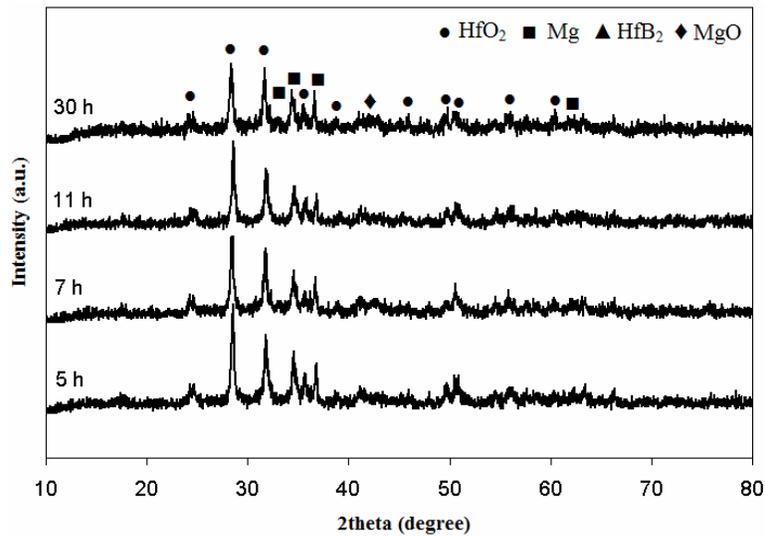
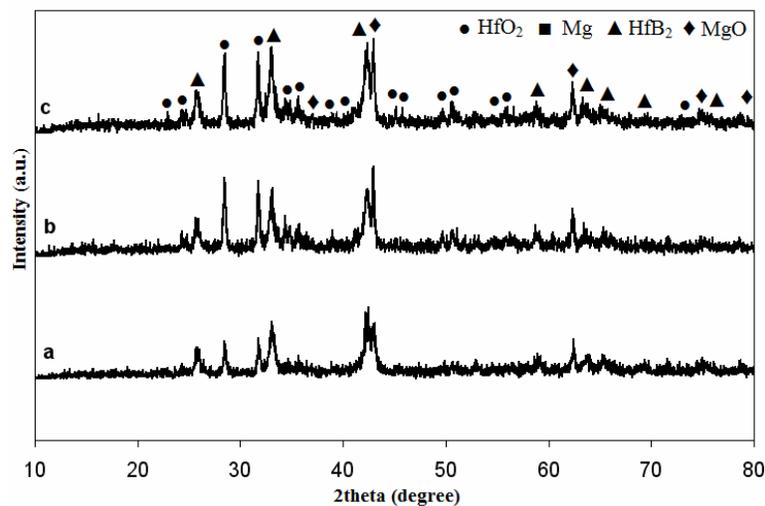Figure 1: XRD patterns of the powder mixtures after 5, 7, 11 and 30 h milling

Figure 2: XRD patterns of the milled powder mixtures after annealing at 1100°C for 6 h, a: 5 h, b: 7 h and c: 11 h

After 5, 7, 11 and 30 h milling, the powder mixtures were annealed at 900-1300°C during 6 h. During annealing, the reaction starts and HfB_2 phases occur. Figure 2 demonstrates the XRD patterns of the powder mixtures after 5, 7 and 11 h milling and annealing at 1100°C for 6 h. The XRD peaks in Figure 2 represent the growing of HfB_2 phase with prolonging milling time. High temperature allows the reduction of HfO_2 and B_2O_3 in the presence of Mg. It is not surprising to see the increasing MgO peak as HfB_2 phase grows. At the end of 6 h annealing, there is no unreacted Mg in the powder. The intensities of HfO_2 are expected to decrease with the increasing HfB_2 phase but they still increase and keep approximately the same HfB_2/HfO_2 ratios.

Figure 3 shows the XRD patterns of the powder mixtures after 5, 7 and 11 h milling and annealing at 1300°C for 6 h. XRD peaks of HfB_2 become greater with increasing temperature, comparatively with the Figure 2. It is also seen from the Figure 3 that shorter milling time and sufficient annealing temperature are appropriate for obtaining HfO_2-HfB_2 composite powder with small amounts of MgO. As seen from the Figure 3 that the intensities of MgO decrease compared with the Figure 2. MgO phase reacts with the quartz boats at 1300°C and it causes Mg_2SiO_4 formation. Also, 5 h milled and annealed product gives approximately the same XRD pattern with the others in Figure 5, except the lower intensities of HfO_2.

XRD patterns of 30 h milled and annealed (at different temperatures and durations) powder mixtures are shown in Figure 4. The incubation of HfB_2 is observed after annealing at 900°C during 6 h and the intensities of HfO_2 and Mg peaks are so small, like the reaction have just started. The spectrum likes neither a crystalline form nor an amorphous form. The suggested reason is that these conditions are sufficient to start the reaction, but it is inadequate to have the whole crystal structure. Figure 4 demonstrates that the peaks of HfB_2 increase with increasing annealing temperature. This is clear especially in (b) and (d) from 900°C to 1300°C.
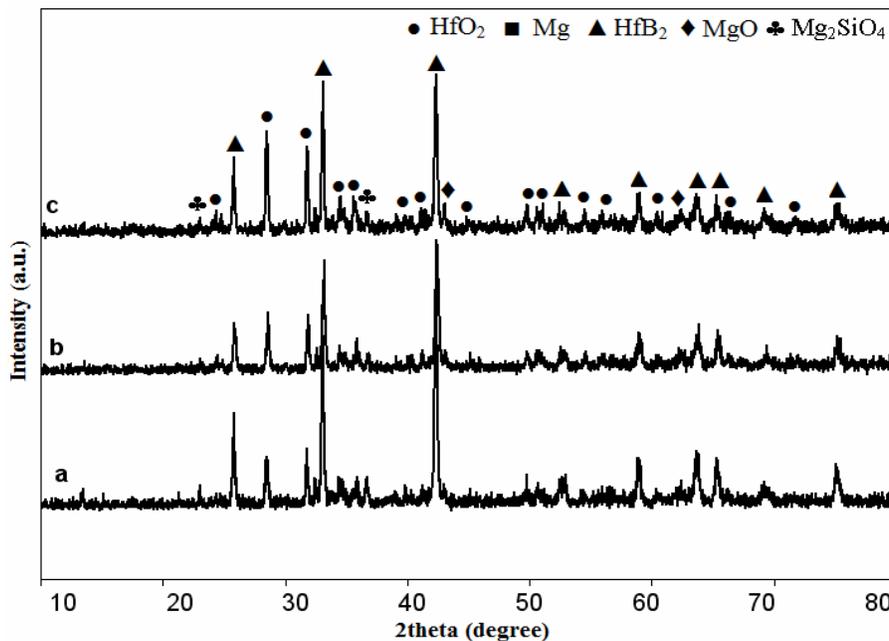

Figure 3: XRD patterns of the milled powder mixtures after annealing at 1300°C for 6 h, a: 5 h, b: 7 h and c: 11 h
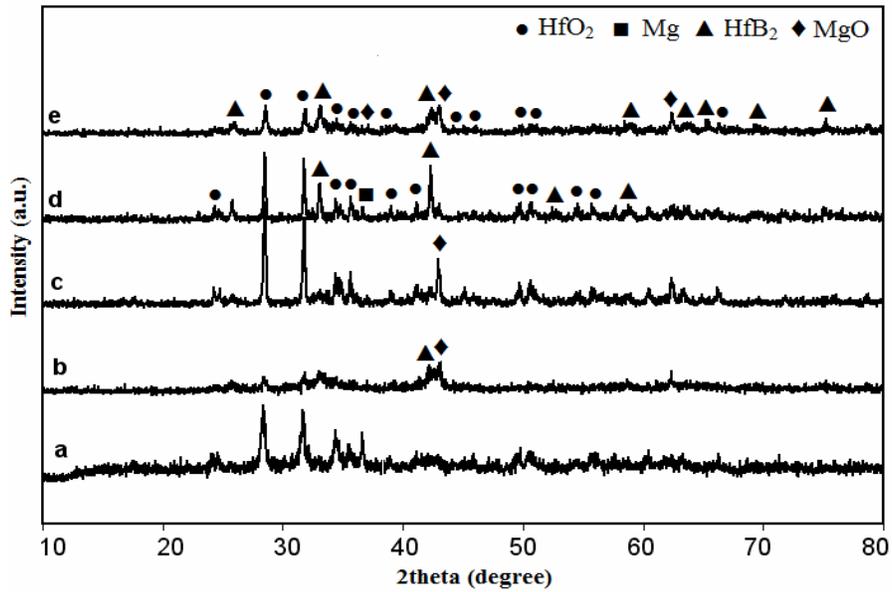
Figure 4: XRD patterns of the 30 h milled and annealed powder mixtures, a: milled; b: at 900°C for 6 h; c: at 1100°C for 6 h; d: at 1300° for 6 h; e: at 1100°C for 12 h
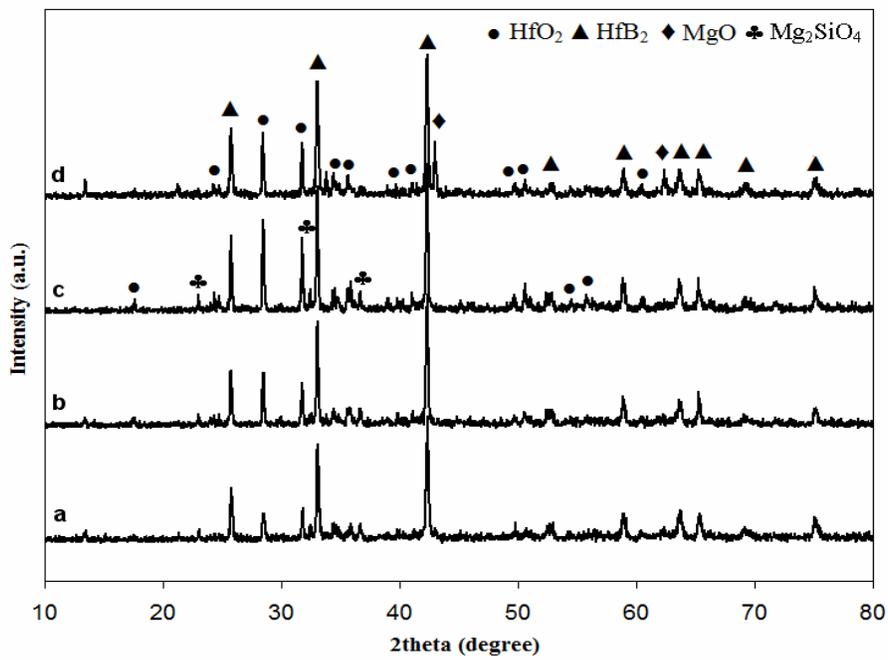

Figure 5: XRD patterns of the 5 h milled and at 1300°C annealed powder mixtures, a: for 6 h; b: for 12 h; c: for 18 h; d: for 12 h, in alumina boat
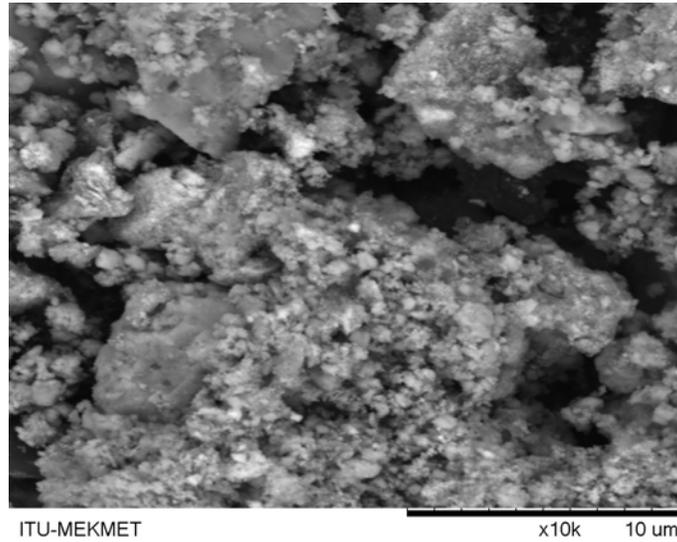
Figure 6: SEM image of 5 h milled powder mixtures

Due to the good results in short milling duration, 5 h milled powders were annealed in higher annealing times. Figure 5 shows that the XRD patterns of 5 h milled and annealed powders (for 6 h, 12 h and 18 h) at 1300°C. 5 milled powders were annealed during 12 h in alumina (Al_2O_3) boat because of the formation of Mg_2SiO_4 compound with the use of quartz boat. Figure 5 (d) points out that there was no trace of reaction between MgO and Al_2O_3 as proved by occurrence of MgO phase.
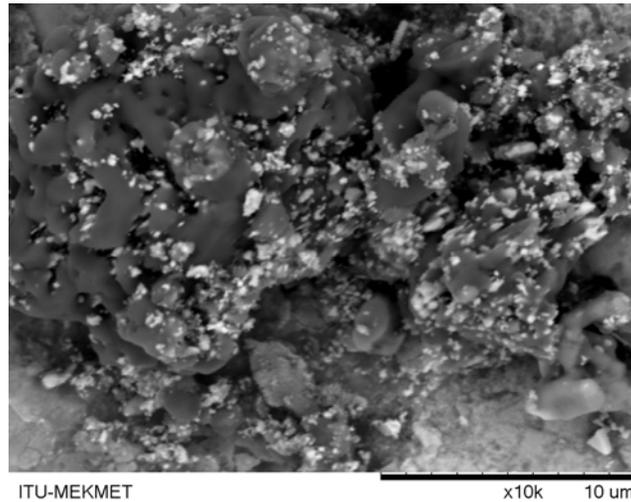

Figure 7: SEM image of 5 h milled and at 1300°C for 6 h annealed powder mixtures

Figure 6 displays the SEM image of 5 h milled powder mixtures. The particle size of powders ranges from 8 μm to 200 nm. Figure 7 demonstrates the SEM image of 5 h milled and annealed (at 1300°C for 6 h) powder mixtures. Nucleation, grain growth,

formation of new phases and coarse particles can be seen from Figure 7. Figure 8 shows that the SEM image of powder mixtures after 5 h milling and at 1300°C for 12 h annealing in alumina boat.
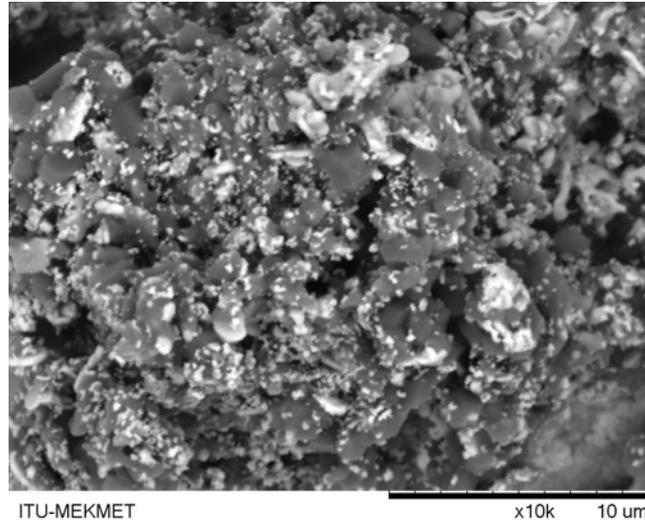

Figure 8: SEM image of 5 h milled and at 1300°C for 12 h annealed powder mixtures (alumina boat)

CONCLUSION

HfO_2-HfB_2 composite powder has been successfully obtained by high-energy ball milling and annealing of HfO_2-B_2O_3-Mg powder mixtures. 5 h milled and at 1300°C for 12 h annealed powder mixture (in alumina boat) gave the best XRD pattern. When alumina boat is used, there is only MgO phase and no additional compound. MgO can be easily removed by washing with distilled water and ethanol due to the insolubility of HfO_2 and HfB_2. Thus, the formation of the composite powder has been accomplished with short milling duration and subsequent annealing.

ACKNOWLEDGEMENTS

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