Cohesive zone modeling of grain boundary microcracking induced by thermal anisotropy in titanium diboride ceramics

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Abstract
This paper addresses the residual stresses and their effect on microcracking in polycrystalline ceramic materials. Residual stresses at microstructural level in titanium diboride ceramics, as a result of thermal expansion anisotropy, were analyzed by finite element method using Clarke's model. Damage mechanics based cohesive zone model was applied to study grain boundary microcracking, propagation and arrest. Quantitative relations between temperature variation, grain boundary energy, grain size, final microcrack length as well as microcracking temperature are established.

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1. Introduction
Grain level thermal expansion anisotropy in polycrystalline ceramics will induce residual stresses during the cooling from sintering temperature. The residual stresses exert a strong influence on the mechanical integrity of materials. Depending on the grain size and grain boundary energy, microcracking occurs and the strength and fracture toughness will be reduced. Several numerical and experimental studies on predicting and measuring the residual stresses in polycrystalline ceramics have been reported in the literature [1–4]. Most of the papers focused on polycrystalline alumina, zirconia/alumina composites, silicon carbide-reinforced alumina, silicon carbide/silicon nitride composites [5]. The residual stresses in another technological important material – titanium diboride (TiB2), are less understood. TiB2 is a ceramic material with high strength, hardness and melting point, and good wear resistance. It is an attractive candidate for the cathode material in the aluminum electrolysis process, because of its good wetting ability with liquid aluminum and good electrical conductivity and chemical inertness at high temperature [6–8]. However, microcracking as a result of residual stresses and mechanical property degradation due to liquid aluminum penetration at grain boundary, are some of the potential limiting factors for wide industrial application as cathode material [9]. This paper studies the residual stresses in single phase TiB2 due to thermal expansion anisotropy and their effect on microcracking initiation and arrest.

In general there are two methods to analyze the residual stresses in ceramic materials: one is micromechanical model based deterministic method [10–15] and another is real microstructure based statistical method [3,4,16–18]. The former method will be used in this study. A representative finite element model based on the micromechanical model by Clarke [10] is constructed and a damage mechanics based cohesive zone model approach is applied to simulate the subsequent microcracking. Clarke’s model consists of four grains surrounded by the thermally isotropic material
Fig. 1. Clarke’s model: four thermal anisotropic grains surrounded by a thermal isotropic matrix material.

Fig. 2. Microstructure of TiB₂ hot pressed without additives. Circles in the figure show the possible four grain junctions.

Fig. 3. Temperature dependent Young’s modulus for TiB₂ [7].
the grain (Fig. 5). The region consists of only square elements. The same model but with different grain sizes has been used. The model contains about 18,000 elements and a similar number of nodes. The used mesh model proved, after a sensitivity analysis, to be suitable to describe the system. Refining the mesh at the grain-matrix boundary did not change significantly the results concerning stress distribution and crack size. The only difference between the grains and matrix materials concerns the thermal properties. Two types of analyses have been carried out. In the first analysis no cracking is permitted along the grain boundaries. The purpose of this type of analysis is to investigate the residual stress fields. In the second type of analysis, a cohesive zone model is applied which allows the prediction of microcracking. ABAQUS has been used for both analyses.

2.3. Cohesive zone model

The microcracking along the grain boundary is modeled by the cohesive zone model in ABAQUS. Cohesive elements were used by Nguyen et al. to describe the cracking behavior in solid oxide fuel cell’s materials and a comparison between discrete and continuum modeling capacity was performed in [15]. The cohesive model is characterized by a traction–separation law [19]. Fig. 6 schematically shows the cohesive zone element and the traction–separation relation. The law characterizing these elements describes a damage initiation criterion and the damage evolution. The cohesive zone behavior is assumed to be linear-elastic initially until a critical traction/displacement has been reached. Beyond the critical stress, an irreversible damage process will begin. The damage of the material is described by the rate of degradation of the material stiffness after the above mentioned critical traction/displacement has been reached. The basic parameters necessary to describe the traction–separation law are two among the critical traction ($t_0$), the critical separation ($\delta_c$) and the cohesive, or fracture energy ($G_c$) [19]. When the cohesive zone model is used to model the grain boundary separation, the cohesive energy is equivalent to the grain boundary energy density. It should be noted that symmetry conditions have been utilized in the finite element analysis.

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**Fig. 4.** Thermal expansion coefficients used in the study [7].

**Fig. 5.** Finite element model for the residual stress and microcracking analyses: entire model with the grain of 50 μm indicated by a black thick line.

**Fig. 6.** Schematic plot of the cohesive zone elements and traction–separation law used in the analysis.
and the reported $G_c$ in the following is half of the total grain boundary separation energy (density). This study focuses on brittle fracture in ceramic materials and the damage evolution model used here is a simplification of the model presented by Tvergaard and Hutchinson [19]. In the cohesive zone modeling, the tractions will decrease once a critical traction value is reached, until they are zero. When the traction reaches zero, material separation, i.e., microcracking, will occur. Because the residual stress field is a self-balanced stress field, the residual stress field will be re-distributed due to the initiation and propagation of a microcrack. As mentioned in Tvergaard and Hutchinson [19], the exact form of the traction–separation law may not be critical for microcracking prediction. Microcracking is determined by the cohesive energy and critical traction values. The critical traction is usually not known and in the present analysis, a critical traction of 1000 MPa has been used. The effect of the critical traction’s value on the simulation results will be discussed later. The elastic stiffness of the cohesive zone has been assumed to the same as the bulk material 565 GPa, independent of the temperature. A very small thickness ($10^{-8}$ mm) has been used for the cohesive elements.

3. Results

3.1. Residual stress field in TiB$_2$

An analytical study on the residual stress distribution has been carried out by Clarke [10]. In the following, the numerical results from the current analysis are presented and compared with the ones by Clarke. Fig. 7a shows the residual stress distribution of the opening stress along the $x$-axis at three different temperatures ($1415$ °C, $734$ °C and $20$ °C) for the case with grain size $50$ μm. As it can be expected, the maximum tensile stress occurs in the center of the model where it is prone to microcracking. The stress decreases with the $x$, i.e. while moving from the center of the reference system toward the positive $x$ direction, and becomes compressive at a distance about 0.55 times of the grain size. A compressive stress peak occurs at the interface with the matrix material. The compressive stress in the matrix material will decrease and approach zero at the outer free boundary. It is interesting to observe that the maximum opening stress in the middle of the model for the TiB$_2$ material could be as large as 3000 MPa. The maximum compressive stress is about half of the tensile peak stress. It should be noted that microcracking will not only depend on the peak tensile stress value. Most importantly, it depends on the total energy available in the material system.

The opening stresses in Fig. 7a have been normalized by a reference stress $\sigma^*$ in Fig. 7b. The reference stress $\sigma^*$ is defined as [10,12,20]:

$$\sigma^* = -E(T)\varepsilon_{22} (\Delta T) = E(T)\Delta x \Delta T,$$

where $E$ is the Young’s modulus; $\Delta x = x_{\text{max}} - x_{\text{min}}$ and $x$ are the thermal expansion coefficients; $\Delta T$ corresponds to $T_{\text{init}} - T_{\text{room}} = (T_{\text{init}}-20)$ °C. The Young’s modulus values
used in the normalization are 514, 542 and 565 GPa for temperatures 1415 °C, 734 °C, and 20 °C, respectively. It can be seen that the opening stresses at different temperatures can be well normalized by using the reference stress (Fig. 7b). The reference stress is related to the use of the Eshelby technique in the analysis of the deformation of a grain in a polycrystalline structure subjected to thermal stresses.

Attempts have also been made to normalize the opening stresses for different grain sizes at room temperature (Fig. 7c). In Fig. 7c the opening stress fields at $T = 20$ °C for the three grain sizes have been normalized by a reference stress value of $\sigma_r = 365.9$ MPa, calculated with the corresponding values of Young’s modulus and strain.

It can be seen that the residual stresses distribution during the cooling process can be normalized by temperature and grain size. An important conclusion which can be drawn from Fig. 7c is that the residual stress field is dependent on the grain geometry but independent of the grain size. This is because that in the residual stress analysis no length scale is involved. In the following it will be shown that the grain size plays a crucial role in microcracking.

### 3.2. Microcracking

In the second type of analysis, the cohesive zone model described in section II, has been applied to study the residual-stress-driven microcracking and its intrinsic relationships with the microstructure parameters. Three grain sizes have been analyzed and for each grain size several grain boundary energy values have been used to study the microcrack length. The analysis is quasi-static and no dynamic effect related to the microcrack propagation, has been considered.

#### 3.2.1. Re-distribution of the residual stresses

Fig. 8 shows the opening stress distributions for the case with grain size $l = 50 \mu$m and grain boundary separation energy density $G_c = 0.33$ and 0.025 N/mm, respectively. In the following, the expressions “grain boundary energy” or “cohesive energy” refer to grain boundary separation energy density. It can be found from Fig. 8a that for the case with $G_c = 0.33$ N/mm, the critical traction has been reached when the temperature cooled down to about 1030 °C. Further cooling induces damage at the grain boundary and irreversible deformation will occur. The maximum opening stress is controlled by the critical traction value specified. In order to balance the damage occurred in the tensile part, the residual stress will be redistributed and the magnitude of the compressive stress will be increased.

For the case with a lower grain boundary energy $G_c = 0.025$ N/mm, Fig. 8b, significant crack growth will occur at room temperature. The stress will be redistributed and both the peak tensile stress and zero stress point will move along the positive $x$ direction.

Fig. 9a and b shows the stress distribution contours for the component $\sigma_{22}$ in the grain area at different stages of the cooling process. Fig. 10 shows the stress temperature history in the center of the model ($x = 0, y = 0$) for the cohesive energy $G_c = 0.025$ N/mm. The stress is first linearly increasing with temperature and then, after reaching the specified critical traction for the damage criterion, it decreases. For the case analyzed, it seems that at about 1030 °C the maximum traction’s value has been reached. After that point, the stress decreases with the temperature. The shape resembles the plot of the used damage criterion which represents the traction–separation law. At about 181 °C the opening stress decreases to zero and according to the definition, material separation and microcracking occurs at this material point. It should be noted that microcracking depends on grain size and grain boundary energy.

#### 3.2.2. Microcracking and microcrack length

Experimental studies [21,22] have shown that microcracking due to residual stress will occur once the grain size has reached a critical value. With the damage based
cohesive zone model approach, the critical grain boundary energy for microcracking, or the critical grain size at which microcracking occurs can be predicted. For the model with grain size 50 μm, Fig. 11 shows the opening stress distribution along the x-axis at room temperature for different values of grain boundary energy. At room temperature, the damage due to residual stress for the case with $G_c = 1$ N/mm is not large enough to cause microcracking. Microcracking will just occur for the case with grain boundary energy about 0.03 N/mm and significant amount of microcrack propagation will occur for the case with grain boundary energy 0.02 N/mm.

It can be clearly seen that for the same grain size the lower the grain boundary energy, the easier the microcrack will initiate and the longer the final microcrack length. It is interesting to note that even the final distribution of the residual stress is disturbed by the critical grain boundary energy; the peak value of the compressive stress is rather insensitive to the grain boundary energy.

Fig. 12 plots the predicted final microcrack length vs. the critical grain boundary energy for the three grain sizes. It is interesting to note that the microcrack length has a decreasing but linear relation with the grain boundary energy and the grain size has a strong influence on the values of the critical grain boundary energy for microcracking $G_c$. For a material with larger grain size, the crack will occur easily (i.e. for smaller values of $G_c$) and higher grain boundary energy is needed to avoid microcracking.

One important aspect in manufacturing ceramics is to avoid microcracking. The above analysis indicates that residual stress induced microcracking can be avoided by either reducing grain size or improving grain boundary energy. For the case with grain size 50 μm, a grain boundary energy value larger than about 0.03 N/mm is necessary to avoid microcracking in TiB$_2$. This grain boundary energy is equal to the reported maximum fracture toughness for TiB$_2$, 6.2 MPa $\sqrt{\text{m}}$ [7].

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Fig. 9. Stress distribution contours of $\sigma_{zz}$ in the grain, for grain size 50 μm and $G_c = 0.025$ N/mm, (a) at $T = 882 \degree C$; (b) at $T = 20 \degree C$.

Fig. 10. Opening stress $\sigma_{zz}$ in $x = 0$ during the cooling process, grain size 50 μm, $G_c = 0.025$ N/mm.

Fig. 11. Final stress distribution along the x-axis in the grain, at $T = 20 \degree C$, for different values of the cohesive energy (N/mm), $l = 50 \mu m$. 

Fig. 12. Plot of predicted final microcrack length vs. the critical grain boundary energy for the three grain sizes.
Fig. 13 shows the calculated critical grain boundary energy vs. grain size. For a given grain size, if the grain boundary energy is larger than the one shown in the figure, no microcracking will occur. On the other hand, for a fixed grain boundary energy value, the critical grain size for avoiding microcracking can be calculated. The critical grain boundary energy shown in Fig. 13 has been fitted by the following equation:

\[ G_c = 0.0006l + 0.00014 \]  

(2)

where \( G_c \) has the unit N/mm and grain size \( l \) has a unit of \( \mu \)m.

These data could be important for material design: known the grain boundary energy of the microstructure, the critical grain size can be estimated. The link among the critical grain size, the temperature variation and other material and process parameters may be useful. Exposure to liquid aluminum at high temperatures, for example, can cause the degradation of the boundary energy. This theme will be addressed in a companion paper. The present relation has been compared with the models available in the literature [22–26] in Fig. 14. In general a linear relation between the critical grain size (or critical particle size) and the surface fracture energy is expected:

\[ l_c = m \frac{\gamma_f}{E \cdot (\Delta \alpha \cdot \Delta T)^2} \]  

(3)

where \( m \) is a coefficient, \( \gamma_f \) the surface fracture energy which corresponds to \( G_c \) in this study. In Fig. 14, the following values for TiB\(_2\) have been used: \( E = E(T = 20 \, ^\circ\text{C}) = 565 \, \text{GPa}, \Delta \alpha = \alpha_{\text{max}} - \alpha_{\text{min}} = 2.8 \times 10^{-6} \, ^\circ\text{C}^{-1} \) and \( \Delta T = T_{\text{fin}} - T_{\text{init}} = -1480 \, ^\circ\text{C} \). The literature models are based on simplified analytical solutions. A comparison of the literature models with experimental results, for various materials, has been carried out by Rice and Pohanka in [22] together with a discussion of the way to estimate the parameters. For a given grain boundary energy, the first model listed by Rice and Pohanka yields the lowest critical grain size: the coefficient \( m \) is about 10.7. The one by Cleveland and Bradt [23] lies in the middle as well as the present study, with a proportionality coefficient of about 15. The largest value of the predicted critical grain size is given by the third model listed in [22] with \( m \approx 20 \). The exact value of the coefficient \( m \) depends on the grain structure of the material and the model assumptions.

The first model in [22] refers to Davidge and Green’s work [24]. This 3D model describes the cracking in composites made of a glassy matrix with embedded ceramic spherical particles. Four glasses differing by the thermal expansion coefficients have been experimentally studied. In the absence of applied stresses, when the particle has a thermal expansion coefficient higher than that of the matrix, the presence of flaws near a particle and the fulfillment of an energy criterion are necessary for cracking to occur. The first model represents the critical particle size...
derived from energy balance. The second model listed in [22] concerns JFP Clarke’s study [25] which focuses on intergranular cracking as a result of the growth of an existing grain boundary pore for two adjacent hexagonal grains. The energy for crack growth along the grain boundary comes from two sources, strain relaxation around a growing crack and relief of residual strains in the two neighboring grains. The Griffith energy balance method together with two conditions, one about the initial crack size and the other about the crack growth length, has been applied to derive a relation among grain size and other parameters. The third model in [22] is from the analysis of the crack propagation at interface between two dissimilar materials by Mulville et al. [26]. A fracture criterion in terms of strain energy release rate has been developed to determine the fracture resistance of interfacial cracks. Experiments on specimens of epoxy bonded to aluminum were also done to compare with the analytical results. Cleveland and Bradt’s [23] relation is derived from an energy criterion for the case of pseudobrookite structure, with high level of thermal expansion anisotropy. Assuming dodecahedral grains, an expression for the total energy is given. This is used to obtain, from an approximated energy balance, the critical grain size as a function of the above mentioned parameters.

It can be observed that all the considered models concern slightly different situation than the one in the present study but still are indicative for the understanding of the role of the involved factors in the relation ‘critical grain size-critical grain boundary energy’.

3.2.3. Microcracking temperature

Microcracking usually starts at a higher temperature than room temperature. Microcracking temperature is an important process parameter and has been experimentally studied in the literature. Several empirical works have been carried out [27,28]. With the damage-mechanics-based cohesive model approach, the microcracking temperature for a given grain size and grain boundary energy can be predicted.

Fig. 15 displays the evolution of microcracking with temperature for different values of grain boundary energy. The crack size is remaining zero until a critical temperature at which the crack starts. The crack will increase its size while the temperature further decreases. Obviously microcracking starts at a higher temperature for the cases with lower values of grain boundary energy.

3.2.4. Effect of cooling temperature range

The residual stress field and consequently the microcracking behavior are proportional to the temperature variation the material is subjected to. A lower starting temperature of the cooling process will result in lower stress, lower microcracking temperature and shorter final microcrack length.

Fig. 16 shows the final stress distributions for two cases with starting temperatures 1000 °C and 1500 °C, respectively. For the case with starting temperature $T_{\text{init}} = 1000$ °C, at room temperature the damage process has just been initiated and the residual stress field is not sufficient to cause microcracking. However, for the case with starting temperature $T_{\text{init}} = 1500$ °C, a microcrack has not only initiated in the center but also propagated for 7.5 μm upon reaching the room temperature.

4. Discussion and concluding remarks

Residual stress due to thermal anisotropy plays an important role in mechanical properties of polycrystalline ceramics. The residual stress field and associated microcracking in TiB₂ ceramics has been studied for the first time using finite element method. Three grain sizes, 10, 20 and 50 μm, have been considered. The Clarke model has been
used to represent microstructure features and cohesive zone model is applied to model the material microcracking process. It should be noted that two dimensional plane stress model has been used and no dynamic effect was considered in modeling the microcracking and propagation. It has been demonstrated that microstructural level residual stress distribution is solely determined by the microstructure and sintering process parameters. The calculation of residual stress does not involve a length scale and the residual stress distribution can be normalized by both the grain size and cooling temperature. The calculated peak tensile residual stress does not involve a length scale and the residual stress distribution is solely determined by the microstructure and sintering process parameters. The calculation of residual stress is solely determined by the microstructure and has been demonstrated that microstructural level residual stress distribution to microcracking and propagation. It has been demonstrated that microstructural level residual stress distribution is solely determined by the microstructure and sintering process parameters. The calculation of residual stress does not involve a length scale and the residual stress distribution can be normalized by both the grain size and cooling temperature. The calculated peak tensile residual stress can be as high as 3000 MPa for TiB₂ while the compressive peak stress is approximately half of the tensile peak. On the other hand, microcracking due to thermal residual stress is strongly dependent on the grain size. Even though the distribution is the same, material with large grain size has more available elastic energy and is prone to microcracking.

With the damage-mechanics-based cohesive zone model, a quantitative relation between the grain boundary energy, grain size and microcrack length has been established. The critical grain boundary energy has been shown to be linearly proportional to the grain size – larger grain size needs higher grain boundary energy to avoid residual-stress-induced microcracking. True critical grain boundary energy value for a material is difficult to measure and almost no data are available for TiB₂. The critical grain boundary energy value predicted by this model can be related to the macroscopic fracture toughness. However, the macroscopic fracture of TiB₂ depends on many factors, residual stress, sintering additives, fracture modes, et al. It is out of the scope of the present study to perform well defined experimental study to verify the predictions. Nevertheless the predicted critical grain boundary energy agrees with the experimental observations of macroscopic fracture reported in [7]: residual stresses and consequent grain boundary cracking contribute partly to the weakening and macroscopic cracking of the material. The following comparison is concerned with the understanding of the “grain-boundary-cracking” contribution to the macroscopic fracture toughness. The calculated minimum grain boundary energy for avoiding microcracking are 0.0302, 0.01225 and 0.0061 N/mm for the cases with grain sizes 50, 20 and 10 µm, respectively. For TiB₂ material, the maximum measured macroscopic fracture toughness has been reported to be 6.2 MPa√m [7] which corresponds to \( G_c = 0.03 \) N/mm. The predicted critical grain boundary energy has been converted to critical stress intensity factor and is compared with the statistical relation between grain size and macroscopic fracture toughness by Munro [7] in Fig. 17. If the maximum fracture toughness is assumed to be 6.2 MPa√m, the present analysis indicates that even no microcracking occurs, little or no additional external load can be carried out for the material with grain size 50 µm. According to the analysis, maximum fracture toughness can only occur at smaller grain size. Munro observed the grain size which results in the maximum fracture toughness is about 8–10 µm. It should be noted that a large scatter exists in the data compiled by Munro since they refer to materials with different chemical impurity content and subjected to different test conditions, and no fracture modes (mechanisms) were distinguished in the statistics. It can also be observed that two trends are present in the statistical fracture toughness – grain size relation. When the grain size is less than about 8 µm the fracture toughness increases with the increase of grain size, while the trend becomes opposite when the grain size is larger than about 8 µm.

The residual stress analysis shows that about 55% of the grain size close to the four grain junction center is under tensile stress. The final microcrack length is dependent on the grain size and grain boundary energy. The analysis with 10 µm grain size shows that if the grain boundary energy is small enough, a microcrack length approaching half of its grain size (5 µm) can be reached at room temperature.

In this study, the interface has no thickness and large cohesive zone interface stiffness \( (5.6 \times 10^{13} \text{ N/mm}^2) \) is preferred. However, large stiffness may induce numerical problems such as spurious oscillations of the tractions in an element [29]. The shape of the traction–separation curve has a very weak influence on the fracture/damage process. The cohesive energy and the critical traction are the fundamental parameters describing the microcracking process. Increasing cohesive energy will delay the damage process for a given grain size. The exact value of the critical stress is not known. A value of 1000 MPa for the critical traction has been chosen for the cohesive traction–separation law. Other values have also been used to study the microcracking behavior. A lower value of the critical stress for separation results in a slightly shorter crack length. Further work should be spent on designing experimental methods to determine the critical stress.
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