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Effect of powder treatment on injection moulded zirconia ceramics

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Abstract

Agglomerated fine zirconia powder was exposed to dry and wet ball milling and to wet mixing. The subject of study was the effect of powder treatment on the disintegration of agglomerated particles, on the rheological properties of thermoplastic ceramic mixtures, and on the properties of sintered yttria-stabilized tetragonal zirconia polytrystalline ceramics (Y-TZP). Test specimens in the shape of bars and discs were produced by injection moulding of ceramic mixtures containing 52.5 and 49 vol% of powder. The powder treatment was found to yield improved rheological properties of ceramic mixtures and improved mechanical properties of sintered specimens in the case of 52.5 vol% of powder in the ceramic mixture. However, the same or even better mechanical properties of sintered components were found when the loading of ceramic mixture was reduced to 49 vol% of powder and non-treated powder was used. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Defects; Injection moulding; Mechanical properties; Microstructure-final; Milling; ZrO_2

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystalline ceramics (Y-TZP) attracts considerable attention mainly because of its excellent mechanical properties. In order to obtain optimum properties very fine and extremely pure powder with narrow particle size distribution should be used for the preparation of ceramic components. Employing such powders for injection moulding of ceramic components presents a number of problems not only as regards binder removal[1] but also the preparation of a homogeneous ceramic mixture of appropriate rheological properties.[2] Even with very intensive mixing of the ceramic mixture not all the agglomerates present will eventually be disintegrated.[3] The presence of agglomerated particles can affect the rheological behaviour of ceramic mixtures[4] and consequently also the quality of injection moulded components. It has also been shown that agglomerates present in fine powders markedly affect the sintering process[5] and impair the properties of sintered ceramics.[6] The treatment of agglomerated fine powders prior to the production of ceramic suspension for injection moulding is thus a possible means of obtaining a homogeneous ceramic mixture and, subsequently, a uniform and compact structure of the sintered component. The particles appearing after the disintegration of agglomerates should be capable of remaining in dispersed state and not forming new agglomerates. This can be achieved by repulsive interaction of the layers of dispersive substance adsorbed on the surface of ceramic particles.[7] Stearic acid is often used with oxidic ceramic particles as a dispersive surfactant acting on the principle of steric stabilization.[8] Apart from being a dispersive substance, stearic acid acts also as a wetting agent reducing the viscosity of the ceramic mixture.[8] Substances with a longer chain than that of stearic acid are considered more effective in steric stabilization due to the larger thickness of the layer with grafted molecules of the dispersant.[9] For the required results to be obtained, however, the proportion of these substances in the binder must be greater than in the case of stearic acid.[9]

The objective of the present work was to compare various methods of treating agglomerated fine powder and applying stearic acid, and to evaluate the effect of these treatments on the properties of Y-TZP ceramics produced by injection moulding.

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2. Experimental

2.1. Materials

For the preparation of injection moulded specimens, yttria-stabilized tetragonal zirconia powder TZ-3YS (Tosoh Corp., Japan) was used, which contained 5.2 wt% of Y_2O_3. According to the manufacturer the size of crystallites was 36 nm and the specific surface was 6.4 m^2/g. The ceramic suspension was formed using a binder containing type Elvax 250 ethylene-vinyl acetate copolymer (EVA) (Du Pont de Nemours, USA), type 52/54 paraffin wax (Koramo, CR) and a dispersant. Used as dispersant and surfactant was type 1.00671 stearic acid (Merck, Germany). Xylene (Lachema, CR) was used as the solvent for stearic acid and also as the liquid medium for wet milling and mixing.

2.2. Preparation of specimens

Prior to being mixed with the binder, zirconia was dried at 120°C for 90 min and, when necessary, treated together with stearic acid. The composition of the ceramic mixtures and the method of powder treatment are given in Table 1. Dry milling was performed for 24 h in a ball mill with rubber lining and Al_2O_3 milling balls. Wet milling was performed for 24 h in a planetary mill with zirconia ceramic vessels and Al_2O_3 milling balls. The mass ratio of xylene to zirconia powder was 3:5. The powder was mixed in xylene (the mass ratio of xylene to powder was 2.5:1) in the absence of milling bodies at a temperature of 100 to 120°C under vigorous stirring for a period of 2 h. Subsequent to wet milling or mixing the xylene was evaporated and the powder dried at 120°C. Ceramic mixtures were prepared with two different volumes of ceramic powder in the mixture, namely 52.5 vol% (mixtures marked 1) and 49 vol% (mixtures marked 2). The ceramic mixtures were kneaded in a two-blade kneader (HKD 0.6T, IKA Labortechnik, Germany) at a temperature of 110 to 120°C for a period of 1.5 h. Test specimens were prepared on an injection moulding machine (Allrounder 220M, Arburg, Germany) in the shape of discs (dia. 42–2.1 mm) and bars (3.5×4.65–60 mm). The temperature of the injection barrel was 160–160–155–150–140°C (nozzle to feed). The rate of injection was 15 $cm^3\ s^{-1}$ and hold pressure was 60 MPa. Binder removal took place in nitrogen atmosphere at a heating rate of 10°C h^{-1} up to a temperature of 500°C and after that at a heating rate of 120°C h^{-1} up to 800°C. During binder removal the discs were embedded in activated carbon ($d_{50} = 2.8$ μm) while the bars were freely suspended during extraction. High-temperature sintering took place in a superkanthal furnace with air atmosphere at a temperature of 1500°C for a period of 2 h. The rate of heating to the sintering temperature was 100°C h^{-1}.

Table 1
Composition of ceramic mixtures and powder treatment methods

Mixture	ZRO_2 (wt%)	EVA (wt%)	Paraffin wax (wt%)	Stearic acid (wt%)	Powder treatment
S1	87.8	6	4	2.2	Without treatment
X1	87.8	6	4	2.2	Wet mixing
DM1	87.8	6	4	2.2	Dry ball milling
WM1	87.8	6	4	2.2	Wet ball milling
S2	86.2	6.8	4.5	2.5	Without treatment
X2	86.2	6.8	4.5	2.5	Wet mixing

2.3. Evaluation methods

The particle size distribution was established on a laser diffraction analyzer (LA-500, Horiba, Japan). The shape of ceramic particles and the microstructure of ceramic specimens were examined with the aid of scanning electron microscopy (JXA-840, Jeol, Japan). The rheological behaviour of ceramic mixtures was investigated on a capillary rheometer (Galaxy V, Kayeness, USA) with a nozzle of 1 mm in diameter and 30 mm in length. Measuring was performed in the range of shear rates from 10^2 to $10^3\ s^{-1}$ at temperatures from 110 to 150°C. The shear rate values were corrected to the non-Newtonian behaviour of mixtures by means of the Weissenberg–Rabinowitsch method.[10] The density in sintered components was established from disc dimensions by calculation. The size of grains in ceramic specimens was determined as the average grain size established from the micrograph of thermally etched microstructure using the intercept procedure and multiplied by a factor of 1.62.[11] The mechanical properties of sintered components were established on a universal test gear (Z020, Zwick, Germany). Flexural strength was established on bars of 4×3 mm in cross-section in four-point arrangement according to the European Standard EN 843-1 while biaxial flexural strength was established on the discs by the ring-on-ring method according to ISO 13356. The specimens were tested as fired, without machining. Statistically significant differences of individual sets of strength values were exposed to the nonparametric two-sample Wilcoxon test at a significance level of $\alpha = 0.05$. The Weibull graphs were plotted with a probability estimate of $P = (i\text{-}0.5)/n$, where i is the order of specimens arranged by ascending strength, and n is the total number of specimens. The Weibull modulus was calculated using the maximum likelihood method in keeping with the European Prestandard ENV 843-5.

3. Results

3.1. Effect of powder treatment on particle size distribution

The nature of the powder used can be seen from Fig. 1. The powder was formed by primary particles of 0.1 to

0.3 μm in size. These particles formed compact aggregates of up to 1 μm in size and they in turn formed more porous agglomerates of up to 50 μm in size. Large agglomerates were disintegrated by milling or mixing into primary particles and hard aggregates. Only in the case of the powder treated by dry milling agglomerates of up to 25 μm were also found in a micrograph of the powder (see Fig. 2). Fig. 3 gives a graph of particle size distribution of untreated and treated powders. The mean size of particles ranged from 0.45 to 0.56 μm. The highest value of the mean particle size was established for untreated powder, the lowest for dry-milled powder. For no powder did the largest particles exceed 2 μm in size.

3.2. Rheology of ceramic mixtures

All the ceramic mixtures displayed pseudoplastic behaviour over the whole range of temperatures examined. The dependence of shear stress on shear rate was described by the power law. The exponent of power law, *n*, for individual types of ceramic mixture and temperature are given in Table 2. The lowest values (0.44–0.46) were established for the mixture with dry-milled powder, the values for the other ceramic mixtures ranged between 0.51 and 0.65. Fig. 4 gives the dependence of viscosity on shear rate for the ceramic mixtures under study at the temperature of injection (140°C). By their viscosity the ceramic mixtures could be divided into two groups. The mixtures with 49 vol% of ceramic powder were of lower viscosity, those with 52.5 vol% of ceramic powder were of higher viscosity. An exception to this was mixture DM1, prepared from dry-milled powder. The viscosity of this mixture with 52.5 vol% of ceramic powder was lower than that of comparable mixtures and it was close to the viscosity of mixtures with a lower powder volume portion. At temperatures of 110 and 120°C this mixture displayed the lowest viscosity of the mixtures investigated. The temperature dependence of viscosity of the ceramic mixtures at a shear rate of 200 s^{-1} is shown in Fig. 5. The activation energies of viscous flow were calculated by the Andrade equation[12] and they are given in Table 2. The lowest activation energy, 14.2 kJ mol^{-1}, was established for mixture DM1

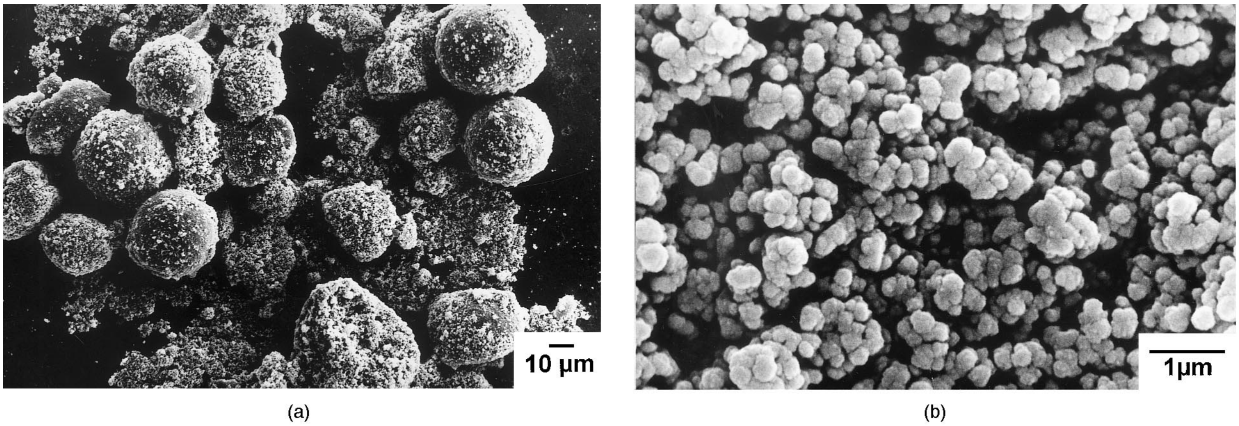

Fig. 1. SEM micrographs of the untreated zirconia powder showing (a) large agglomerates and (b) microstructure within the agglomerates.

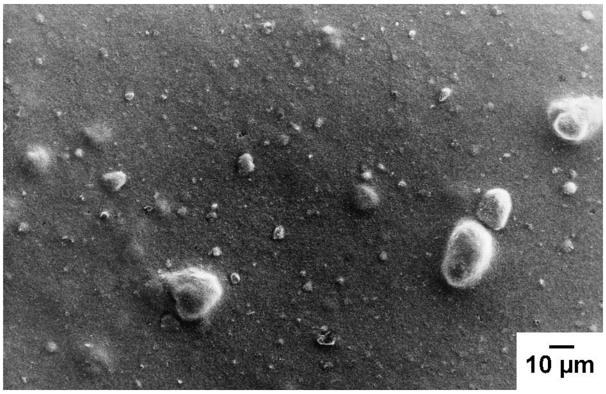

Fig. 2. SEM micrograph of the dry ball milled zirconia powder.

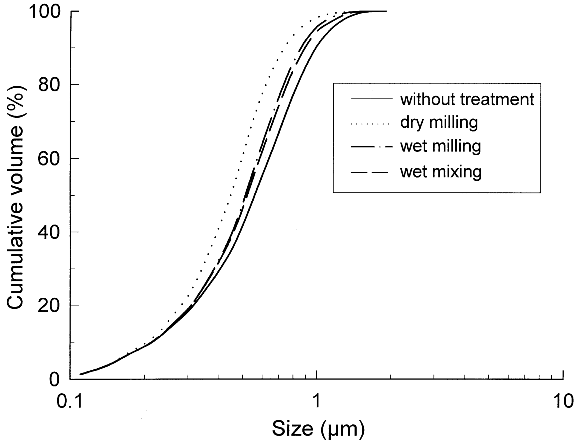

Fig. 3. Particle size distribution of untreated and treated zirconia powders.

(dry-milled powder, powder content in the mixture 52.5 vol%), the highest, 28.7 kJ mol^{-1}, for mixture S1 (untreated powder, powder content in the mixture 52.5 vol%).

3.3. Properties of sintered specimens

The shrinkage of sintered specimens was established for the thickness and diameter of the disc and for both sides of the bar cross-section, and it is given in Table 3.

Table 2
Activation energy of viscous flow (E_η) at shear rate 200 s^{-1} and power law exponent (n) of ceramic mixtures

Mixture	E_η (kJ mol^{-1})	n(–)				
		110°C	120°C	125°C	140°C	150°C
S1	28.7	0.57	0.55	0.57	0.54	0.60
X1	24.1	0.65	0.65	0.63	0.59	0.55
DM1	14.2	0.46	0.45	0.46	0.44	0.45
WM1	26.4	0.63	0.57	0.60	0.61	0.58
S2	24.1	0.56	0.58	0.57	0.56	0.51
X2	24.0	0.59	0.57	0.55	0.56	0.56

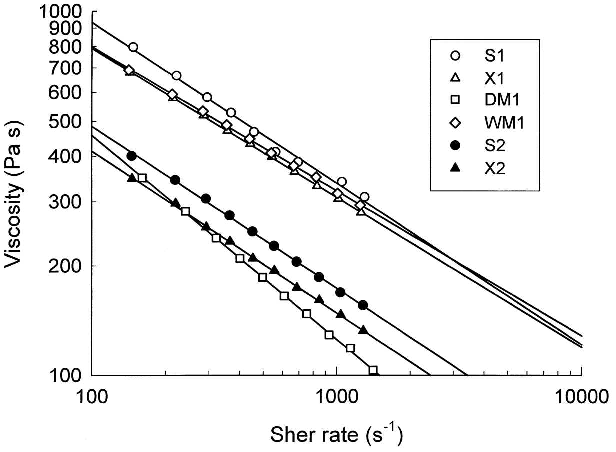

Fig. 4. Rheological behaviour of zirconia mixtures at 140°C.

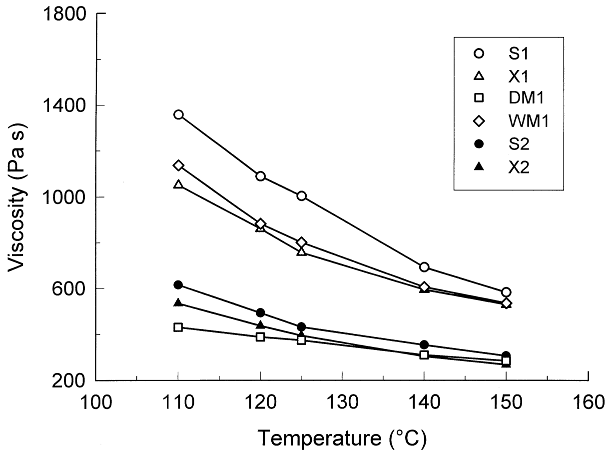

Fig. 5. The temperature dependence of viscosity of zirconia mixtures.

The shrinkage of specimens prepared from mixtures S1, X1 and WM1 (powder content 52.5 vol%) was similar (~19.5%) for both types of shape and for both dimensions measured. The specimens prepared from mixtures S2 and X2 (powder content 49 vol%) displayed a higher degree of shrinkage and its values were again similar for both types of body and dimensions measured. The lowest degree of shrinkage was obtained with specimens prepared from mixture DM1 (dry-milled powder, powder content in the mixture 52.5 vol%). With these specimens differences in shrinkage were established not only between individual specimen shapes but also between the disc diameter and disc thickness (18.5% vs 17.6%).

The density was determined for the discs (Table 3) and it corresponded to the shrinkage. For the specimens prepared from mixtures with the same volume fraction of ceramic powder the density was the higher the higher was the shrinkage. The discs prepared from mixtures S1, X1 and WM1 exhibited the highest density (99.6 to 99.7% of theoretical density). The specimens prepared from mixtures S2 and X2 with 49 vol% of powder exhibited lower values, 98.7 and 98.9% t.d., respectively. The lowest density was established for specimens prepared from mixture DM1, namely 97.6% t.d.

The strength values established for sintered discs and bars, and the calculated Weibull moduli are given in Table 4. For the discs prepared from mixtures with higher powder loading, i.e. S1, X1, WM1 and DM1, the powder treatment had no statistically significant effect on the strength. However, from the Weibull graph in Fig. 6 it is evident that powder treatment, dry and wet milling in particular, narrowed down the scatter in strength values. In S1 discs there appeared several markedly lower strength values. The discs prepared from mixtures with a lower volume (49 vol%) of untreated powder exhibited the highest average strength and the highest Weibull modulus ($\sigma = 679$ MPa, $m = 11.8$). The strength of S2 discs was statistically significantly higher than in discs with a higher powder loading in the mixture and even discs X2 prepared from treated powder and with the same volume fraction of

Table 3
Linear shrinkage and relative density of sintered discs and bars

Sample	Disc			Bar	
	Linear shrinkage (%)		Density (% t.d.)	Linear shrinkage (%)	
	Diameter	Thickness		Short side	Long side
S1	19.5	19.4	99.6	19.5	19.4
X1	19.6	19.6	99.6	19.6	19.5
DM1	18.5	17.6	97.6	18.3	18.0
WM1	19.5	19.1	99.7	19.5	19.6
S2	21.0	20.8	98.7	21.0	20.9
X2	21.2	21.4	98.9	21.0	20.8

powder did not achieve comparable values. A comparison of the strength values for bars (Fig. 7) revealed a different effect of powder treatment on the strength of sintered bars from that established for discs. In mixtures with higher powder loading the treatment of powder increased the strength of bars statistically significantly. The strength values increased in this sequence: S1, X1, DM1. On the contrary, the bars prepared from mixtures with a lower powder loading did not exhibit any significant difference in strength. Statistically, the bars prepared from untreated powder S2 had a similar strength (772 MPa) as the best bars prepared from DM1 mixtures with a higher powder volume (737 MPa). With regard to the small number of values for most types of ceramics the Weibull modulus of strength values of bars was not established. The structure of all sintered specimens was similar (see Fig. 8), it was formed by regular grains whose average size was about 0.6 μm. In the structure of specimens prepared from powders treated by ball milling, debris of alumina were found (see Fig. 9) whose size did not exceed 10 μm.

Table 4
Average strength (σ), standard deviation (s) and Weibull modulus (m) determined for sintered discs by biaxial flexural test and for sintered bars by four-point flexural test

Sample	Disc				Bar		
	σ (MPa)	s (MPa)	m (–)	Number of tests	σ (MPa)	s (MPa)	Number of tests
S1	566	186	3.6	27	583	31	9
X1	538	133	4.7	20	651	77	11
DM1	553	106	5.6	30	737	114	29
WM1	601	62	10.0	15	–	–	–
S2	679	60	11.8	20	772	95	10
X2	569	131	5.5	27	735	80	9

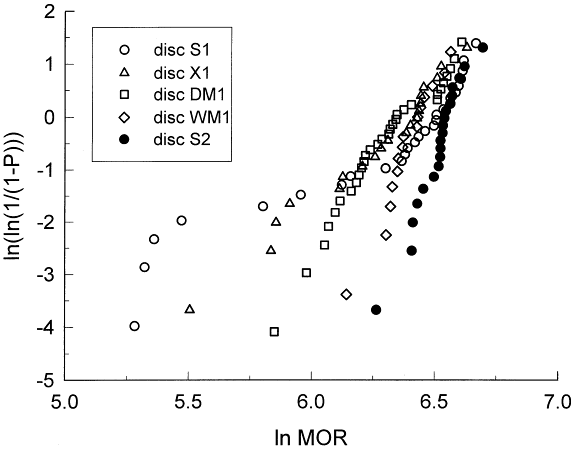

Fig. 6. The Weibull plot of biaxial flexural strength of sintered discs.

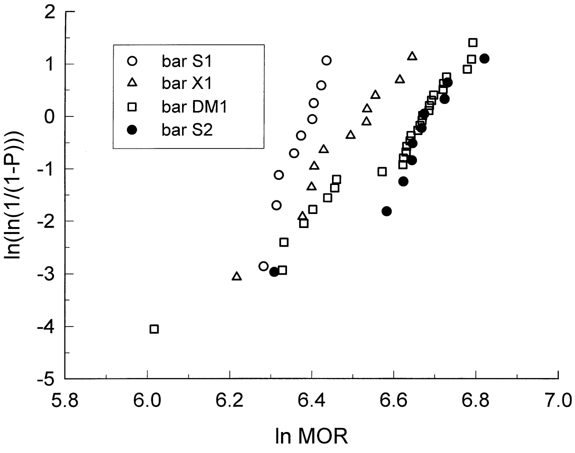

Fig. 7. The Weibull plot of four-point flexural strength of sintered bars.

4. Discussion

The treatment of powder slightly affected the particle size distribution. With treated powders there was a small decrease in the mean particle size, the greatest shift towards finer particles in comparison with untreated powder being observed in the dry-milled

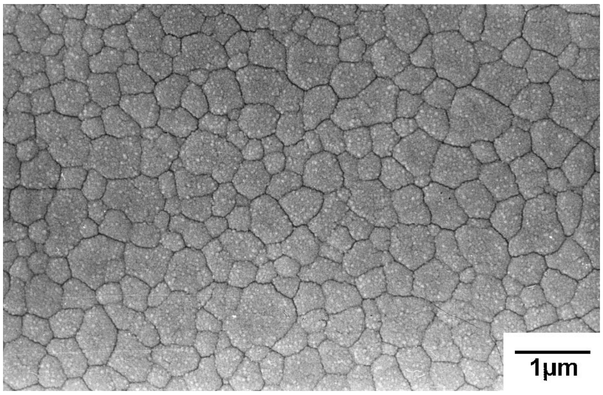

Fig. 8. SEM micrograph showing the microstructure of a sintered bar DM1.

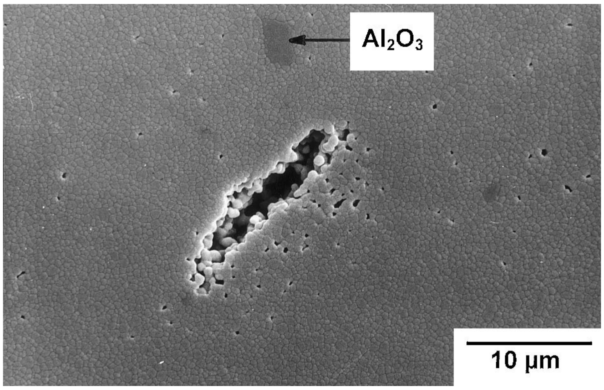

Fig. 9. SEM micrograph showing a large pore in the structure of a sintered bar DM1 and debris of alumina balls.

powder. In the case of this powder, however, and the same as with untreated powder, the ultrasonic dispersion of powder during particle size analysis resulted in the disintegration of large agglomerates since the analysis did not reveal particles of 25 to 50 μm in size that were clearly visible in the micrographs of these powders (Figs. 1 and 2). As will be shown below, however, the stronger agglomerates present in dry-milled powder, in contrast to soft agglomerates in untreated powder, were not disintegrated completely during the mixing of ceramic mixture. A mixture was thus formed which was made up of a powder with broad particle size distribution and probably also with smaller specific surface. Such powder provides for a more compact arrangement than powders with a narrower particle size distribution. Together with the smaller specific surface this explains the lower viscosity of the ceramic mixture with dry-milled powder when compared with the other ceramic mixtures with the same volume fraction of powder. The lower value of the exponent of power law ($n = 0.44$) describing the pseudoplastic behaviour of ceramic mixture DM1 was related to the possibility of the irregular agglomerated particles being orientated and arranged in the direction of shear stress at high shear rates. Orientated packing of non-spherical particles due to the shear stresses appearing during the filling of disc cavity with this ceramic mixture was probably the cause of anisotropic sintering which manifested itself by considerable differences between the shrinkage values of the diameter and the thickness of the sintered disc. Fig. 10 gives a fracture surface with distinct agglomerates in the structure of DM1 bars after binder removal. The lowest shrinkage value and a density of only 97.6% t.d. as established for the sintered specimens prepared from ceramic mixture DM1 also evidenced the presence of agglomerates in the structure of green ceramic body. A picture of the microstructure of a sintered DM1 bar (Fig. 9) reveals the uniform porosity with tiny pores of up to 0.5 μm and a defect 15 μm in size caused by non-uniform sintering of irregularly packed agglomerated particles.

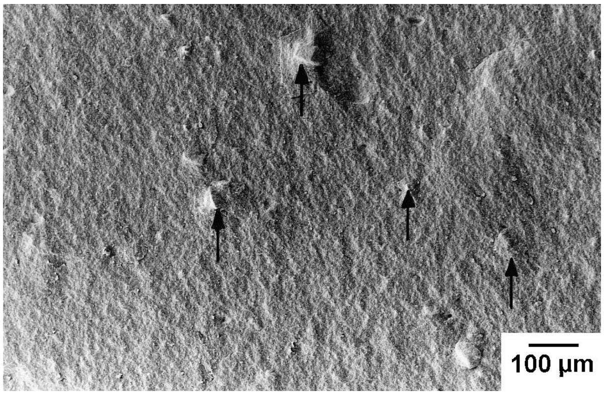

Fig. 10. SEM micrograph showing agglomerates on the fracture surface of a debinded bar DM1.

The average grain size found in the microstructure of all sintered components (0.6 μm) corresponded approximately to the mean particle size in the initial powder. These particles formed by hard and compact aggregates, which were impossible to disintegrate even in powder treatment, are likely to have remained preserved also during the mixing of ceramic mixture, and due to the preferred sintering of compact structure[13] they formed grains in sintered ceramics.

The results have shown the different effect of powder treatment on the strength of discs and bars. To explain this finding the size of critical defect must be considered, The size of a critical defect near the surface of the tensile side of the bar can be estimated from the values of flexural strength, σ, and fracture toughness, K_{IC}, using the modified Griffith's equation:

$$a = \left(\frac{K_{IC}}{\sigma Y}\right)^2$$

where $2a$ is the size of defect and Y is the shape factor. The shape factor value is $Y = 1.45$ for elliptical defects with half-axis radius $a/c = 0.5$ and $Y = 1.63$ for semi-elliptical defects with the same half-axis ratio.[14] The fracture toughness established for ceramic specimens prepared from mixture DM1 was 4.7 MPa $m^{1/2}$.[15] Having found from measurements that the strength values were from 410 to 890 MPa, then the maximum sizes of calculated critical defects ranged from 50 to 250 μm for elliptical defects, and from 40 to 200 μm for semi-elliptical defects. The estimated dimensions of critical defects were two orders of magnitude larger than the grain size in sintered specimens and they were also several times larger than the defects caused by non-uniform sintering of the irregular structure of agglomerated particles. It can thus be assumed that the critical defects in bars were not related to the particle arrangement alone in the ceramic mixtures. The highest strength values were obtained for bars prepared from mixtures with the lowest viscosity (S2, DM1, X2). On the contrary, bars prepared from mixture S1 with the highest activation energy, i.e. mixtures whose viscosity increased with decreasing temperature more markedly than in the other mixtures, exhibited the lowest strength values. The appearance of critical defects was thus related to the viscosity of ceramic mixtures and impaired disintegration and dispersion of particles, i.e. the presence of agglomerated particles in the structure of debinded component was not decisive in determining the strength of sintered bars. The critical defects appeared probably as flow marks and weld lines when the narrow and long cavity of the bar was filled with the ceramic mixture. Similar defects appearing on injection-moulded fine-grained zirconia components were reported by Song and Evans[16] in whose opinion these defects were due to the low temperature of injected ceramic mixture and the low injection pressure. In the case of discs the nature of filling the mould cavity with ceramic mixture was different, the path of ceramic mixture in the mould was shorter and the differences in viscosity had no significant effect on the strength of discs. It was only in the discs prepared from mixture S1 with the highest activation energy that a few very low strength values were found which were due to the defects appearing during the filling of mould cavity with ceramic mixture of poor rheological behaviour. Fig. 11 shows the fracture surface of a disc whose strength was 238 MPa. Seen on the fracture surface is a defect with a cavity formed due to imperfect filling of the mould with ceramic mixture. The part of the defect reaching to the surface and the stress appearing in the vicinity of this defect during sintering made it possible for a surface crack to develop from which the fracture propagated when the disc had been loaded (the area of crack initiation is marked with arrows in the fracture surface micrograph). In the case of the other discs of low strength values (< 250 MPa) too, defects were found on the fracture surface at the point of initiation of fracture propagation that were associated with mould filling. If we disregarded these low values, the Weibull modulus of S1 discs would increase to $m = 6.7$ with a higher determination coefficient of the line in the Weibull graph ($r^2 = 0.96$), which lends support to the assumption that specimens with low strength values contained a different type of defect compared with the other discs. Although statistical analysis of the strength of discs prepared from mixtures with a higher powder loading (52.5 vol%) did not reveal any statistically significant difference, the twofold value of the Weibull modulus of the WM1 discs in comparison with the other discs suggested that wet milling made it possible to prepare a mixture with satisfactory rheological properties and still with regular particle dispersion. This yielded ceramics with a narrower size distribution of critical defects and the scatter of strength value was reduced. But both for the bars and the discs the same or even better mechanical properties were established, in comparison with the other specimens, in case of specimens prepared from mixture S2 (non-treated powder, 49 vol% of powder). As regards the strength of bars, the low viscosity of this mixture was decisive. Results obtained for the discs showed, however, that mixing the ceramic mixture in the kneader made it possible to sufficiently disperse the particles of agglomerated powder even without its prior treatment. So that, it follows from the results that treating the powder had a favourable effect in particular on the rheological behaviour of mixtures with higher powder loading while improved disintegration and dispersion of particles of treated powder in the ceramic mixture as compared with non-treated powder was not evidenced. On the contrary, in the case of dry milling, strong agglomerates were formed. Although from the viewpoint of mechanical properties of sintered components the application of mixture with non-treated powder and lower powder loading (49 vol% of powder) appears to be most advantageous, its applicability may be limited by the pronounce tendency to warping during binder removal or by the lower density of sintered component.

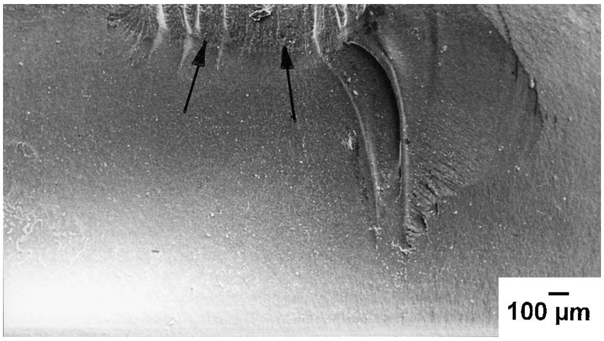

Fig. 11. SEM micrograph of fracture surface of a sintered disc S1 (arrows indicate the area of crack initiation).

5. Conclusions

During the preparation of the ceramic mixture it was possible to disintegrate large agglomerates present in the applied zirconia powder even in the case that the powder had not been treated prior to mixing with the binder. Powder treatment had a favourable effect on the rheological behaviour of the ceramic mixtures with 52.5 vol% of powder and thus made it possible to improve the mechanical properties of sintered components. The high activation energy of viscous flow of the mixture with untreated powder led to the appearance of critical defects, which had their origin in the stage when the mould was being filled with ceramic mixture. Reducing the volume portion of powder in the ceramic mixture to 49 vol% yielded better rheological properties also in the mixture prepared from untreated powder. Specimens prepared from this mixture displayed in all cases strength and Weibull modulus values that were higher than or comparable with specimens prepared from the other mixtures.

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