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## Densification of Ultra-Refractory Transition Metal Diboride Ceramics

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### Abstract:

*The densification behavior of transition metal diboride compounds was reviewed with emphasis on ZrB<sub>2</sub> and HfB<sub>2</sub>. These compounds are considered ultra-high temperature ceramics because they have melting temperatures above 3000°C. Densification of transition metal diborides is difficult due to their strong covalent bonding, which results in extremely high melting temperatures and low self-diffusion coefficients. In addition, oxide impurities present on the surface of powder particles promotes coarsening, which further inhibits densification. Studies prior to the 1990s predominantly used hot pressing for densification. Those reports revealed densification mechanisms and identified that oxygen impurity contents below about 0.5 wt% were required for effective densification. Subsequent studies have employed advanced sintering methods such as spark plasma sintering and reactive hot pressing to produce materials with nearly full density and higher metallic purity. Further studies are needed to identify fundamental densification mechanisms and further improve the elevated temperature properties of transition metal diborides.*

**Keywords:** Transition metal diborides; Densification; Sintering; Hot pressing.

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### 1. Introduction

Transition metal diborides (TMB<sub>2</sub>s) have been researched for many years as materials for use in extreme environments.<sup>1-7</sup> Several TMB<sub>2</sub>s, including TiB<sub>2</sub>, ZrB<sub>2</sub>, HfB<sub>2</sub>, and TaB<sub>2</sub>, are considered to be ultra-high temperature ceramics (UHTCs) because they have melting temperatures in excess of 3000°C. Other TMB<sub>2</sub>s such as OsB<sub>2</sub> and ReB<sub>2</sub> have received attention as novel superhard materials.<sup>8-10</sup> The TMB<sub>2</sub>s possess unusual combinations of properties such as metal-like thermal and electrical conductivities with ceramic-like hardness and elastic modulus, which result from a complex combination of covalent, metallic, and ionic bond characteristics.<sup>11-13</sup> Because of their properties, TMB<sub>2</sub>s are proposed for use at extreme temperatures, heat fluxes, radiation levels, strain rates, or chemical reactivities that exceed the capabilities of existing materials. Some of the potential applications typically mentioned for TMB<sub>2</sub>s include hypersonic aerospace vehicles, rocket motors, scramjet engines, lightweight armor, high-speed cutting tools, refractories for molten metal contact applications, plasma-facing materials for nuclear fusion reactors, and fuel forms for advanced nuclear fission reactors.<sup>5,14-22</sup> The same characteristics that give TMB<sub>2</sub>s their remarkably high melting temperatures and hardness values also make TMB<sub>2</sub>s difficult to densify.

The densification of ceramic materials can be accomplished by a number of methods. Many commercial ceramics are produced by pressureless sintering of parts fabricated by powder processing methods.<sup>23-25</sup> Some ceramics are difficult to densify by pressureless

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sintering, but this can be overcome by using alternative densification methods that simultaneously apply elevated temperatures with pressure and/or an external field in methods such as hot pressing, hot isostatic pressing, or spark plasma sintering.<sup>26,27</sup> The mechanisms for sintering involve transport of material through solid, liquid, or vapor phases.<sup>28</sup> Mechanisms that promote densification include grain boundary diffusion, lattice diffusion when the source of material is the grain boundaries, or plastic flow.<sup>29</sup> Other mechanisms such as surface diffusion, lattice diffusion when the source of material is particle surfaces, or evaporation-condensation lead to coarsening without densification. In practice, coarsening and densification occur simultaneously.<sup>26</sup> The six mechanisms listed above are limiting cases where either densification or coarsening is predominant, but, in some cases, competition between the processes leads to limiting densities. More detailed discussions of sintering mechanisms and kinetics can be found in a number of sources and will not be reviewed further herein.<sup>23-31</sup>

The purpose of this paper is to critically evaluate published studies of the densification behavior of nominally pure TMB<sub>2</sub> ceramics with the focus on ZrB<sub>2</sub> and HfB<sub>2</sub>. Ceramics containing significant additions of SiC, MoSi<sub>2</sub>, or other second phases are intentionally excluded from consideration in this manuscript.

## 2. Historic Reports

Historic densification studies are considered those ranging from the initial reports of TMB<sub>2</sub> synthesis into the early 1990s. This era was dominated by initial evaluations of TMB<sub>2</sub>s as part of the space race activities in the U.S.S.R. and the U.S., but included efforts that extended through the 1980s and into the early 1990s.

Initial synthesis methods for diborides were reported in the late 1800s and early 1900s.<sup>32-35</sup> These and other early studies focused on the phases formed and did not discuss densification. Starting in the 1960s, Kislyi et al. published a number of studies on the behavior of UHTCs, including some of the first reported studies of the densification behavior of TMB<sub>2</sub> powders. The group emphasized that the directional nature of the strong covalent bonds in diborides inhibited diffusion and prevented shrinkage.<sup>36</sup> That report also noted that densification of commercial ZrB<sub>2</sub> was activated by impurities, but the materials reported therein did not reach full density by pressureless sintering.<sup>36</sup> The same group investigated vacuum sintering of TiB<sub>2</sub>, which revealed that non-densifying mass transport mechanisms such as surface diffusion and evaporation-condensation were active below 1800°C for materials with oxygen impurities.<sup>37</sup> The addition of Mo to ZrB<sub>2</sub> enhanced densification and allowed for full densification, which was attributed to viscous flow.<sup>38</sup> In contrast, W additions were noted to decrease densification due to a volume increase associated with the dissolution of W into the ZrB<sub>2</sub> structure.<sup>39</sup> Taken together, the published papers indicated mixed success in the densification of TMB<sub>2</sub>s. While some insight was gained into densification behavior, different results were observed for different TMB<sub>2</sub>s, which indicated that different extrinsic effects (e.g., impurities) controlled the observed behavior.

About the same time as the studies by Kislyi et al., researchers at ManLabs in the U.S. were studying TMB<sub>2</sub>s as part of a series of projects sponsored by the U.S. Air Force.<sup>40</sup> In one effort, densification behavior of fifteen different ZrB<sub>2</sub> and HfB<sub>2</sub> compositions were evaluated.<sup>41</sup> Hot pressing was the predominant method used for densification, but other techniques including hot isostatic pressing, plasma spraying, arc casting, hot forging, and pyrolytic deposition were also examined.<sup>41</sup> The densification mechanism of ZrB<sub>2</sub> was analyzed by fitting displacement during hot pressing to various diffusion models. Based on the fit to the grain boundary diffusion model shown in Fig and the values of diffusivity, Kaufman and Clougherty concluded that densification proceeded by diffusion through a liquid film at the grain boundaries.<sup>41</sup> In contrast, densification of HfB<sub>2</sub> with a coarse starting particle size was slower and the highest density reached was ~92%.<sup>42</sup> A subsequent study

found that  $\text{HfB}_2$  with an initial particle size of less than  $5 \mu\text{m}$  reached nearly full density at the relatively modest temperature of  $1800^\circ\text{C}$  with a pressure of  $\sim 1.5 \text{ GPa}$ .<sup>43</sup> The overall conclusions from the ManLabs studies were that none of the TMB2s that had been examined were phase pure and that densification of all of the TMB2s was affected by oxide impurities.<sup>41</sup> Based on the results of these studies, most subsequent investigations utilized hot pressing with addition of sintering aids that would react with and remove oxygen impurities to produce dense TMB2 ceramics.

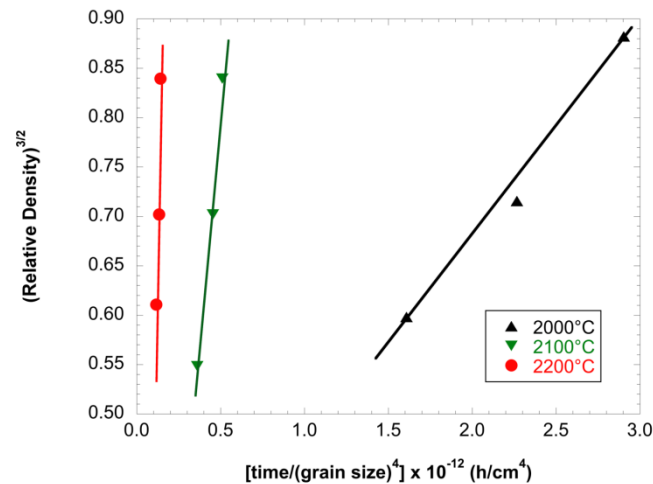
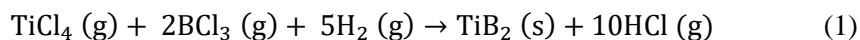


Fig. 1. Relative density to the  $3/2$  power as a function of sintering time divided by grain size to the fourth power showing that densification of  $\text{ZrB}_2$  was consistent with grain boundary diffusion. Replotted from data in Ref. 41, which is a public domain source.

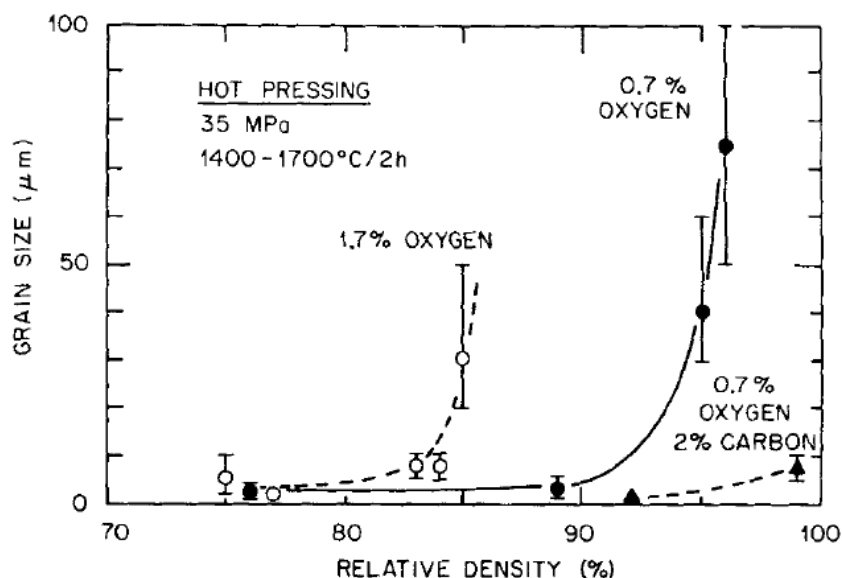
Metallic sintering aids have been widely reported for enhancing the densification of TMB2s. For example, Cech et al. reported the addition of up to 3 wt% Fe, Ni, or Co to enhance the densification of  $\text{ZrB}_2$ .<sup>44</sup> A decrease in the lattice parameters of  $\text{ZrB}_2$  was noted indicating dissolution of part of the transition metals into the TMB2 lattice. Similar metal additions have been reported to enable pressureless sintering of  $\text{TiB}_2$  ceramics.<sup>45,46</sup> The use of transition metals was effective in promoting densification due to the formation of a liquid phase. However, the presence of transition metals results in the formation of eutectics at temperatures below  $1500^\circ\text{C}$ , which precludes the use of the resulting ceramics at extreme temperatures. To minimize the introduction of low-melting compounds, several historic studies also examined the efficacy of non-metallic additions on the densification behavior of TMB2s. The ManLabs reports noted improvements in densification for compositions rich in either boron or the transition metal compared to nominally stoichiometric TMB2s.<sup>41,42</sup> In addition, improved sintering was also noted for additions of C, SiC or ZrC, though specific mechanisms were not discussed.<sup>41</sup> Subsequent to the initial reports, results from the ManLabs studies on the effects of densification conditions and sintering additives on properties were compiled and summarized by Fenter.<sup>47</sup>

As noted above, several of the historic studies recognized that impurities impacted the densification behavior of TMB2s. Kaufman and Clougherty reported attempts to purify TMB2s by HF leaching with mixed results.<sup>41</sup> While impurity levels decreased for  $\text{ZrB}_2$ , the same treatments on  $\text{HfB}_2$  powders resulted in dissolution of most of the starting powder. Unfortunately, even purified  $\text{ZrB}_2$  powders still contained high enough levels of impurities to have an adverse effect on densification behavior. Two historic studies stand out for not only recognizing the role of oxygen impurities in densification of TMB2s, but isolating and controlling their impact. Baumgartner and Steiger synthesized  $\text{TiB}_2$  with a low oxygen content by a gas phase reaction (Reaction 1).<sup>48</sup> Particles less than  $0.5 \mu\text{m}$  wide with a platelet

morphology were produced. The authors reported >99 % relative density for pressureless sintering temperatures of 2100°C or higher with a diffusion-controlled mechanism.



Building on those results, Baik and Becher used a combination of carbon additions and comminution to sinter a commercial  $\text{TiB}_2$  to nearly full density.<sup>49</sup> They concluded that limiting the oxygen content of the  $\text{TiB}_2$  powders to 0.5 wt% or lower inhibited vapor phase coarsening and promoted densification. As shown in Fig. , reducing the oxygen content from 1.7 to 0.7 wt% resulted in an increase in relative density from ~85 to ~95 % with final grain sizes in the range of 30  $\mu\text{m}$  to 70  $\mu\text{m}$ . The addition of carbon to the powder containing 0.7 wt% oxygen to further react with and remove oxygen impurities enabled nearly full densification (>99 %) with a grain size of less than 10  $\mu\text{m}$ . For  $\text{TiB}_2$ , consideration of grain size is important because spontaneous microcracking that reduces strength, elastic modulus, and hardness occurs for grain sizes above ~15  $\mu\text{m}$ .<sup>50</sup> Hence, not only did Baik and Becher define a method for densifying  $\text{TiB}_2$ , but their method also controlled grain growth to enable production of  $\text{TiB}_2$  ceramics with properties that were consistent with the intrinsic behavior of the material.



**Fig. 2.** Grain size as a function of relative density for hot pressed  $\text{TiB}_2$  powders with various oxygen contents. Reprinted from Ref. 49.

These historic studies were remarkable for the volume of research conducted and the impact that they had on subsequent research. For example,  $\text{ZrB}_2$  and  $\text{HfB}_2$  were identified as the most promising candidates for aerospace applications based on initial oxidation studies<sup>42</sup> and have been the focus of efforts for use at ultra-high temperatures in oxidizing environments since then. Specifically for densification, these historic studies identified the critical aspects of chemical purity, composition, particle size, and oxygen content that provided the foundation for many of the recent studies of the intrinsic behavior of the TMB2s.

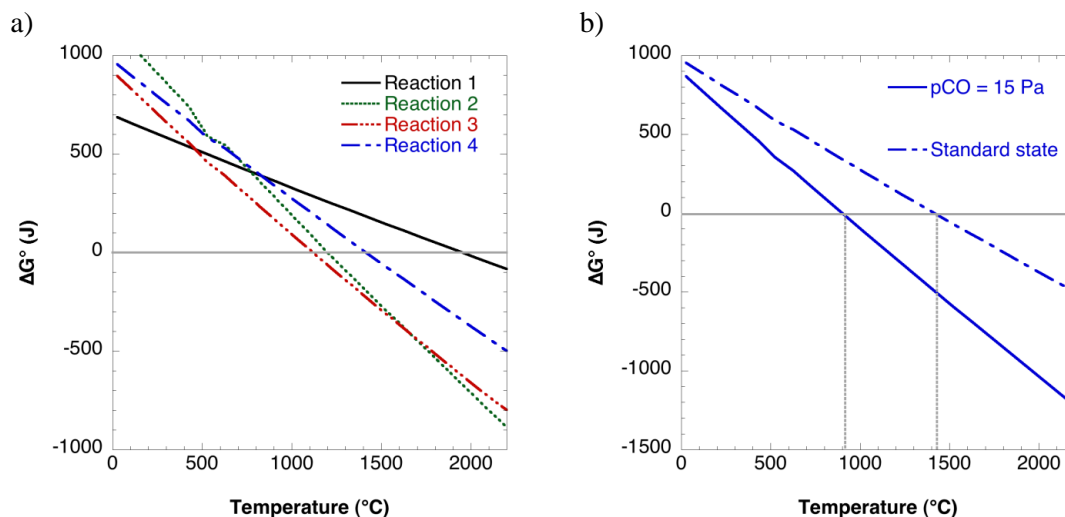
### 3. Recent Studies

Research on UHTCs experienced a resurgence of interest in the 1990s, which was motivated by the worldwide interest in hypersonic aviation. The extreme environments associated with sustained hypersonic flight led to the search for materials that could withstand

temperatures of 2000°C or higher, heat fluxes of hundreds of W/cm<sup>2</sup>, and thermal shock, all in an oxidizing environment.<sup>12,51-53</sup> For nominally pure materials, densification methods can be grouped into three main categories: 1) pressure-assisted methods such as hot pressing and spark plasma sintering; 2) pressureless sintering methods; and 3) reaction-based densification.

### Pressure assisted densification

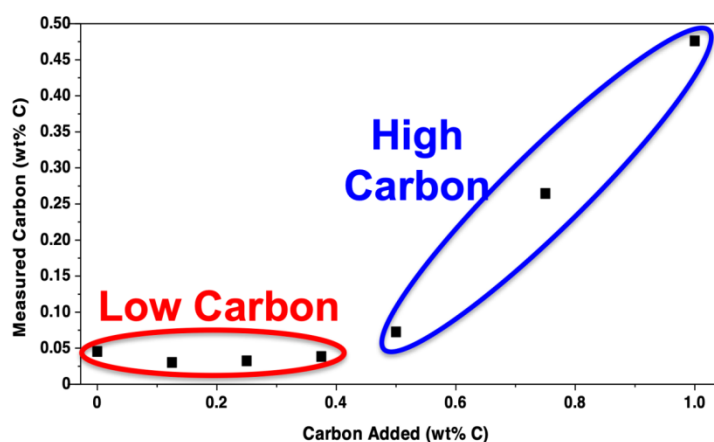
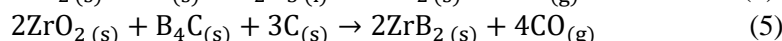
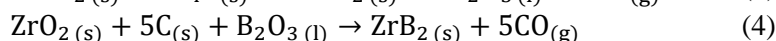
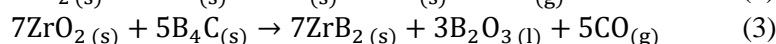
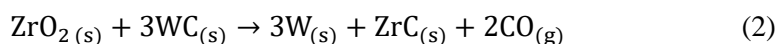
Densification of nominally pure TMB2s (i.e., without intentional addition of second phases such as SiC or MoSi<sub>2</sub>) is most commonly accomplished through the use of hot pressing.<sup>14</sup> Hafnium diboride has been studied less than ZrB<sub>2</sub>, but several studies have examined its densification behavior. Opeka et al. produced dense HfB<sub>2</sub> by hot pressing at 2160°C with the addition of HfH<sub>2</sub> as a densification aid.<sup>54</sup> The group from ISTECH used the addition of transition metal silicides to promote densification of HfB<sub>2</sub> by hot pressing<sup>55,56</sup> or spark plasma sintering,<sup>57-59</sup> generally achieving nearly full density at temperatures as low as 1800°C with additives such as MoSi<sub>2</sub>, but HfB<sub>2</sub> only reached about 80% at 2200°C without additives. Additional studies have revealed the effects of pressure,<sup>60</sup> solid solution additives,<sup>61</sup> and stoichiometry of boron carbide<sup>62</sup> on densification. From these studies, full densification of HfB<sub>2</sub> appears to require temperatures of at least 2100°C in combination with additives that promote densification and alter microstructure development.



**Fig. 3.** (a) Change in standard Gibbs' free energy of reaction for reactions that promote oxygen removal from diboride particle surfaces and (b) the effect of furnace pressure on the favorability of Reactions 2-5. Reprinted with permission from Reference 81.

A variety of sintering aids have been used to promote densification of TMB2s by hot pressing including transition metals,<sup>63-66</sup> nitrides,<sup>67-69</sup> and oxides.<sup>70-72</sup> However, the presence of low melting temperature phases, particularly those that promote liquid phase sintering, compromises the elevated temperature mechanical behavior of TMB2 ceramics.<sup>73</sup> Additives that react with and promote removal of oxides are attractive for densification of TMB2s. For example, MoSi<sub>2</sub> and other silicides have been shown to promote densification by removing oxide impurities from the surfaces of grains by a combination of mechanisms.<sup>57,58,74-77</sup> Additives such as C, B<sub>4</sub>C, WC, or their combinations promote densification by reacting with surface oxides and removing oxygen in the form of CO gas through thermodynamically-favorable processes as shown by Reactions 2-5.<sup>78,79</sup> These reactions are endothermic and become favorable at elevated temperatures as shown by the point where change in standard state Gibbs' free energy for the reactions becomes negative. The use of reduced pressures

(e.g., mild vacuum) during heating can further enhance densification by making the oxygen-removal reactions favorable at lower temperatures b) compared to standard state (i.e., partial pressure of 1 atm for each gaseous species). Harrington et al.<sup>80</sup> provided direct evidence of carbon reacting with surface oxide impurities by comparing the amount of carbon added to batches to the amount of carbon retained in the final ceramics (Figure 4). Below a critical content of about 0.5 wt% carbon added, the retained carbon contents in the ceramics were below ~0.05 wt% and the ceramics had elevated retained oxygen contents.<sup>80</sup> For additions in this range, all of the carbon that had been added was consumed by reaction with oxygen impurities, but not all of the oxygen impurities were removed (i.e., carbon was the limiting reactant). Carbon additions that resulted in this behavior were in what was termed the “low carbon” regime. Once the critical threshold value of carbon additions was reached, oxygen content in the ceramics was minimized (i.e., was below ~0.1 wt%) and any excess carbon added to the ceramic was retained in the form of carbon inclusions in the final ceramic.<sup>80</sup> Carbon additions that resulted in this behavior were termed the “high carbon” regime, which occurred with oxygen as the limiting reactant. Taken as a whole the use of reactive additives is an attractive approach for promoting densification of TMB2 ceramics as this approach offers the ability to enhance densification while also controlling microstructure development by limiting grain growth during densification.<sup>81</sup>

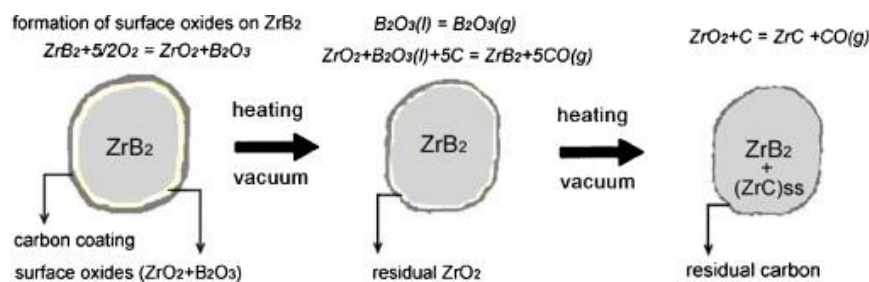


**Fig. 4.** Measured carbon content in  $\text{ZrB}_2$  content as a function of nominal carbon additions showing that the initial carbon additions are consumed by reaction. Replotted with data from Ref. 83 with permission.

### Pressureless Sintering

Although TMB2s can be difficult to densify even when external pressure is applied, a number of studies have reported pressureless sintering to nearly full density. Pressureless sintering provides a number of potential advantages including the ability to densify complex shapes made by additive manufacturing,<sup>82-84</sup> colloidal processing,<sup>85,86</sup> or other routes<sup>87</sup> as well as densify the internal structure present in foams or other intentionally porous bodies.<sup>88</sup> As with hot pressing, metal additives can be used to promote pressureless sintering,<sup>66,89-92</sup> but result in formation of liquid phases that are deleterious to mechanical integrity above 1500°C. Several studies have reported the use of  $\text{MoSi}_2$  and other silicides as densification aids to

promote pressureless sintering of TMB2s.<sup>56,93-96</sup> Additives that react with and remove oxygen impurities such as C,<sup>97,98</sup> B,<sup>99</sup> B<sub>4</sub>C,<sup>100-104</sup> WC,<sup>105,106</sup> or their combinations<sup>107,108</sup> have also been shown to promote pressureless sintering when the starting particle size of the TMB2 is sufficiently small to enable pressureless sintering.<sup>78,107</sup> Some reports also describe enhanced sintering with the addition of metallic species that substitute onto metal sites in the lattice of the primary TMB2 (e.g., addition of TiB<sub>2</sub> to ZrB<sub>2</sub> to form a (Zr,Ti)B<sub>2</sub> solid solution),<sup>109-112</sup> although the mechanisms are not understood. While starting particle size is an important factor in the pressureless sintering of TMB2 ceramics, removal of oxygen impurities from particle surfaces is critical. If oxygen content is above the critical threshold value of about 0.5 wt%,<sup>49,78</sup> then grains coarsen, which inhibits densification.<sup>51</sup> Because oxygen is insoluble in the TMB2 lattice, oxygen impurities can be removed using additives that react with and remove them from the particle surfaces. Carbon is a particularly effective additive when added as a thin layer on the outside of TMB2 particles, as can be done using soluble carbon precursors such as phenolic resin.<sup>97</sup> As illustrated in Fig. , carbon can be distributed evenly over the particle surface<sup>97</sup> to minimize the diffusion distance required for reaction of the sintering aid with the oxide impurities compared to the addition of isolated particles of the sintering aids. Overall, pressureless sintering is a highly attractive densification method for TMB2s based on the ability to produce complex shapes and ease of mass production compared to pressure-assisted densification methods.



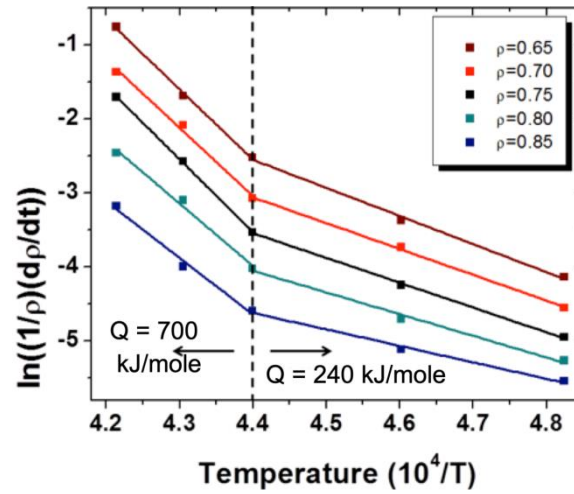
**Fig. 5.** Schematic representation of the removal of oxide impurities from ZrB<sub>2</sub> particle surfaces using carbon coated by deposition from phenolic resin solution. Used by permission from Ref. 97.

### Reactive Sintering

Several different reaction-based processes have been used to densify TMB2 ceramics.<sup>113</sup> The most common reactive process is direct reaction of the desired TM with boron.<sup>114-115</sup> Other processes including magnesio-thermal reduction of oxides,<sup>116,117</sup> borothermal reduction of oxides<sup>118</sup> or nitrides,<sup>119</sup> and reactive pressureless sintering,<sup>120</sup> The potential advantages of reactive processes include producing materials with higher purity and lowering densification temperatures, both of which can lead to improved properties.<sup>121-124</sup> For direct synthesis from elemental precursors (or TM hydrides), reaction is thought to proceed by diffusion of B into the TM through the developing TMB2 reaction layer,<sup>114</sup> although oxide impurities are often found in the resulting ceramics. Further refinement of microstructure and minimization of oxide impurities is possible by controlling the ratio of TM to B in the reactants and/or adding carbon to react with and remove oxygen during synthesis.<sup>125</sup> Observation of exothermic “gas-burst” phenomena led to formation of dense TMB2 ceramics with a unique duplex microstructure consisting of ZrB<sub>2</sub> platelets in a matrix of equiaxed grains, which led to improved strength at room temperature.<sup>126</sup> Reactive hot pressing has been used to study the densification mechanisms of TMB2 ceramics during the intermediate stage of sintering and revealed that densification was controlled by grain boundary diffusion below 2100°C and lattice diffusion at higher temperatures as illustrated in Fig. .<sup>127</sup> Hence, reaction-



based processes are a versatile and effective way not only to produce dense TMB2s, but also offer the ability to study fundamental densification mechanisms and improve sintering.



**Fig. 6.** Activation energy plot showing the densification rate of  $ZrB_2$  ceramics produced by reactive hot pressing in the low temperature (greater than  $4.4 \text{ K}^{-1}$  inverse temperature  $\times 10^4$ ) and high temperature (less than  $4.4 \text{ K}^{-1}$  inverse temperature  $\times 10^4$ ). Used by permission from Ref. 127.

#### 4. Summary and Outlook

Transition metal diboride ceramics can be densified by methods including hot pressing, pressureless sintering, and reaction-based processes. While starting particle size influences densification, the critical requirement for full densification of TMB2s is minimization of oxygen-containing impurities on the particle surfaces, which appear to function by minimizing grain coarsening and promoting densifying sintering mechanisms. Recent studies have revealed important fundamental aspects of densification of TMB2s including the effect of temperature on predominant densification mechanism, pathways for removal of oxygen impurities using reactive additives, and methods to control microstructure development during hot pressing.

Despite the recent progress that has been made, a number of unanswered questions remain. Some areas for potential future research include:

1. Sintering and grain growth mechanisms: Both historic and recent studies have examined sintering mechanisms. The materials in both studies contained oxygen impurities. In the historic study, the oxide formed a nearly-continuous grain boundary phase while in the recent study, oxide inclusions were present in the final ceramic. The opportunities for future mechanism studies include identifying initial stage sintering mechanisms, identifying intermediate stage sintering mechanisms in materials with lower oxygen impurity contents, studying final stage sintering mechanisms, and elucidating grain growth mechanisms. Evaluation of the effects of solid solution additives and second phases is also needed. Knowledge of sintering mechanisms will enable better control of microstructure development during densification and, therefore, the ability to control properties of the final ceramics.
2. Oxygen impurity effects: While the presence of oxygen impurities has been correlated to inhibited densification and enhanced grain coarsening, more detailed studies are needed to identify the mechanisms and kinetics of the processes involved. One recent study<sup>128</sup> has taken a step in this direction by applying high-resolution

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characterization methods to study the mechanisms of oxygen removal from particle surfaces, but additional studies are needed to determine values for surface energies, identify reactions, and derive analytical expressions to describe behaviors.

3. Emerging trends: This review summarized studies of hot pressing, spark plasma sintering, pressureless sintering, and reactive processes for densifying TMB2s. Some emerging areas for additional research include studying densification mechanisms and kinetics for flash sintering of TMB2s,<sup>129,130</sup> examining densification behavior of high entropy TMB2s, and utilizing computational methods including data mining to maximize the understanding of the densification behavior of TMB2 ceramics.

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**Сажетак:** *Изучавана је денсификација боридних једињења са посебним освртом на  $ZrB_2$  и  $HfB_2$ . Сматра се да су ова једињења керамике примењиве на ултра-високим температурама, јер им је температура топљења преко 3000 °C. Денсификација ових једињења је тешка због њихове јаке ковалентне везе, која резултује високим температурама топљења и ниским коефицијентом дифузије. Додатно, кисеоничне нечистоће које се налазе на површини честица праха чине површину храпавијом, што додатно успорава згушњавање. Студије пре 1990. Углавном користе топло пресовање. Те студије откривају механизме синтеровања и тврде да су нечистоће испод 0.5 wt% потребне за ефектно скупљање. Скорашње студије укључују напредне методе као што су синтеровање у плазми и рективно топло пресовање да би добили материјале скоро потпуно густе и са високим степеном чистоће. Потребна су даља истраживања да би се утврдили фундаментални механизми згушњавања и да би се побољшала својства борида на високим температурама.*

**Кључне речи:** *ди-бориди, згушњавање, синтеровање, топло пресовање.*

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