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Synthesis and characterization of dense ultra-high temperature thermal protection materials produced by field activation through spark plasma sintering (SPS): I. Hafnium Diboride

U. ANSELMI-TAMBURINI
Department Chemical Engineering and Materials Science, University of California, Davis, CA, 95616, USA

Y. KODERA
*Department of Materials Chemistry and the High-Tech Research Center,
Ryukoku University, Seta, Ohtsu, Japan*

M. GASCH
ELORET Corp., NASA Ames Research Center, Moffett Field, CA 94035-1000, USA

C. UNUVAR, Z. A. MUNIR*
Department Chemical Engineering and Materials Science, University of California, Davis, CA, 95616, USA

M. OHYANAGI
*Department of Materials Chemistry and the High-Tech Research Center,
Ryukoku University, Seta, Ohtsu, Japan*

S. M. JOHNSON
*Thermal Protection and Materials Systems Branch, NASA Ames Research Center,
Moffett Field, CA 94035-1000, USA*

The consolidation of HfB_2 by sintering and reactive sintering using the field-activated process of the spark plasma sintering (SPS) method was investigated. Sintering of the diboride at 1900°C under a pressure of 95 MPa did not result in dense materials. In contrast, reactive sintering at 1700°C produced about 98% dense HfB_2 with a 10 min hold at temperature. In contrast to previous observations, the reaction between the elements and the consolidation of the resulting diboride did not coincide, the latter occurring at a much higher temperature. The reaction mechanism between B and Hf during reactive sintering was investigated. Measured rates of growth of the HfB_2 were found to be in agreement with calculated values from diffusion couple experiments, suggesting that the current did not play a significant role in the reactivity.

1. Introduction

The development of hypersonic flight vehicles has been the driving motivation for the search for ultra-high temperature ceramics (UHTCs) to be used for the leading edges of sharp-bodied re-entry vehicles. Among the materials that have attracted considerable attention in recent years are the borides of group IVb transition metals, with the diborides of hafnium and zirconium being the most promising. Their high melting temperatures and relatively good oxidation resistance provide the promise of operating in an oxidizing environment at temperatures in the range 1900–2500°C [1]. Effort to develop such high temperature materials began in the 1960s [2] and experimental work on the enhancement of the oxidation resistance of the

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*Author to whom all correspondence should be addressed.

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borides through a second phase addition was carried out [2]. Addition of SiC was found to enhance oxidation resistance with the optimum level reported to be 20 vol% [3]. In addition to improving the oxidation resistance of the diboride, the second phase SiC also served as a sintering aid and as grain growth inhibitor [1]. Other additives were also investigated, including elemental carbon, chromium, aluminum, and tantalum, but the results were generally not satisfactory to the proposed application. Addition of silicide phases of the metal of the diboride or the silicides of other metals were also widely investigated [4–6]. Details of these investigations and a review of the oxidation studies of the diborides have recently been provided in the comprehensive work of Opeka *et al.* [7].

In the majority of reported studies, the preparation of dense bodies of the diborides was accomplished through hot-pressing, resulting in materials with a wide range of (typically large) grain sizes and consequently a considerable variation in the mechanical properties [1].

An early attempt to densify HfB_2 was made by Kalish and Clougherty by hot-pressing [8]. They obtained fully dense samples only when the temperature exceeded 1840°C and under a very high pressure (800 MPa). Densification was also achieved by reactive sintering, using elemental powders [9]. Although this approach facilitated densification, it nevertheless required extreme conditions (2160°C for 3 h with 27.3 MPa) in order to obtain a sample with a final porosity between 5 and 10%. In addition, the samples contained significant contamination from carbon, in the form of HfC.

The use of field activation to sinter or reactively sinter materials has recently been shown to provide an effective means to densify high temperature materials in a relatively short time [10]. A variation of this technique is the spark plasma sintering (SPS) method in which pulsed DC current is applied simultaneously with a uniaxial pressure. In this paper we report results of an investigation on the formation of dense hafnium diboride by sintering and by reactive sintering using the SPS method. In subsequent publications we will report on the effect of additives on the sintering of this boride.

2. Experimental materials and methods

The characteristics of the powders used in this study are reported in Table I. Boron powders with different purity levels, and different handling procedures were explored in order to assess the influence of these parameters on the properties of the final product. For the sintering of HfB_2, typically about 15 g of powders were poured in a graphite die having an internal diameter of 19 mm and a length of 38 mm. In reactive sintering experiments, stoichiometric amounts of powders of boron and hafnium were mixed in an agate mortar before introduction in the die. In some cases the boron powders were annealed in a vacuum furnace for three hours in order to reduce adsorbed gas contamination. To reduce the interaction between the reacting mixture and the graphite die, several layers of graphite foil were placed between the inside surfaces of the die and the sample. The external surface of the die was lined with graphite felt. This was done to reduce radiation heat losses and thus the power required to reach high temperature. In an alternative approach high purity boron was used without any annealing but all powder handling was done in a glove box (VAC Omnilab) under an atmosphere of purified argon (<0.5 ppm of oxygen and <1 ppm of moisture). To prevent contamination during the transfer from the glove box to the SPS apparatus, the die was wrapped in Parafilm.

TABLE I Characteristics of starting materials

Material	Supplier	Purity (%)	Grain size
Hf	Cerac	99.8	−325 mesh
B	Cerac	99.9	$<1\ \mu$m
B	Alfa	99	−325 mesh
HfB_2	Cerac	99.5	−325 mesh

Sintering was done in a Sumitomo SPS unit (model 1050) under a vacuum of $3 \cdot 10^{-2}$ Torr. While this level of vacuum has a nominally significant oxygen partial pressure, the presence of carbon (in the die and punches) results in a very low oxygen partial pressure in the vicinity of the sample at the sintering temperatures [11]. Various final (hold) temperatures and load pressures were explored in order to find the optimal conditions. In most cases a low pressure was applied first and was increased to a higher level when shrinkage was observed. This was done particularly in the case of reactive sintering. In this case the initial pressure was the lowest possible compatible with a good electrical contact between plungers and die. This minimized the possibility of explosion in the event of large outgassing from the boron powder. The temperature was monitored using a single-color pyrometer focusing on the external surface of the die. In some cases the temperature was also measured using a thermocouple placed in a hole drilled along the axis of the lower plunger of the die. The thermocouple in this arrangement was less then 1 mm below the lower surface of the sample. A C-type thermocouple with wires 125 μm thick was used. Unless otherwise stated the temperatures reported in the following refer to pyrometer measurements.

In order to gain a better understanding of the reaction mechanism in reactive sintering, experiments were stopped at different stages of the thermal cycle. At the end of the each experiment the sample was cut, polished, and examined using X-ray diffraction (Scintag XDS 2000), optical and SEM (Philips XL-30 SFEG) microscopy.

3. Results and discussion

Table II shows examples of the experimental conditions and the final densities obtained for the sintering of pure hafnium diboride samples, as well as those prepared by

TABLE II Experimental parameters and final densities of sintered and reactively sintered hafnium diboride

Starting powder	Hold temp (°C)	Hold time (min)	Pressure (MPa)	Relative density (%)
HfB_2 (15g)	1800	10	30–85	62.4
HfB_2 (15g)	1900	10	80–95	86.8
HfB_2 (15g)	1900	10	95	85.5
Hf+2B (3.5g)	1900	0	30	98.4
Hf+2B (7g)	1900	0	63–95	97.9
Hf+2B (10g)	1700	10	63–95	97.7
Hf+2B (10g)	1900	3	63–95	97.1

reactive sintering of the diboride from the elements. These results show that sintering of dense diboride is not accomplished even when using a temperature as high as 1900°C and a pressure of 95 MPa with a holding time of 10 min. The highest relative density obtained in this case was less than 87%. Using hot-pressing, Kalish and Clougherty [8] obtained fully dense hafnium diboride samples at temperatures near those used here (above 1840°C), but by using pressures almost an order of magnitude higher (800 MPa).

Significantly higher relative densities were obtained using reactive sintering. At 1700°C and a pressure of 95 MPa, reactive sintering produced samples, which were about 98% dense with a 10 min hold. Reactive sintering has also been used previously. Opeka *et al.* [9] coupled reactive sintering with hot-pressing, but their results were not particularly satisfactory. Despite temperatures as high as 2160°C and a holding time of 3 h under an applied pressure of 27.5 MPa, the samples contained 5–10% porosity. The reason for the improvement in the final density when reactive sintering is used instead of plain densification of the compound is still not clear and will be discussed later.

The reaction between Hf and B is highly exothermic and can easily produce conditions similar to self-propagating high-temperature synthesis (SHS) if a hot spot acts as an ignition source for the reaction. The theoretical adiabatic temperature for such reaction is 3706°C, and the reaction process is usually associated with a fast release of adsorbed gases, leading typically to retained porosity in the product phase [12]. In the confinement of the die, rapid gas release can lead to explosion. For this reason reactive sintering experiments were performed using two levels of pressure, the initial level being relatively low to ensure the non-destructive release of the gases in the case of a combustion reaction. The pressure was increased at the later stages, when the reaction between the elements commences, as judged by the abrupt shrinkage associated with molar volume change.

The heating rate used for all the experiments was 100°C min^{-1}. A typical profile of temperature, pressure, and shrinkage for the cases of sintering and reactive sintering are shown in Fig. 1a and b, respectively. In the case of the sintering of the diboride compound, Fig. 1a, the pressure was kept constant at a value of 105 MPa. The densification of HfB_2 appears to start at about 1450°C, and becomes significant only at temperatures above 1550°C. In the case of reactive sintering, Fig. 1b, the pressure is kept very low initially and then increased quickly at a temperature corresponding to the onset of the densification observed for HfB_2 (around 1450°C). This produces the large sharp displacement (shrinkage) observed in Fig. 1b. In some cases, however, evidence for reaction was seen in the early stages of the process (i.e., at low temperatures), and it is believed to be the consequences of self-propagating reactions initiated by a hot spot in the electrically heated die. In this case a very sharp displacement is observed at temperatures well below 1000°C, corresponding the combustion reaction. However, despite the apparent large difference in experimental conditions, samples obtained with or without an initial combustion do not show a significant difference in the final properties as long as the final temperature and the final pressure are the same.

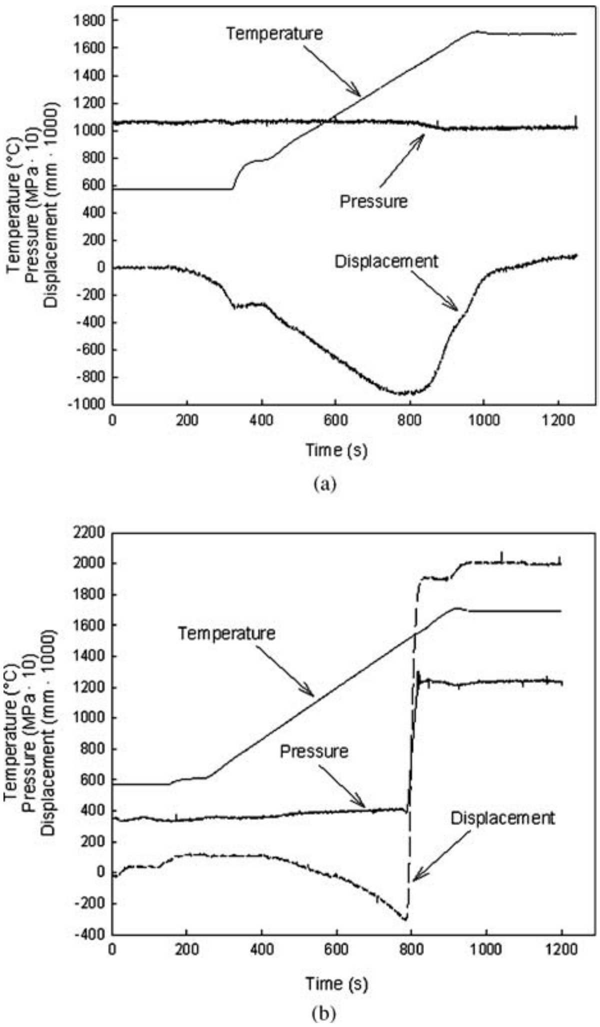


Figure 1 (a) Time evolution of SPS parameters during the densification of pure HfB_2. (b) Time evolution of SPS parameters during the reactive sintering of a stoichiometric mixture Hf+2B.

An example of typical microstructure of samples of HfB_2 obtained through reactive sintering is shown in Fig. 2a and b. These figures confirm the high relative density of these samples and the relatively small dimension of the grains. The small dark regions seen in the optical

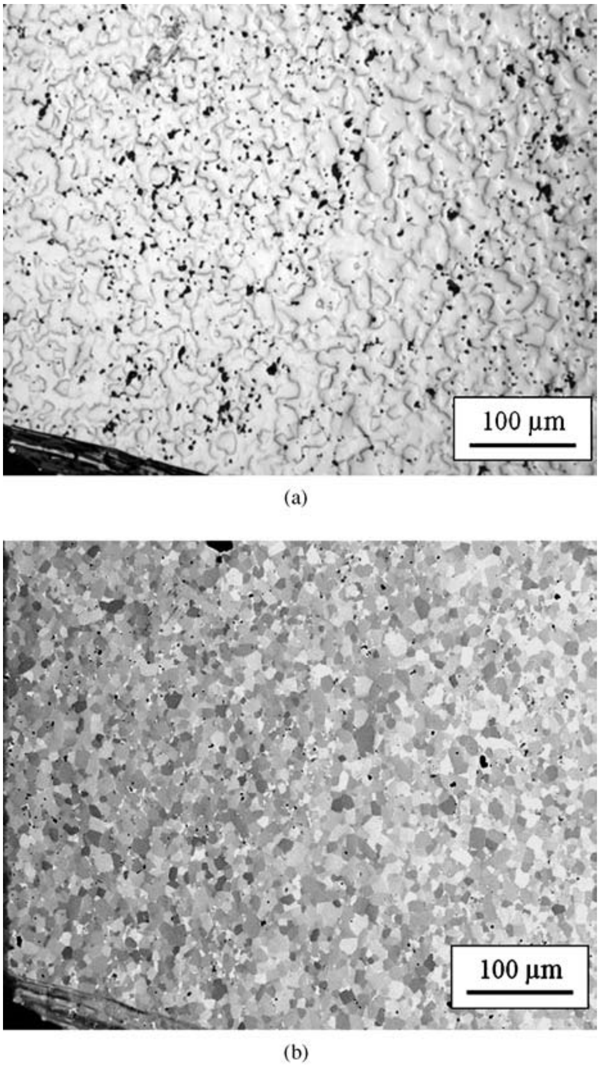


Figure 2 (a) Optical micrograph of a sample of HfB_2 obtained through reactive sintering (powder handling in glove box). Heating rate 100°C/min; final temperature 1700°C (optical pyrometer); hold pressure 120 MPa. (b) SEM image of the same area shown in Fig. 2a.

micrograph, Fig. 2a are not pores, but are the phase HfO_2. The SEM image of the same region, shown in Fig. 2b does not show any evidence of the oxide phase, since it is indistinguishable from the boride in both secondary electron (SE) and back-scattered electron (BSE) modes. The presence of hafnium oxide in sintered hafnium diboride has been previously reported by Clougherty *et al.* [13]. It is due to the nearly unavoidable presence of oxides in the starting powders. In the case of conventional sintering of HfB_2 the oxide is likely present as a surface layer on the grain of the powders of the boride. In reactive sintering this problem becomes much more serious because of the tendency of boron to react with oxygen and moisture forming boron oxide. Since the XRD signal of the oxide is too small for quantitative evaluation, an estimate on the amount of this phase was obtained from the optical micrograph of polished samples through image analysis. Up to 10 vol% of oxide can be detected in typical samples obtained through reactive sintering using low purity boron handled in air. However, when high purity boron was used and the powders were handled under a controlled atmosphere in a glove box, the oxide level was reduced considerably, to a level below 3 vol%.

3.1. Reaction mechanism

The results presented above show that high density hafnium diboride can be prepared through reactive sintering under pressure within a relatively short hold time by the field activation method (SPS). Depending on temperature, the hold time varied from zero (at 1900°C) to 10 min (at 1700°C). In contrast, the sintering of diboride did not result in high density under corresponding times and temperatures. These observations underscore the need for a better understanding of the relationship between the reaction to form the diboride and its densification.

In order to provide such an understanding, the measured temperatures need to reflect the condition of the sample and not the die. As indicated above, temperatures for this work were measured by a pyrometer focused on the surface of the die. As we have shown in a previous work [14], there can be significant difference between the two readings. In this case however, the appropriate thermocouple, the type-C thermocouple (W5%Re–W25%Re) could not be used over the entire temperature range, since it reacted quickly with the carbon of the die at temperatures above 1500°C. Fig. 3 shows a comparison between the temperature measured by the pyrometer (focused on the external surface of the die) and the temperature measured by a type-C thermocouple in contact with the sample for thermocouple temperatures values up to 1500°C. It can be seen that the two temperatures differ by a significant amount, in excess of 200°C at higher temperatures. In view of the experimental limitation indicated above, we have used an extrapolation of this figure to determine the temperature of the sample in the higher range. In the following we will use this extrapolation in reporting the temperatures relative to samples obtained at higher

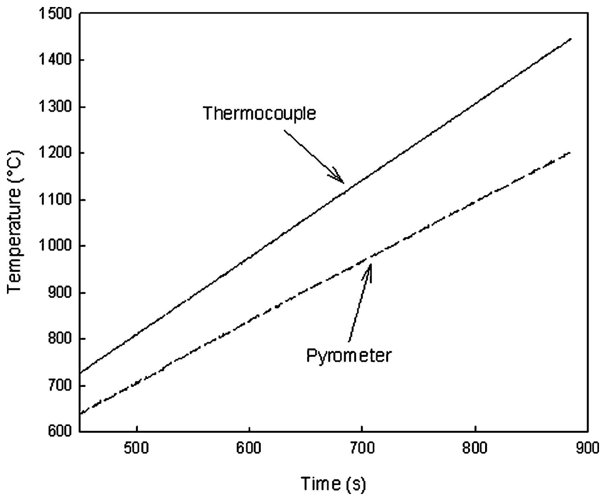
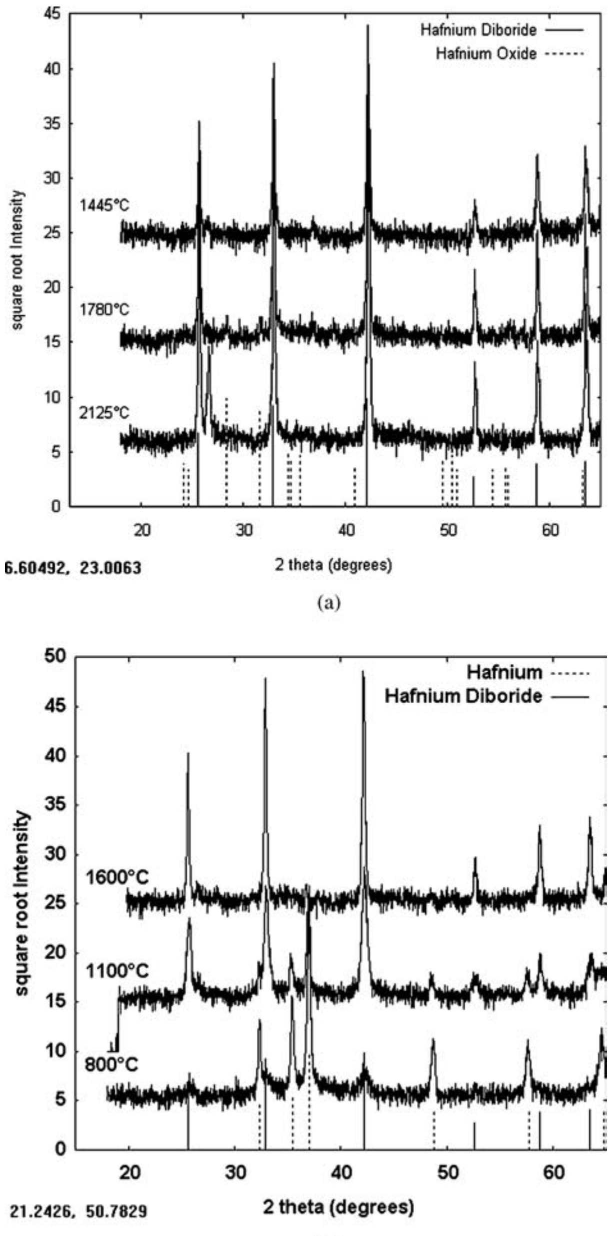


Figure 3 Comparison between the temperature measurements obtained using an optical pyrometer focused on the external surface of the die and a thermocouple positioned inside one of the plungers and in contact with the sample lower surface.



(a)

(b)

Figure 4 (a) XRD of polished samples whose SPS reactive sintering cycle was interrupted at different temperatures. The heating rate was 100°C min^{-1} and the pressure was 35 MPa. The temperature was detected with an optical pyrometer. These experimental values have been corrected to real sample temperature extrapolating the data of Fig. 3. (b) XRD of polished samples whose SPS reactive sintering cycle was interrupted at different temperatures. The heating rate was 100°C min^{-1} and the pressure was 35 MPa. The temperature was detected with a thermocouple positioned at less then 1 mm from the sample lower surface.

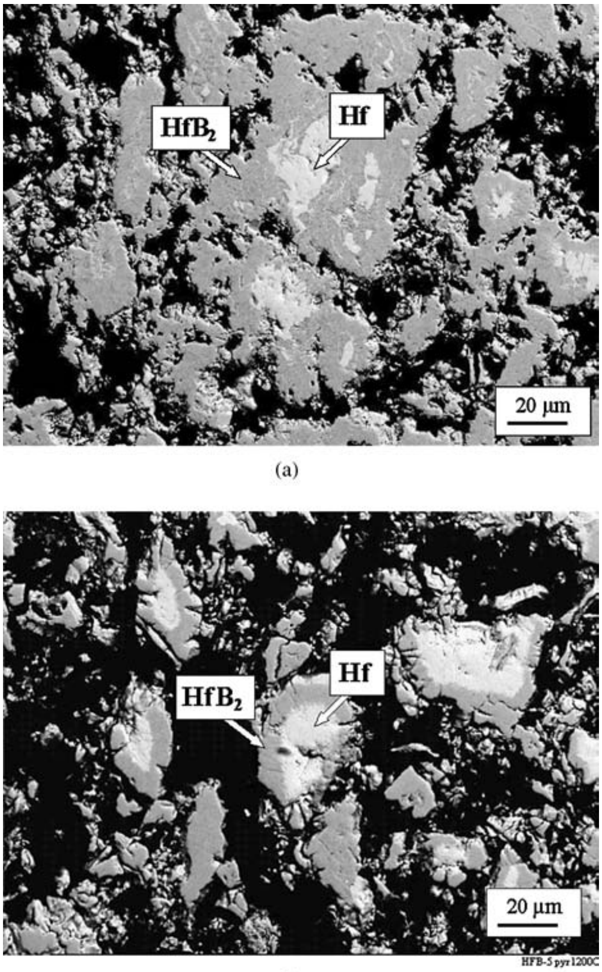
temperatures, where the temperature was detected using a pyrometer.

The enhanced densification obtained with reactive sintering is investigated by stopping the process at different temperatures during the heating process. Fig. 4a shows the XRD patterns of samples whose reaction and densification were stopped at three different temperatures. The peak at 2-theta value of 27° is for graphite and it reflects the surface contamination from the die. The other peaks are all for the HfB_2 phase and are the same for all three temperatures. This implies that the reaction to form the boride had taken place at as a low a sample temperature as 1445°C. As was seen from Fig. 1, densification becomes significant only above about 1450°C when detected with the pyrometer, corresponding to 1780°C on the sample. This suggests that in this system densification is not associated with the formation reaction as is sometimes observed in SPS experiments [15]. Additional experiments were made to determine the temperature at which the reaction commences. The XRD patterns of samples heated to much lower temperatures are shown in Fig. 4b. In this case temperatures were directly measured by a thermocouple placed inside the lower plunger. These patterns indicate that the reaction occurs at even lower temperatures. In fact only in the pattern of a sample heated to 800°C is there evidence for elemental hafnium.

Further insight on the reaction mechanism can be obtained from SEM observations of samples heated to different temperatures. Fig. 5a shows the microstructure of a sample heated to 1780°C whose XRD pattern is reported in Fig. 4a. As indicated above, the pattern does not show any evidence for unreacted Hf, but the SEM microstructure shows the presence of Hf in the core of what were the original Hf grains. The microstructure of the sample heated to 1445°C, Fig. 5b, shows an even greater difference. In this case the microstructure shows a considerable fraction of unreacted Hf, in contrast with the XRD results. This difference between XRD and SEM results is a consequence of the different sample preparation techniques used for the two techniques. The XRD patterns were obtained on the surfaces of samples after they were polished with coarse sandpaper, while the SEM images were obtained on sections of the samples which were subjected to a careful metallographic preparation in order to avoid grains pullout. The method of surface preparation and the very low penetration depth of X-rays in hafnium diboride render the XRD information not representative of the grains interior. However, despite these differences, both XRD and SEM results confirm that at the temperature corresponding to the onset of the densification (at around 1780°C) the conversion of the elements into the compound is nearly complete. This result confirms that densification is not associated to any significant extent with the reaction forming the diboride.

The SEM observations further suggest that the reaction between boron and hafnium takes place over a relatively wide temperature range (probably limited by the diffusion of boron into the hafnium grains) and is not associated with any evident modification in the microstructure of the starting Hf powders. Evidence for a reaction is seen at as a low a temperature as 1100°C.

The absence of any clear correlation between the synthesis reaction and the densification leaves unanswered the question of why reactive sintering produced higher final densities. Two possible alternative explanations can be put forward. The first involves the possibility that the *in situ* formation of the boride phase can produce a mi-



(a)

(b)

Figure 5 (a) SEM image of sample whose SPS sintering cycle was interrupted at 1450°C as measured by the pyrometer. This corresponds to a sample temperature of 1780°C. The heating rate was 100°C min^{-1} and the pressure was 35 MPa. (b) SEM image of sample whose SPS sintering cycle was interrupted at 1200°C as measured by the pyrometer. This corresponds to a sample temperature of 1445°C. The heating rate was 100°C min^{-1} and the pressure was 35 MPa.

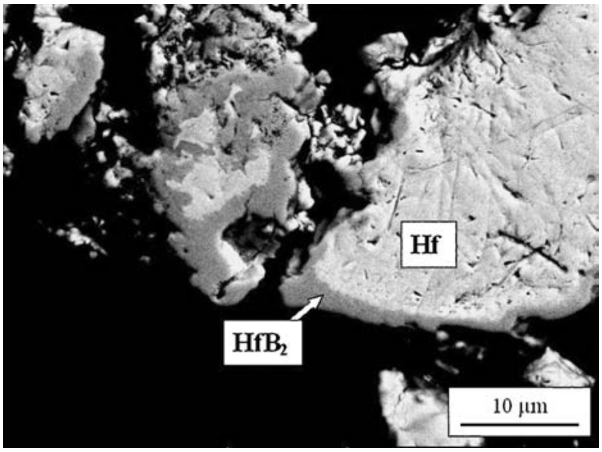


Figure 6 SEM image of a sample whose SPS sintering cycle was interrupted at 1100°C. The temperature was measured using a thermocouple. The heating rate was 100°C min^{-1} and the pressure was 35 MPa.

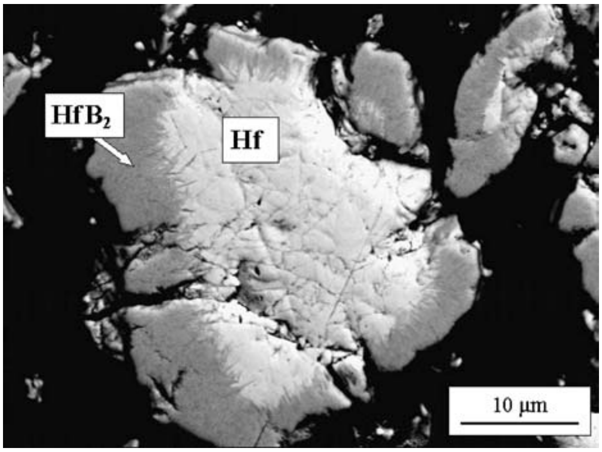


Figure 7 SEM image on sample whose SPS sintering cycle was interrupted at 1200°C as measured by the pyrometer. This corresponds to a sample temperature of 1445°C. The heating rate was 100°C min^{-1} and the pressure was 35 MPa.

crostructure more favorable for the following densification. This interpretation, however, does not seem likely, as the images of Figs 5–7 show. During the chemical reaction the microstructure of the boride remains very similar to that of the original Hf powder. A second possible explanation involves the absence of any surface contamination (particularly oxide) when the diboride is formed *in situ*. Under conditions inside the graphite die, the partial pressure of oxygen is very low, as has been indirectly seen by the loss of stoichiometric oxygen from zirconia [11]. This explanation seems to be the more likely from the evidences we obtained so far.

The SEM images also provide insight on the diffusion process which leads to the formation of the product. The only literature account on the kinetics of the reaction between hafnium and boron is that provided by Samsonov and Zhunkovskii [16]. These authors suggested that gas-phase mass transfer plays a major role in the interaction. For total gas pressure below 10^{-3} Torr, gas phase transport becomes dominant and thus no direct contact between the reactants is necessary. This pressure is not much lower than the nominal pressure in the SPS, 3×10^{-2} Torr. This would explain the fairly homogeneous thickness of the product layer observed even in the early stages of the interaction (see Fig. 6). The cited authors also reported the formation of an irregular interface between the metal and the boride layer for all metals of the group IVB. Our observations show similar features. As can be seen in Fig. 7 the interface between the unreacted Hf core and the boride layer is not planar, but has narrow, needle-like regions of HfB_2 projecting into the Hf matrix. The Hf itself shows signs of embrittlement, probably due to the formation of a solid solution.

Samsonov and Zhunkovskii [16] reported values for the parabolic growth constant for the reaction between Hf and B and its dependence on temperature. This allows a comparison with the layer thicknesses we observe in the SEM images of partially reacted samples. Such a comparison can provide an indication of the possible alteration in the reaction kinetics induced by the current during the SPS experiments.

Since the experiments from which the SEM images of Figs 5–7 were obtained were not isothermal, the comparison cannot be made using the usual parabolic growth law, but a numerical simulation based on the differential form of the same law including the temperature dependence of the growth constant must be used. We start with the parabolic law in the form,

$$\frac{dx}{dt} = \frac{k}{x} \tag{1}$$

where x is the product layer thickness, k the parabolic growth constant, and t is time. This form assumes a planar interface between the two reacting phases. This is an acceptable approximation in the reaction between powders when the early stages of the interaction are considered. It also assumes that the boron is uniformly distributed on the surface of the hafnium grains. This condition can be satisfied if boron is transferred by a gas phase. The dependence of the growth constant on temperature is given by Samsonov and Zhunkovskii [16] as:

$$k = 5 \times 11^{-3} \exp\left(-\frac{24000}{T}\right) \tag{2}$$

The numerical integration of Equation 1 was performed considering a heating rate of 100°C min^{-1}, the same as that used in the SPS experiments. Fig. 8 shows the results of these calculations. The figure shows the sample temperature *vs*. time and the corresponding layer thickness obtained from the integration of Equation 1 using the temperature dependence of k as expressed by Equation 2. The results are in a fairly good agreement with the layer thicknesses observed in this work. Fig. 6, for example, shows a thickness of the diboride layer of about 1 μm for a sample heated to 1100°C at 100°C/min. The simulation based on Equations 1 and 2 shows similar results. Fig. 7 shows a sample that was heated to 1445°C. In these conditions a layer thickness around 5 μm is expected on the basis of the diffusion model (Fig. 8) and a very similar layer thickness is observed in the image. These results lead to the conclusion that the rate of the chemical interaction observed during the reactive sintering of hafnium boride in the SPS agrees quite well with the data obtained from diffusion couple experiments. This would indicate that the electric current did not play a significant role in the reaction between boron and hafnium. However, this indirect conclusion must be substantiated with diffusion couple experiments in the SPS, as has been done recently for the case of Mo-Si couples [17].

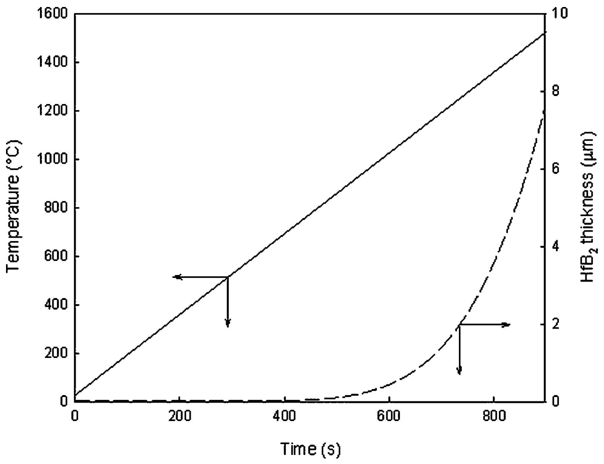


Figure 8 Results of the numerical integration of Equation 1 for the non-isothermal layer growth of HfB_2 on Hf.

4. Conclusions

The consolidation of HfB_2 was investigated by the sintering of the diboride and by the reactive sintering of elemental boron and hafnium powders. Sintering and reactive sintering were investigated in the field activated method of the spark plasma sintering (SPS) method. The sintering of the diboride phase at 1800°C with a 10 min hold time and a maximum pressure of 85 MPa did not result in a highly consolidated product, reaching a relative density of only 62%. In creasing the temperature and pressure, to 1900°C and 95 MPa, respectively, increased the final density, but the product was far from fully dense (about 87%).

In contrast to the above, the simultaneous synthesis and consolidation of the diboride (reactive sintering) produced dense (about 98%) product at 1700°C with a hold time of 10 min and an applied uniaxial pressure of 95 MPa. At 1900°C, a similarly high density could be achieved with zero hold time. The absence (or low level) of impurity on the formed HfB_2 phase (under a very low oxygen partial pressure within the graphite die) is put forth as an explanation for the difference in behavior between sintering and reactive sintering.

The reaction mechanism between B and Hf during reactive sintering was investigated by terminating the reaction at various temperatures. Evidence for reaction between the elements is seen at as a low a temperature as 1100°C, but the completion of the reaction extended over a relatively wide temperature range. An important observation is the lack of association of the reaction with the densification. Densification was observed at a temperature where the conversion to the diboride was complete.

Microstructural observations on partially reacted samples provided information on the growth rate of HfB_2 on the surfaces of Hf grains. The rates of growth of the product layer were found to be in agreement with calculated values from diffusion couple experiments, suggesting that the current did not play a significant role in the reactivity.

Acknowledgements

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