Mechanism for Densification of Yttria-Stabilized Tetragonal Zirconia Powder by Electric Current-Activated/Assisted Sintering*

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The effect of electric current-activated/assisted sintering (ECAS) on the densification of a mechanically milled 3Y-TZP ceramic powder was investigated. The changes in temperature ($T$) and relative density ($\rho$) with time during ECAS under a uniaxial pressure of 90.5 MPa in a closed die were measured for different heating conditions. From the results, densification rate ($\dot{\rho}$) vs. $T$ and $\rho$ vs. $\rho$ curves were interpolated for different fixed heating rates ($T$) of 0.1 to 2.0 K/s. Although the values of $\rho$ at fixed temperatures or relative densities increase with increasing $T$, the values of $T$ and $\rho$ corresponding to the peaks of $\rho$ were almost constant at 1300 K and 0.8, respectively, irrespective of $T$. The stress exponent ($n$) estimated from log-log plots of $\dot{\rho}$ and the effective stress ($\sigma_{\text{eff}}$) increased monotonically with increasing $T$; however, the values of $n$ re-estimated using $\sigma_{\text{eff}}$ compensated for threshold stress ($\sigma_0$) were approximately 2, irrespective of $T$. In addition, the activation energy ($Q$) estimated from the $\sigma_{\text{eff}}$ vs. $1/T$ Arrhenius plot was 450 ± 20 kJ/mol. These values of $n$ and $Q$ were similar to those for creep experiments reported by Melendo et al., which suggests that densification of 3Y-TZP powder compacts by ECAS proceeds through grain boundary sliding affected by $\sigma_0$ as well as creep deformation in the intermediate stress region.

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1. Introduction

Electric current-activated/assisted sintering (ECAS) has been expected to become a powerful tool for the fabrication of nanocrystalline bulk materials, especially that of tetragonal zirconia polycrystals stabilized by 3 mol% Y$_2$O$_3$ (3Y-TZP). In this sintering process, use of ball-milled powder compacts enables extremely brief densification at relatively low temperatures of 1200 to 1400 K without apparent grain growth. However, rapid densification, which is the advantage of ECAS, makes quantitative analysis difficult. Granger et al. have investigated the relationship between the densification rate ($\dot{\rho}$) and the relative density ($\rho$), which can be converted to effective stress ($\sigma_{\text{eff}}$) for porous compacts, at fixed temperatures ($T$) during densification of 3Y-TZP powder compacts by ECAS. They have suggested that the stress exponent ($n$) increased monotonically from 2.0 to 4.8 with increasing $T$. However, their study was focused on the densification behavior under isothermal conditions after rapid heating. Most rapid densification progresses during heating; therefore, it has not been clarified whether the densification behavior that corresponds to small changes in $\rho$ and $\dot{\rho}$ under isothermal conditions represents the rapid densification behavior corresponding to extremely large changes in $\rho$ and $\dot{\rho}$ during heating.

The densification kinetics of pressureless sintering are generally expressed using a function of $T$, grain size ($d$) and $\rho$. On the other hand, in the case of creep deformation, the steady-state creep strain rate ($\dot{\varepsilon}$) becomes a function of $T$, $d$ and flow stress ($\rho$ is a constant). Typically, creep experiments are conducted at various constant flow stresses at a fixed temperature and/or various constant temperatures at a fixed flow stress in order to estimate $n$ and/or the activation energy for creep deformation. In contrast, for pressureless sintering during the initial stage of sintering ($\rho$ below 0.92) the values of $\dot{\rho}$ at a fixed value of $\rho$, which increase continuously during isothermal heating, are measured at various constant temperatures to estimate the activation energy for densification ($Q$). Here, one value of $\dot{\rho}$ at a fixed value of $\rho$ should be obtained from one powder compact when held at one temperature: the so-called isothermal method. However, the values of $\dot{\rho}$ are often measured from one powder compact heated at a fixed heating rate, instead of a fixed temperature: the so-called constant heating rate method. One value of $\dot{\rho}$ at a fixed value of $\rho$ and the corresponding value of $T$ are obtained from $\rho$–$T$ and $\dot{\rho}$–$T$ curves for one powder compact heated at a fixed heating rate. Thus, the values of $\dot{\rho}$ at a fixed value of $\rho$ at various temperatures are obtained for several powder compacts heated at various constant heating rates.

The temperature range required for pressureless sintering of 3Y-TZP powder compacts by ECAS is too low for pressureless sintering. Thus, the densification kinetics seems to be expressed by the creep deformation formula, in which $\dot{\varepsilon}$ is converted to $\dot{\rho}/\rho$. However, rapid densification proceeds mainly during high-speed heating, and thus it is difficult to measure $\dot{\rho}$ at the isothermal condition. Recently, the rapid densification behavior of 3Y-TZP powder compacts under ECAS at a fixed applied pressure of 46.5 MPa have been analyzed by Kumagai using a quasi-constant heating rate method. The values of $\dot{\rho}$ at a fixed temperature under various effective stresses, which were converted from $\rho$ for estimation of $n$, and the values of $\dot{\rho}$ at a fixed effective stress at various temperatures for estimation of $Q$ were obtained from the $\rho$–$T$ and $\dot{\rho}$–$T$ curves at fixed heating rates of 0.1 to 2 K/s. Unfortunately, although the applied current for resistance heating was constant during ECAS, the heating rate was not constant, but decreased monotonically with increasing densification time. Thus, the $\rho$–$T$ and $\dot{\rho}$–$T$ curves at the various fixed heating rates were constructed by interpolating...
data points that corresponded to the values of $\rho$, $\tilde{p}$ and $T$ at the moment of the required heating rate on the $\rho$–$T$ and $\tilde{p}$–$T$ curves. The estimated values of $n$ and $Q$ compensated for threshold stress ($\sigma_0$) in Ref. 9) were 1.9 and 460 $\pm$ 26 kJ/mol, respectively.

The purpose of this study is to investigate the densification behavior of 3Y-TZP powder compacts by ECAS at 90.5 MPa, which is higher than 46.5 MPa employed in Ref. 9), and discuss the influence of the applied pressure for powder compact on the densification mechanism.

2. Experimental Procedures

A high purity powder of tetragonal zirconia stabilized by 3.0 mol% yttria (High Purity Chemicals Co. Ltd., Japan) was used in this study. The supplier provided the following impurity content in mass%: Al 0.001, Fe 0.001 and Ti 0.002. The 3Y-TZP powder was mechanically milled at a rotational speed of 420 rpm for 1.6420 $\times$ 10$^6$ s (19 days) in an Ar atmosphere using a planetary ball-mill system (Pulverisette-6, Fritsch, Germany). An yttria-stabilized zirconia vessel and balls were used to prevent contamination during the milling process. The diameter of the balls was 5 mm and the weight ratio of ball to powder was 10 to 1.

The mechanically milled 3Y-TZP powder (2.00 $\times$ 10$^{-3}$ kg) was packed in a cylindrical graphite die with inner and outer diameters of 10 and 45 mm, respectively, and a height of 40 mm, and pressed at a constant uniaxial pressure of 90.5 MPa by upper and bottom graphite plungers with diameters of 10 mm and lengths of 30 mm. After evacuating the chamber to 10 Pa, a short rectangular pulse with a current used in this study, full densification was achieved within an extremely short period of approximately 400 s. Figure 3 shows XRD patterns obtained for the as-milled powder (Fig. 3(a)) and the powder compact consolidated at 1000 A (Fig. 3(c)). Figure 3(b) shows an XRD pattern for comparison, of the powder compact obtained by interrupting the ECAS treatment (indicated by arrows in Figs. 1 and 2) after the start of rapid densification. Broad peaks typical of an amorphous structure are evident in the XRD pattern of the as-milled powder (Fig. 3(a)). In contrast, sharp crystalline peaks of tetragonal zirconia solid solution ($t$-ZrO$_2$) are observed in the XRD pattern for the powder compact consolidated at 1000 A (Fig. 3(c)). The SEM image presented in Fig. 4

Fig. 1 Temperature as a function of time for 3Y-TZP powder compacts consolidated at 90.5 MPa and fixed currents of 700 to 1000 A.
shows that the fully densified bulk consists of an extremely fine equiaxed grain structure. The XRD pattern shown in Fig. 3(b) for the powder compact interrupted during ECAS treatment was quite similar to that for the fully densified bulk (Fig. 3(c)). The average crystallite sizes estimated by the Scherrer method using the three main peaks of 111, 202, and 311 for the dense (Fig. 3(c)) and porous (Fig. 3(b)) samples were similar at 24 and 22 nm, respectively. These results indicate that rapid densification occurs after total crystallization of t-ZrO$_{2s}$ and proceeds without apparent grain growth.

Figures 5 and 6 show $\dot{\rho}$ vs. $T$ and $\dot{\rho}$ vs. $\rho$ plots, respectively. In both cases, $\dot{\rho}$ increased with increasing current and the peaks of $\dot{\rho}$ shifted to the higher side of $T$ or $\rho$. However, it should be noted that $T$ for all samples in Figs. 5 and 6 were not constant, but decreased continuously with increasing consolidation time (see Fig. 7). Data points corresponding to $T = 0.1, 0.2, 1$ and 2 K/s on the five $\dot{\rho}$-$T$ curves in Fig. 5 and the five $\dot{\rho}$-$\rho$ curves in Fig. 6 were selected to obtain the $\dot{\rho}$ vs. $T$ and $\dot{\rho}$ vs. $\rho$ interpolation curves at fixed heating rates, which are plotted in Figs. 8 and 9, respectively. The $\dot{\rho}$ vs. $T$ and $\dot{\rho}$ vs. $\rho$ interpolation curves obtained in the present study are shown with solid lines, while the dashed lines represent the previously reported interpolation curves for the same amorphous 3Y-TZP powder compacts consolidated at a low pressure of 46.5 MPa.$^9$ Figure 8 shows that $T$ corresponding to the peaks of $\dot{\rho}$ from
the present data was almost constant at approximately 1300 K, irrespective of \(T\). This value was lower than \(T\) of approximately 1350 K for the previously reported data (dashed lines). In addition, \(\rho_{C26}\) corresponding to the peaks of \(\rho_{C26}/C26\) for the present data was also constant at approximately 0.80 (see Fig. 9). However, this value was close to \(\rho_{C26}\) of approximately 0.79 for the previous reported data (dashed lines).

Figure 10 shows the \(\rho\) vs. \(T\) interpolation curves at fixed heating rates constructed using the data points in Figs. 8 and 9. The previously reported \(\rho\) vs. \(T\) interpolation curves at fixed heating rates for ECAS at 46.5 MPa\(^9\) are also shown for comparison (dashed lines).

Moreover, both of the \(\rho\)-\(T\) curves for high pressure (solid lines) and low pressure (dashed lines) in Fig. 10 had smooth S-shaped profiles with a similar onset-temperature of approximately 1050 K. However, the slope of the high pressure \(\rho\)-\(T\) curve at a fixed heating rate was larger than that of the corresponding low pressure \(\rho\)-\(T\) curve. Thus, the finishing temperature for rapid densification under high pressure was lower than that under low pressure. As a result, the temperatures corresponding to the peaks of \(\rho\) at the fixed heating rates for high pressure were lower than those for low pressure, as shown in Fig. 8.
3.2 Activation energy and stress exponent

In the case of pressureless sintering, the driving force of densification in the initial stage of sintering (ρ below 0.92) is a reduction of surface energy of the powder particles. The high-energy solid-vapor interface is replaced by a low-energy solid-solid interface through neck growth by atomic diffusion. However, even though the sintering temperature is sufficiently high for diffusion, the densification rate decreases rapidly with decreasing neck curvature, and thus decreasing surface tension. On the other hand, a long period of time is required for densification when the sintering temperature is too low for atomic diffusion. In the case of pressureless sintering of 3Y-TZP compacts, it has been reported that apparent densification was not observed during heating from 1400 to 1428 K at temperatures below 1463 K. Thus, densification by ECAS is considered to proceed through high-temperature plastic deformation and/or grain boundary sliding, rather than by neck growth.

The densification kinetics for pressure sintering, i.e., hot-pressing for powders, can be expressed by the steady-state creep strain rate formula, in which \( \dot{\varepsilon} \) is replaced by \( \dot{\rho}/\rho \), as follows:12)

\[
\dot{\rho}/\rho = A \frac{G_{\text{eff}} b}{kT} \left( \frac{b}{d} \right)^n \left( \frac{\sigma_{\text{eff}}}{G_{\text{eff}}} \right)^n D_0 \exp \left(-\frac{Q}{RT}\right)
\]

where \( A \) is a dimensionless constant, \( G_{\text{eff}} \) is the effective shear modulus of the powder compacts, \( b \) is the Burgers vector, \( k \) is the Boltzmann constant, \( T \) is absolute temperature, \( d \) is the grain size, \( p \) is the grain size exponent, \( \sigma_{\text{eff}} \) is the effective stress, \( n \) is the stress exponent, \( D_0 \) is the frequency factor, \( Q \) is the activation energy and \( R \) is the gas constant. The room-temperature shear modulus for porous materials (\( G'_{\text{eff}} \)) is often expressed using the shear modulus for the fully dense bulk (\( G_{\text{th}} \)) and the initial relative density (\( \rho_0 \)) as follows:13,14)

\[
G'_{\text{eff}} = G_{\text{th}} \left( \frac{\rho}{\rho_0} \right) (1 - \frac{2}{3} \rho_0) \]

However, the author has used \( G'_{\text{eff}} \) for the porous 3Y-TZP materials obtained experimentally by Luo et al.15) in the range from 0.63 to 0.93 for \( \rho_0 \) as follows:

\[
G'_{\text{eff}} \text{ [MPa]} = 66.1 \times 10^3 - 116 \times 10^3 \times (1 - \rho) \]

In addition, the high-temperature shear modulus for porous materials (\( G_{\text{eff}} \)) is given by eq. (5):16)

\[
G_{\text{eff}} \text{ [MPa]} = G_{\text{th}} \times 10^3 - 13.3 T
\]

Assuming the powder is comprised of ideal spherical particles, \( \sigma_{\text{eff}} \) is then given by eq. (6), using the applied stress for powder compact (\( \sigma \)), \( \rho \) and \( \rho_0 \) in the initial stage of sintering (\( \rho \) below 0.92):5,7)

\[
\frac{\sigma_{\text{eff}}}{\sigma} = \frac{1 - \rho_0}{\rho^2 (\rho - \rho_0)}
\]

The crystallite size was almost constant at 22 to 24 nm during ECAS; therefore, \( p \) and \( d \) in eq. (3) were also considered to be constant. When \( T \) is constant, eq. (3) can be rewritten as follows:

\[
\ln \left( \frac{1}{G_{\text{eff}}} \cdot \frac{\dot{\rho}}{\rho} \right) = n \cdot \ln \left( \frac{\sigma_{\text{eff}}}{G_{\text{eff}}} \right) + \ln B
\]

where \( B \) is a dimensionless constant and \( B = (Ab/kT) \cdot (b/d)^p D_0 \exp(-Q/RT) \).

Fig. 11 Stress exponent calculated using eq. (7) for 3Y-TZP powder compacts consolidated at 90.5 MPa. The applied stress (\( \sigma \)) is converted to effective stress (\( \sigma_{\text{eff}} \)) using the relative density (see eq. (6)). The values of densification rate and relative density at fixed temperatures for data points are obtained from the interpolation curves in Figs. 8 and 10, respectively. Results for 3Y-TZP powder compacts consolidated at 46.5 MPa are also shown for comparison (dashed lines).

Many studies concerning creep of 3Y-TZP bulk materials have suggested the presence of the three regions of \( n: n = 1 \) in the low stress region, \( n = 2 \) in the high stress region and \( n > 3 \) in the intermediate stress region.17–21) In addition, creep deformation has been reported to proceed by Nabarro-Herring (N-H) diffusional creep in the low stress region and by grain boundary sliding in the high stress region.15–21) The high value of \( n > 3 \) is considered to be due to the inhibition of grain boundary sliding by the existence of \( \sigma_{\text{th}} \) and the “natural” value of \( n = 2 \) can be obtained using (\( \sigma = \sigma_{\text{th}} \)) instead of \( \sigma \) in the creep deformation formula.3,7–21) If the continuous increase in \( n \) in the present ECAS experiments (see Fig. 11) is due to the existence of \( \sigma_{\text{th}} \) as well as creep, the natural value of \( n = 2 \) will be obtained by replacing \( \sigma_{\text{eff}} \) with \( (\sigma_{\text{eff}} - \sigma_{\text{th}}) \) in eq. (3).

Equation (3) can be rewritten by replacing \( \sigma_{\text{eff}} \) with \( (\sigma_{\text{eff}} - \sigma_{\text{th}}) \) as follows:

\[
\frac{\dot{\rho}}{\rho} = A \frac{G_{\text{eff}} b}{kT} \left( \frac{b}{d} \right)^p \left( \frac{\sigma_{\text{eff}} - \sigma_{\text{th}}}{G_{\text{eff}}} \right)^n D_0 \exp \left(-\frac{Q}{RT}\right)
\]

where \( \sigma_{\text{th}} \) is a function of \( T \) and expressed as follows:17–19)

\[
\sigma_{\text{th}} = C \exp \left( \frac{Q_{\text{th}}}{RT} \right)
\]

where \( C \) is a dimensionless constant and \( Q_{\text{th}} \) is the activation energy related to \( \sigma_{\text{th}} \), i.e., energy required to overcome the
pining force by Y³⁺ segregation at the grain boundaries. Thus, when \( T \) is constant, eq. (8) can be rewritten as follows:

\[
\left( \frac{1}{G_{\text{eff}}} \cdot \frac{\dot{\rho}}{\rho} \right) = B \left( \frac{\sigma_{\text{eff}} - \sigma_0}{G_{\text{eff}}} \right)^n
\]  

(10)

In order to estimate \( \sigma_0 \), a \([\left(1/G_{\text{eff}}\right) \cdot \left(\rho/\rho\right)]^{1/2}\) vs. \((\sigma_{\text{eff}}/G_{\text{eff}})\) plot at fixed temperatures, i.e., \( n = 2 \) in eq. (10), is constructed as shown in Fig. 12. All the data points were on the corresponding straight lines. Thus, we obtained the values of \( \sigma_0/G_{\text{eff}} \) corresponding to zero of \( \rho/\rho \) in eq. (10). Figure 13 shows an Arrhenius plot of \( \sigma_0/G_{\text{eff}} \) vs. reciprocal \( T \). The value of \( Q_0 \) estimated from the slope of the straight line was 100 ± 30 kJ/mol, which is close to 120 kJ/mol for creep experiments with 3Y-TZP powder compacts consolidated at 90.5 MPa. Results for 3Y-TZP powder compacts consolidated at 46.5 MPa are also shown for comparison (dashed lines).

The activation energy for densification can be calculated using eq. (8). When \( \rho \) and thus \( \sigma_{\text{eff}} \) is constant, eq. (8) can be rewritten using the average \( n \) value of 2 as follows:

\[
\ln \left( \frac{T}{G_{\text{eff}}} \cdot \frac{\dot{\rho}}{\rho} \right) / \left( \frac{\sigma_{\text{eff}} - \sigma_0}{G_{\text{eff}}} \right)^2 = \frac{-Q}{RT} + \ln C
\]  

(11)

where \( C = (Ab/k) \cdot (d/\overline{d})^p \cdot D_0 \) is a dimensionless constant. Figure 15 shows an Arrhenius plot of temperature-, effective shear modulus-, effective stress- and threshold stress-compensated densification rate vs. reciprocal temperature, when \( n = 2 \) in eq. (8) (see eq. (11)).
obtained from the \(\dot{\rho} \sim \rho\) (Fig. 9) and \(T \sim \rho\) (Fig. 10) curves, respectively. All the data points except \(\rho\) of 0.90 fit well on a straight line and the estimated activation energy for densification was \(450 \pm 20\text{kJ/mol}\). This value is relatively smaller than \(570 \pm 30\text{kJ/mol} \) obtained from creep experiments with 3Y-TZP\(^{20}\) but similar to \(460 \pm 40\text{kJ/mol}\) by other researchers\(^{17-19}\) and \(460 \pm 26\text{kJ/mol}\) obtained from the ECAS of 3Y-TZP under low pressure.\(^{9}\)

Figure 16 shows the previously reported activation energies for \(\text{Zr}^{4+}\) lattice diffusion (\(Q_{l}\), \(\text{Zr}^{4+}\) grain boundary diffusion (\(Q_{gb}\)) and densification (\(Q\)) in yttria-stabilized zirconia. (SC and PC denote single crystal and polycrystals, respectively.)

![Fig. 16 Activation energies for \(\text{Zr}^{4+}\) lattice diffusion (\(Q_{l}\), \(\text{Zr}^{4+}\) grain boundary diffusion (\(Q_{gb}\)) and densification (\(Q\)) in yttria-stabilized zirconia. (SC and PC denote single crystal and polycrystals, respectively.)](image)

However, based on the results presented in Fig. 16, we can consider that \(Q_{l}\) (\(\text{Zr}^{4+}\)) for 3Y-ZrO\(_2\) tetragonal single crystals (if apparent) is close to \(Q_{l}\) (\(\text{Zr}^{4+}\)) for 8-32Y-ZrO\(_2\) cubic single crystals.

Unfortunately, reports concerning \(Q_{gb}\) have been significantly limited. It is well known that grain boundary diffusion of \(\text{Zr}^{4+}\) in ZrO\(_2\)-Y\(_2\)O\(_3\) polycrystals is strongly affected by dopants or impurities. Nakatani et al.\(^{26}\) have reported that the flow stress in 3Y-TZP was strongly affected even by a small amount (0.2 mol%) of cation doping. They have suggested that the doping of ions with small ionic radii causes a decrease of the flow stress, due to acceleration of \(\text{Zr}^{4+}\) grain boundary diffusion by grain boundary segregation of the doped-ions. In addition, Kowalski et al.\(^{27,28}\) have reported that the ratio of \(Q_{gb}/Q_{l}\) (\(r\)) was 0.67 (= 340 kJmol\(^{-1}\)/505 kJmol\(^{-1}\)) for \(\text{Ti}^{4+}\), of which the ionic radius of 0.068 nm is smaller than that of 0.084 nm for \(\text{Zr}^{4+}\), but \(r\) was 1.10 (= 367 kJmol\(^{-1}\)/333 kJmol\(^{-1}\)) in Ca\(^2+\)-doped 8Y-CZP with a larger ionic radius of 0.112 nm. The Y\(^{3+}\) ion, which has a large ionic radius of 0.1019 nm, has also been reported to segregate at grain boundaries with an enrichment factor of above 2.\(^{29}\) Thus, the segregation of Y\(^{3+}\) at grain boundaries seems to disturb the \(\text{Zr}^{4+}\) grain boundary diffusion. Sakka et al.\(^{30}\) have reported that \(Q_{l}\) and \(Q_{gb}\) estimated by inter-diffusion experiments using cubic polycrystalline 16Y\(_2\)O\(_3\)-84(Zr\(_1-x\)Hf\(_x\))O\(_2\) with \(x = 0.020\) and 0.100 were 391 and 309 kJ/mol, respectively. In addition, Swaroop et al.\(^{35}\) have reported that \(Q_{gb}\) for tetragonal polycrystalline 3Y-TZP was 370 kJ/mol. In both cases, \(Q_{gb}\) are smaller than the corresponding \(Q_{l}\), however, the temperature ranges of 1857–2389 K and 1673–1873 K are relatively higher than the typical creep-test temperatures of up to 1723 K.\(^{17}\)

Melendo et al.\(^{17}\) have suggested that the creep deformation in the intermediate and high stress regions is controlled by \(\text{Zr}^{4+}\) lattice diffusion, because their estimated activation energy for creep (460 \pm 40 kJ/mol) was higher than the values of \(Q_{gb}\) for 3Y-TZP\(^{29}\) and 16Y-CZP\(^{30}\) but close to the values of \(Q_{l}\) for 8-32Y cubic single crystals.\(^{23}\) The value of 450 \pm 20 kJ/mol for rapid densification obtained in this study is similar to the above mentioned activation energy for creep,\(^{17}\) which suggests that the rapid densification proceeded through the same diffusion path as that for creep deformation. The pinning force for grain boundary sliding by the grain boundary segregation of Y\(^{3+}\) increases with decreasing temperature (see eq. (9)). Thus, further experiments concerning \(\text{Zr}^{4+}\) diffusion in 3Y-TZP at the low temperatures up to 1723 K are required to clarify whether the densification behavior is controlled by \(\text{Zr}^{4+}\) lattice diffusion, \(\text{Zr}^{4+}\) grain boundary diffusion or by different diffusion paths.

Regarding \(n\) in the case of creep deformation; when \(\sigma\) is sufficiently high to neglect the influence of \(\sigma_{0}\), \(n\) has the “natural” value of 2. Unfortunately, the existence of a high stress region during rapid densification by ECAS has not been clarified, because the present value of 90.5 MPa is close to the fracture strength of the graphitie die and plungers. However, as shown in Fig. 11, \(n\) at the highest value of \(\sigma_{eff}\) without compensation for \(\sigma_{0}\) was 2.4 and close to 2, which suggests the possibility of a high stress region of \(n = 2\), although further investigation is required.
4. Conclusion

The densification behavior of mechanically-milled 3Y-TZP powder compacts by ECAS at a constant pressure of 90.5 MPa was investigated. The obtained $\rho$–$T$ and $\rho$–$p$ curves at fixed currents were converted to $\rho$–$T$ and $\rho$–$p$ curves at fixed heating rates by interpolating selected data points. As a result, the values of $\rho$ at fixed temperatures or relative densities increased with increasing heating rates, but $T$ and $\rho$ corresponding to the peaks of $\rho$ were almost constant at 1300 K and 0.8, respectively, irrespective of the heating rate. The present value of 1300 K was lower than the previously reported value of 1350 K for lower pressure of 46.5 MPa; however, the present value of 0.8 for $\rho$ was close to the previously reported value of 0.79.

The values of $n$ estimated from log-log plots of $\rho$ and $\rho$ at fixed temperatures, in which $\rho$ were converted to effective stress, increased from 2.4 to 4.8 with increasing temperature. However, all the values of $n$ compensated for $\sigma_0$ were constant at approximately 2. The activation energy for rapid densification estimated from an Arrhenius plot of $\rho$ compensated for $\sigma_0$ vs. reciprocal temperature at fixed relative densities from 0.65 to 0.90 was 450±20 kJ/mol. The estimated values of $n$ and $Q$ were similar to the previously reported values from creep experiments and ECAS under the low pressure of 46.5 MPa. In conclusion, the present rapid densification of mechanically milled 3Y-TZP powder compacts by ECAS under high pressure is considered to proceed by grain boundary sliding as well as creep deformation in the intermediate stress region and densification by ECAS under low pressure.

REFERENCES


Appendix

- $b$: Burgers vector (m)
- $d$: Grain size (m)
- $D_D$: Appropriate diffusion coefficient (m$^2$/s)
- $E_{eff}$: Effective elastic modulus for powder compact (Pa)
- $E_a$: Elastic modulus for fully dense bulk (Pa)
- $G_{eff}$: Effective shear modulus for powder compact (Pa)
- $G_h$: Shear modulus for fully dense bulk (Pa)
- $H$: Height of powder compact (m)
- $H_b$: Height of fully dense bulk (m)
- $k$: Boltzmann constant (J/mol·K)
- $n$: Stress exponent
- $\rho$: Grain size exponent
- $Q$: Activation energy for densification (J/mol)
- $Q_0$: Activation energy for threshold stress (J/mol)
- $R$: Gas constant (J/mol·K)
- $T$: Absolute temperature (K)
- $T$: Heating rate (K/s)
- $\rho$: Relative density of powder compact
- $\rho_0$: Initial relative density of powder compact
- $\rho$: Densification rate (/s)
- $\sigma$: Applied stress for powder compact (Pa)
- $\sigma_{eff}$: Effective stress for powder compact (Pa)
- $\sigma_0$: Threshold stress (Pa)