In Process Nanocrystalline Control Consolidation of the Amorphous ZrO₂-20 mol% Al₂O₃ Powder

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The instrumented pulse electric discharge consolidation method is used to provide a way of in process nanocrystalline control densification of the amorphous ZrO₂-20 mol% Al₂O₃ powder as prepared by rotating-arm reaction ball milling. The cylindrical compact height (h_f) of the amorphous ZrO₂-20 mol% Al₂O₃ powder is found to be a dominant process variable; at 1 mm, it leads to the densification prior to major crystallization after a high relative density of roughly 0.86 at 800 K, and significant decreases down to 1284 K in temperature necessary to obtain the full densification under 100 MPa. The rapid densification for amorphous and nanocrystalline supersaturated cubic ZrO₂-20 mol% Al₂O₃ is fairly well expressed by an Arrhenius-type equation of Newtonian viscous flow: $\eta_p = \eta_{p0} \exp(Q/kT)$ having greatly decreasing apparent activation energy Q from 300 to 72 kJ mol⁻¹ and process viscosity η_p at 1200 K with decreasing h_f from 14.6 to 1 mm. The Berkovich indentation testing permits us to derive a relatively low level of 4.4 GPa for the value of the yield stress at room temperature in the full-density nanocrystalline ZrO₂-20 mol% Al₂O₃ sample having the Vickers hardness number of approximately 800 DPN.
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1. Introduction

The nanocrystalline ceramics is one of the most promising materials to achieve the innovative mechanical property such as high-strain-rate superplasticity at low temperature and extremely high fracture toughness, when one can actually obtain the full densification combined with the nanocrystalline synthesis with the grain size less than a few ten nanometers. Therefore, the bulk nanocrystalline synthesis has been the subject of much attention in the field of nanoceramic processing. To the best of our knowledge, we are the first to find the solid state amorphization by mechanical alloying¹⁾ the oxide ceramics powder mixture, ZrO₂-20 mass% Al₂O₃, while there have been various amorphous powder production methods including the alkoxy method,²⁾ spray pyrolysis³⁾ and rapid quenching.⁴⁾ At the same time, we have successfully prepared the full-density product of the nanocrystal, as synthesized via crystallization, below 30 nm for the crystallite size by employing the spark pressure sintering, as we here use this term for the pulse electric discharge consolidation, of the amorphous powder. Alternatively, there has been build-up processing of bulky nanocrystal such as the high pressure condensation of nanoparticles synthesized via inert gas deposition.⁵⁾ However, thus-obtained nanocrystalline ceramic mostly consists of single element or molecule and is a porous and small mass product, so that one presently finds it difficult to exhibit outstanding mechanical properties inherent to the nanocrystal.

Our non-equilibrium solid state powder processing comprises of mechanical alloying and spark pressure sintering on the basis of the concepts of reaction milling⁶⁾ and intelligent sintering⁷⁾ respectively, and is expected to develop a variety of the bulk nanocrystalline synthesis of the ceramics analogous to the case of the alloy.⁸⁾ We here are going to develop a way of in process nanocrystalline control densi-

fication of the amorphous ZrO₂-20 mol% Al₂O₃ powder by varying the compact height in spark pressure sintering.

2. Experimental Procedures

The amorphous oxide ceramic powder was prepared by mechanical alloying (MA) the powder mixture, ZrO₂-20 mass% Al₂O₃ with the weight 4.9 N (0.5 kgr) using the rotating-arm reaction ball milling with temperature control.⁹⁾ The chemical analysis identifies the composition of (ZrO₂)₈₀(Al₂O₃)₂₀ with the external Fe element of a few percent for the amorphous particle. The crystallization of the amorphous ZrO₂-20 mol% Al₂O₃ powder was examined in argon atmosphere by a differential scanning calorimeter (DSC) using the heating rate of 0.5 K s⁻¹.

The amorphous ZrO₂-20 mol% Al₂O₃ powder was packed into the graphite die with an inner diameter of 10 mm and an outer diameter of 45 mm, and then consolidated at various compact heights under an applied pressure (σ) of 100 MPa using the spark pressure sintering apparatus equipped with the feeding of rectangular pulse and direct current (dc) superimposing alternative current. The graphite die temperature is measured via the thermocouple and corrected by the temperature profile along a radius of the die to estimate the temperature at the surface of the compact. The displacement (Z) measures a linear shrinkage of the compact in real time by correcting the thermal expansion of the graphite plungers in heating. The apparent relative density (D_a) of the powder compact is deduced from a relation of $D_a = h_f / (Z_f - Z + h_f)$ where h_f and Z_f are the height and displacement at full-density.

The porosity of the consolidated product is obtained by the lineal analysis on the polished surface of a half-cut mid-section as observed by optical microscopy. The bulky sample is characterized by X-ray diffraction using CuK α ; its average crystallite size is calculated by X-ray peak broadening at the

Fig. 1 The DSC curves for the amorphous ZrO_2 -20 mol% Al_2O_3 powder as synthesized at the milling time of 6.7×10^5 s by the rotating-arm reaction ball milling. This figure includes the case of the multilayered powder obtained at the milling time of 1×10^4 s.

half of the maximum using the Scherer formula. The Berkovich indentation with a three-sided pyramidal indenter is carried out for the fully dense ZrO_2 -20 mol% Al_2O_3 sample under various applied loads up to 2 N at a loading rate ranging from 7.2 to 1.4 $\text{mN}\cdot\text{s}^{-1}$ in the depth-sensing indentation system (Shimadzu DUE-201S).

3. Results

3.1 Solid state amorphous powder synthesis

Figure 1 shows the thermal stability of the amorphous ZrO_2 -20 mol% Al_2O_3 powder prepared at 6.7×10^5 s by rotating-arm reaction ball milling in a differential scanning calorimeter using the heating rate of 0.5 K s^{-1} . This figure includes the multilayered (ML) ZrO_2 -20 mass% Al_2O_3 powder as synthesized at the milling time of 1×10^4 s just prior to the solid state reaction for the amorphous synthesis. The baseline is obtained from the DSC curve of the second run. For the amorphous ZrO_2 -20 mol% Al_2O_3 powder, the first exothermic DSC peak is due to the crystallization to the supersaturated cubic having the onset temperature (T_x) of 850 K and the completion temperature (T_{af}) of 1073 K, and an endothermic peak seems to appear just before crystallization; its onset temperature of 800 K here is coupled with the glass transition temperature (T_g). With further increasing temperature, the secondary sharp exothermic peak appears as is characterized by peak temperature (T_{p2}), and is seen to superimpose a broad exothermic peak that has the nearly same temperature's range from 1100 to 1450 K as that of heat generation during the solid state reaction of ML ZrO_2 -20 mass% Al_2O_3 powder to single tetragonal phase. Note that a broad temperature's range of $T_{af} < T < T_{p2}$ in supersaturated cubic is appropriate for a model experiment of rapid densification during heating of nanocrystal below approximately 10 nm in crystallite size.

Besides, the present result on crystallization of amorphous ZrO_2 -20 mol% Al_2O_3 is similar to that of the alkoxy

Fig. 2 The temperature, displacement and current density under an applied stress of 100 MPa as a function of time. Measurement is taken during spark pressure sintering of the amorphous ZrO_2 -20 mol% Al_2O_3 powder using a constant dc of 600 A after the feeding of rectangular pulse.

method.²⁾ However, the amorphous ceramic powder synthesized by the conventional methods has the inhomogeneity of amorphous structure and the mixing of the impurities that may affect on the crystallization and metastable transformation. Now, we can say that the attrition milled amorphous ZrO_2 -20 mol% Al_2O_3 powder shows clear processes of crystallization and non-equilibrium phase transformation due to the homogeneous amorphous structure obtained by kinetically process control, while as milled powder used in this study may still retain the unreacted powder having the volume fraction of several percent as estimated from the enthalpy ratio.

3.2 Consolidation process control by varying compact height

Figure 2 shows the temperature at the surface of the compact, the plunger displacement and direct current versus processing time with the initial heating rate of 5 K s^{-1} , when the pressure of 100 MPa is applied in the case of $h_f = 9.8$ mm. This measurement was taken during the spark pressure sintering of the attrition milled amorphous ZrO_2 -20 mol% Al_2O_3 powder under dc of 600 A, following the feed of the rectangular pulse current of 800 A with 30 s. The characteristic temperatures, T_g , T_{af} and T_{p2} as obtained at the heating rate of 0.5 s^{-1} in DSC are depicted in the figure, but last two are actually lower than those of 5 K s^{-1} in the case of the spark pressure sintering. The amorphous ZrO_2 -20 mol% Al_2O_3 powder compact shows a definite densification from roughly 800 K up to near T_{af} , following a small shrinkage below T_g , and then a rapid densification between T_{af} and T_{p2} in nanocrystalline cubic ZrO_2 -20 mol% Al_2O_3 . Finally, the tetragonal and monoclinic ZrO_2 -20 mol% Al_2O_3 compact shows a large monotonic displacement at the constant temperature of 1337 K.

Fig. 3 The apparent relative density versus temperature and time in the spark pressure sintering of the amorphous $\text{ZrO}_2\text{-20mol\%Al}_2\text{O}_3$ powder compacts at various heights.

Figure 3 shows the apparent relative density of the amorphous $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ powder compact in a range of h_f from 1 to 14.6 mm by employing the spark pressure sintering under the pressure of 100 MPa. In the case of the lowest height of 1 mm, the amorphous $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ powder compact shows a definite shrinkage prior to major crystallization up to T_{af} , following a deviation at T_g from a baseline expressing thermal expansion, and then obtains the full densification at 1284 K in heating. Moreover, it is noteworthy to describe that the amorphous $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ powder compact with $h_f = 1.7$ and 1 mm have the considerably high relative density of approximately 0.86 at the maximum below T_g . With increasing height from $h_f = 2.3$ to 14.6 mm, the temperature necessary for a rapid densification in nanocrystalline cubic $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ increases, and consequently resulting in an increase in densification by monotonic and tetragonal phases. Figure 4 shows the relative density versus consolidation temperature for the $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ sample with various heights under the applied pressure of 100 MPa. The temperature (T_f) necessary to obtain the full densification shows a great decrease from 1456 to 1284 K with decreasing height from 14.6 to 1 mm.

3.3 Bulk nanocrystalline synthesis via crystallization

Figure 5 shows X-ray diffraction patterns for $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ products consolidated at various temperatures for the holding time of 600 s and as attrition milled amorphous powder. The bulky nanocrystalline $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ sample shows a single cubic phase of extended solution below 1150 K, and then a monoclinic phase above 1205 K that is the onset temperature of secondary sharp exothermic DSC peak of the amorphous $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ powder. The X-ray peak of tetragonal $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ appears at the consolidation temperature of 1250 K within the accuracy of this experiment. This result indicates that cubic $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$, which is the stable phase at high temperatures, undergoes the metastable transformation to monoclinic with or without tetragonal phase. In the former case, the tetragonal phase comes from unreacted

Fig. 4 The relative density as a function of temperature for consolidated $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ compacts with different heights under an applied pressure of 100 MPa.

Fig. 5 X-ray diffraction patterns for consolidated $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$, as synthesized via crystallization at various temperatures. This figure includes the case of the amorphous $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ powder prepared by rotating-arm reaction ball milling.

ML involved in as milled amorphous $\text{ZrO}_2\text{-20 mol\%Al}_2\text{O}_3$ powder. The further study will be needed to draw the conclusion on the phase transition that is still the subject in controversy even for commercial zirconia ceramics.¹⁰⁾

Figure 6 shows the average crystallite size, as obtained

Fig. 6 The average crystallite size as deduced from 111 peaks of cubic, tetragonal and monoclinic phases as a function of temperature for the ZrO₂-20 mol%Al₂O₃ sample consolidated under 100 MPa.

from X-ray peak 111, of the cubic, tetragonal and monoclinic phases versus the temperature for the consolidated ZrO₂-20 mol%Al₂O₃ sample. The cubic crystallite size is 11 nm at the minimum below approximately 1100 K, following an increase with increasing temperature from 1150 K. The crystallite sizes of monoclinic and tetragonal ZrO₂-20 mol%Al₂O₃ are 12 and 11 nm at the minimum respectively, and retain a considerable low value of approximately 20 nm even at the highest temperature of this experiment. The control of consolidation temperature is effective to a variety of nanocrystalline synthesis in the attrition milled amorphous ZrO₂-20 mol%Al₂O₃ powder.

3.4 Instrumented dynamic indentation test

Figure 7 shows the load-indentation depth curve for the fully dense ZrO₂-20 mol%Al₂O₃ sample synthesized at 1360 K using the loading rate of 1.4 mN·s⁻¹ in dynamic Berkovich hardness testing. Figure 8 is the optical micrograph of the polished surface of the half-cut mid-section of the fully dense ZrO₂-20 mol%Al₂O₃ product with the indent. The tetragonal and monoclinic nanocrystalline ZrO₂-20 mol%Al₂O₃ shows a smooth loading curve up to the applied load of 2 N without any fracturing and crack formation around the corners of triangular pyramidal indentation as shown in Fig. 8. The dynamical indent shows the depth (d_1) at loading, being equal to the depth (d_2) after the holding for 60 s in the case of the lowest loading rate, and leaves the plastic strain of 0.4 after unloading. The d_1 is found to decrease with increasing loading rate up to 7.2 mN·s⁻¹ and then gradually approaches to d_2 under the applied load, indicating the presence of a loading-rate dependence. Whereas, the Vickers hardness number is approximately 800 GPN with tetragonal and monoclinic crystallite size of 13 and 17 nm for the consolidated ZrO₂-20 mol%Al₂O₃ sample.

4. Discussion

4.1 Process model for electric filed assisted consolidation

The sintering strain rate ($\dot{\epsilon}_s$) is defined by

Fig. 7 The load versus indent depth curve for the fully dense nanocrystalline powder compact, consolidated at 1360 K, of monoclinic and tetragonal ZrO₂-20 mol%Al₂O₃ in dynamic Berkovich indentation testing at the loading rate of 1.4 mN·s⁻¹.

Fig. 8 The optical micrograph of the full-density nanocrystalline ZrO₂-20 mol%Al₂O₃ powder compact with Berkovich indent.

$$\dot{\epsilon}_s = (1/D)(dD/dt) \quad (1)$$

where D is the relative density of the powder compact. The densification rate, (dD/dt) at the constant heating rate, (dT/dt) is given by a relation of $dD/dt = (dD/dT)(dT/dt)$.¹¹⁾ When the densification occurs during Newtonian viscous flow, the sintering strain rate is written by

Fig. 9 The process viscosity under constant dc against the reciprocal temperature for the spark pressure consolidation of the amorphous ZrO_2 -20 mol% Al_2O_3 powder with various final compact heights.

$$\dot{\epsilon}_s = \sigma_{\text{eff}}/3\eta_p \quad (2)$$

where η_p is the process viscosity and σ_{eff} is the effective stress applied to the contacted area between sintering particles. The effective stress for a lower density compact with $0.64 < D < 0.9$ is given by a relation of $\sigma_{\text{eff}} = \sigma(1 - D_0)/D^2(D - D_0)$ where D_0 is the relative density at the onset of densification. Then, the dependence of the process viscosity on temperature here is given by the Arrhenius-type equation of Newtonian viscous flow:

$$\eta_p = \eta_{p0} \exp(Q/kT) \quad (3a)$$

$$\ln \eta_p = \ln \eta_{p0} + Q/kT \quad (3b)$$

where η_{p0} is the viscosity coefficient and Q is the apparent activation energy.

Figure 9 shows the process viscosity under the applied pressure of 100 MPa as a function of reciprocal temperature for consolidated ZrO_2 -20 mol% Al_2O_3 compacts having four different heights. The η_p is obtained by the densification at the initial heating rate of 5 K s^{-1} at the maximum, correcting thermal expansion of the sample, as shown in Fig. 3. In the case of $h_f = 1 \text{ mm}$, the process viscosity for the amorphous ZrO_2 -20 mol% Al_2O_3 compact is below $10^{11} \text{ Pa}\cdot\text{s}$ that is recognized as the value of T_g ,⁽¹²⁾ and shows a good linearity, permitting the derivation of the value of 72 kJ mol^{-1} for the apparent activation energy; so these indicating the densification during Newtonian viscous flow in the supercooled liquid. On the other hand, the densification of nanocrystalline cubic ZrO_2 -20 mol% Al_2O_3 compact, being plotted by eq. (3b), is characterized not by the single straight line⁽¹⁾ compensating the effect of heating rates on the densification

Fig. 10 The applied load as a function of the depth of the indenter hold for 60 s under various applied loads for the nanocrystalline ZrO_2 -20 mol% Al_2O_3 sample consolidated at 1376 K. The prediction from the finite element method of an elastic perfectly-plastic solid is displayed by the solid curved line.

curve, but by decreases in viscosity coefficient at 1200 K and the slope with decreasing h_f from 14.6 to 1.7 mm. The former is accounted for by an increase in amorphous volume accompanied by a decreasing crystallite size⁽⁸⁾ in nanocrystalline cubic ZrO_2 -20 mol% Al_2O_3 . The latter causes a decrease from 160 to 300 kJ mol^{-1} in apparent activation energy, manifesting an effect of electric field (E_c), which is varied by the height of sample squeezed between both plungers, on the densification during viscous flow of nanocrystalline cubic according to a relationship of $\eta_p = \eta_{p0} \exp\{Q(E_c)/kT\}$.

With these information, the electric field is thought to be another dominant process variable in spark pressure sintering for the occurrence of a low temperature densification, which ought to occur under an extremely high pressure, in amorphous and/or nanocrystalline ZrO_2 -20 mol% Al_2O_3 . While, a spatial distribution of high quasi-isostatic pressure inside the thin disk should be considered for a further discussion of the process control methodology and micro-mechanism involved.

4.2 Plastic deformation at ambient temperature

Let us evaluate the yield stress (σ_y) at the room temperature in the full-density nanocrystalline ZrO_2 -20 mol% Al_2O_3 sample. With the numerical analysis of the finite element method, Larsson and Giannakopoulos present the relationship⁽¹³⁾ between load (P) and indentation depth (d) in Berkovich indentation:

$$P = 1.273(\tan 24.7^\circ)^{-2} \sigma_y (1 + \sigma_{\text{fow}}/\sigma_y) \times (1 + \ln E \tan 24.7^\circ / 3\sigma_y) d \quad (4)$$

where σ_{fow} is the flow stress, E is Young's modulus. Figure 10 shows the indent depth (d_2) after holding for 60 s under various applied loads for nanocrystalline monoclinic and tetragonal ZrO_2 -20 mol% Al_2O_3 as synthesized at 1376 K. The adoption of d_2 is presently reasonable considering some uncertainty of indentation properties such as loading rate dependence. When assuming the non-strain hardening in a nanocrystalline solid,⁽¹⁴⁾ the prediction of the

eq. (4), as depicted as the solid line, has been done to get a good fit for the experimental result, having the proper value ($0.8E_c$) where E_c is the value of 138 GPa for Young's modulus in the literature. Now, we have a level of 4.4 GPa for the value of the yield stress for consolidated nanocrystalline ZrO_2 -20 mol% Al_2O_3 with the crystallite size of 13 and 17 nm. This relatively small value is acceptable for the consolidated ZrO_2 -20 mol% Al_2O_3 sample having the level of 800 DPN for the Vickers hardness number. The yield stress will be an important material parameter for the better understanding and formulation of unique strengthening in nanocrystalline ceramics.

5. Conclusions

For the attrition milled amorphous ZrO_2 -20 mol% Al_2O_3 powder compact, a decrease from 14.6 to 1 mm in compact height results in the rapid densification in supercooled liquid and nanocrystalline cubic as expressed by Arrhenius-type equation of Newtonian viscous flow with a decreasing activation energy from 300 to 72 kJ mol⁻¹. A great decrease to 1100 K in consolidation temperature makes it possible to synthesize a variety of bulky nanocrystalline ZrO_2 -20 mol% Al_2O_3 sample having a nearly threshold value of approximately 10, 11 and 12 nm for the crystallite size of cubic, monoclinic and tetragonal phases respectively. The

yield stress is derived at 4.4 GPa in Berkovich indentation testing under the lowest loading rate for the nanocrystalline ZrO_2 -20 mol% Al_2O_3 sample.

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