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Superplastic Deep Drawing of Tetragonal Zirconia Ceramics at 1160°C

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Abstract

Superplastic forming under biaxial tension of tetragonal zirconia (Y-TZP) is investigated by pushing a hemispherical punch (radius 6 mm) on Y-TZP which was placed on a ring with an inner diameter of 16·7 mm. Dense Y-TZP samples with a grain diameter of 125 nm could be elongated to a dome height of at least 8 mm at a temperature as low as 1160°C. Such elongations could not be achieved at this very low temperature when the ceramic had a grain diameter of 250 nm. At a grain size of 250 nm differences in deformation behaviour were observed for different types of Y-TZP powders. This is explained by the fact that at higher cavity concentration in the sintered compact the sample deforms at lower forces but fractures at lower elongations.

1 Introduction

Hot forming of ceramics is strongly related to the occurrence of superplasticity, which is defined as its ability to undergo large elongations during tensile deformation.[1] Yttria doped tetragonal zirconia polycrystalline (Y-TZP) materials are the most investigated and most promising superplastic ceramics. Analysis of superplasticity in ceramics is either performed in compression[2–4] or in tension.[5–7] In both cases the mechanism for superplasticity is identical and is usually attributed to some kind of grain-boundary process. The grain-boundary morphology after these deformation tests differs however. Under compression the grain-boundary morphology is improved (more ‘dense’) and residual flaws are eliminated provided appropriate compression conditions are chosen.[8,9] In tension nucleation and growth of internal cavities often occurs.[5,6]

It is generally accepted that superplastic deformation rates can be enhanced by reducing the grain size. Recently it was found that for compressing single-phase Y-TZP at 1200°C the initial strain rate increases by a factor of 4 if the grain size decreases from 200 to 100 nm.[8] From these results it was concluded that real superplastic deformation (strain rate $> 10^{-4}\ \mathrm{s}^{-1}$) is possible at relatively low temperatures (1200°C) and a relatively low stress of 50 MPa if the grain size is in the nanoscale range (100 nm), while no second phases (like CuO) are present.

The utility of superplastic ceramics in industrial forming (e.g. deep drawing) necessitates ceramics which sustain both tensile and compressive strains.[10] For that reason results on stretching (or deep drawing) of ceramics under biaxial tension are important. In this paper deep drawing results are described on Y-TZP with varying grain sizes (250 and 125 nm). Also the influence of experimental conditions (punch displacement rate and operation temperature) on deep drawing are examined. Two types of powders are used, with different agglomerate morphology. This morphology influences the defect(cavity)-size and concentration in the dense ceramic and it is shown in this paper that it therefore also influences deep-drawing behaviour.

2 Experimental Procedure

The Y-TZP ceramic materials were made from two different types of powder. One powder was a commercially available TZ3Y powder (Tosoh Co., Japan), containing 5·8 at% Y. This powder typically has a BET surface area of $20\ \mathrm{m}^{-2}\ \mathrm{g}^{-1}$, while

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the agglomerates are spherical (granulated).[11] A primary crystallite size of 34 nm was calculated from X-ray line broadening data.[11] The second zirconia powder with 5 at% Y was prepared by precipitation of a metal chloride solution in an excess of ammonia. The hydroxide gel is thoroughly washed to remove chlorine ions and free water and afterwards calcined at 500°C to obtain a nanocrystalline (crystallite size 8 nm) weakly, irregularly agglomerated powder (specific surface area $120\,m^{-2}\ g^{-1}$).[11] From both powders green compacts were made by first uniaxially pressing at 44 MPa in a die (diameter 48 mm) and subsequent isostatically pressing at 400 MPa.

Deformation by means of deep drawing was performed on 3 different Y-TZP materials, coded A, B and C for respectively a TZ3Y Tosoh powder compact sintered at 1300°C and 2 compacts of 'chloride' powders sintered at 1300°C and 1070°C. More details of the materials used for deformation are given in Table 1. Grain sizes were determined from SEM pictures of polished and thermally etched samples using the linear intercept method and the correction factor as given by Mendelson.[12]

Deep drawing tests were performed on several discs of each material. All discs were machined to a diameter of 25 mm and a thickness of 1 mm. Prior to the tests the samples were polished on one side (diamond paste 0·3 μm) and annealed at 1000°C (heating/cooling 2°C min^{-1}). The discs were placed on a cylindrical SiC ring with an inner diameter of 16·7 mm. A hemispherical punch with radius of 6 mm was pushed on the non-polished side of the ceramic using two different velocities (0·6 and 0·3 mm min^{-1}) while the force was monitored. The tests were performed in air at 1150, 1160 and 1210°C using a screw-driven universal testing machine (Zwick 1478, FRG). The axial displacement was measured externally during all tests. Identical experimental conditions were used in Ref. 13.

3 Results

The results in Table 1 indicate that very fine-grained and dense Y-TZP with a grain size of 125 nm can be made, when starting with real nanocrystalline (chloride precipitation prepared) powders. By using the same consolidation and sintering procedure the Tosoh TZ3Y compact is only dense after sintering at 1300°C resulting in a grain size of 250 nm, as is also observed by Theunissen *et al.*[14] Using this set of samples the influence of starting powder and ceramic grain size on deformation behaviour can be analysed.

Table 1. Samples used for deformation tests by deep drawing

Code	*Atom % Y*	*Sinter temperature (°C)*[a]	*Sinter time (h)*	*Grain size (nm)*
A[b]	5·8	1300	3	250
B[c]	5	1300	3	250
C[c]	5	1070	10	125

[a] All samples have a relative density of 96–98%.
[b] Powder from Tosoh corporation.
[c] Powder prepared by precipitation.[11]

In Fig. 1 the displacement of the punch and the resulting force on the ceramic are given during deep drawing at 1210°C for materials which all have the same grain size (250 nm). Here the influence of punch velocity and the type of starting powder used are clearly visible. If higher displacement rates are used the chance of fracturing during deep drawing increases (compare e.g. B1 and B2; fracturing is indicated in the figure by an arrow downwards). At lower displacement rates the material can be stretched to a height of 8 mm without fracture and was interrupted (as indicated by *i* in Fig. 1). From Fig. 1 it is also clear that lower punch velocities require less force for identical displacements and that Tosoh ceramics require higher forces for the same displacement (compare e.g. A2 and B2). All these differences will be discussed in the next section.

In Fig. 2 a photograph is given of Tosoh samples A1 and A2. At low punch rates a dome without macrocracks is formed, while at higher rates fracture occurs. Fracture mainly origins at places of maximum displacement as was also observed by Wu and Chen.[15] In Fig. 3 three specimens of material B are shown after deformation. In this

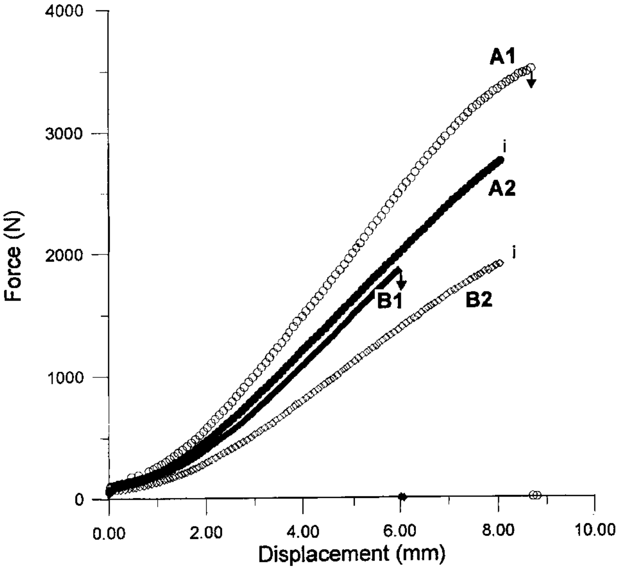

Fig. 1. Displacement versus applied force during deep drawing at 1210°C of several Y-TZP's with identical grain size (250 mm sample A and B; see Table 1). A1 and B1: displacement rate 0·6 mm min^{-1}; A2 and B2: displacement rate: 0·3 mm min^{-1}.

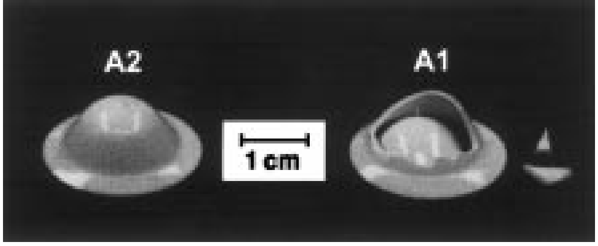

Fig. 2. Sample A2 (0·3 mm min^{-1}) and A1 (0·6 mm min^{-1}) after deformation tests as given for Fig. 1.

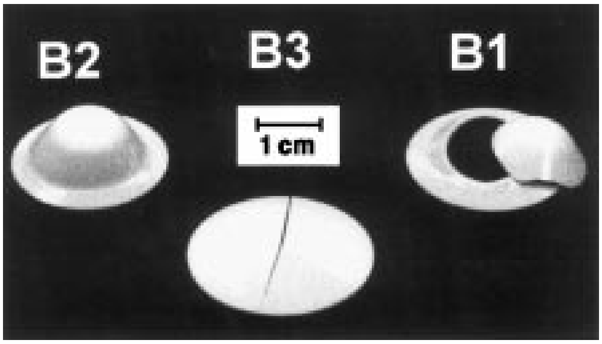

Fig. 3. Sample B ('chloride' gain size 250 nm) after deformation tests. B2: deformed at 1210°C with 0·3 mm min^{-1} (height: 8 mm); B3: deformed at 1150°C with 0·3 mm min^{-1} (almost no deformation); B1: deformed at 1210°C with 0·6 mm min^{-1} (height at fracture 6 mm)

figure B1 and B2 show the influence of punch rate, while sample B3 was deformed with the same rate (0·3 mm min^{-1}) as sample B1 but at a lower temperature (1150°C instead of 1210°C). Sample B3 fractured after deformation of only 1 mm. So for Y-TZP samples with a grain size of 250 nm deep drawing as described in this paper can not be performed at 1150°C.

In Fig. 4 it is shown that at a relatively high punch rate of 0·6 mm min^{-1} Y-TZP with a grain size of 125 nm (sample C1) could be deep-drawn at 1210°C to a height of 10 mm without fracture while the coarser-grained samples fracture after punch displacements of 6 and 8·5 mm (A1 and B1 respectively).

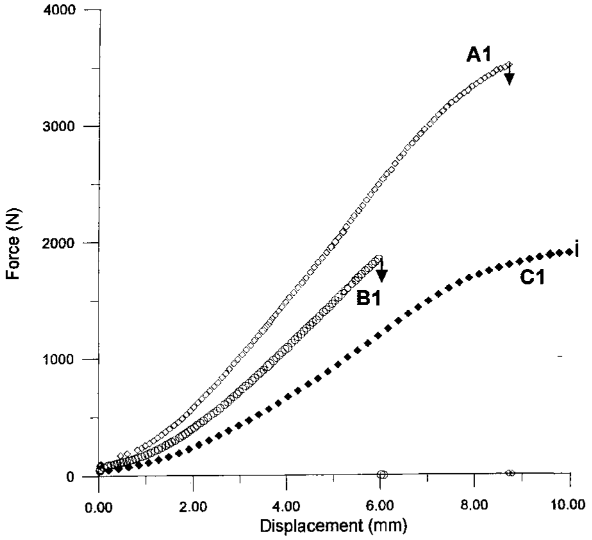

Fig. 4. Displacement versus applied force during deep drawing at 1210°C of several Y-TZP's with different grain sizes [250 and 125 nm (B and C)] and different starting powders (A and B); displacement rate 0·6 mm min^{-1}.

Forming of sample C under several experimental conditions is shown in Fig. 5. For Y-TZP with a grain size of 125 nm deep drawing is possible at a temperature as low as 1160°C (sample C3). The experimental conditions for this sample are almost identical to the one for the coarser grained sample B3 (Fig. 3) where almost no deformation was possible. At a higher punch rate (0·6 mm/min) the fine-grained sample C can still be elongated at 1150°C to a height of 4·3 mm before fracture (C2 in Fig. 5).

4 Discussion

4.1 Influence of grain size on deep-drawing

From the results given in this paper clearly a strong improvement in deep-drawing behaviour is visible if grain size is reduced. These results will now be discussed in terms of superplasticity. The grain-size effect on superplasticity is often observed in literature and can be explained by the fact that grain-boundary sliding or an interface reaction are the dominant deformation modes.[4,16,17] The strain rate ($\dot{\varepsilon}$) in high-temperature deformation is usually described by:[1]

$$\dot{\varepsilon} = \mathrm{A}\frac{\sigma^n}{d^p}\exp\left(-\frac{Q}{\mathrm{RT}}\right) \tag{1}$$

where A is a numerical constant, σ the flow stress and n its exponent, d the grain size with exponent p, Q the apparent activation energy and RT has its usual meaning. For dense zirconia with grain sizes of 300 nm or more, often an exponent $p = 1$ is observed,[1,18] while for Y-TZP with grain sizes in

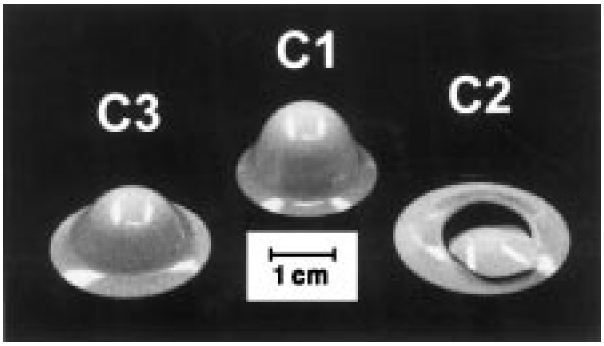

Fig. 5. Y-TZP samples with grain size of 125 mm after deformation tests; C3: deformed at 1160°C with 0·3 mm min^{-1} (height: 8 mm); Cl: deformed at 1210°C with 0·6 mm min^{-1} (height: 10 mm); C2: deformed at 1150°C with 0·6 mm min^{-1} (height at fracture 4·3 mm).

the range 100–200 nm an indication for $p = 2$ is given.[8] In other words: reducing the grain size still gives sufficient high strain rates at lower temperatures.[8] From this literature result it can be concluded that by decreasing the grain size to the nanoscale range the deep drawing ability for Y-TZP is still present at relatively low temperatures as is confirmed by the results from this study.

The possibility for deep drawing or bulging of Y-TZP at 1160°C without second phase additions, as reported in this paper, is to our knowledge unique. Very often in literature a deformation temperature of 1450–1550°C is used for tensile elongation experiments[5,7,12,17] or for biaxial gas-pressure deformation.[20] Wu and Chen[15] report superplastic bulging at 1150°C. In these experiments however CuO is added to Y-TZP as a second phase, which acts as a liquid grain-boundary phase during deformation,[15] while the experiments described in this paper concern single phase Y-TZP.

4.2 Deformation temperature and punch rate

It is demonstrated that the experimental conditions (temperature and punch rate) influence deformation. This influence can be explained in terms of cavity formation during tensile deformation. It is well established that superplastic deformation under tension of metals and ceramics is associated with the concurrent development of internal cavities.[5,6,18] In ceramics these cavities nucleate at grain boundaries and can become considerably larger than the average grain size with areas up to several square microns.[6,19,21] At a certain concentration and/or size the cavities are interlinking which is associated with the onset of tensile failure. Under a constant strain rate the degree of cavitation increases with a decrease in deformation temperature.[6] This is obvious and also visible from the results in Figs 3 and 5.

By increasing the punch rate the maximum elongation decreases while a higher force is necessary for obtaining the same displacement (compare e.g. A2 and A1 in Fig. 1). The relation between punch rate and force, necessary for a certain displacement, will now be discussed in terms of the phenomenological law as given in eqn (1). For sample A1 a force of 2500 N (F_1) is necessary for obtaining a displacement of 6 mm at a punch rate of 0·6 mm min^{-1} (v_1), while the same displacement is achieved at a punch rate of 0·3 mm min^{-1} by using a force of about 2000 N (F_2) on an identical surface area (v_2; sample A2 in Fig. 1). The ratio of the stresses applied on sample A1 and A2 is identical to the ratio of the forces (F_1/F_2). The ratio of strain rates is identical to the ratio of the punch rates (v_1/v_2). In this way a relation between the ratios of strain rates and stresses for samples with identical grain size can be written as follows:

$$\frac{v_1}{v_2} = \left(\frac{F_1}{F_2}\right)^n \qquad (2)$$

From this equation a stress exponent (n) of 3 is calculated, using the above mentioned data. This value was confirmed by comparing several force ratios at different displacements for the samples A1 and A2 as well as for the couple B1 and B2. It is difficult to calculate the stress on the samples under these experimental conditions but it is assumed that a maximum stress of 30 MPa is imposed on a sample when applying a load of 2500 N (which is the maximum load used; see Fig. 1) for forming a hemisphere with a radius of 6 mm. A stress exponent of 3 was also observed by Owen and Chokshi for Y-TZP at low stress while a transition stress was defined by these authors above which $n = 2$.[17] For Y-TZP having a grain size of 0·4 mm, this transition stress was 40 MPa and its value increases with decreasing grain size.[17] It is therefore assumed that the deep drawing experiments on samples with grain sizes $\leqslant 250$ nm as described in this paper are below the transition stress.

A stress exponent 3 for deforming Y-TZP at low stresses was also mentioned in Refs 6, 19 and 22–24. Owen and Chokshi suggested that $n = 3$ arises from an interface reaction controlled process for grain boundary sliding. Since grain boundary sliding is also the dominant strain contributing process when a stress exponent of 2 is found these authors suggest that the difference in stress exponent is attributed to a difference in impurity concentration at grain boundaries.[17] In compacts with identical overall impurity concentration the level of segregation of Y^{3+} and impurities to grain boundaries decreases with decreasing grain sizes because grain-boundary volume is increasing. This lower 'impurity' concentration at the grain boundaries will lead to a decrease in non-stoichiometry at the grain boundaries and therefore less defects are present. Defects have negative effect on grain boundary plasticity. By using this assumption Owen and Chokshi[17] argued that at small grain sizes, where almost no segregation is present, an increase in stress will lead to a stronger enhancement in strain rate than for larger grains with a larger segregation level. This discussion also implies that when a stress exponent of 3 is found the strain rate is less sensitive to impurities.

The punch rate dependence as mentioned in this paper (Fig. 1) can also qualitatively be explained by the phenomenon of cavity formation. Cavity growth during tensile deformation can either be a diffusion controlled or a plasticity controlled process.[6]

Diffusion of vacancies along the grain boundaries into cavities, which is an important mechanism in metals, plays little or no role in ceramics as indicated by Langdon and co-workers.[6,21] If cavities should grow by this diffusion mechanism then it is expected that the degree of cavitation increases with *decreasing* strain rate which is not observed. The lack of rounded or spherical cavities as found by Langdon and co-workers[6,21] is according to these authors also a strong evidence for cavity growth by means of another process than diffusion. It is expected that in ceramics some kind of a plasticity controlled cavity growth process occurs during tensile deformation.[6] In that case cavity growth is dependent upon the level of applied stress and the growth rate of cavities increases with increasing strain rate and/or decreasing temperature.[6,21] Because of the stronger cavity growth at higher strain rate also higher stresses are present in the ceramics.[21] This explains the higher forces necessary for the same displacement at higher punch rates.

4.3 Influence of powder morphology

The influence of starting powder on deep drawing is clearly visible from the results shown in Fig. 1. In order to obtain the same displacement under identical experimental conditions higher forces are necessary for the Tosoh ceramic (sample A) than for the 'chloride' ceramic (sample B). At a punch rate of 0·6 mm min^{-1} sample A can be deformed up to 8·6 mm, while sample B fractures after a displacement of 6 mm (A1 and B1 in Fig. 1). The deformation experiments as described in this paper can be analysed by a stress exponent $n = 3$ and therefore plasticity is likely to be independent on impurity level. As the influence of impurity concentration is ruled out the observed difference in deformability will be explained by the model of cavity concentration in the sintered compact and further cavity formation during deep drawing.

In a recent paper[25] the influence of powder morphology on compaction and sintering behaviour is discussed for the same powders, while using the same consolidation and sintering procedures as described in this paper. The Tosoh powder (A) consists of uniform spherical agglomerates, while the 'chloride' derived powder (B) has irregular shaped agglomerates.[11,25] This irregular agglomerates of 'B' result in improper die filling and therefore in defects in the green compact and flaws or cavities in the sintered product.[25] The Tosoh powder gives a better die filling, resulting in lower defect concentration and fewer and smaller cavities in the sintered compact.[25] A higher concentration of defects or cavities in the sintered compact can lead to an acceleration in creep rate.[4] So creep is easier if the ceramic contains more cavities prior to deformation as is observed for sample B ('chloride') if compared with A (Tosoh). However more and larger cavities prior to deformation results in cavity interlinking at lower force and/or displacement and therefore in easier fracturing (compare B1 and A1 in Fig. 1).

5 Conclusions

Biaxial deformation by deep drawing is investigated as a severe test for superplastic deformation of Y-TZP ceramics. Ceramics with a grain size of 125 nm can be deformed to a hat-shaped sample with a dome-height of 8 mm by deep drawing a disc at very low temperature (1160°C), while Y-TZP with a grain size of 250 nm needs higher deformation temperatures. In all cases no second phase was present, which is often used in literature as a method for improving plasticity or decreasing deformation temperatures.

In general, samples fracture at lower displacements when the temperature is lower and/or the punch rate used for deformation is higher. This dependence can be explained by the phenomenon that during deep drawing, cavities are more easily formed at lower temperature or higher displacement rates and consequently a faster interlinkage of cavities occurs to a critical size for fracture. It is expected that a plasticity controlled cavity growth process takes place during tensile deformation of these ceramics.

The morphology of the starting powder also influences deformation. If compared with spray dried spherical agglomerated powders, a powder with irregularly-shaped agglomerates results in more defects in the green compact and more and larger flaws or cavities in the sintered product. This higher cavity concentration in the non-deformed ceramic leads to a larger creep rate at identical force but also fracturing of the ceramic at lower force and elongation occurs.

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