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# Effect of small amounts of additives on the sintering of high-purity Y-TZP

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Superfine Y-TZP powders of high purity were prepared by using clean-room facilities. The effects of several kinds of minute or small amounts of additives on the densification and microstructural development of the Y-TZP powder were investigated. It was found that $\leqslant 1$ wt% ferric or calcium oxides did not affect the densification of the Y-TZP powder compacts, while the addition of sodium oxides retarded the densification and that of copper oxide accelerated it, and these effects are most obvious at an additive level of 1 wt%. The retardation of the densification by sodium oxide was found to result from the agglomeration effect of the powder, and the formation of the eutectic liquid phase between zirconia and copper oxides promoted the densification and grain growth during sintering of copper oxide-doped powder. In addition, sodium and copper oxides both destabilize the tetragonal Y-TZP and lead to the formation of monoclinic phase.

## 1. Introduction

Small amounts of additives or impurities are very important in the processing of advanced ceramics. In some cases, small or even minute amounts of additives can promote densification and substantially improve the microstructures which develop, but in other cases, they may not work or they may even impede the sintering and degrade the microstructure. Therefore, the study of the effect of additives on the processing, especially the sintering behaviour and microstructure development of ceramics, has long been one of the most interesting and significant themes in ceramic science. Taking the $MgO$-$Al_2O_3$ system as an example, only 0.25 wt% MgO plays an important role in the densification and microstructural development of $Al_2O_3$ [1–3], and the studies on this case continue [4], but the results are still controversial, one of the difficulties in this study being that the purity of alumina itself cannot be ensured, and the effect of magnesia may sometimes be altered by other impurities.

Y-TZP material is one of the candidates for practical use because of its excellent mechanical properties at room temperature which resulted from the phase transformation toughening effect. The processing of this material has been studied extensively [5–8]. However, the effect of small amounts of additives on the sintering behaviour has not been investigated in detail, partly because of the reason mentioned above for alumina. By purifying the raw materials and preparing the powder through the use of clean-room facilities, the difficulty with the purity of the material itself can be overcome.

## 2. Experimental procedure

### 2.1. Powder preparation

Industrial zirconium oxychloride was used as the raw material. A large amount of impurities in the material was found, mainly silicon and sodium oxides, as shown in Table I. A method of filtration–recrystallization was employed for the purification: first filtering the solution of the raw materials to remove the insoluble impurities like silica, and then heating the solution to evaporate large amounts of solvents upto close to its solubility limit; after cooling the solution to room temperature, needle-like small crystals were produced with some uncrystallized, yellow-coloured solution in between. After filtration again and washing with ethanol, pure white crystalline zirconium oxychloride was obtained. If the impurity level did not exceed that expected, the purified zirconium oxychloride was used for powder preparation. Other raw materials, like yttrium nitrate, were not purified because of their relatively high purity levels and the small amount used.

The mixed solution of $Zr^{4+}$ and $Y^{3+}$ was prepared from the purified zirconium oxychloride and yttrium nitrate, and the yttria content in the final powder was designated to be 3 mol%. The hydroxide coprecipitation method with ammonia was used for the preparation of the powder precursor. After removing $Cl^-$

TABLE I Impurity levels in zirconium oxychloride raw material

| Element[a] | Content before purification (p.p.m.) | Content after purification (p.p.m.) |
|---|---|---|
| Na | 6510 | ND |
| Si | 240 | 8 |
| Ti | 130 | 1 |
| Al | < 20 | < 20 |
| Mg | 3 | 1 |

[a] Other elements are either not detected by X-ray fluorescence or less than 3 p.p.m. by ICP-AES.

until it could not be detected by 10% $Ag^+$, some amount of *iso*-butanol was added into the coprecipitates and the mixture was then distilled. The mixed vapour was extracted and cooled, and water and *iso*-butanol separated from each other, then water was removed and *iso*-butanol was refluxed. The cycle was repeated until all the water was removed, and thus non-aqueous powder precursors were obtained. The distilled precursors were then dried by rotating evaporation at around 60 °C with a reduced gas pressure.

To prevent the incomplete decomposition of the organics, the precursor was calcined step wisely 200 °C, 2 h; 400 °C, 2 h; finally 600 °C, 2 h. After calcination, Y-TZP powders were obtained.

## 2.2. The addition of additives

Calcium, ferric, sodium and copper oxides were selected as the additives, and calcium, sodium, and copper acetates, and ferric oxalate as the additive precursors. Because all the acetates are soluble in water, they were added in the Y-TZP powder in the form of solutions. To distribute the additives homogeneously, the volume of the acetate solutions was designed to be able to wet the powders thoroughly, and the amount of additives added was adjusted by controlling the solution concentration. Ferric oxalate is insoluble in water, so only suspensions were prepared for addition. The addition levels were 0.01, 0.1, and 1 wt% for all kinds of additives. The doped powders were dried and calcined step wisely again from 400 °C, 1 h; 600 °C, 1 h; and finally to 750 °C, 2 h, to decompose any organics completely.

During the above steps, the distillation and rotating evaporation were conducted in a clean room of 10 000 $m^{-3}$ (particle number per cubic metre) grade, because in both steps the materials were in closed containers. The other steps were carried out in a clean room of 100 $m^{-3}$ grade.

## 2.3. Forming and sintering

The doped and undoped powders were cold isostatically pressed directly at 300 and 600 MPa for 1 min in rubber moulds. The compacted samples were then sintered by either heating with a constant rate or isothermally at fixed temperatures. The heating rate was 10 °C $min^{-1}$, and the highest sintering temperature was 1550 °C.

TABLE II Impurity levels in Y-TZP powder prepared in a clean room

| | Fe | Mg | Si | Ca | Na | Cu | Al |
|---|---|---|---|---|---|---|---|
| Content (p.p.m.) | 7 | 4 | 15 | 11 | < 10 | < 2 | < 10 |

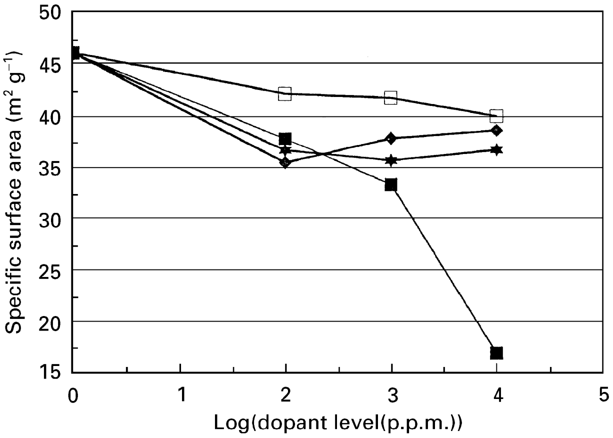

*Figure 1* Relations between the specific surface area and the dopant level. (■) Sodium oxide, (◆) calcium oxide, (★) ferric oxide, (□) copper oxide.

## 2.4. Characterization of the powders, compacts and the sintered bodies

The possible existing elements were detected by X-ray fluorescence spectroscopy (XRFS) qualitatively, and then the detected elements were quantitatively analysed with atomic emission spectroscopy (AES–ICP) for the raw materials before and after purification, and for the prepared powders. The BET multipoint adsorbing technique was used for the measurement of the specific surface area of the powders. The pore-size distribution of the compacts was detected by mercury porosimetry. The sintered bodies were then characterized with SEM for their microstructure and with X-ray diffraction (XRD) for their phase structure.

# 3. Results

## 3.1. The properties of the powders and compacts

### 3.1.1. The purity of the powders

Table I shows the impurity levels of the as-received and recrystallized zirconium oxychlorides. The main impurities in the as-received materials were silicon, sodium, and titanium. After filtration and recrystallization, the three elements were removed thoroughly. Other elements not listed in the table were not detected by XRFS.

The impurity levels in the powders prepared are listed in Table II. The powders were still pure enough because they were prepared in clean rooms. If other elements undetected by XRFS are not taken into account, the total amount of impurities is lower than 60 p.p.m. Therefore, as the minimum doping level is 0.01 wt%, the effect of impurities contained by the powder itself will not be considered.

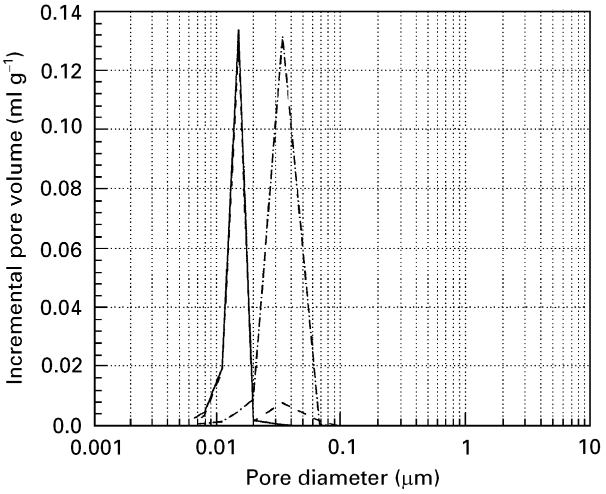

*Figure 2* Pore-size distributions of the $Na_2O$-doped Y-TZP powder compacts. (——) pure Y-TZP, (– – –) 0.1% $Na_2O$, (–·–) 1% $Na_2O$.

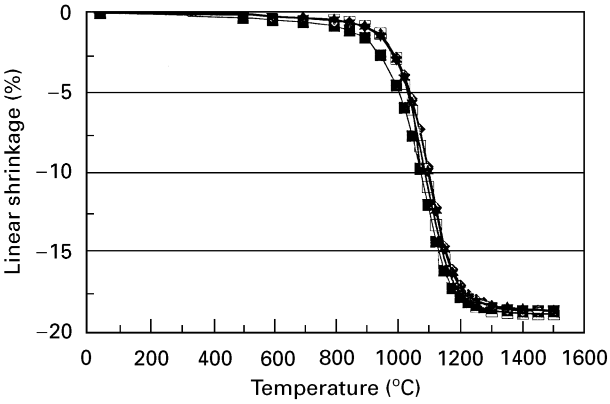

*Figure 3* Linear shrinkage versus temperature plots for calcium oxide-doped Y-TZP during heating at a constant rate (10 °C min$^{-1}$): (■) 0 p.p.m., (◆) 100 p.p.m., (★) 1000 p.p.m., (□) 10 000 p.p.m.

### 3.1.2. *The specific surface area*

Fig. 1 shows the specific surface area of the differently doped powders. It can be seen that the addition of sodium oxide can lower the specific surface area significantly, while the others do not.

### 3.1.3. *The pore-size distributions of the compacts*

The results of mercury porosimetry measurement shows that pure and up to 1 wt% calcium, ferric and copper oxides-doped Y-TZP powder compacts have almost the same single peak pore-size distribution characteristics, indicating that the addition of up to 1 wt% calcium, ferric and copper oxides do not change the particle packing behaviour of the Y-TZP powders. However, the addition of even 0.1 wt% sodium oxide does, as shown in Fig. 2, a distribution peak at larger size resulting. At 1 wt% doping level, only the larger pores were present in the compacts.

## 3.2. Densification behaviour

Figs. 3–6 show the relationships between the linear shrinkage and temperature for the different kinds of powders during heating at a constant rate of 10 °C min$^{-1}$. The addition of up to 1 wt% calcium oxide did not affect the densification of the powder compacts. A small effect can be found with 0.1 and 1 wt% ferric oxides, but this is relatively small compared to the effects of copper or sodium oxides. The addition of sodium oxide retarded the densification and increased the sintering temperature, while copper

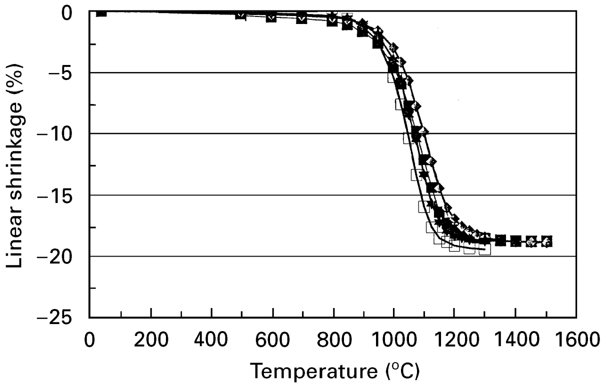

*Figure 4* Linear shrinkage versus temperature plots for ferric oxide-doped Y-TZP during heating at a constant rate (10 °C min$^{-1}$); for key, see Fig. 3.

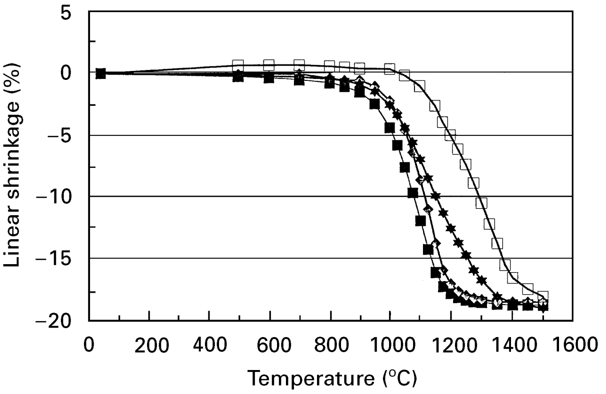

*Figure 5* Linear shrinkage versus temperature plots for sodium oxide-doped Y-TZP during heating at a constant rate (10 °C min$^{-1}$); for key, see Fig. 3.

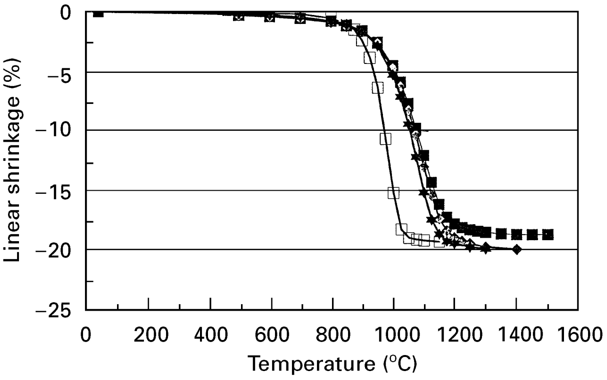

*Figure 6* Linear shrinkage versus temperature plots for copper oxide-doped Y-TZP during heating at a constant rate (10 °C min$^{-1}$); for key, see Fig. 3.

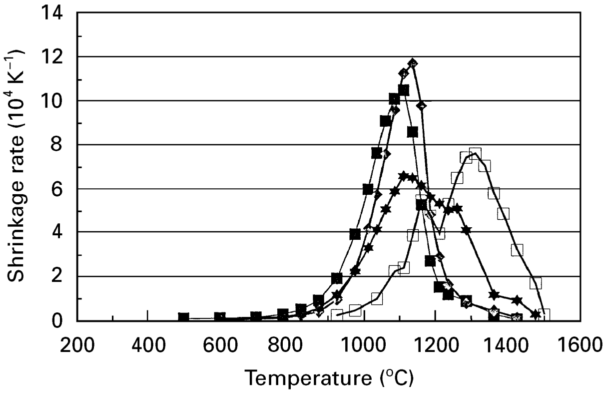

*Figure 7* Linear shrinkage rate versus temperature plots for sodium oxide-doped Y-TZP during heating with constant rate (10 °C min$^{-1}$); for key, see Fig. 3.

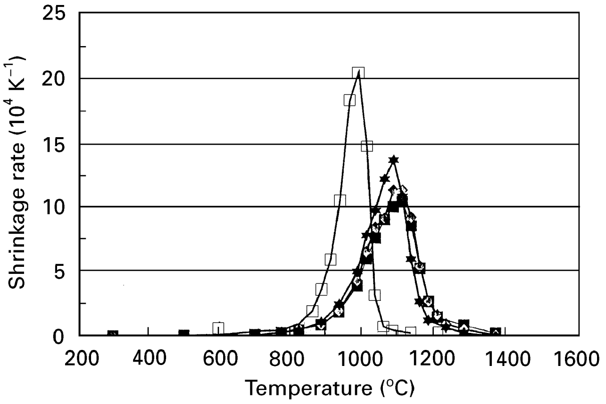

*Figure 8* Linear shrinkage rate versus temperature plots for copper oxide-doped Y-TZP during heating at a constant rate (10 °C min$^{-1}$); for key, see Fig. 3.

oxides promoted the densification and decreased the sintering temperature. The most significant effect could be found at the doping level of 1 wt%.

Converting the data in Figs. 5 and 6 into shrinkage rate – temperature relations, the effect on shrinkage rate can be more clearly seen, as shown in Figs. 7 and 8. The addition of 1 wt% copper oxide enhanced the densification rate and lowered the sintering temperature by 200–250 °C; only 0.1 wt% sodium oxide lowers the densification rate significantly, and leads to the occurrence of two maximum rates during heating at a constant rate.

### 3.3. Phase composition of the powders and the sintered bodies

The experimental results show that the tetragonal phase of 3Y-TZP materials can be maintained to above 1550 °C during sintering, without transformation to the monoclinic phase. This feature is unchanged when doped with 1 wt% or less calcium and ferric oxides, or with 0.1 wt% or less sodium and copper oxides. However, when 1 wt% copper or sodium oxides were doped, larger amounts of monoclinic phase were observed in sintered bodies, and also even in powders, as illustrated in Table III.

### 3.4. The microstructure development

No significant effects of calcium and ferric oxides on the microstructure formation were observed in this study. The presence of 1 wt% sodium oxide can impede the grain growth of Y-TZP to some extent, while when 1 wt% copper oxide was added, the grain-growth promoting effect became most obvious, as can be seen in Fig. 9. In addition, 1 wt% sodium oxide-doped samples were found to be cracked after sintering at 1550 °C for 2 h. Although 1 wt% copper oxide-doped samples were not cracked, a large amount of microcracks can be observed under the microscope.

## 4. Discussion

### 4.1. The effect of sodium oxide on the densification and microstructure development

No systematic $Na_2O$–$ZrO_2$ and $Na_2O$–$Y_2O_3$ binary phase diagrams nor $Na_2O$–$ZrO_2$–$Y_2O_3$ ternary phase diagram could be found. The effects of the compound formation between $Na_2O$–$ZrO_2$–$Y_2O_3$ as second phases are believed to be limited because the content of sodium oxide is not higher than 1 wt%. In addition, data on the solubility of $Na_2O$ in $ZrO_2$ or $Y_2O_3$ are rare; a solubility of 3.5% $Na_2O$ in $ZrO_2$ at 1600–1700 °C were reported [9].

Sodium oxide is easy to deliquesce, but this problem is not considered during high-temperature sintering. It sublimates at around 1275 °C [10], therefore the formation of liquid phase is out of the question.

From the data of specific surface area and pore-size distribution measurements, however, one of the main reasons for the retardation of the densification by

TABLE III Monoclinic phase contents in doped Y-TZP powders and materials

| Materials | 750 °C, 2 h calcined | 1100 °C, sintered | 1250 °C, sintered | 1400 °C, sintered | 1550 °C, sintered |
|---|---|---|---|---|---|
| Pure Y-TZP | 0 | 0 | 0 | < 1 | < 1 |
| 0.1 wt% $Na_2O$ | 0 | | | < 1 | 1 |
| 1 wt% $Na_2O$ | 18 | | | 60 | 63 |
| 1 wt % ferric oxide | 0 | | | | 0 |
| 0.1 wt% copper oxide | 0 | | | | 3 |
| 1 wt% copper oxide | 22 | 75 | 67 | 76 | 68 |

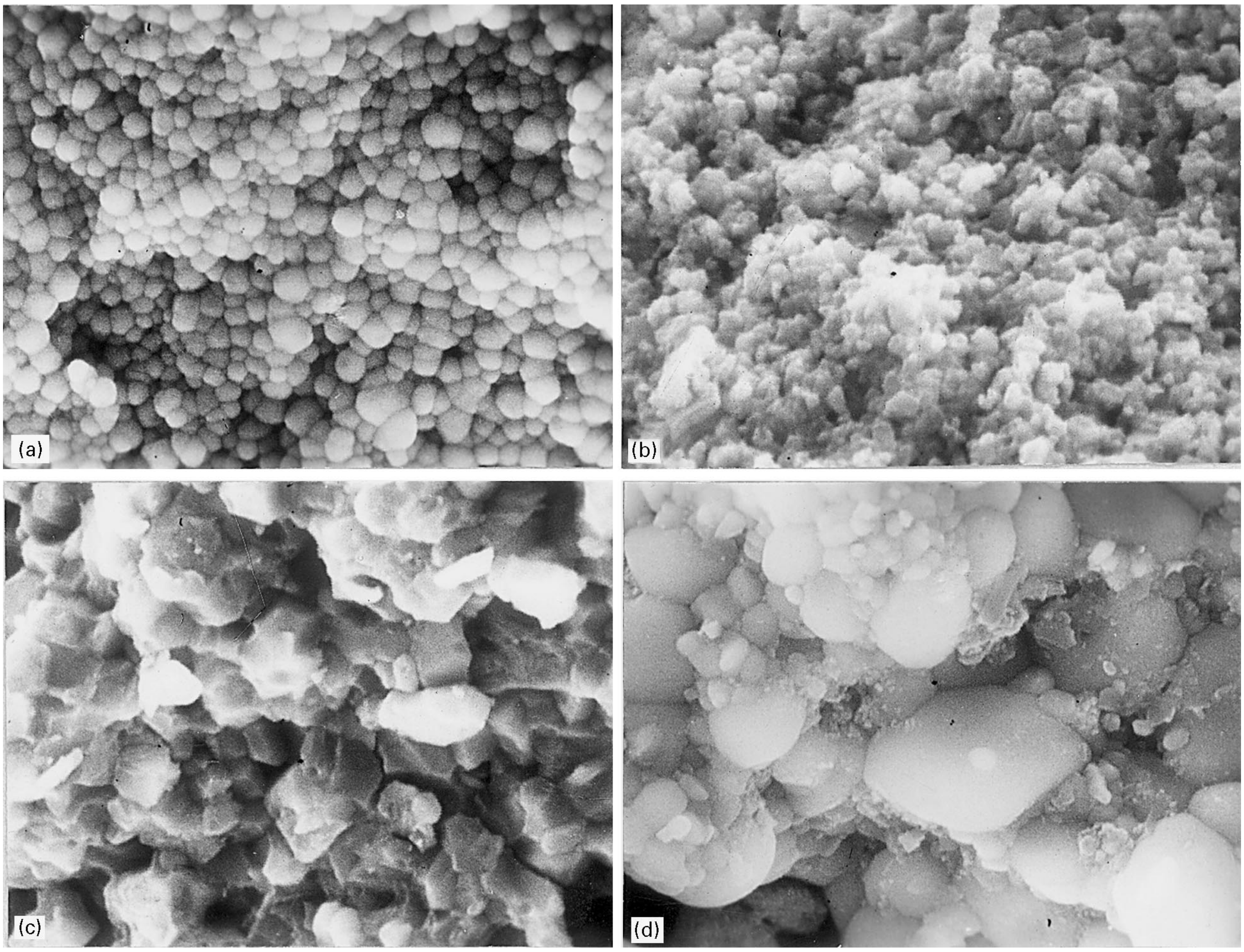

*Figure 9* SEM microstructures of (a) pure Y-TZP (1550 °C, 2 h), (b) doped with 1 wt% sodium oxide (1550 °C, 2 h), (c, d) doped with 1 wt% copper oxide sintered at 1400 and 1550 °C for 2 h, respectively.

sodium oxide can be inferred to be the formation of agglomerates between the primary Y-TZP particles, which leads to the decrease of specific surface area and the formation of larger pores. The larger inter-particle pores are more stable thermodynamically, on the one hand, but also more difficult to remove kinetically, than the smaller pores, on the other.

The phenomenon for the occurrence of two maximum values of shrinkage rate during heating for 0.1 and 1 wt% $Na_2O$-doped samples can be related to the sublimation of sodium oxide, as the sublimation temperature of sodium oxide is very close to those where the maximum values appear.

It is no clear reason for the effect of sodium oxide on the phase stability of Y-TZP. The three possible explanations might be: (1) the possible formation of solid solution and/or eutectic phase between $Na_2O$ and $Y_2O_3$ leading to the decrease of $Y_2O_3$ content in $ZrO_2$; (2) partial solution of $Na_2O$ in the $ZrO_2$ lattice, leading to the decrease of the Gibb's energy and interfacial energy of the monoclinic phase, and thus promoting the phase transformation from tetragonal to the monoclinic; and (3) $Na_2O$ is distributed homogeneously on the surface of Y-TZP particles and/or at the interface between Y-TZP grains, increases the surface and/or interfacial energy of Y-TZP, and therefore destabilizes Y-TZP. In the above three possibilities, the third one is the most unlikely, because if the presence of $Na_2O$ on the interface of Y-TZP particles or grains has increased the interface energy, it would prefer to accumulate and remain separated from Y-TZP particles and/or grains. The grain-growth inhibition by sodium oxide might have resulted from the second particle pinning or solute drag effect by $Na_2O$ or $Na_2O$–$Y_2O_3$ at the interface between Y-TZP grains [11, 12].

### 4.2. The effect of copper oxide on the densification and microstructural development

In contrast to the effect of sodium oxide, the addition of copper oxide can significantly promote the densification and grain growth of Y-TZP. According to the phase diagram of $CuO(Cu_2O)$–$ZrO_2$ [13], at 1130 °C a eutectic phase between copper oxide and zirconium oxide will form. Although the ternary phase diagram of $CuO(Cu_2O)$–$Y_2O_3$–$ZrO_2$ is not available, it is certain that the melting point of the ternary system of $CuO(Cu_2O)$–$Y_2O_3$–$ZrO_2$ will be lower than 1130 °C. So we can believe with confidence that the promotion of both densification and grain growth of Y-TZP by copper oxide is led by the eutectic phase formation between $CuO(Cu_2O)$–$Y_2O_3$–$ZrO_2$, which enhances the species diffusion ability and is responsible for pore removal and grain growth.

In addition to the possible explanations mentioned above for sodium oxide, another reason for the destabilization of tetragonal phase by copper oxide, is probably the greatly promoted grain growth of Y-TZP, producing a grain size which exceeds the critical value for the stability of tetragonal Y-TZP (the critical grain size is about 0.8–1.2 μm), leading to the phase transformation to the monoclinic.

## 5. Conclusions

The doping with 0.01–1 wt% sodium, calcium, ferric and copper oxides, of highly pure Y-TZP powder, has the following effects on the sintering behaviour:

1. At not higher than 1 wt% doping level of calcium or ferric oxides, the densification process is approximately unaffected. The addition of sodium oxide and copper oxide can dramatically retard and promote the densification process, and increase and decrease the sintering temperature for Y-TZP, respectively.
2. One of the main reasons for the retardation of the densification of Y-TZP by sodium oxide is the formation of agglomerates between the primary particles, while the promotion of densification by copper oxide is believed to result from the formation of a eutectic phase below 1130 °C.
3. The presence of calcium or ferric oxides in Y-TZP material do not affect the phase stability of Y-TZP, but sodium or copper oxides at the 0.1 or 1 wt% level destabilize the tetragonal phase and promote phase transformation to the monoclinic phase.
4. The addition of 0.1 and 1 wt% copper oxide promotes the grain growth of Y-TZP significantly.

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