

Research Article

Mechanical Properties of ZTA: Correlation with Structural Properties and Influence of Ageing

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We report the mechanical and thermal properties of industrial Zirconia Toughened Alumina (ZTA) composites for different compositions of zirconia and yttria, paying a special attention to possible ageing. As a result a correlation between the structural properties and the in-fine performances is obtained; in particular, depending on mechanical properties expected by the customer, optimum composites compositions are indicated.

1. Introduction

One-third of the population of the developed countries will be more than 60 years old in 2014 and will be exposed to osteoarthritis or osteoporosis. As a consequence, about 600.000 total hip replacements are performed each year in Europe, and this number should increase of more than 10% per year during the next 10 years [1]. The demand for well-integrated, long-lasting implants is therefore very high, although current feedback is not fully acceptable. Hip joints, for example, are generally limited to maximum 15–20 years lifetime, due to failures or aseptic loosening (resulting from osteolysis related to wear debris in the case of metal-polyethylene prostheses). Ceramic-ceramic hip implants have been introduced in orthopedics since they show decreased wear rates and they lower the risk of aseptic loosening. They are today considered as the most promising materials to improve implant lifetime. Unfortunately, the risk of failure associated with the use of alumina and the lack of *in vivo* stability of zirconia have dampened their widespread use so far. This is why most of research and industrial development are now focused on ZTA. The use of zirconia particles with tetragonal phase (t-ZrO₂) inside alumina leads indeed to a toughening of alumina, while preserving *a priori* a better stability *in vivo* when compared to zirconia alone [1–4].

The stability conditions of the t-ZrO₂ are more or less well known, but most of the fundamental studies which have been published obviously deal with samples synthesized at a laboratory scale which show very different results according to process conditions. The situation is even worse in the case of composites: when zirconia is put in an alumina matrix to form ZTA composites, the balance between parameters which compete to stabilize the t-ZrO₂ is completely changed and is hardly known. In particular the structural and mechanical properties of these composites are also strongly samples-dependent due to different routes of elaboration [5–8]. Indeed the ZTA production includes many steps of heat treatments, milling, spray-dry, shaping, and sintering, all those steps affecting the stability of zirconia and the final mechanical properties. That is why we have recently published a study of the structural properties of industrial ZTA composites for different compositions of zirconia and yttria at the main stages of the process and compared them with those of monolithic doped and undoped zirconia [9]: influences on phases stability, lattice parameters, homogeneous and nonhomogeneous strains, particles, and crystallites sizes were considered and discussed. The structural state of a given compound was explained from a very delicate balance of three competing effects, yttria doping, strain effect, and size

effect: the first and third ones were shown stabilizing the tetragonal phase relatively to the monoclinic phase and destabilizing the tetragonal phase relatively to the cubic phase, whereas the second one is doing the opposite. In addition to this competition, local effects were also considered for a full understanding of the microscopic situation: the two most prominent ones are microstrains and the inhomogeneous distribution of yttria which both increase the metastable coexistence of phases. This latter effect induces a core-shell structure of the grains. This complex situation was shown to have strong consequence from industrial point of view and explain many divergences and conflicting reports in the literature about nominally chemically identical compounds.

In the present paper we report the thermal and mechanical properties of these materials, paying a special attention to possible ageing. As a result a correlation between the structural properties and the in-fine performances is obtained; in particular, depending on mechanical properties expected by the customer, optimum composites compositions are indicated.

2. Experimental Procedures

2.1. Synthesis of Materials and Microstructures. The alumina and zirconia raw powders are produced by the Nanoe Company (France) via an industrial process close to a method of coprecipitation at low temperature. These raw powders are then mechanically milled in aqueous media. The alumina is doped with 1000 ppm of MgO as a sintering additive. Zirconia with x content of yttrium (ZxY) ranging between 0 and 8 mol% is milled at high rates to form composites containing from 2.5 to 50 wt% of zirconia. Hereafter we use the conventional notation: for example, A50Z8Y is a composite with 50 wt% of zirconia doped with 8 mol% of yttrium. The spray-dried granules are uniaxially pressed (320 MPa) to obtain pellets with 20 mm diameter and 2 mm thickness. The pellets are sintered at 1500°C during 7 h. In order to analyze the microstructures of the sintered composites, the pellets are mirror-polished with diamond paste until 1 μm , thermally etched at 1450°C for 1 h and gold-coated to avoid charging effects. These analyses are carried out using scanning electronic microscopy (SEM) Leo Gemini 1530.

2.2. X-Ray Diffraction. Room temperature high resolution X-ray diffraction patterns are collected on a highly accurate two-axis diffractometer with an 18 kW copper Rigaku rotating anode generator, using the Bragg Brentano geometry and equipped with a Rigaku furnace. Rietveld refinements of XRD data allowing determination of complete sets of structural data (even though we show in this paper only a few parts of these sets), lattice parameters, phases mixing, microstrains, and so forth are performed using the Jana 2006 package [10].

2.3. Mechanical Characterization. Vickers hardness, threshold for fatigue crack propagation, and bending strength have been measured for each composition of samples. Young modulus and hardness have also been measured by nanoindentation for some compositions, in order to compare values to

Vickers hardness. These indentations have been performed with a Wolpert Testwell indenter on polished pellets which were thermally relaxed at 1200°C. Vickers indentation hardness has been measured with a load of 10 kg, that is, 98.1 N and Young's modulus determined using a mixing law with 400 GPa for alumina and 200 GPa for zirconia. The fracture threshold K_{I0} has been determined several days after indentation in order to get cracks stabilization after slow propagation: in this case it has been shown that Anstiss' formula allows calculating K_{I0} crack propagation threshold, which characterizes the delayed fracture risk [11]. This method allows us to get a trend of the fracture threshold K_{I0} with the composition of ZTA even if we noted an overestimation of K_{I0} obtained compared to K_{I0} usually obtained by double torsion or stable indentation crack growth in bending tests. Bending tests have been performed by averaging measurements on 20 as-fired bars of each composition using a 3-point bending Instron 4505 machine. 100 nanoindentations of 50 or 100 nm depth every 5 μm were performed on relaxed and polished pellets. These two values of penetration were chosen in order to get the whole response of the composite (case of 100 nm) or to get individual response of alumina and zirconia by indenting only one grain of each material (case of 50 nm).

3. Results

3.1. Structural Measurement Results. We have studied two types of samples: as-fired samples and the so-called "aged samples" which are as-fired samples that have been put afterward in a hydrothermal vessel with water and placed during 24 hours in a furnace at 140°C (440 K) in order to study the effects of ageing. We have also compared the behavior of zirconia and composites.

3.1.1. Thermal Evolution of As-Prepared Samples. We have recorded X-ray diffraction Rietveld patterns of sintered monolithic zirconia and ZTA composites between typical room temperature and 1300°C (1600 K). Temperature-dependence of phase ratio and volumes of phase are shown Figures 1 and 2 for different amount of yttria, that is, Z0Y, Z3Y, and aged-Z3Y.

It is well known that undoped zirconia exhibits a sequence of two-phase transformations from room temperature to high temperature, that is, monoclinic-tetragonal-cubic transitions. Normally the m-ZrO₂ is observed at room temperature but stabilization of the high temperature t-ZrO₂ at room temperature is performed by different way in order to allow toughening by phase transformation [5]. Indeed if the t-ZrO₂ is retained at room temperature, when an external stress is applied, this metastable phase turns back into the stable m-ZrO₂ with an increase of volume of 4%. This increase of 4% of volume opposes to the cracks propagation. This phenomenon is the origin of the outstanding mechanical properties of zirconia. Several ways (which may compete) exist to stabilize the tetragonal zirconia down to room temperature: chemical and doping composition (e.g., Y₂O₃), grain size below a critical size R_c [12, 13], strains effect due to alumina matrix, and so forth, which have been discussed in our previous article [9]. That is why it is important to determine the temperature range of stability of the metastable t-ZrO₂.

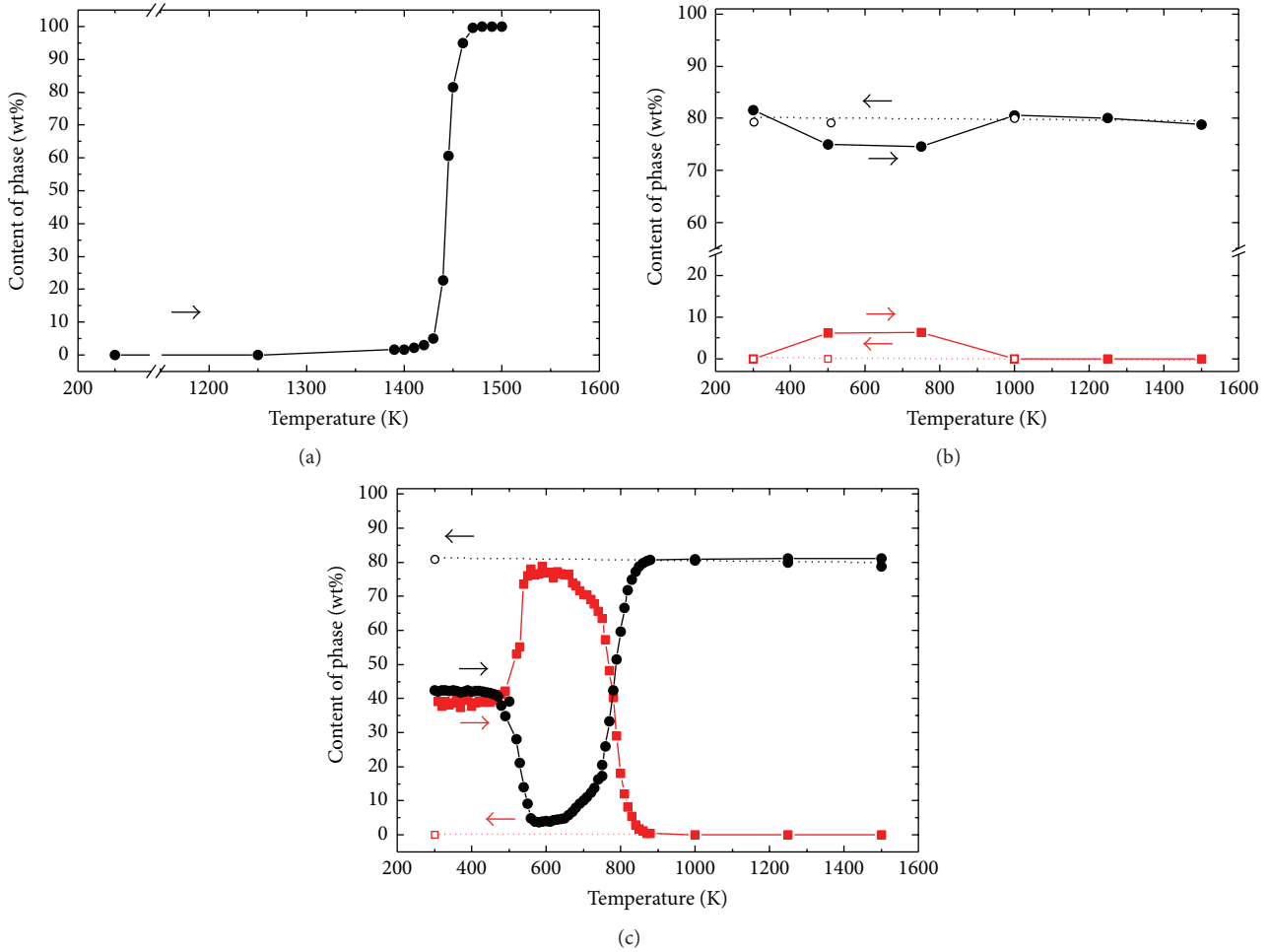


FIGURE 1: Dependence of the content of zirconia phases on the temperature: (a) Z0Y, (b) Z3Y, and (c) aged-Z3Y; black for the t-ZrO₂ and red for the m-ZrO₂; full line: heating; dash line: cooling.

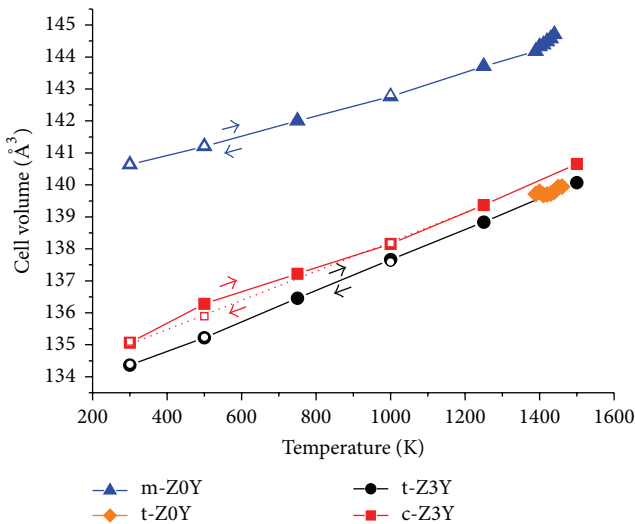


FIGURE 2: Dependence of the cell volumes on the temperature; full line: heating; dash line: cooling.

At room temperature in Z0Y we have observed the m-ZrO₂ and when heating the complete transformation towards the t-ZrO₂ occurs at $T \approx 1480$ K (1180°C). This t-m transformation induces a substantial increase in volume ($\approx 4\%$ Figure 2). Doping with yttria induces in Z3Y a metastable stabilization of the tetragonal phase (≈ 80 wt%) at room temperature with the smallest amount of c-ZrO₂ (≈ 20 wt%), and the m-ZrO₂ has completely disappeared (Figure 1(b)). On heating between ≈ 470 K (170°C) and ≈ 570 K (270°C) a small amount of t-ZrO₂ retransforms into the m-ZrO₂ (Figure 1(b)) but the situation reverses at higher temperature due to the m-t transformation up to the highest temperature (1500 K). This induces a small anomaly (Figure 2) on the temperature-dependence of the c-ZrO₂ volume, but no anomaly (to the precision of measurements) in the t-ZrO₂. On cooling, no evolution is observed and the initial state is recovered. During the whole cycle the c-ZrO₂ ratio did not change. Increasing doping with zirconia up to Z8Y induces at room temperature a c-ZrO₂ majority phase (≈ 70 wt%) which coexists with ≈ 30 wt% of t-ZrO₂ (not shown). Thermal cycling induces no

change in phase ratio and linear evolutions of the volumes are observed (not shown).

The appearance of a small amount of m-ZrO₂ in Z3Y when heating is characteristic of an *in situ* ageing phenomenon. Indeed as a small steam amount in the furnace is unavoidable, the m-ZrO₂ phase appears in the temperature range where the ageing kinetics are the highest [14]. This small amount of m-ZrO₂ retransforms afterward into the t-ZrO₂ because of the m-t transition. Further heating at high temperature eliminated the residual steam and no further ageing is observed. In Z8Y this phenomenon is not observed, which is an indication of strong stabilization of the c- and t-ZrO₂, and is an indication of probable insensibility of this compound to ageing, as we demonstrate below.

As a general observation, increasing the yttria content leads to an increase of lattice volume of every zirconia phase, as observed (Figure 2). This evolution is expected: the substitution of zirconium by yttrium with (i) higher ionic size and with different valences results in (ii) the creation of oxygen vacancies, both effects leading to an increase of the atomic distances and thus of the lattice volume.

Regarding the composites we have studied A20Z3Y and A10Z1.5Y compositions. In A20Z3Y at room temperature the compound gets ≈75 wt% of the t-ZrO₂ and ≈25 wt% of the c-ZrO₂, and this phase ratio does not change whatever the temperature is which means that the anomalies observed in Z3Y are not detected anymore. This indicates that A20Z3Y is not sensible to ageing which we have checked below. A10Z1.5Y is at room temperature completely in the t-ZrO₂, and no temperature evolution is observed. Volumes of phases monotonously increase with temperature.

3.1.2. Thermal Evolution of Aged Samples. In Z3Y, strong changes are observed at room temperature between as-fired and aged samples (Figures 1(b) and 1(c)): indeed before ageing ≈80 wt% of t-ZrO₂ and ≈20 wt% of c-ZrO₂ were observed, while after ageing ≈40 wt% monoclinic phase has appeared, c-ZrO₂ has slightly diminished to ≈15 wt%, and the t-ZrO₂ is reduced to ≈45 wt%. Moreover during a further heating (Figure 1), an additional ageing is also observed as in the nonaged sample. Indeed at ≈540 K (240°C) almost all of the t-ZrO₂ transform into the m-ZrO₂ which retransforms at higher temperature into the t-ZrO₂: at ≈880 K (580°C) it has completely disappeared. During the whole process the c-ZrO₂ phase ratio does not change, and no anomaly is observed in the volumes evolutions (not shown). On cooling the high temperature phase ratios are retained. This result is rather remarkable, and even though many defects have been created during the whole cycling, it is interesting to notice that heating up to 1500 K has fully eliminated the m-ZrO₂ created both by the preliminary ageing and by the subsequent heating run.

Regarding the composites, at room temperature a detailed analysis of as-fired samples has already been published [9] for many concentrations of zirconia and yttria, and we just recall here that, for nonaged AZ3Y compounds, phase ratios of t- and c-ZrO₂ are almost independent of the zirconia concentration and are ≈85 wt% and ≈25 wt%, respectively: that is, no monoclinic phase is observed. After 24 h of ageing procedure, an amount of 1 wt% of monoclinic phase

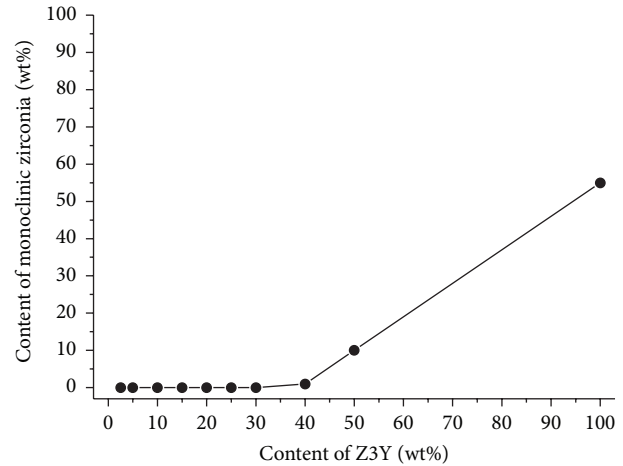


FIGURE 3: Dependence of the content of transformed zirconia on the zirconia content after 24 h of ageing treatment.

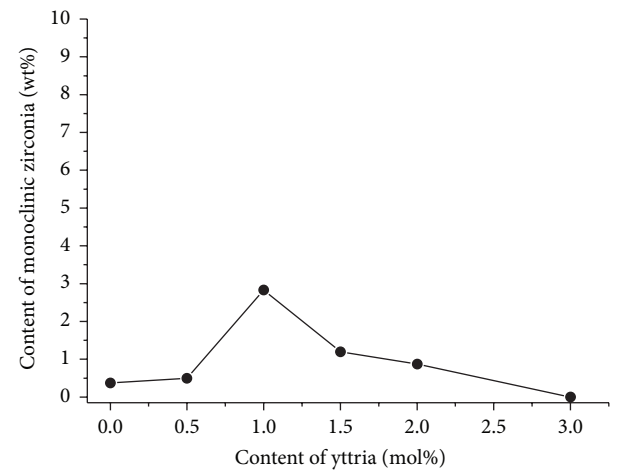


FIGURE 4: Dependence of the content of transformed zirconia on the yttria content in A25Z composites.

is detected for concentration of 40 wt% (Figure 3) which linearly increases at higher content: in the A50Z3Y content only 10 wt% of m-ZrO₂ has appeared.

As no ageing is detected for concentration below ≈35 wt% of Z3Y, we have also examined in A10ZY compounds the influence of yttria content. In fact for yttria content equal and below 3 mol% no ageing is detected, including the case of A10Z0Y, which indicates that even without doping the t-ZrO₂ is stable enough, in particular because of size effect [9] to resist ageing. On the contrary in the case of A25ZY, m-ZrO₂ exists before ageing for content below 1.5 mol% of yttria and gets a significant phase ratio in A25Z0Y (65 wt%) and 35 wt% of t-ZrO₂. After ageing there is a weak increase of the m-ZrO₂ which peaks around 1 mol% of yttria content (Figure 4).

3.2. Mechanical Measurements Results. We have studied the influence of sintering temperature, zirconia composition, and yttria doping on Vickers hardness, threshold for crack propagation, and bending strength.

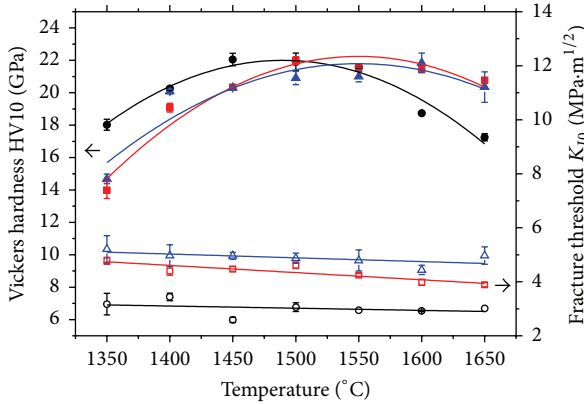


FIGURE 5: Dependence of the mechanical properties on the sintering temperature (black: Al_2O_3 , red: A10Z3Y , and blue: A25Z3Y).

3.2.1. Influence of the Sintering Temperature on Mechanical Properties. We have already reported [9] that the optimum sintering temperature regarding the density and the limitation of grain growth stands around 1500°C . Here we have checked the consequences of this choice for the mechanical properties. A10Z3Y and A25Z3Y composites have been sintered at temperatures between 1500°C and 1650°C and compared with monolithic alumina (Figure 5). Regarding Vickers hardness, both composites display very similar values, due to their close compositions with an optimum close to 1550°C . Below this temperature the highest values are obtained for bulk alumina, which is a well-known result: alumina shows a higher hardness than zirconia, even at low values of density. Above 1550°C however both composites get higher values, because alumina grain size in composites is smaller than in bulk, due to mutual inhibition of grains growth when sintering a composite (see Figure 7 in [9]), which allow a better hardness.

On the contrary, the fracture threshold of A25Z3Y composite is higher than in A10Z3Y composite, both of them have been higher than in bulk alumina (Figure 5). They all display a monotonic evolution with a slow decrease at increasing sintering temperature: at low sintering temperature, a strong amount of porosity is observed, inducing high value of threshold, but at higher temperature although an optimal density is obtained, increasing of grain size prevents the existence of any optimum for this physical property. Therefore, the choice of 1500°C as sintering temperature appears to be a good compromise and assures a good density, small grain size, and good mechanical properties. In order to check the measurement of hardness and also to check whether Young's modulus follows a rule of mixtures we have also performed nanoindentation. In addition to composite sintered in classical condition, that is, at 1500°C , we have also studied samples sintered at higher temperature (1650°C) because they have higher grains size which make easy to get individual response of grains. The results are summarized in Table 1.

The values obtained for hardness are comparable to those obtained by the same method in the literature [15, 16]. Although within the standard deviation they are on average higher than those from Figure 5 as classically observed for

TABLE 1: Results of nanoindentation.

Compound	Hardness (GPa)	Young's modulus (MPa)
Al_2O_3	31 (5)	442 (45)
Z3Y	16 (3)	256 (41)
$\text{A10Z3Y-1650}^\circ\text{C}$	30 (7)	434 (65)
$\text{A25Z3Y-1500}^\circ\text{C 100 nm}$	27 (7)	394 (66)
$\text{A25Z3Y-1500}^\circ\text{C 50 nm}$	28 (3)	391 (31)
$\text{A25Z3Y-1650}^\circ\text{C}$	27 (7)	410 (58)

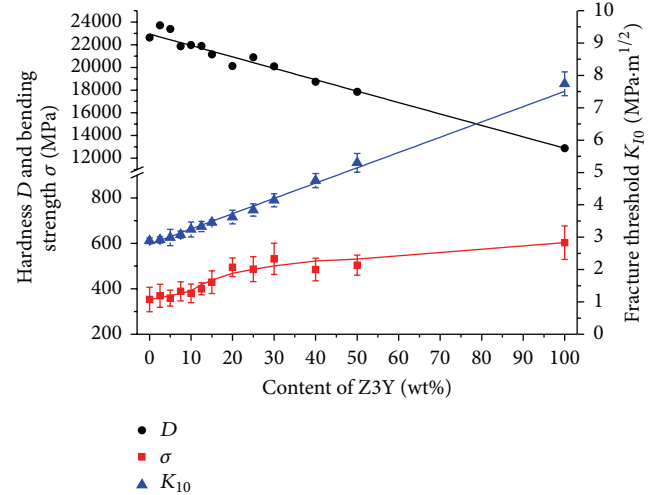


FIGURE 6: Dependence of the mechanical properties on the Z3Y zirconia content.

this kind of measurements which provide higher values than microindentation, they also follow a rule of mixture. Young's modulus is a little bit higher than the classical values (about 10%) and also follows the rule of mixture.

3.2.2. Influence of the Zirconia Content on Mechanical Properties. A quasi-linear dependence of Vicker hardness is observed in AZ3Y composites between both end members, that is, monolithic alumina (highest value) and monolithic zirconia (lowest value) (Figure 6), which is an expected result and indicates a classical mixing law for this property. Similarly a linear but opposite evolution of fracture threshold is also obtained for the same reason, as zirconia gets a better value than alumina. Bending strength evolution is almost linear with zirconia concentration excepted between ≈ 15 wt% and 40 wt% compositions which display slightly highest values, whose origin is not clear. The A25Z3Y composition was also tested using a 4-point bending machine and the bars were prepared according to the standard ISO 14704. The value obtained in this way was 900 MPa.

3.2.3. Influence of the Ytria Content on Mechanical Properties. Vickers hardness, threshold for fatigue crack propagation, and bending strength have been studied for A10ZY and A25ZY composites for different amount of yttria (Figure 7). Hardness increases monotonically with yttria content for both composites. The threshold in A10ZY is almost constant

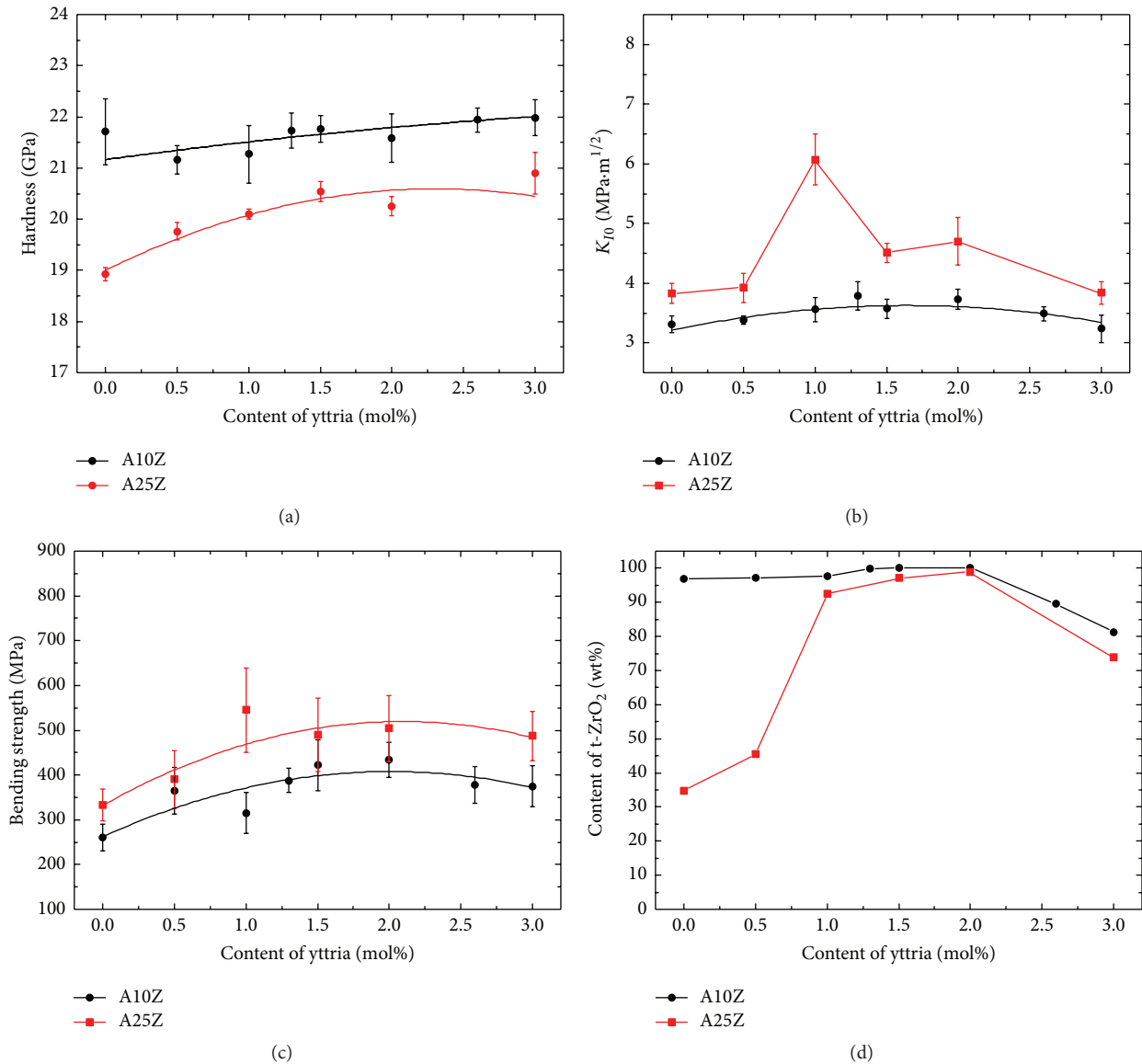


FIGURE 7: Dependence of the mechanical properties on the yttria content: (a) hardness, (b) fracture threshold K_{I0} , (c) bending strength, and (d) content of t-ZrO₂.

whatever the content of yttria is whereas in A25ZY an optimum is observed between 1 and 2 mol%. The same type of observation can be done in the evolution of bending strength: in A10ZY it is monotonous but in A25ZY an optimum is observed in the same concentration range. These two interesting points are discussed below.

4. Summary and Discussions of Results

We have observed in the AZ3Y composite that ageing starts above ≈ 35 wt% of zirconia (Figure 3) whereas values of 20–30 wt% are commonly reported in the literature. This is due to the good homogeneity of the composites and the small zirconia grain size [9]: the tetragonal phase is stabilized by size effect. This effect also explains the absence of any ageing in A10Z composite even in the case of A10Z0Y where the

t-ZrO₂ stabilization by doping is not at play. However, for higher amount of zirconia (i.e., larger grain size) we have observed ageing in A25Z when the amount of yttria is below 3 mol%: the size effect is not enough to stabilize the t-ZrO₂ at small amount of yttria and a small amount of monoclinic phase appears, with a maximum value for 1 mol%. This effect is explained by the phase ratio evolution with yttria content in this compound (Figure 7). Indeed around 1 mol% of yttria a drastic transformation from t- to m-ZrO₂ appears: the t-ZrO₂ is close to instability and retransforms by ageing, whereas this effect is not observed in A10Z (Figure 7) because the t-ZrO₂ is stable in the whole range of concentration. We have also observed that maximal mechanical properties are rather between 1 and 2 mol% compared to 3 mol% of yttria content (Figure 7) as it is reported in monolithic zirconia [9], because the amount of t-ZrO₂ is maximum (Figure 7). This points out

the fact that, if needed, embedding zirconia particles inside an alumina matrix changes its mechanical properties and allow optimizing the properties by an adequate doping.

5. Conclusions

According to this study, sintering composites at 1500°C is a good compromise and assures a good density, small grain size, and good mechanical properties. These properties have been shown to follow a mixing law between zirconia and alumina with monotonic evolution: no optimum composition of zirconia exists. This means that the choice of zirconia composition will depend on what is the desirable property is: if maximal hardness is required, a small amount of zirconia should be chosen; on the contrary if maximal bending strength and threshold for fatigue crack propagation are wanted, a higher concentration of zirconia should be used. Regarding yttria doping, maximal properties were observed between 1 and 2 mol% of yttria, concentrations which correspond to the highest amount of tetragonal phase, that is, maximal zirconia toughening of mechanical properties. However, this is at the same range of yttria content that the ageing is the highest: at these concentrations the t-ZrO₂ is at its optimum capacity to transform into the m-ZrO₂ and induces the phase transformation toughening. On the other hand, our study has shown that in A25Z composites no ageing is observed below 35 wt% of zirconia, due to the small grain sizes of zirconia and good homogeneity of the composites. Therefore, if a good ageing resistance is needed, such as, for instance, in orthopedic hips prosthesis, a ≈1.5 mol% doping of yttria should be chosen; on the contrary, if strong ageing resistance is not required, such for wear resistance, a 1 mol% yttria doping could be chosen to maximize the mechanical properties.

Competing Interests

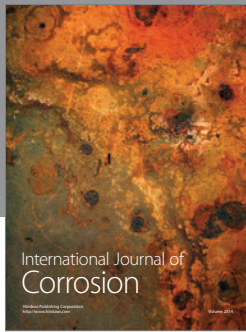
The authors declare that they have no competing interests.

Acknowledgments

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